

THE BEHAVIOUR OF Pt-BASED ALLOYS AT HIGH TEMPERATURE

March 2008

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A dissertation submitted to the faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Master of Physical Metallurgy.

DECLARATION:

I, Wendy Tshawe declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in Physical metallurgy in the University of Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in any other University.

.....

Signature

This Day of 2007

ABSTRACT

Previously published work on the development of the Pt-based superalloys for high temperature and special applications, as well as phase equilibria work, showed that there were problems and uncertainties with the available Pt-Al phase diagram.

The aim of the current work was to make a comprehensive study of all relevant phases, and to clarify the phase boundaries of the phases: (Pt), Pt₃Al (all temperature versions), Pt₂Al (both phases), β and Pt₅Al₃, by use of higher resolution SEM and XRD.

A displacive transformation was confirmed for cubic Pt₃Al to tetragonal Pt₃Al and from high temperature Pt₂Al to low temperature Pt₂Al. The β -phase was observed to be present, the phase reactions were confirmed and the eutectic composition was found. The Pt₆Al₂₁ phase was identified instead of Pt₅Al₂₁, and was deduced to be a different interpretation of the same phase, although the former had been described as a metastable phase. The phases and phase boundaries were found to generally agree with Massalski, and disagreed with Oya *et al.*'s phase diagram.

DEDICATION

This thesis is dedicated to my loving
Parents: Siphiwo and Nozuko Tshawe, my Creator God and me

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to the following people and organisations that made this project a success:

- ❖ To my supervisor, Lesley Cornish, your patience, your teaching, your words, has all made me a better person today. I am certainly better than I was before I met you, thank you.
- ❖ MINTEK for their resources, support and permission to publish these results.
- ❖ DST/NRF Centre of Excellence in Strong Materials.
- ❖ Mintek personnel: Dr. Alistair Douglas, Lizelle Glaner, Edson Muhuma, Bernard Joja, Alain Mwamba, Iris Klingbiel, Rainer Süss, thanks for a great contribution to this project.
- ❖ My special friend James Aluha Lulizi, thanks for your support during this time.
- ❖ To my family: my parents and siblings, your presence, love and support has given me hope and strength to press on.
- ❖ Finally, to God, who is the reason for what I do, His constant support, favor and unfailing love has got me where I am.

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1 INTRODUCTION

1.1 Introduction and background

Platinum and nickel are two of the highly successful elements used at high temperature applications that can maintain their mechanical properties and corrosion resistance [1987Sim]. They have similar structure and chemistry, but platinum has a higher melting point (1769°C for platinum compared to 1455°C for nickel) and higher corrosion resistance than nickel [2003Cor, 2004Süs, 2006Mal].

Previous developments have shown that nickel-based superalloys (NBSAs) are highly successful at high temperature applications without losing their mechanical properties [1987Sim]. However, because nickel-based superalloys are reaching their temperature limit for operation in turbine engines, there is a need for new high temperature alloys that could still maintain their mechanical properties. The reason is that greater thrust, reduced fuel consumption and lower pollution could be achieved. Platinum has therefore been targeted to replace nickel for some high temperature applications. Recent studies conducted on platinum alloys have revealed superior corrosion properties for platinum with similar structure to the NBSAs [2006Mal]. Due to the fact that platinum and nickel possess an fcc structure, they are therefore too soft to be used as pure metals. However, there are strengthening mechanisms available with these elements which allow use at high temperatures, such as alloying, resulting in precipitation and solid solution strengthening [1987Sim]. Alloying platinum with a number of elements like aluminium, zirconium, titanium and many other elements form high temperature compounds [1990Mas]. Platinum-based alloys are used in industrial applications, such as catalysts, as well as the investment and jewellery; and nickel-based superalloys are used in turbine engines, among other high temperature applications.

Much work was done at Mintek, and a number of ternary and quaternary Pt-based alloys have been proven to exhibit the same two-phase structure (γ/γ') as nickel-based superalloys

[2001Hil, 2002Cor, 2003Cor]. A quaternary alloy composition has been optimised for the best microstructure and hardness. Studies have shown that the quaternary alloy $\text{Pt}_{84}:\text{Al}_{11}:\text{Ru}_2:\text{Cr}_3$ has the best structure produced yet in the programme [2002Cor, 2003Cor].

Work has begun on establishing a thermodynamic database for Pt-Al-Ru-Cr alloys using Thermo-CalcTM to optimise the descriptions of the phases and allow phases and compositions of selected alloys to be derived [2003Cor, 2004Cor, 2006Cor], and further work has been done to enhance the mechanical and oxidation properties of the alloys [2000Hil1, 2001Süs1, 2003Fai, 2006Mal]. The Pt-Al binary phase diagram is the basis for the high order phase diagrams being developed, there are two different versions, and clarity is needed.

Some features of the platinum-aluminium phase diagram have previously been determined, but the platinum-rich region showed uncertain information. McAlister and Kahan's review [1986McA] reported a displacive transformation of a high-temperature cubic Pt_3Al (γ') to a tetragonal low-temperature variant (γ'_2) at 1280°C , whereas Oya and Mishima [1987Oya] reported the transformation of cubic Pt_3Al to tetragonal Pt_3Al ($\gamma' \rightarrow \gamma'_2$) at 340°C , and an additional transformation $\gamma'_1 \rightarrow \gamma'_2$ ($\text{DOc} \rightarrow \text{DO'c}$) at 127°C . These structures are shown in Chapter 2. The phase boundaries of the phase diagrams also differed.

The aim of this project therefore is to confirm the phases and phase boundaries already reported by McAlister and Kahan's review [1986McA], and these phases are: (Pt), Pt_3Al (all temperature versions), Pt_2Al (both phases), β and $\text{Pt}_5\text{Al}_{21}$. An experimental procedure is outlined, followed by results and discussion; a conclusion will be drawn from the results obtained.

2 LITERATURE REVIEW

2.1 Platinum and Platinum Group Metals

Platinum group metals (PGMs) are six specific metals belonging to the transition group of metals in the periodic table. The six metals (platinum, palladium, rhodium, ruthenium, iridium and osmium), together with gold, occur naturally in close association and have strong chemical similarities. In Westbrook and Fleischer's review [1995Wes], it was reported that these elements share properties such as inert softness, relatively high density, environmental resistance, good corrosion resistance, and are collectively called the precious metals. Yamabe-Mitarai, Koizumi, Murakami, Ro, Maruko and Harada [1996Yam], Yamabe-Mitarai, Ro, Maruko, Yokokawa and Hirada [1997Yam1], and Yamabe-Mitarai, Koizumi, Murakami, Ro, Maruko and Harada [1997Yam3] reported that most of the platinum group metals have low affinity for oxygen, and referred to systems based on iridium, rhodium and platinum as refractory superalloys, because of their ability to be used at very high temperatures. Ruthenium and osmium are hexagonal close packed (hcp); the rest of the metals are face-centered cubic structures.

2.2 Platinum

Vander Voort's review [1984Van] indicated that platinum is an expensive precious metal and has an fcc structure, hence it is very soft with a Vickers hardness of under 50HV in the annealed condition. This means it cannot be used alone because it deforms easily, and so is mixed with other materials. Platinum-based alloys are currently mainly used in the autocatalytic applications as well as jewellery. Sims, Stoloff and Hagel [1987Sim] reported that platinum additions can be used to enhance the protective properties by improving diffusional stability and adhesion of oxide scales in NBSA coatings. Alloys based on platinum were reported to be more chemically inert than those based on iridium and rhodium [1997Yam].

2.3 Nickel-based superalloys

Much attention has been given in developing Ni-based superalloys (NBSAs), which comprise many small, strained-coherent, $L1_2$ ordered particles in a softer fcc matrix, which are very stable at high temperatures (1455°C). The NBSA developments have been extensively reviewed by Sims *et al.* [1987Sim]. The use of NBSAs at very high temperatures does not coarsen the precipitates too quickly, because the structure of the particles is closely related to that of the matrix, which is energetically favourable [1987Sim]. Therefore, the surface area energy is similar, hence there is limited driving force. These small ordered particles slow down the movement of dislocations, which causes the superalloys to have high temperature strength and toughness. However, their use at elevated temperatures is currently limited by the melting point of Ni, 1455°C [1987Sim].

Currently, the NBSAs are operating at up to 90% of the melting point of Ni, 1455°C and so are reaching their temperature limit for operating in turbine engines [1987Sim]. There is therefore a need for new alloys to further increase operational temperatures of these engines, to achieve greater thrust, reduced fuel consumption and lower pollution. Pt-Al alloys hold great promise because they have been used as coatings on Ni-based superalloys [1987Sim, 1972Bug]. According to Wolf and Hill [2000Wol], selected intermetallic compounds were found to have interesting properties such as: good diffusional resistance, high temperature strength, high melting points, good oxidation resistance and low densities for performance in service regimes, which could exceed the Ni-based superalloys.

Compared to nickel (1455°C), platinum has a much higher melting point, 1769°C, the same fcc structure, similar chemistry and higher corrosion resistance. Therefore, Pt-based alloys are being developed at Mintek as potential alloys to replace NBSAs [2000Wol, 2001Hil, 2003Cor, 2006Cor]. However, platinum-based superalloys cannot replace NBSAs entirely, on account of higher price and higher density, but will only be used in specific applications [2000Wol]. Massalski's phase diagrams [1990Mas] indicate that platinum can be alloyed with a number of elements such as: aluminium, zirconium and titanium to form high temperature compounds. Low temperature stable phases are also formed, such as: Pt_3Cr ,

Pt₃Ga, Pt₃In, Pt₃Mn, Pt₃Zn and Pt₃Co [1990Mas]. However, Darling, Selman and Rushforth [1970Dar] reported that alloying additions must be carefully controlled to avoid decreasing the alloys' environmental resistance.

2.4 Development of Pt-based alloys at Mintek

2.4.1 Background

Work at Mintek was carried out, firstly in the development of platinum-based superalloys for high temperature and special applications as the potential alloys to replace NBSAs, and subsequently for the development of a thermodynamic database using Thermo-CalcTM. Wolf and Hill [1999Wol] confirmed the co-existence of the Pt solid solution phase (fcc) with an ordered f.c.c. (L1₂) Pt₃Al phase, which is similar in structure to the (Ni)-Ni₃Al system. It was well established that long-term ageing of the nickel-base superalloys gives rise to mismatch dislocation substructures, and these can be delineated by etching [1991Wol]; similar features were observed optically on etched Pt-Al surfaces [1999Wol]. Pt₈₉Al₁₁ alloys were heat treated for 1 hour at 1480°C, followed by ageing at 1100°C and quenched. An etching response was found to vary as a function of heat treatment time and composition, and the alloys showed typical age-hardening curves during isothermal annealing as shown in Figure 2.1.

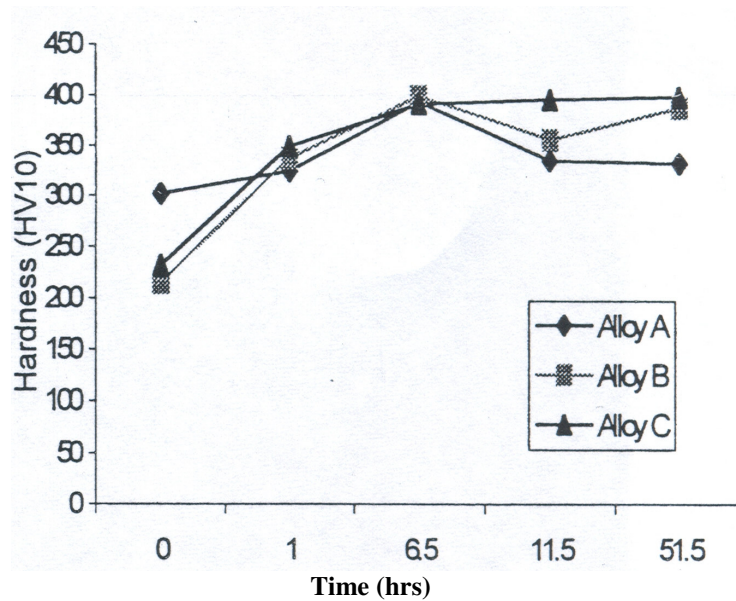


Figure 2.1. Age-hardening of the nominal $\text{Pt}_{89}\text{Al}_{11}$ alloys during isothermal annealing at 1100°C [1999Wol].

Wolf and Hill [2000Wol] further confirmed the presence of the (Pt)- Pt_3Al alloy which was similar in structure to the (Ni)- Ni_3Al system in terms of morphology as indicated in Figure 2.2. However, there are some limiting factors that have been identified in the Pt-Al binary system such as:

- Unstable high-temperature L_{12} phase at room temperature [2002Hil1]
- Possible limited resistance of the matrix phase to deformation by solid solution strengthening [1994Nab]
- High temperature oxidation properties and
- Volume fraction of the γ' phase.

Therefore, ternary and higher order alloying additions were considered to address these challenges [2000Wol].

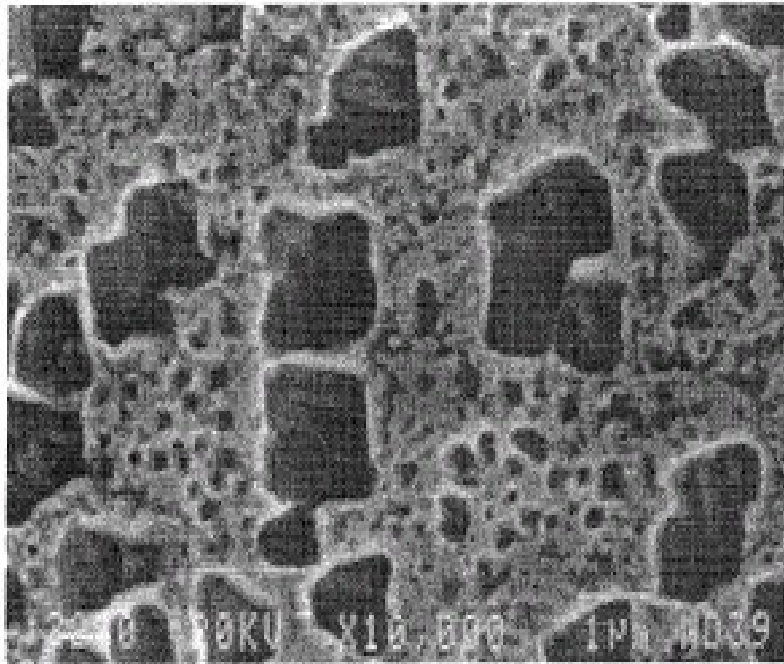


Figure 2.2. Cuboidal Pt_3Al precipitates in $Pt_{88}Al_{12}$, which has been solution heat treated and aged at $1350^{\circ}C$ [2000Wol].

2.4.2 Stabilization of cubic Pt_3Al

Hill, Cornish, Ellis and Witcomb [2001Hil1] reported that both Pt-Al-Cr and Pt-Al-Ti had a potential for developing the (Pt)- Pt_3Al microstructure. Hill, Adams, Biggs, Ellis, Hohls, Taylor and Wolff's investigation [2002Hil1] on high temperature Pt-Al-Z alloys (where Z = Ru, Re, W, Mo, Ti, Ta and Cr) showed microstructures similar to (Ni)- Ni_3Al . Studies on the high temperature Pt-Al-Z alloys (where Z = Ru, Re, W, Mo, Ni, Ti, Ta and Cr) showed the presence of microstructures similar to Ni and Co-based superalloys, and alloys could withstand greater extremes of temperatures [2002Hil1]. Süss and Volkl [2002Süs1] performed studies on selected ternary alloys of Pt-Al-Z (where Z = Ti, Cr, Ru, Ta and Ir) to improve phase stability of the alloys. Cr, Ti, Ta stabilised the $L1_2$ form of Pt_3Al while Ru and Ir stabilised the lower temperature $D0'c$ type structure, and Ru was a solid solution strengthener [2001Hil1, 2002Hil1, 2002Süs]. TEM work results showed that the precipitates disappeared at temperatures well below $1300^{\circ}C$, therefore, further additions to stabilise the small precipitates would be beneficial [2006Dou].

2.4.3 High temperature strengthening of Pt-based superalloys

The effects of different substitutional alloying additions on the high temperature compressive strengths of Pt-Al-Z alloys (where Z = Ti, Cr, Ru, Ta and Re) were studied, and a higher strength above 1150°C than the commercial Ni-based superalloys was reported to exist [2001Hil2]. According to Hill, Biggs, Ellis, Hohls, Taylor and Wolff [2001Hil3], the Pt-Al-Ta alloy had the highest proof stress compared to Pt-Al-Ru and Pt-Al-Cr as shown in Figure 2.3. The ternary elements of Pt-Al-Z (where Z = Ti, Cr, Ru, Ta and Ir) were selected to improve the high-temperature mechanical properties of the alloys, and results showed higher stress-rupture strength and good ductility for Pt-Al-Cr and Pt-Al-Ru [2002Süs]. The alloys showed promising mechanical properties at room temperature, and a high resistance to crack initiation and propagation, with hardness values higher than 400HV [2001Hil3]. Keraan and Lang [2003Ker] did further studies on Pt₈₀:Al₁₄:Cr₃:Ru₃, Pt₈₆:Al₁₀:Ru₄ and Pt₈₆:Al₁₀:Cr₄ alloys to investigate mechanical properties and formability for high temperature use. Compression testing at various deformation temperatures and strain rates showed that the Pt₈₀:Al₁₄:Cr₃:Ru₃ alloy had higher temperature strength than the Pt₈₆:Al₁₀:Cr₄ alloy due to higher volume fraction of the intermetallic precipitates, and the solid solution strengthening effect of ruthenium.

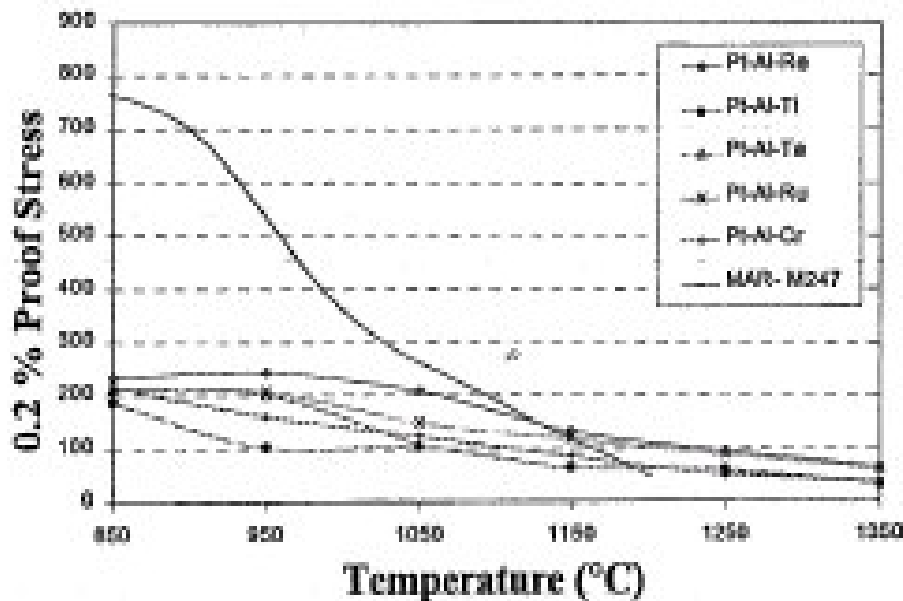


Figure 2.3. Temperature dependence of the 0.2% flow stress of the ternary Pt-Al-X alloys [2001Hil3].

Douglas, Neethling and Cornish [2004Dou2] reported that there is solid solution strengthening in the (Pt) matrix, as well as strengthening provided by the Pt₃Al precipitates in the Pt₈₆:Al₁₀:Ti₄ alloy. The strengthening mechanisms were:

- the presence of the high density of dislocations
- the size difference between the ternary alloying atom, Ti (atomic radius 129pm), and the other atoms comprising the γ' precipitate, Pt (139pm) and Al (143pm)-dilatational strengthening.

Chown and Cornish [2003Cho], and Glaner and Cornish [2003Gla] studied cobalt and nickel additions to the Pt-Al alloys to improve solid solution strengthening, and Co additions were found to further improve formability [2004Cho]. However, there was less solution strengthening than expected upon Ni additions [2003Gla].

Tensile tests undertaken on the Pt-Al-Cr and Pt-Al-Ru, and the best Pt-Al-Cr-Ru composition alloys were very encouraging [2004Süs1]. These tensile tests undertaken at ambient temperatures corresponded to those of the other high temperature alloys previously reported [2004Süs1, 2006Cor].

A TEM study was made on a series of Pt₈₆:Al₁₀:X₄ alloys (where X = Cr, Ru, Ti, Ir and Ta) to analyse the dislocation content, precipitation and microstructure of samples compressed at different temperatures [2004Dou2], and to investigate the changes in the microstructure of Pt-Al alloys using *in situ* heating up to 1100°C [2006Dou]. The Pt₃Al phase transformation was found at a much lower temperature (~359°C) than that given by Massalski and Kahan (~1280°C) [1986McA], and was in better agreement with Oya and Mishima [1987Oya].

2.4.4 Lattice mismatch between the two phases

The (Pt)-Pt₃Al interface is semi-coherent, resulting to a lattice mismatch between the two phases. In order to understand the lattice mismatch, an extensive TEM investigation was carried out on the elastically strained samples of Pt:Al:X ternary alloys (where X = Ru, Cr, Ta, Ti and Ir) [2001Dou1, 2001Dou2, 2002Dou, 2003Dou, 2003San]. Figure 2.4, shows a misfit dislocation network in the precipitate/matrix interface found in the Pt-Al-Cr system, which relaxed the resultant lattice strain [2001Dou2]. Douglas, Neethling, Santamarta, Schryvers and Cornish [2003Dou], Santamarta, Neethling, Schryvers and Douglas [2003San], Douglas [2004Dou1] and Douglas, Neethling, Santamarta, Schryvers and Cornish [2007Dou] investigated the dislocation distribution and misfit strain on the (Pt)-Pt₃Al microstructure using a TEM to understand the structural changes in the low temperature Pt₃Al precipitates. Results indicated that there was a modification of the D0'c unit cell, mD0'c:

- The mD0'c *c*-axis was 1.5 times the length of the *c*-axis of the D0'c unit cell (D0'c).

The *c*-axis of the unit cell of the precipitate was aligned along an *a*-axis of the matrix unit cell, thus a matrix-precipitate (Pt)-Pt₃Al orientation relationship formed in order to relieve the lattice strain as shown in Figure 2.4 (d).

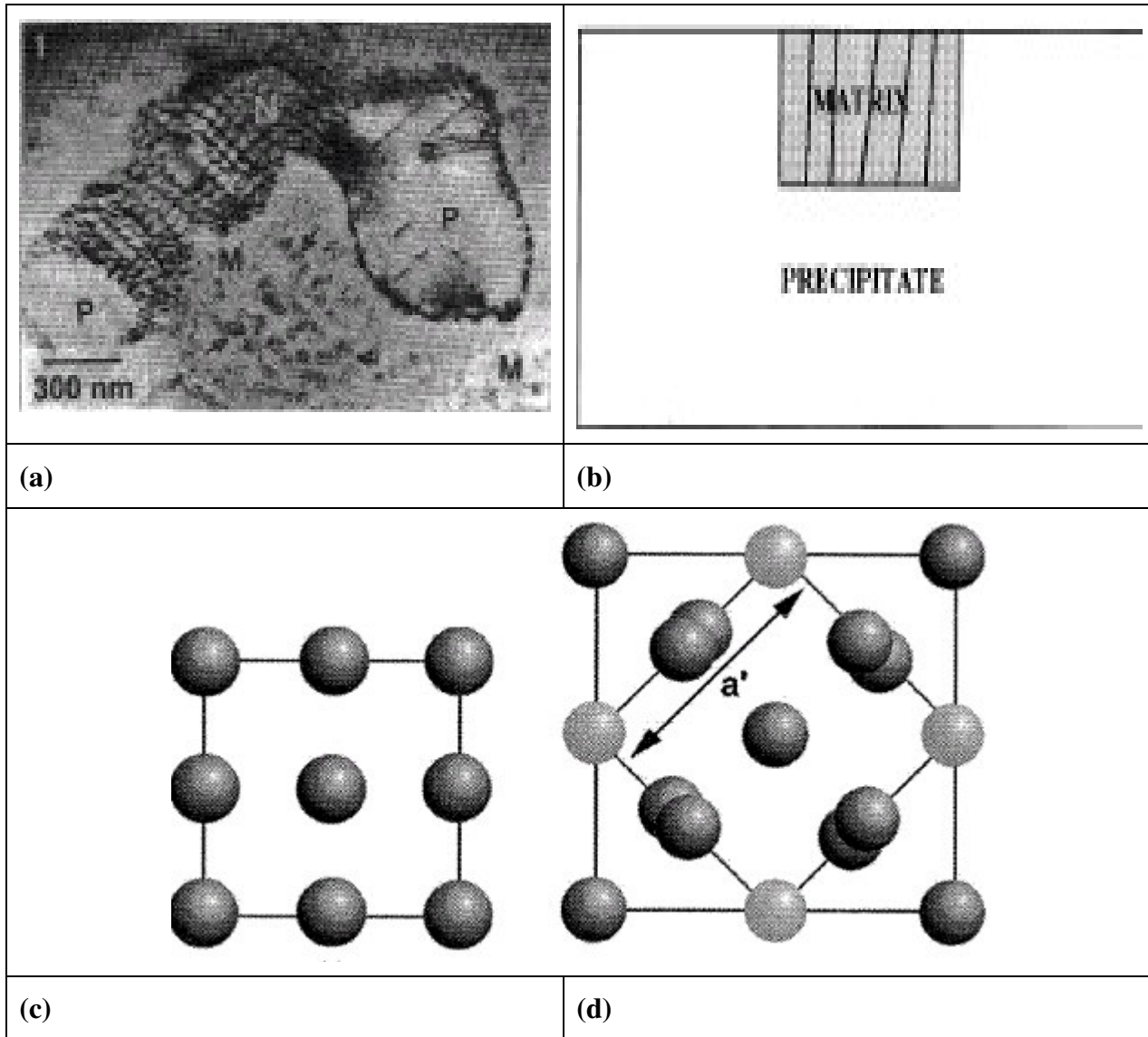


Figure 2.4. (a) TEM bright-field image of a $\text{Pt}_3(\text{Al,Cr})$ precipitate in a (Pt,Al,Cr) matrix with a dislocation network, (b) Schematic illustration of the matrix/precipitate position perpendicular to foil surface through the region of the dislocation network, (c) (001) projection of the fcc unit cell of the (Pt) phase, (d) (001) projection of the modified $\text{D0}'\text{c}$ unit cell of the Pt_3Al phase [2001Dou2].

2.4.5 High temperature oxidation properties in Pt-based superalloys

Hill, Adams, Biggs, Ellis, Hohls, Taylor and Wolff's [2002Hil2] preliminary investigation on the oxidation behaviour of ternary Pt-Al-X alloys (where X = Re, Ta, Ti, Cr and Ru) at higher temperatures showed different oxidation behaviour for the different alloys. Increased susceptibility of the alloys to internal oxidation was found in Pt-Al-Re and Pt-Al-Ta alloys and a protective layer did not form. On the other hand, Pt-Al-Ti formed discontinuous

aluminium and titanium oxides prior to the formation of the continuous alumina layer, which showed reasonably good oxidation resistance [2002Hil2, 2001Hil1]. The Pt-Al-Cr and the Pt-Al-Ru alloys showed a continuous alumina film which provided protection for the alloys. In the investigation carried out on the ternary Pt-Nb-Ru, Pt-Ti-Ru and Pt-Al-Z (where Z = Ni, Ru, Re) compositions, it was found that a thin external aluminium-oxide layer had formed, while the underlying metal had not been attacked on the samples alloyed with Al. Additionally, the Pt-Ti-Ru and Pt-Nb-Ru alloys oxidised internally by the formation of Ti-oxide and Nb-oxides respectively [2001Hil3]. Since Pt-Al-Z alloys had the best oxidation resistance, it was decided that later work would only be on these alloys.

High temperature oxidation properties of the Pt-Al-Z (Z = Ti, Cr, Re, Ru, Ta and Ir) alloys were studied by Süß, Hill, Ellis and Wolff [2001Süs1]. Al additions were increased to accelerate oxide scale formation [2001Süs2]. Further studies on Pt-Al-X (where X = Ru, Re, W, Mo, Ni, Ti, Ta and Cr) were carried out, and Pt-Al-Re had weaker oxidation resistance, Pt-Al-Cr and Pt-Al-Ru alloys formed a protective external alumina film [2002Hil1].

Studies by Fairbank [2003Fai] on the Pt-Rh-Hf and Pt-Rh-Zr alloys showed good mechanical properties of Pt-Rh-Hf (better than Pt-Ti-Cr), but the oxidation resistance was very poor. Maledi, Potgieter, Sephton, Cornish, Chown and Süß [2006Mal] reported Pt alloys to have superior corrosion properties relative to both coated and uncoated Ni-based superalloys under high temperature conditions (~ 900°C).

2.4.6 Increasing the volume of cubic Pt₃Al

Most of the strength in the alloys comes from the Pt₃Al precipitates as in NBSAs [1987Sim]. Pt-Al-Cr was very promising with regards to oxidation resistance and high temperature stability, but had a low volume fraction of the Pt₃Al precipitates [2001Süs2]. Therefore, trials were made on a range of Pt-Al-Cr-Ru alloys to increase the volume fraction in order to enhance the alloy's creep properties. In order to increase the proportion of Pt₃Al (γ') precipitates, several alloys were prepared [2002Cor]. Compositions were selected based on the ternary Pt-Al-Cr and Pt-Al-Ru samples [2002Cor]. In an attempt to improve the microstructure, one alloy was heat treated twice, resulting in better distributed precipitates

which is a desired structure, than the alloy heat treated only once (Figure 2.5) [2001Hil4, 2002Cor].

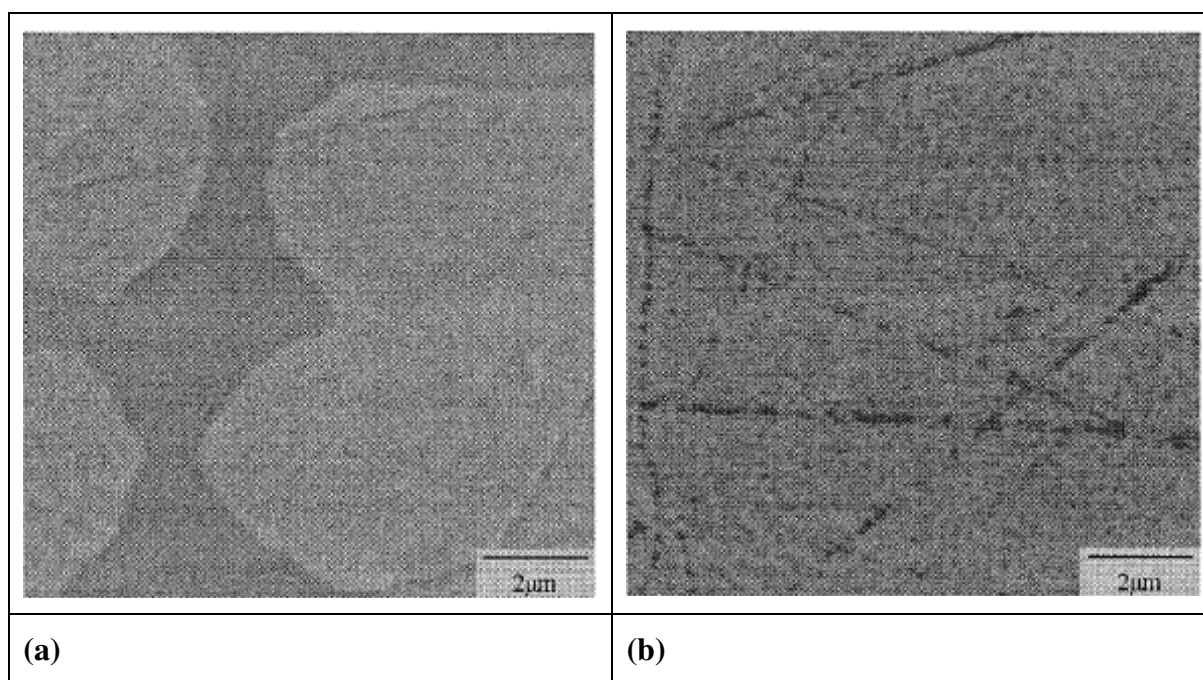


Figure 2.5. SEM BSE image of the two types of two-phase alloys (a) heat treated once, with precipitates which are twice as large than those of (b) heat treated twice, showing fine and evenly distributed precipitates of (Pt) and $\sim\text{Pt}_3\text{Al}$ [2002Cor].

2.4.7 X-Ray studies

As part of the larger project to develop and optimise Pt-based alloys for high temperature use, X-ray studies were carried out to help identify phases observed in the Pt-Al-Ru [2003Pri1, 2003Pri2, 2006Ngw] and Pt-Cr-Ru [2004Süs2, 2004Süs3, 2006Ngw] systems.

2.4.8 Building a database for Pt-based Superalloys

The development of the thermodynamic database is to facilitate further development of the Pt-based alloys. The database will enable the thermodynamic description of the phases from the experimental results already acquired and new phases to be optimised, and ultimately predict an alloy's phases without necessarily undertaking further experimental work.

CALPHAD methods are being used to derive the database [2006Wat1, 2006Wat2, 2007Cor]. The alloys based on the Pt-Al-Cr-Ru quaternary system showed very encouraging results in terms of microstructure and hardness [2004Süs1, 2005Pri], and so the database was developed on these elements (Figure 2.6) [2006Wat1, 2006Wat2]. Currently, the database contains the elements platinum, aluminium, chromium and ruthenium [2006Cor2, 2007Cor]. Where the component phase diagram had inconsistencies or phase diagram information was needed, experimental phase diagram work was undertaken.

A preliminary version of the database was constructed from the thermodynamic data sets of the binary systems. Then an extrapolation into the ternary system was made from the binary systems, and experimental phase data were compared to the calculated ones [2006Cor2]. After subsequent ternary work, it was found that the following binary phase diagrams needed more work: Pt-Al, Cr-Pt and Cr-Ru.

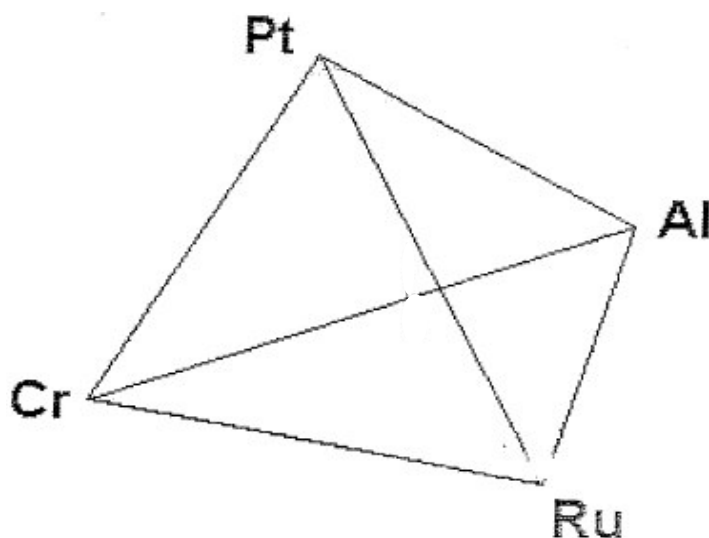


Figure 2.6. Schematic diagram of the Pt-Al-Cr-Ru System, showing four ternary systems and six binary systems [2006Cor2].

The Pt-Al-Cr-Ru system was optimized in Thermo-CalcTM by studying the four component ternary systems which are shown schematically in Figure 2.6. In order to build the Pt-Al-Cr-Ru database, comparisons of the experimental binary and ternary systems with those calculated had to be undertaken [2006Cor2]. Good agreement was found when Pt-Al-Cr and

Pt-Cr-Ru phase diagrams were extrapolated from the binaries [2003Süs, 2006Süs, 2008Süs], as well as for Pt-Al-Ru [1999Hil, 2000Big, 2001Big, 2005Pri].

2.5 Pt-Al binary System

2.5.1 Studies on the Pt-Al phase diagram

Chourigine [1912Cho1, 1912Cho2] gave the first report on the liquidus and solidus of the Pt-Al phase diagram, which was based on thermal analyses covering the range 0 to 36.4 at.% Pt. However, their data were later considered unreliable because of doubtful purity of samples, and disagreements with the later measurements by Huch and Klemm [1964Huc]. Huch and Klemm [1964Huc] conducted their studies using thermal analyses, metallographic, X-ray diffraction (XRD) and density measurements over the range 0 to 100 at.% Pt and their results are as shown in Figure 2.7.

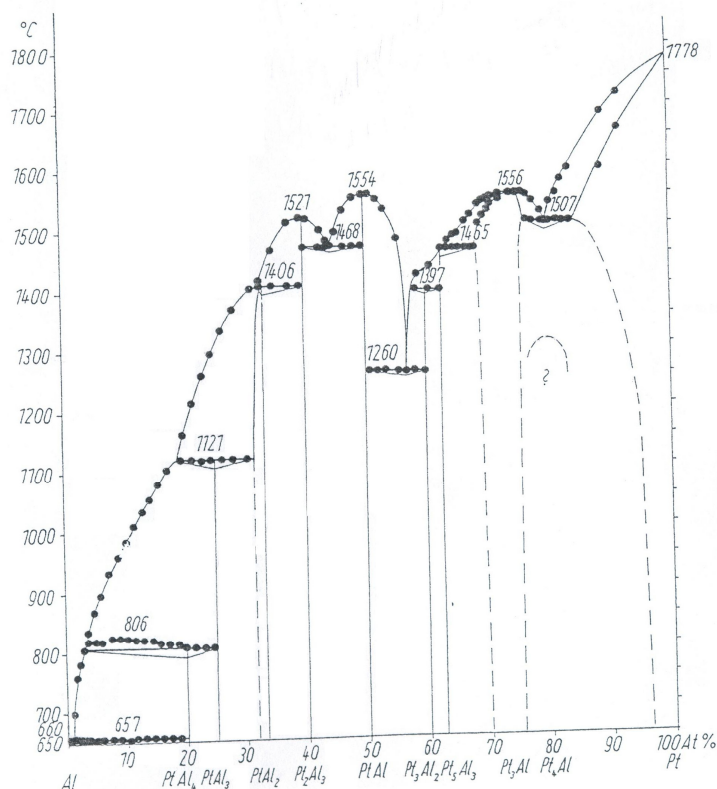


Figure 2.7. Thermal analyses over the range of 0 to 100 at.% in the Pt-Al binary system [1964Huc].

A phase transformation of Pt_4Al was shown (dotted line in Figure 2.7) at $\sim 1300^\circ\text{C}$. (Pt) comprised ~ 4 at.% Al at low temperatures (at $\sim 650^\circ\text{C}$). There were uncertainties about the phases and phase boundaries, with most phase boundaries in the Pt-rich side being shown as dotted lines (Figure 2.7): (Pt), Pt_4Al , Pt_3Al and PtAl_2 . Some of the phases were shown as line compounds (Figure 2.7): PtAl_4 , PtAl_3 , Pt_2Al_3 , PtAl , Pt_3Al_2 and Pt_5Al_3 .

Platinum solubility in the terminal (Al) solid solution at 657°C and above was minimal. The data points for the $\text{L} + \text{PtAl}_3 \rightarrow \text{PtAl}_4$ reaction was interpreted as a three-phase field. Similarly, this was done for the $\text{L} + \text{PtAl}_2 \rightarrow \text{PtAl}_3$ reaction. The PtAl_2 phase boundary in the Al-rich side was shown to be uncertain below 1127°C (Figure 2.7).

Darling *et al.* [1970Dar] employed microprobe analyses, metallographic methods and X-ray lattice parameter studies to determine the solvus of (Pt) over a wide range of temperatures as indicated in Figure 2.10. Several data points of the liquidus and solidus of the terminal (Pt) solid solution were found to be consistent with Huch and Klemm's phase diagram results [1964Huc]. Darling's [1970Dar] results of the solvus of (Pt) were also consistent with the X-ray parameter studies of Schubert [1978Sch] and Schaller [1979Sch], as indicated in Figure 2.10.

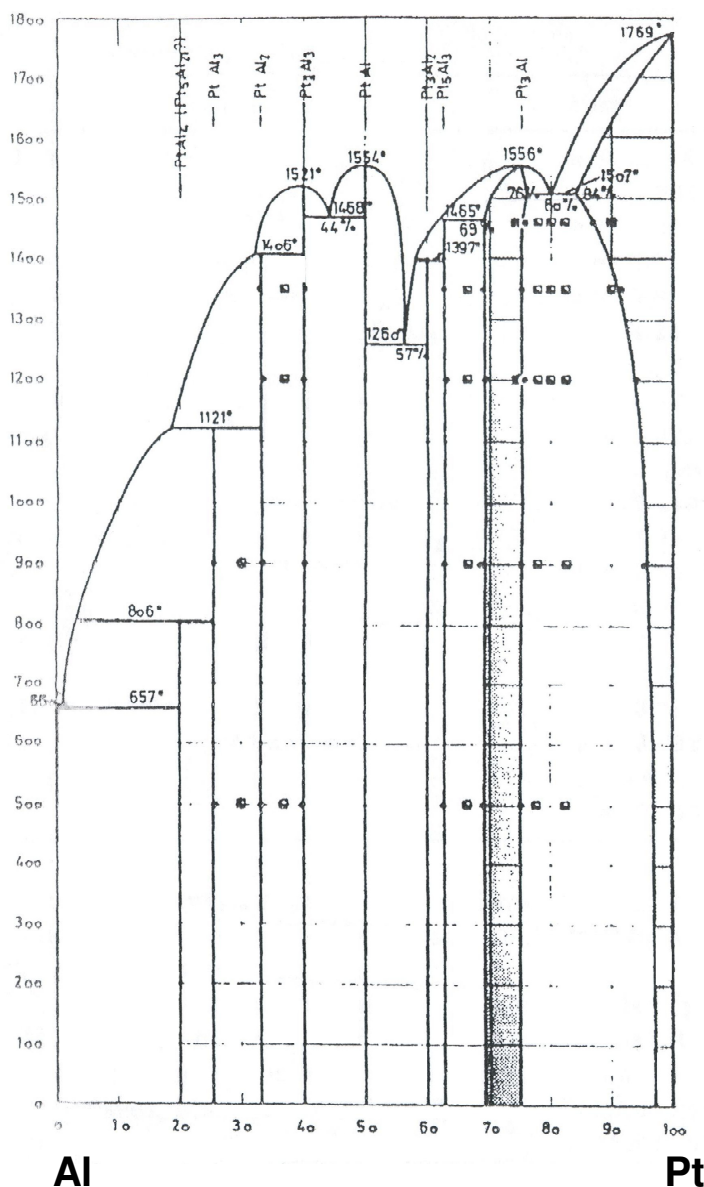


Figure 2.8. Thermal analyses of the Pt-Al binary system, showing no evidence of the existence of Pt_2Al phase [1976Gue].

Guex and Feschotte [1976Geu] also performed selected microprobe analyses after heat treatment of the samples in the range 500°C to 1350°C for a longer period of time than Chattopadhyay and Schubert [1975Cha1]. Most of the phases were identified as line compounds (Figure 2.8): PtAl_2 , $\text{Pt}_5\text{Al}_{21}$, PtAl_3 , PtAl_2 , Pt_2Al_3 , PtAl , Pt_3Al_2 , Pt_5Al_3 and Pt_3Al . A transformation for the Pt_3Al phase was reported to occur at 1200°C [1976Gue], thus at lower temperatures relative to Huch and Klemm [1964Huc]. Guex and Feschotte [1976Gue] found no evidence of the existence of Pt_2Al phase in the 66.5 at.% Pt samples. The samples

and heat treatment temperatures were indicated as dots at selected temperatures, as shown in Figure 2.8 [1976Geux]. The (Pt) contained ~3 at.% Al at low temperatures (below ~500°C).

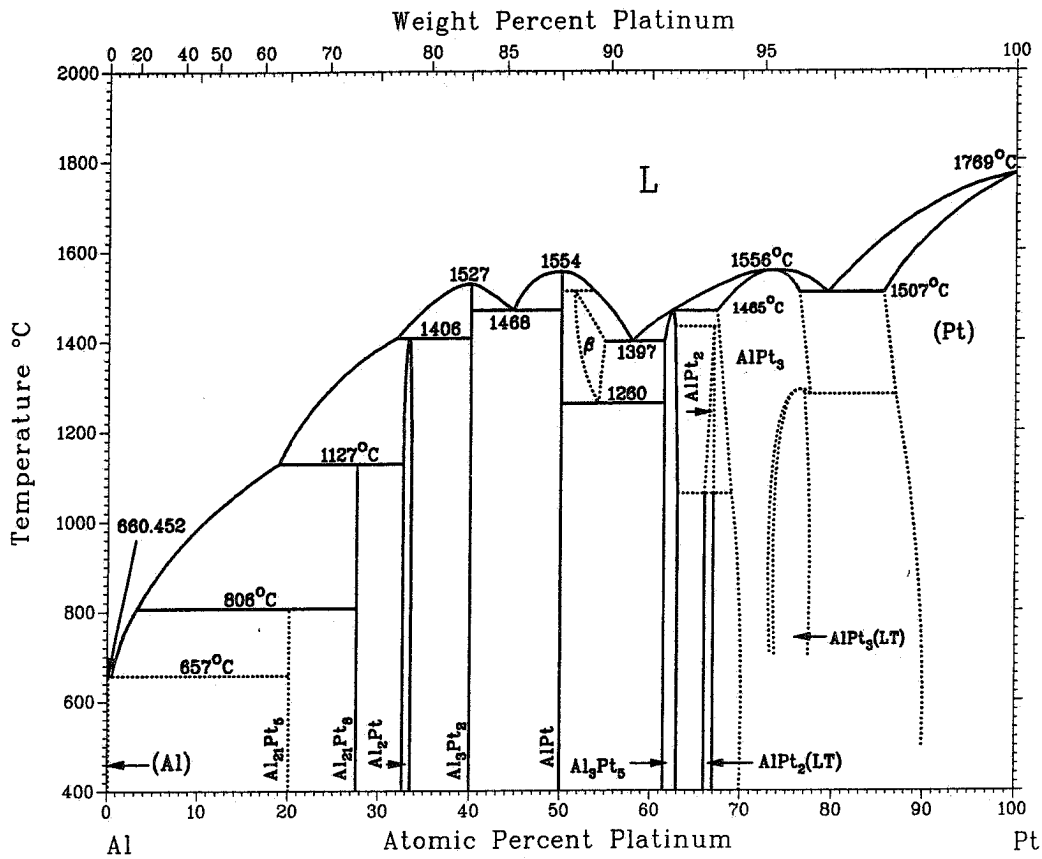


Figure 2.9. Pt-Al phase diagram of McAlister and Kahan [1986McA].

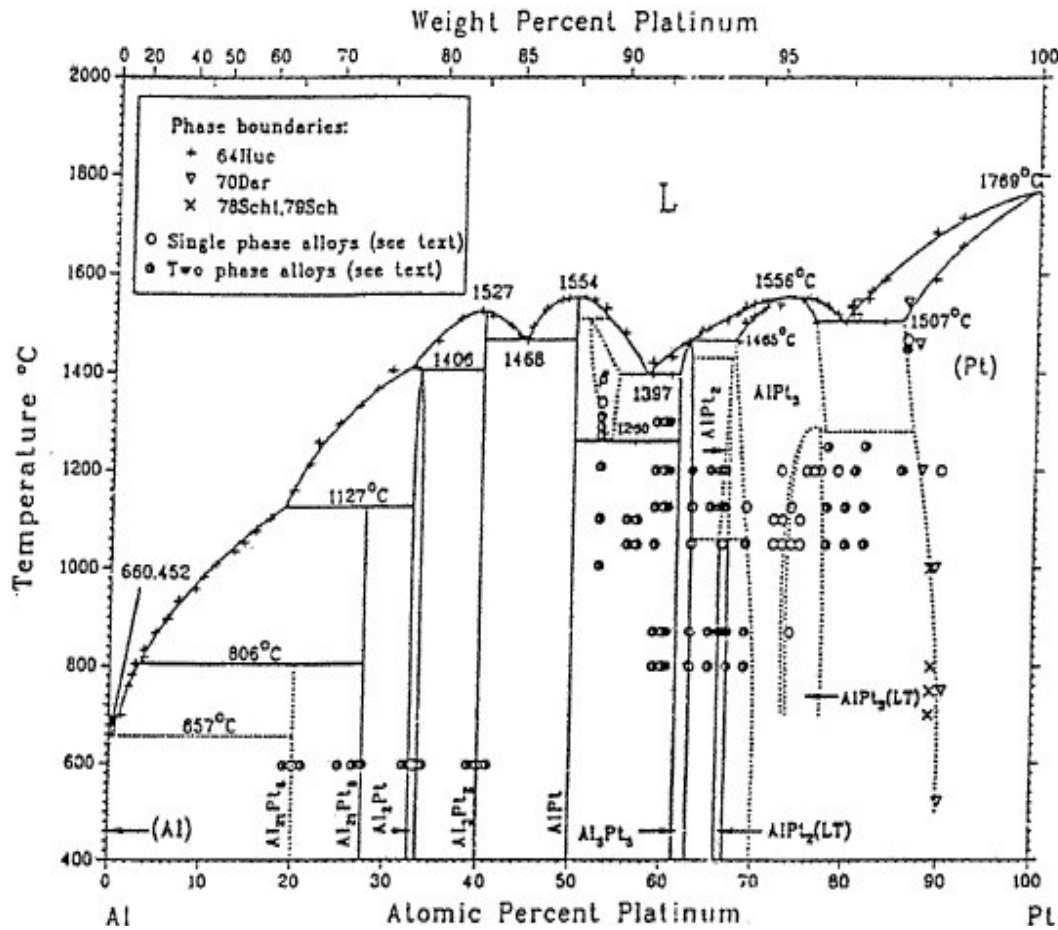


Figure 2.10. Pt-Al phase diagram showing comparison of the data between different sources [1986McA].

There are currently two conflicting phase diagrams: that of McAlister and Kahan [1986McA] (Figures 2.9 and 2.10), and that of Oya and Mishima [1987Oya] (Figure 2.11). The major differences, which are crucial in the development of Pt-based alloys using the $\sim$ Pt₃Al precipitates in a platinum solid solution, are the phase transformation temperatures in cubic to tetragonal $\sim$ Pt₃Al and the number of types of the $\sim$ Pt₃Al phases.

McAlister and Kahan [1986McA] made an assessment of the Pt-Al phase diagram as given in Figure 2.9 from the thermal data of Huch and Klemm [1964Huc], Darling, Selman and Rushforth [1970Dar], Guex and Feschotte [1976Geu] and Schubert [1978Sch]. They reported a displacive transformation of a high-temperature cubic Pt₃Al (γ') to a tetragonal low-temperature variant (γ'_2) at 1280°C as shown in Figure 2.9. However, Oya and Mishima [1987Oya] reported the transformation of cubic Pt₃Al to tetragonal Pt₃Al ($\gamma' \rightarrow \gamma'_2$) at 340°C,

and an additional transformation $\gamma'_1 \rightarrow \gamma'_2$ ($\text{DOc} \rightarrow \text{DO'c}$) at 127°C as shown in Figure 2.11. The structures of phases are given in Table 2.1. Table 2.3 shows a comparison of reactions and reaction temperatures from McAlister and Kahan [1986McA] and Oya and Mishima [1987Oya].

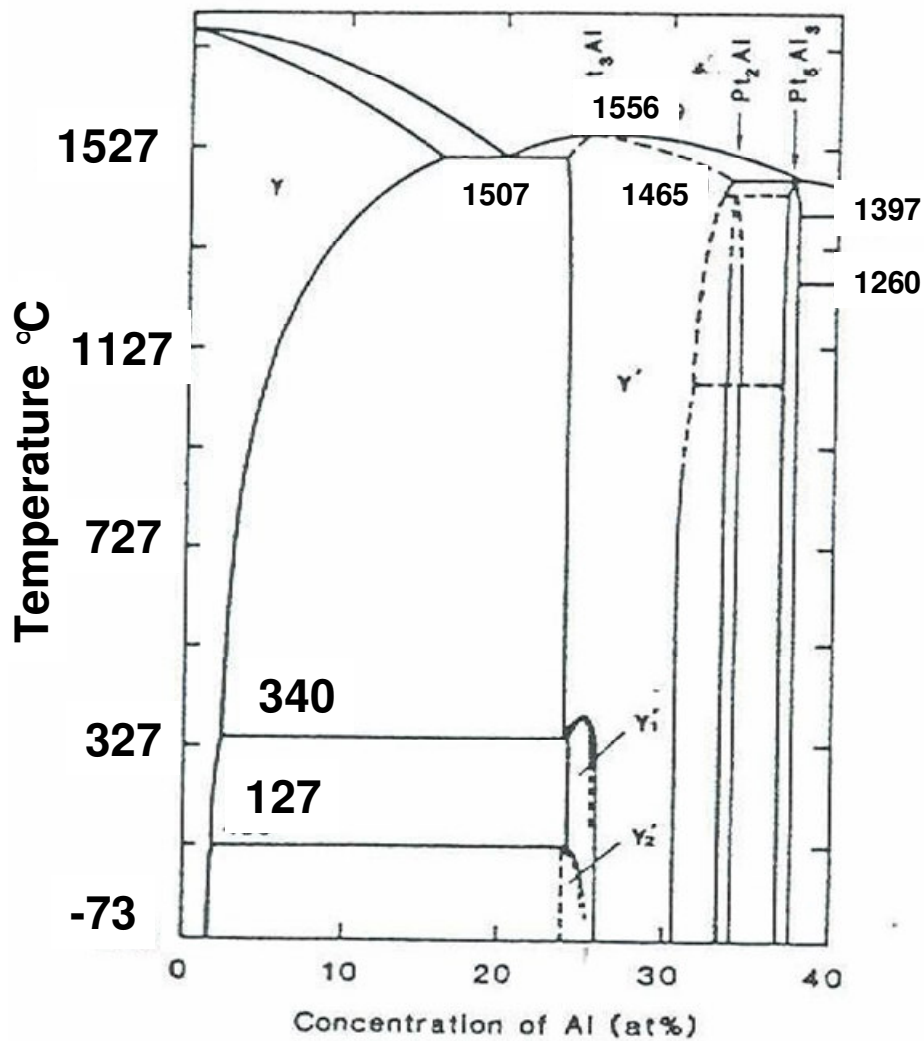


Figure 2.11. Partial Pt-Al phase diagram [1987Oya].

Table 2.1. Pt-Al crystal structure data [1986McA].

Phase	Homogeneity range (at. % Pt)	Space group	Prototype	Reference
(Pt)	83.8 to 100	$Fm\bar{3}m$	Cu	-
Pt ₃ Al	67.3 to 77.7	$Pm\bar{3}m$	AuCu ₃	[1962Bro, 64Huc]
Pt ₃ Al [LT]	74 to 78	P_4/mbm	Pt ₃ Ga(l)	[1975Cha1]
Pt ₂ Al (LT)	66 to 67	$Pmma$	Pt ₂ Ga(LT)	[1976Cha]
Pt ₂ Al	66 to 67	$Pnma$	PbCl ₂	[1975Cha1]
Pt ₅ Al ₃	61.5 to 63	$Pbam$	Ge ₃ Rh ₅	[1964Huc]
β	51 to 56	$Pm\bar{3}m$	CsCl	[1978Bha]
PtAl	50	$p2_13$	FeSi	[1956Sch, 1963 Fer]
Pt ₂ Al ₃	40	$P3m1$	-	[1978Bha]
PtAl ₂	31.5 to 33.5	$Fm\bar{3}m$	CaF ₂	[1937Zin, 1963Fer, 1982Ell]
Pt ₈ Al ₂₁	27	14 ₁ a	-	[1968Eds, 1982Ell]
Pt ₅ Al ₂₁	19.2	-	-	[1964Huc, 1980Pia]
(Al)	~0	$Fm\bar{3}m$	Cu	[Pearson2]

Table 2.2. Pt-Al lattice parameter data, measurements made at 25°C except for β at 1340°C [1986McA].

Phase	Unit cell dimensions (nm)					References
	at. % Pt	Structure	a	b	c	
(Pt)	88.0	fcc	0.39	-	-	[1979Sch]
Pt ₃ Al(LT)	74.0	Pt ₃ Ga	0.55	-	0.781	[1975Cha1]
Pt ₃ Al	72.8	AuCu ₃	0.39	-	-	[1962Bro]
Pt ₂ Al (LT)	66.6	Pt ₂ Ga (LT)	1.63	0.392	0.544	[1976Cha]
β	53.0	Cubic CsCl	0.31	-	-	[1978Bha]
PtAl	50	cubic B20	0.49	-	-	[1956Sch]
Pt ₂ Al ₃	40	hexagonal Al ₃ Ni ₂	0.42	-	0.52	[1963Fer]
PtAl ₂	-	cubic CaF ₂	0.60	-	-	[1937Zin]
Pt ₈ Al ₂₁	27	tetragonal	1.30	-	1.07	[1968Eds]
Pt ₅ Al ₂₁	19.2	cubic	1.92	-	-	[1964Huc]
(Al)	0	fcc	0.405	-	-	[Pearson2]

Table 2.3. Comparison of the reactions of the Pt-Al Phase Diagrams [1986McA, 1987Oya].

Reaction	Compositions of the respective phases			T(°C) [1986McA]	T (°C) [1987Oya]	Reaction type
$L + Pt_3Al \leftrightarrow Pt_5Al_3$	62.3	67.3	62.5	1465	1465	Peritectic
$L + PtAl \leftrightarrow \beta$	50	53.7	51.5	1510	-	Peritectic
$\beta \leftrightarrow PtAl + Pt_5Al_3$	54.2	50	61.5	1260	-	Eutectoid
$L \leftrightarrow \beta + Pt_5Al_3$	55.7	57.9	66.5	1397	-	Eutectic
$Pt_2Al \leftrightarrow Pt_2Al$ (LT)	-	67	-	1060	1050	Solid state
$Pt_5Al_3 + Pt_3Al \leftrightarrow Pt_2Al$	62.7	67	67.5	1430	1433	Peritectoid
$Pt_3Al \leftrightarrow Pt_3Al$ (LT) + (Pt)	77.7	77	87	1280	340	Eutectoid
$Pt_3Al \leftrightarrow Pt_3Al$ (LT)	-	76.5	-	1290	386	Displacive
$L \leftrightarrow Pt_3Al$		73.2		1556	1556	Congruent
$L \leftrightarrow Pt_3Al + (Pt)$	79.5	76.4	85.7	1507	1507	Eutectic
$L \leftrightarrow (Pt)$	100			1769	1762	Melting point
$L \leftrightarrow PtAl$	-	50	-	1554	-	Congruent
$L + PtAl_2 \leftrightarrow Pt_8Al_{21}$	18.8	32.6	27.5	1127	-	Peritectic
$Pt_2Al \leftrightarrow Pt_2Al$ (LT)	-	67	-	1060	-	Solid state
$L + Pt_8Al_{21} \leftrightarrow Pt_5Al_{21}$		27.5	19.2	806		Peritectic
$L \leftrightarrow Pt_5Al_{21} + (Al)$	0.4	0	19.2	657	-	Eutectic
$L \leftrightarrow Pt_2Al_3$	40	-	-	1527	-	Congruent
$L \leftrightarrow Al$	0	-	-	660.5	-	Melting point

2.5.2 (Pt) phase

The Pt-rich end of the Pt-Al phase diagram has a terminal solid solution (Pt) which has an fcc (Cu prototype) structure [1964Huc]. At 1510°C, 14 at.% Al dissolves in the platinum solid solution [1964Huc, 1970Dar], 10 at.% Al dissolves at 1200°C [1962Bro] and 5 at.% Al dissolves at 300°C [1979Sch]. Platinum was reported to react exothermally with aluminium [1970Dar].

2.5.3 Pt₃Al phases

In the two conflicting phase diagrams (McAlister and Kahan [1986McA] (Figure 2.9) and Oya and Mishima [1987Oya] (Figure 2.11)), the major differences are the phase transformation temperatures for cubic to tetragonal Pt₃Al and the number of types of the Pt₃Al phases. McAlister and Kahan [1986McA] reported one transformation for the Pt₃Al phase: a high-temperature cubic Pt₃Al (γ') to a tetragonal low-temperature variant (γ'_2) at 1280°C. However, Oya and Mishima [1987Oya] reported the transformation of cubic Pt₃Al to

tetragonal Pt_3Al ($\gamma' \rightarrow \gamma'_1$) at 340°C , and an additional transformation $\gamma'_1 \rightarrow \gamma'_2$ ($\text{DOc} \rightarrow \text{DO}'\text{c}$) at 127°C . The consecutive transformations $\gamma' \rightarrow \gamma'_1 \rightarrow \gamma'_2$ ($\text{L1}_2 \rightarrow \text{DOc} \rightarrow \text{DO}'\text{c}$) are martensitic in nature as shown in Figure 2.12. Bronger and Klemm [1962Bro] suggested the ordered phase transformation of Pt_3Al at temperatures below 1300°C in the duplex region by the reaction between Pt_3Al and the primary solid solution, and this finding was confirmed by Geux and Feschotte [1976Geu].

The high temperature cubic $\text{L1}_2 \text{Pt}_3\text{Al}$ has an ordered fcc structure of AuCu_3 type ($a = 0.3876$ nm), with a space group of $Pm\bar{3}m$ (Table 2.1) [1962Bro, 1964Huc]. This cubic Pt_3Al phase has a solubility range of 67.3 at.% Pt to 77.7 at.% Pt (Table 2.1) [1962Bro, 1964Huc]. The L1_2 phase melts congruently at 1556°C [1964Huc, 1976Geu]. Cubic Pt_3Al forms a eutectic at 1507°C with (Pt) (Table 2.3).

The lower temperature tetragonal Pt_3Al phase was reported to have a DOc lattice ($a = 0.5459$ nm, $c = 0.7806$ nm), with a distorted fct structure contained within the DOc lattice (Figure 2.13); and a solubility range of 74 at.% Pt to 78 at.% Pt (Table 2.1). A space group of $P4/m\bar{b}m$, based on the Pt_3Ga , was reported, although there is a resemblance with the space group of the $I_4/m\bar{c}m$ and prototype Ir_3Si , and the Pt_3Ga lattice was reported to be a more primitive lattice (Table 2.1) [1962Bro, 1975Cha, 1985Vil].

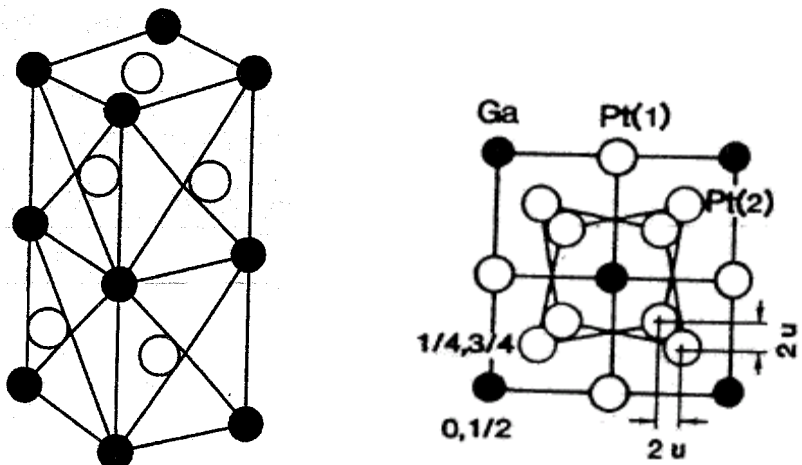
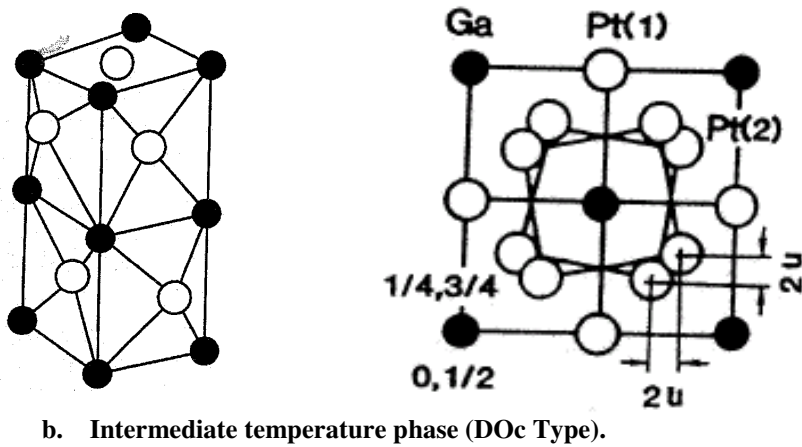
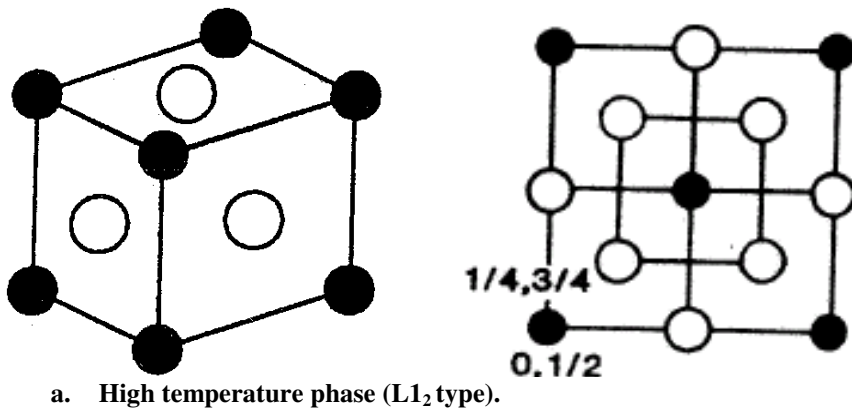


Figure 2.12. High, intermediate and low temperature crystal structures of Pt_3Al phases ($L1_2$, DOc and DOc') shown as viewed along the $\langle 001 \rangle$ [1987Oya].

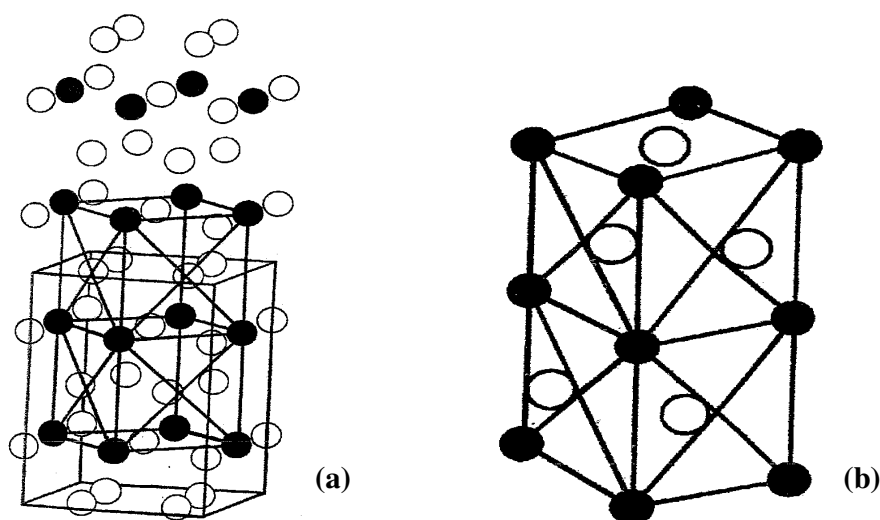


Figure 2.13. (a) The DOc' unit cell of the Pt_3Al tetragonal structure (low temperature), contains a distorted fct lattice, also shown in (b). The Pt atoms (white) lie offset from the centre of the faces and the Al atoms (black) sit at the corners of the cell. In (b) for clarity, only the Pt atoms on the top and front faces are shown [1987Oya].

DTA results showed that the cubic Pt_3Al phase (γ') which exists with the (Pt) is stable to at least above 600°C and γ'_2 is stable between $\sim 600^\circ\text{C}$ and $\sim 400^\circ\text{C}$, as shown in Figure 2.14 [1987Oya]. The DTA results by Oya and Mishima [1987Oya] showed that the intermediate phase (γ'_1) is stable over a narrow composition range ($10 < x < 25$ at.% Al) and under a small temperature interval ($> 600^\circ\text{C}$) as shown in Figure 2.14. The tetragonal Pt_3Al phase reacts with the primary solid solution to form a eutectoid reaction at 1280°C (Table 2.3) [1964Huc, 1970Dar]. Phase analyses showed that Pt_3Al phase boundary narrows with decreasing temperature (Figures 2.7, 2.8, 2.9 and 2.11).

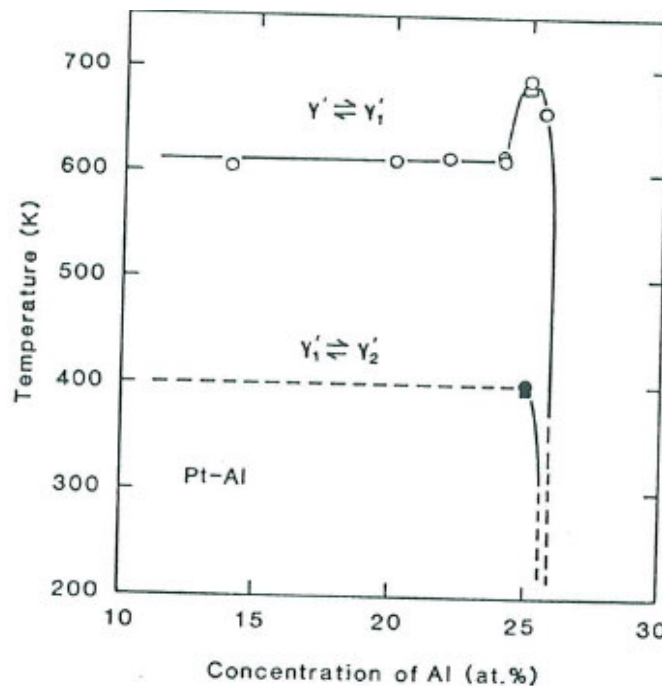


Figure 2.14. Composition dependence of the transformation temperatures of $\gamma' \rightarrow \gamma_1'$ and $\gamma_1' \rightarrow \gamma_2'$ in Pt-Al alloys, circle marks were obtained by DTA and square marks by dilatometry [1987Oya].

Biggs [2001Big] derived a method to differentiate between the two forms of Pt_3Al and (Pt), using the peak splitting of the tetragonal phase. This is shown as a flow chart in Figure 2.15.

Douglas, Neethling, Santamarta, Schryvers and Cornish [2003Dou] suggested a tetragonal unit cell (mD0'c) with c-axis 1.5 times the D0'c unit cell at 1350°C as shown in Figure 2.16, which is contrary to the previously published results [1986McA, 2000Hil]. A TEM micrograph showing a Pt_3Al precipitate containing a number of stacked plates, which is the characteristic of alloys undergoing a martensitic transformation, in a (Pt) solid solution matrix is shown in Figure 2.17. Recent work [2006Dou], using *in situ* heating in a TEM, reported the Oya *et al.* diagram [1987Oya] to be more correct, with the resulting transformation of Pt_3Al phase at much lower temperatures than reported by McAlister and Kahan [1986McA]. However, workers on a parallel project in Germany [2004Wen] showed better agreement with McAlister and Kahan [1986McA]. Thus, there is a possibility that very minor impurities are responsible since the platinum comes from different sources [2006Cor].

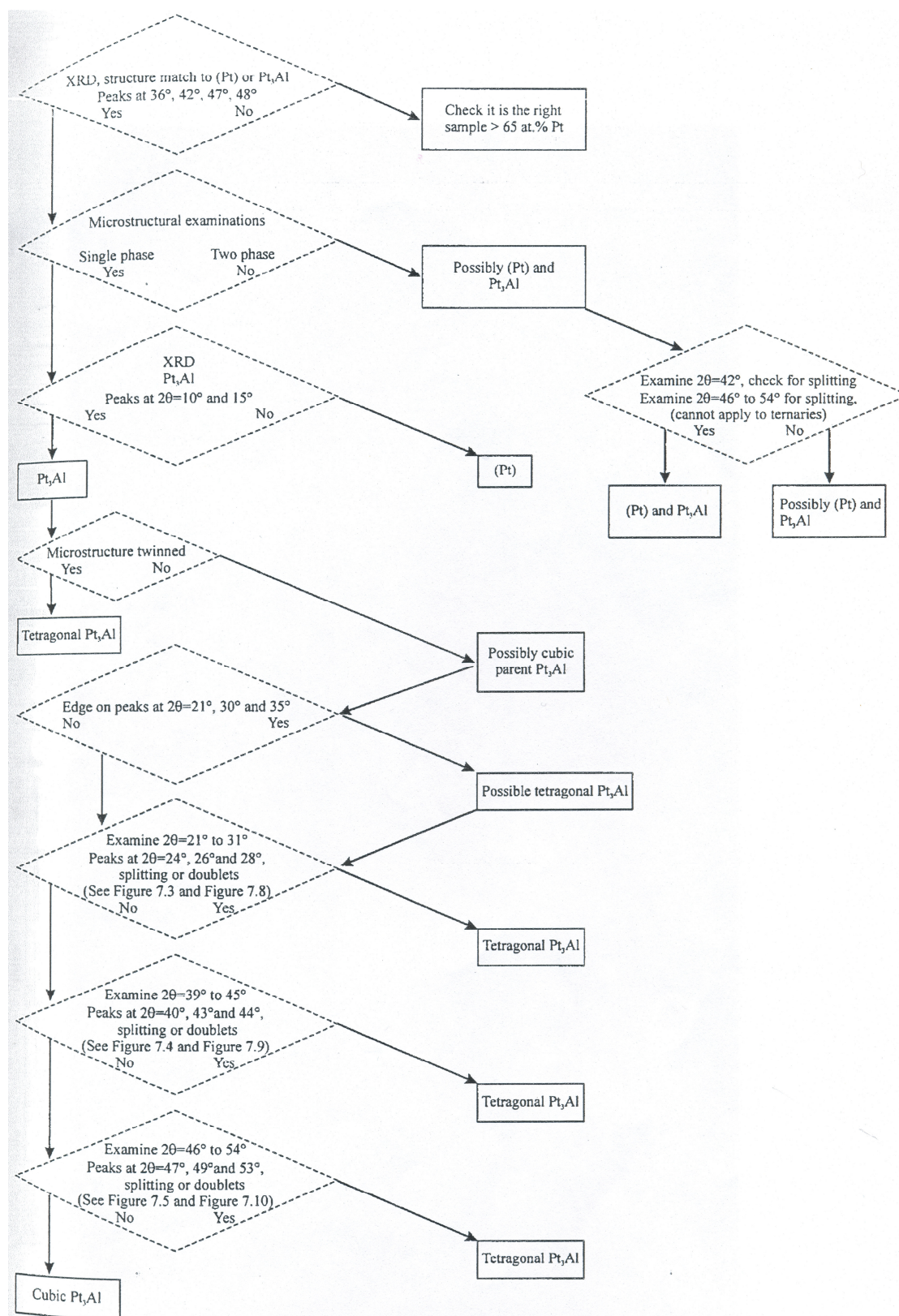


Figure 2.15. Methodology for distinguishing between the two forms of Pt₃Al and platinum solid solution phases [2001Big].

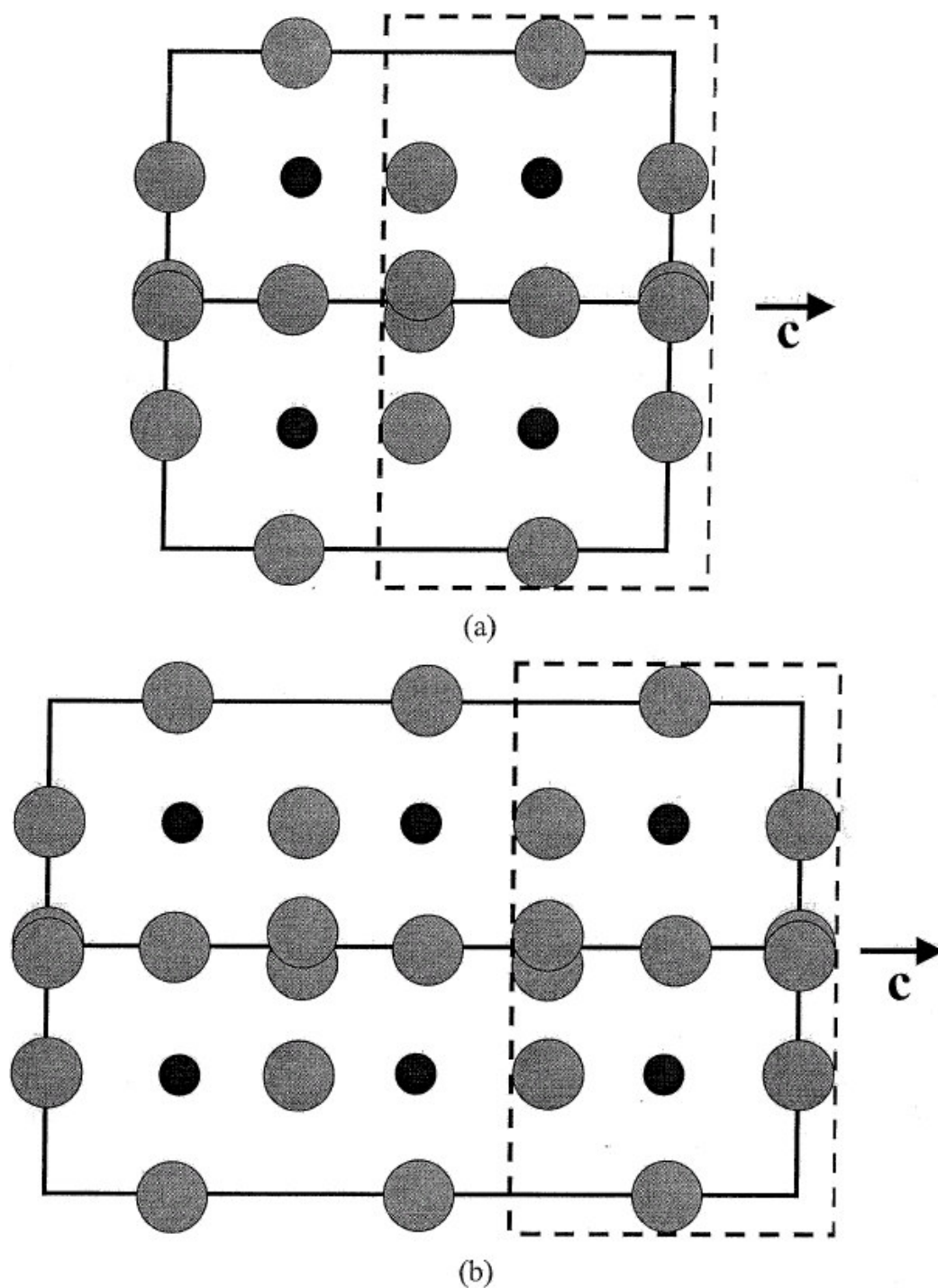


Figure 2.16. (a) Unit cell of the D0'c structure, (b) unit cell of the modified D0'c (mD0'c) unit cell [2003Dou].

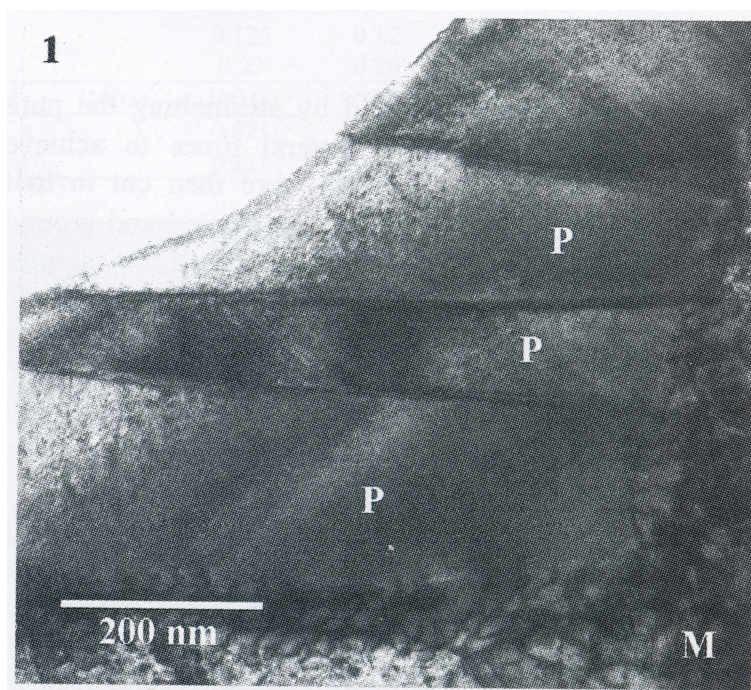


Figure 2.17. Bright- field TEM micrograph of a typical Pt₃Al precipitate, containing a number of stacked plates (P), characteristic of alloys undergoing a martensitic transformation in a (Pt) solid solution matrix (M) [2003Dou].

2.5.4 Pt₂Al phase

Chattopadhyay and Schubert [1975Cha1, 1976Cha], and Chatterji, Decries and Fleischer [1975Cha2] reported two crystal variants of Pt₂Al: a high-temperature variant with a PbCl₂ structure and a low-temperature variant with a low-temperature Pt₂Ga structure (Table 2.1). Both variants have a solubility range of 66 to 67 at.% Pt. The transformation of the high temperature to low temperature Pt₂Al phase was reported by Chattopadhyay and Schubert [1975Cha1, 1976Cha], and Chatterji *et al.* [1975Cha2] at 1060°C, although the nature of the transformation was not known. The unit cell parameters of the Pt₂Al phases were reported by Chattopadhyay and Schubert [1976Cha], and vary between high and low-temperature conditions (Table 2.2). However, these results contradicted the work of Guex and Feschotte [1976Gue], who found no evidence of the existence of Pt₂Al phase (Figure 2.8). Subsequent work by Biggs [2001Big1] and Biggs, Hill, Cornish and Witcomb [2001Big2] confirmed the presence of the Pt₂Al phase in the Pt₃Al matrix of the 68.8 at.% Pt sample, as shown in Figure 2.18.

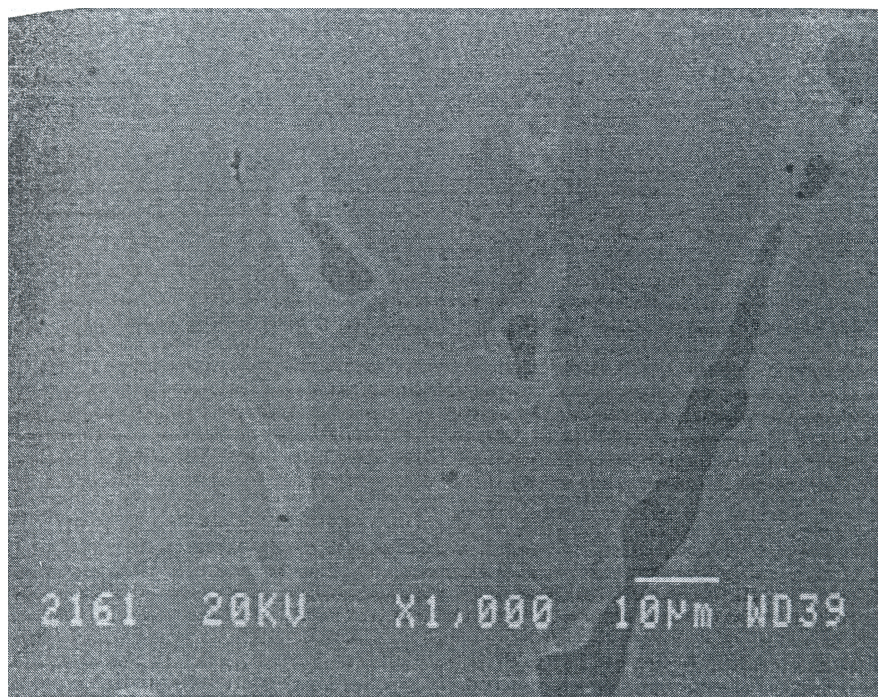


Figure 2.18. Scanning electron micrograph, backscattered mode, showing the 68.8 at.% Pt–Al sample, arc-melted, OPS polished: grey matrix (Pt₃Al phase, 69 at.% Pt) and dark phase with a white halo (Pt₂Al, 66.2 at.% Pt) [2001Big].

2.5.5 Pt₅Al₃ phase

Pt₅Al₃ is a rhombohedral phase of Rh₅Ge₂-type with a solubility range of 61.5 to 63 at.% Pt [1964Huc] (Table 2.1). At 62.5 at.% Pt, Pt₃Al reacts peritectically to form Pt₅Al₃ at 1465°C [1986McA, 1987Oya] (Table 2.3). McAlister and Kahan reported a peritectoid reaction between Pt₃Al + Pt₅Al₃ which forms Pt₂Al at 1430°C and 67.5 at.% Pt [1986McA], while Oya and Mishima [1987Oya] reported it at 1433°C (Table 2.3).

Prins, Cornish and Boucher [2005Pri] confirmed the presence of Pt₅Al₃ from the β -phase decomposition according to the reaction: $\beta \rightarrow \text{PtAl} + \text{Pt}_5\text{Al}_3$ in ternary alloys.

2.5.6 The β -phase

Thermodynamically plausible curvatures of the $\beta/\beta + L$ and $\beta/\beta + \text{Pt}_5\text{Al}_3$ boundaries and the peritectic reaction ($L + \text{PtAl} \rightarrow \beta$) were previously reported by Chouriguine [1912Cho1, 1912Cho2]. The β -phase was observed metallographically by Chattopadhyay and Schubert [1975Cha1], and Bhan and Kudielka [1978Bha] as a cubic CsCl type phase, stable above 1260°C, with a solubility range of 51 to 56 at.% Pt (Table 2.1). The eutectic ($L \rightarrow \beta + \text{Pt}_3\text{Al}_5$) which occurs at about 54 at.% Pt and 1397°C, and a eutectoid ($\beta \rightarrow \text{PtAl} + \text{Pt}_3\text{Al}_5$) which occurs at 1260°C between 50 to 60 at.% Pt were reported by Huch and Klemm [1964Huc] (Table 2.3). However, McAlister and Kahan [1986McA] regarded the β -phase as uncertain. Prins *et al.* [2005Pri] confirmed the existence of the β -phase in the Al-Pt-Ru ternary for an alloy of $\text{Al}_{42}:\text{Pt}_{56}:\text{Ru}_2$ (at.%) composition, and showed it decomposed to $\sim\text{PtAl}$ and $\sim\text{Pt}_5\text{Al}_3$ as shown in Figure 2.19. This is important, because if a binary phase exists in the ternary it also has to exist in the binary.

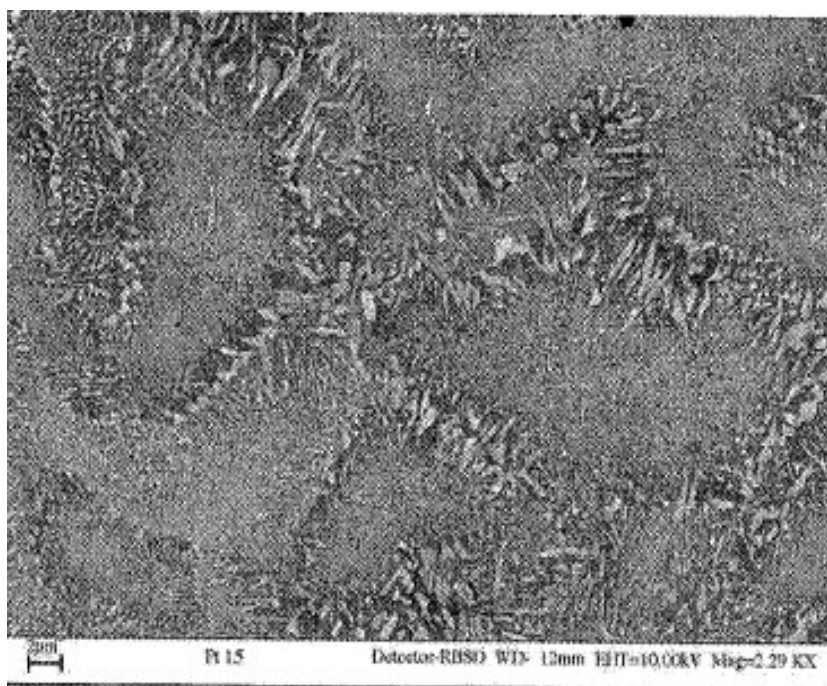


Figure 2.19. SEM image in backscattered mode of $\text{Al}_{42}:\text{Pt}_{56}:\text{Ru}_2$ (at.%) showing the varying morphology for eutectic (coarser) and prior dendritic (finer) regions: Pt_5Al_3 (light) and PtAl (dark) [2005Pri].

2.5.7 PtAl phase

PtAl was reported to have a cubic B20 and FeSi structure, a composition of 50 at.% Pt and a congruent melting point at 1554°C [1956Sch, 1963Fer] (Tables 2.1, 2.3). A eutectoid reaction of $\beta \rightarrow \text{PtAl} + \text{Pt}_3\text{Al}_5$ at 1260°C was reported by Huch and Klemm [1964Huc] as mentioned above.

2.5.8 Pt₂Al₃

The Pt₂Al₃ phase has a structure related to hexagonal Al₃Ni₂, with lattice parameters of $a = 0.42$ nm and $c = 0.52$ nm, and a 40 at.% Pt composition [1963Fer] (Tables 2.1, 2.2). Pt₂Al₃ melts congruently at 1527°C [1964Huc]. This phase was identified by Huch and Klemm [1964Huc], who used thermal analysis, metallographic, X-ray diffraction (XRD) and density measurements. Prins *et al.* [2005Pri] reported the presence of Pt₂Al₃ phase as part of the eutectic reaction of: $L \rightarrow \text{PtAl} + \text{Pt}_2\text{Al}_3$ in the ternary alloy of Al₅₂:Pt₄₀:Ru₈ (at.%) composition, as shown in Figure 2.20.

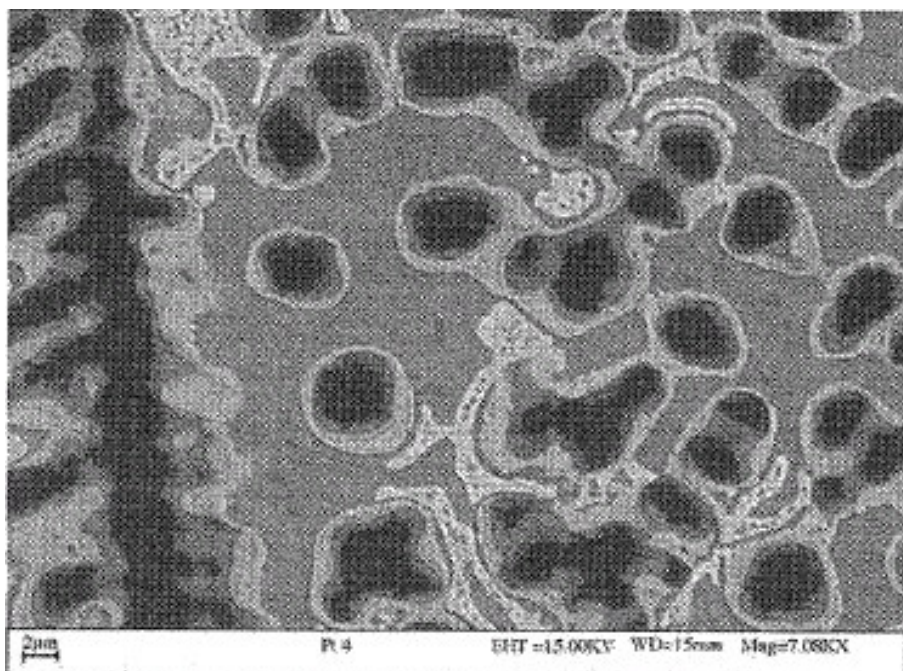


Figure 2.20. SEM image in backscattered electron mode of Al₅₂:Pt₄₀:Ru₈ showing RuAl (dark), PtAl (light) and Pt₂Al₃ (medium) [2005Pri].

2.5.9 PtAl₂

PtAl₂ is of cubic CaF₂ type [1937Zin] (Table 2.1), with the lattice parameter of $a = 0.599$ nm, and a solubility range of 31.5 to 33.5 at.% at 850°C [1937Zin, 1963Fer, 1982Ell] (Table 2.2). Huch and Klemm [1964Huc] used thermal analysis, metallographic, X-ray diffraction (XRD) and density measurements, to confirm the presence of this phase. Prins *et al.* [2005] reported the presence of the PtAl₂ phase, observed as part of the peritectic reaction ($L + \text{RuAl}_2 \rightarrow \text{PtAl}_2$) in the Al₆₂:Pt₆:Ru₃₂ (at.%) alloy as shown in Figure 2.21.

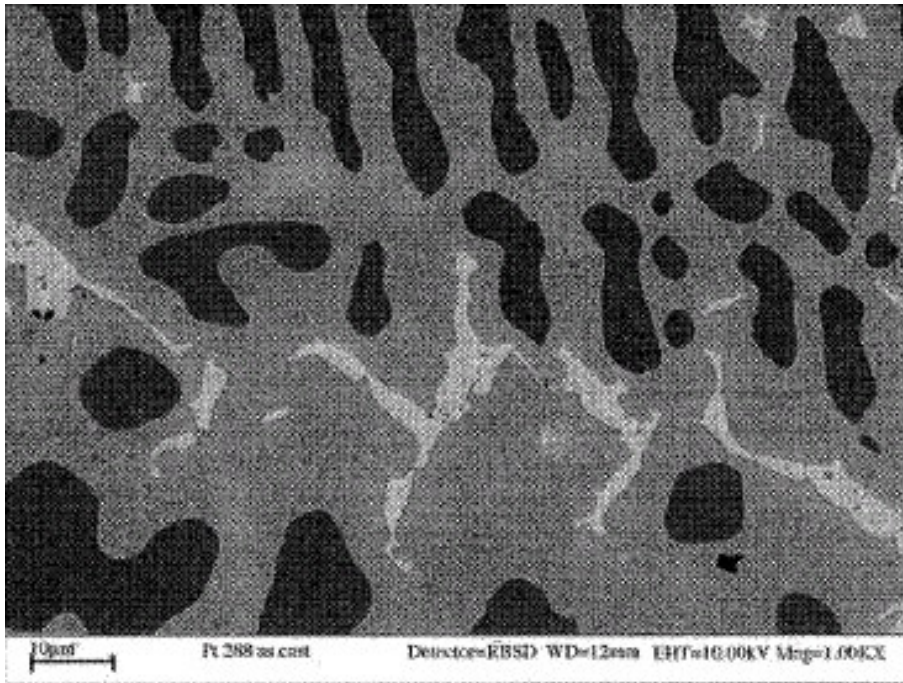


Figure 2.21. SEM image in the backscattered electron mode of Al₆₂:Pt₆:Ru₃₂ showing RuAl (dark), RuAl₂ (medium contrast) and lastly very irregular light patches of PtAl₂.

2.5.10 Pt₈Al₂₁

Pt₈Al₂₁ has a tetragonal crystal structure (Table 2.1) with lattice parameters of $a = 1.30$ nm and $c = 1.07$ nm [1968Eds], and a composition of 27 at.% Pt [1968Eds, 1982Ell] (Table 2.2).

2.5.11 Pt₆Al₂₁

This phase is not included on the phase diagram of McAlister and Kahan [1986McA]. Piatti and Pellegrini [1980Pia] reported the hyper-eutectic hexagonal Pt₆Al₂₁ phase, after metallographic, density measurements and X-ray diffraction at 657°C, as a metastable phase. It was identified as metastable phase because a slow, but significant, transformation from hexagonal to cubic Pt₅Al₂₁ (which is the phase in equilibrium with Al at the eutectic reaction ($L \rightarrow (Al) + Pt_5Al_{21}$) composition) over a period of several hours at 200°C was found [1980Pia].

2.5.12 Pt₅Al₂₁

On the basis of XRD and density studies, Huch and Klemm [1964Huc] identified the cubic Pt₅Al₂₁ phase, and this finding was confirmed by the metallographic, density studies and X-ray diffraction of Piatti and Pellegrini [1980Pia]. Pt was reported to be practically insoluble in (Al), therefore a eutectic mixture of $L \rightarrow (Al) + Pt_5Al_{21}$ with the composition of 0.1 at.% Pt at 657°C in the as-quenched alloys was reported to occur [1974Ton] (Table 2.3). The Pt₅Al₂₁ has a composition of 19.2 at.% Pt (Table 2.1).

2.5.13 (Al) phase

Aluminium is face centred cubic with a lattice parameter of $a = 0.405$ nm (Table 2.2) [1964Huc]. Huch and Klemm [1964Huc] reported that there was no homogeneous solid solution obtained in the 2 at.% Pt alloy, as platinum appeared to segregate rapidly to the interdendritic areas of the solidifying film. Therefore, the solubility of Pt in (Al) was negligible (Figure 2.6) [1964Huc], and this finding was confirmed by Piatti and Pellegrini [1980Pia].

2.5.14 Calculated diagrams

Wu and Jin [2000Wu] performed an assessment on the Pt-Al binary phase diagram using the CALPHAD method (Figure 2.22). The calculated phase diagram showed a good fit to the liquidus and solidus when compared with the experimental data from Huch and Klemm [1964Huc], Darling *et al.* [1970Dar] and Schubert [1978Sch] (Figure 2.23). The calculated [2000Wu] and experimental results [1964Huc] of the invariant equilibria are compared in Table 2.4. However, Wu and Jin [2000Wu] showed only one Pt₃Al phase and ignored the lower temperature phases, therefore they did not reflect the ordering transformations. They also did not include the Pt₂Al and the β -phase owing to the lack of experimental data.

Table 2.4. Comparison of calculated and experimental invariant reactions in Al-Pt system [2000Wu].

Reaction	Comparisons of respective phases (at.% Pt)			(°C)	Ref
$L \rightarrow Pt_3Al + (Pt)$	79.5	76.4	85.7	1780	[1964Huc]
	80.1	76.6	82.1	1775	[2000Wu]
$L \rightarrow Pt_3Al_2 + PtAl$	44.7	40	50	1741	[1964Huc]
	44.1	39.9	50	1766	[2000Wu]
$L + Pt_3Al \rightarrow Pt_5Al_3$	62.3	67.3	62.5	1738	[1964Huc]
	62.4	64.2	62.5	1736	[2000Wu]
$L \rightarrow PtAl + Pt_5Al_3$	58.2	50	62.5	1695	[1964Huc] [2000Wu]
$L + Pt_3Al_2 \rightarrow PtAl_2$	31.8	40	33.3	1679	[1964Huc]
	31.2	39.9	33.3	1677	[2000Wu]
$L + PtAl_2 \rightarrow Pt_8Al_{21}$	18.8	32.6	27.5	1400	[1964Huc]
	17.5	33.3	27.6	1400	[2000Wu]
$L + Pt_8Al_{21} \rightarrow Pt_5Al_{21}$	3.1	27.5	19.2	1079	[1964Huc]
	5	27.6	19.2	1082	[2000Wu]
$L \rightarrow (Al) + Pt_5Al_{21}$	0.4	0	19.2	930	[1964Huc]
	0.7	0	19.2	928	[2000Wu]
$L \rightarrow Pt_3Al$	73.2	73.2	-	1829	[1964Huc]
	74.2	74.2	-	1835	[2000Wu]
$L \rightarrow PtAl$	50	50	-	1827	[1964Huc]
	50	50	-	1826	[2000Wu]
$L \rightarrow Pt_2Al_3$	40	40	-	1800	[1964Huc]
	40	40	-	1795	[2000Wu]

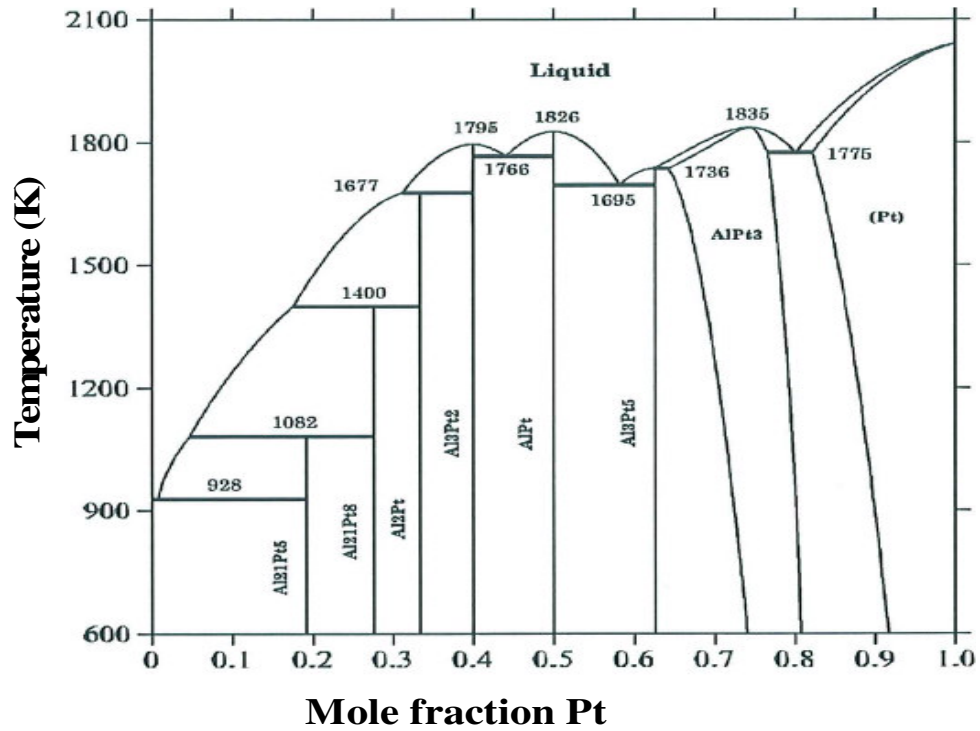


Figure 2.22. Calculated Pt-Al phase diagram [2000Wu].

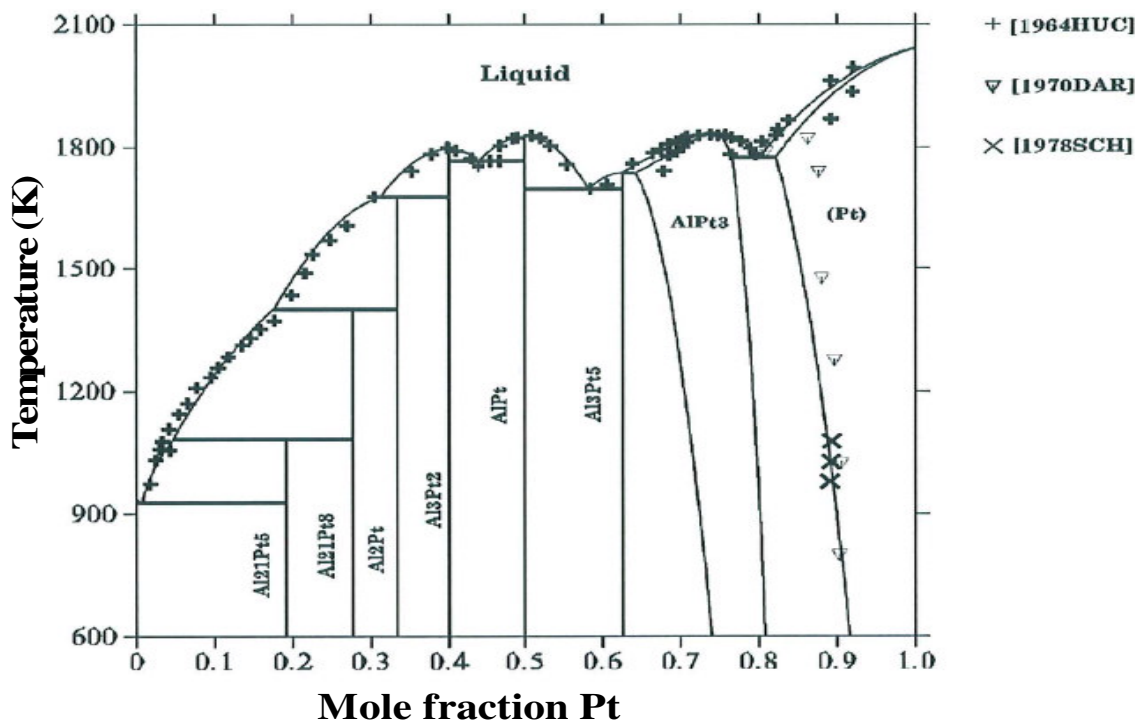


Figure 2.23. Comparison of the calculated [2000Wu] and experimental Pt-Al phase diagrams from [1964Huc, 1970Dar, 1978Sch].

Therefore, Prins and Cornish [2002], Prins, Sundman, Cornish and Stumpf [2003Pri], Prins [2004Pri] and Prins *et al.* [2005Pri] undertook a reassessment in order to include:

- ordering behaviour of Pt_3Al ,
- existence of the β -phase and
- the existence of the Pt_2Al phases.

All the phases except for Pt_3Al were modelled as stoichiometric line compound phases; and Pt_3Al phase was described using the four-sublattice compound energy formalism (4SL CEF) which was suggested by Sundman [1998Sun] to treat the order-disorder relation in fcc structures (Al and L_{12}) (Figure 2.23).

The calculated compositions and temperatures of the invariant reactions for the intermetallic phases were found to be in general good agreement with those reported experimentally. However, there were some areas in less good agreement, mostly due to the model being used, which required more data than could be provided. These are:

- Pt_3Al phase forms at a too high Pt content due to symmetry of the 4SL CEF model used
- The β phase was modelled as a line compound (for lack of data), and the assumed stoichiometry influenced the equilibria.
- Pt_5Al_3 formed congruently in the calculation [2004Pri] and not by peritectic reaction as observed experimentally [1986McA] (Table 2.5).

The comparison between the optimised phase diagram [2004Pri] and the experimental data from the literature [1986McA] is shown in Figure 2.24. The reactions for PtAl , β and the Pt_2Al phases are enlarged in Figure 2.25.

Table 2.5. Experimental and calculated invariant temperatures and compositions for the Pt-Al system [2004Pri].

Reaction and composition (at.% Pt)	Reaction Temperature[°C]	Reference
L $\leftrightarrow$ Pt ₃ Al + (Pt) 79.5 76.4 85.7 83.7 81.1 99.0	1507 1475	[1986McA] [2004Pri]
PtAl + L $\leftrightarrow$ β 50.0 53.7 51.5 50.0 58.0 52.0	1510 1179	[1986McA] [2004Pri]
L $\leftrightarrow$ Pt ₂ Al ₃ + PtAl 44.47 40.0 50.0 46.7 40.0 50.0	1468 1497	[1986McA] [2004Pri]
L + Pt ₃ Al $\leftrightarrow$ Pt ₅ Al ₃ 62.3 67.3 62.5	1465	[1986McA] [2004Pri]
Pt ₅ Al ₃ + Pt ₃ Al $\leftrightarrow$ Pt ₂ Al 62.7 67.0 67.5 62.5 72.0 66.5	1430 1428	[1986McA] [2004Pri]
L + Pt ₂ Al ₃ $\leftrightarrow$ PtAl ₂ 31.8 40.0 33.3 40.0 40.0 33.3	1406 1398	[1986McA] [2004Pri]
L $\leftrightarrow$ β + Pt ₅ Al ₃ 55.7 57.9 66.5 58.0 52.0 62.5	1397 1450	[1986McA] [2004Pri]
β $\leftrightarrow$ PtAl + Pt ₄ Al ₃ 54.2 50.0 61.5 52.0 50.0 62.5	1260 1260	[1986McA] [2004Pri]
L + PtAl ₂ $\leftrightarrow$ Pt ₈ Al ₂₁ 18.8 32.6 27.5 30.0 33.3 27.5	1127 1131	[1986McA] [2004Pri]
L + Pt ₈ Al ₂₁ $\leftrightarrow$ Pt ₅ Al ₂₁ 3.1 27.5 19.2 9.0 27.5 19.2	806 827	[1986McA] [2004Pri]
L $\leftrightarrow$ (Al) + Pt ₅ Al ₂₁ 0.4 0.0 19.2 4.0 3.0 19.2	657 637	[1986McA] [2004Pri]
L $\leftrightarrow$ Pt ₃ Al 73.2 73.2 75.3 75.3	1556 1604	[1986McA] [2004Pri]
L $\leftrightarrow$ PtAl 50.0 50.0 50.0 50.0	1554 1554	[1986McA] [2004Pri]
L $\leftrightarrow$ Pt ₂ Al ₃ 40.0 40.0 40.0 40.0	1527 1527	[1986McA] [2004Pri]
L $\leftrightarrow$ Pt ₅ Al ₃ 62.5 62.5	1527	[2004Pri]

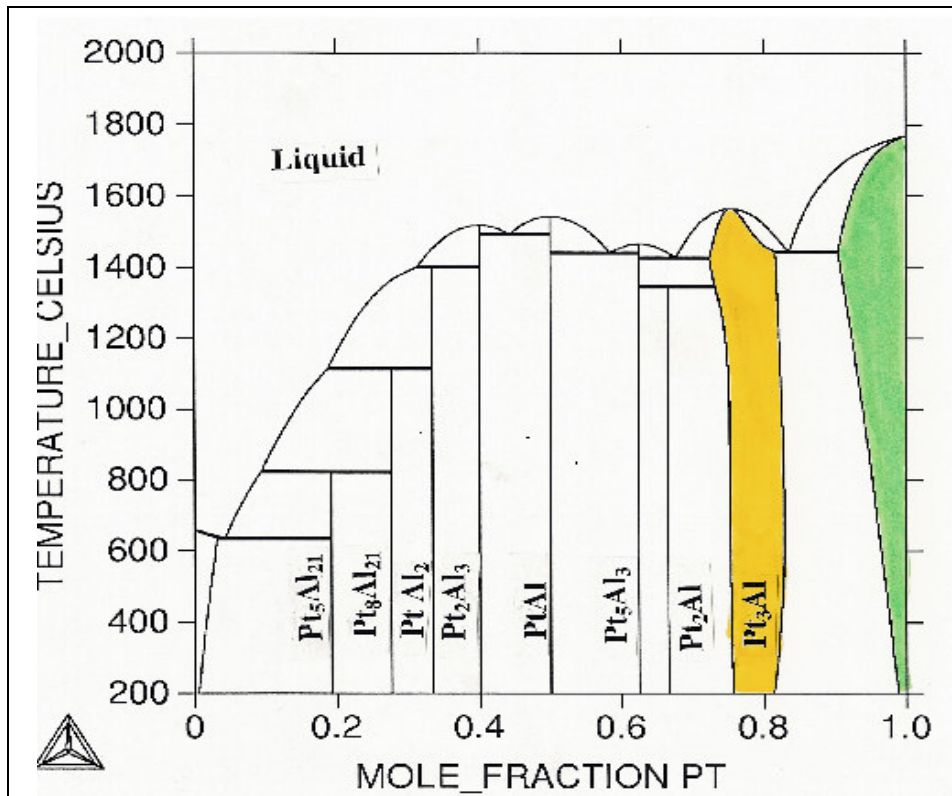


Figure 2.24. Calculated Pt-Al phase diagram [2004Pri].

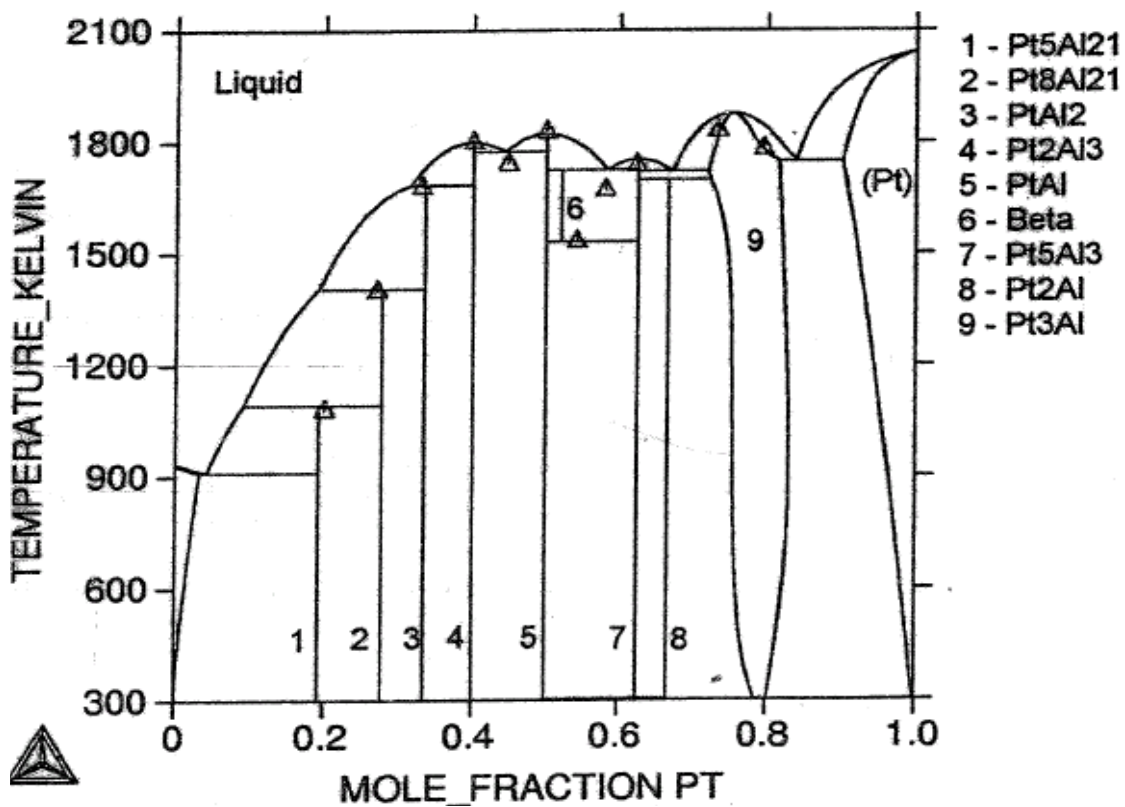


Figure 2.25. Calculated Al-Pt phase diagram compared with experimental invariant data points from the literature [1986McA, 2004Pri].

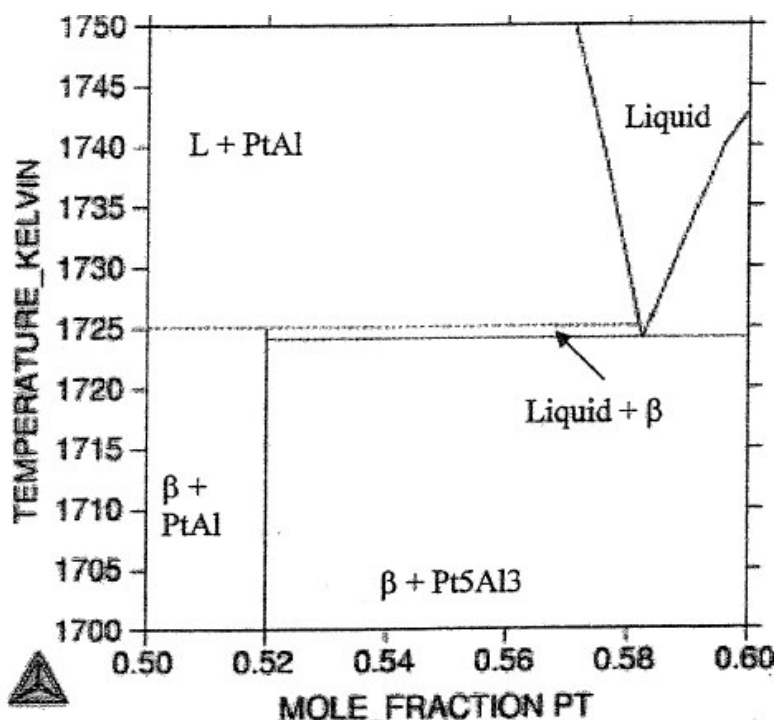


Figure 2.26. Partial Pt-Al binary system showing the reactions for the PtAl, β and Liquid phases [2004Pri].

Aim of this work

The aim of the current work is to make a comprehensive description of all relevant phases, and to clarify the phase boundaries of the phases: (Pt), Pt_3Al (all temperature versions), Pt_2Al (both phases), β and $\text{Pt}_5\text{Al}_{21}$. Also the reaction temperatures of the transformations of Pt_3Al and Pt_2Al needed to be verified. The formation temperature of PtAl_2 and β needed to be confirmed, as did the eutectoid decomposition of β . $\text{Pt}_5\text{Al}_{21}$ is shown as a line compound with uncertainty; this needed to be resolved. In order to do this, sample compositions were targeted as: 81.5, 75, 72, 67, 64, 53.5, 51, 24, 16 at.% Pt. Mintek's new Nova NanoSEM facilitated this work, since there was higher resolution.

3 EXPERIMENTAL PROCEDURE

3.1 Sample manufacture

The aluminium and platinum elements were 99.9 % purity, attained in the solid form. The alloy samples were made from the two elements, by adding them together in the targeted amounts, then melting them in a button-arc furnace under argon and Ti oxygen getter, on a water-cooled copper hearth. The samples were turned at least three times for improved homogeneity. Most actual compositions of the samples were close to the required compositions. Since the samples solidified on a water-cooled hearth, the dendrites grew away from the hearth, resulting in a preferred orientation in that growth direction. This affected the peak intensities in XRD.

3.2 Heat treatment

Samples were cut into halves using Secotom-10 cutting wheel with technilube (coolant) as a lubricant. Half a button for each composition was examined in the as-cast condition, while the rest of the samples were heat treated at respective temperatures. The heat treatment range was from 600°C to 1500°C for 1000 hours followed by a water quench. All the samples were examined metallographically.

3.3 Metallographic preparation

The samples were mounted in conducting bakerlite and ground to 1200 grit on SiC paper. Polishing was done using RotoPol-11 machine OPS-polishing. The aim of this polishing was to remove as much crystal damage (resulting from mechanical polishing) as possible from the surface of the sample.

3.4 Scanning electron microscopy (SEM-EDS)

A JOEL JSM-840A (SEM) equipped with an EDS facility was used to examine samples at higher magnifications, in the backscattered electron mode (BSE) to show atomic number contrast differences, and to measure the compositions of the phases observed. The phase analyses were carried out on polished samples and the results quoted are the average of at least four composition determinations. A Nova-NanoSEM (HRSEM) was also used for higher magnifications in the backscattered electron (BSE) mode in order to obtain a clearer image of the phases observed. Pure Pt and Al were used as the calibration standards.

3.5 X-Ray Diffraction

X-ray diffraction (XRD) analyses were carried out on polished samples (both as-cast and heat treated) using a Siemens Kristalloflex D500 with Mo K-alpha radiation. A scan with a step-size of 0.02° per minute was run from a starting position of $2\theta = 10^\circ$ to $2\theta = 55^\circ$. Spectra were matched with standard spectra from the International Centre for Diffraction Data (ICDD) for the expected phases [2005ICD], and the file references are given in Table 3.1.

3.6 Hardness

The hardness of the alloys was measured using Vickers hardness tester. A 5kg load was used, with at least 5 analyses carried out to obtain an average hardness value, and the dwell time was ~10 seconds. The hardness indentation was studied for the presence of cracks.

Table 3.1. XRD database information for the phases studied [2005ICD] (Cu radiation used).

Element / phase	Crystal structure	Space group	PDF Number	Cell parameters (nm)			Molecular weight	λ
				α	β	γ		
Pt	Fcc-cubic	$Fm\bar{3}m$ (225)	040802	3.9231	-	-	195.09	1.5406
Pt ₃ Al	Cubic	$Pm\bar{3}m$ (221)	657545	3.8775	-	-	612.25	1.5406
Pt ₃ Al	Tetragonal	$P4/mbm$ (127)	481815	5.4485	-	7.8144	612.25	1.5406
Pt ₂ Al	Orthorhombic	$Pnma$ (62)	290069	5.4007	4.0547	7.8985	417.16	1.5406
Pt ₂ Al	Orthorhombic	$Pmma$ (51)	380740	16.297	3.921	5.439	417.16	1.5406
Pt ₅ Al ₃	Orthorhombic	$Pbam$ (55)	651302	5.41	10.7	3.95	1056.39	1.5406
PtAl	Cubic	$P213$ (198)	653299	4.866	-	-	222.07	1.5406
Pt ₂ Al ₃	Hexagonal	$P\bar{3}m1$ (164)	659707	4.209	-	10.35	471.12	1.5406
PtAl ₂	Fcc-cubic	$Fm\bar{3}$ (225)	658551	5.91	-	-	249.05	1.5406
Pt ₈ Al ₂₁	Tetragonal	P (0)	391287	28.84	-	27.11	3313.20	-
Pt ₆ Al ₂₁	Hexagonal	P (0)	351179	13.02	-	9.61	1737.15	1.5406
Al	Fcc-cubic	$Fm\bar{3}m$ (225)	851327	4.0494	-	-	26.98	1.5406

3.6.1 Rationale for the selection of alloy compositions

Nine platinum-aluminium alloys of different chemical compositions were selected, and exposed to different temperature conditions. The compositions were as follows: 81.5 at.% Pt, 75 at.% Pt, 72 at.% Pt, 67 at.% Pt, 64 at.% Pt, 53.5 at.% Pt, 51 at.% Pt, 24 at.% Pt and 16 at.% Pt. The purpose for the selection of the compositions at 81.5 at.% Pt, 75 at.% Pt and 72 at.% Pt was to check the placement of the Pt_3Al phase boundaries, and to find where the Pt_3Al phase transformation is. The 67 at.% Pt and 64 at.% Pt compositions were selected to confirm the existence of Pt_2Al phase, the phase boundaries and the dashed horizontal line at 1060°C . The 53.5 at.% Pt and 51 at.% Pt compositions were selected to confirm the existence of the β -phase, which was reported to form in a peritectic reaction ($\text{L} + \text{PtAl} \rightarrow \beta$) at 1397°C and to decompose in a eutectoid ($\beta \rightarrow \text{PtAl}$ and Pt_5Al_3) at 1260°C . The purpose for the selection of the 24 at.% Pt and 16 at.% Pt compositions was to confirm the existence of the $\text{Pt}_5\text{Al}_{21}$ in the aluminium-rich side of the Pt-Al system [1986McA].

4 RESULTS

4.1 Accuracy and reliability of analytical techniques

One of the regions of interest on the Pt-Al phase diagram has phases of small width very close together. In some instances when the minor phase was present, it was only possible to do fewer analyses than the usual five as there were not always sufficient large areas of the phase. In many circumstances, a phase had dark precipitates evenly distributed throughout the sample, and the analysis collected X-rays from the surrounding phases, thus the analyses of phases in such circumstances were not accurate. The phase descriptions are given for observations in the backscattered electron mode.

An HRSEM with EDS was used to analyse the samples, and the EDS analyses were done at room temperature. One challenge with this system was that aluminium evaporated during the high temperature heat treatments because of its high vapour pressure, and it was confirmed by the data scatter in EDS measurements. The XRD also confirmed the presence of aluminium oxide in some of the samples. The overall phase analyses for each sample was measured at very low magnifications ($\approx X500$ mag.), and occasionally some scatter in the data was experienced because of low homogeneity. As a result of these uncertainties, the degree of accuracy was reduced.

Establishing the particular phases and whether a martensitic-type transformation had occurred relied heavily on XRD and metallographic observations. The difference between the two forms of Pt_3Al shown by Villars and Culvert [1985Vil] was subtle, and it was not a trivial task to distinguish between the phases. To be able to detect which phase was present between the high and the low temperature Pt_3Al phases, peaks were made more resolvable. A singlet or absence of peaks indicated that the sample probably contained the cubic Pt_3Al phase, while peak splitting usually indicated the presence of the tetragonal Pt_3Al phase [2001Big], unless the apparent split would be attributed to a different phase. The high and low temperature Pt_3Al phases were analysed using a procedure of expanding the 2θ scale, in order to

differentiate the existence of these two phases. Biggs [2001Big] derived a model of differentiating between the two phases which was used to further verify the presence of the two phases (Figure 2.10). Casting on a cooled surface meant that dendrites of a specific orientation grew, giving a preferred orientation in the sample. Texture is very important, because in highly textured samples, the peaks in the XRD spectrum [2005ICD] have different intensities from those expected. This could mean that peaks are not observed. The effect of preferred orientation from casting made distinction between the two forms of Pt_3Al even more difficult.

The XRD machine used for analyses was unable to rotate the sample about itself, which would reduce the effect of texture. In most of the XRD spectra, there was no precise match between the phase intensities from the XRD database [2005ICD] and the intensities of the experimental peaks, because the samples had preferred orientation due to arc-melting. The shift in the experimental peaks relative to the database peaks is due to the original atoms being substituted by other atoms of different sizes.

4.2 Phase analyses for the 81.5 at.% Pt samples

4.2.1 Nominal 81.5 at.% Pt sample in the arc-melted condition

On cooling from solidification, the (Pt) phase solidified first into coarse dendrites (Figure 4.1). In the solid state, fine, discrete dark precipitates were formed in the dendrites. The dark phase formed as part of a eutectic mixture between the dendrite arms, nucleating from the dendrites at different directions and combining to form mismatches between the colonies growing together with different orientations of growth (Figure 4.1(b)).

The overall composition was in the two-phase region ((Pt) and Pt_3Al) of both published phase diagrams [1986McA, 1987Oya], and was within the expected composition of the alloy (Table 4.1). The phases were very small and close together, which would result to imprecise measurements. The EDS composition for the light phase was in the two-phase region, and it

was assumed to be the (Pt) phase, but due to the presence of the dark precipitates, the spot analyses would have included those precipitates. The dark phase was assumed to be Pt₃Al, although its composition was in the two-phase field ((Pt) and Pt₃Al) of Oya and Massalski's phase diagrams [1986McA, 1987Oya].

The solidification sequence was:

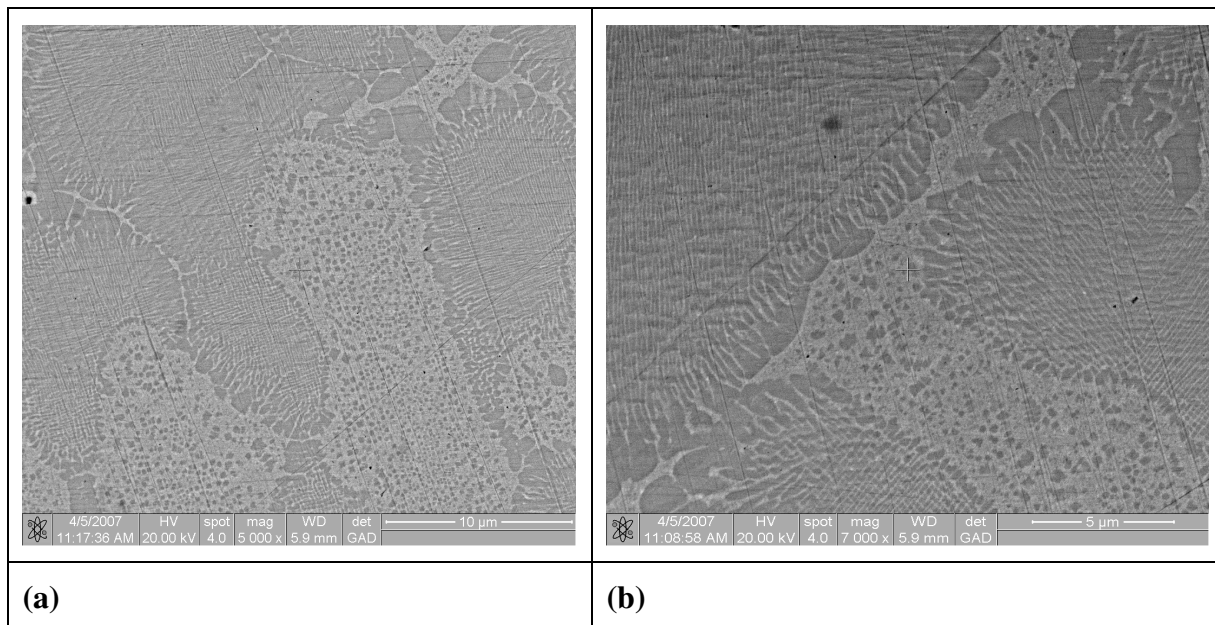
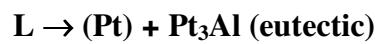
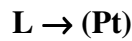


Figure 4.1. BSE-SEM image for nominal 81.5 at.% Pt in the arc-melted condition, showing (Pt) dendrites (light) with Pt₃Al precipitates inside, surrounded by a (Pt) + Pt₃Al (dark) eutectic.

Table 4.1. EDS analysis for the nominal 81.5 at.% Pt sample in as-cast condition.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
81.5 at.% Pt in arc-melted condition	Overall	81.7 ± 1.2	18.3 ± 1.2	-
	Light	85.5 ± 0.9	14.5 ± 0.9	mainly (Pt)
	Dark	80.2 ± 0.8	19.8 ± 0.8	mainly Pt ₃ Al

Table 4.2. XRD database [2005ICD] information for the nominal 81.5 at.% Pt sample in as-cast condition.

2 θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
10.5	3.88	100	6	-	28	-
14.9	2.74	110	30	-	20	-
18/18.0/18.3	2.27/2.24/ 2.23	111/111/202	100	100	99	100
20.8	1.96	200	12	53	-	-
23.6/23.5	1.74/1.74	210/114	4	-	9	5
29.6/30	1.39/1.37	220/220	40	31	23	-
33.8	1.22	332	4	-	-	10
34.9	1.18	311	12	33	-	-
36.5	1.13	222	6	12	-	-
42.4	0.98	400	0.6	6	-	-
46.4/46.9	0.9/0.9	331/331	16	22	9	-
47.7/48.3	0.88/0.87	420/420	18	20	9	-

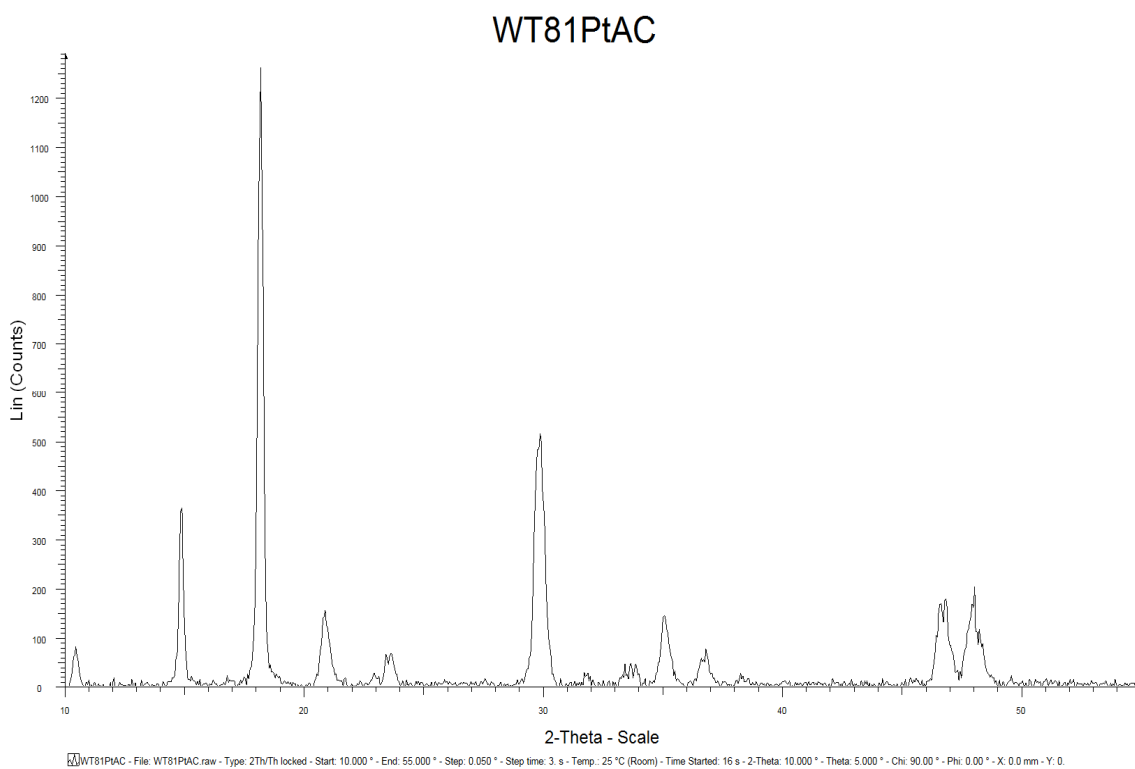


Figure 4.2. Raw XRD spectrum for the nominal 81.5 at.% Pt sample in as-cast condition.

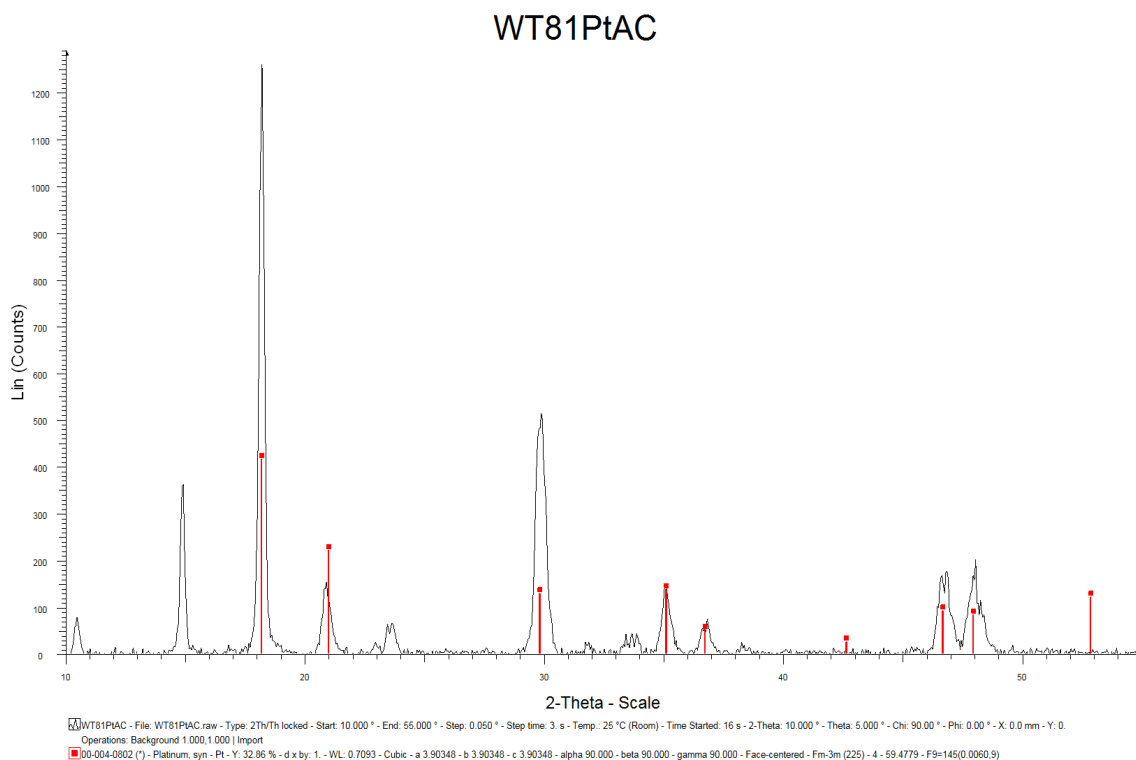


Figure 4.3. XRD trace showing peaks of Pt for the nominal 81.5 at. % Pt sample in as-cast condition.

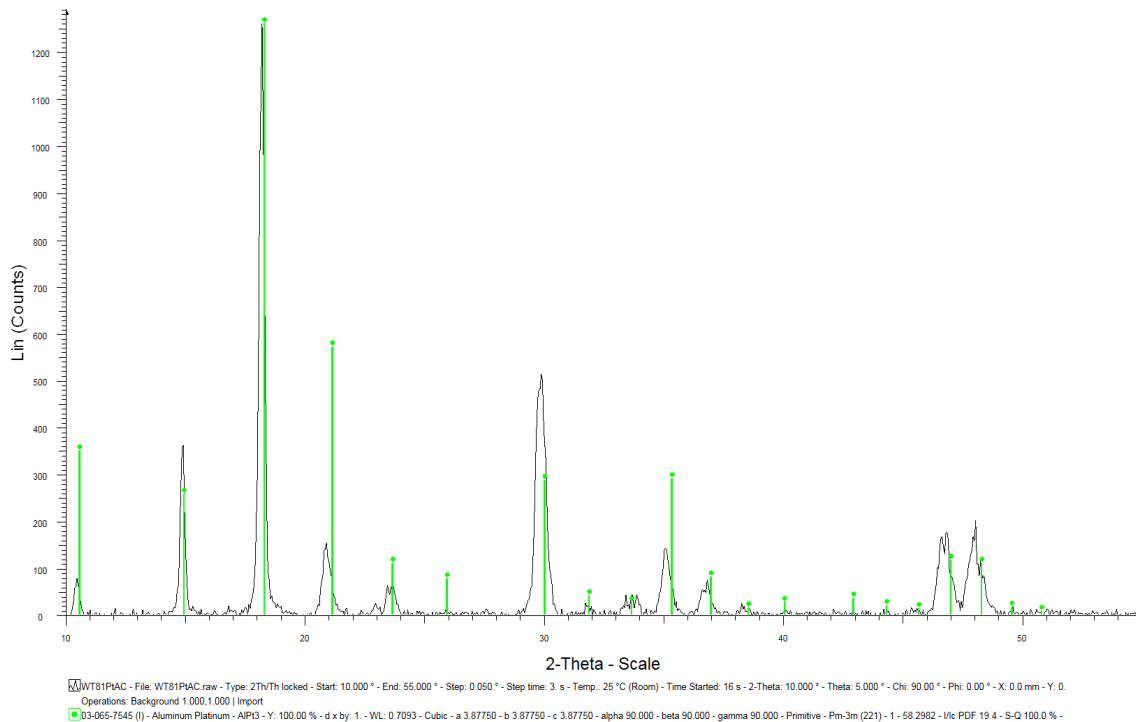


Figure 4.4. XRD trace showing peaks of cubic Pt_3Al for the nominal 81.5 at. % Pt sample in as-cast condition.

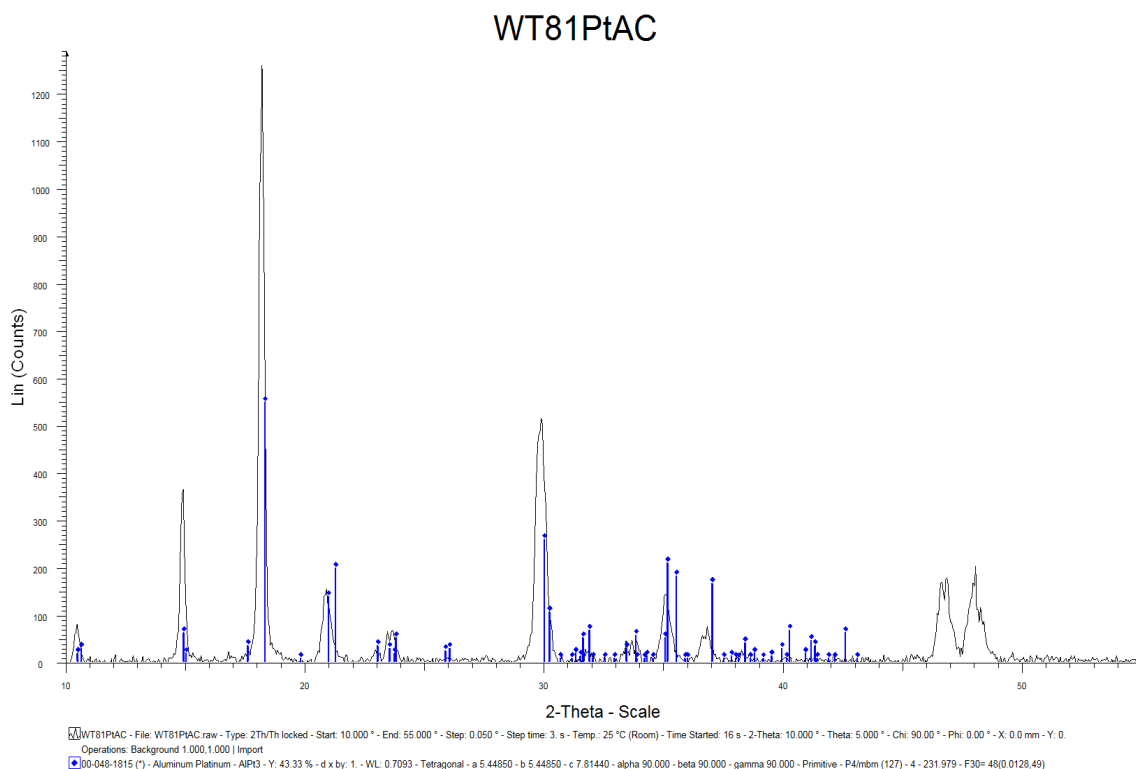


Figure 4.5. XRD trace showing peaks of tetragonal Pt_3Al for the nominal 81.5 at. % Pt sample in the as-cast condition.

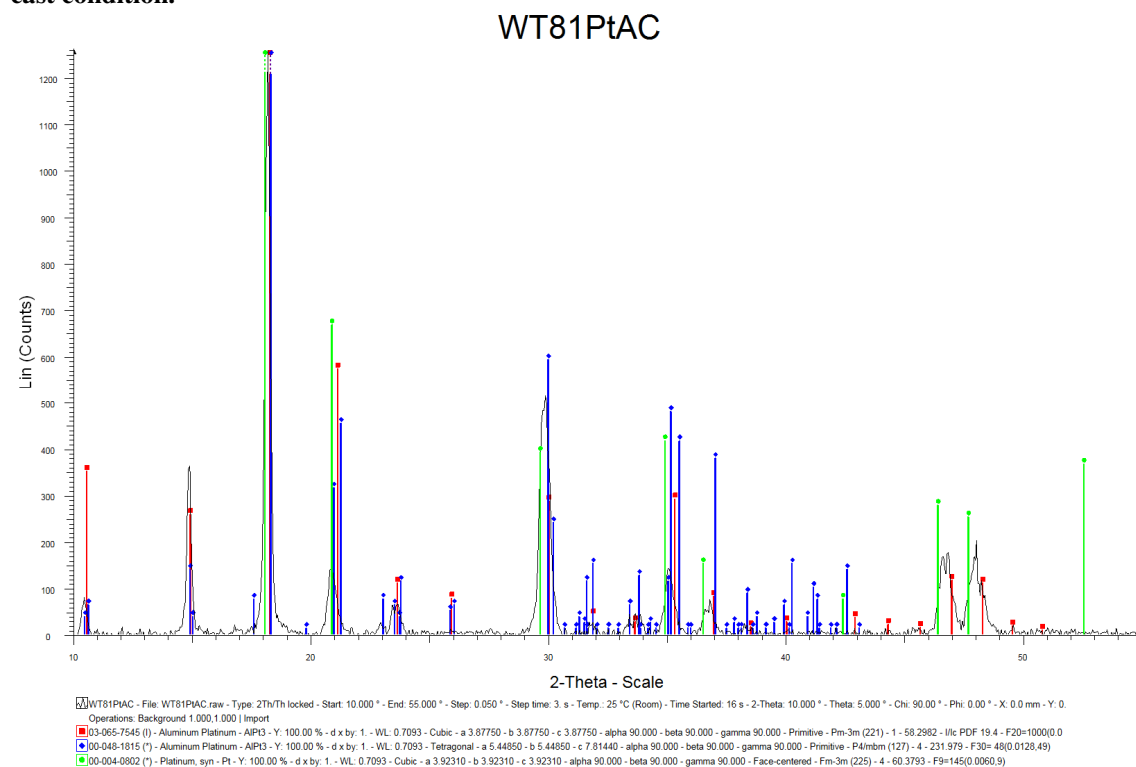


Figure 4.6. XRD trace showing peaks of cubic and tetragonal Pt_3Al and Pt for the nominal 81.5 at. % Pt sample in the as-cast condition.

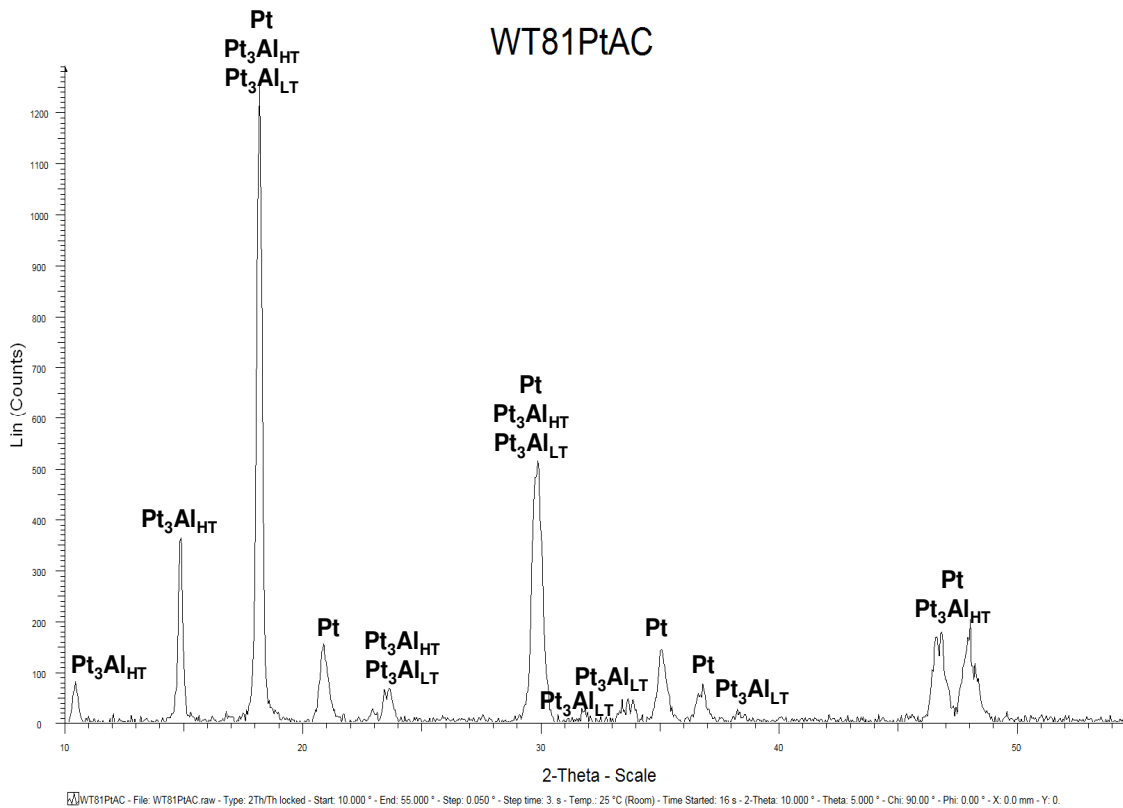


Figure 4.7. XRD pattern for the nominal 81.5 at.% Pt sample showing the phases in the as-cast condition.

The XRD spectrum had broad peaks, high counts and high signal to background noise (Figure 4.2). The broad peaks suggested the presence of a range of lattice parameters which was likely for the as-cast structure. The spectrum had few peaks suggesting a simple structure. A consistent slight shift to the left was observed for both the cubic and the tetragonal Pt_3Al phases, due to the presence of more Pt (Figure 4.3). Comparison with the peaks from the XRD database [2005ICD], confirmed the presence of three phases: (Pt), cubic and tetragonal Pt_3Al phases (Table 4.2). The presence of the (Pt) phase was shown in Figure 4.3 where there was a match on the peaks at $2\theta = \sim 18^\circ, \sim 21^\circ, \sim 30^\circ, \sim 35^\circ, \sim 37^\circ, \sim 42.5^\circ, \sim 47^\circ$ and $\sim 48^\circ$ with negligible shift. According to Biggs [2001Big], the peaks at $2\theta = \sim 10.5^\circ$ and $\sim 15^\circ$ indicated the presence of at least one of the Pt_3Al phases. The microstructure was not observed to be twinned, indicating the cubic parent Pt_3Al phase. The presence of the cubic Pt_3Al phase was shown in Figure 4.4, where singlet peaks are at $2\theta = \sim 10.5^\circ, \sim 15^\circ, \sim 18^\circ, \sim 30^\circ, \sim 35^\circ, \sim 47^\circ$ and $\sim 48.2^\circ$, which are different from (Pt), although the intensities of the experimental peaks and the database peaks did not match, due to preferred orientation on casting. In Figure 4.5,

peak splitting which identified tetragonal Pt_3Al was shown by peaks at $2\theta = \sim 18^\circ$, $\sim 23.5^\circ$, $\sim 30^\circ$, $\sim 32^\circ$, $\sim 34^\circ$ and 38.5° , which were different from the cubic Pt_3Al , with a slight shift to the left. The strongest peak was at $2\theta = \sim 18^\circ$ and it was due to all three phases (Table 4.2).

4.2.2 Nominal 81.5 at. % Pt sample annealed at 1500°C

The microstructure looks as-cast with large pores, coarse dendrites and a coarse and sparse eutectic because it has partially melted (Figure 4.8(a)). This means that the furnace was actually running at a higher temperature than set, because the eutectic temperature is actually 1507°C [1986McA]. A rim of a very light phase surrounded the dendrites. According to the EDS spectrum, the very light phase was Pt, with the Pt peaks at $2\theta = \sim 2^\circ$, and the difference in contrast could be due to edge effects (Figure 4.9). The overall composition was in the (Pt) phase field of the published phase diagrams [1986McA, 1987Oya]. The dark phase was assumed to be Pt_3Al , although it had a higher platinum content than expected (Table 4.3), and its composition was in the (Pt) phase region. The light phase was assumed to be (Pt) [1986McA, 1987Oya].

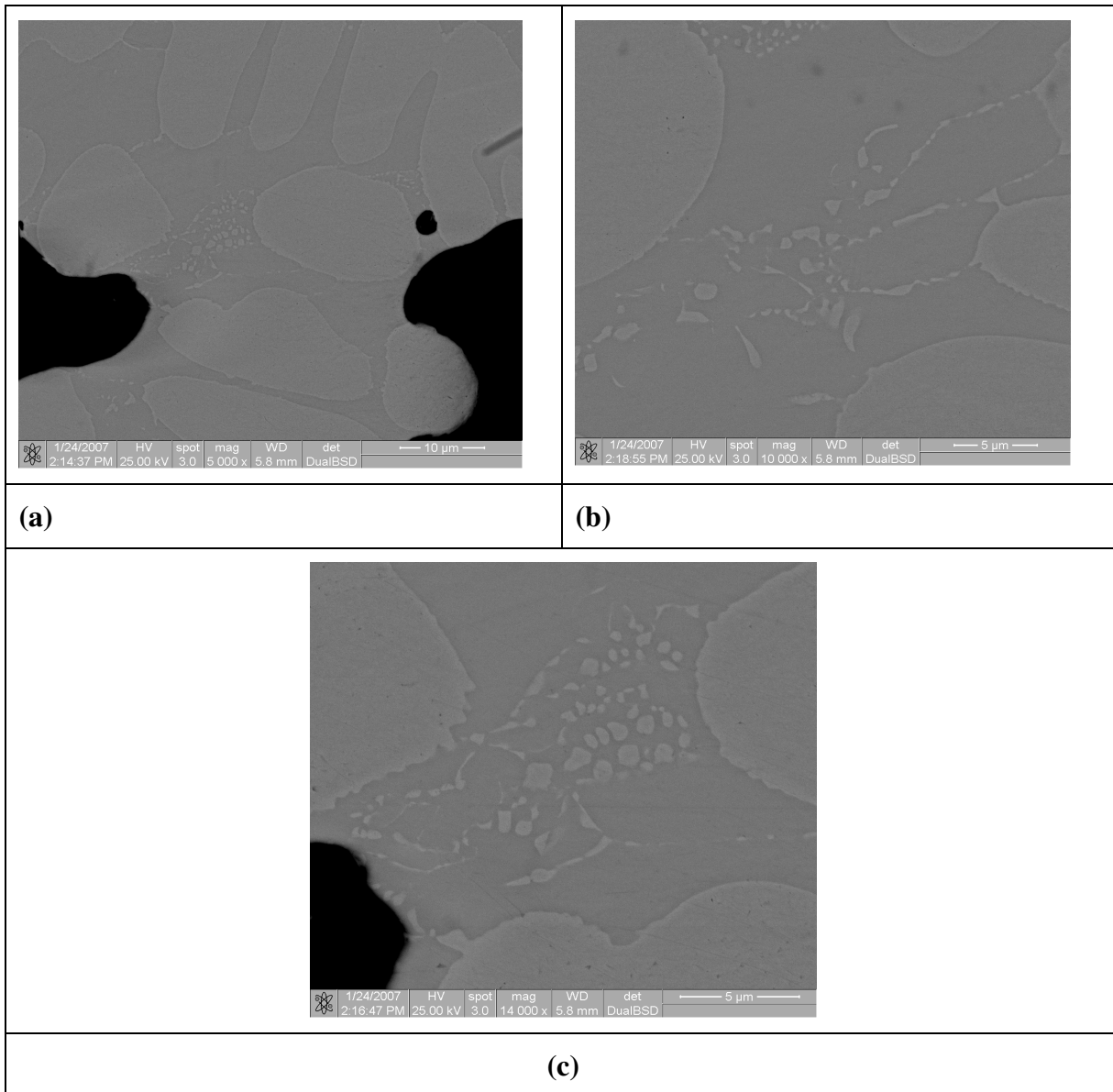


Figure 4.8. BSE-SEM images at different magnifications for the nominal 81.5 at.% Pt sample annealed at 1500°C for 1000 h, showing light (Pt) dendrites surrounded by a lighter rim and a (Pt) and Pt₃Al (dark) sparse eutectic observed between the dendrites.

Table 4.3. EDS analysis for the nominal 81.5 at.% Pt sample annealed at 1500°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1500°C for 1000 hours and W/Q	Overall	95.4 ± 1.7	4.6 ± 1.7	-
	Light	96.7 ± 0.4	3.3 ± 0.4	(Pt)
	Dark	94.0 ± 1.5	6.0 ± 1.5	Pt ₃ Al
	Light rim	97.7 ± 0.4	-	(Pt)

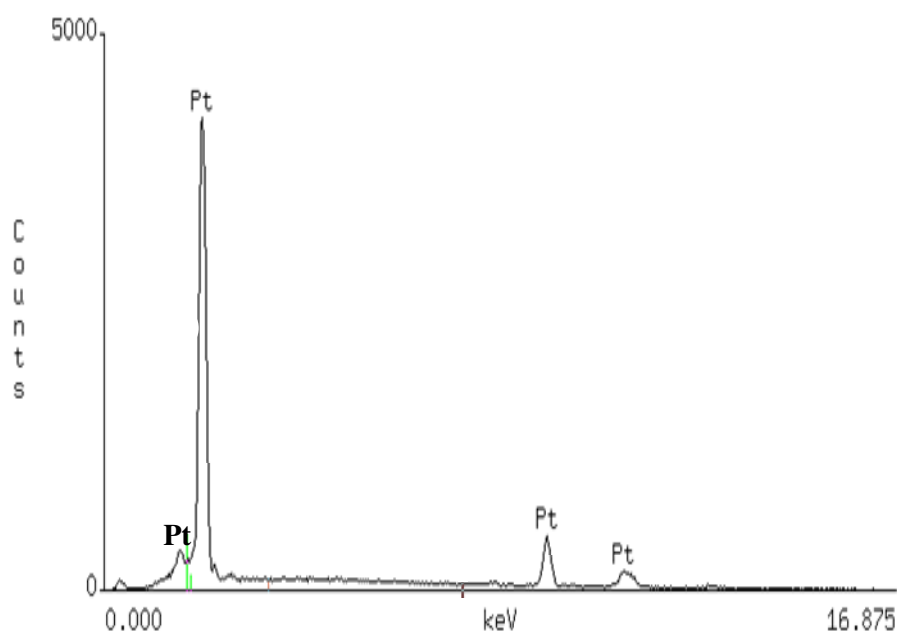


Figure 4.9. EDS spectrum, showing peaks for Pt for the 81.5 at.% Pt sample annealed at 1500°C.

Table 4.4. XRD database [2005ICD] information for the nominal 81.5 at.% Pt sample annealed at 1500°C.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
14.9	2.74	112	4	-	-	11
18/18.0/18.3	2.27/2.24/ 2.23	111/111/202	100	100	99	100
20.8/21.1/21.2	1.96/1.94/1.93	200/200/220	28	53	-	-
23.6/23.8	1.74/1.72	210/310	16	-	9	9
26	1.59	204	3	-	-	4
29.6/29.9	1.39/1.37	220/220	20	31	23	-
31.9	1.29	314	6	-	-	12
34.9/35.3	1.18/1.17	222/311	16	33	23	-
36.5/36.9	1.13/1.12	222/222	10	12	6	-
46.4/46.9	0.9/0.9	331/331	10	3	9	-

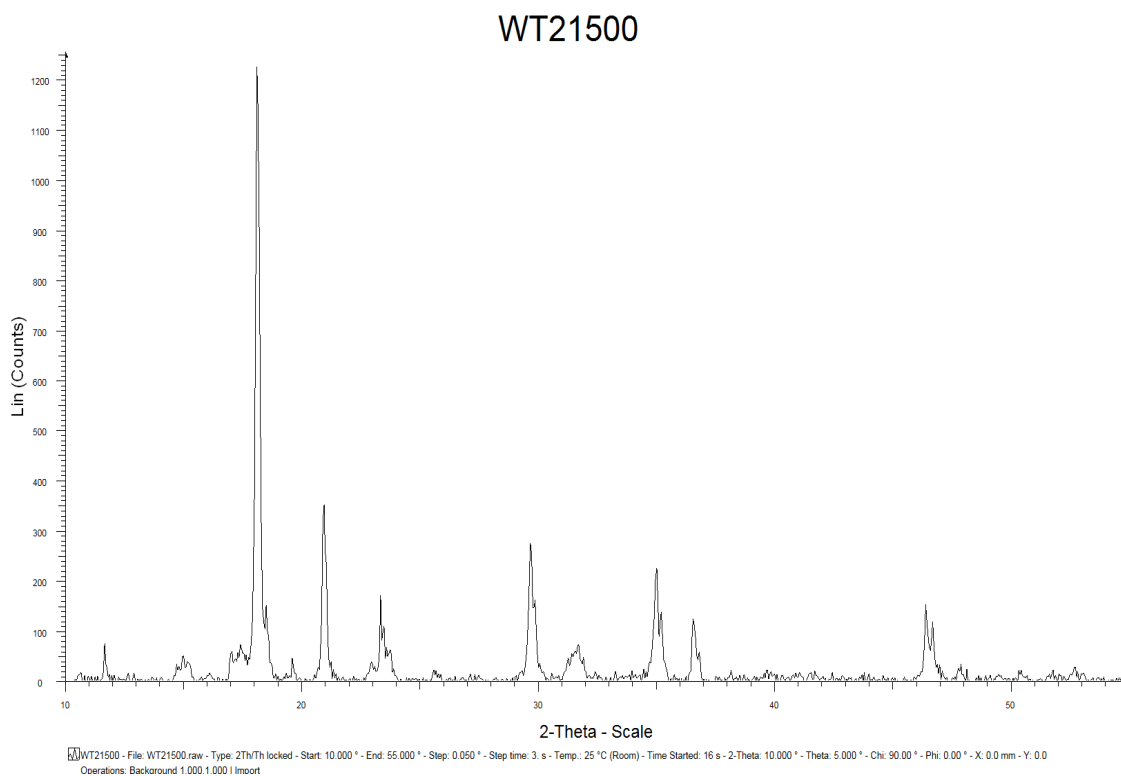


Figure 4.10. Raw XRD spectrum for nominal 81.5 at.% Pt annealed at 1500°C.

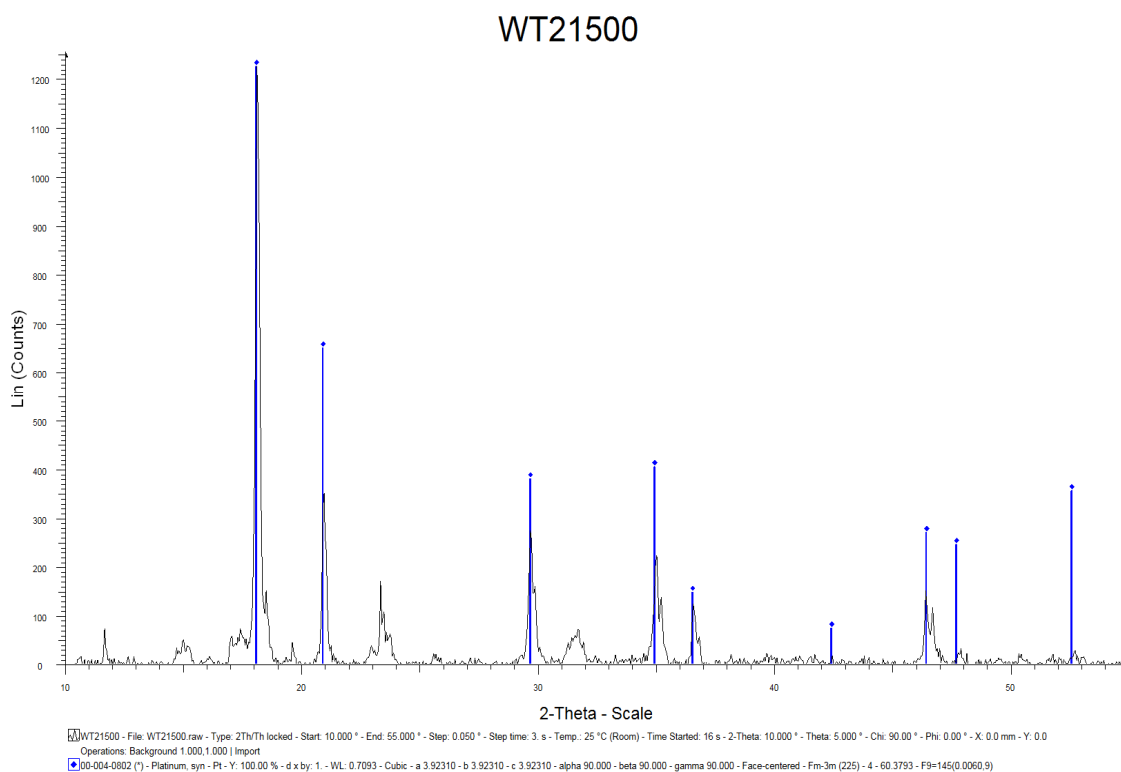


Figure 4.11. XRD trace showing peaks of Pt for the nominal 81.5 at.% Pt sample annealed at 1500°C.

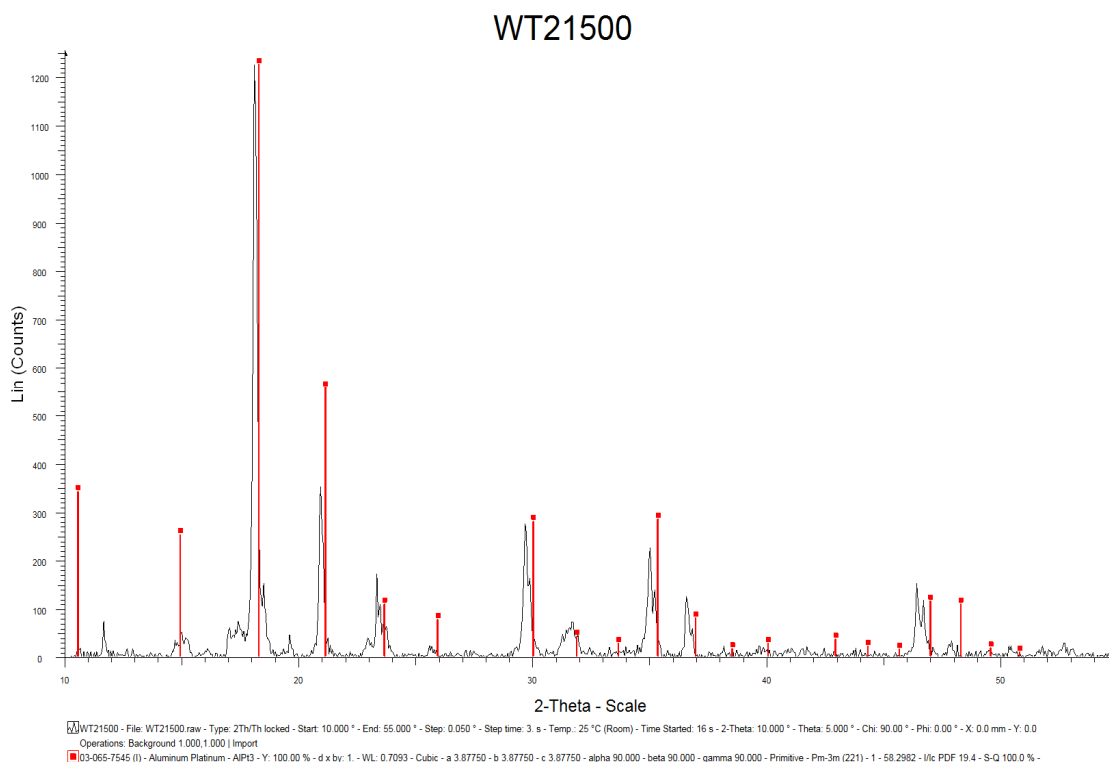


Figure 4.12. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 81.5 at. % Pt sample annealed at 1500°C.

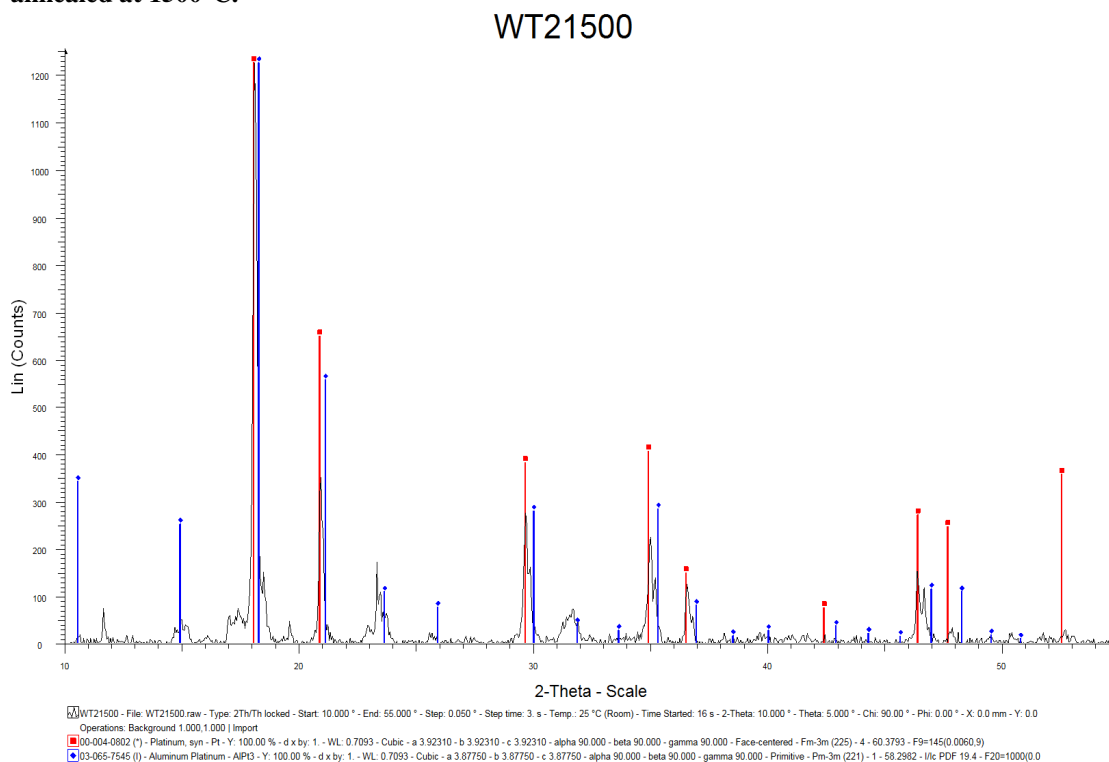


Figure 4.13. XRD trace showing peak overlap between Pt and the cubic Pt_3Al phase.

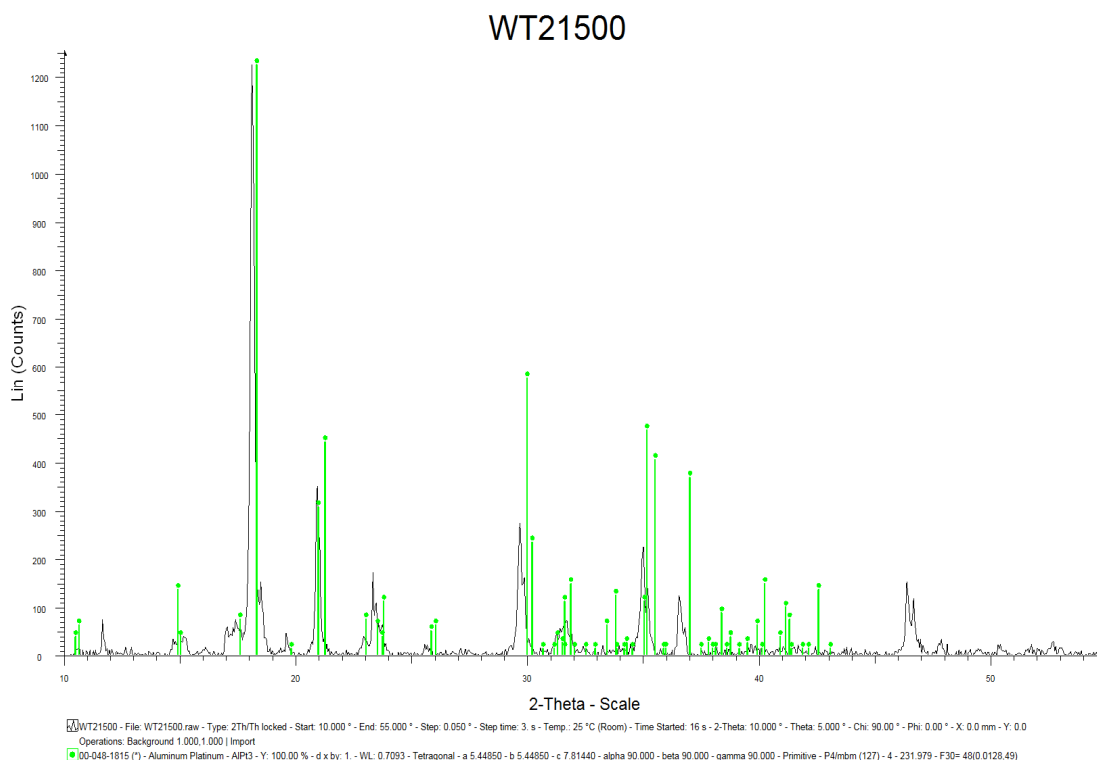


Figure 4.14. XRD trace showing peaks of the tetragonal Pt_3Al phase for the nominal 81.5 at. % Pt sample annealed at 1500°C.

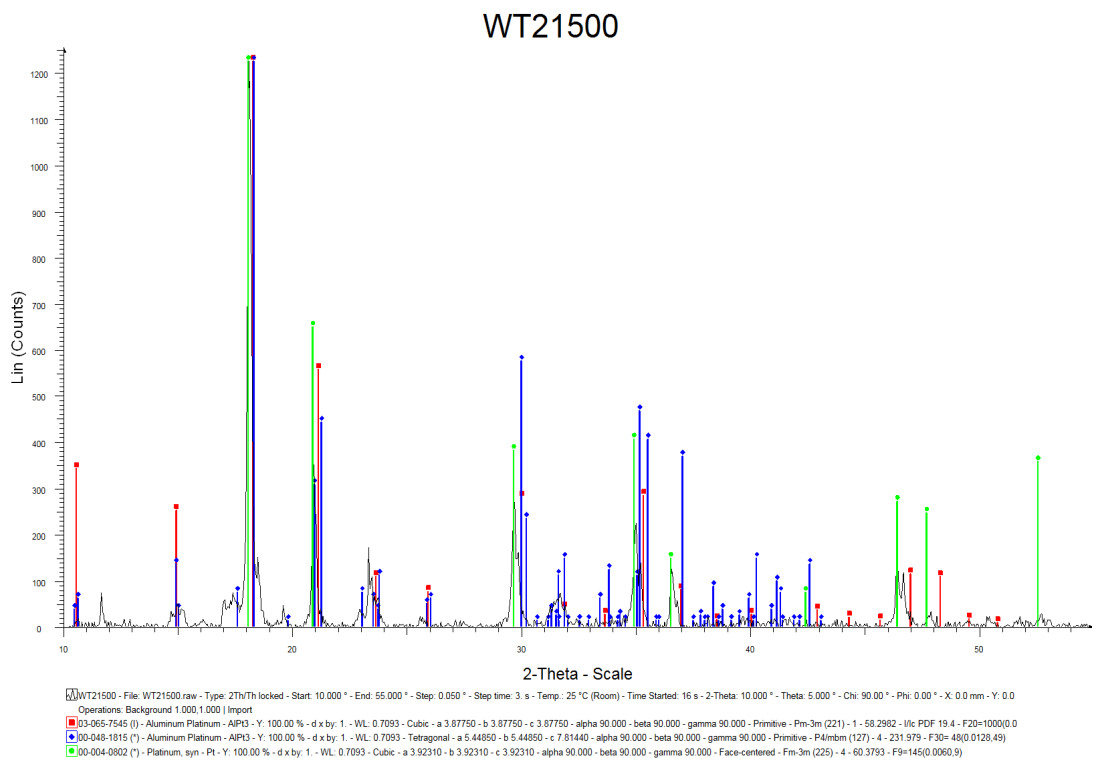


Figure 4.15. XRD trace showing peaks of the cubic and tetragonal structures of Pt_3Al and Pt for nominal 81.5 at. % Pt annealed at 1500°C.

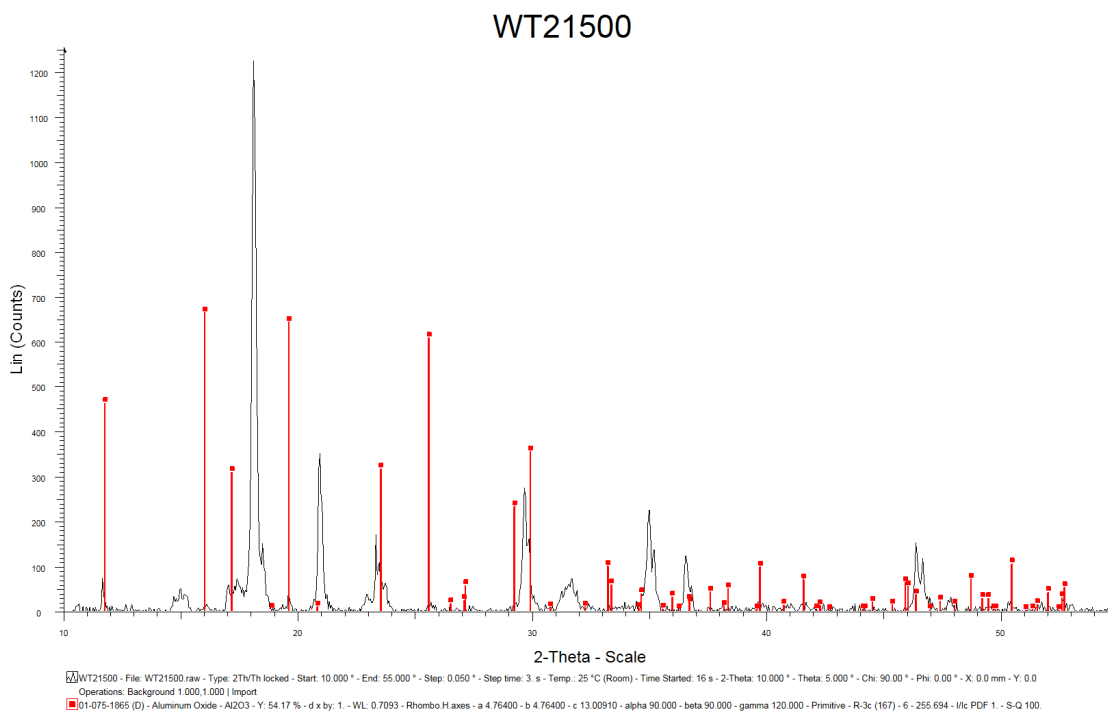


Figure 4.17. XRD pattern showing the phases in the nominal 81.5 at.% Pt sample annealed at 1500°C.

The XRD spectrum had broad peaks, high counts and high signal to background noise (Figure 4.10). According to the XRD database [2005ICD], the high and low temperature Pt_3Al phases as well as the (Pt) phase were identified (Table 4.4). The presence of (Pt) was shown by a match of the peaks at $2\theta = \sim 18^\circ, \sim 21^\circ, \sim 30^\circ, \sim 35^\circ, \sim 37^\circ$ and 46.5° with a negligible shift as shown in Figure 4.11. The presence of the peaks at $2\theta = \sim 15^\circ$ indicated that the sample contained at least one of the Pt_3Al phases [2001Big]. A match of singlet peaks which identified cubic Pt_3Al , which are different from (Pt) are at $2\theta = \sim 18^\circ, \sim 24^\circ, \sim 30^\circ, \sim 35^\circ, \sim 37^\circ$ and $\sim 47^\circ$, with a slight shift to the left as indicated in Figure 4.12, and the peaks at $2\theta = \sim 30^\circ, \sim 35^\circ, \sim 37^\circ$ appeared as split, but this is because of peak overlap between the (Pt) and cubic Pt_3Al phases as shown in Figure 4.13. In Figure 4.14, peak splitting for tetragonal Pt_3Al was observed at: $2\theta = \sim 15^\circ, \sim 18^\circ, \sim 24^\circ, \sim 26^\circ$ and $\sim 32^\circ$ with a slight shift to the right. The peaks at $2\theta = \sim 12^\circ, \sim 17^\circ$ and 19.5° matched aluminium oxide with a negligible shift to the right (Figure 4.16). The peak at $2\theta = \sim 18^\circ$ was formed by all three phases as indicated in Figure 4.17. Relative to the as-cast spectrum, peak intensity at $2\theta = \sim 48^\circ$ decreased because of preferred orientation during casting. There was no peaks at $2\theta = 10.5^\circ$.

4.2.3 Nominal 81.5 at.% Pt sample annealed at 1400°C

Heat treatment at 1400°C resulted in the coarsening of the two phases (Figure 4.18), with a coarsened eutectic mixture observed between the dendrite arms. The dendrites had dark precipitates nucleated throughout. The overall EDS composition was that targeted and in the two-phase region ((Pt) + Pt_3Al_{HT}) [1986McA, 1987Oya] (Table 4.5). The presence of the dark precipitates in the dendrites may have decreased the expected EDS composition for the light phase, because the spot analyses picked up the surrounding precipitates. The dark phase was on the Pt_3Al phase boundary in Massalski and Oya's phase diagrams [1986McA, 1987Oya]. The dark phase had an error of ~ 1.7 at.% due to small regions of the phase.

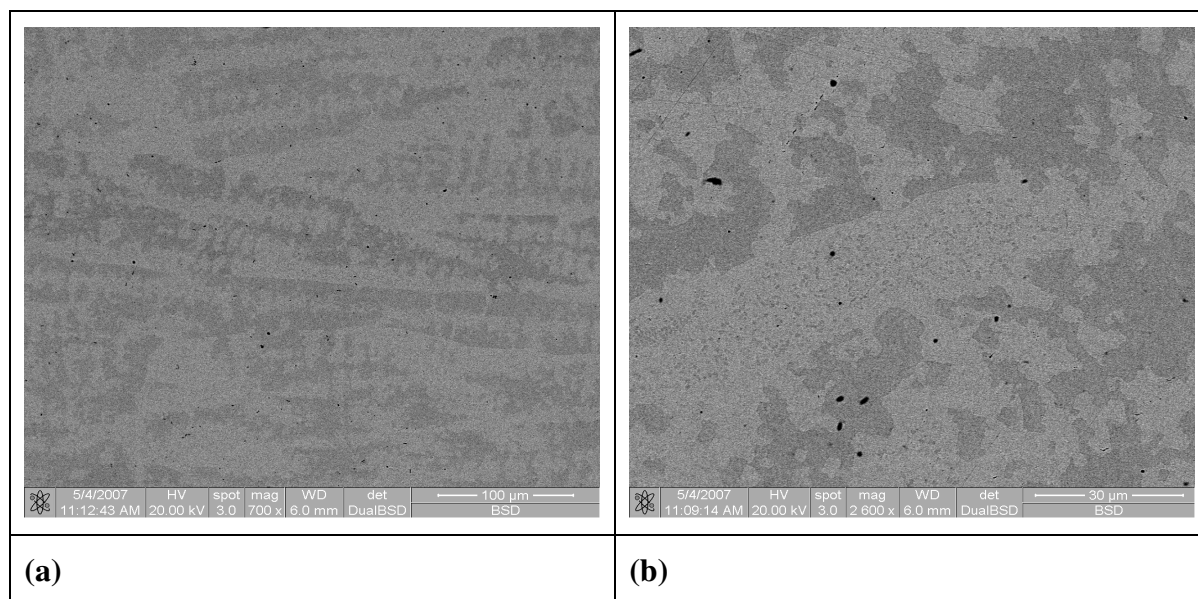


Figure 4.18. BSE-SEM image for nominal 81.5 at.% Pt annealed at 1400°C for 1000 h, showing light (Pt) dendrites with Pt₃Al precipitates inside, surrounded by a coarsened (Pt) + Pt₃Al eutectic mixture.

Table 4.5. EDS analysis for the nominal 81.5 at.% Pt sample annealed at 1400°C.

Condition	description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1400°C for 1000 hrs and W/Q	Overall	85.8 ± 1.0	14.2 ± 1.0	-
	Light	88.3 ± 0.6	11.7 ± 0.6	(Pt)
	Dark	77.1 ± 1.7	22.9 ± 1.7	Pt ₃ Al

Table 4.6. XRD database [2005ICD] information for the nominal 81.5 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
18/18.0	2.27/2.24	111/111	65	100	99	-
20.8/21.1/21.2	1.96/1.94	200/200	9	53	45	-
23	1.78	213	11	-	-	6
26	1.58	312	9	-	-	5
29.6/29.9	1.39/1.37	220/220	41	31	23	-
31.9	1.29	300	100	-	32	12
33.8	1.22	332	9	-	-	10
34.9	1.18	311	9	33	-	-
38.5	1.08	431	13	-	-	7
41	1.0	415	9	-	-	8

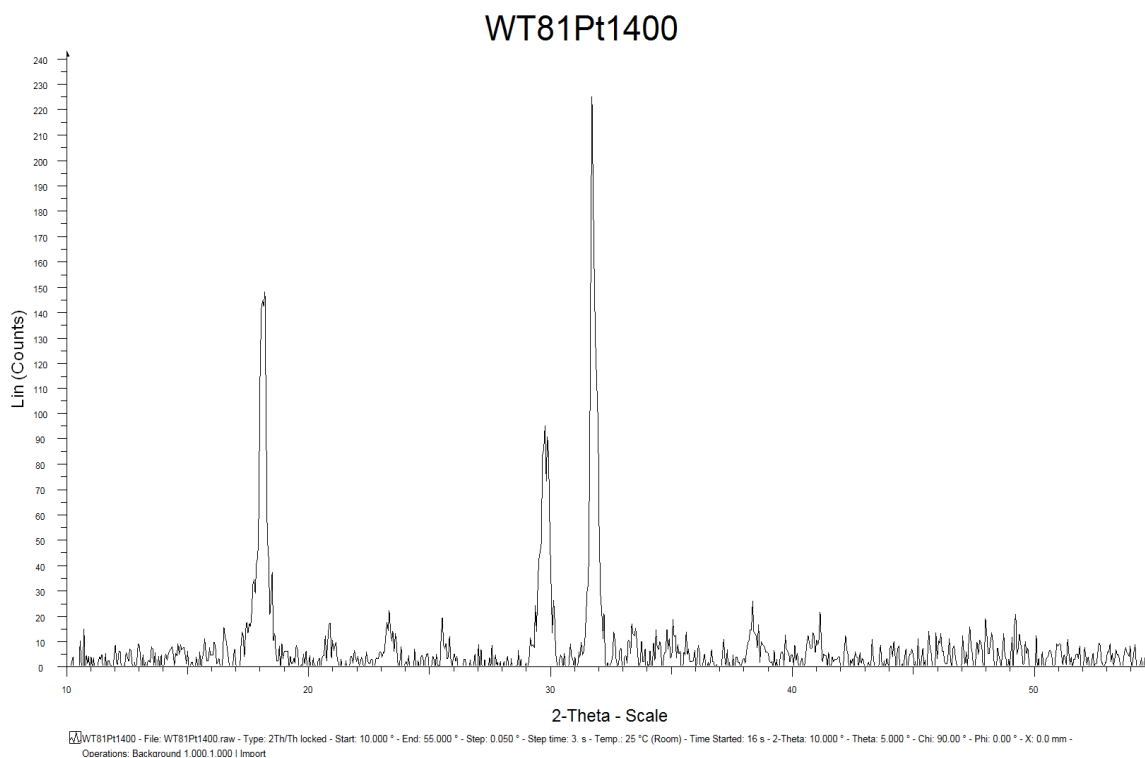


Figure 4.19.Raw XRD spectrum for the nominal 81.5 at. % Pt sample annealed at 1400°C.

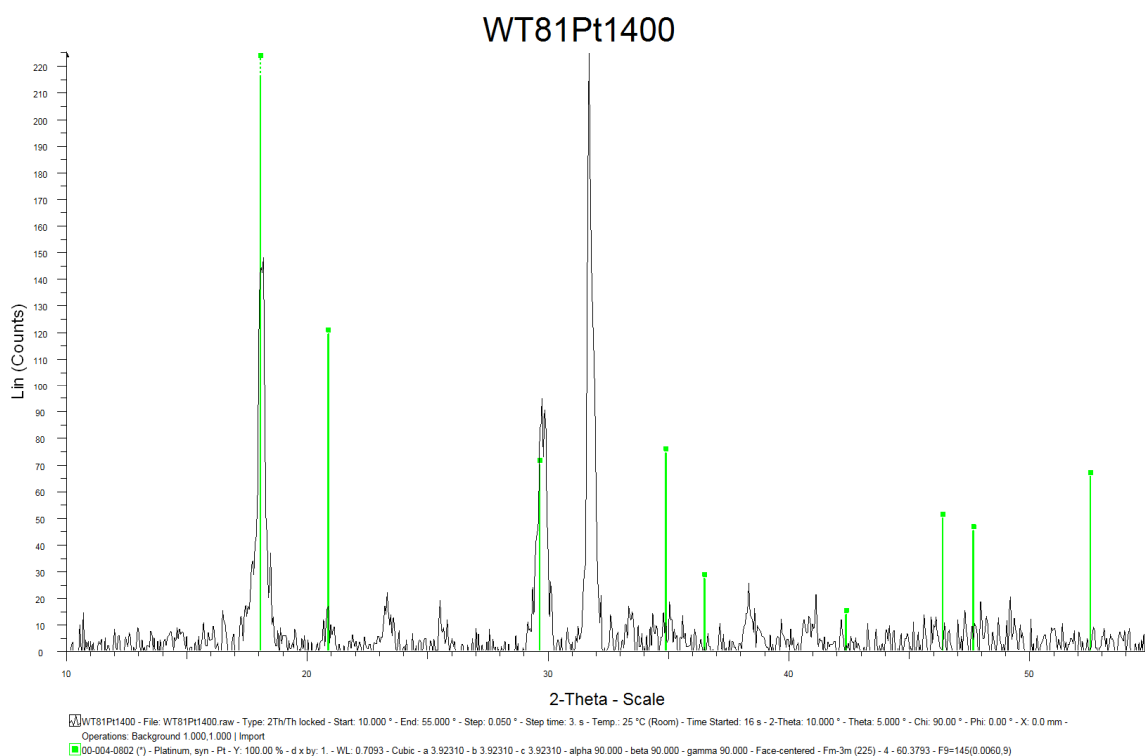


Figure 4.20. XRD trace showing peaks for Pt for the nominal 81.5 at. % Pt sample annealed at 1400°C.

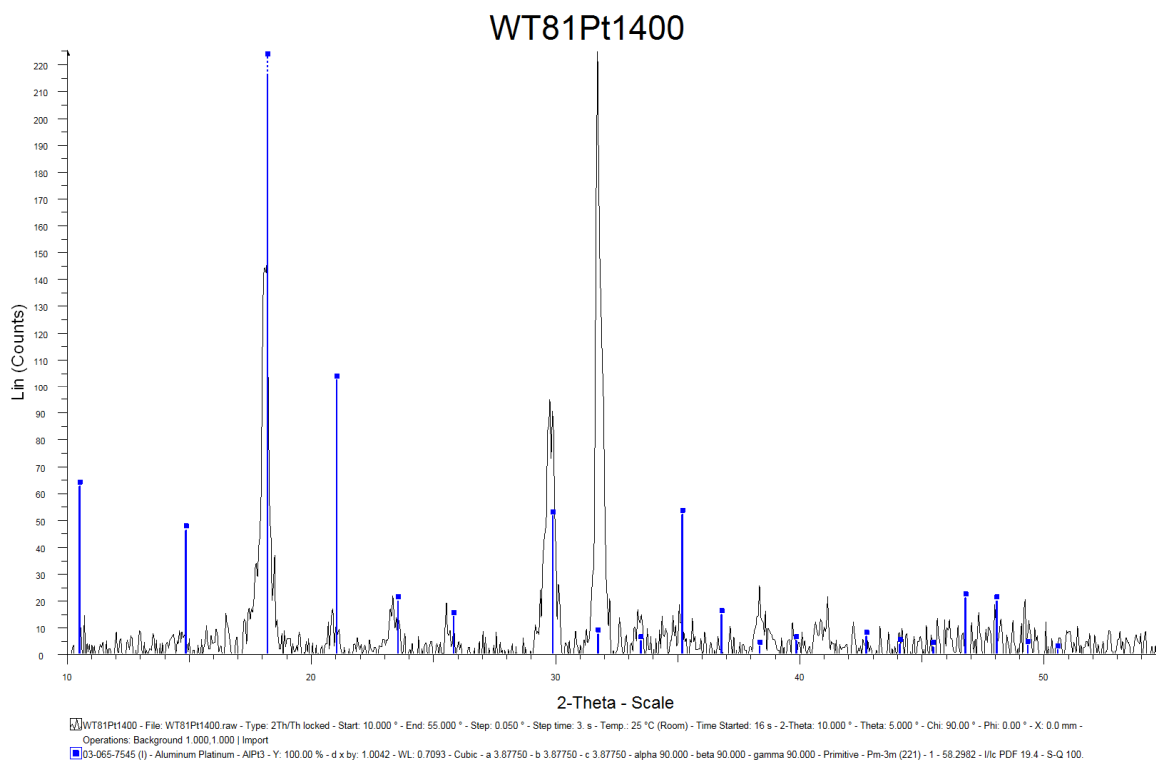


Figure 4.21. XRD trace showing peaks for the cubic Pt_3Al phase for the nominal 81.5 at.% Pt sample annealed at 1400°C.

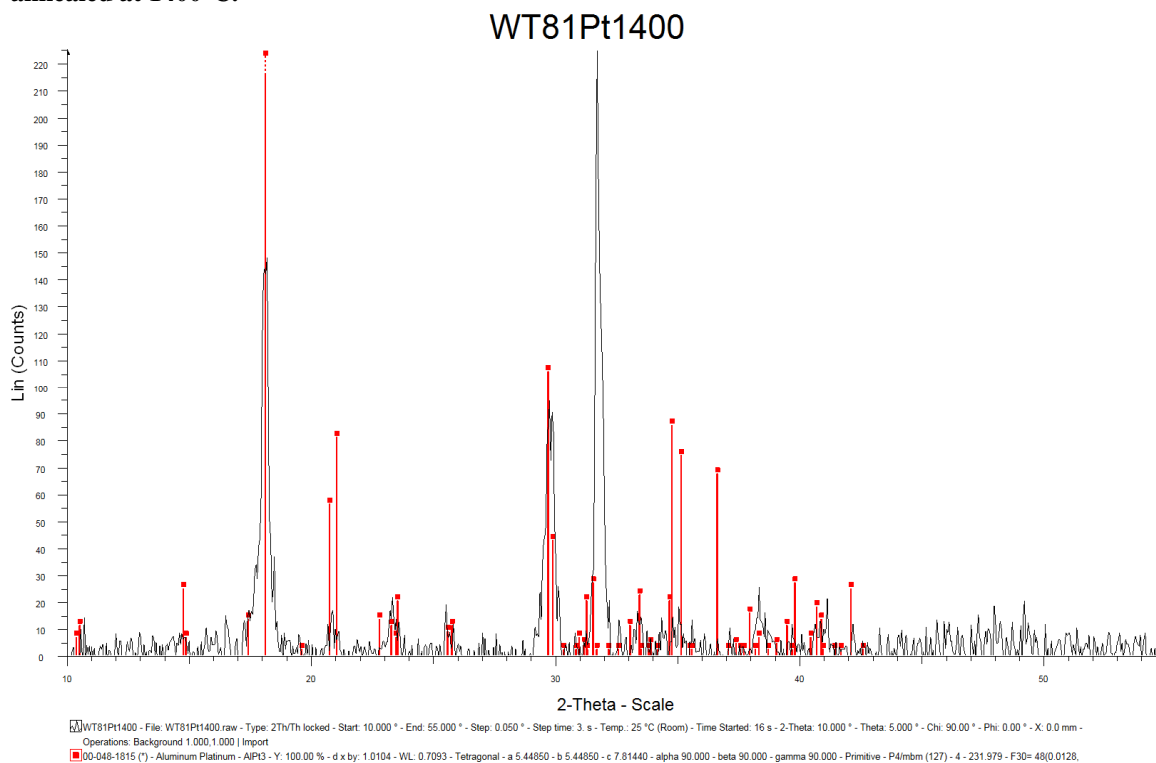


Figure 4.22. XRD trace showing peaks for the tetragonal Pt_3Al phase for the nominal 81.5 at.% Pt sample annealed at 1400°C.

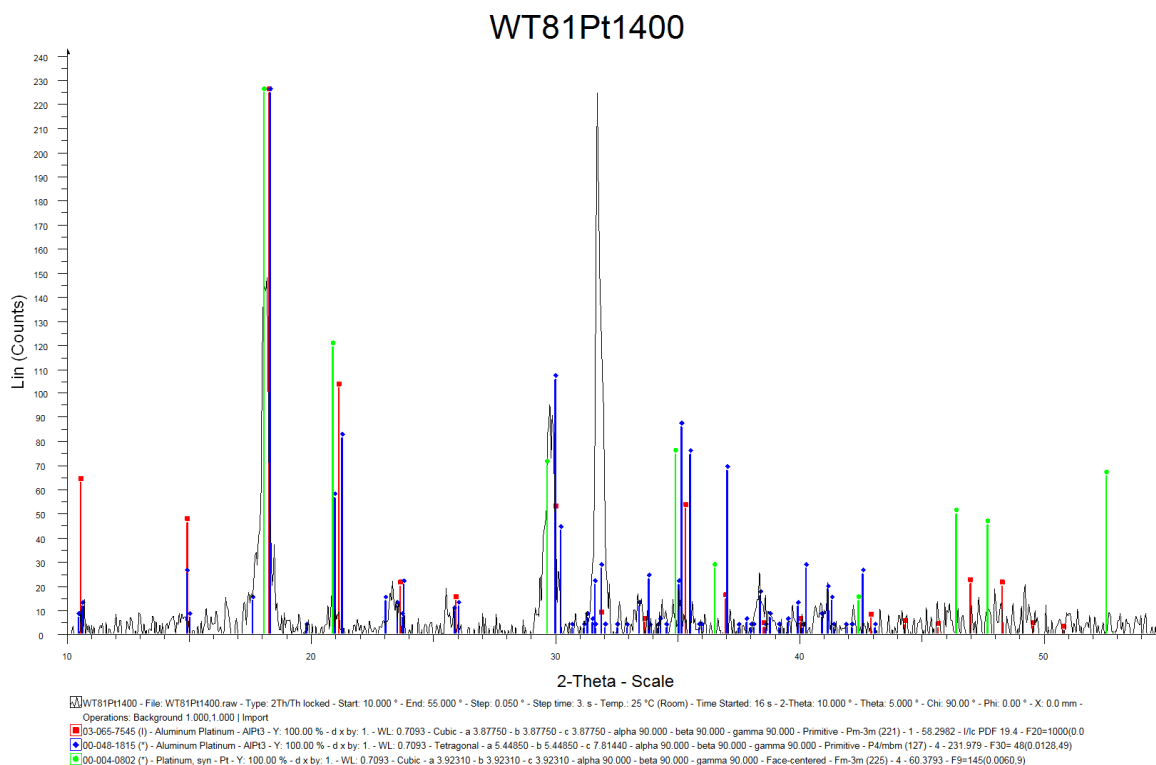


Figure 4.23. XRD trace showing peaks for the cubic and tetragonal Pt_3Al structures and Pt for the nominal 81.5 at. % Pt sample annealed at 1400°C.

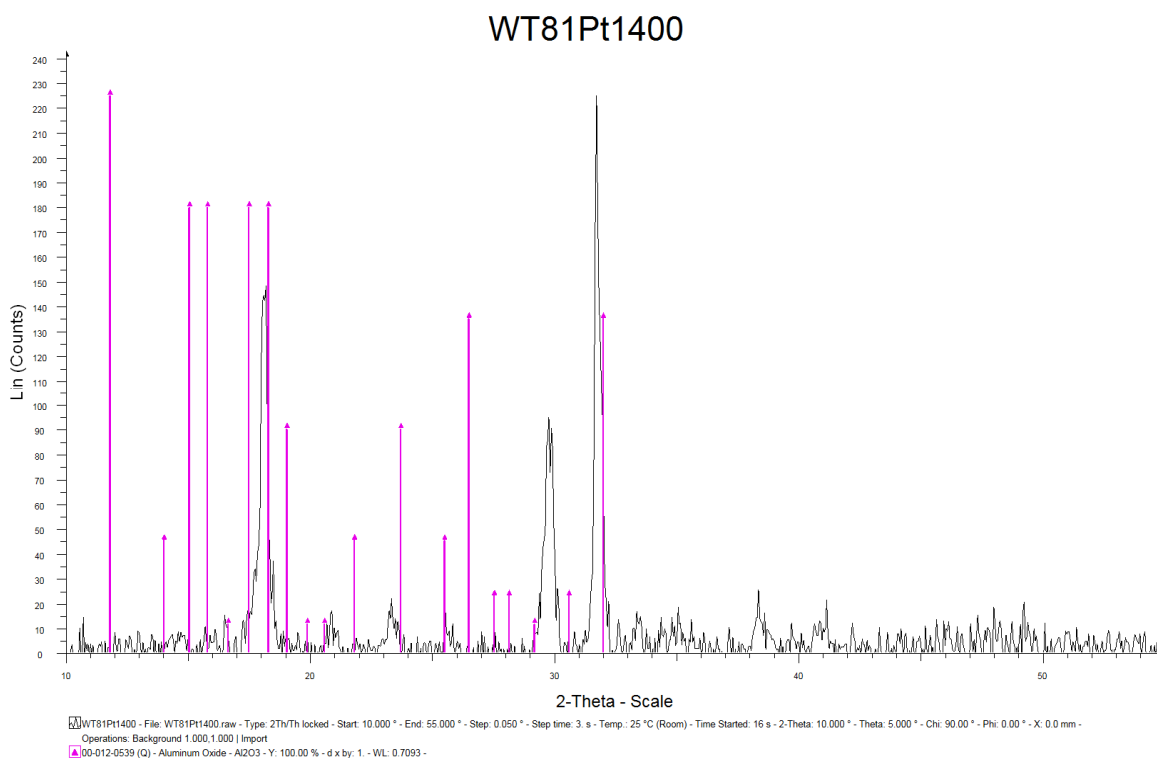


Figure 4.24. XRD trace ($2\theta = 10^\circ$ to 55°) identifying the presence of aluminium oxide for the nominal 81.5 at. % Pt sample annealed at 1400°C.

Relative to the as-cast spectrum, the spectrum of the sample annealed at 1400°C was very noisy and only major peaks could be clearly observed, thus the peaks at $2\theta = \sim 47^\circ$ and $\sim 48^\circ$ could not be observed. The spectrum showed the strongest peak at $2\theta = \sim 32^\circ$, which matched both high and low temperature Pt_3Al phase as well as aluminium oxide (although only one large peak was found), while the two previous samples (as-cast and heat treated at 1500°C) had the strongest peaks at $2\theta = 18.2^\circ$.

4.2.4 Nominal 81.5 at.% Pt sample annealed at 1300°C

Annealing at 1300°C resulted in irregular coarsened dendrites, with a coarsened eutectic mixture between the dendrites. A very light rim which was too small for analysis was observed around the dendrites (Figure 4.26), and the dendrites had dark precipitates nucleated within. There was porosity in the microstructure. The overall EDS composition was in the expected composition range (Table 4.7), with a very large error of ± 5.4 at.% Pt. The light phase composition was in the two-phase region of the phase diagrams [1986McA, 1987Oya], identifying (Pt), and the dark phase was close to the eutectoid composition in Massalski's phase diagram [1986McA], and in the Pt_3Al phase field in Oya and Mishima's phase diagram [1987Oya], confirming the Pt_3Al phase.

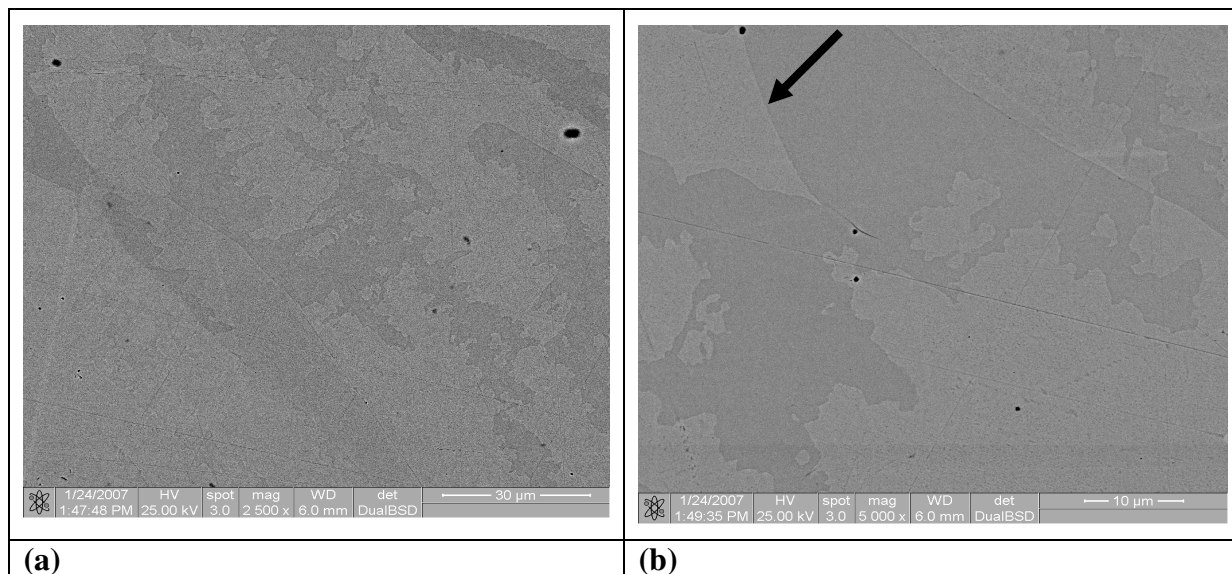


Figure 4.26. BSE-SEM image for nominal 81.5 at.% Pt annealed at 1300°C for 1000 h, showing light (Pt) dendrites with Pt₃Al precipitates throughout, surrounded by a very light rim and a coarsened (Pt) and Pt₃Al (dark) eutectic between the dendrites.

Table 4.7. EDS analysis for the nominal 81.5 at.% Pt sample annealed at 1300°C for 1000 h.

Condition	description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1300°C for 1000 hrs and W/Q	Overall	80.9 ± 5.4	19.1 ± 5.4	-
	Light	85.9 ± 0.6	14.1 ± 0.6	mainly (Pt)
	Dark	75.9 ± 0.9	24.1 ± 0.9	mainly Pt ₃ Al

Table 4.8. XRD database information [2005ICD] for the nominal 81.5 at.% Pt sample annealed at 1300°C.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
18/18.0/18.3	2.27/2.24/ 2.23	111/111/202	16	100	99	-
20.8/21.1/21.2	1.96/1.94	200/200	14	53	45	-
23	1.78	213	7	-	-	6
23.8	1.72	310	56	-	-	9
26.0	1.58	312	11	-	-	5
29.9	1.37	224	5	-	-	47
34.9/35.1	1.18/1.18	311/206	50	33	-	38
46.4/47	0.9/0.89	331/331	61	22	9	-
47.7/48.3	0.88/0.87	420/420	100	20	9	-

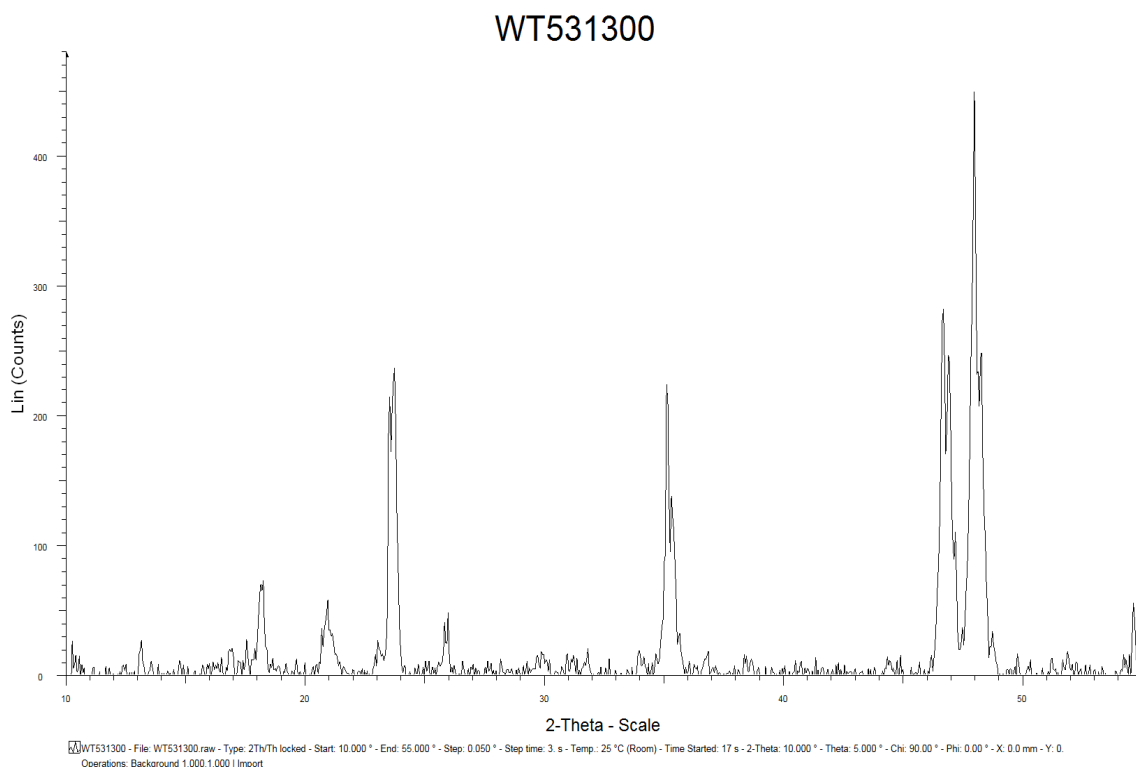


Figure 4.27. Raw XRD spectrum for the nominal 81.5 at.% Pt sample annealed at 1300°C.

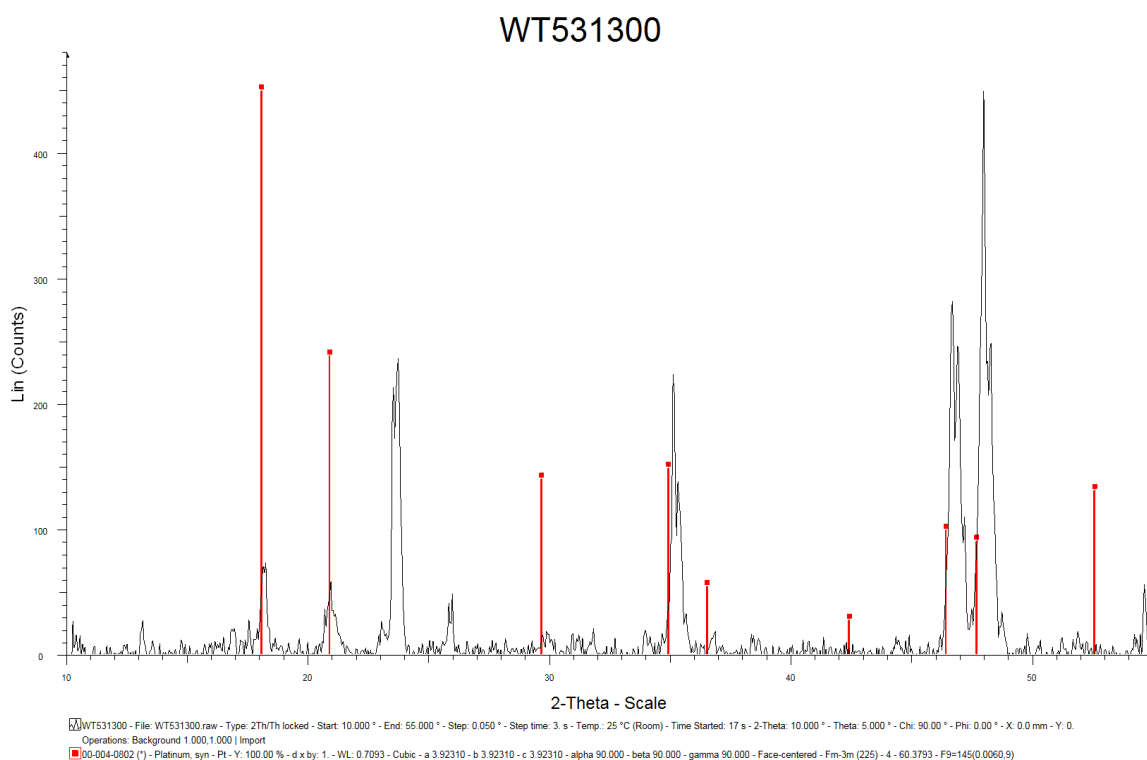


Figure 4.28. XRD trace showing peaks for Pt for the nominal 81.5 at.% Pt sample annealed at 1300°C.

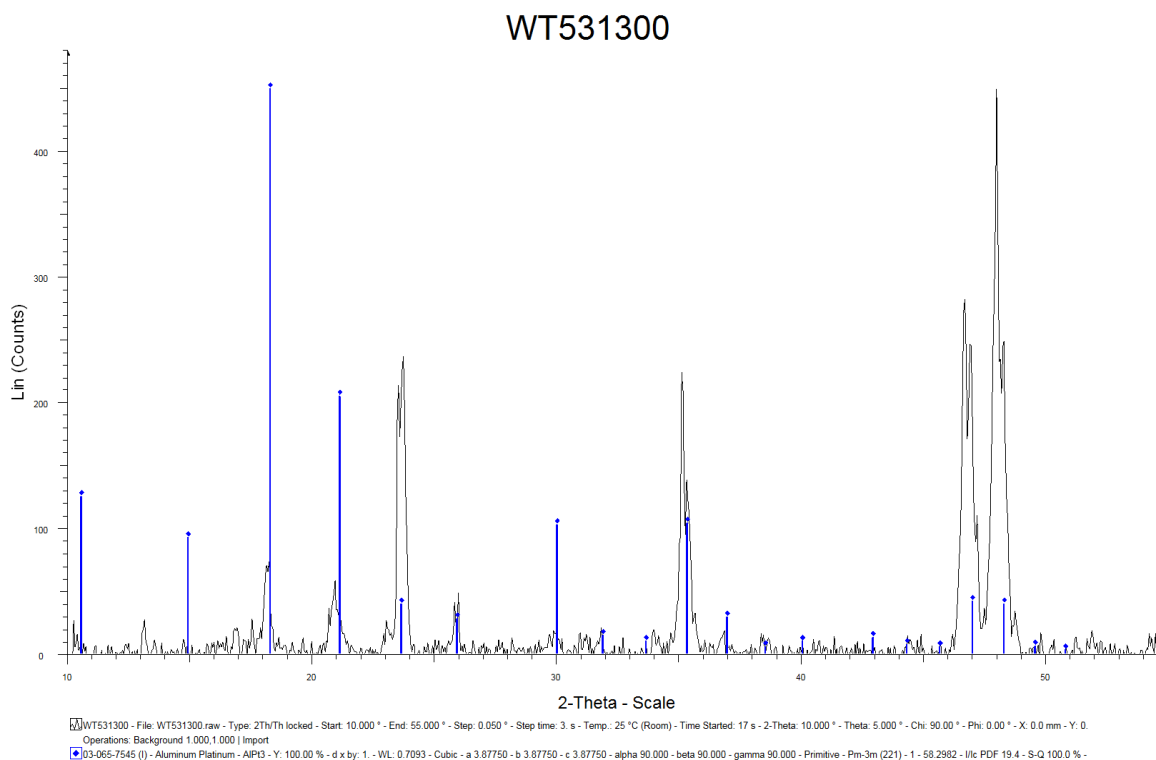


Figure 4.29. XRD trace showing peaks for cubic Pt_3Al for the nominal 81.5 at. % Pt sample annealed at 1300°C.

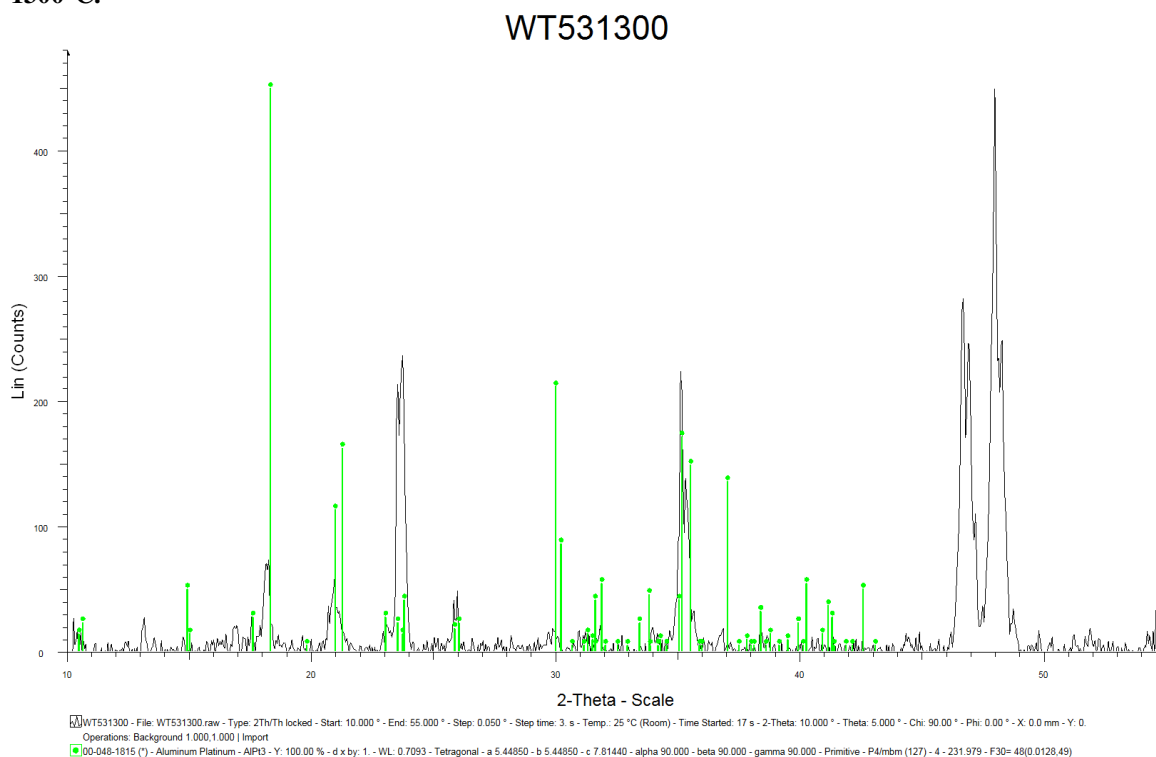


Figure 4.30. XRD trace showing peaks for the tetragonal Pt_3Al phase for the nominal 81.5 at. % Pt sample annealed at 1300°C.

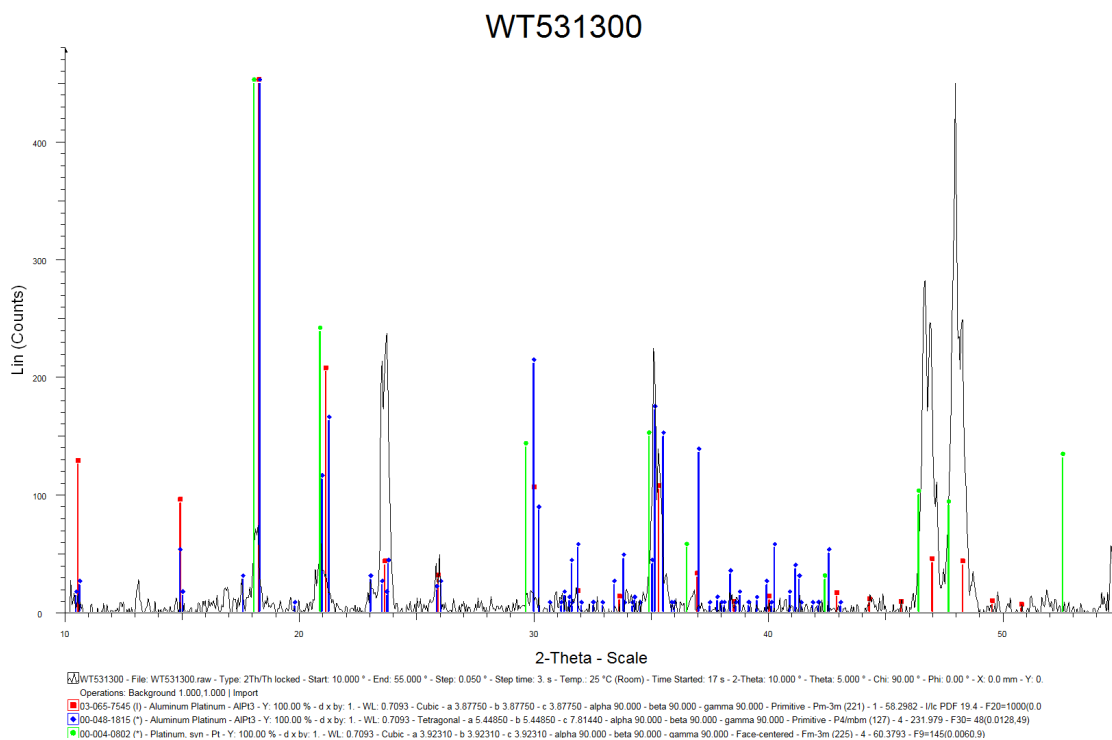


Figure 4.31. XRD trace showing peaks for cubic and tetragonal Pt_3Al and Pt for the nominal 81.5 at.% Pt sample annealed at 1300°C.

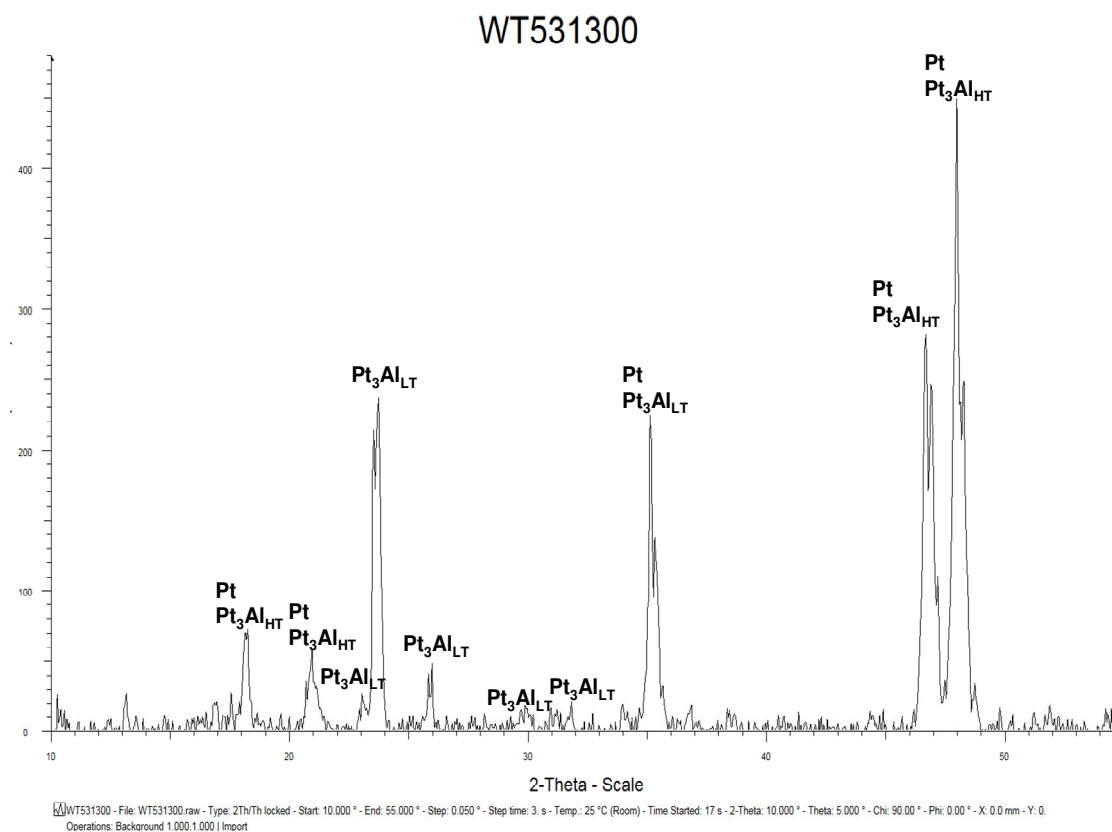


Figure 4.32. XRD pattern showing the phases in the nominal 81.5 at.% Pt sample annealed at 1400°C.

The XRD spectrum was not good, it had broad peaks, fairly low counts, low signal to background noise and had highest peaks towards the end ($2\theta = \sim 48^\circ$) (Figure 4.27). Comparison with the database [2005ICD] showed the presence of the high and low temperature Pt_3Al phases and (Pt) (Table 4.8). The peaks at $2\theta = \sim 18^\circ$, $\sim 21^\circ$, $\sim 35^\circ$, $\sim 47^\circ$ and $\sim 48^\circ$ identified (Pt), with a slight shift to the right, as shown in Figure 4.28. The presence of the peak at $2\theta = 10.5^\circ$ indicated that the sample contained at least one of the Pt_3Al phases [2001Big]. The microstructure was not twinned which is an indication of the presence of the parent cubic Pt_3Al phase, which was identified by the singlet peaks at $2\theta = \sim 18^\circ$, $\sim 21^\circ$, $\sim 47^\circ$ and $\sim 48^\circ$, which were different from the (Pt) phase as shown in Figure 4.32, with a slight shift to the left (Figure 4.27). However, in Figure 4.29, the sample clearly had peak splitting at $2\theta = \sim 23^\circ$, $\sim 26^\circ$, $\sim 30^\circ$, $\sim 31^\circ$ and $\sim 35^\circ$ which identified the tetragonal Pt_3Al , (and are different from (Pt) and cubic Pt_3Al phase peaks), with a slight shift to the left. There was no match for the peak at $2\theta = \sim 13^\circ$ (Figure 4.32).

Relative to the as-cast spectrum, the spectrum of the sample annealed at 1300°C had a noisy background and more peak splitting. Relative to the as-cast spectrum, the spectrum had the strongest peak at $2\theta = \sim 48^\circ$, while the peak at $2\theta = \sim 18^\circ$ had relatively low intensity compared to the as-cast and alloys annealed at 1500°C and 1400°C . The peak at $2\theta = \sim 15^\circ$ has disappeared relative to the as-cast spectrum, and new peaks at $2\theta = \sim 13^\circ$ and $2\theta = \sim 26^\circ$ have formed (Figure 4.29). The peak at $2\theta = \sim 26^\circ$ was also present in samples annealed at 1400°C , and matched tetragonal Pt_3Al phase. The XRD trace at $2\theta = \sim 24^\circ$, $\sim 47^\circ$ and $\sim 48^\circ$ had lower intensities relative to the database [2005ICD], therefore, the sample had preferred orientation.

4.2.5 Nominal 81.5 at. % Pt sample annealed at 1100°C

After heat treatment at 1100°C , the microstructure showed coarsened irregular dendrites, with a coarsened eutectic mixture observed between the dendrite arms (Figure 4.33). The dendrites were less coarse relative to the as-cast sample and samples annealed at 1500°C , 1400°C and 1300°C . Unlike the previous samples (annealed at 1400°C and 1300°C), the phases in the

microstructure had a different contrast (Figure 4.29). The overall composition was close to the original alloy composition, and was in the two-phase region of the phase diagrams ((Pt) and Pt₃Al) (Table 4.9) [1986McA, 1987Oya]. According to the EDS results, the light phase was in the (Pt) phase field of Massalski's phase diagram [1986McA], and in the two-phase region of Oya's phase diagram [1987Oya]. The dark phase was in the Pt₃Al phase field [1986McA, 1987Oya].

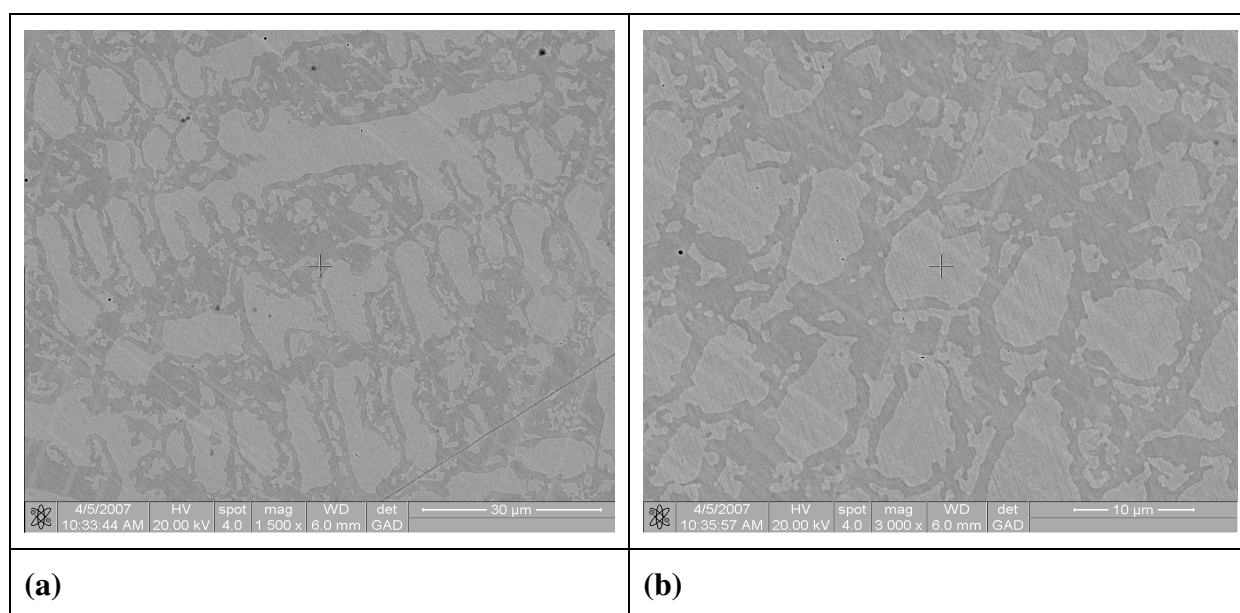


Figure 4.33. BSE-SEM image for the nominal 81.5 at. % Pt sample annealed at 1100°C for 1000 h, showing light (Pt) dendrites surrounded by a coarsened (Pt) + Pt₃Al eutectic.

Table 4.9. EDS analysis for the nominal 81.5 at. % Pt sample annealed at 1100°C for 1000 h.

Condition	Phase	Pt (at. %)	Al (at. %)	Phase
Annealed at 1100°C for 1000hrs and W/Q	Overall	79.2 ± 2.0	20.8 ± 2.0	-
	Light	89.0 ± 0.2	11.0 ± 0.2	(Pt)
	Dark	75.8 ± 0.5	24.2 ± 0.5	Pt ₃ Al

Table 4.10. XRD database [2005ICD] information for the nominal 81.5 at.% Pt sample annealed at 1100°C.

2 θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
10.5	3.88	100	7	-	28	-
14.9	2.74	110	27	-	20	-
18/18.0/18.3	2.27/2.24/ 2.23	111/111/202	51	100	99	100
20.8	1.96	200	56	53	-	-
23	1.78	213	2	-	-	6
26.0	1.58	312	4	-	-	5
29.6/29.9	1.39/1.37	220/224	65	31	-	47
31.8	1.29	314	9	-	-	12
34.9/35.3/35.1	1.18/1.17/1.18	311/311/206	100	33	23	38
42.6	0.98	008	7	-	-	11
46.4	0.9	331	9	22	-	-
47.7	0.88	420	9	20	-	-

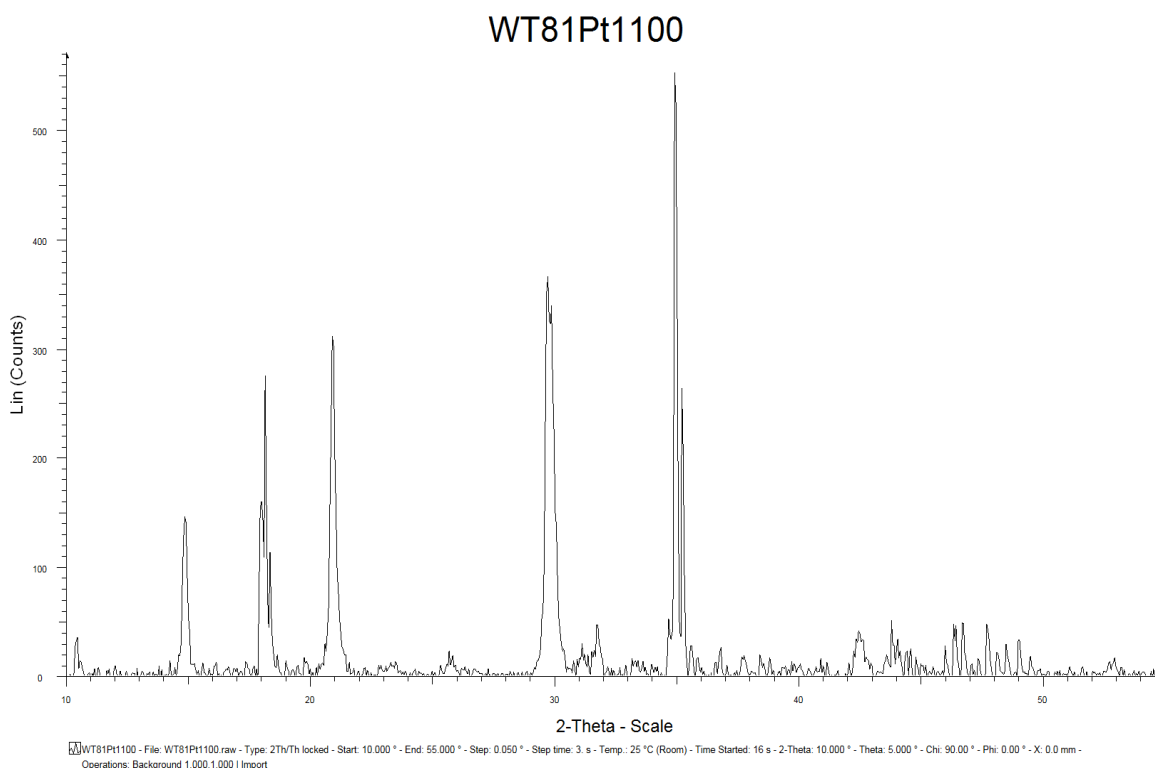


Figure 4.34. Raw XRD spectrum for the nominal 81.5 at.% Pt sample annealed at 1100°C.

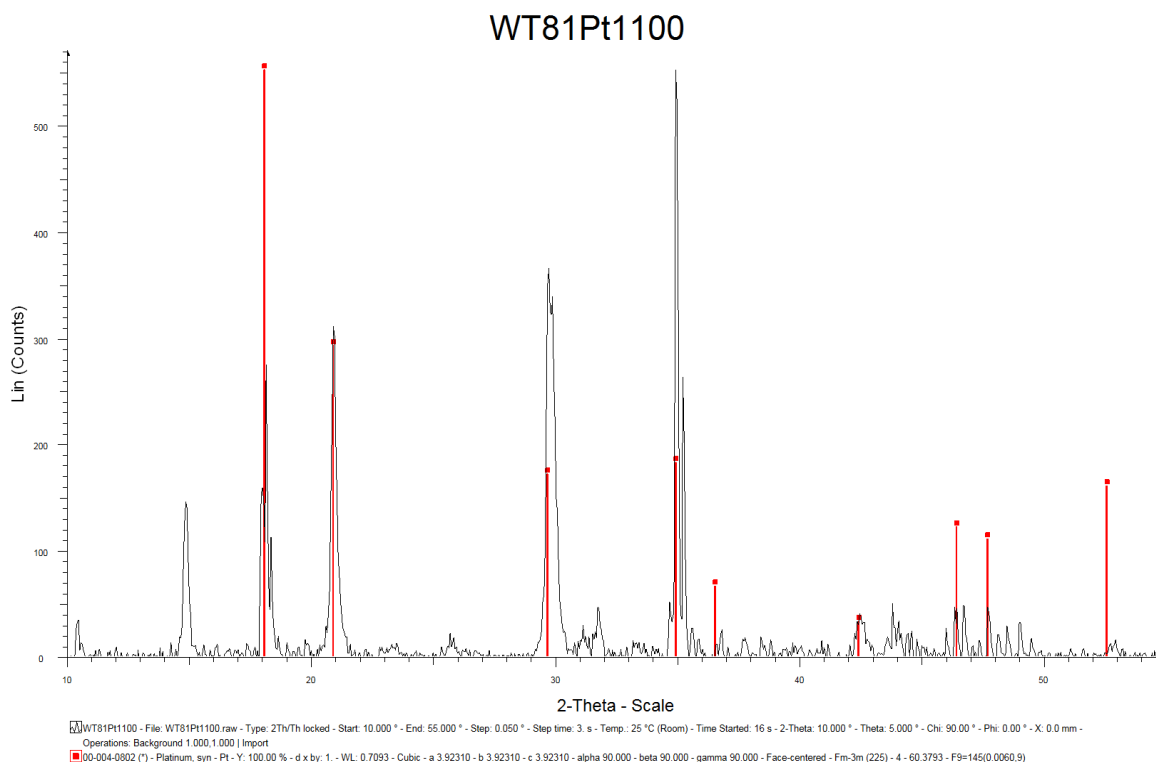


Figure 4.35. XRD trace showing peaks of Pt for the nominal 81.5 at. % Pt sample annealed at 1100°C.

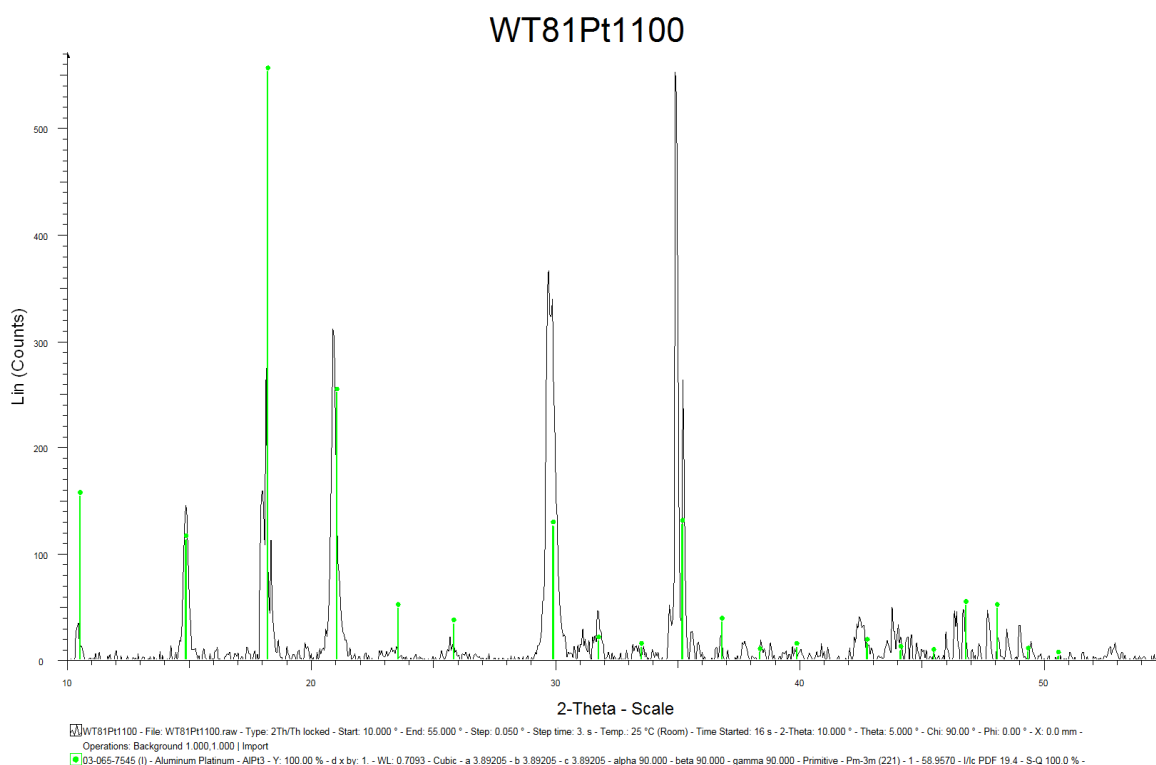


Figure 4.36. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 81.5 at. % Pt sample annealed at 1100°C.

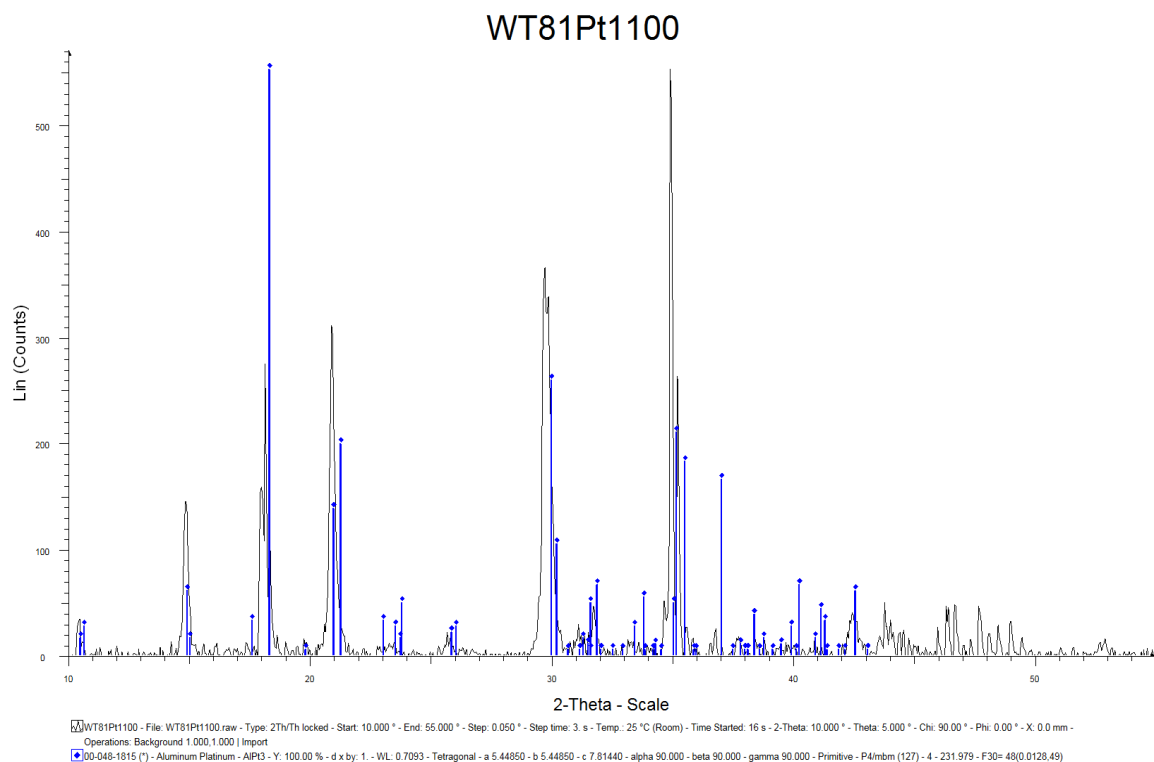


Figure 4.37. XRD trace showing peaks of the tetragonal Pt_3Al phase for the nominal 81.5 at.% Pt sample annealed at 1100°C.

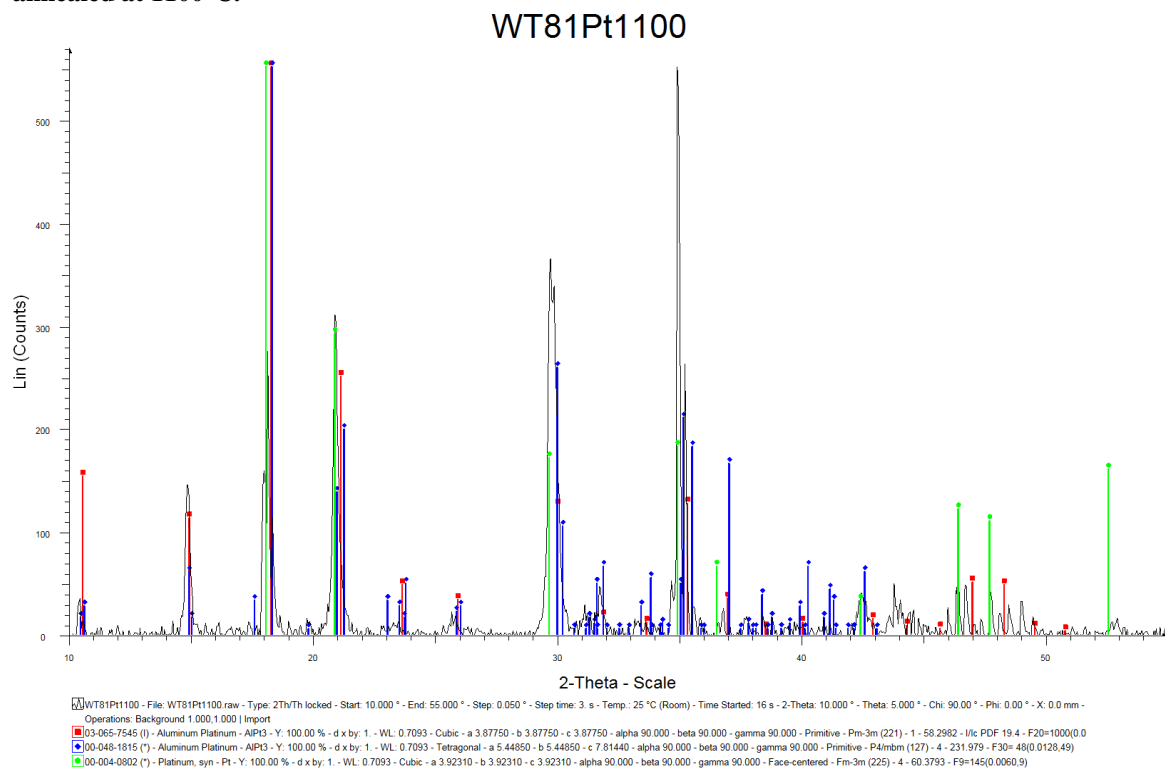


Figure 4.38. XRD trace showing peaks of the cubic and tetragonal Pt_3Al structures and Pt for the nominal 81.5 at.% Pt sample annealed at 1100°C.

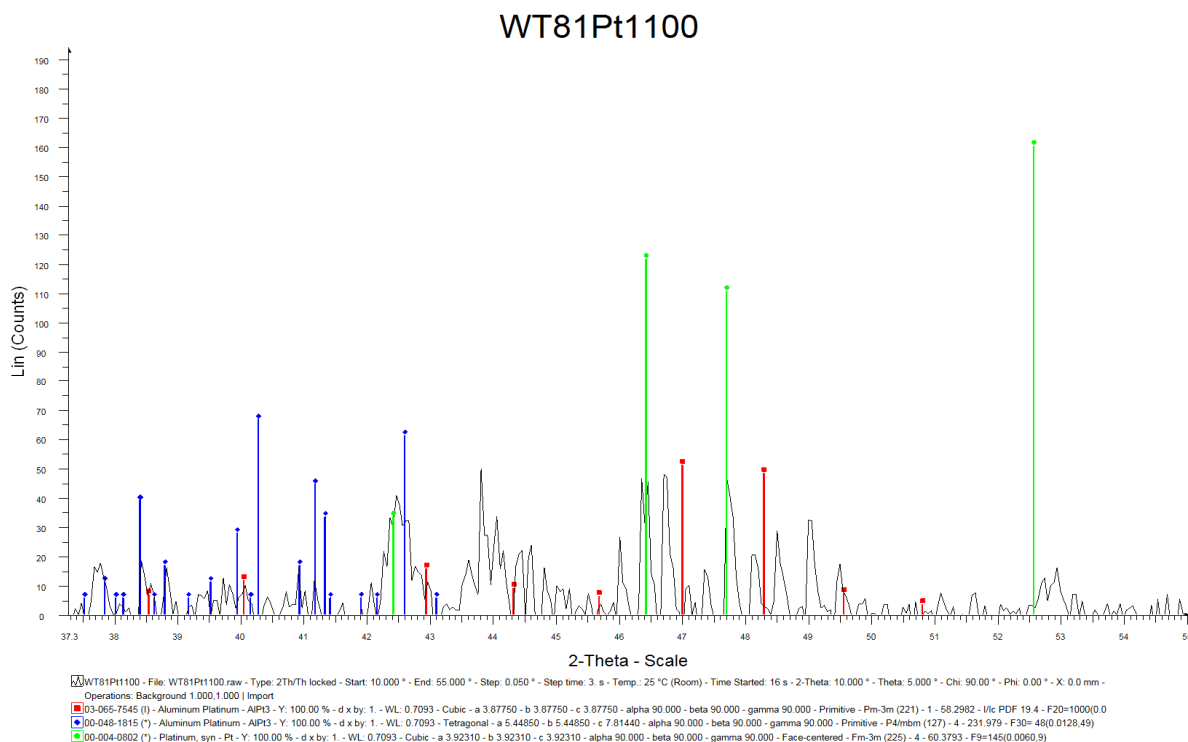


Figure 4.39. XRD trace ($2\theta = 37.3^\circ$ to 55°) distinguishing between cubic and tetragonal Pt_3Al structures and Pt for the nominal 81.5 at. % Pt sample annealed at 1100°C .

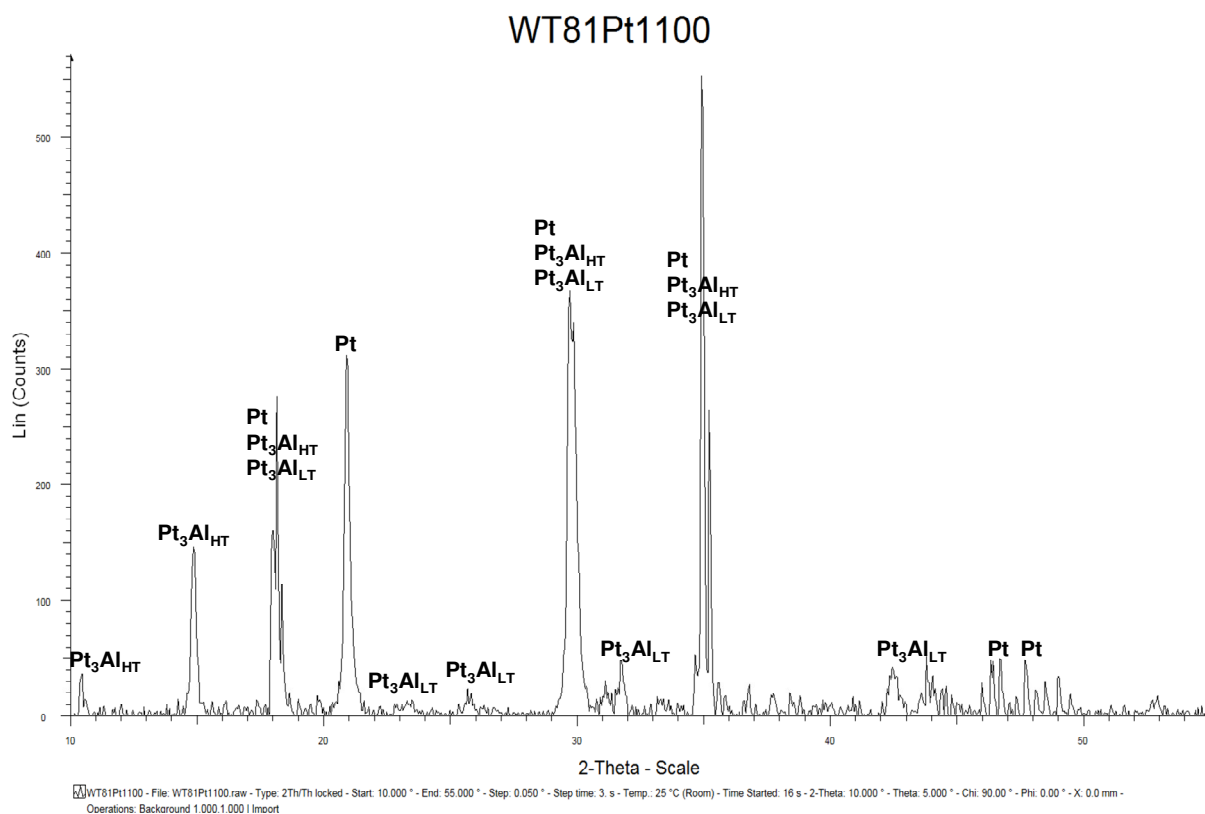


Figure 4.40. XRD pattern showing the phases in the nominal 81.5 at. % Pt sample annealed at 1100°C .

The XRD spectrum had broad peaks, fairly low counts and high signal to background noise (Figure 4.34). The major peak intensities of the spectrum increases as 2θ increases (Figure 4.34). In comparison with the database [2005ICD], the high and low temperature Pt_3Al phases and (Pt) were present (Table 4.10). The peaks which identified (Pt) are $2\theta = \sim 18^\circ$, $\sim 21^\circ$, $\sim 30^\circ$, $\sim 35^\circ$, 46.5° and $\sim 48^\circ$ with a negligible shift as shown in Figure 4.35. The peaks towards the end are expanded for a better view as shown in Figure 4.39. Biggs [2001Big], reported that the peaks at $2\theta = 10.5^\circ$, $\sim 15^\circ$ indicated that the sample contained at least one of the Pt_3Al phases. In Figure 4.36, the singlet peaks at $2\theta = 10.5^\circ$, $\sim 15^\circ$, $\sim 18^\circ$ and $\sim 35^\circ$ identified the cubic Pt_3Al phase, and are different from the (Pt) peaks, with a negligible shift. In Figure 4.37, there was peak splitting from the tetragonal Pt_3Al phase at $2\theta = \sim 18^\circ$, $\sim 23^\circ$, $\sim 26^\circ$, $\sim 30^\circ$, $\sim 32^\circ$, $\sim 35^\circ$, $\sim 43^\circ$ and $\sim 44^\circ$, which are different from (Pt) and cubic Pt_3Al peaks, with a slight shift to the left. Based on the information above, it was concluded that all three phases were present as shown in Figure 4.40.

Relative to the as-cast and previous samples, the spectrum had the strongest peak at $2\theta = \sim 35^\circ$ (Figure 4.34), while the as-cast sample and the sample heat treated at 1500°C had the strongest peak at $2\theta = \sim 18^\circ$, the sample annealed at 1400°C had the strongest peak at $2\theta = \sim 32^\circ$, and the sample annealed at 1300°C had the strongest peak at $2\theta = \sim 48^\circ$. Relative to the as-cast spectrum, new peaks for the tetragonal Pt_3Al phase at $2\theta = \sim 31^\circ$, $\sim 43^\circ$ and 44° were found. The peak at $2\theta = \sim 37^\circ$ has disappeared and the peaks at $2\theta = \sim 47^\circ$ and 48° had lower intensities relative to the as-cast spectrum. Therefore the spectrum showed a reduced preferred orientation compared to the as-cast condition.

4.3 Phase analyses for the 75 at.% Pt samples

4.3.1 Nominal 75 at.% Pt in the arc-melted condition

After solidification, the sample had a two-phase microstructure. The microstructure had coarse grains, with a minor white grain boundary phase, the platinum solid solution, with dark precipitates nucleated throughout (Figure 4.41). There were some patches of the light phase within the dark phase, thus the dark phase had a high error of ~1.2 at.% Pt (because the analyses were affected by the light phase). The overall composition was higher in Pt than targeted, which was probably due to errors in weighing rather than melting, especially considering that all the nominal 75 at.% samples had much more Pt than would be the case if Al was lost, and was in the two-phase region ((Pt) and Pt₃Al) (Table 4.11) [1986McA, 1987Oya]. The light phase composition was in the (Pt) phase region, and the composition was higher than the target. The dark phase was in the two-phase region ((Pt) and Pt₃Al) of the phase diagrams [1986McA, 1987Oya]. However, the dark phase was identified as Pt₃Al [1986McA].

The solidification sequence was:

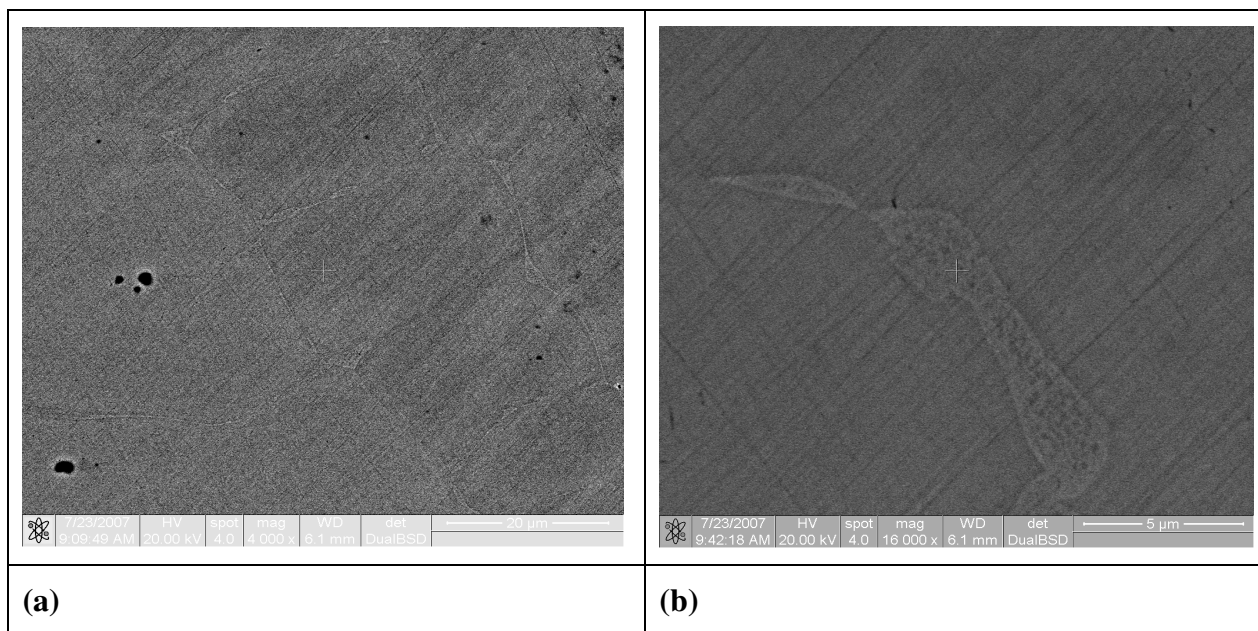
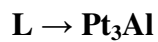


Figure 4.41. BSE-SEM image for the nominal 75 at.% Pt sample in the as-cast condition, showing the light (Pt) phase mainly along the grain boundaries as a eutectic and Pt_3Al as the dark phase.

Table 4.11. EDS analysis for the nominal 75 at.% Pt sample in the as-cast condition.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
75 at.% Pt sample in arc-melted condition	Overall	85.1 ± 2.5	14.9 ± 2.5	-
	Light	87.9 ± 0.1	12.1 ± 0.1	Mainly (Pt)
	Dark	77.7 ± 1.2	22.3 ± 1.2	Mainly Pt_3Al

Table 4.12. XRD database information [2005ICD] for the nominal 75 at.% Pt sample in the as-cast condition.

2 θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
10.6	3.85	110	4	-	-	5
14.9/14.9	2.74/2.74	110/112	100	-	20	11
17.5	2.33	211	23	-	-	6
18	2.27	111	44	100	-	-
21.2	1.93	220	16	-	-	36
23.8	1.72	310	11	-	-	9
29.9	1.37	224	16	-	-	47
31.9	1.29	314	7	-	-	12
34.9/35.3	1.18/1.17	311/311	36	33	23	-
38.4	1.08	431	21	-	-	7
49.6	0.85	421	64	-	1	-

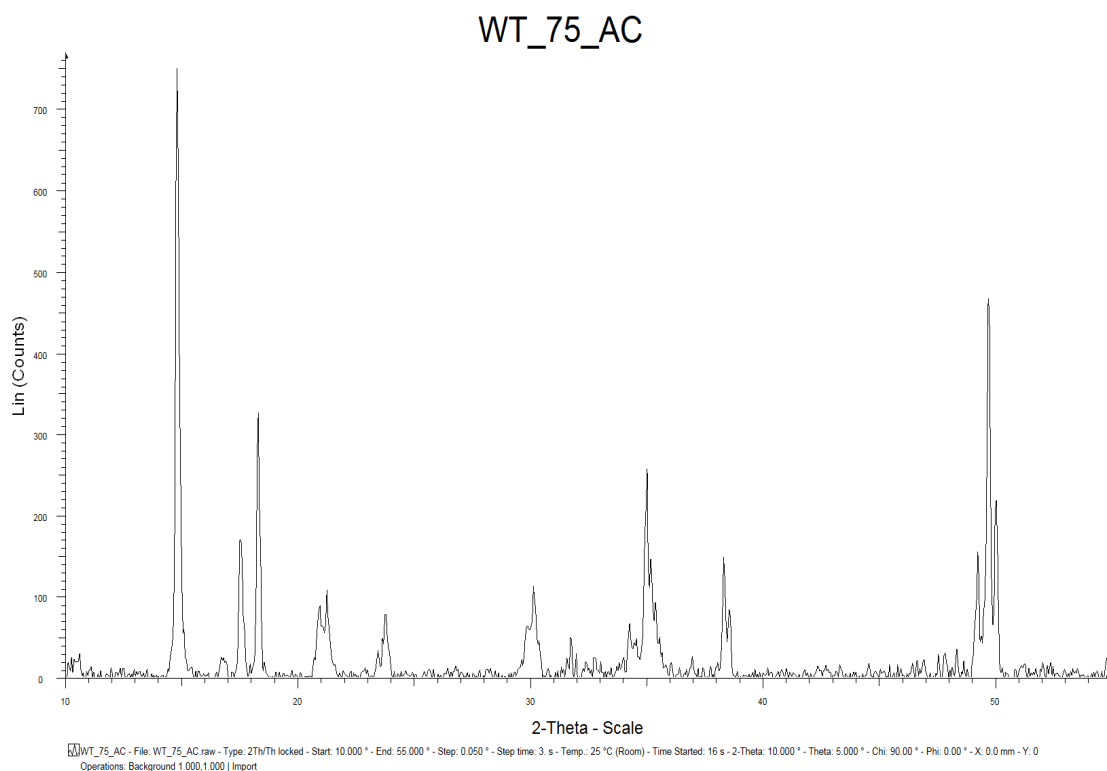


Figure 4.42. Raw XRD spectrum for the nominal 75 at.% Pt sample in the as-cast condition.

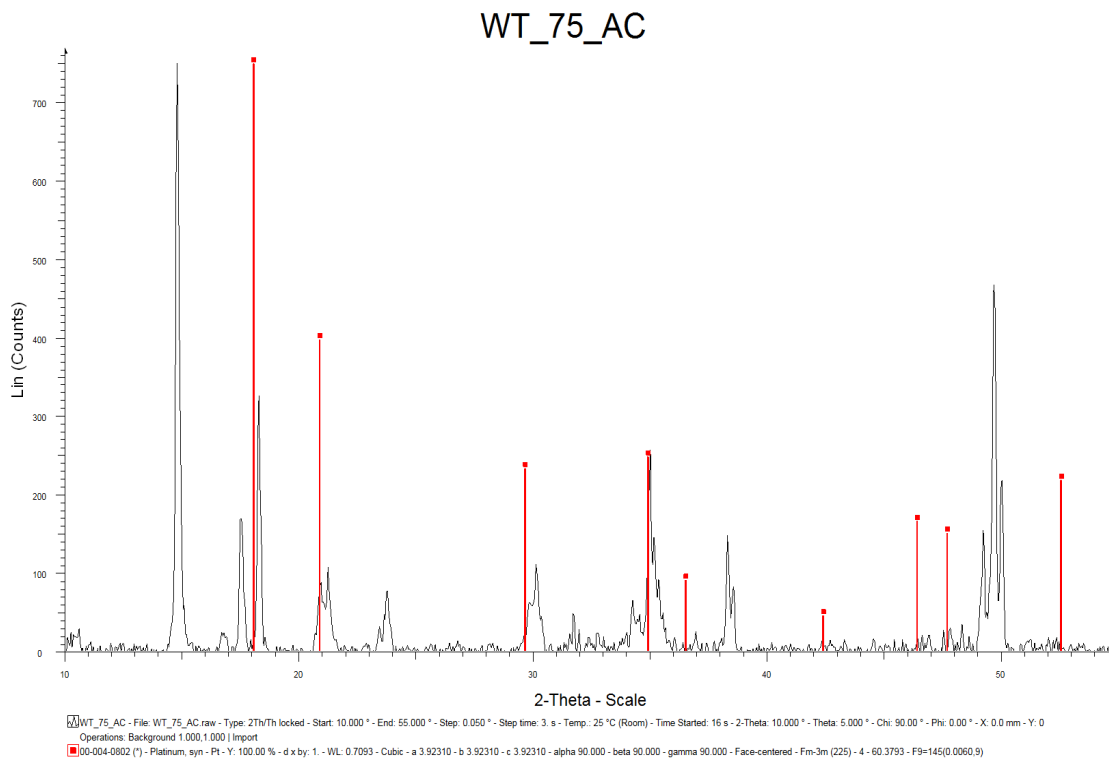


Figure 4.43. XRD trace showing peaks of Pt for the nominal 75 at.% Pt sample in the as-cast condition.

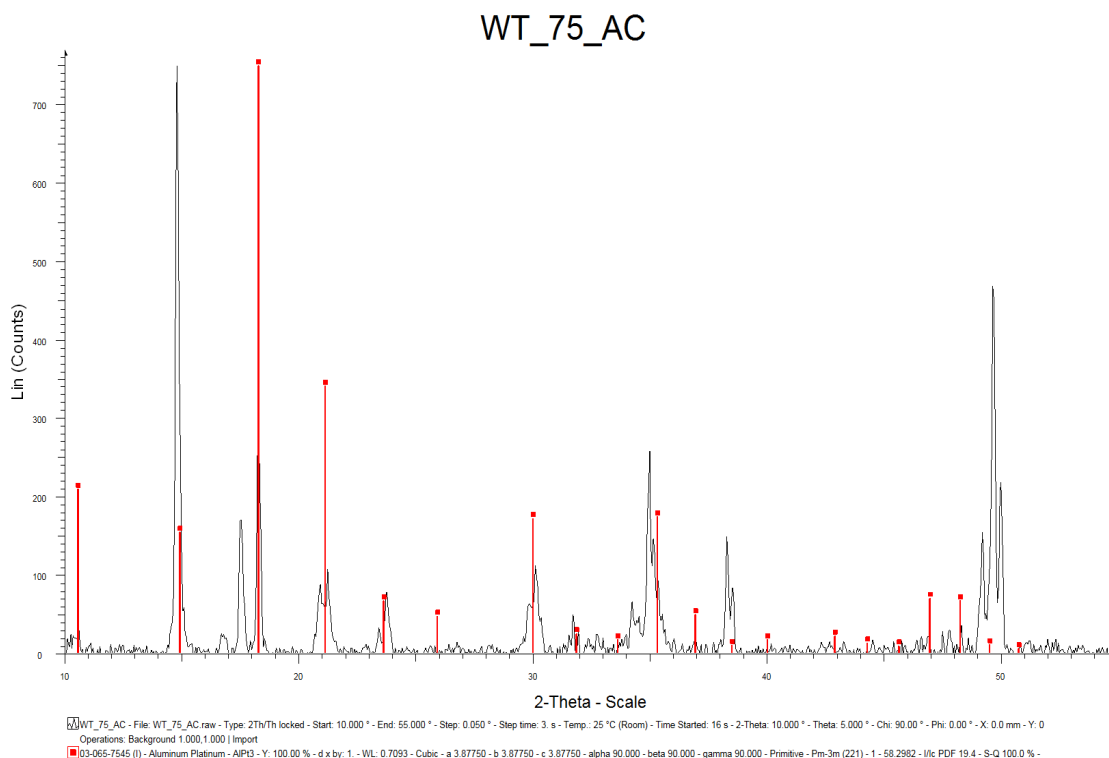


Figure 4.44. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 75 at.% Pt sample.

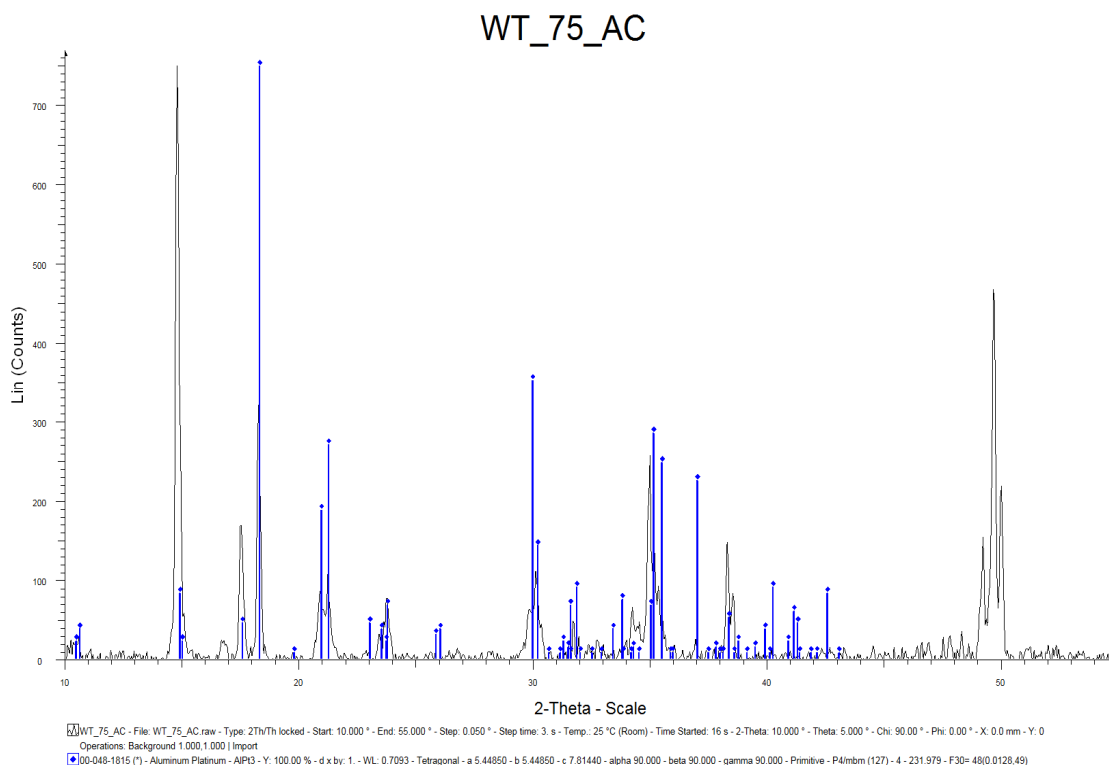


Figure 4.45. XRD trace showing peaks of tetragonal Pt_3Al for the nominal 75 at. % Pt sample in the as-cast condition.

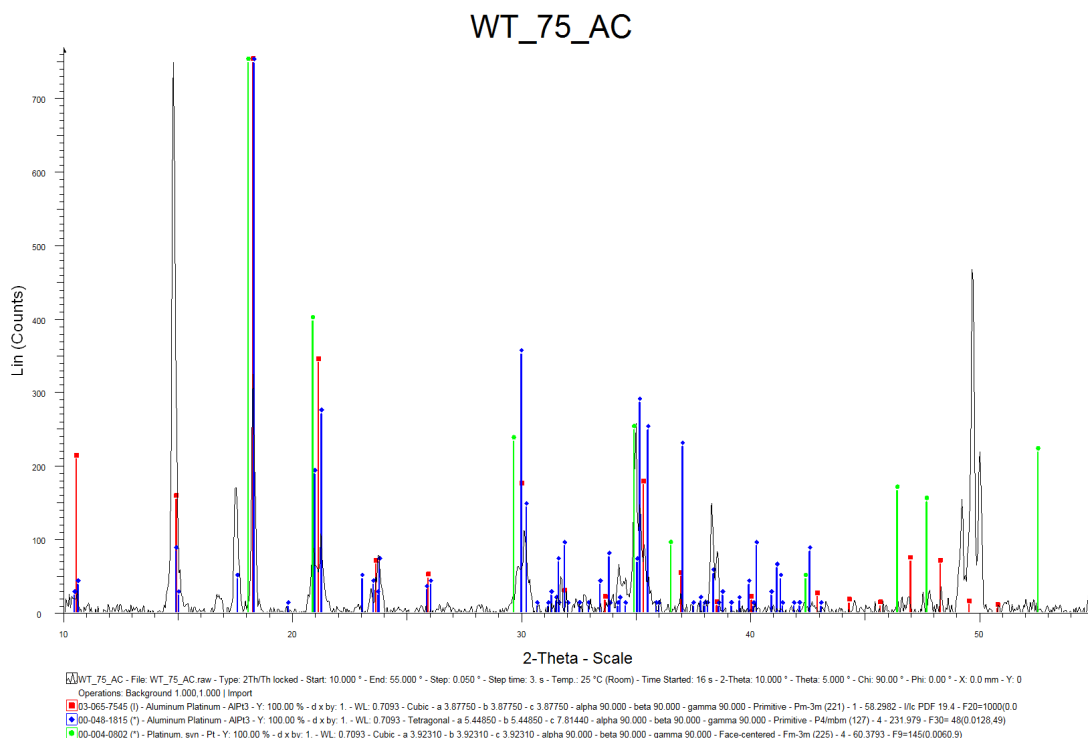


Figure 4.46. XRD trace showing peaks of cubic and tetragonal Pt_3Al and Pt for the nominal 75 at. % Pt sample in the as-cast condition.

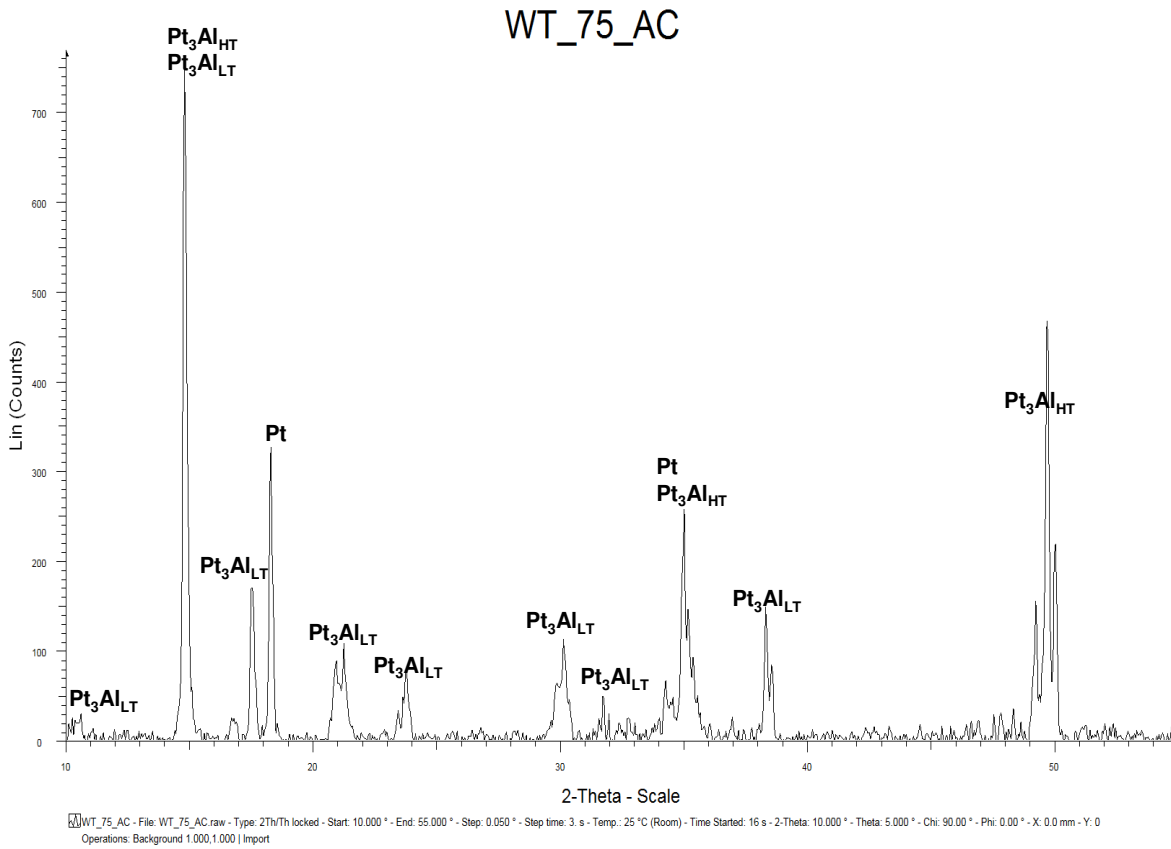


Figure 4.47. XRD pattern showing the phases in the nominal 75 at. % Pt sample in the as-cast condition.

The XRD spectrum had broad peaks, high counts and a good signal to background noise (Figure 4.42). The XRD database [2005ICD] confirmed the presence of high and low temperature Pt_3Al phases as well as the (Pt) phase (Table 4.12). The (Pt) phase was identified by peaks at $2\theta = \sim 18^\circ$ and $\sim 35^\circ$, with a slight shift to the right Figure 4.43. The peaks at $2\theta = 10.5^\circ$ and $\sim 15^\circ$ indicated the presence of at least one of the Pt_3Al phases [2001Big]. In Figure 4.44 the singlet peaks at $2\theta = \sim 15^\circ$, $\sim 35^\circ$ and $\sim 50^\circ$, which are different from the (Pt) peaks, indicated the cubic Pt_3Al phase with a slight shift to the left. In Figure 4.45, there is peak splitting at $2\theta = 10.5^\circ$, $\sim 15^\circ$, 17.5° , $\sim 21^\circ$, $\sim 24^\circ$, $\sim 30^\circ$, $\sim 32^\circ$ and 38.5° , and these peaks are different from (Pt) and cubic Pt_3Al peaks, with a negligible shift (Figures 4.45 and 4.47). There was no match for the peak at $2\theta = 16.8^\circ$, which is only a small peak (Figure 4.47). Based on the above information, it was assumed that all three phases were present in the microstructure as shown in Figure 4.47.

4.3.2 Nominal 75 at.% Pt sample annealed at 1400°C

Heat treatment at 1400°C resulted in the coarsened dark precipitates nucleated throughout a light matrix (Figure 4.48). The precipitates were quite small and were very close together, which resulted in inaccurate EDS measurements for both phases. The as-cast microstructure had the light phase only in the grain boundaries (Figure 4.41), while the sample heat treated at 1400°C showed a two-phase mixture throughout the sample. The overall composition of the microstructure was in the two-phase region of both published phase diagrams [1986McA, 1987Oya]. The light phase was in the (Pt) phase region [1986McA], but at the (Pt) phase boundary in Oya's phase diagram [1987Oya]. The dark phase was assumed to be Pt_3Al phase and it was in the two-phase region of both phase diagrams [1986McA, 1987Oya], and it was too small to analyse (Table 4.13).

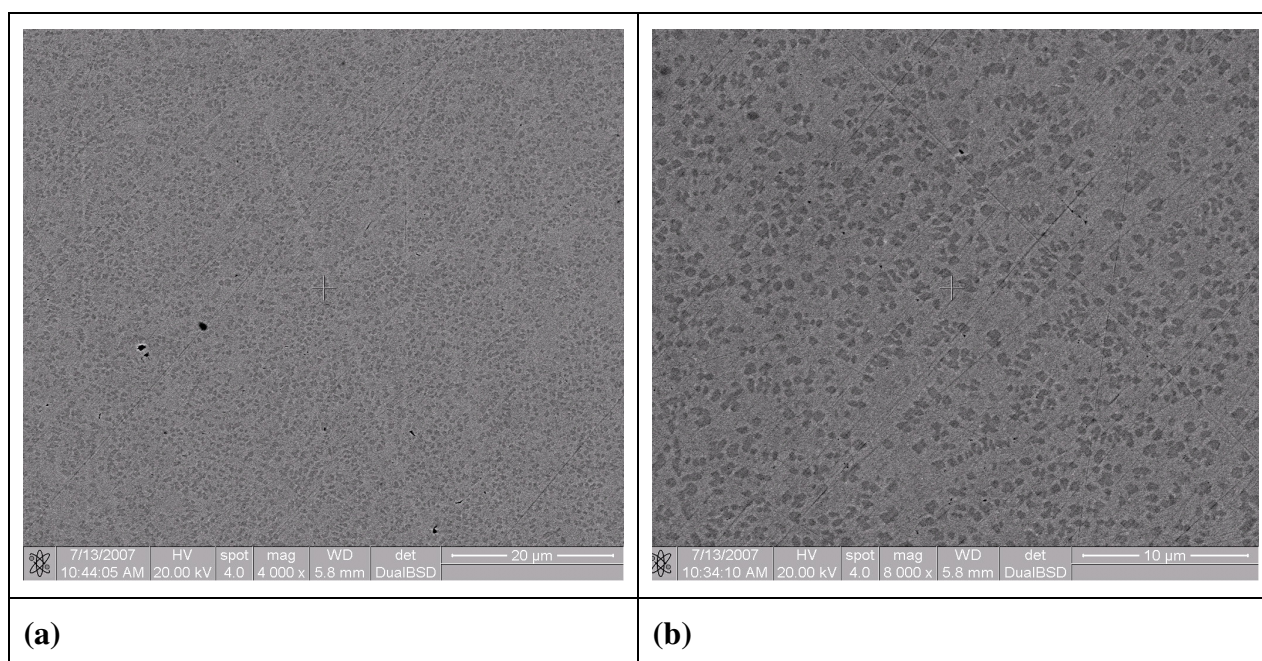


Figure 4.48. BSE-SEM image for nominal 75 at.% Pt annealed at 1400°C, showing light (Pt) phase and Pt_3Al phase (dark precipitates).

Table 4.13. EDS analysis for the nominal 75 at.% Pt sample annealed at 1400°C for 1000 h.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
75 at.% Pt annealed at 1400°C for 1000 hrs then W/Q	Overall	86.1 ± 0.8	13.9 ± 0.8	-
	Light	88.8 ± 0.8	11.2 ± 0.8	(Pt)
	Dark	79.0 ± 1.0	21.0 ± 1.0	Pt ₃ Al

Table 4.14. XRD database information [2005ICD] analysis for the nominal 75 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}
10.4	3.88	100	6	-	28
14.9/14.9	2.74/2.74	110/112	4	-	20
18/18.0	2.27/2.24	111/111	2	100	99
20.8/21.1	1.96/1.94	200/200	100	53	45
23.6	1.73	210	8	-	9
29.6/29.9	1.39/1.37	220/220	21	31	23
34.9/35.3	1.18/1.17	222/311	6	33	23
42.5	0.98	400	-	6	-
38.5	1.07	320	4	-	12
46.4/47	0.9/0.89	331/331	8	22	9
47.7/48.3	0.88/0.87	420/420	81	20	9

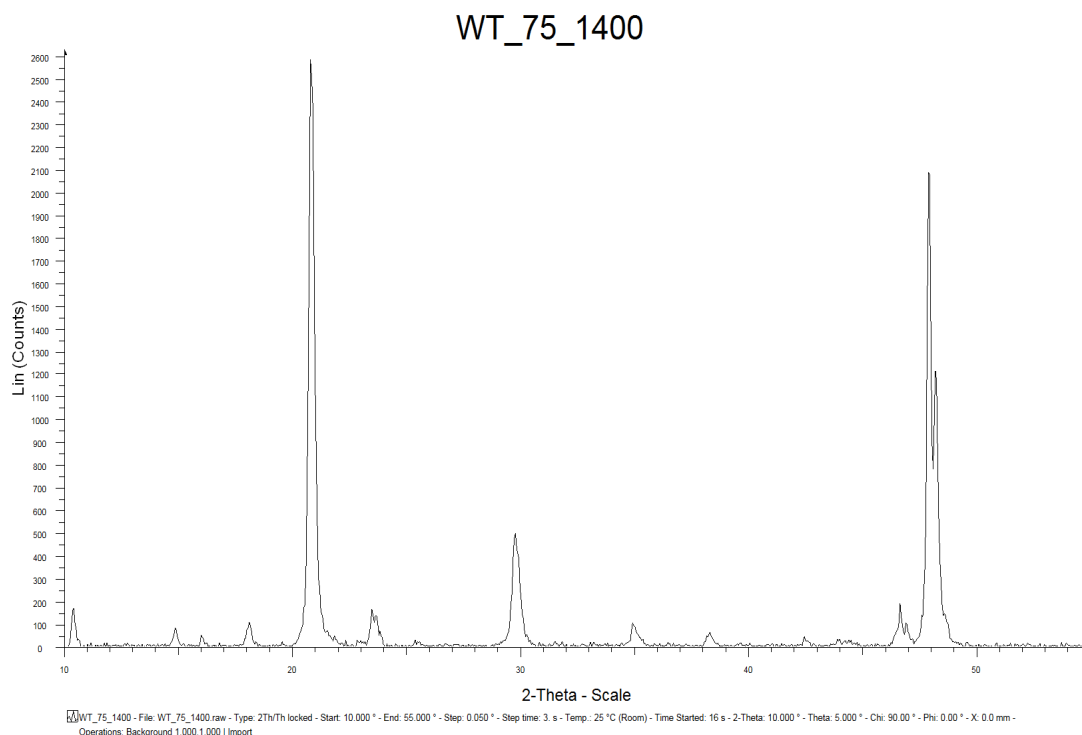


Figure 4.49. Raw XRD spectrum for the nominal 75 at.% Pt sample annealed at 1400°C.

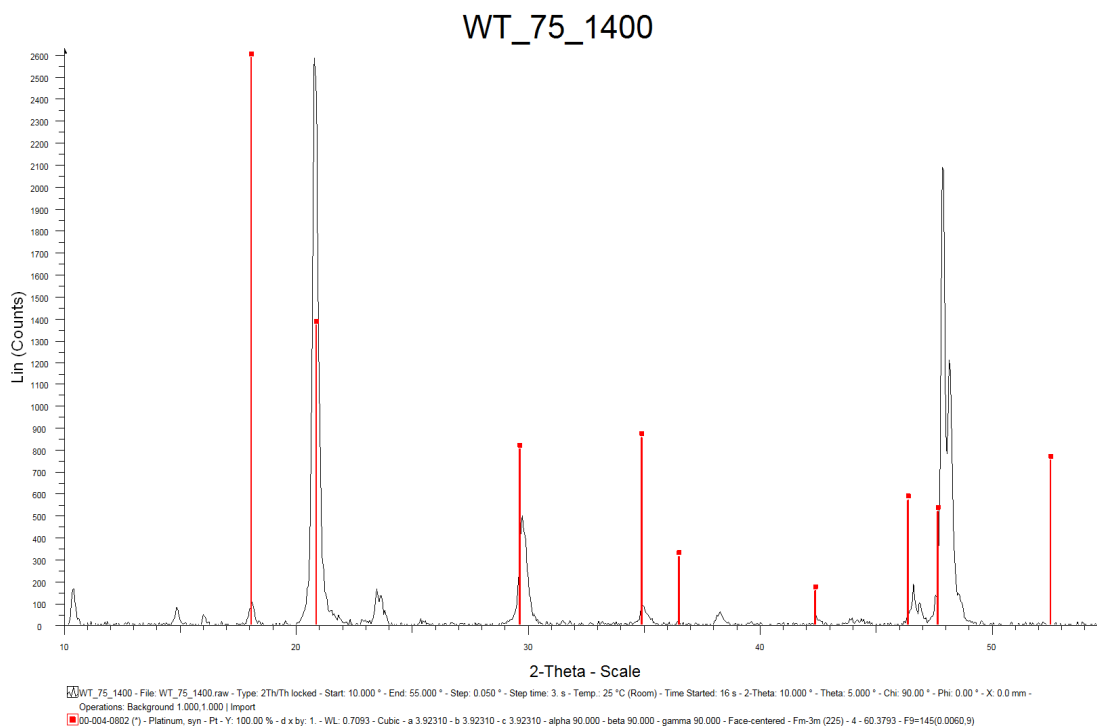


Figure 4.50. XRD trace showing peaks of Pt for the nominal 75 at.% Pt sample annealed at 1400°C.

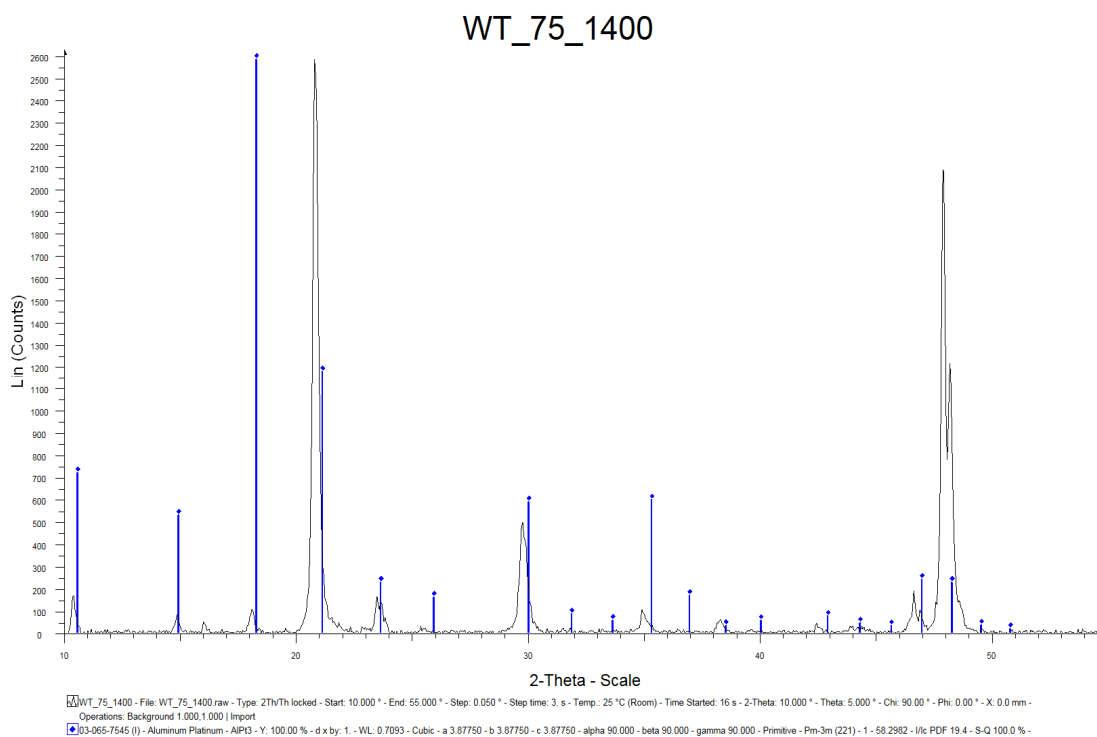


Figure 4.51. XRD trace showing peaks of the cubic Pt₃Al phase for the nominal 75 at.% Pt sample annealed at 1400°C.

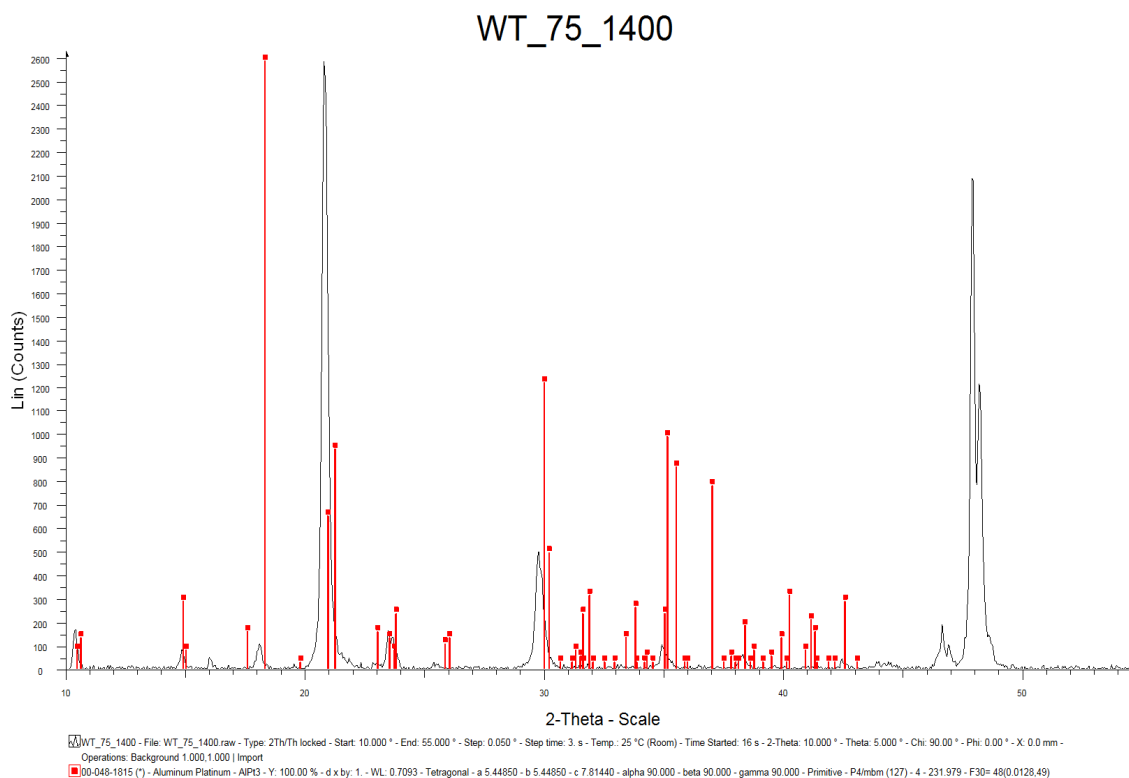


Figure 4.52. XRD trace showing peaks of tetragonal Pt_3Al for the nominal 75 at.% Pt sample annealed at 1400°C .

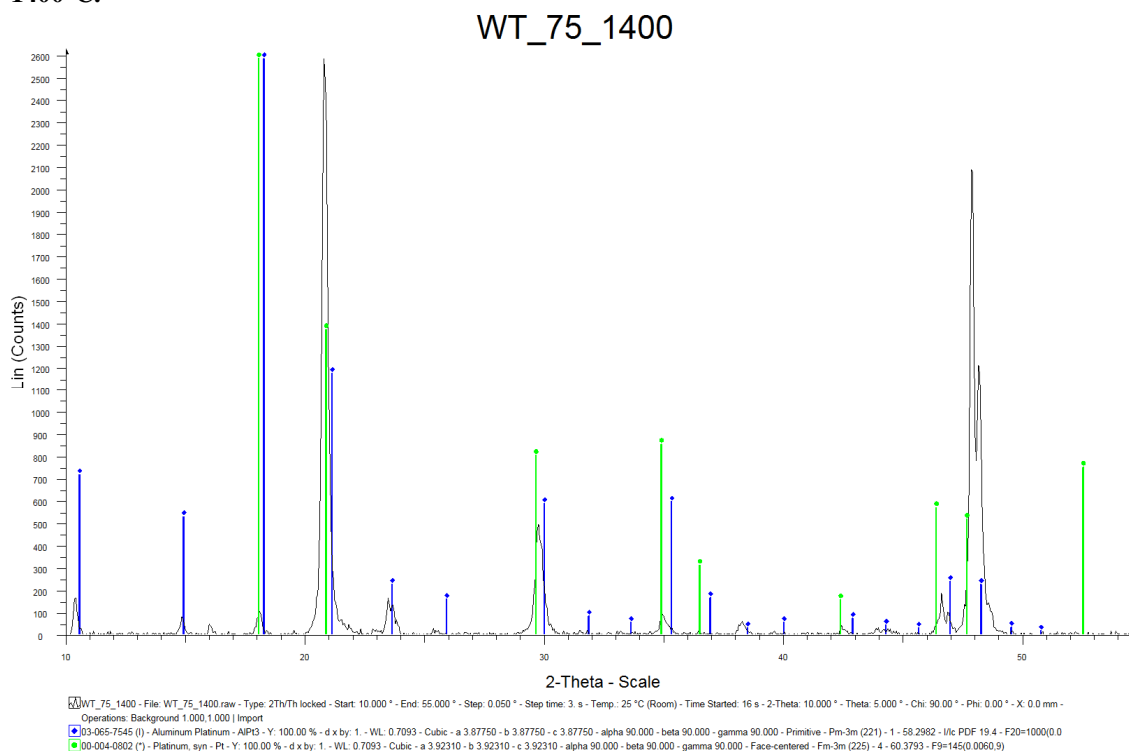


Figure 4.53. XRD trace showing peaks of Pt and cubic Pt_3Al for the nominal 75 at.% Pt sample annealed at 1400°C .

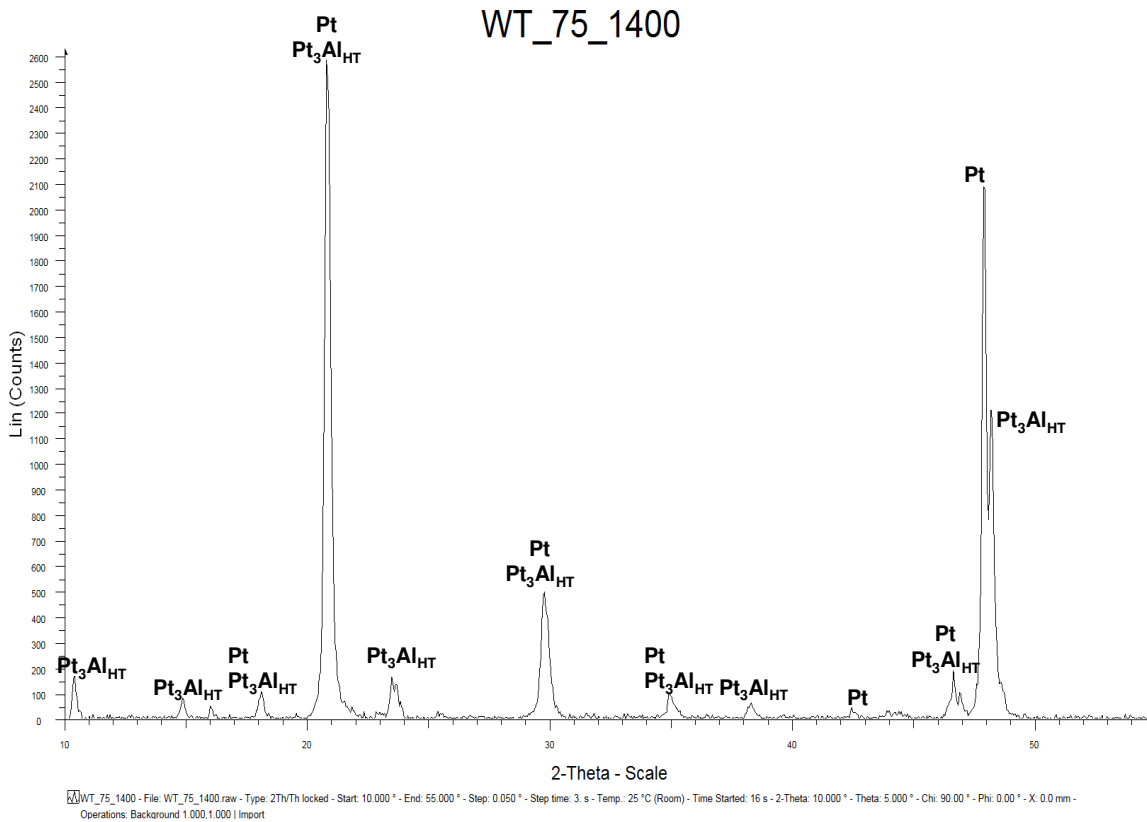


Figure 4.54. XRD pattern showing the phases in the nominal 75 at.% Pt sample annealed at 1400°C.

The XRD spectrum had fairly broad peaks, high counts, high signal to background noise (Figure 4.49), and few peaks, reflecting a simple structure, with less peak splitting than the as-cast spectrum. The XRD spectrum [2005ICD] showed a good match for cubic Pt₃Al and (Pt) (Table 4.14). A good match for (Pt) was observed at $2\theta = \sim 18^\circ, \sim 21^\circ, \sim 30^\circ, \sim 35^\circ, 42.5^\circ, \sim 47^\circ$ and $\sim 49^\circ$, with a slight shift to the right (Figure 4.50). Biggs [2001Big], reported that the peaks at $2\theta = 10.5^\circ$ and $2\theta = \sim 15^\circ$ indicated that the sample contained at least one of the Pt₃Al phases. In Figure 4.51, singlet peaks from cubic Pt₃Al were observed at $2\theta = \sim 10.5^\circ, \sim 15^\circ, \sim 18^\circ, \sim 21^\circ, \sim 24^\circ, \sim 30^\circ, \sim 35^\circ, \sim 38.5^\circ, \sim 47^\circ$ and $\sim 48^\circ$, which was different from (Pt), with a slight shift to the right. A small peak at $2\theta = \sim 16^\circ$ was not identified. Based on the information mentioned above, two phases were present in the microstructure as shown in Figure 4.53. Relative to the as-cast spectrum, the sample had the strongest peak at $2\theta = \sim 21^\circ$, which was from the cubic Pt₃Al and (Pt) phases (Figure 4.54). Peaks at $2\theta = \sim 15^\circ, \sim 18^\circ$ and 38.5° , had relatively low intensities compared to the as-cast spectrum.

4.3.3 Nominal 75 at.% Pt sample annealed at 1300°C

There was a single phase in the centre of the microstructure and a two-phase region at the edge (Figure 4.55). The two-phase mixture was a light phase with dark precipitates nucleated throughout. The zone at the edges was richer in platinum than the single phase region in the centre. The sample showed evidence of the evaporation of aluminium during the heat treatment process since there was less Al at the edge, and the microstructure was different. The individual phases at the edge layer could not be analysed accurately as the phases were fine and close together. The overall composition was ~4 at.% Pt higher in platinum than the targeted composition, and was in the Pt_3Al phase field of Massalski's phase diagram [1986McA], while it was in the two-phase field in Oya's phase diagram [1987Oya] (Table 4.14). The light phase was in the (Pt) phase region [1986McA], although it was in the two-phase field in [1987Oya]. The dark phase was fairly close to the eutectoid composition of Massalski [1986McA], and in the Pt_3Al phase field in Oya and Mishima's phase diagram [1987Oya].

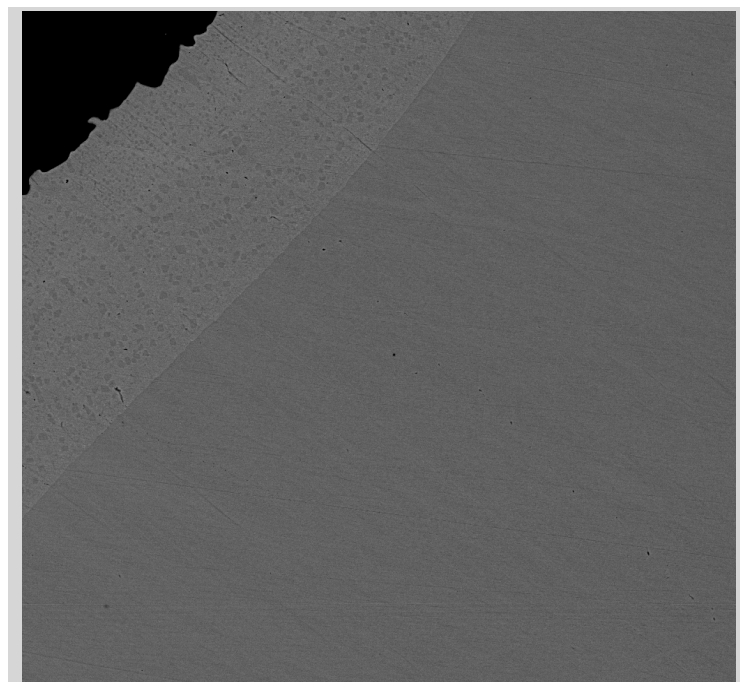


Figure 4.55. BSE-SEM image for nominal 75 at.% Pt annealed at 1300°C, showing light phase (towards the edge) of the Pt_3Al (dark phase) and (Pt).

Table 4.15. XRD analyses for nominal 75 at.% Pt annealed at 1300°C for 1000 h.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
75 at.% Pt sample annealed at 1200°C	Overall	79.1 ± 0.01	20.9 ± 0.01	Pt ₃ Al
	Edge	89.0 ± 1.8	11.0 ± 1.8	(Pt) + ~Pt ₃ Al
	Centre	76.5 ± 0.6	23.5 ± 0.6	Pt ₃ Al

Table 4.16. XRD database information [2005ICD] for the nominal 75 at.% Pt sample annealed at 1300°C for 1000 h.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
10.5	3.88	100	9	-	28	-
14.9	2.74	110	55	-	20	-
18/18.2/18.3	2.27/2.24/ 2.24	111/111/202	85	100	99	100
20.8	1.96	200	16	53	-	-
23.8	1.72	310	16	-	-	9
26.0	1.58	312	7	-	-	5
29.6/29.9/29.9	1.39/1.37/1.37	220/220/224	100	31	23	47
31.9	1.29	314	11	-	-	12
36.5/36.9	1.13/1.12	222/222	11	12	6	-
40.2	10.3	512	9	-	-	12
47.7/48.3	0.88/0.87	420/420	12	20	9	-

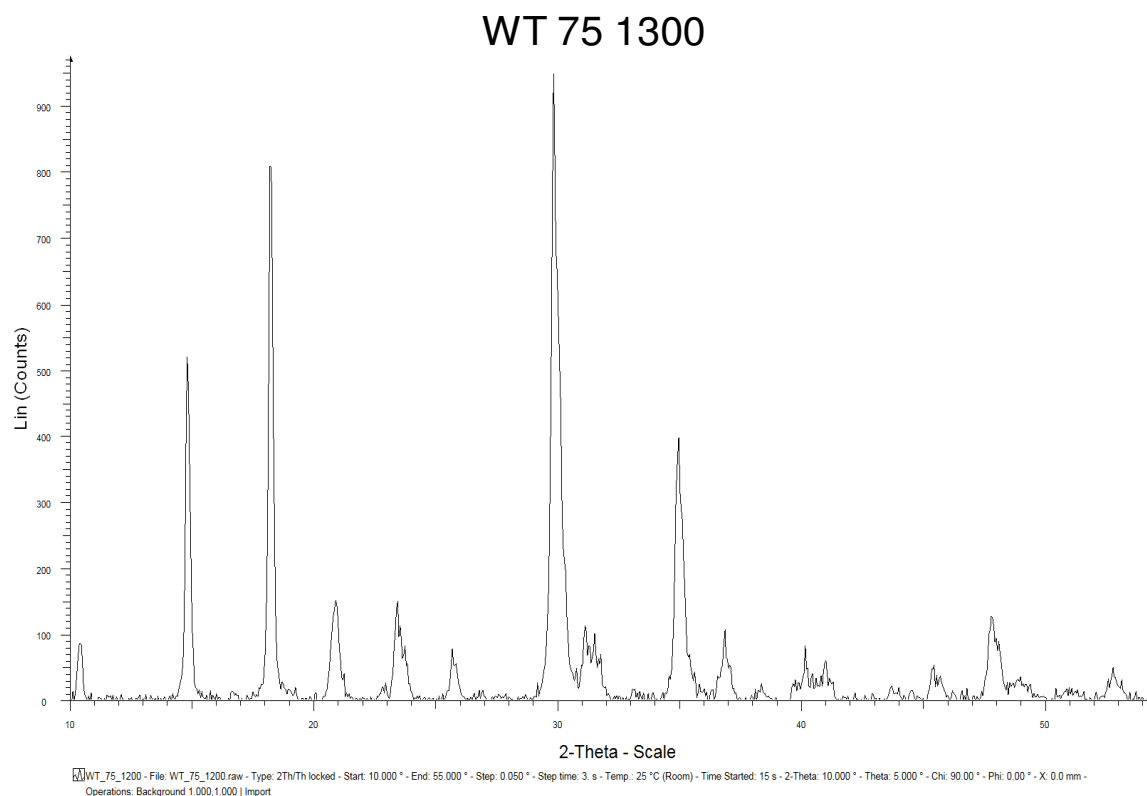


Figure 4.56. Raw XRD spectrum for the nominal 75 at.% Pt sample annealed at 1300°C.

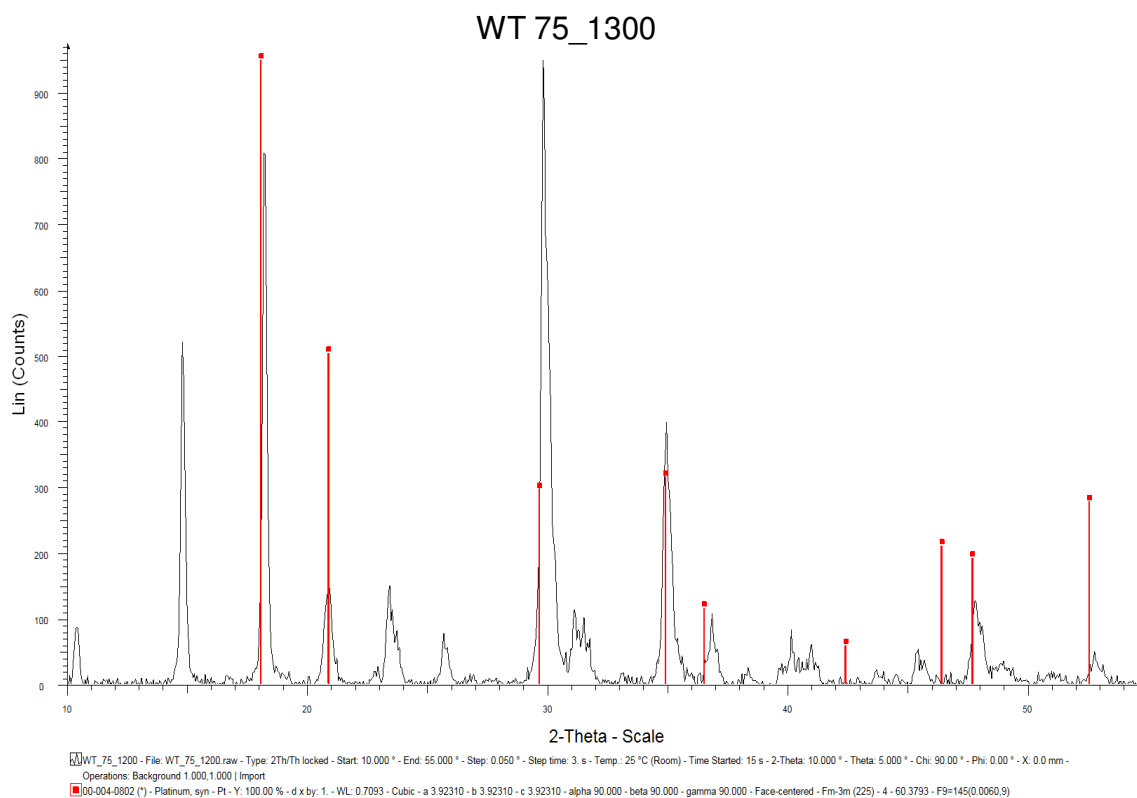


Figure 4.57. XRD trace showing peaks of Pt for the nominal 75 at.% Pt sample annealed at 1300°C.

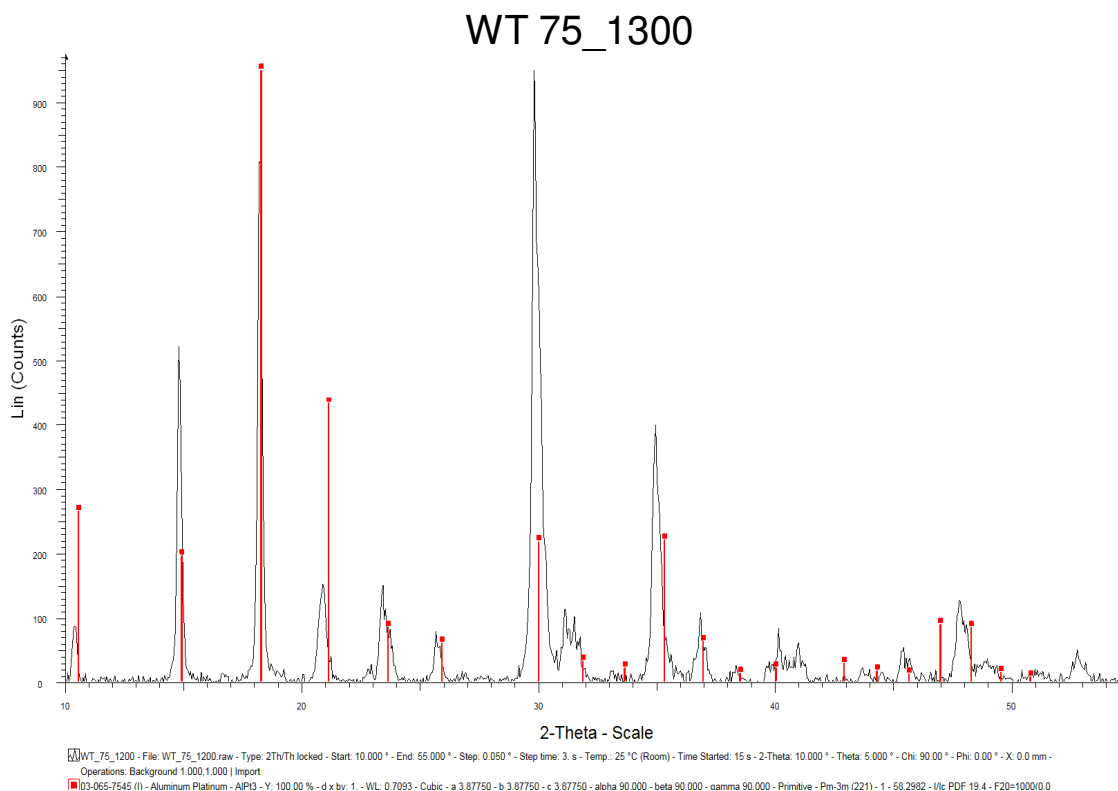


Figure 4.58. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 75 at.% Pt sample annealed at 1300°C .

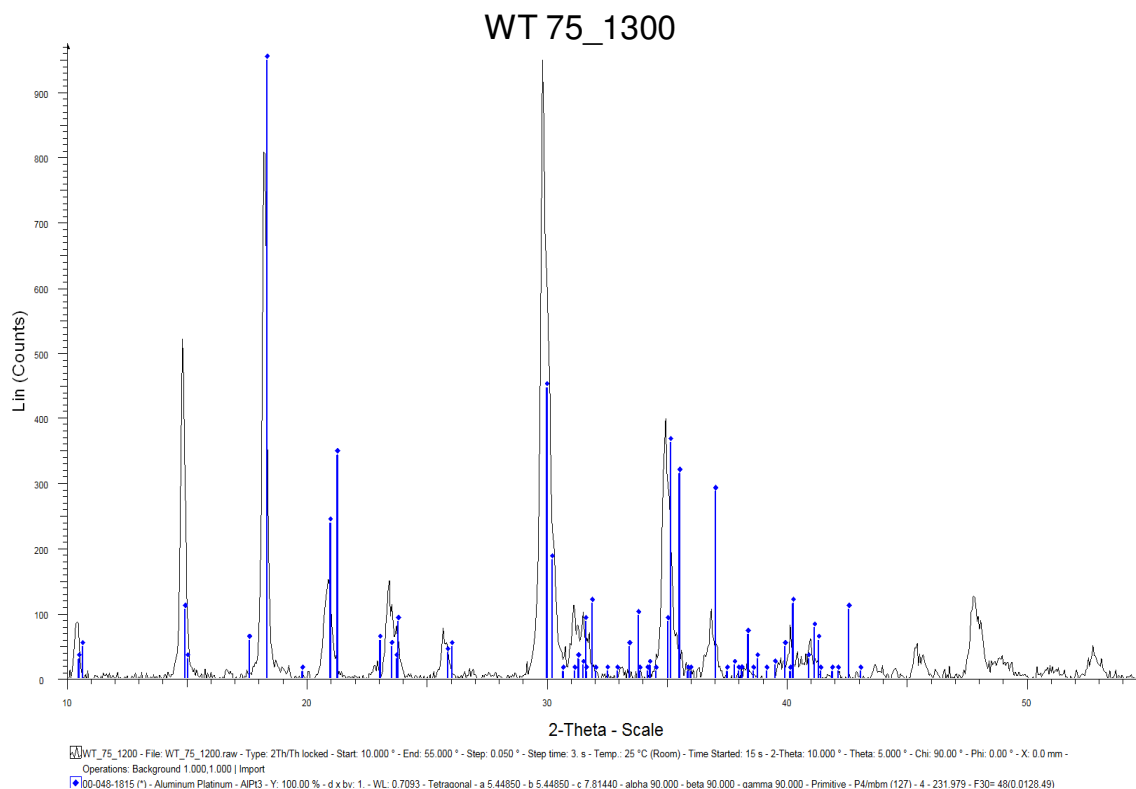


Figure 4.59. XRD trace showing peaks of the tetragonal Pt_3Al phase for the nominal 75 at.% Pt sample annealed at 1300°C .

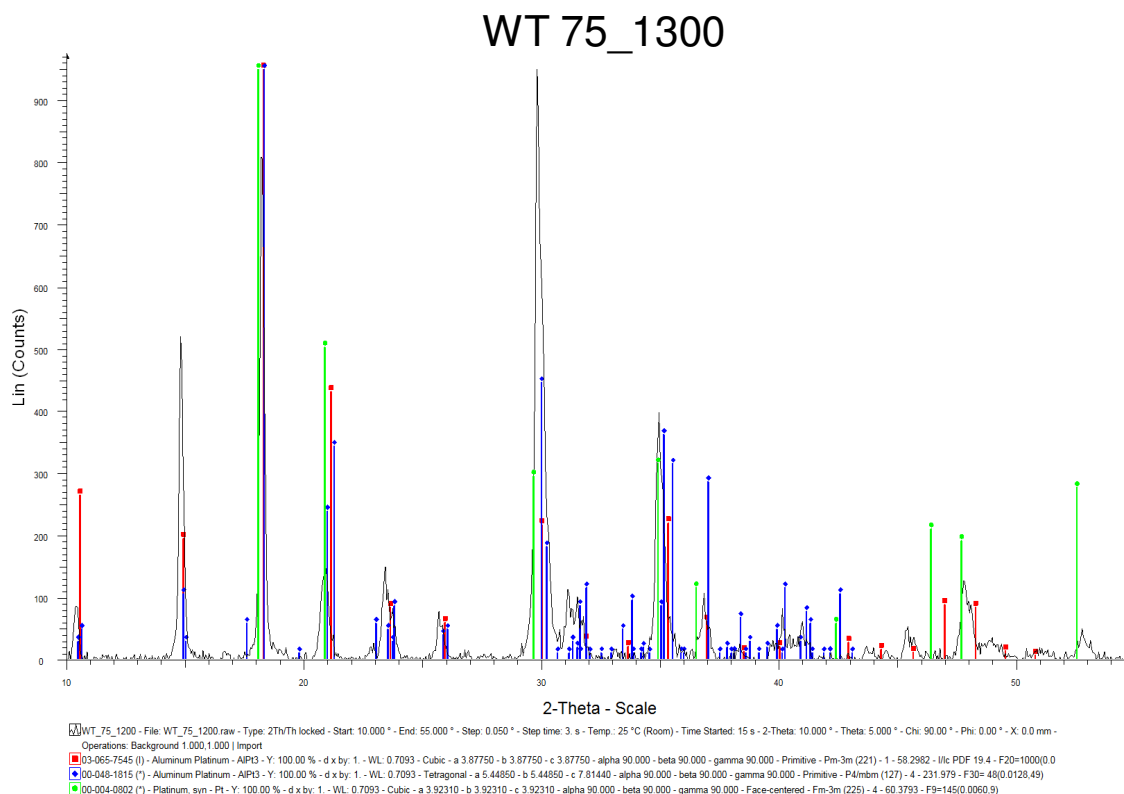


Figure 4.60. XRD trace showing peaks of the cubic and tetragonal Pt_3Al structures and (Pt) phases for the nominal 75 at. % Pt sample annealed at 1300°C.

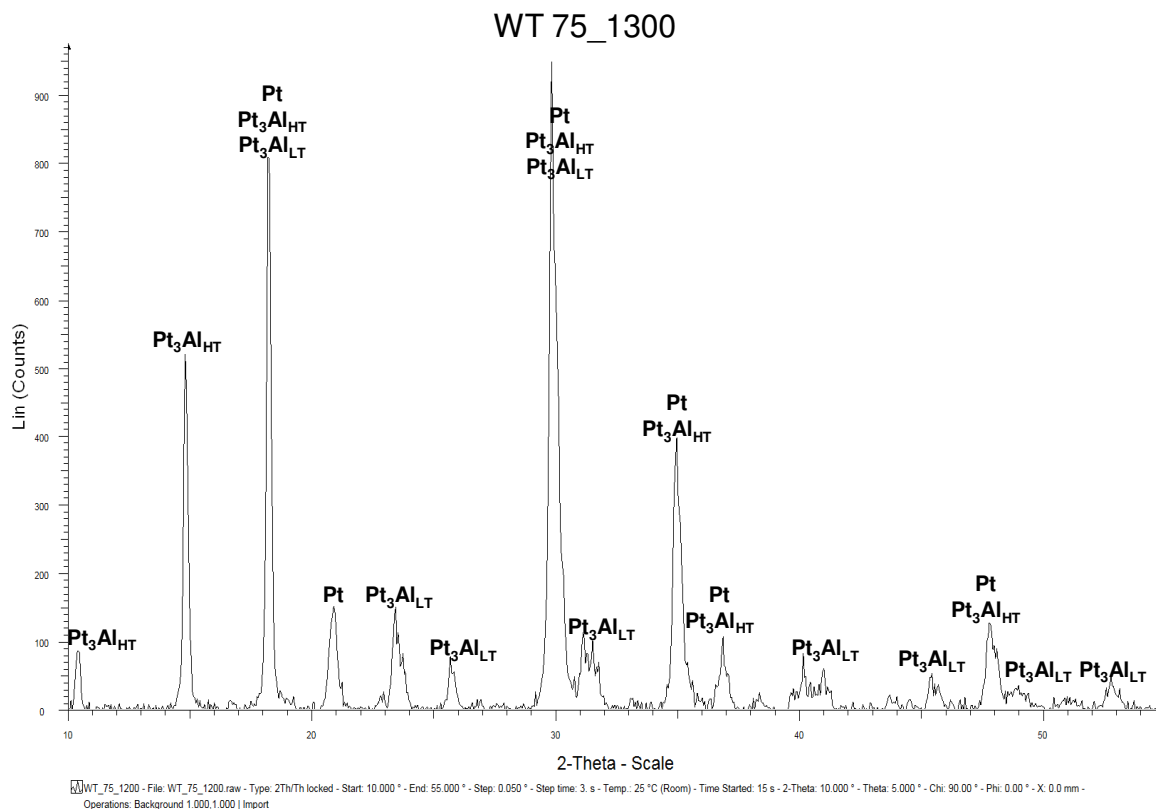


Figure 4.61. XRD pattern showing the phases in the nominal 75 at. % Pt sample annealed at 1300°C.

The XRD spectrum had broad peaks, high counts and high signal to background ratio (Figure 4.56). The spectrum was almost similar to the as-cast spectrum. The XRD database [2005ICD] confirmed the presence of high and low temperature Pt₃Al and (Pt) (Table 4.16). The peaks which matched the (Pt) phase were: $2\theta = \sim 18^\circ, \sim 21^\circ, \sim 30^\circ, \sim 35^\circ, \sim 37^\circ$ and $\sim 48^\circ$, with a slight shift to the right (Figure 4.57), and the singlet peaks at $2\theta = 10.5^\circ, \sim 15^\circ, \sim 18^\circ, \sim 30^\circ, \sim 35^\circ, \sim 37^\circ$ and $\sim 48^\circ$ were from the cubic Pt₃Al phase, with a slight shift to the right as shown in Figure 4.58. Peak splitting at $2\theta = \sim 18^\circ, \sim 24^\circ, \sim 26^\circ, \sim 30^\circ, \sim 32^\circ, \sim 40^\circ, \sim 46^\circ, \sim 49^\circ$ and $\sim 53^\circ$, was from the tetragonal Pt₃Al phase, with a slight shift to the left as shown in Figure 4.59 and Figure 4.61. According to the information above, three phases were assumed to be present in the microstructure as indicated in Figure 4.61.

The as-cast spectrum had the highest peak at $2\theta = \sim 15^\circ$ from cubic Pt₃Al and the sample annealed at 1300°C had the highest peak at $\sim 30^\circ$ from all three phases ((Pt), cubic Pt₃Al and tetragonal Pt₃Al phases). New peaks from the tetragonal Pt₃Al phase were observed at $2\theta = \sim 26^\circ, \sim 40^\circ, \sim 46^\circ, \sim 49^\circ$ and $\sim 54^\circ$, and the spectrum was more split, mainly towards the end. The peak at $2\theta = \sim 15^\circ$ from cubic Pt₃Al phase had lower intensity in the 1300°C sample than in the as-cast spectrum, and the peaks at $2\theta = \sim 47^\circ$ and $2\theta = \sim 48^\circ$ were similar to the peaks of the spectrum of the sample annealed at 1400°C, but had a lower intensity. Therefore, the sample has reduced preferred orientation compared to the as-cast sample.

4.3.4 Nominal 75 at.% Pt sample annealed at 1200°C

Heat treatment at 1300°C resulted in a mixture of very small and larger ($\sim X10$) dark precipitates randomly distributed throughout (Figure 4.62). A similar microstructure was observed in the sample annealed at 1400°C, where the precipitates had coarsened. The phases were fine and close together, giving to imprecise EDS measurements. The overall composition of the sample was in the two-phase region of both phase diagrams [1986McA, 1987Oya]. The light phase was at the (Pt) phase boundary of Massalski's phase diagram [1986McA], and in the two-phase region of Oya *et al.*'s phase diagram [1987Oya] and had an error of ~ 1.8 at.%. The dark phase was at the Pt₃Al phase boundary [1986McA, 1987Oya], but it is realised that the dark phase was too small to analyse accurately, although bigger

precipitates were observed in certain areas of the microstructure such as the region highlighted in Figure 4.62c.

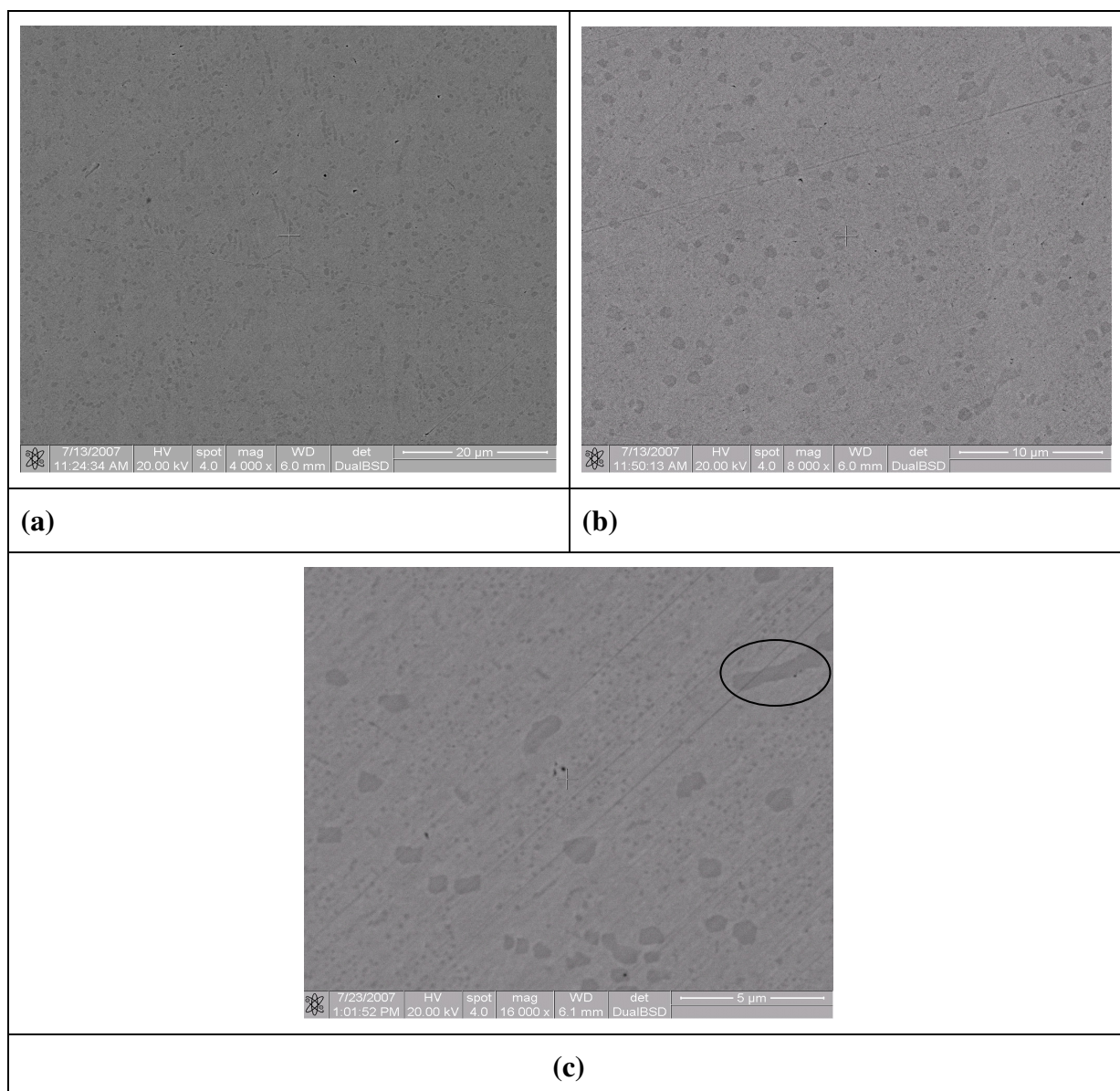


Figure 4.62. BSE-SEM image for nominal 75 at.% Pt annealed at 1200°C, showing light (Pt) phase and Pt₃Al phase (dark precipitates) at different magnifications.

Table 4.17. EDS analysis for the nominal 75 at.% Pt sample annealed at 1200°C for 1000 h.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
75 at.% Pt sample annealed at 1300°C	Overall	84.6 ± 0.8	15.4 ± 0.8	-
	Light	87.9 ± 1.8	12.1 ± 1.8	mainly (Pt)
	Dark	77.8 ± 0.3	22.2 ± 0.3	mainly Pt ₃ Al

Table 4.18. XRD analysis for nominal 75 at.% Pt annealed at 1200°C for 1000 h.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) (Pt)	I (%) Pt ₃ Al _{HT}
14.9	2.74	110	2	-	20
18/18.2	2.27/2.24	111/111	100	100	99
20.8/21.1	1.96/1.94	200/200	5	53	45
29.6/29.9	1.39/1.37	220/220	17	31	23
34.9	1.18	222	0.8	33	-
36.5/36.9	1.13/1.12	222/222	15	12	6

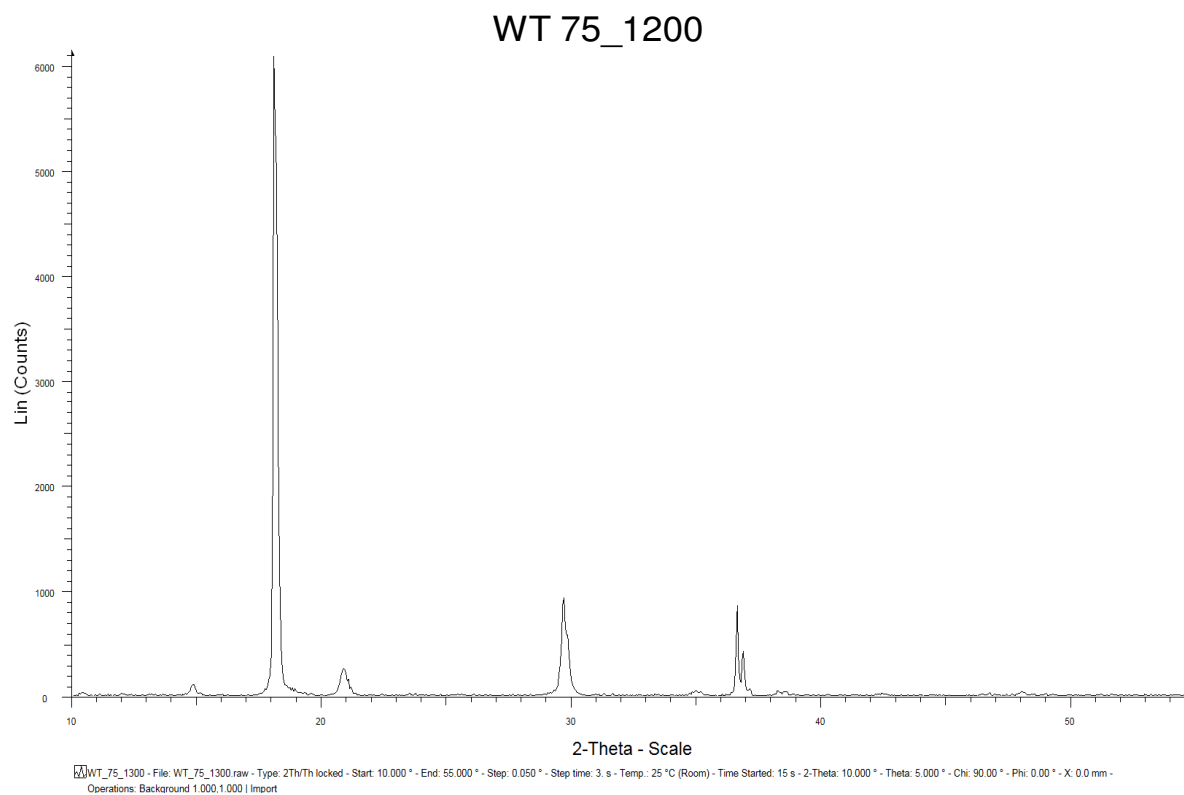


Figure 4.63. Raw XRD spectrum for the nominal 75 at.% Pt sample annealed at 1200°C.

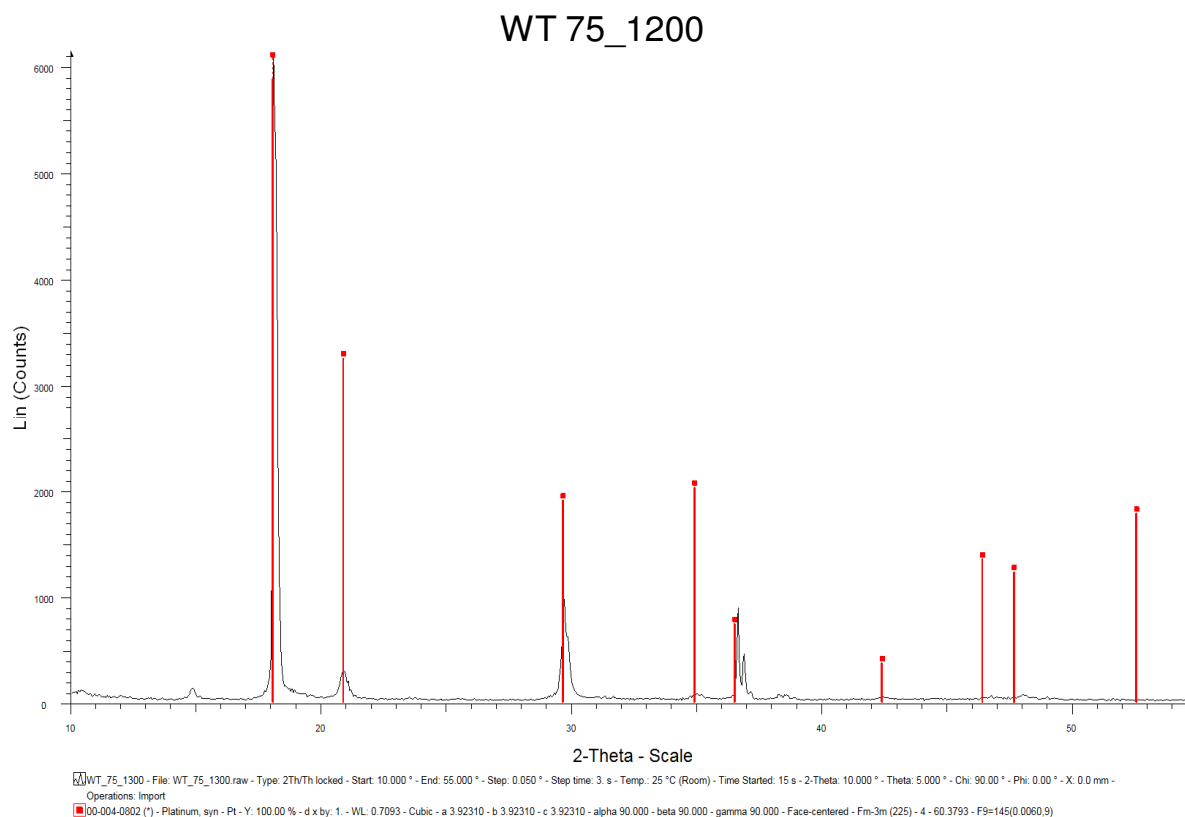


Figure 4.64. XRD trace showing peaks of Pt for the nominal 75 at.% Pt sample annealed at 1200°C.

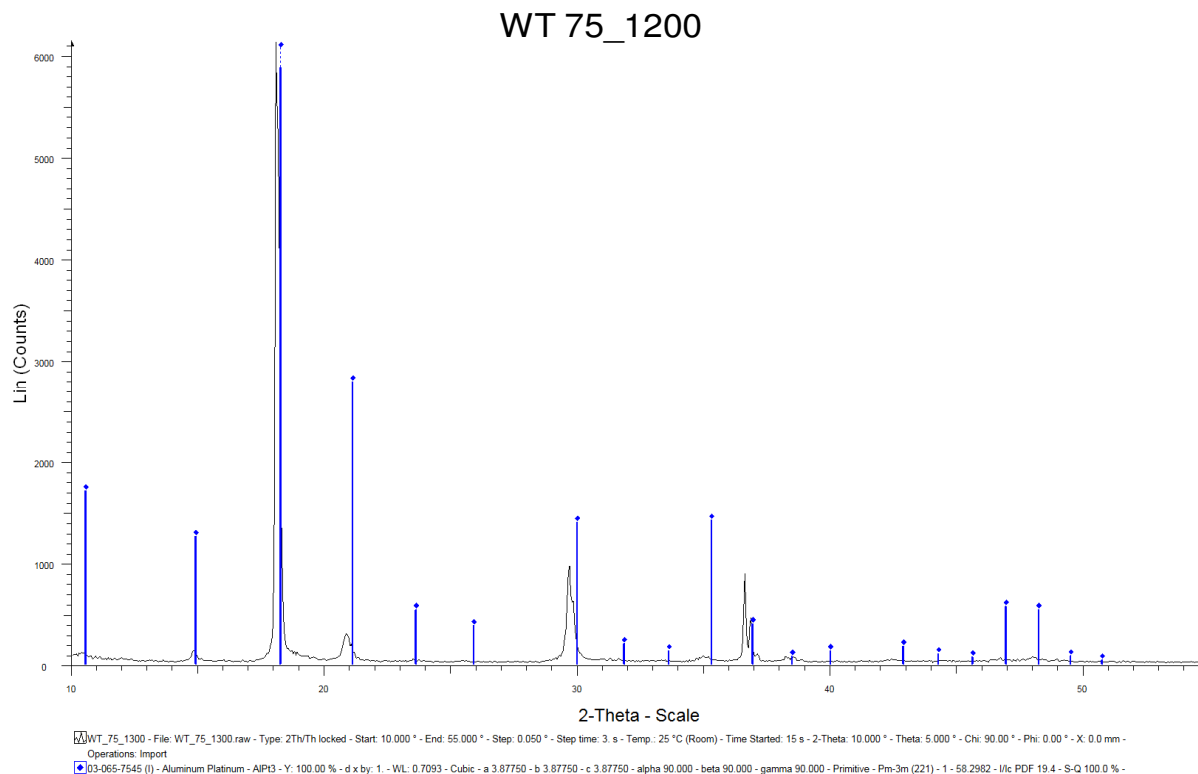


Figure 4.65. XRD trace showing peaks of cubic Pt₃Al for the nominal 75 at.% Pt sample annealed at 1200°C.

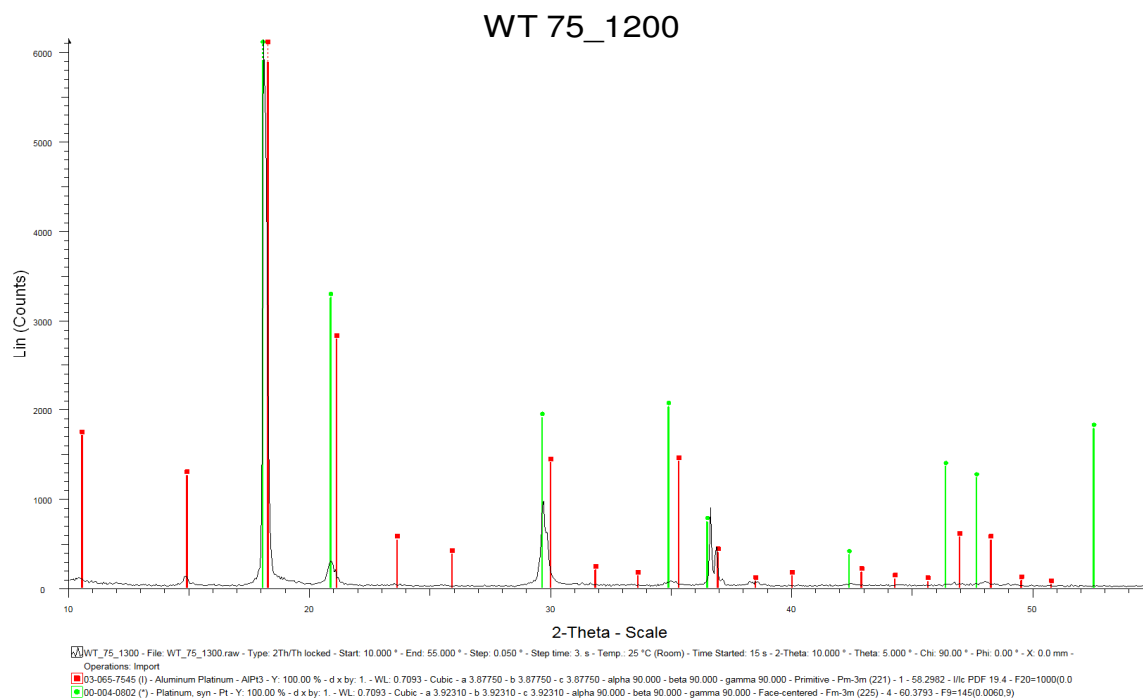


Figure 4.66. XRD trace showing peaks of Pt and cubic Pt_3Al for the nominal 75 at.% Pt sample annealed at 1200°C.

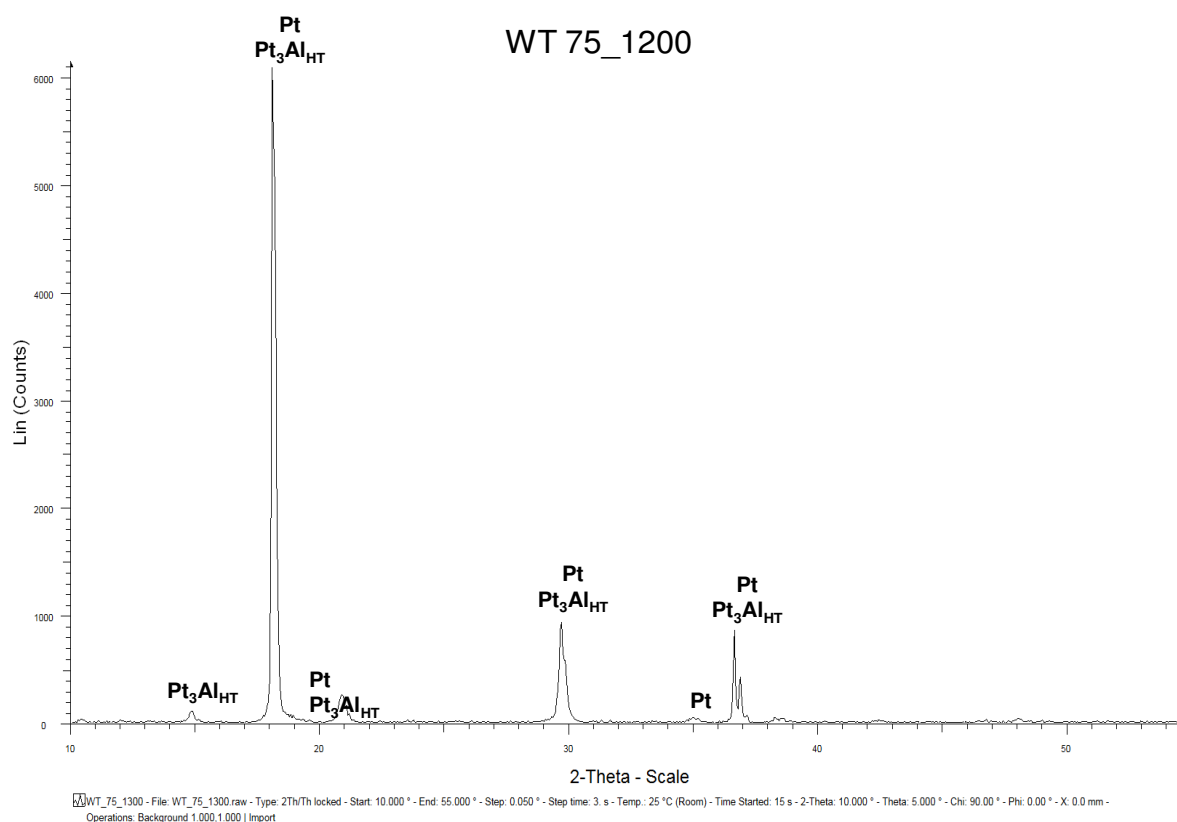


Figure 4.67. XRD pattern showing the phases in the nominal 75 at.% Pt sample annealed at 1200°C.

The XRD spectrum had only a few sharp peaks, very high counts and high signal to background ratio (Figure 4.63). The XRD spectrum [2005ICD] confirmed the presence of cubic Pt₃Al and (Pt) (Table 4.18). The presence of (Pt) is indicated in Figure 4.64, where a match at $2\theta = \sim 18^\circ, \sim 21^\circ, \sim 30^\circ, \sim 35^\circ$ and $\sim 37^\circ$, with a slight shift to the right. In Figure 4.65, cubic Pt₃Al is indicated by the peaks at $2\theta = \sim 15^\circ, \sim 18^\circ, \sim 21^\circ, \sim 30^\circ$ and $\sim 37^\circ$, which were different from the (Pt) peaks, with a slight shift to the left. Based on the above information two phases were assumed to be present in the microstructure as shown in Figure 4.67.

There are no unmatched peaks, so the tetragonal Pt₃Al phase was not present. The spectrum had the strongest peak at $2\theta = \sim 18^\circ$, while the as-cast spectrum had the strongest peak at $2\theta = \sim 15^\circ$, and the sample annealed at 1400°C had the strongest peak at $2\theta = \sim 21^\circ$. The peaks from the tetragonal Pt₃Al phase which were observed in the as-cast spectrum disappeared in the spectrum of the sample annealed at 1200°C, and these were: $2\theta = 10.5^\circ, 17.5^\circ, \sim 24^\circ$ and $\sim 32^\circ$. Therefore, the tetragonal Pt₃Al phase disappeared after heat treatment at 1200°C. Relative to the as-cast spectrum (Figure 4.42) the peaks at $2\theta = 16.8^\circ$ and 17.5° had disappeared, while the peaks at $2\theta = \sim 15^\circ, \sim 35^\circ, \sim 46^\circ$ and $\sim 47^\circ$ had relatively very low intensities.

4.4 Phase analyses for the 72 at.% Pt samples

4.4.1 Nominal 72 at.% Pt sample in the arc-melted condition

The HRSEM studies revealed a single phase, although the structure was difficult to resolve (Figure 4.68). According to the EDS results in Table 4.19, the overall composition was at the Pt₃Al phase boundary of both published phase diagrams [1986McA, 1987Oya].

The solidification sequence was:

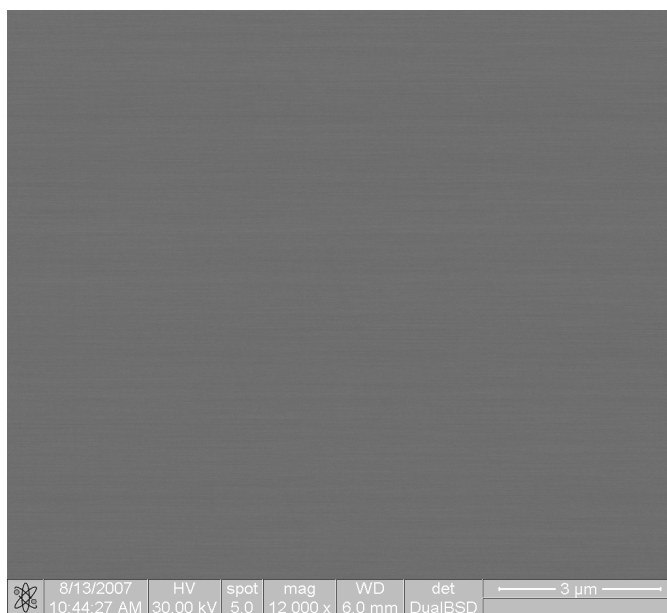
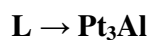


Figure 4.68. BSE-SEM image for nominal 72 at.% Pt in the as-cast condition, showing a Pt_3Al single phase.

Table 4.19. EDS analysis for the nominal 72 at.% Pt sample in the as-cast condition.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
72 at.% Pt arc-melted condition	Overall	76.4 ± 0.8	23.6 ± 0.8	Pt_3Al

Table 4.20. XRD database information [2005ICD] for the nominal 72 at.% Pt sample in the as-cast condition.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) $\text{Pt}_3\text{Al}_{\text{HT}}$	I (%) $\text{Pt}_3\text{Al}_{\text{LT}}$
10.5	3.88	100	26	28	-
14.9	2.74	110	6	20	-
18.2	2.24	111	39	99	-
21.1	1.94	200	100	45	-
23.6	1.73	210	9	9	-
26.0	1.58	312	4	-	5
29.9	1.37	220	7	23	-
35.1	1.18	206	26	-	38
42.9	0.97	400	7	3	-

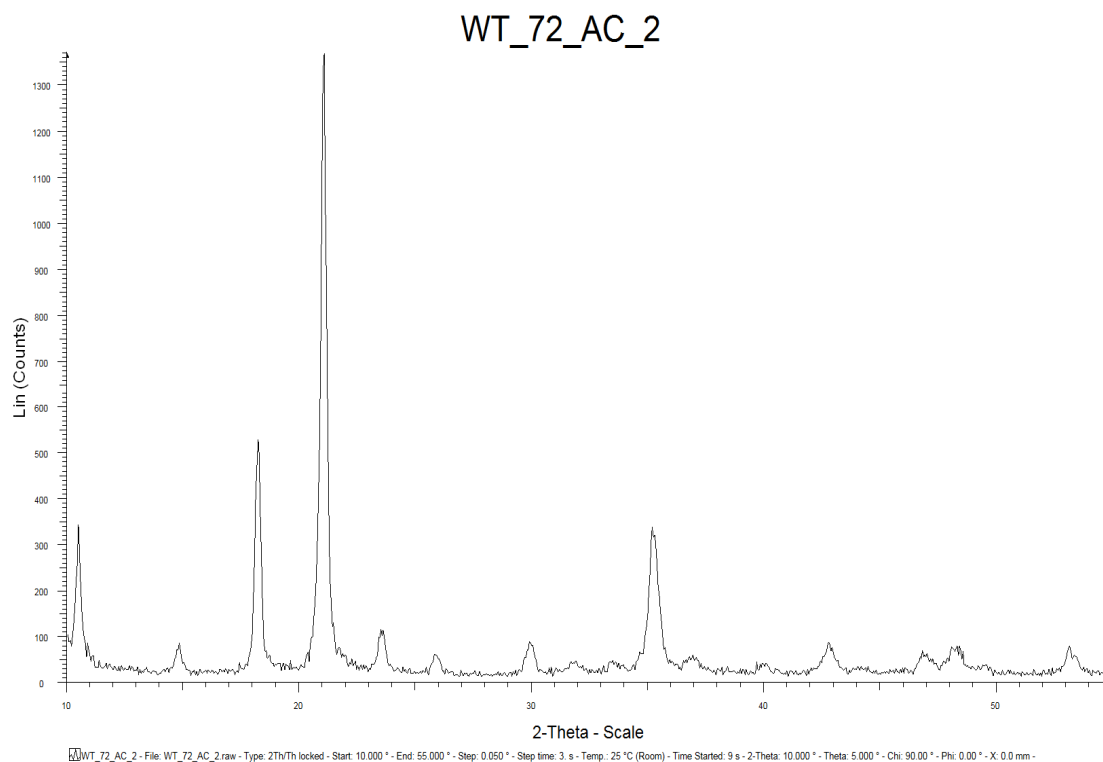


Figure 4.69. Raw XRD spectrum for the nominal 72 at.% Pt sample in the as-cast condition.

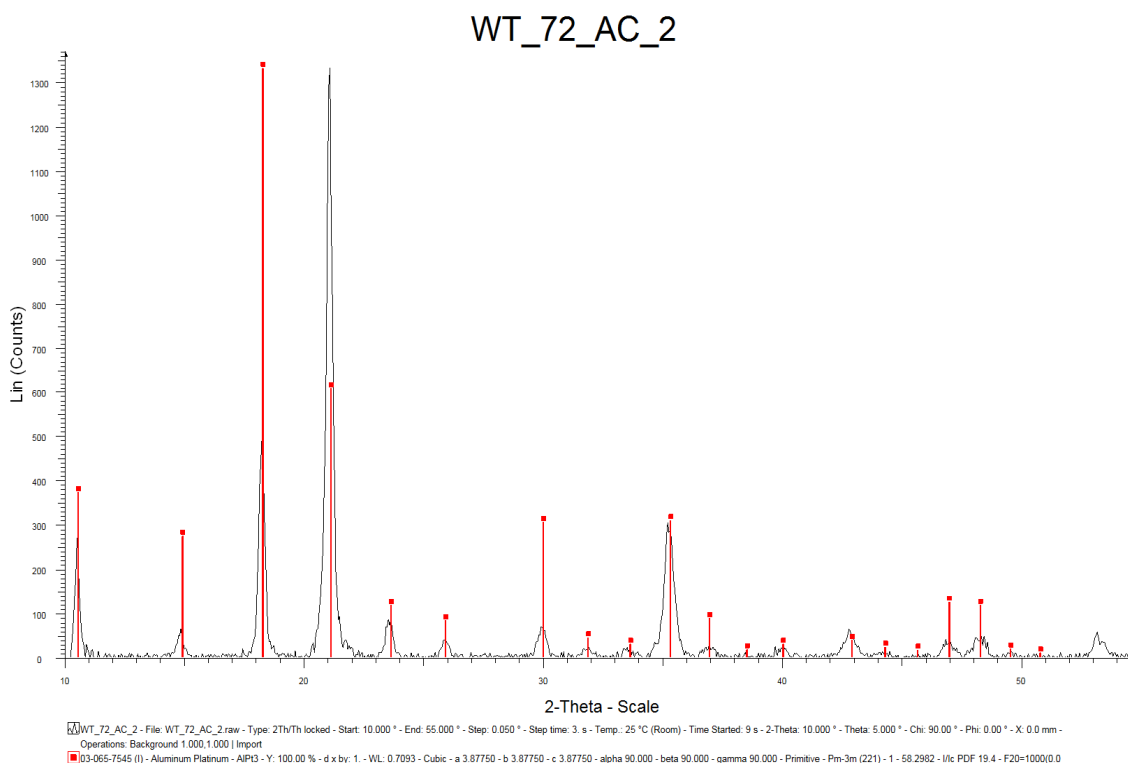


Figure 4.70. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 72 at.% Pt sample in the as-cast condition.

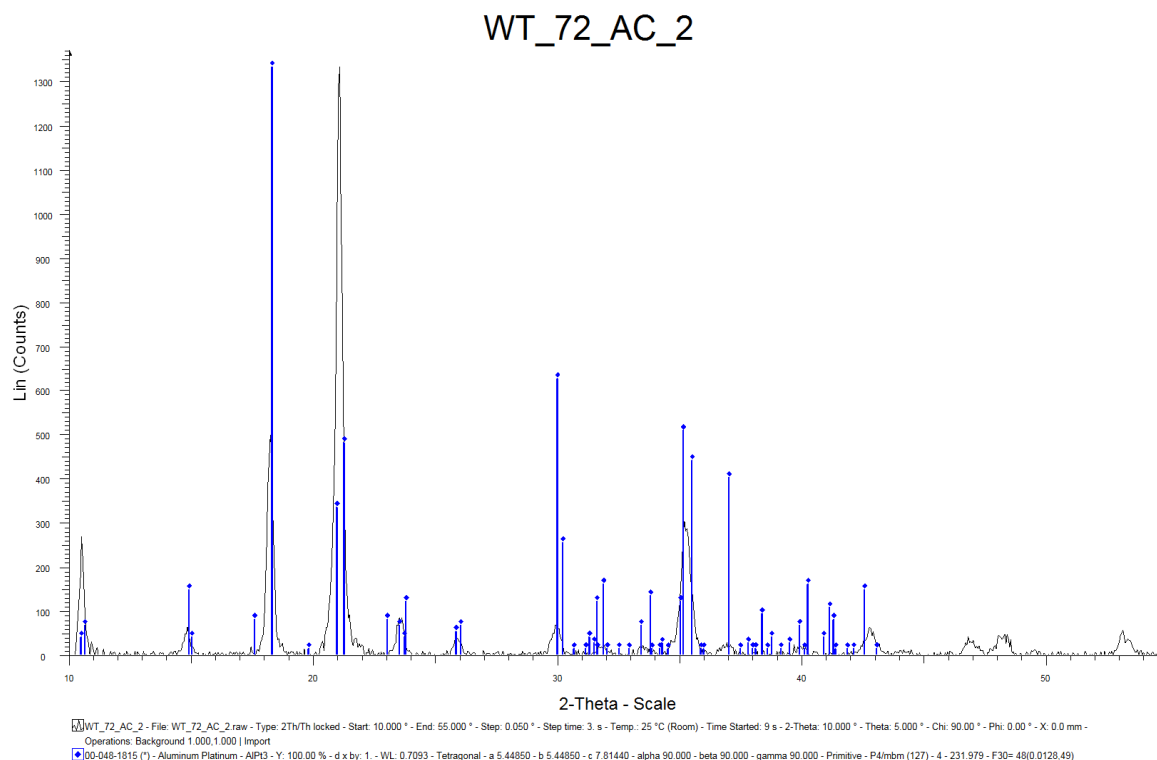


Figure 4.71. XRD trace showing peaks of the tetragonal Pt_3Al phase for the nominal 72 at.% Pt sample in the as-cast condition.

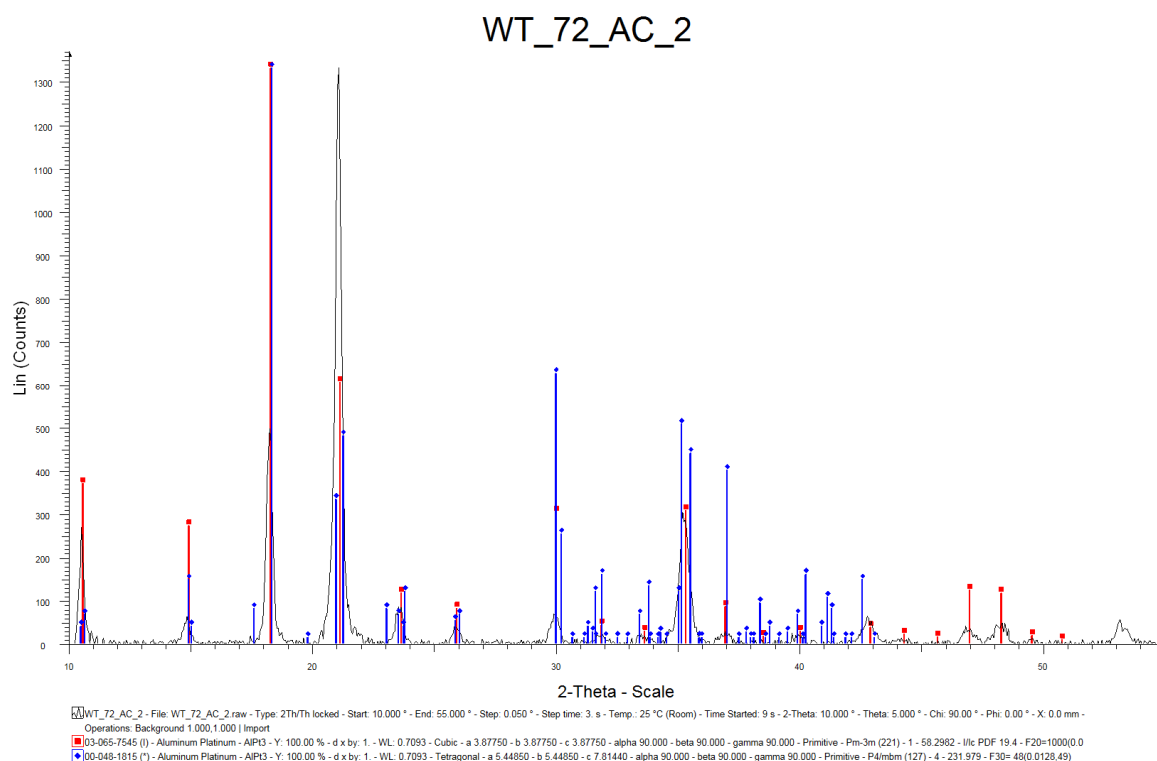


Figure 4.72. XRD trace showing peaks of the cubic and tetragonal structures for the nominal 72 at.% Pt sample in the as-cast condition.

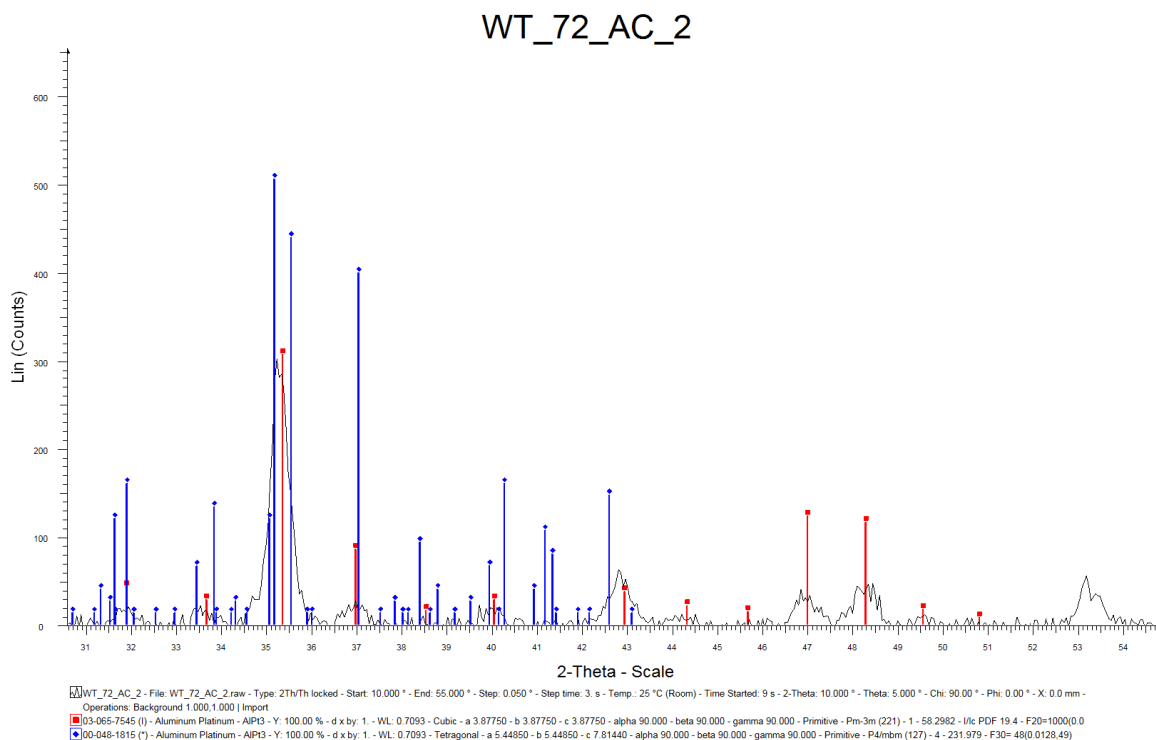


Figure 4.73. XRD trace ($2\theta = 30.5^\circ$ to 55°) distinguishing between the cubic and tetragonal Pt_3Al structures for the nominal 72 at.% Pt sample in the as-cast condition.

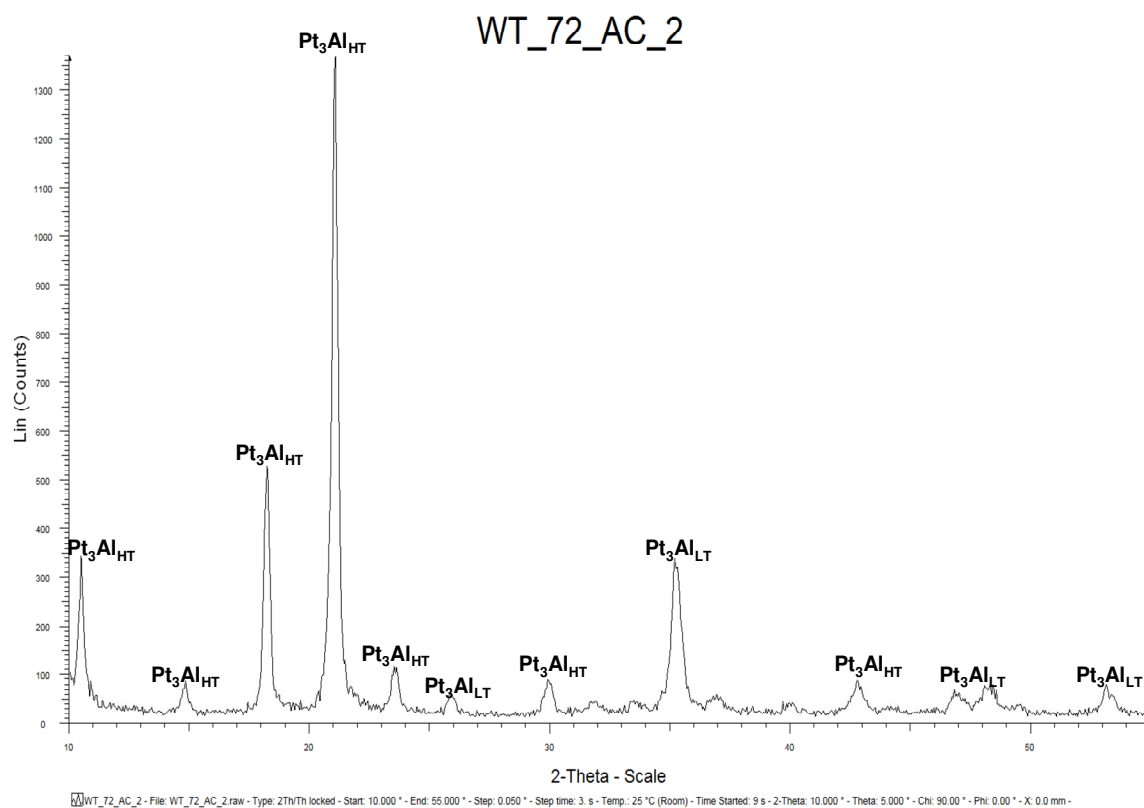


Figure 4.74. XRD pattern showing the phases in the nominal 72 at.% Pt sample in the as-cast condition.

The XRD spectrum had broad peaks, high counts and high signal to background noise (Figure 4.69). The XRD spectrum [2005ICD] showed a very good match for both the cubic and tetragonal Pt₃Al phases (Table 4.20), including a fairly good match for the intensities. The presence of the peaks at $2\theta = 10.5^\circ$ and $\sim 15^\circ$ indicated that the sample contained at least one of the Pt₃Al phases according to Biggs [2001Big]. The singlet peaks from cubic Pt₃Al phase were: $2\theta = 10.5^\circ$, $\sim 15^\circ$, $\sim 18^\circ$, $\sim 21^\circ$, $\sim 24^\circ$, $\sim 30^\circ$ and $\sim 43^\circ$ with a negligible shift as shown in Figure 4.70, and the peaks from the tetragonal Pt₃Al phase were: $2\theta = \sim 26^\circ$, $\sim 35^\circ$, $\sim 47^\circ$, $\sim 48^\circ$ and $\sim 53^\circ$ with a slight shift to the left as shown in Figure 4.71. Based on the information above, both high and low temperature forms of Pt₃Al were found in the microstructure as shown in Figure 4.74.

Relative to the as-cast spectrum, the spectrum had the strongest peak at $2\theta = \sim 35^\circ$, whereas the as-cast spectrum had the strongest peak at $2\theta = \sim 21^\circ$. The peak at $2\theta = \sim 18^\circ$ from cubic Pt₃Al had a lower intensity than the as-cast spectrum, due to different proportions of the phase in the samples, and peaks at $2\theta = \sim 21^\circ$, $\sim 24^\circ$ and $\sim 30^\circ$ which were from cubic Pt₃Al in the as-cast spectrum, were split after annealing, to match the tetragonal Pt₃Al phase.

4.4.2 Nominal 72 at.% Pt sample annealed at 1200°C

The HRSEM studies showed a single phase (Figure 4.75) which was confirmed by the EDS results. The overall composition was in the tetragonal Pt₃Al phase region of Massalski's phase diagram [1986McA], and in the cubic Pt₃Al phase region of Oya *et al.*'s phase diagram [1987Oya] (Table 4.21).

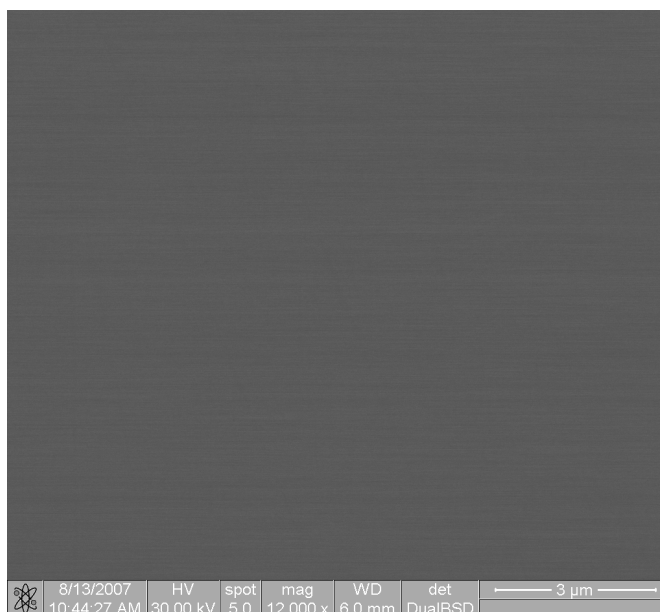


Figure 4.75. BSE-SEM image for nominal 72 at. % Pt annealed at 1200°C, showing a Pt₃Al single phase.

Table 4.21. EDS analysis for the nominal 72 at. % Pt sample annealed at 1200°C for 1000 h.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
1200°C	Overall	76.1 ± 0.2	23.9 ± 0.2	Pt ₃ Al

Table 4.22. XRD database [2005] information for the nominal 72 at. % Pt sample annealed at 1200°C.

2θ	d (Å)	h k l	I (%) Raw spectrum	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
10.4	3.91	002	4	-	3
14.9	2.74	110	18	20	-
17.5	2.33	211	4	-	6
18.2	2.24	111	13	99	-
21.2	1.93	220	20	-	36
23.8	1.72	310	18	-	9
26.0	1.58	312	18	-	5
29.9	1.37	224	9	-	47
31.9	1.29	314	7	-	12
33.8	1.22	332	9	-	10
35.3/35.1	1.17/1.18	311/206	100	23	38
48.3	0.87	420	27	9	-

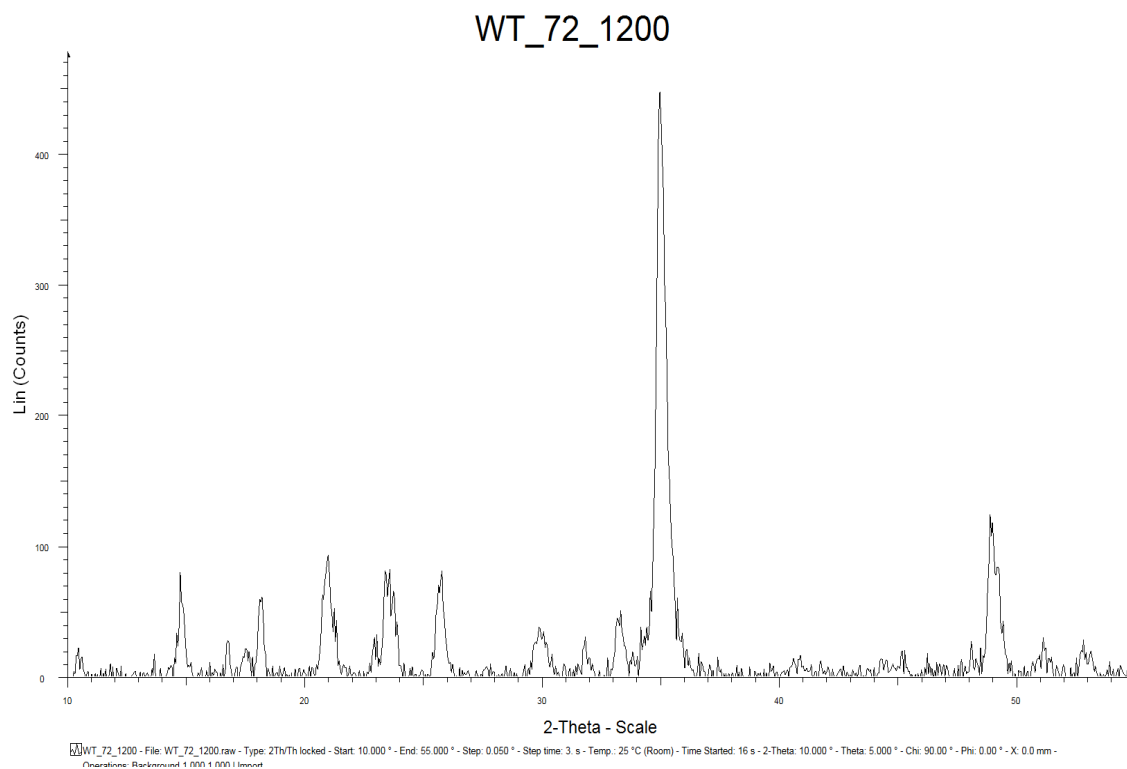


Figure 4.76. Raw XRD spectrum for the nominal 72 at.% Pt sample annealed at 1200°C.

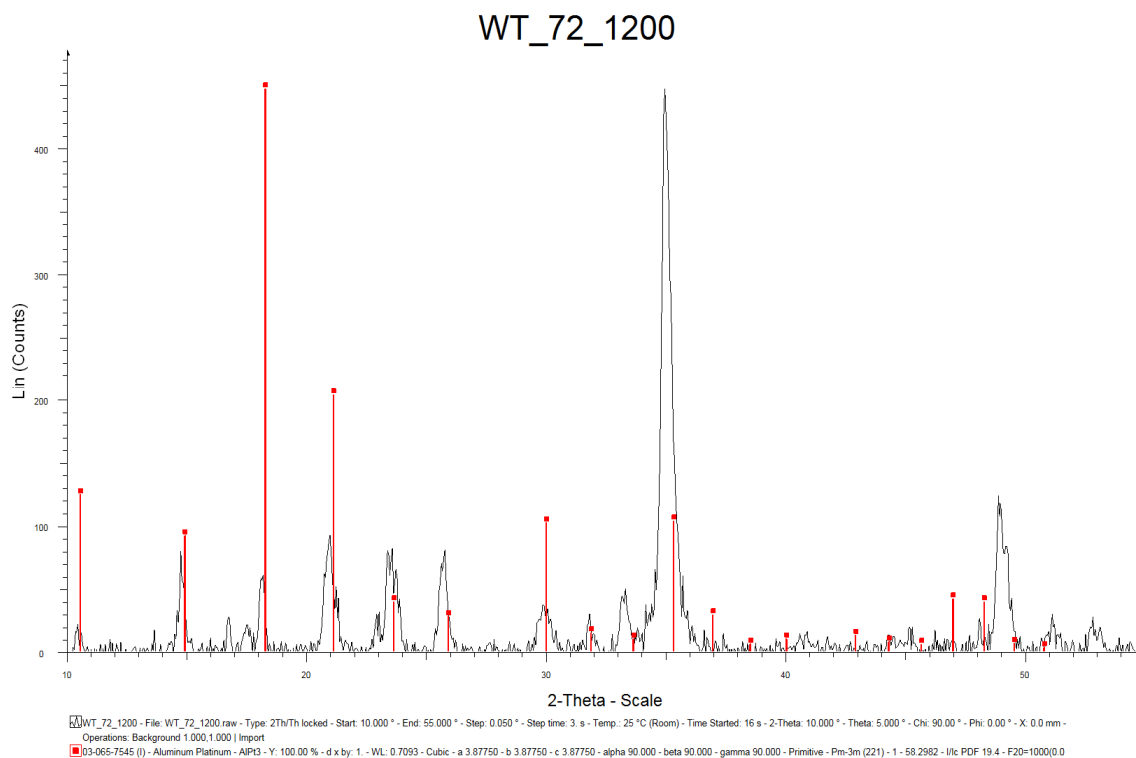


Figure 4.77. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 72 at.% Pt sample annealed at 1200°C.

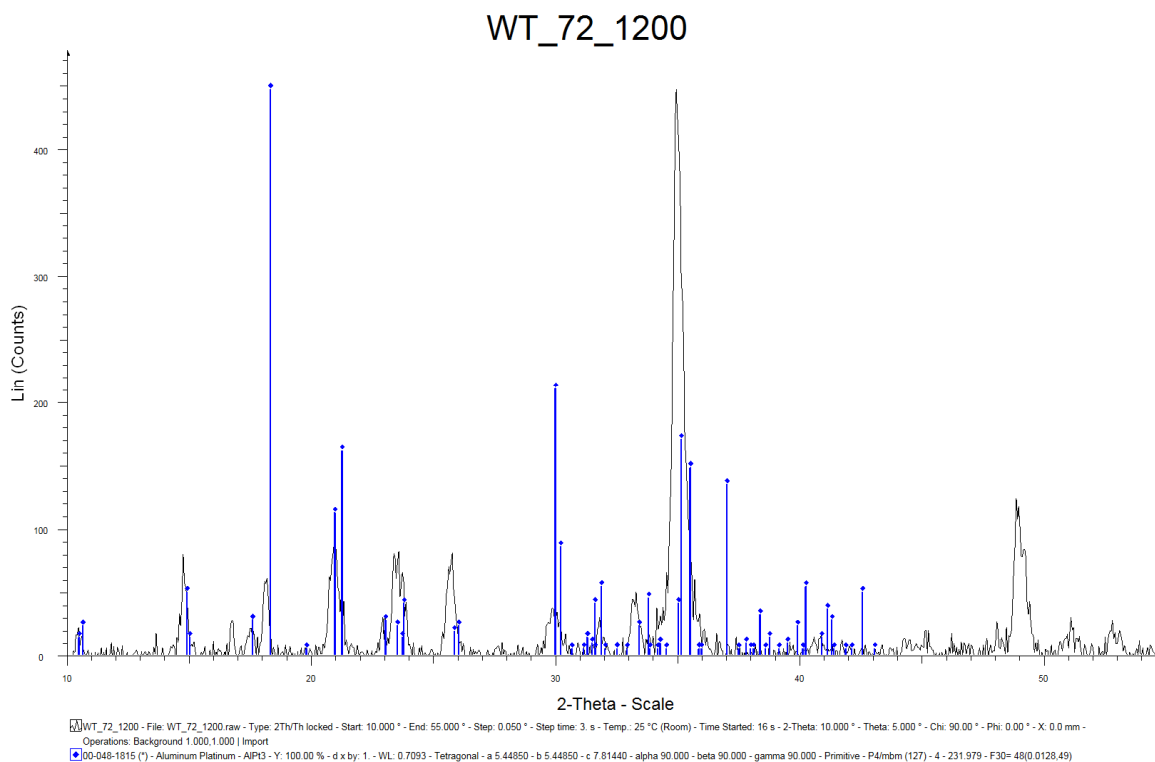


Figure 4.78. XRD trace showing peaks of the tetragonal Pt_3Al phase for the nominal 72 at.% Pt sample annealed at 1200°C.

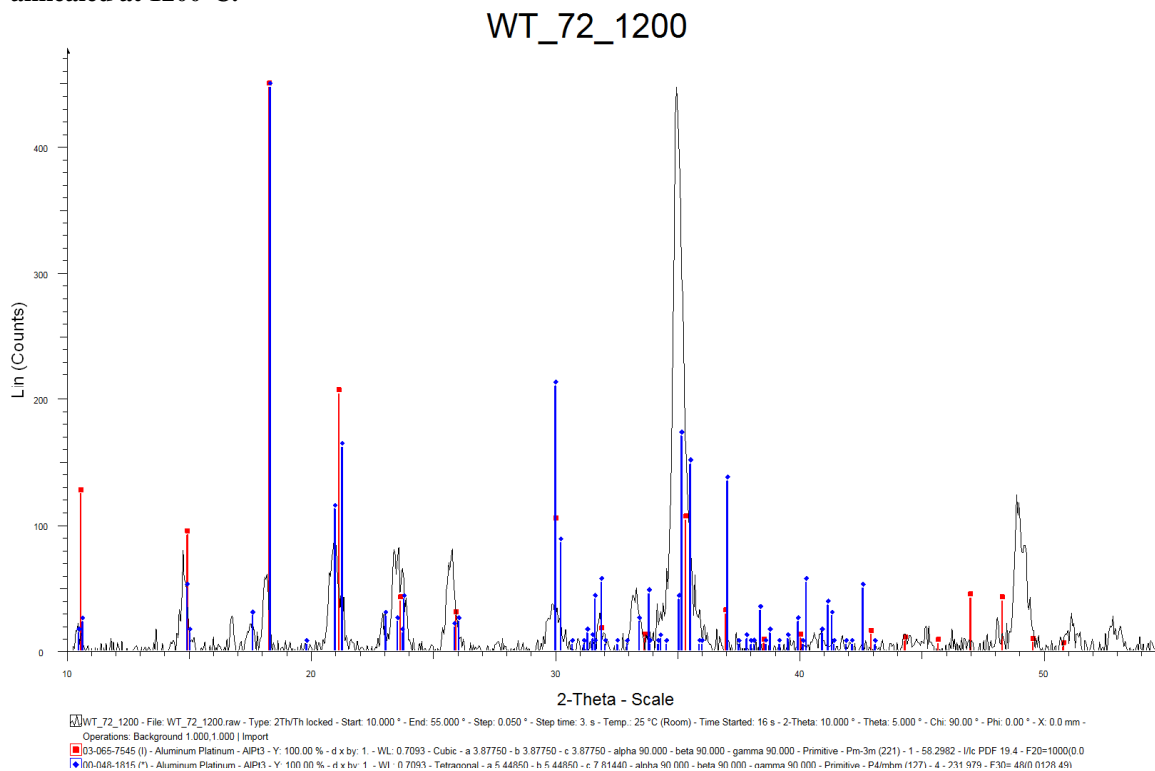


Figure 4.79. XRD trace showing peaks of the cubic and tetragonal Pt_3Al structures for the nominal 72 at.% Pt sample annealed at 1200°C.

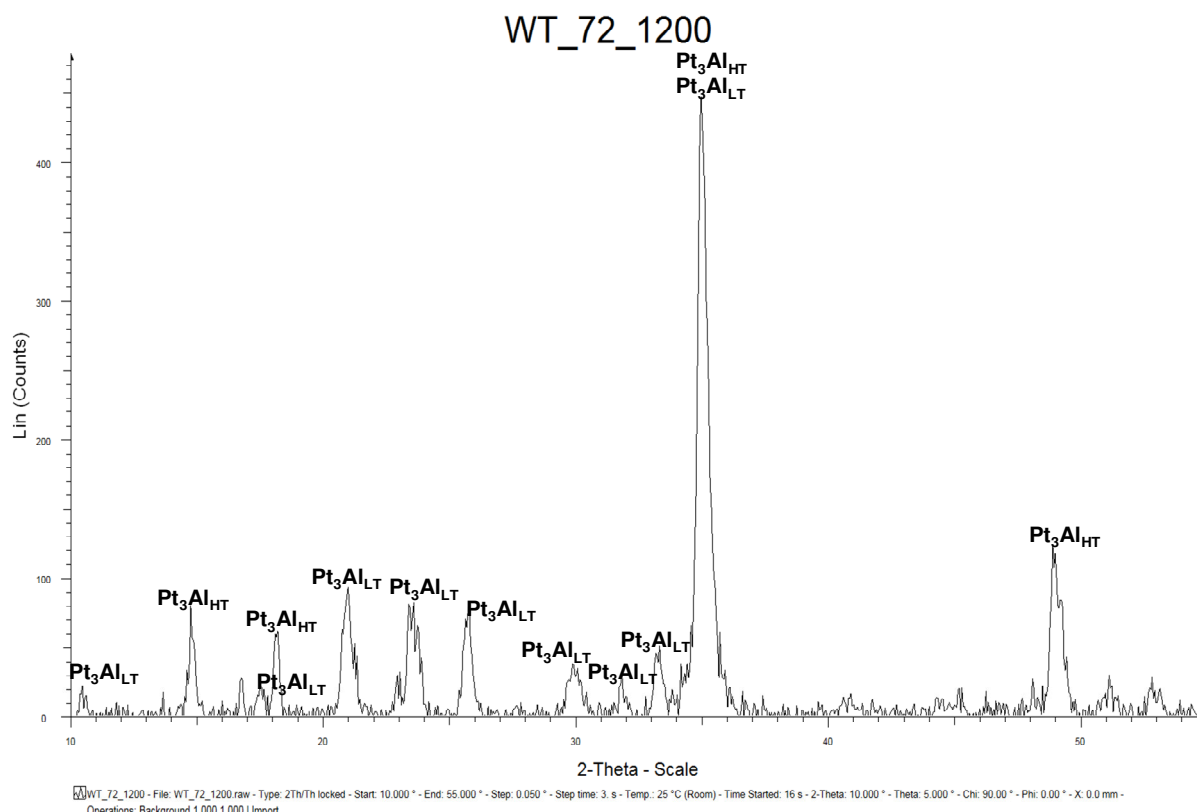


Figure 4.80. XRD pattern showing the phases in the nominal 72 at.% Pt sample annealed at 1200°C.

The XRD spectrum had broad peaks, fairly low counts and a fairly low signal to background noise (Figure 4.76). The spectrum had more peak splitting compared to the as-cast spectrum. The XRD database [2005ICD], confirmed the presence of both high and low temperature Pt_3Al phases (Table 4.22). The peaks at $2\theta = 10.5^\circ$ and $\sim 15^\circ$ revealed the possibility of the presence of at least one of the Pt_3Al phases [2001Big]. The cubic Pt_3Al phase showed a match with singlet peaks at $2\theta = \sim 15^\circ$, $\sim 18^\circ$, $\sim 30^\circ$, $\sim 35^\circ$ and $\sim 49^\circ$ with a slight shift to the left (Figure 4.77), and the peaks from the tetragonal Pt_3Al phase, which are different from cubic Pt_3Al phase were: $2\theta = 10.5^\circ$, 17.5° , $\sim 21^\circ$, $\sim 23^\circ$, $\sim 26^\circ$, $\sim 30^\circ$, $\sim 32^\circ$, 33.5° and $\sim 35^\circ$ with a slight shift to the left as shown in Figure 4.78. Therefore, the sample contained both cubic and tetragonal Pt_3Al phases as shown in Figure 4.80. The peaks at the end of the spectrum had no match, because the database [2005ICD] data ended.

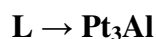
Relative to the as-cast spectrum, the spectrum had the strongest peak at $2\theta = \sim 35^\circ$, whereas the as-cast spectrum had the strongest peak at $2\theta = \sim 21^\circ$. The peaks at $2\theta = \sim 18^\circ$ and $2\theta = \sim 21^\circ$ had lower intensities compared to the as-cast spectrum, indicating that microstructure had less preferred orientation than the as-cast sample.

4.5 Phase analyses for the 67 at.% Pt samples

4.5.1 Nominal 67 at.% Pt sample in arc-melted condition

Initially, the HRSEM showed a two-phase microstructure: light phase and a dark phase (Figure 4.81), and the light dendrites and dark interdendritic phases were analysed with EDS (Table 4.23). Subsequently, it was realised that there was a third phase, which was identified by the difference in contrast. Thus, the dark phase analyses are actually for areas of Pt_2Al and Pt_5Al_3 , which is why they have large error bars. The primary phase solidified as dendrites (light phase) and was assumed to be Pt_3Al . Some of the light phase further reacted peritectically with the liquid and formed Pt_5Al_3 (dark phase), and lastly the light phase and the dark phase reacted peritectoidally to form Pt_2Al (medium contrast phase). There were no laths observed in the microstructure, therefore the high temperature Pt_2Al phase is expected. The medium phase was too small to be analysed accurately, although it was observed from the microstructure (Figure 4.81(b)). The overall EDS composition was in the two-phase region (Pt_3Al and Pt_2Al) of Massalski's phase diagram (Table 4.23) [1986McA]. The alloy was brittle because it disintegrated on removal from the mount during preparation for the XRD analyses.

The solidification sequence was:



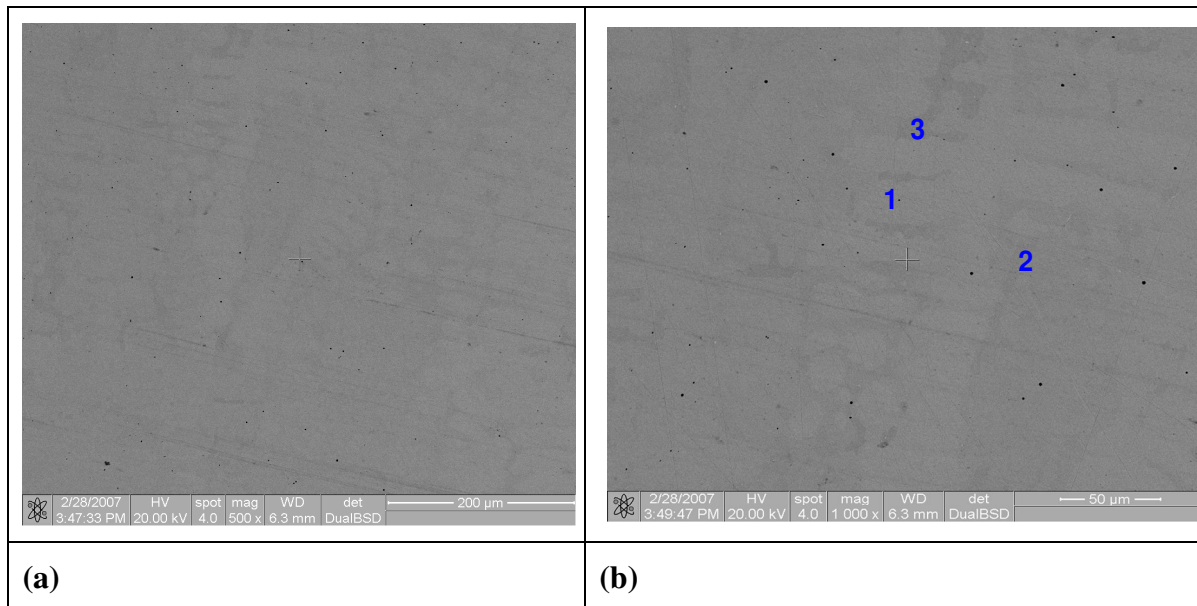


Figure 4.81. BSE-SEM image for nominal 67 at.% Pt in arc-melted condition, showing the dendrites of Pt₃Al (1), surrounded by the light phase (2), and the dark phase between the dendrite structures (3), resulting from a peritectic reaction.

Table 4.23. EDS analysis for the nominal 67 at.% Pt sample in the arc-melted condition.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Arc-melted 67 at.% Pt sample	Overall	67.7 ± 0.5	32.3 ± 0.5	-
	Light	68.7 ± 0.5	31.3 ± 0.5	Pt ₃ Al
	medium	65.2 ± 1.7	34.8 ± 1.7	Pt ₂ Al with Pt ₅ Al ₃

Table 4.24. XRD database [2005ICD] information for the nominal 67 at.% Pt sample in the arc-melted condition.

2 θ	d (Å)	h k l	I (%) Raw spectrum	I (%) Pt ₂ Al _{HT}	I (%) Pt ₃ Al _{HT}	I (%) Pt ₅ Al ₃
10.5	3.88	100	4	-	28	-
11.3	3.61	011	15	25	-	-
12.8	3.19	102	4	33	-	-
13.6	3.0	111	4	53	-	-
14.9	2.74	110	34	-	20	-
18.3	2.24	202	39	-	100	-
18.9	2.16	211	6	73	-	-
21.1/21.7	1.94/1.89	200/203	15	45	23	-
23.6	1.73	210	34	-	9	-
28.9	1.42	115	10	4	-	-
29.8/29.9	1.38/1.37	223/220	100	14	23	-
31.3	1.32	006	4	3	-	-
33.96	1.21	125	52	11	-	-
35.3/34.9	1.17/1.18	311/043	16	-	23	11
37.2	1.11	324	13	7	-	-
40.0	1.04	321	10	-	2	-
48.3	0.87	420	34	-	9	-

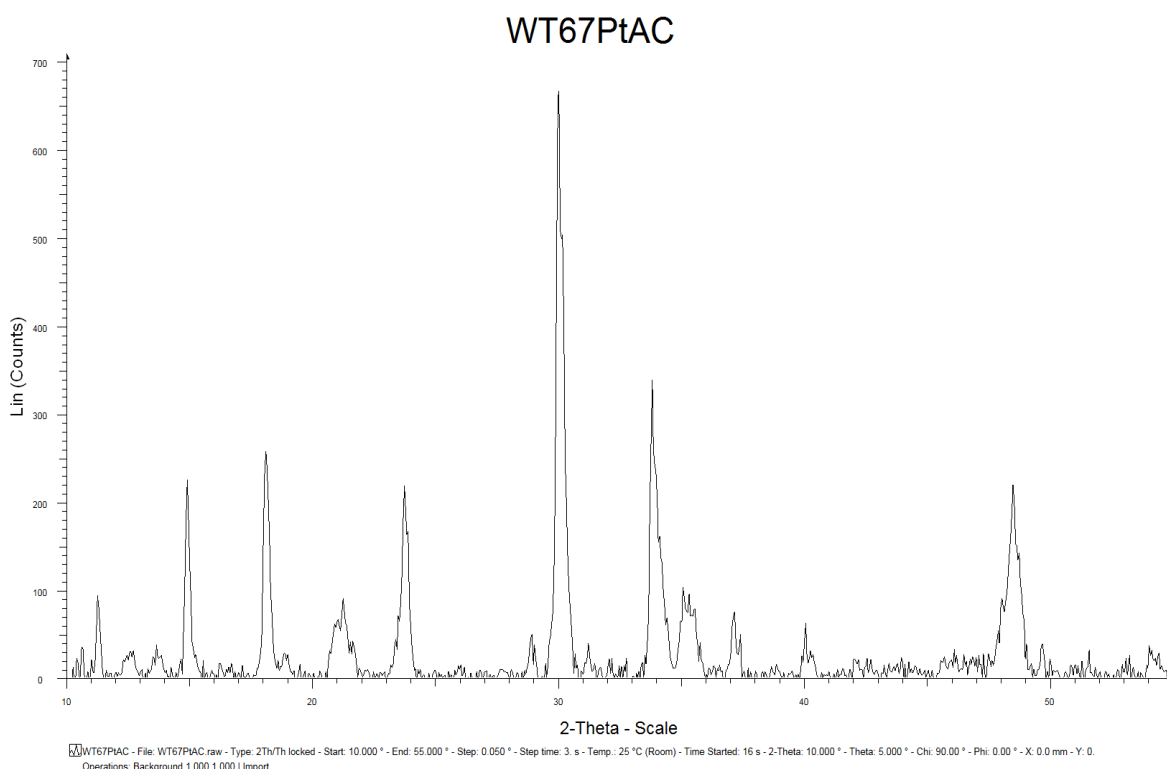


Figure 4.82. Raw XRD spectrum for the nominal 67 at.% Pt sample in the arc-melted condition.

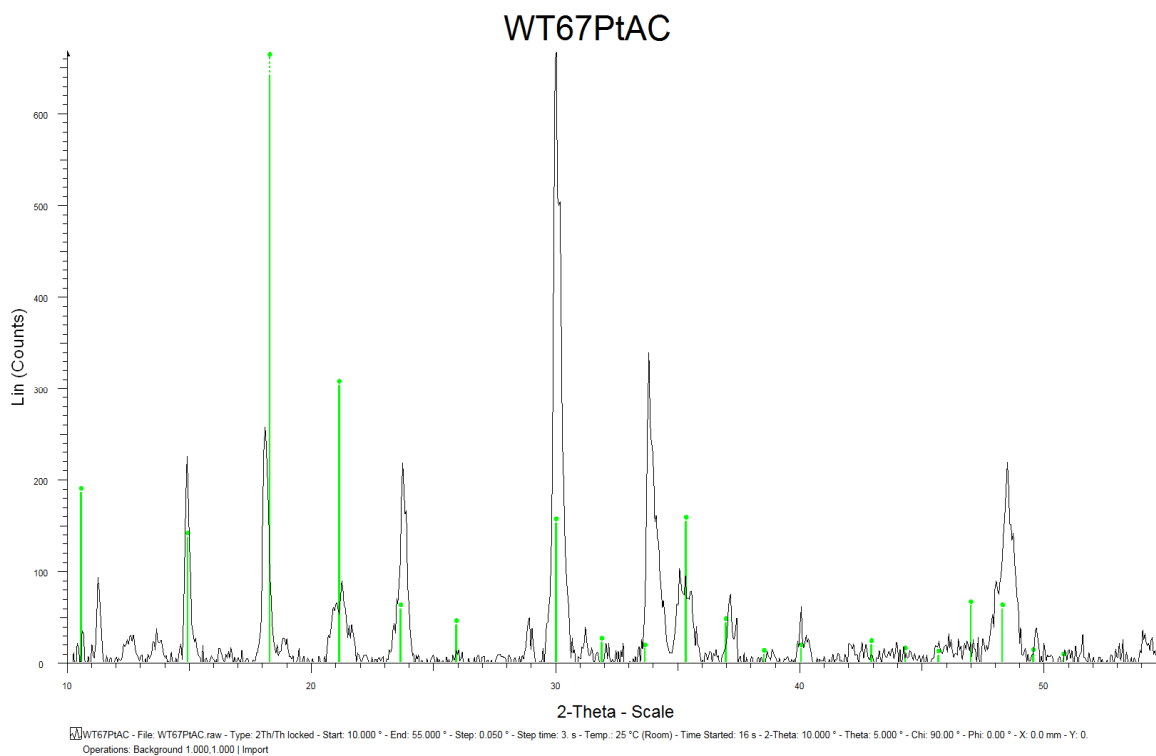


Figure 4.83. XRD trace showing peaks of the cubic Pt_3Al phase for the nominal 67 at.% Pt sample in the arc-melted condition.

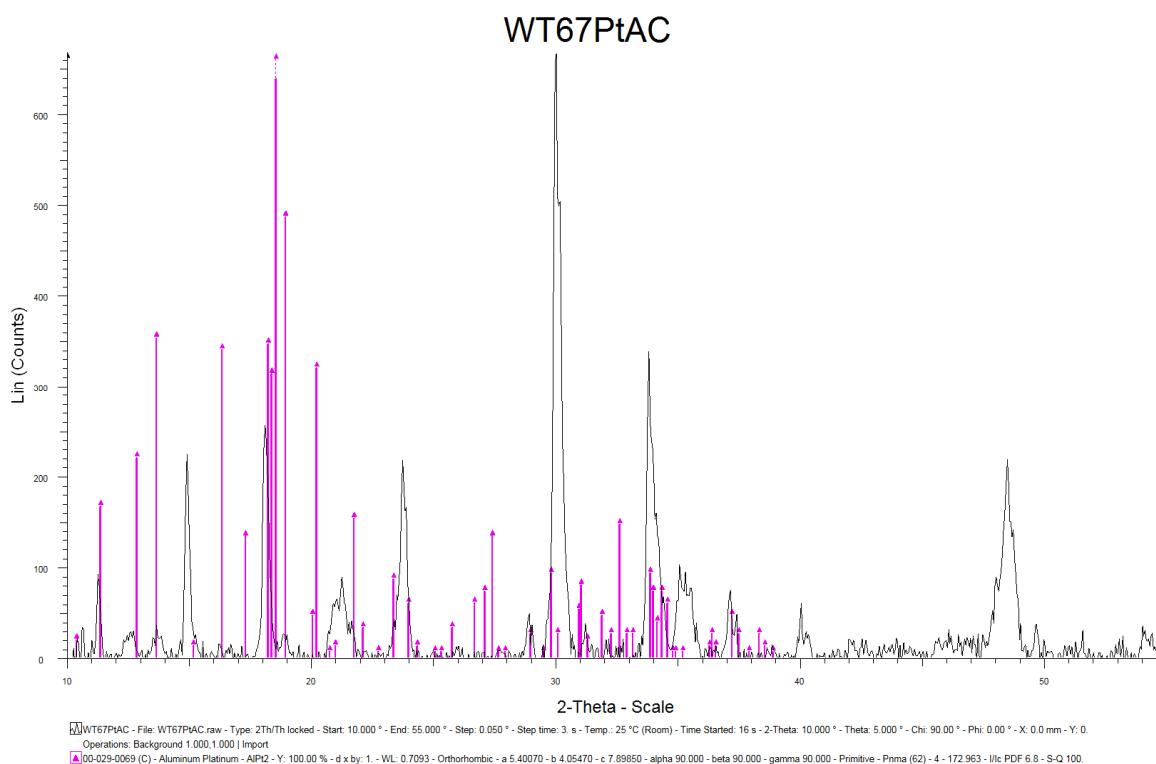


Figure 4.84. XRD trace showing peaks of the high temperature Pt_2Al phase for the nominal 67 at.% Pt sample in the arc-melted condition.

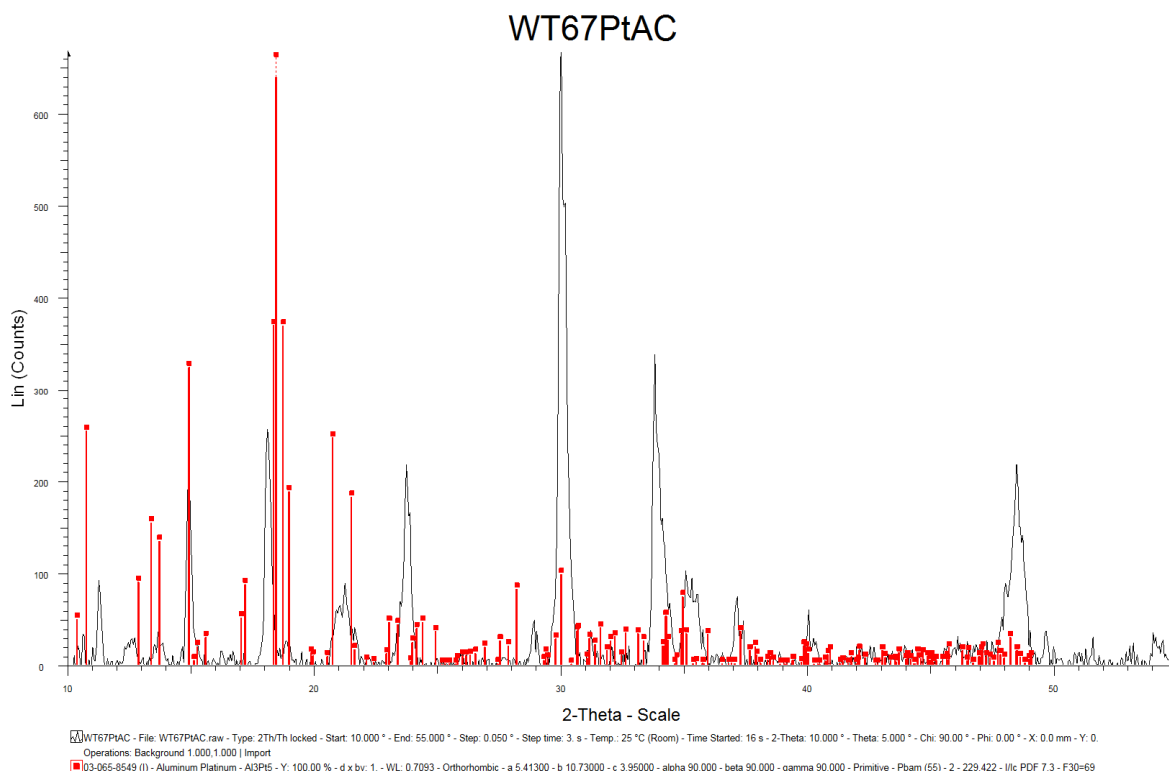


Figure 4.85. XRD trace showing peaks of the Pt_5Al_3 phase for the nominal 67 at. % Pt sample in the arc-melted condition.

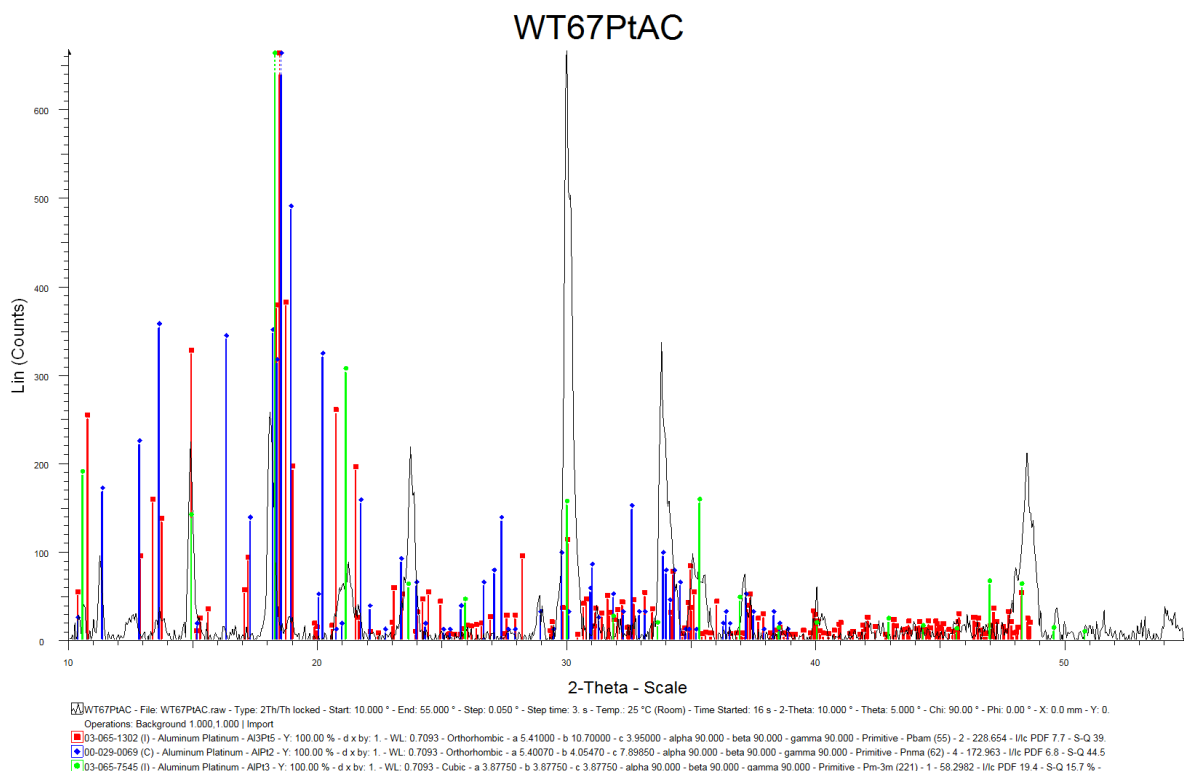


Figure 4.86. XRD trace showing peaks of cubic Pt_3Al , high temperature Pt_2Al and Pt_5Al_3 for the nominal 67 at. % Pt sample in the arc-melted condition.

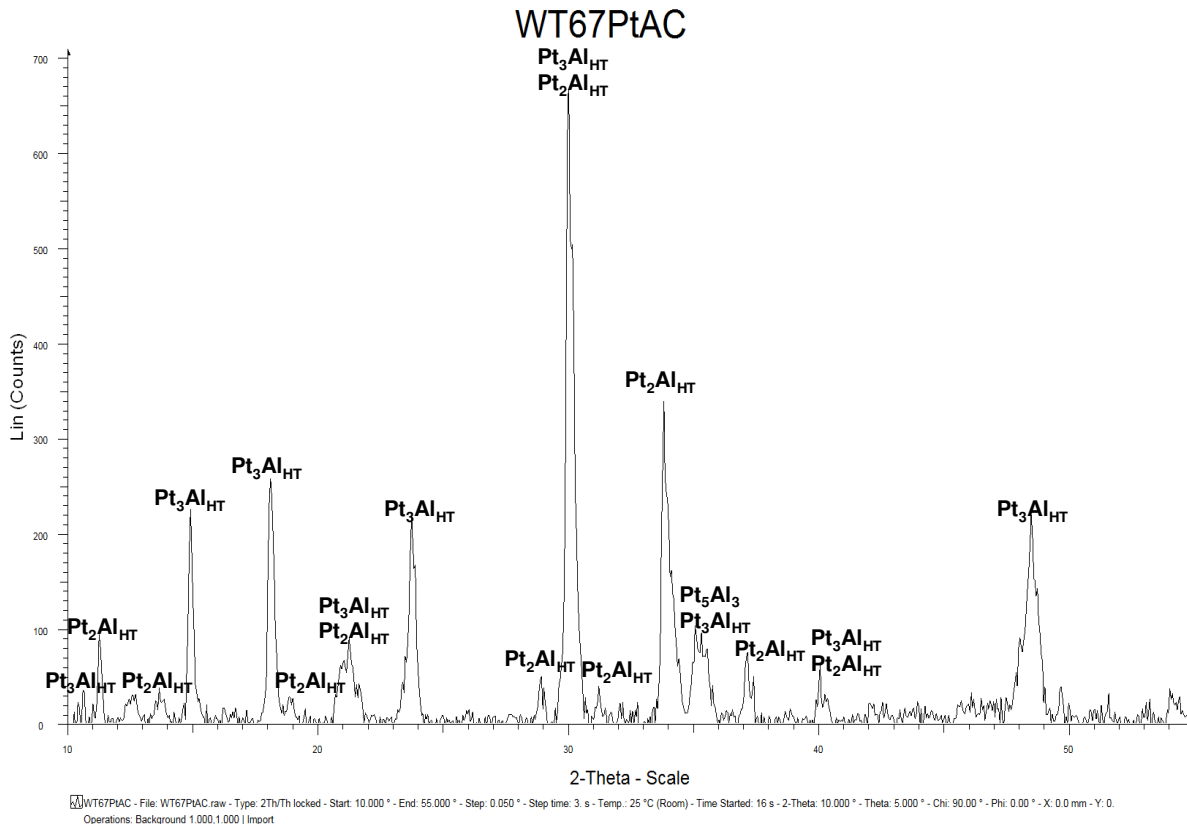


Figure 4.87. XRD pattern showing the phases in the nominal 67 at.% Pt sample in the as-cast condition.

The XRD spectrum had broad peaks, high counts and moderate signal to background ratio (Figure 4.82). The spectrum has few peaks, which resulted in a simple spectrum, although the microstructure had complex phases. The XRD database [2005ICD] showed that there may be a presence of Pt_3Al , Pt_2Al and Pt_5Al_3 phases (Table 4.24). In Figure 4.83, a match of peaks with cubic Pt_3Al phase was observed at $2\theta = 10.5^\circ, \sim 15^\circ, \sim 18^\circ, \sim 21^\circ, \sim 24^\circ, \sim 30^\circ, \sim 35^\circ, \sim 40^\circ$ and $\sim 48^\circ$ with a negligible shift. The presence of the high temperature Pt_2Al phase was shown by the match of peaks at $2\theta = \sim 11^\circ, 12.5^\circ, \sim 14^\circ, \sim 19^\circ, \sim 21^\circ, \sim 29^\circ, \sim 30^\circ, \sim 31^\circ, \sim 34^\circ, \sim 37^\circ$ and $\sim 40^\circ$, which were different from cubic Pt_3Al , with a slight shift to the left (Figure 4.84). The Pt_5Al_3 phase was indicated by the match of the peak at $2\theta = \sim 35^\circ$, with a slight shift to the left (Figure 4.85). Therefore it was assumed that the sample contained the high temperature Pt_3Al , high temperature Pt_2Al and probably Pt_5Al_3 . The strongest peak was at $2\theta = \sim 30^\circ$ and it was from the high temperature Pt_3Al and Pt_2Al phases (Figure 4.87), and was probably because of the preferred orientation originating from solidification after arc-melting.

4.5.2 Nominal 67 at.% Pt sample annealed at 1400°C

Observations on the SEM revealed a single phase (Figure 4.88). The overall composition was in the single-phase region of Massalski's phase diagram [1986McA] (Table 4.25). The alloy was brittle because it disintegrated during the removal of the mount for XRD analysis.

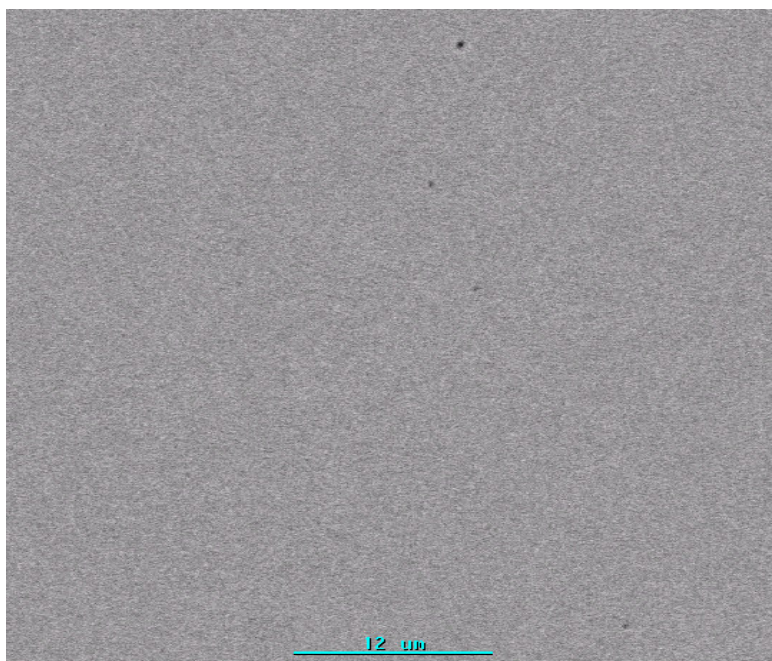


Figure 4.88. BSE-SEM image for the nominal 67 at.% Pt annealed at 1400°C, showing Pt₃Al single phase.

Table 4.25. EDS analysis for the nominal 67 at.% Pt sample annealed at 1400°C for 1000 h.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
1400°C	Overall	71.0 ± 0.5	29.0 ± 0.5	Pt ₃ Al

Table 4.26. XRD database [2005ICD] information for the nominal 67 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) Pt ₃ Al _{HT}	I (%) Raw spectrum
10.5	3.88	100	28	13
14.9	2.74	110	20	17
18.2	2.24	111	99	100
21.1	1.94	200	45	30
29.9	1.37	220	23	23
35.3	1.17	311	23	21
36.9	1.12	222	6	13

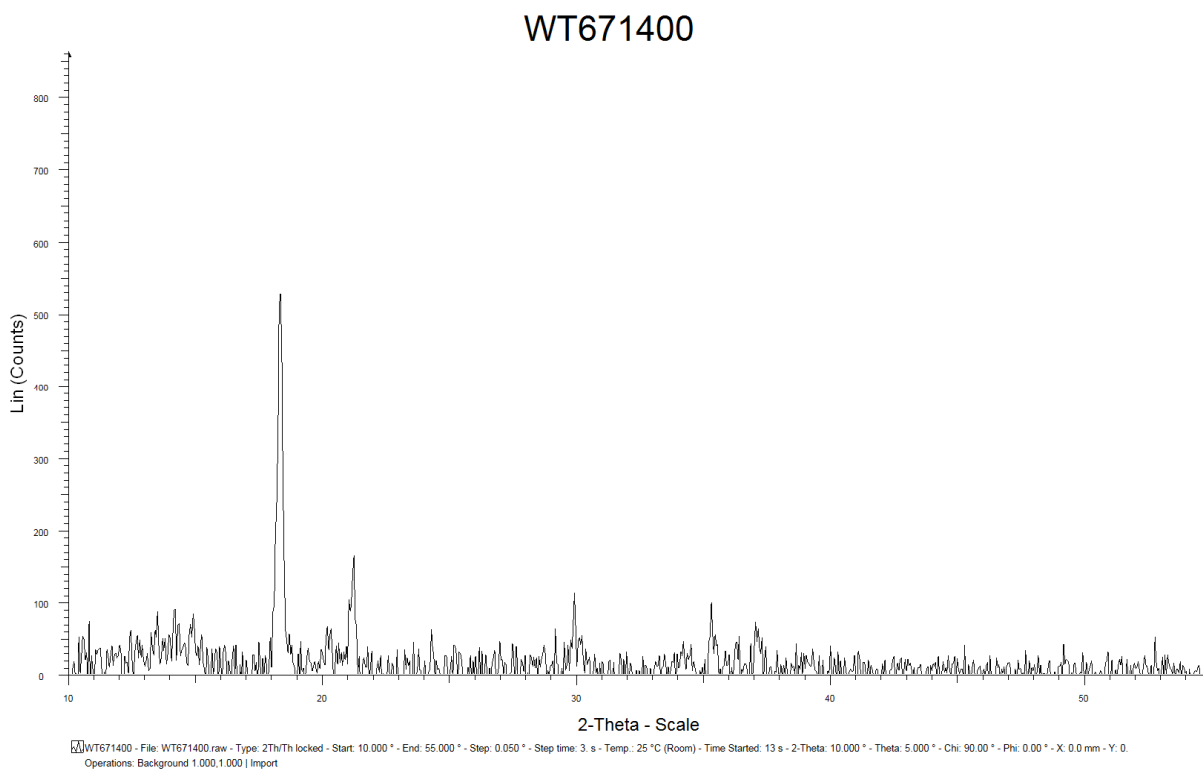


Figure 4.89. Raw spectrum for the nominal 67 at.% Pt sample annealed at 1400°C.

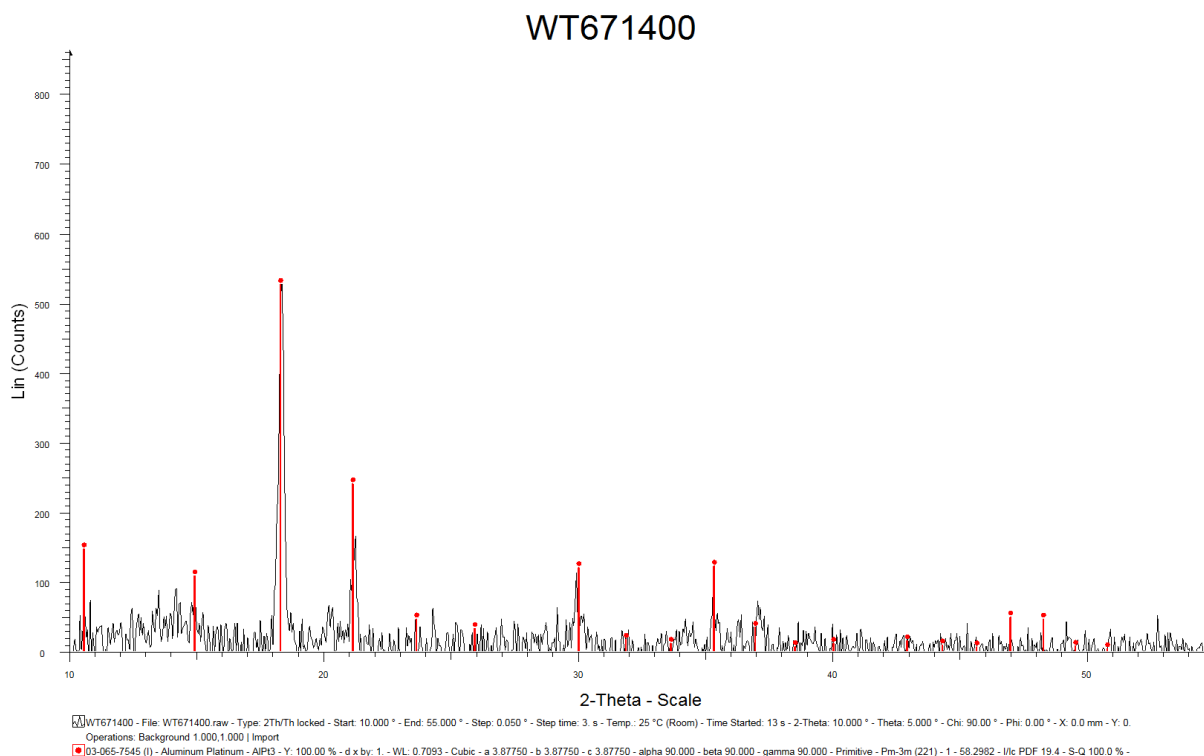


Figure 4.90. XRD trace showing peaks of cubic Pt_3Al for the nominal 67 at. % Pt annealed at 1400°C.

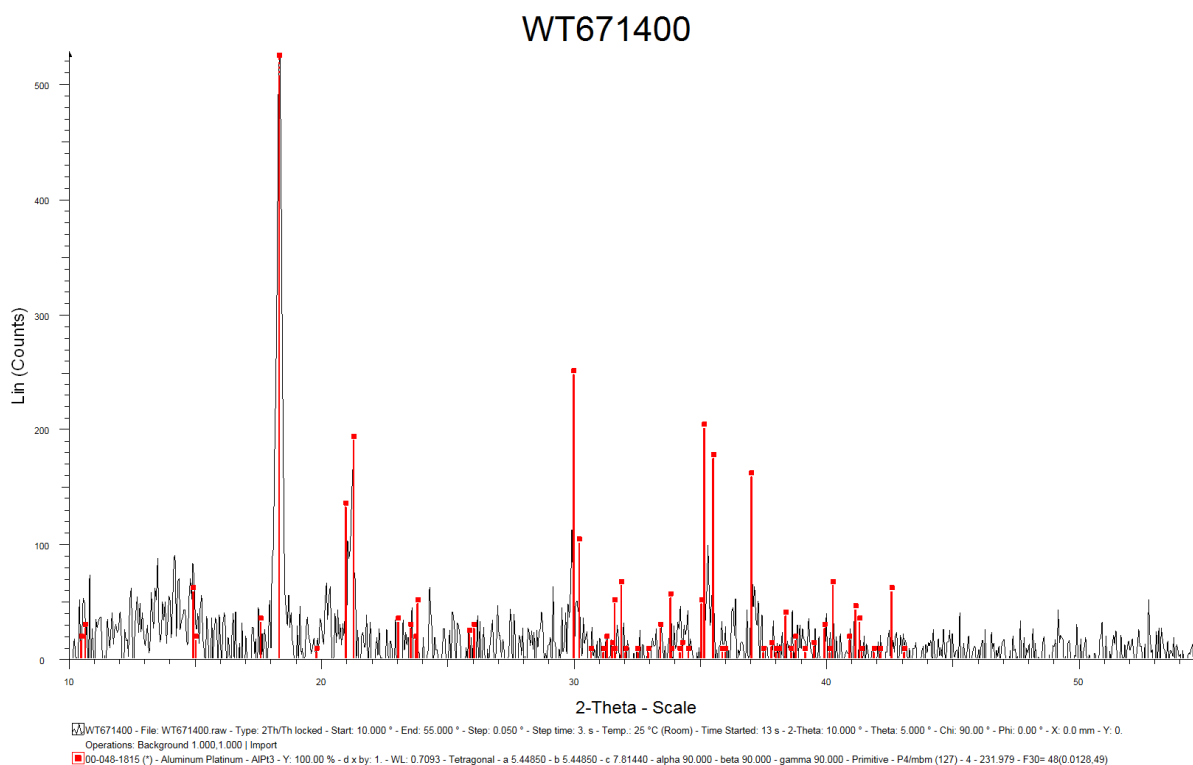


Figure 4.91. XRD trace showing peaks of tetragonal Pt_3Al for the nominal 67 at. % Pt annealed at 1400°C.

The XRD spectrum was very poor with few peaks, low counts and very low signal to background noise (Figure 4.89). Only one phase was expected. The XRD database [2005ICD] showed the presence of cubic Pt₃Al (Table 4.26). In Figure 4.90, a match of all the major peaks for high temperature Pt₃Al was observed at $2\theta = 10.5^\circ$, $\sim 15^\circ$, $\sim 18^\circ$, $\sim 21^\circ$, $\sim 30^\circ$, $\sim 35^\circ$ and $\sim 37^\circ$, with a negligible shift. There was a slight possibility of the presence of the tetragonal Pt₃Al phase (Figure 4.91), but the results were not conclusive, because the spectrum was very poor, and it was difficult to differentiate between the peaks.

Relative to the as-cast spectrum, the spectrum of the sample annealed 1400°C had the strongest peak at $2\theta = \sim 18^\circ$ while the as-cast spectrum had the strongest peak at $2\theta = \sim 30^\circ$, and the rest of the peaks had different intensities. Therefore the microstructure showed less preferred orientation after annealing.

4.5.3 Nominal 67 at.% Pt sample annealed at 1200°C

On heat treatment at 1200°C, the sample formed laths in the dendrites (Figure 4.92(b)). The laths were in the primary phase (light phase). The presence of laths signified a martensitic-like transformation. The dark phase was the second phase between the dendrites that had the laths. The overall composition of the alloy was within the target of the original weighed composition, and was in the two-phase region of Pt₂Al and Pt₃Al phases (Table 4.27) [1986McA]. The lighter phase (laths) was at the Pt₃Al phase boundary, and the dark phase was at the Pt₂Al phase boundary [1986McA]. The dark phase had high errors of $\pm 4.8.0$ at.% Pt.

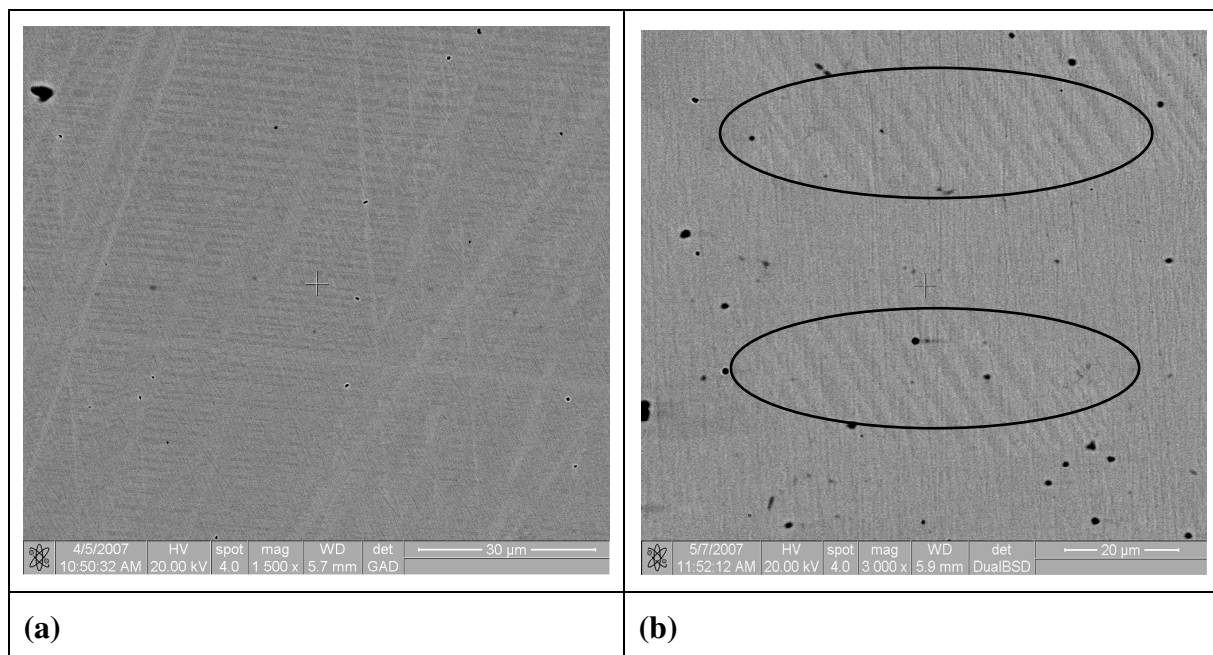


Figure 4.92. BSE-SEM for the nominal 67 at.% Pt sample annealed at 1200°C, showing laths formed on transformation of high temperature Pt_2Al to low temperature Pt_3Al phase.

Table 4.27. EDS analysis for the nominal 67 at.% Pt sample annealed at 1200°C for 1000 h.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1200°C	Overall	67.1 ± 1.0	32.9 ± 1.0	-
	Light	68.8 ± 0.2	31.2 ± 0.2	Pt_3Al (LT)
	Dark	64.9 ± 4.8	35.1 ± 4.8	Pt_2Al

Table 4.28. XRD database [2005ICD] information for the nominal 67 at.% Pt sample annealed at 1200°C.

2 θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₂ Al _{HT}	I (%) Pt ₂ Al _{LT}	I (%) Pt ₃ Al _{HT}
10.6/10.5	3.84/3.88	301/100	77	-	26	28
13.1	3.12	111	4	-	2	-
13.6	3.0	111	38	53	-	-
15.0	2.71	600	9	-	14	-
18.9	2.16	211	100	73	-	-
19.6	2.09	502	5	-	36	-
23.7	1.72	612	33	-	27	-
27.4	1.5	222	48	20	-	-
28.9	1.42	115	4	4	-	-
29.8	1.38	223	9	14	-	-
31.8	1.29	215	5	7	-	-
34.0	1.21	125	5	11	-	-
35.1	1.18	032	28	-	67	-
38.3	1.08	422	11	4	-	-
40.0	1.04	321	14	-	-	2
48.3	0.87	420	26	-	-	9

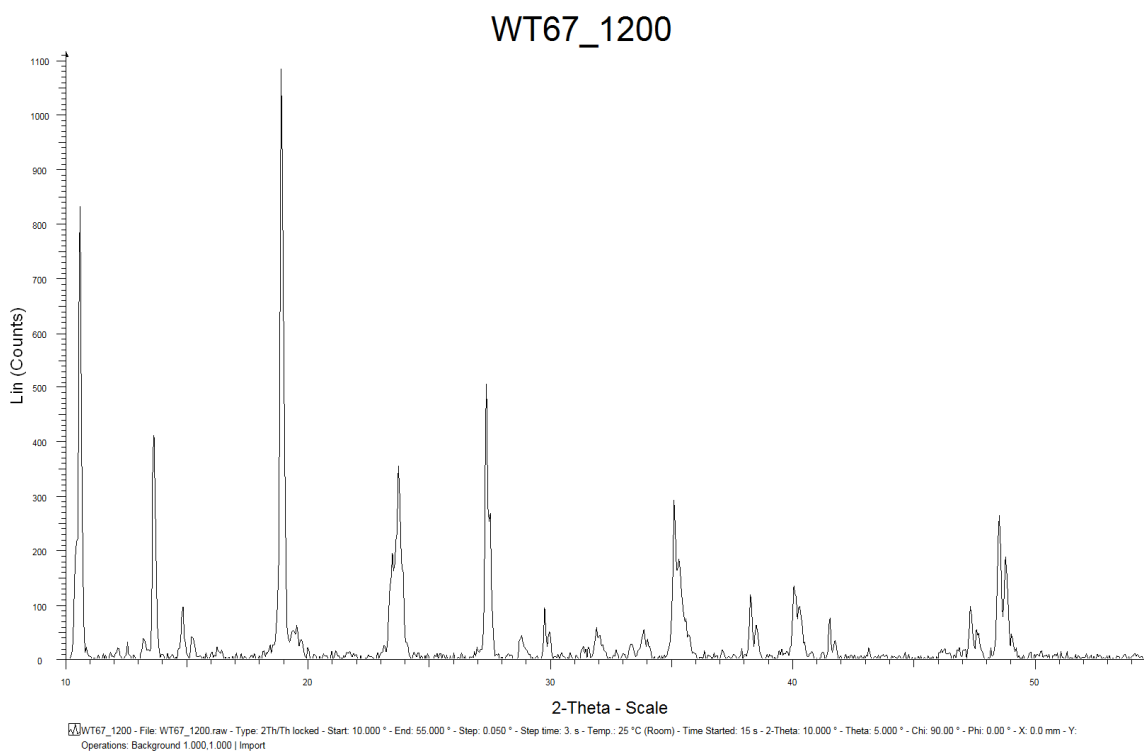


Figure 4.93. Raw XRD spectrum for the nominal 67 at.% Pt sample annealed at 1200°C.

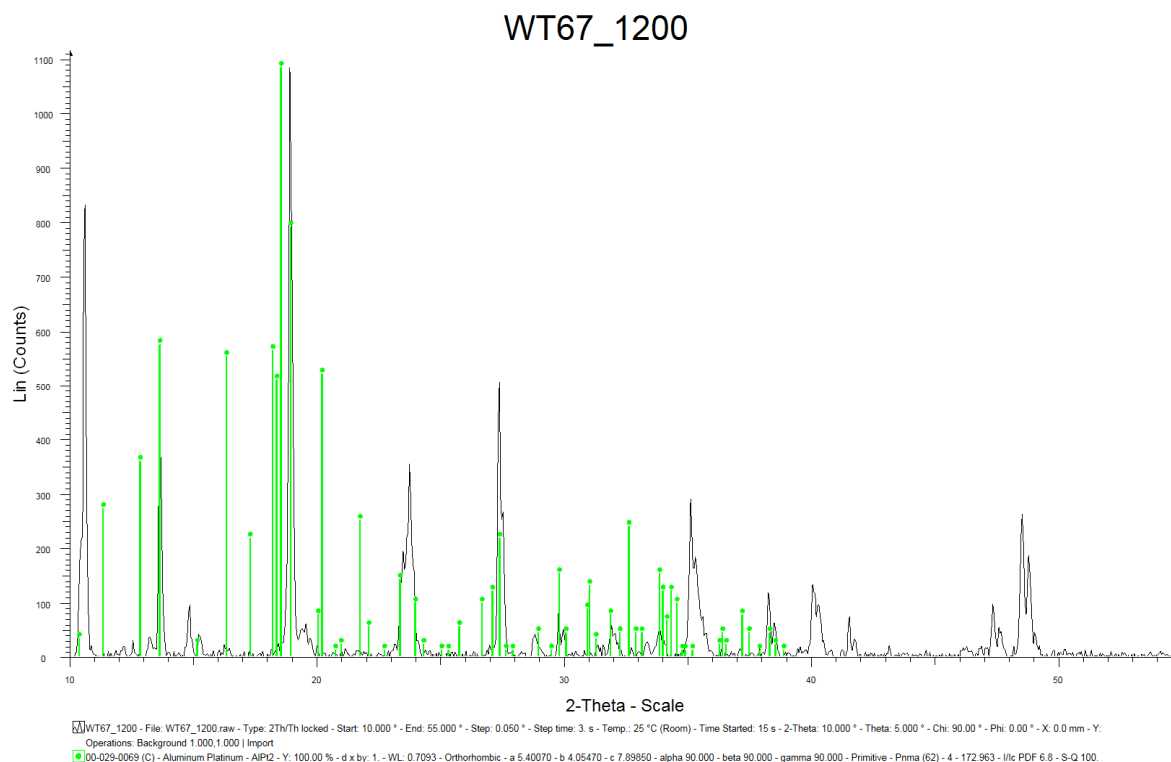


Figure 4.94. XRD trace of high temperature Pt_2Al for the nominal 67 at.% Pt sample annealed at 1200°C.

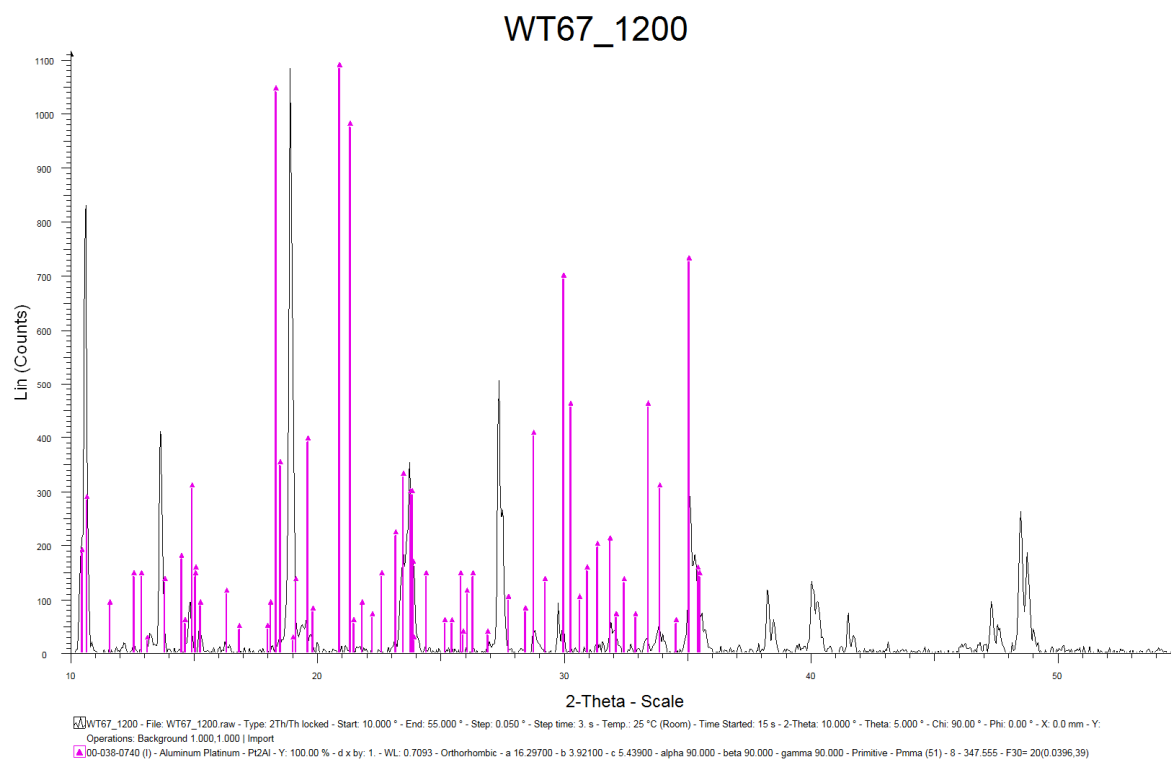
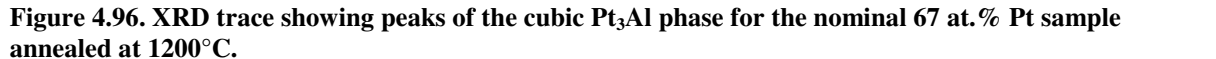


Figure 4.95. XRD trace of low temperature Pt_2Al for the nominal 67 at.% Pt sample annealed at 1200°C.



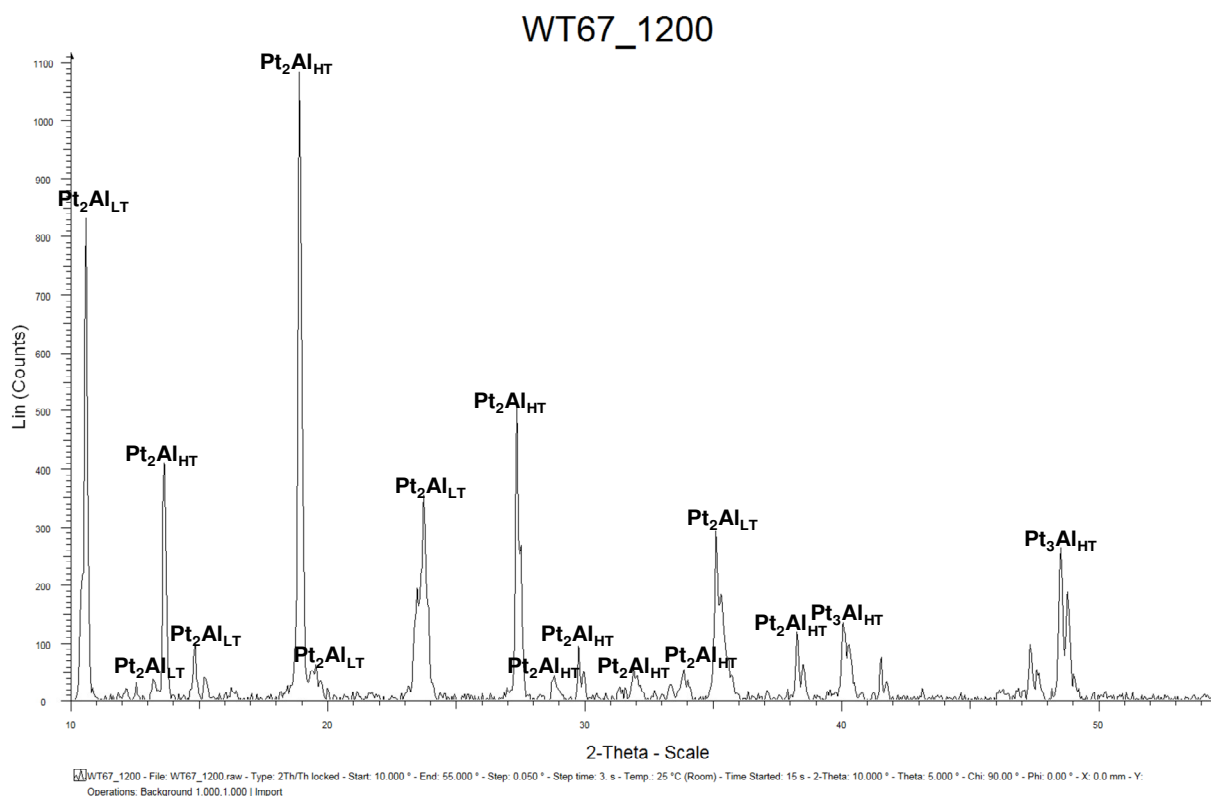


Figure 4.98. XRD pattern showing the phases for the nominal 67 at.% Pt sample annealed at 1200°C.

This was a simple spectrum, with narrower peaks than the as-cast sample, high counts and high signal to background ratio (Figure 4.93). Some of the peaks were in a different position compared to the as-cast sample. According to the XRD database [2005ICD] there was a good match with high and low temperature Pt_2Al , and possibly some Pt_3Al , because the peaks lie close together (Table 4.28). In Figure 4.94, there was a match of peaks with the high temperature Pt_2Al phase at $2\theta = \sim 14^\circ, \sim 19^\circ, \sim 27^\circ, \sim 29^\circ, \sim 30^\circ, 32^\circ, \sim 34^\circ$ and 38.5° , with a negligible shift. The presence of low temperature Pt_2Al was shown by the match of peaks at $2\theta = 10.5^\circ, \sim 13^\circ, \sim 15^\circ, 19.5^\circ, \sim 24^\circ$ and $\sim 35^\circ$ which are different from high temperature Pt_2Al peaks, with a negligible shift in Figure 4.95, and some peaks towards the end of the spectrum were shown to match the cubic Pt_3Al phase, and these were $2\theta = \sim 40^\circ$ and $\sim 49^\circ$ as shown in Figure 4.96. The peaks which did not match towards the end of the spectrum were because the data in the database [2005ICD] ended, and these were: $2\theta = \sim 42^\circ$ and $\sim 44^\circ$. Therefore, three phases were observed in the sample as shown in Figure 4.98.

The as-cast spectrum had the strongest peak at $2\theta = \sim 30^\circ$ from high temperature Pt_3Al and Pt_2Al phases, and the sample annealed at 1200°C had the strongest peak at $2\theta = \sim 19^\circ$ from high temperature Pt_2Al . The spectrum of the sample annealed at 1200°C showed peaks which matched the high temperature Pt_2Al and Pt_3Al phases in the as-cast spectrum. Peaks which matched the low temperature Pt_2Al phase in the annealed spectrum were: 10.5° , $\sim 13^\circ$, $\sim 15^\circ$, $\sim 24^\circ$ and $\sim 35^\circ$. Therefore, sample had a solid phase transformation during annealing.

4.5.4 Nominal 67 at.% Pt sample annealed at 1000°C

The HRSEM revealed a three-phase structure. The light and the grey phases solidified dendritically (Figure 4.99). The grey phase had similar composition to the light phase, although the reason for the difference in contrast is associated with differences in plane orientation, enhanced by OPS polishing. The annealing process rounded the edges observed in the as-cast structure (Figure 4.81). Compared to the annealed sample at 1200°C that had laths, the microstructure of this sample had no visible laths. The overall composition of the microstructure was in the two-phase region ($\text{Pt}_2\text{Al} + \text{Pt}_3\text{Al}$) of Massalski's phase diagram [1986McA]. According to the EDS results, the light phase composition was at the Pt_3Al phase boundary, with an error of ~ 1.2 at.% Pt, and the dark phase composition was at the Pt_2Al phase boundary [1986McA].

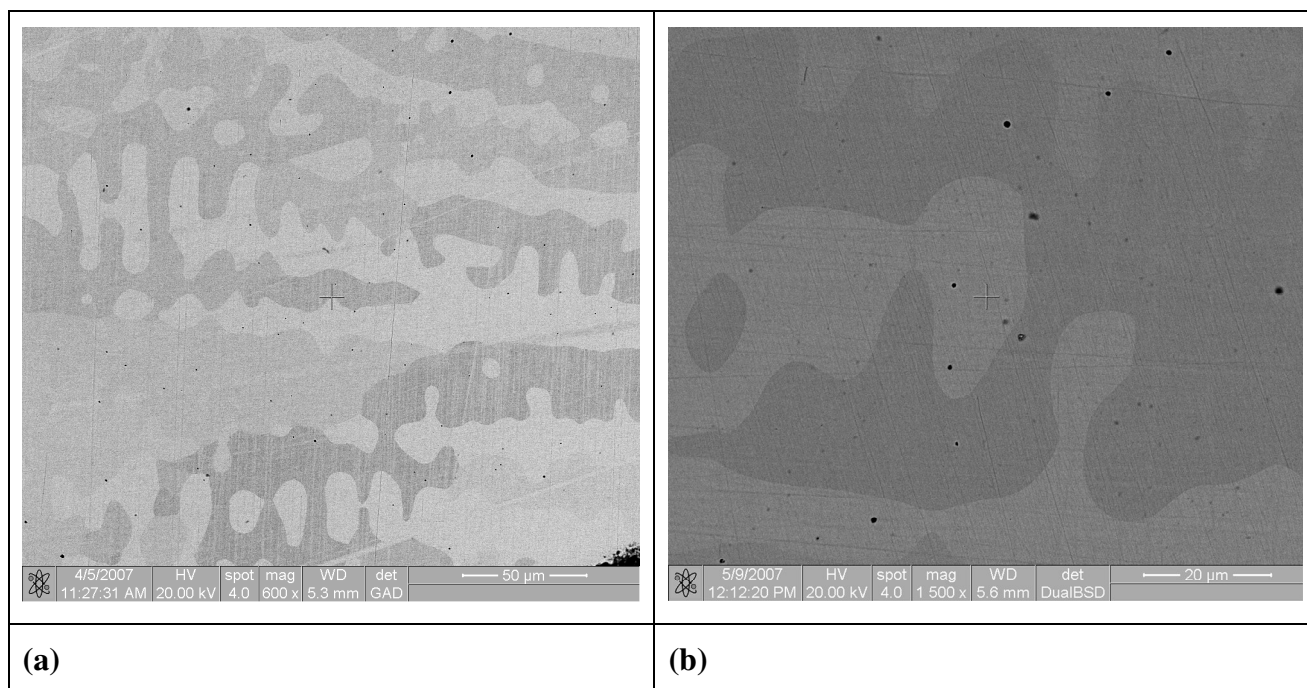


Figure 4.99. BSE-SEM image for nominal 67 at.% Pt annealed at 1000°C, showing Pt₃Al (light and grey) and Pt₂Al (dark).

Table 4.29. EDS analysis for the nominal 67 at.% Pt sample annealed at 1000°C for 1000 h.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1000°C for 1000hrs and W/Q	Overall	67.5 ± 0.5	32.5 ± 0.5	-
	Light	69.7 ± 1.2	30.3 ± 1.2	Pt ₃ Al
	Grey phase	69.7 ± 1.2	30.3 ± 1.2	Pt ₃ Al
	Dark	67.2 ± 0.8	32.8 ± 0.8	Pt ₂ Al

Table 4.30. XRD database [2005ICD] information for the nominal 67 at.% Pt sample annealed at 1000°C.

2 θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₂ Al _{HT}	I (%) Pt ₃ Al _{HT}
11.3	4.45	011	30	25	-
13.6	3.0	111	32	53	-
14.9	2.74	110	15	-	20
17.2	2.37	103	15	20	-
18.2	2.24	111	11	-	99
18.9	2.16	211	100	73	-
20.1	2.03	020	11	48	-
21.7	1.89	203	6	23	-
23.9	1.71	122	17	9	-
27.4	1.5	222	15	20	-
29.8	1.38	223	6	14	-
31.3	1.32	006	15	3	-
32.6	1.26	314	28	22	-
35.3	1.17	311	22	-	23
38.3	1.08	422	11	4	-
47	0.89	331	9	-	9

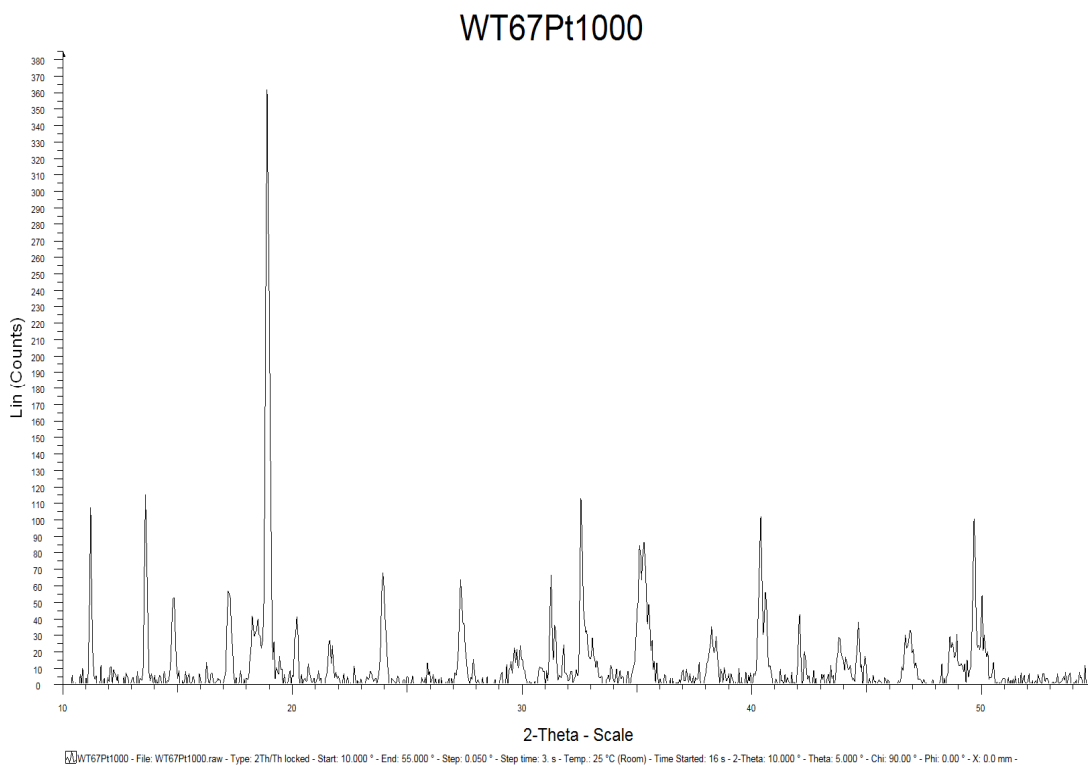


Figure 4.100. Raw spectrum for the nominal 67 at.% Pt sample annealed at 1000°C.

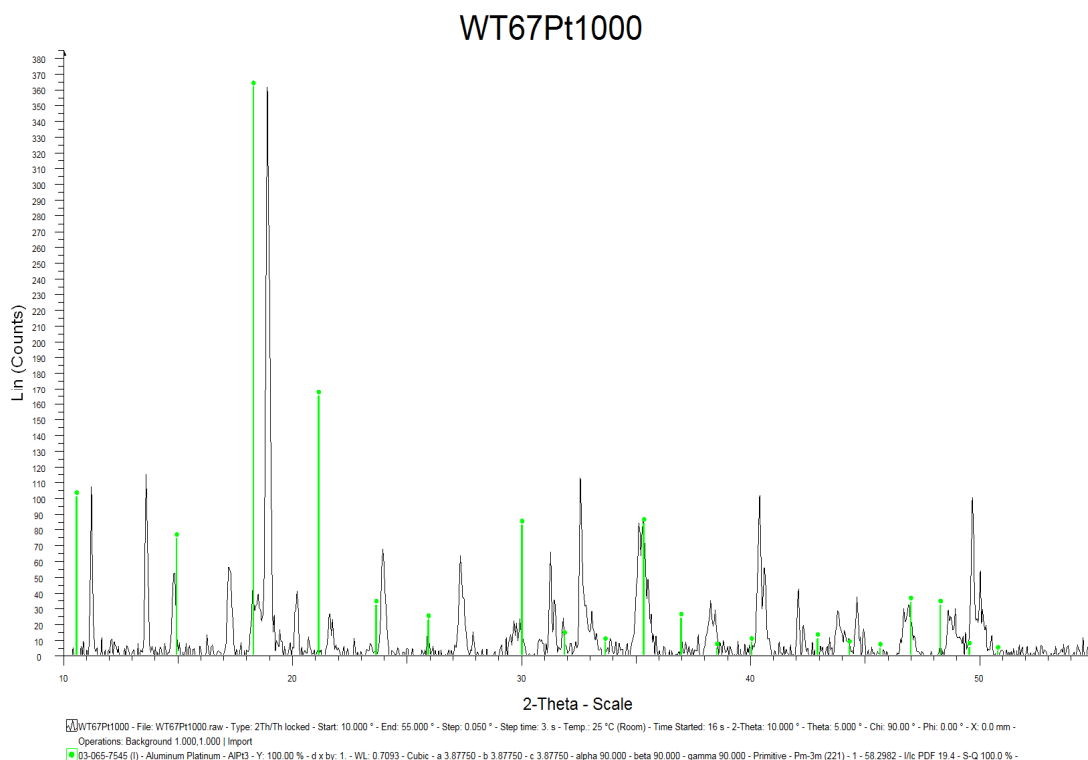


Figure 4.101. XRD traces of cubic Pt_3Al for the nominal 67 at.% Pt annealed at 1000°C.

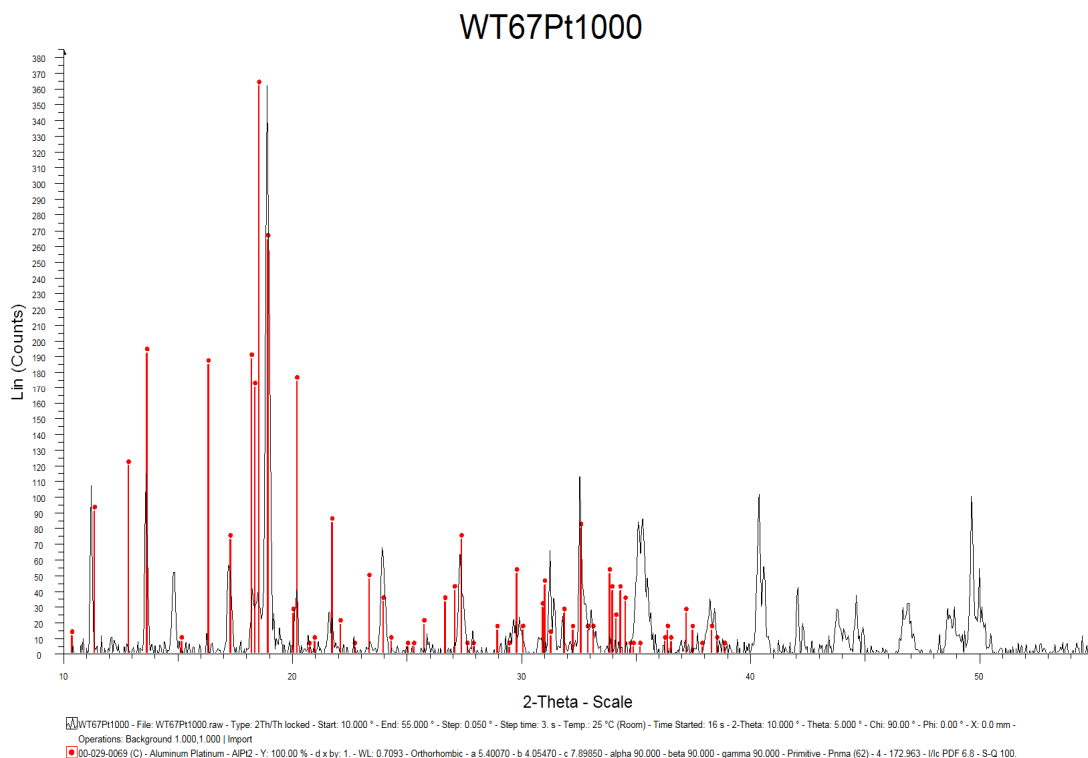


Figure 4.102. XRD traces of high temperature Pt_2Al for the nominal 67 at.% Pt annealed at 1000°C.

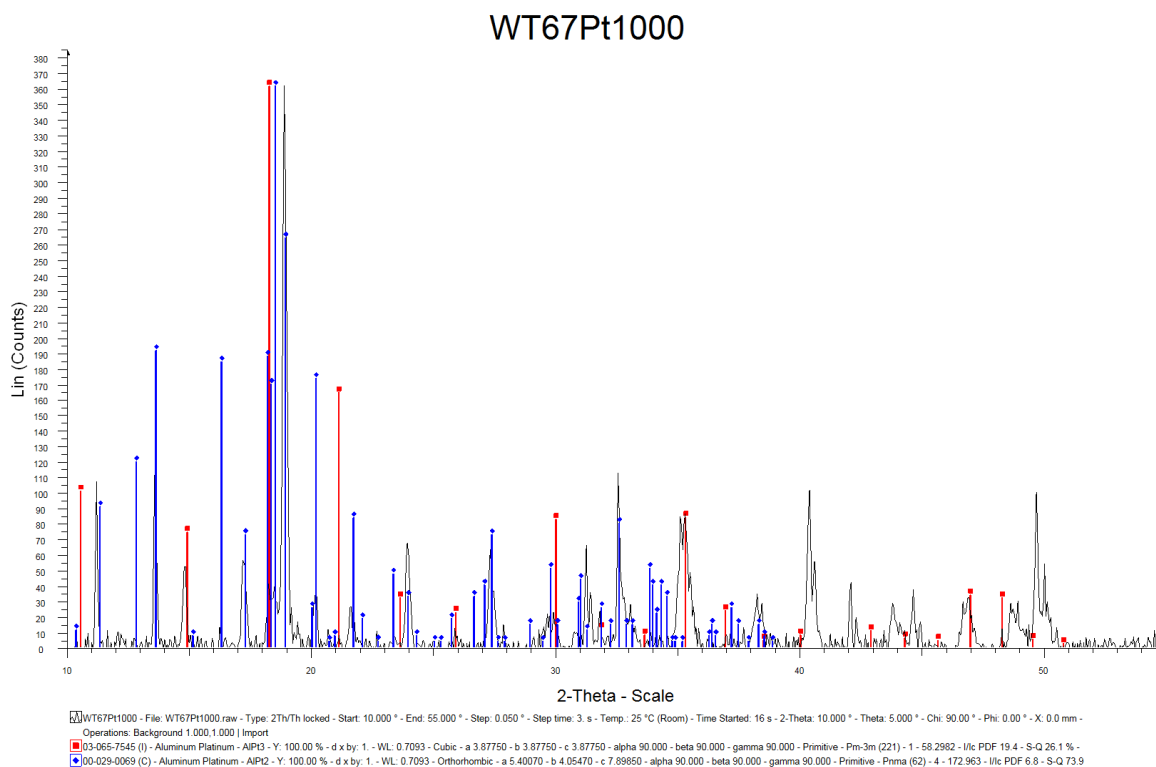


Figure 4.103. XRD trace showing peaks for cubic Pt_3Al and high temperature Pt_2Al for the nominal 67 at. % Pt sample annealed at 1000°C.

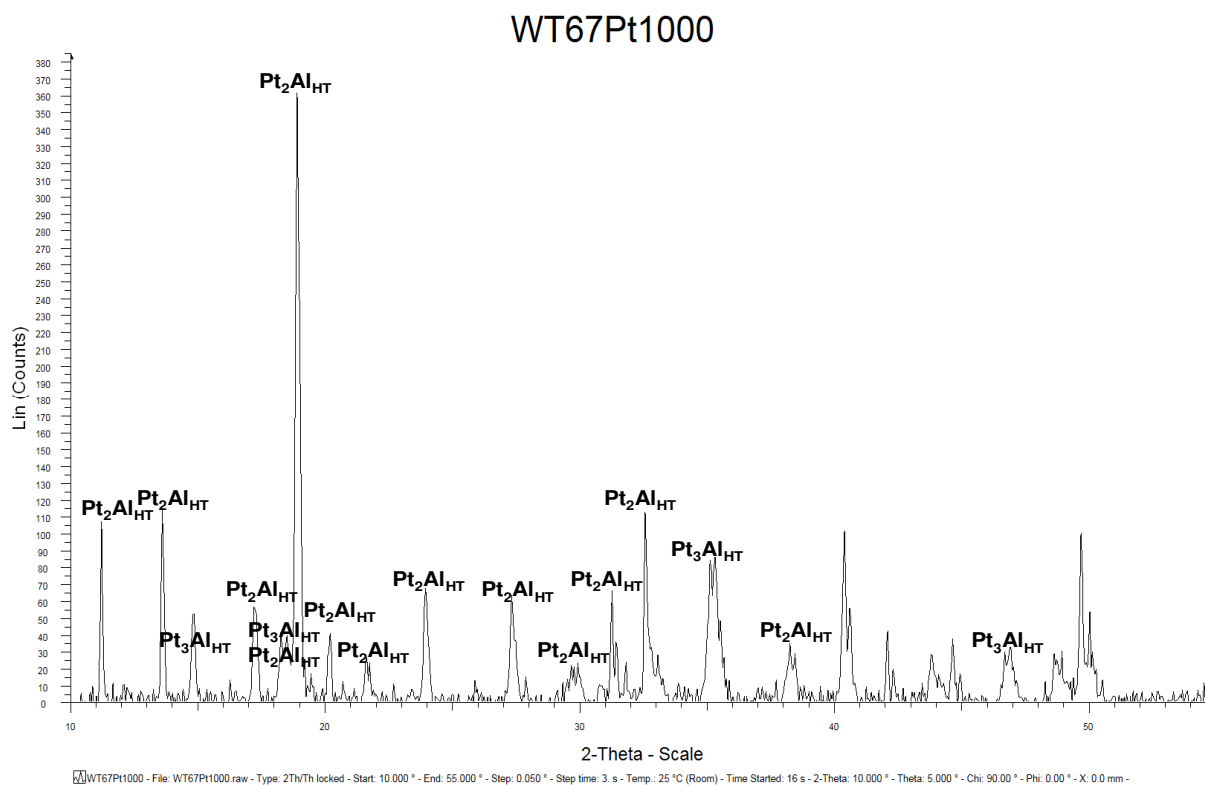


Figure 4.104. XRD pattern showing the phases in the nominal 67 at. % Pt sample annealed at 1000°C.

This was a fairly complex spectrum, with fairly narrow peaks, fairly low counts and a low signal to background ratio (Figure 4.100). The XRD database [2005ICD] showed a good match with high temperature Pt_3Al and Pt_2Al phases (Tables 4.30). In Figure 4.101, a match of peaks with cubic Pt_3Al was observed at $2\theta = \sim 15^\circ, 18.5^\circ, \sim 35^\circ$ and $\sim 47^\circ$, with a slight shift to the left. The presence of high temperature Pt_2Al was indicated by the match of peaks at $2\theta = 11.5^\circ, \sim 14^\circ, 17.5^\circ$, several peaks at $\sim 18^\circ, \sim 20^\circ, \sim 22^\circ, \sim 24^\circ, 27.5^\circ, \sim 30^\circ$, several peaks at 31.5° , several peaks at $\sim 32^\circ$ and $\sim 38^\circ$, which are different from the cubic Pt_3Al peaks, with a negligible shift as shown in Figure 4.102. Therefore, it was assumed that the microstructure contained the high temperature Pt_3Al and Pt_2Al phases as shown in Figure 4.104.

The spectrum of this sample had the strongest peak at $2\theta = \sim 19^\circ$ and the as-cast spectrum had the highest peak at $2\theta = \sim 30^\circ$, while the spectrum of the sample annealed at 1400°C had the strongest peak at $2\theta = \sim 18^\circ$. The as-cast spectrum had a much lower intensity compared to the spectrum of this sample at $2\theta = \sim 19^\circ$, and also the proportions of the high temperature Pt_2Al phase were different in the samples. The peaks above $2\theta = \sim 40^\circ$ did not show a match, because the database data [2005ICD] ended, as indicated in Figure 4.104.

4.6 Phase analyses for the 64 at.% Pt samples

4.6.1 Nominal 64 at.% Pt in the arc-melted condition

The sample solidified to form a single phase as shown in Figure 4.105. The overall composition was in the single phase region of both phase diagrams (Table 4.31) [1986McA]. The composition was higher than expected from the original weighed composition, and this may be due to weighing errors or the loss of aluminium during casting.

The solidification sequence was:

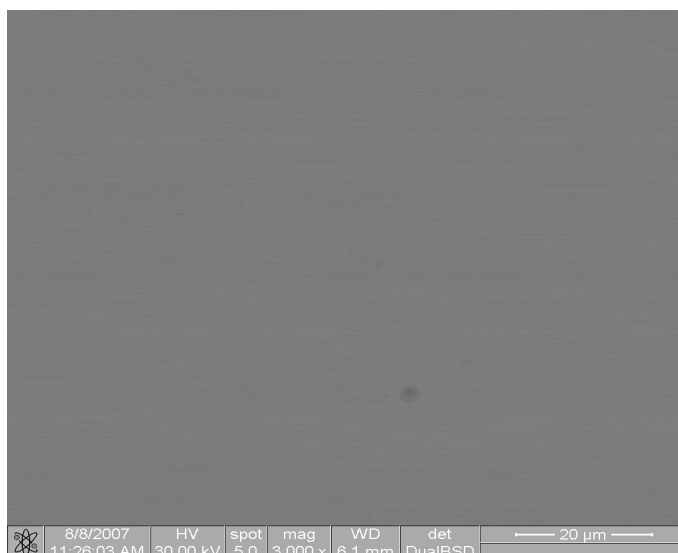
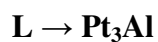


Figure 4.105. BSE-SEM image for nominal 64 at. % Pt in the arc-melted condition, showing a Pt_3Al single phase.

Table 4.31. Phase analysis for the nominal 64 at. % Pt sample in the arc-melted condition.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
Arc-melted	Overall	73.8 ± 0.6	26.2 ± 0.6	Pt_3Al

Table 4.32. XRD database information [2005ICD] for the nominal 64 at. % Pt sample in the arc-melted condition.

2 θ	d (Å)	h k l	I (%) raw spectrum	I (%) $\text{Pt}_3\text{Al}_{\text{HT}}$
10.5	3.88	100	12	28
14.9	2.74	110	15	20
18.2	2.24	111	20	99
21.1	1.94	200	19	45
23.6	1.73	210	13	9
25.9	1.58	211	6	6
29.9	1.37	220	12	23
33.6	1.23	310	9	2
35.3	1.17	311	76	23
38.5	1.07	320	4	1
40.0	1.04	321	8	2
47	0.89	331	100	9
48.3	0.87	420	6	9

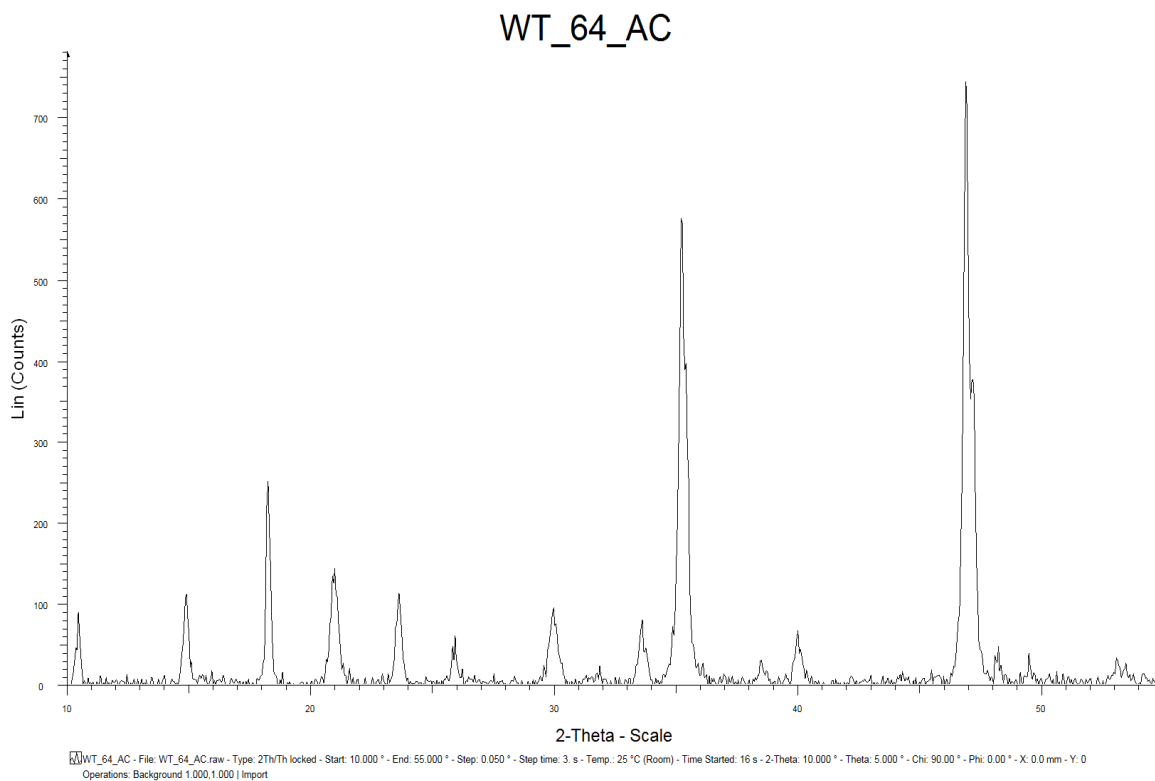


Figure 4.106. Raw XRD spectrum for the nominal 64 at. % Pt sample in the arc-melted condition.

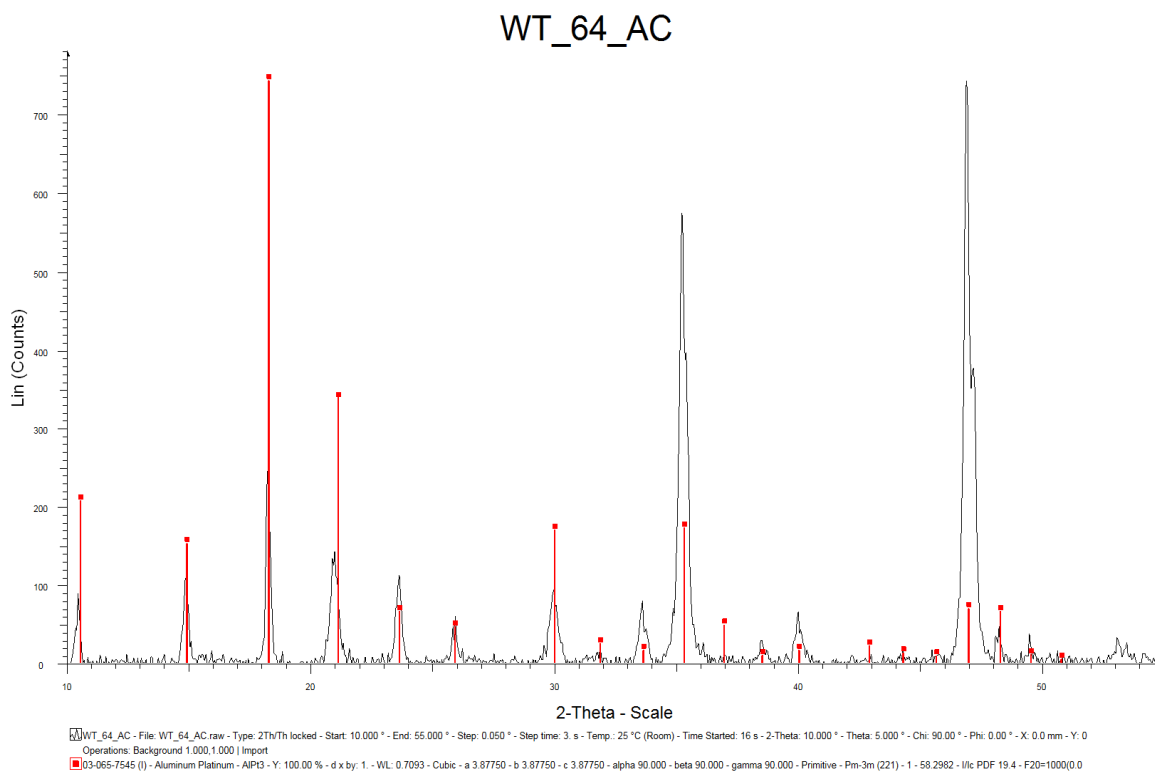


Figure 4.107. XRD trace showing peaks for the cubic Pt_3Al phase for the nominal 64 at. % Pt sample in the arc-melted condition.

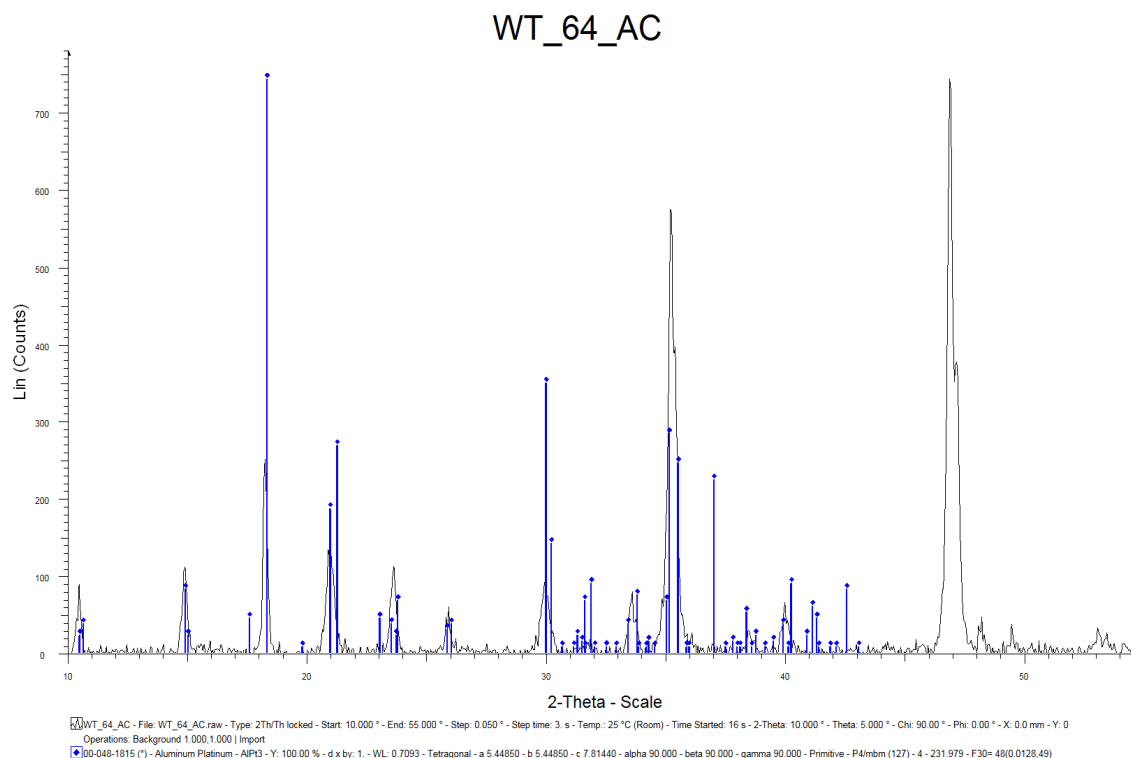


Figure 4.108. XRD trace showing peaks for the tetragonal Pt_3Al phase for the nominal 64 at.% Pt sample in the arc-melted condition.

The XRD spectrum had narrow peaks with fairly low counts and a high signal to background ratio (Figure 4.106). The XRD spectrum [2005ICD], showed that the cubic Pt_3Al phase was present (Table 4.32), because all the peaks were well matched, including a fairly good match for the intensities, with no peak splitting. The matched peaks were: $2\theta = 10.5^\circ$, $\sim 15^\circ$, $\sim 18^\circ$, $\sim 21^\circ$, $\sim 24^\circ$, $\sim 26^\circ$, $\sim 30^\circ$, $\sim 34^\circ$, $\sim 35^\circ$, $\sim 39^\circ$, $\sim 40^\circ$ and $\sim 46^\circ$, and there was minimal peak splitting and only at higher angles, and the tetragonal Pt_3Al is not thought to be present (Figure 4.108).

4.6.2 Nominal 64 at.% Pt annealed at 1400°C

The HRSEM showed a single phase (Figure 4.109). The results were confirmed by EDS in Table 4.33, with the overall composition in the Pt_3Al phase region of Massalski's phase diagram [1986McA]. The composition of the sample was similar (within 2 at.% Pt) to the as-cast sample (Table 4.31), and to the 67 at.% Pt sample annealed at this temperature (Table

4.25). The sample has higher composition than targeted, and this may be due to weighing errors or the loss of aluminium during casting.



Figure 4.109. BSE-SEM image of nominal 64 at.% Pt annealed at 1400°C, showing Pt₃Al single phase.

Table 4.33. Phase analysis for nominal 64 at.% Pt annealed at 1400°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
64 at.% Pt annealed at 1400°C	Overall	71.6 ± 0.4	28.4 ± 0.4	Pt ₃ Al

Table 4.34. XRD database [2005ICD] information for the nominal 64 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₃ Al _{HT}	I (%) Pt ₃ Al _{LT}
14.9	2.74	110	11	20	-
18.2	2.24	111	100	99	-
21.2	1.93	220	19	-	36
29.9	1.37	220	9	22	-
35.5	1.16	422	28	-	33
36.9	1.12	222	11	6	
47	0.89	331	11	9	

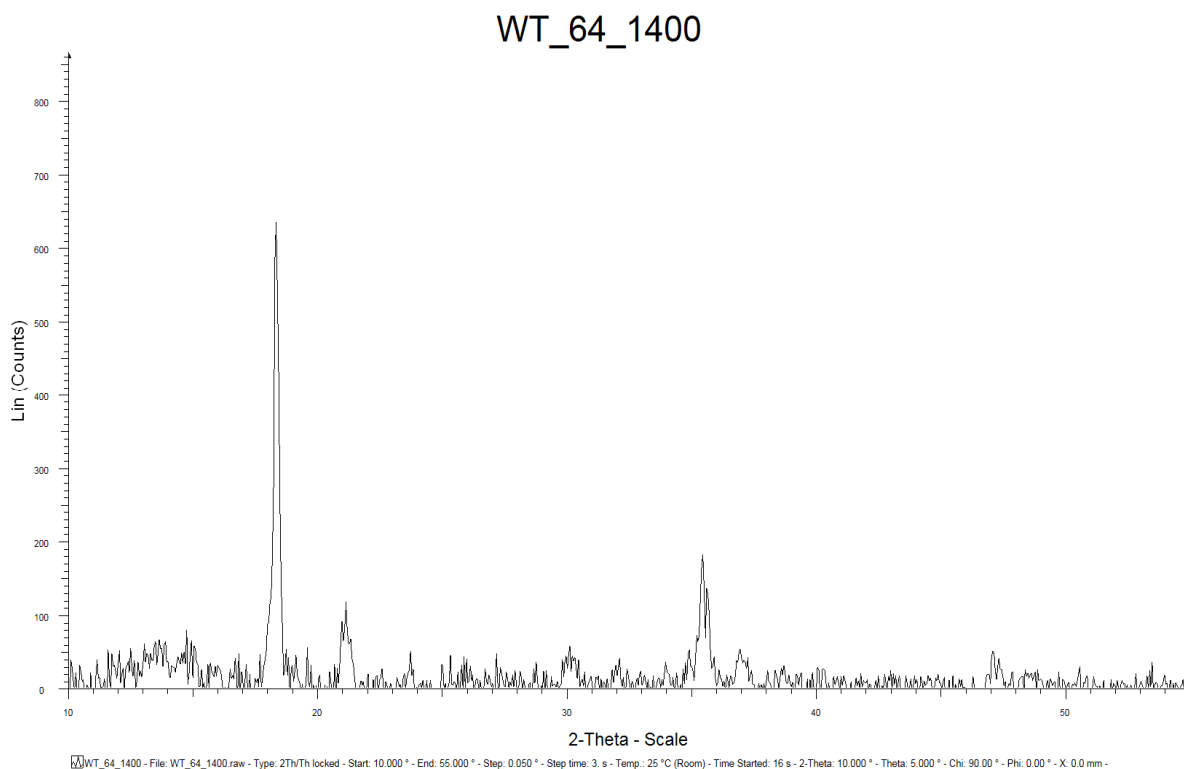


Figure 4.110. XRD spectrum for the nominal 64 at.% Pt sample annealed at 1400°C.

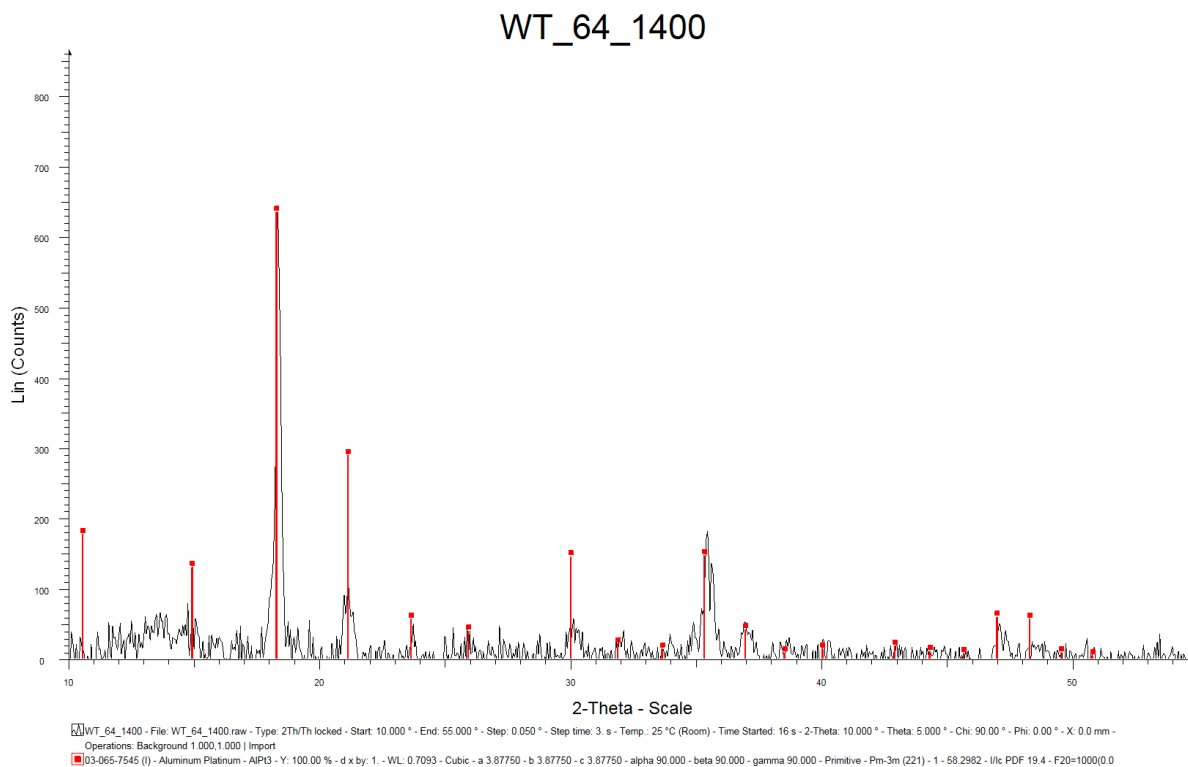


Figure 4.111. XRD trace showing peaks for the cubic Pt_3Al phase for the nominal 64 at.% Pt sample annealed at 1400°C.

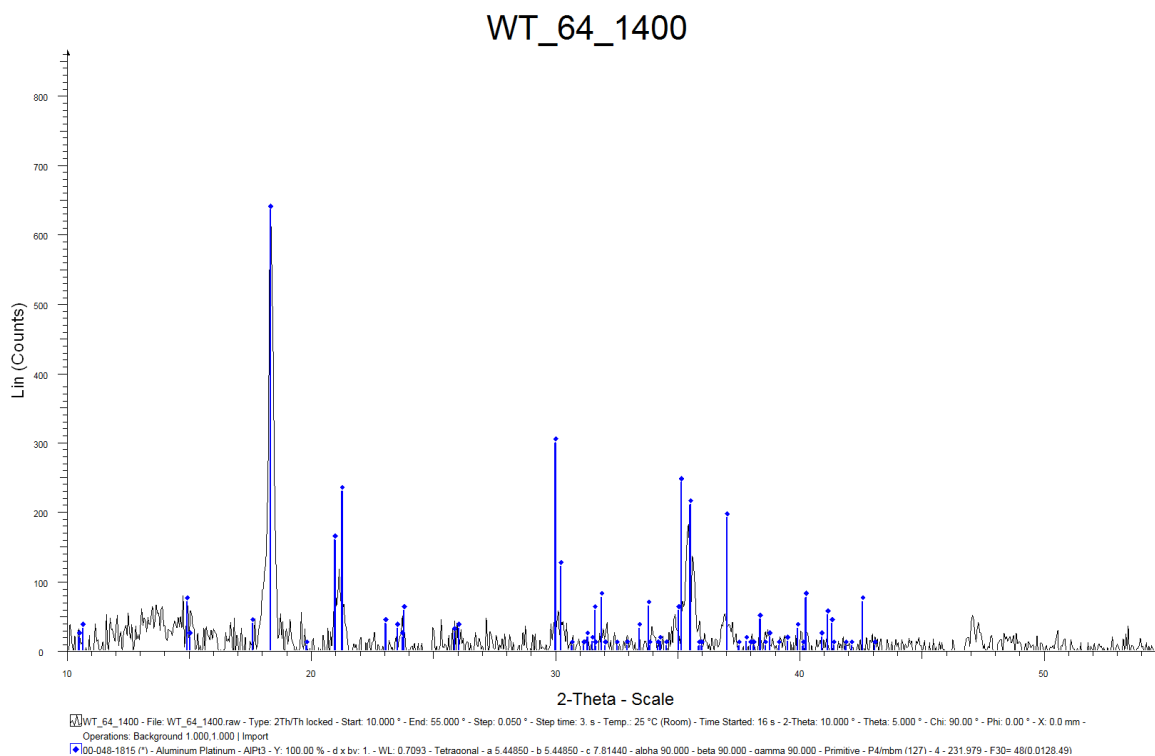


Figure 4.112. XRD trace showing peaks for the tetragonal Pt_3Al phase for the nominal 64 at.% Pt sample annealed at 1400°C .

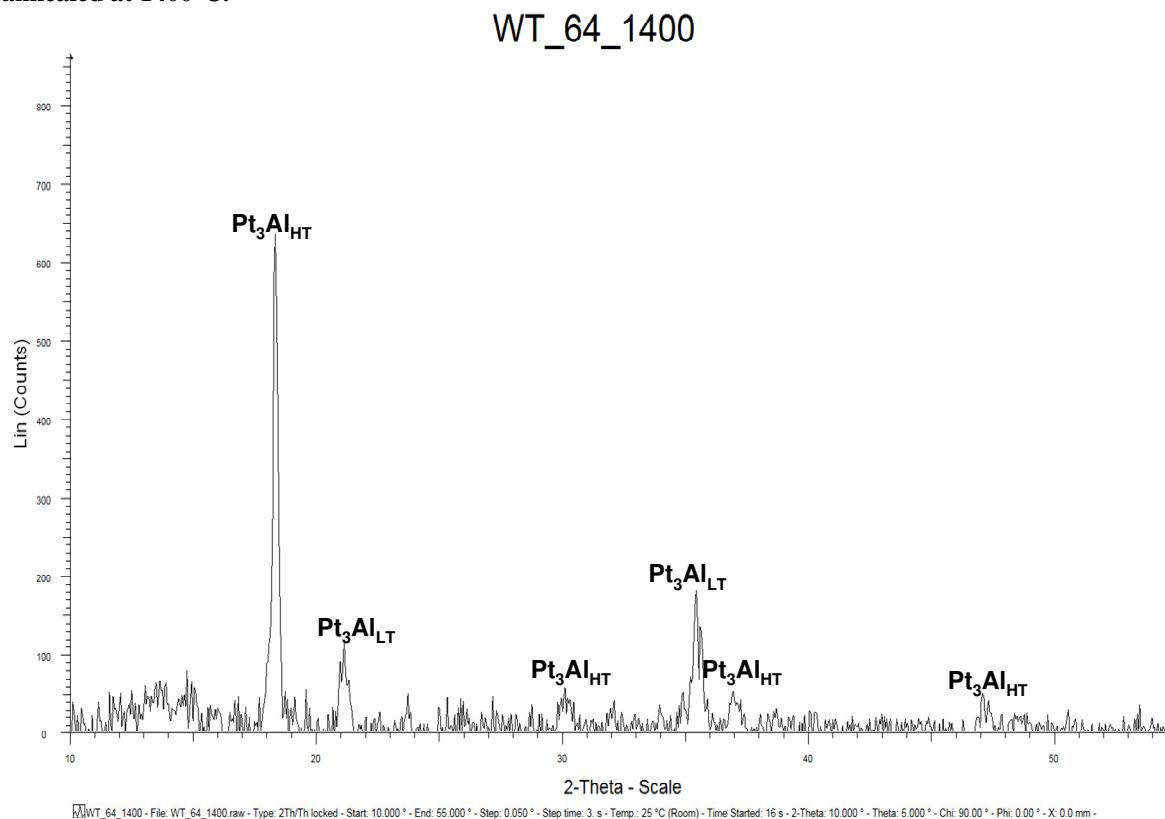


Figure 4.113. XRD pattern showing the phases in the nominal 67 at.% Pt sample annealed at 1400°C .

Figure 4.110 shows a poor spectrum with broad peaks, fairly low counts and a very low signal to background ratio. The spectrum had a very noisy background and therefore, it was difficult to distinguish between the peaks. Comparison with the ICDD [2005ICD] showed the presence of both forms of Pt_3Al (Table 4.34). The cubic Pt_3Al phase showed a good match of the peaks at $2\theta = \sim 15^\circ, \sim 18^\circ, \sim 30^\circ, \sim 37^\circ$ and $\sim 47^\circ$, with a negligible shift (Figure 4.111). Even with a poor spectrum peak splitting from tetragonal Pt_3Al could be observed at $2\theta = \sim 21^\circ$ and $\sim 35^\circ$ (Figure 4.112). Therefore, it was assumed that the sample was mainly cubic Pt_3Al , with possibly some tetragonal Pt_3Al as shown in Figure 4.113.

4.6.3 Nominal 64 at.% Pt sample annealed at 1200°C

Observations in the HRSEM showed a two-phase structure (Figure 4.114) and the overall EDS composition was taken from the two-phase region (Pt_2Al and Pt_5Al_3) of Massalski's phase diagram [1986McA], with a high error of ~ 4 at.% Pt (Table 4.35). The microstructure showed two different contrasts, thought to be different phase regions, and this is also confirmed by the high overall error.

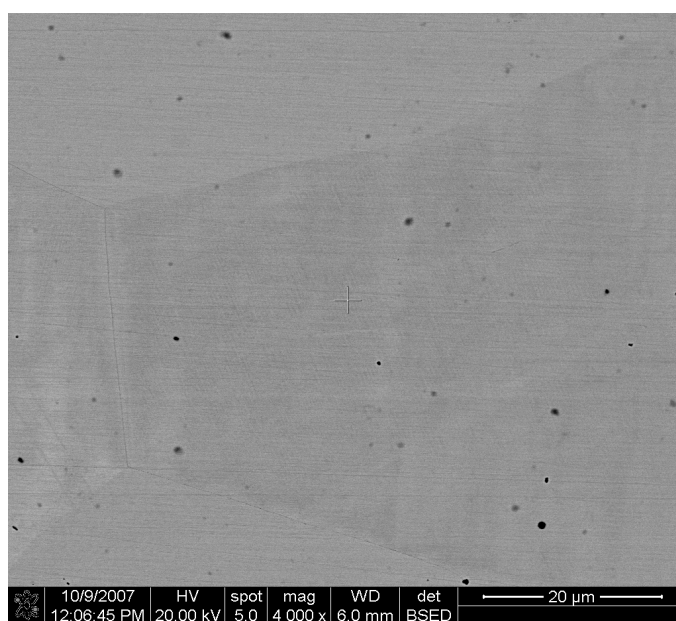


Figure 4.114. BSE-SEM image for nominal 64 at.% Pt annealed at 1200°C, showing a single phase.

Table 4.35. Phase analysis for the nominal 64 at.% Pt annealed at 1200°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
64 at.% Pt annealed at 1200°C	Overall	64.2 ± 4.0	35.9 ± 4.0	-

Table 4.36. XRD analysis for the nominal 64 at.% Pt annealed at 1200°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₂ Al _{HT}	I (%) Pt ₃ Al _{HT}
10.5	3.88	100	10	-	28
11.3	3.61	011	10	25	-
13.6	3.0	111	7	53	-
14.9	2.74	110	12	-	20
16.3	2.5	112	10	51	-
17.2	2.4	103	4	20	-
18.3/18.2	2.25/2.24	210/111	100	52	99
20.1	2.03	020	30	48	-
23.9	1.71	122	7	9	-
25.7	1.59	204	5	5	-
29.8	1.38	223	17	14	-
31.8	1.29	215	7	7	-
34.3	1.20	033	20	11	-
35.3	1.17	311	24	-	23
37.2	1.11	324	8	7	-

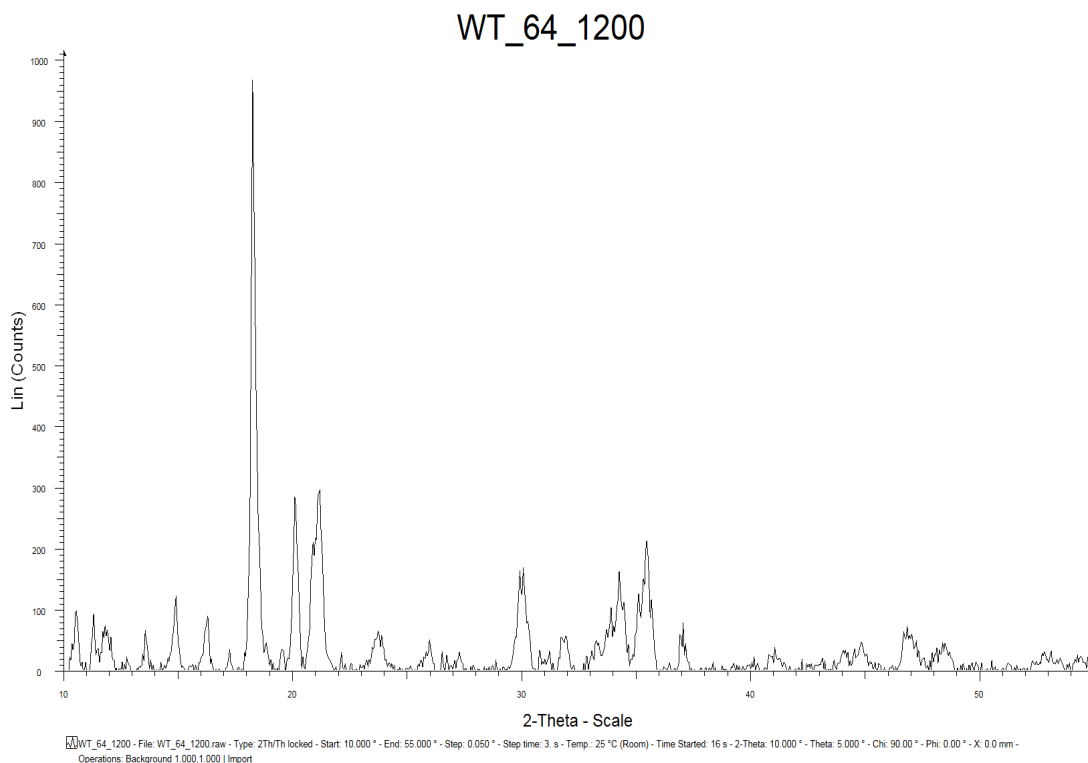


Figure 4.115. Raw XRD spectrum for the nominal 64 at.% Pt sample annealed at 1200°C.

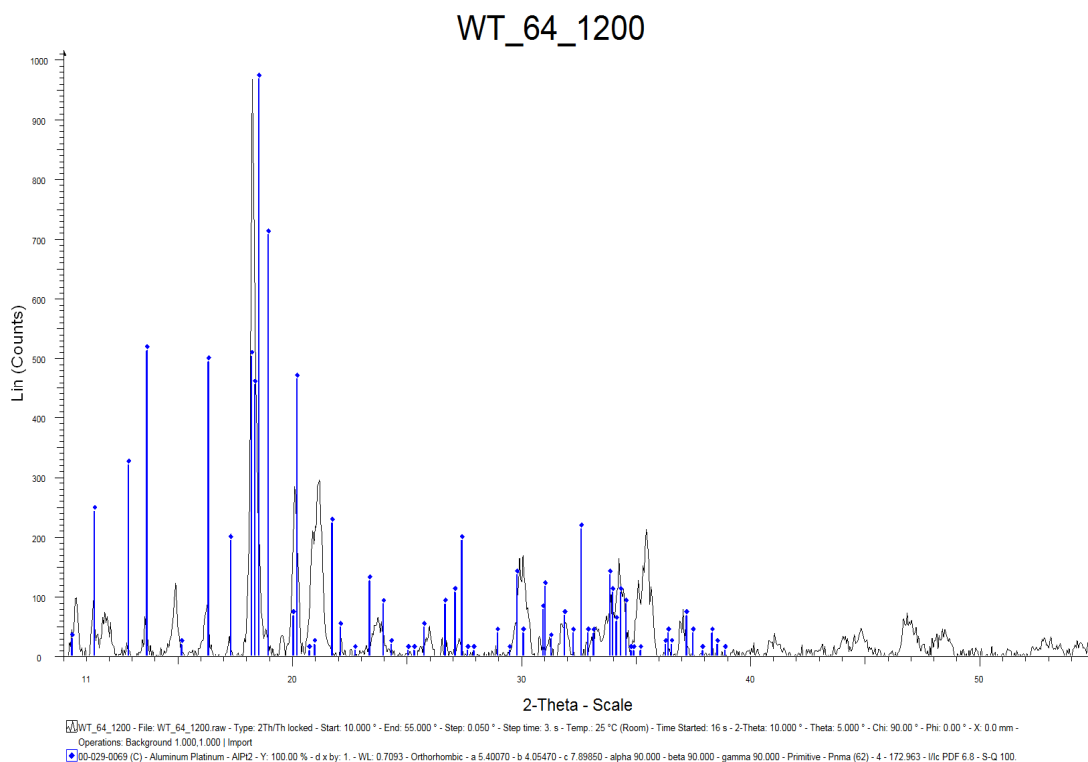


Figure 4.116. XRD trace showing peaks for high temperature Pt_2Al for the nominal 64 at. % Pt sample annealed at 1200°C.

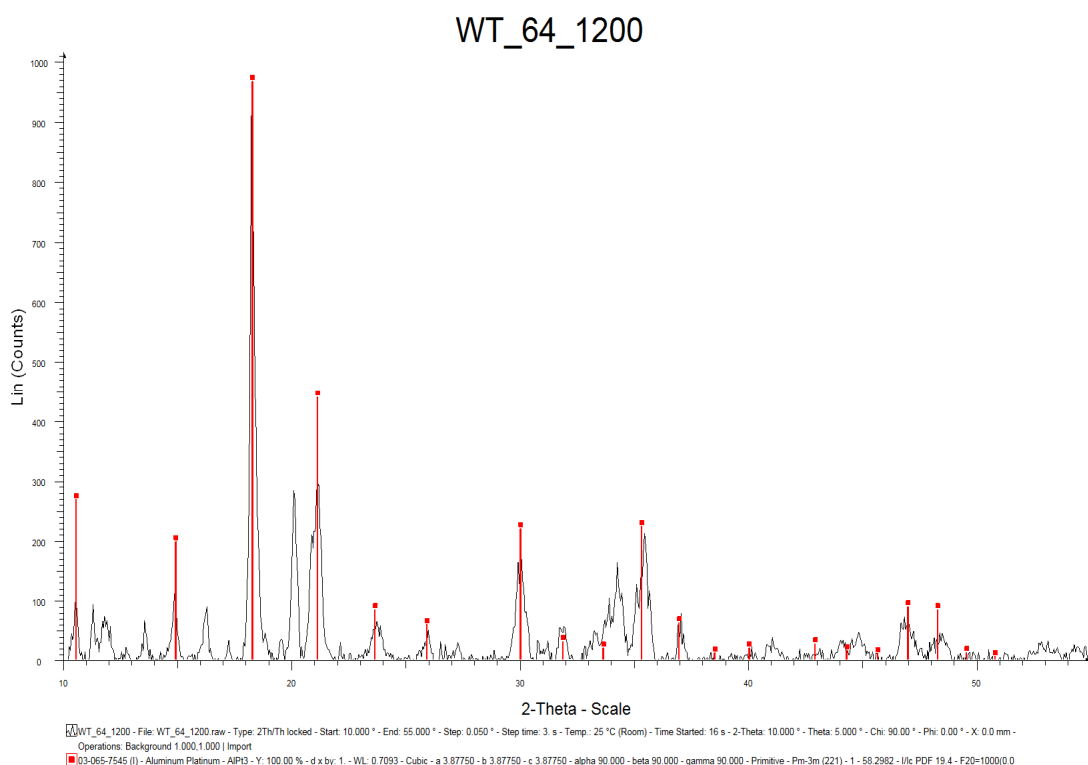


Figure 4.117. XRD trace showing peaks for the cubic Pt_3Al phase for the nominal 64 at. % Pt sample annealed at 1200°C.

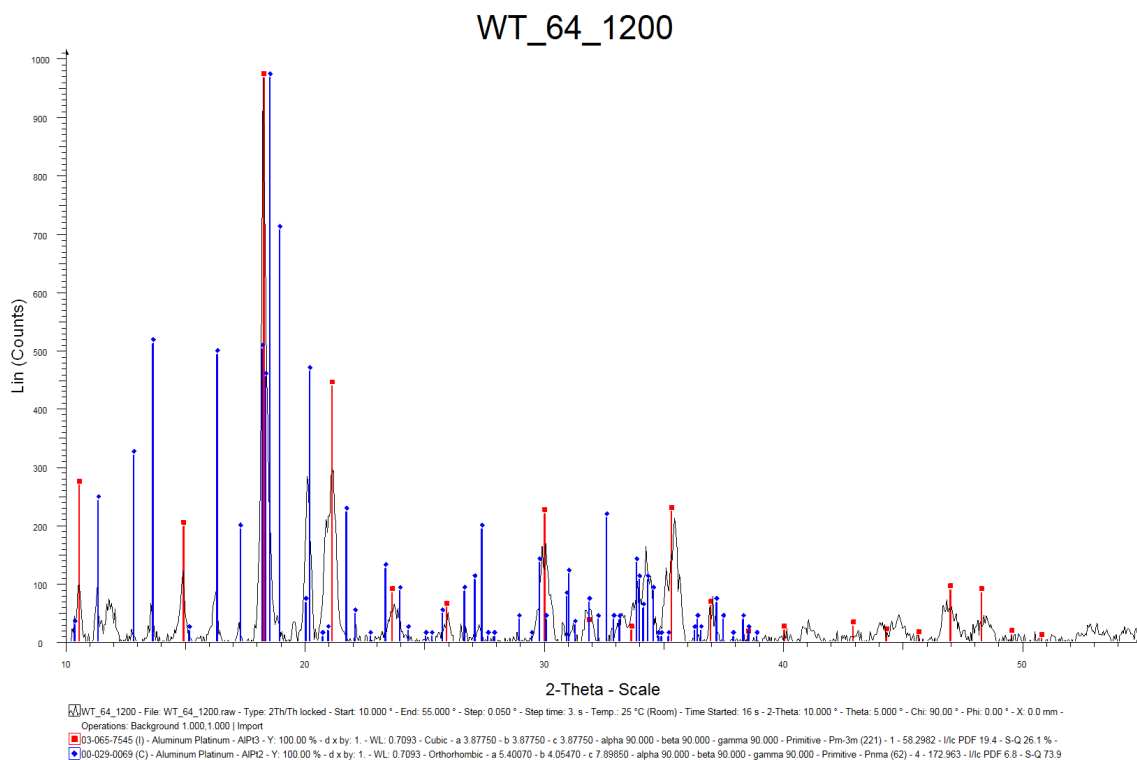


Figure 4.118. XRD trace showing peaks for cubic Pt_3Al and high temperature Pt_2Al for the nominal 67 at.% Pt sample annealed at 1200°C.

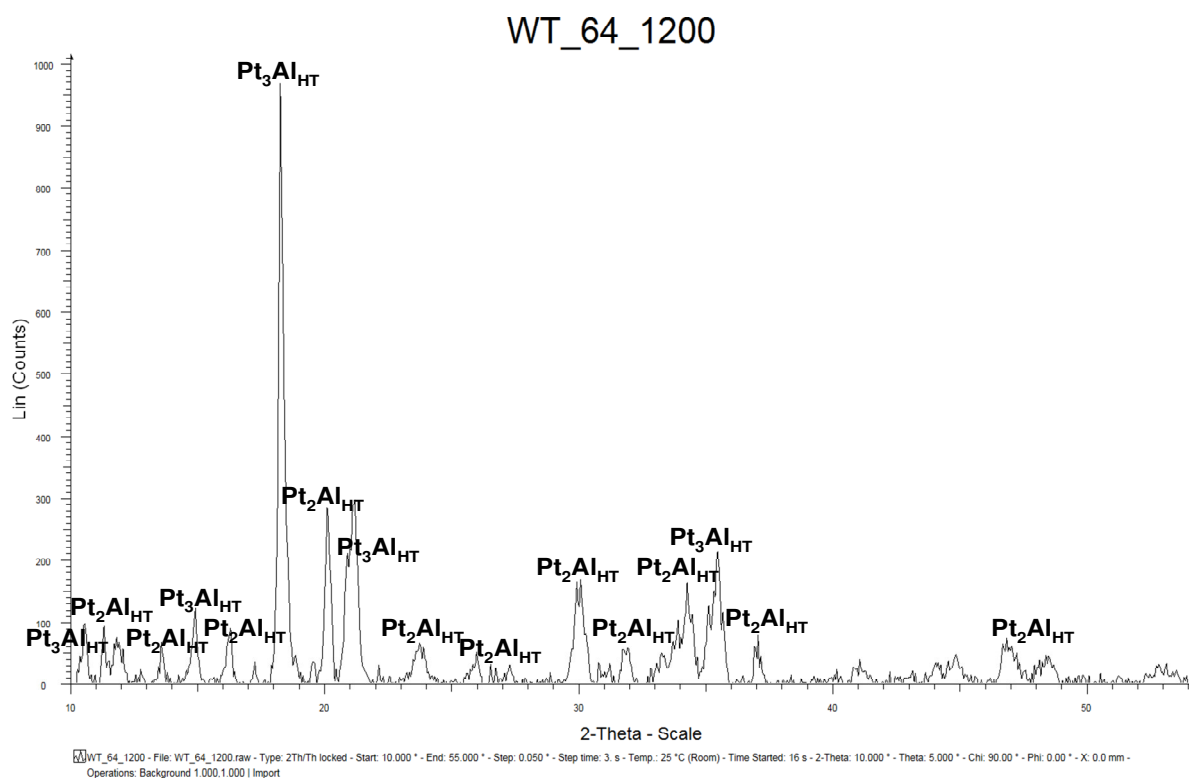


Figure 4.119. XRD pattern showing the phases in the nominal 64 at.% Pt sample annealed at 1200°C.

The XRD spectrum had broad peaks, high counts and a high signal to background ratio (Figure 4.115). Most of the peaks matched high temperature Pt_2Al (Figure 4.116), and these were: $2\theta = 11.5^\circ, \sim 14^\circ, \sim 16^\circ, 17.5^\circ, \sim 18^\circ, \sim 20^\circ, \sim 24^\circ, \sim 26^\circ, \sim 30^\circ, \sim 32^\circ, \sim 34^\circ, \sim 37^\circ, \sim 47^\circ$ and $\sim 48^\circ$, with a slight shift to the left. In Figure 4.117, matches of peaks with cubic Pt_3Al were at $2\theta = 10.5^\circ, \sim 15^\circ, \sim 18^\circ$ and 35.2° , which were different from the high temperature Pt_2Al peaks, with a negligible shift. Only one peak was not matched ($2\theta = \sim 12^\circ$), which could be due to aluminium oxide, although the major aluminium oxide peaks did not match major peaks in the spectrum. Figure 4.120 showed the two phases found in the alloy.

Relative to the as-cast spectrum, the spectrum of the sample annealed at 1200°C generally had strong peaks in the beginning (Figure 4.115), while the as-cast spectrum had strong peaks towards the end (Figure 4.106). The spectrum of the sample annealed at 1200°C had the strongest peak at $2\theta = \sim 18^\circ$, which was from the high temperature Pt_3Al and Pt_2Al phases, while the as-cast spectrum had the strongest peak at $2\theta = \sim 47^\circ$. The microstructure had preferred orientation during casting.

4.6.4 Nominal 64 at.% Pt annealed at 1000°C

The HRSEM (Figure 4.120) showed a single phase which was difficult to resolve. The overall composition of the sample was in the (Pt_3Al and Pt_2Al) region of Massalski's phase diagram [1986McA]. The overall composition was higher in Pt than the targeted composition, and the reason for the high platinum content may be due to the loss of aluminium during melting.

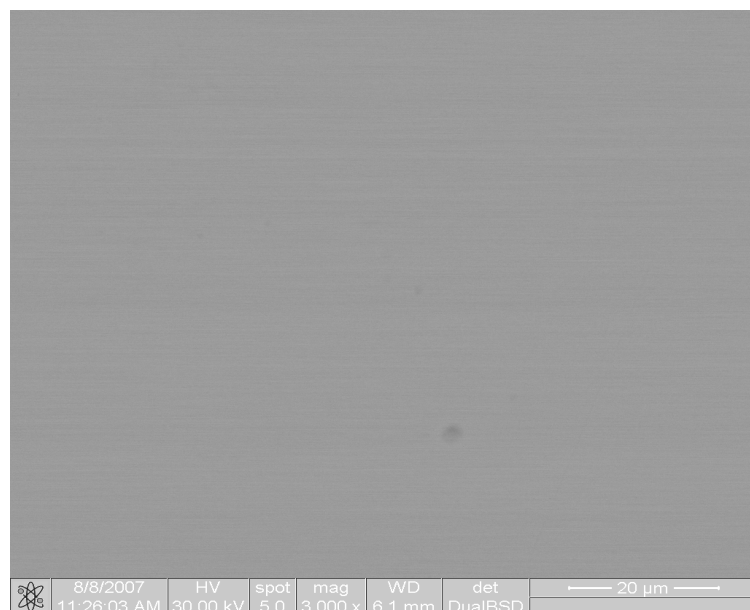


Figure 4.120. BSE-SEM image of nominal 64 at.% Pt annealed at 1000°C, showing Pt₃Al single phase.

Table 4.37. Phase analysis for the nominal 64 at.% Pt sample annealed at 1000°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Arc-melted	Overall	69.7 ± 0.1	30.3 ± 0.1	-

Table 4.38. XRD database [2005ICD] information for the nominal 67 at.% Pt sample annealed at 1000°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt₂Al_{HT}	I (%) Pt₂Al_{LT}
11.3	3.61	011	6	25	-
11.5	3.53	210	6	-	8
12.8	3.19	102	92	33	-
13.1	3.12	111	6	-	2
13.6	3.0	111	37	53	-
16.3	2.51	112	37	51	-
18.2/18.3	2.24/2.23	210/012	97	52	96
18.9	2.16	211	64	73	-
19.6	2.09	502	17	-	36
20.1	2.03	020	4	48	-
21.7/21.8	1.89/1.88	203/711	100	23	8
23.4	1.74	321	5	-	30
24.3	1.69	114	5	2	-
25.7/25.8	1.59/1.59	204/022	26	5	13
26.6	1.54	123	21	9	-
27.4	1.5	222	26	20	-
28.7	1.43	522	12	-	37
29.8/30.6	1.38/1.34	223/713	8	14	9
31.3	1.31	223	13	-	18
31.8/31.8	1.29/1.29	215/323	20	7	19
33.1	1.24	132	9	4	-
33.8	1.22	412	32	14	-
34.5	1.19	231	4	9	-
36.4	1.14	216	6	4	-
37.2	1.11	324	21	7	-
38.3	1.08	422	4	4	-

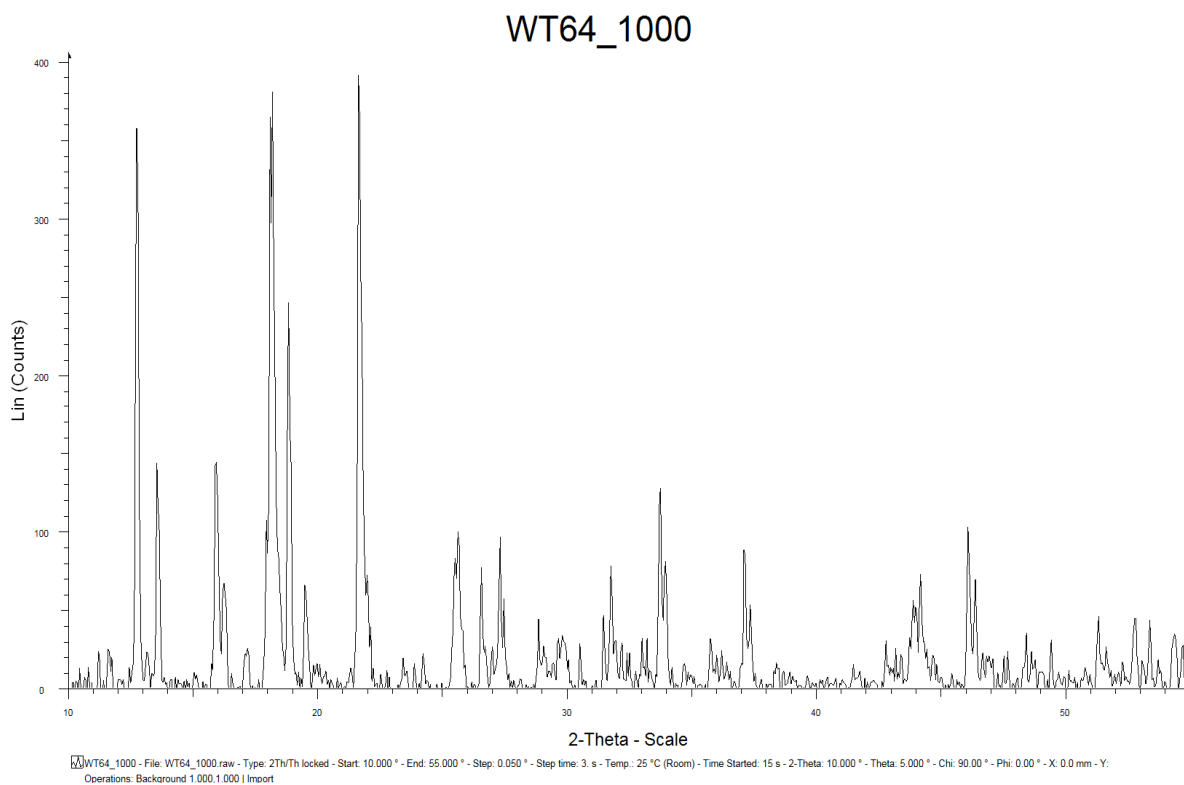


Figure 4.121. Raw XRD spectrum for the nominal 64 at.% Pt sample annealed at 1000°C.

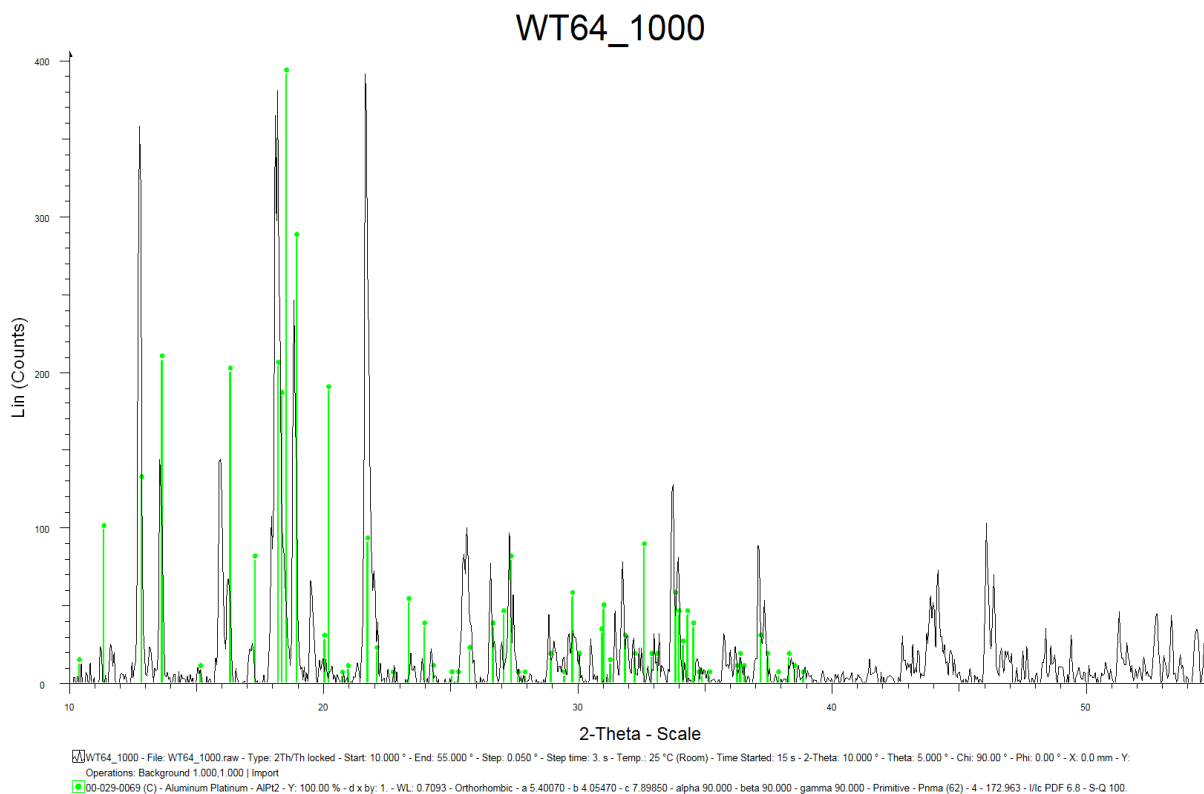


Figure 4.122. XRD trace showing peaks for high temperature Pt_2Al for the nominal 64 at.% Pt sample annealed at 1000°C.

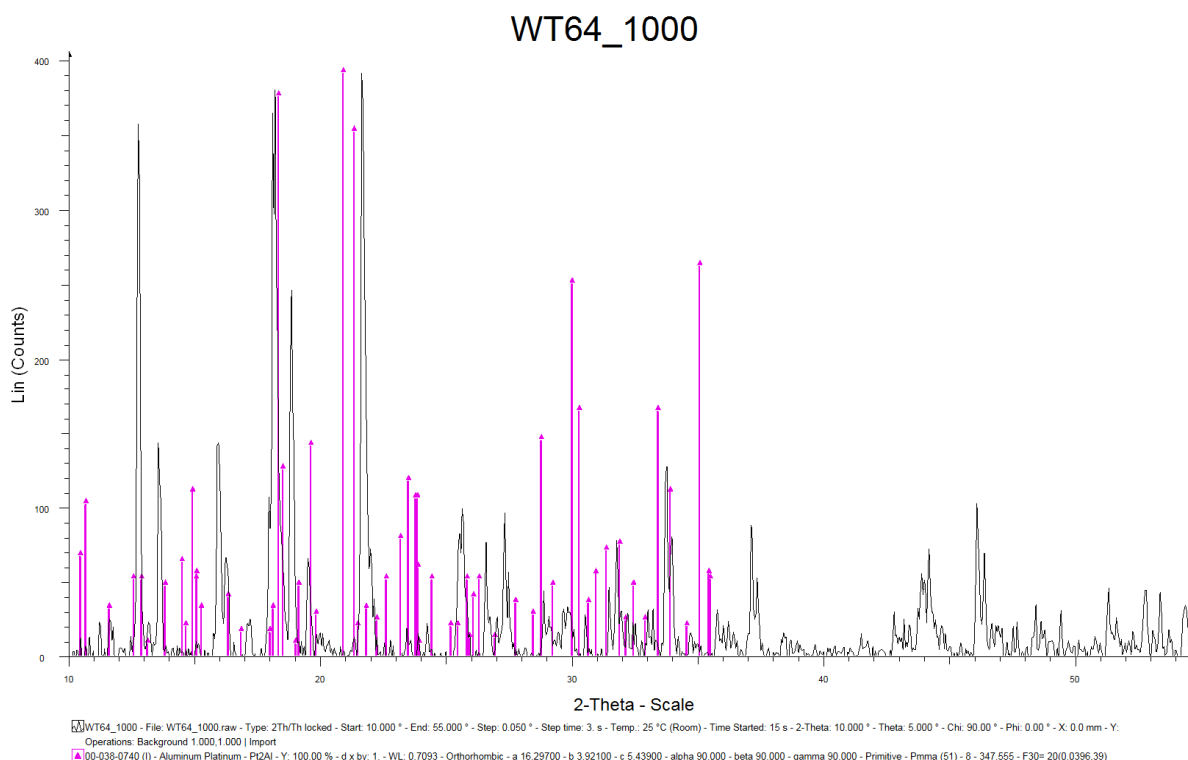


Figure 4.123. XRD trace showing peaks for low temperature Pt_2Al for the nominal 64 at.% Pt sample annealed at 1000°C.

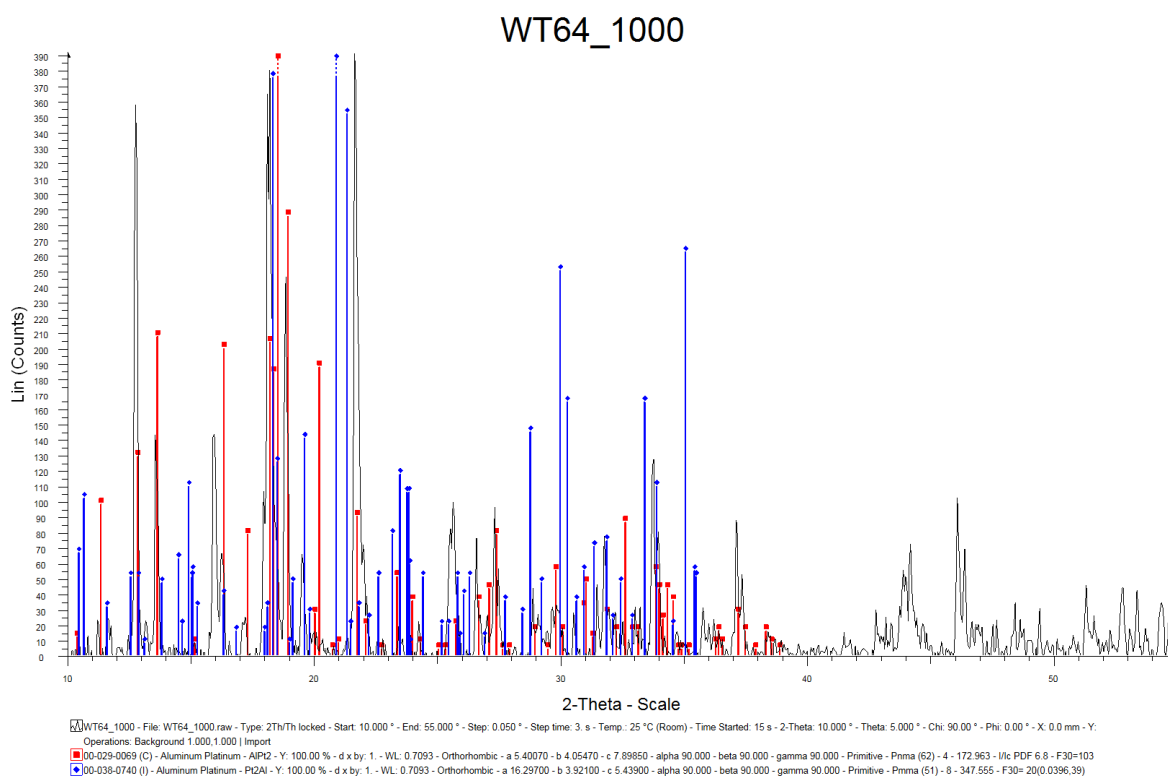


Figure 4.124. XRD trace showing peaks for high and low temperature Pt_2Al for the nominal 64 at.% Pt sample annealed at 1000°C.

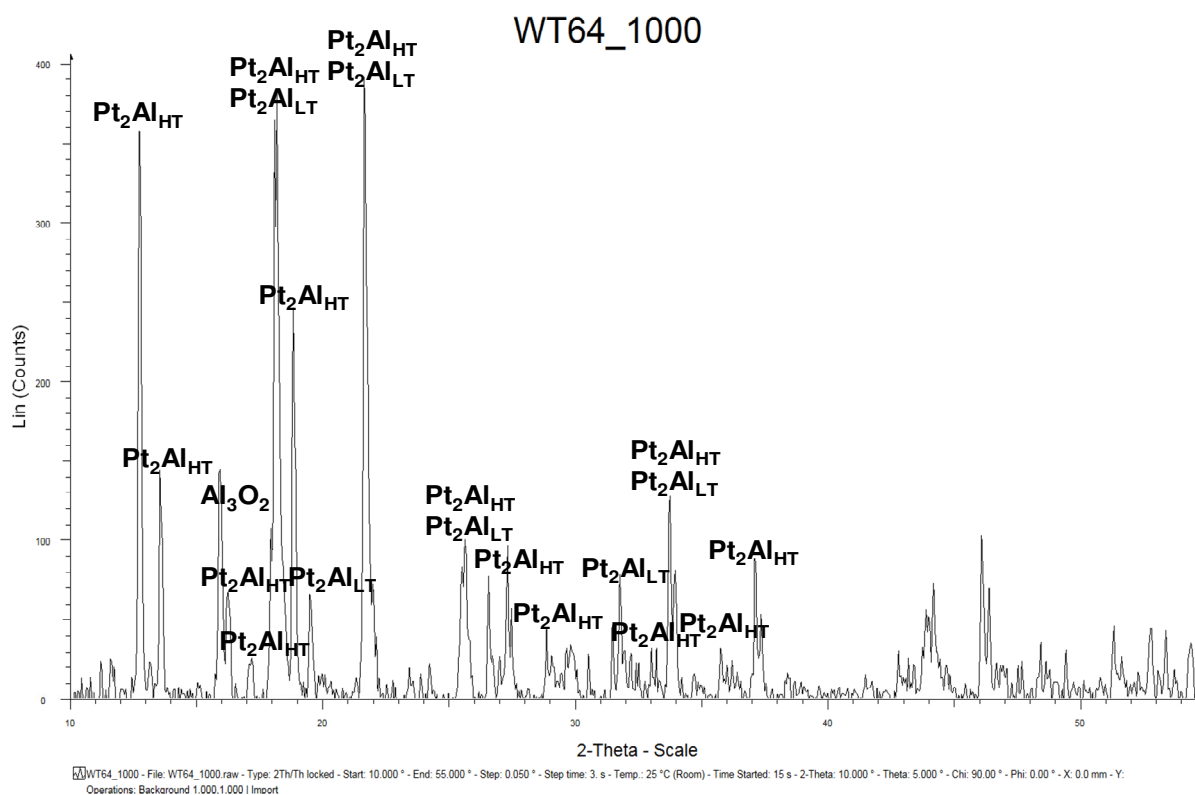


Figure 4.125. XRD pattern showing the phases in the nominal 64 at.% Pt sample annealed at 1200°C.

The spectrum was fairly complex, with broad peaks, low counts and a low signal to background ratio (Figure 4.121). The ICDD [2005ICD] indicated the presence of at least one of the Pt_2Al phases (Table 4.38). In Figure 4.122, a match of peaks with the high temperature Pt_2Al was at $2\theta = 11.2^\circ, \sim 13^\circ, 13.5^\circ, 16.3^\circ, 17.2^\circ, 18.2^\circ, \sim 19^\circ, \sim 20^\circ, 21.5^\circ, \sim 22^\circ, 24.5^\circ, \sim 26^\circ, 26.5^\circ, 27.5^\circ, \sim 30^\circ, 31.2^\circ, \sim 33^\circ, \sim 34^\circ, \sim 35^\circ, 36.5^\circ, \sim 37^\circ$ and $\sim 39^\circ$, with a slight shift to the right. Figure 4.123, showed a match of peaks with the low temperature Pt_2Al , at $2\theta = 11.5^\circ, 13.2^\circ, 18.2^\circ, 19.5^\circ, \sim 22^\circ, 23.5^\circ, \sim 26^\circ, 28.5^\circ, \sim 29^\circ, 30.5^\circ, \sim 32^\circ$, and $\sim 34^\circ$, with a slight shift to the right, but the peaks $2\theta = \sim 16^\circ$ and 25.5° were not matched, unless there was a very strong shift to the right.

The spectrum had three regions with strong peaks, and these were: $2\theta = \sim 13^\circ, \sim 18^\circ$ and $\sim 22^\circ$ (Figure 4.125). The high temperature Pt_2Al matched the peaks at $2\theta = \sim 13^\circ, \sim 18^\circ$ well, while the low temperature Pt_2Al matched the peak at $2\theta = \sim 22^\circ$, although there was a shift and the peaks did not match so well. Relative to the as-cast spectrum, the spectrum was fairly

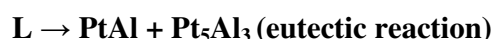
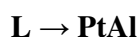
complex, and some of the peaks were in different positions. The spectrum had the strongest peaks at $2\theta = \sim 18^\circ$ and $\sim 22^\circ$ (Figure 4.121), while the as-cast spectrum had the strongest peak at $2\theta = \sim 47^\circ$ (Figure 4.106). The spectrum is very similar to the spectrum of the sample annealed at 1200°C (Figure 4.115). The spectrum of the sample annealed at 1400°C also had the strongest peak at $2\theta = \sim 18^\circ$ (Figure 4.110). Figure 4.125 showed the match of the phases with the major peaks of the spectrum, and the peaks above $2\theta = \sim 40^\circ$ were not matched because the reported data ended [2005ICD].

4.7 Phase analyses of 53.5 at.% Pt samples

4.7.1 Nominal 53.5 at.% Pt sample in the arc-melted condition

EDS analyses (Table 4.39) showed that the dark phase (primary) solidified to form irregular needles (Figure 4.126). Further solidification formed a eutectic mixture of $L \rightarrow \text{PtAl} + \text{Pt}_5\text{Al}_3$. The overall composition was in the two-phase region of Massalski's phase diagram [1986McA].

The solidification sequence according to the microstructure was:



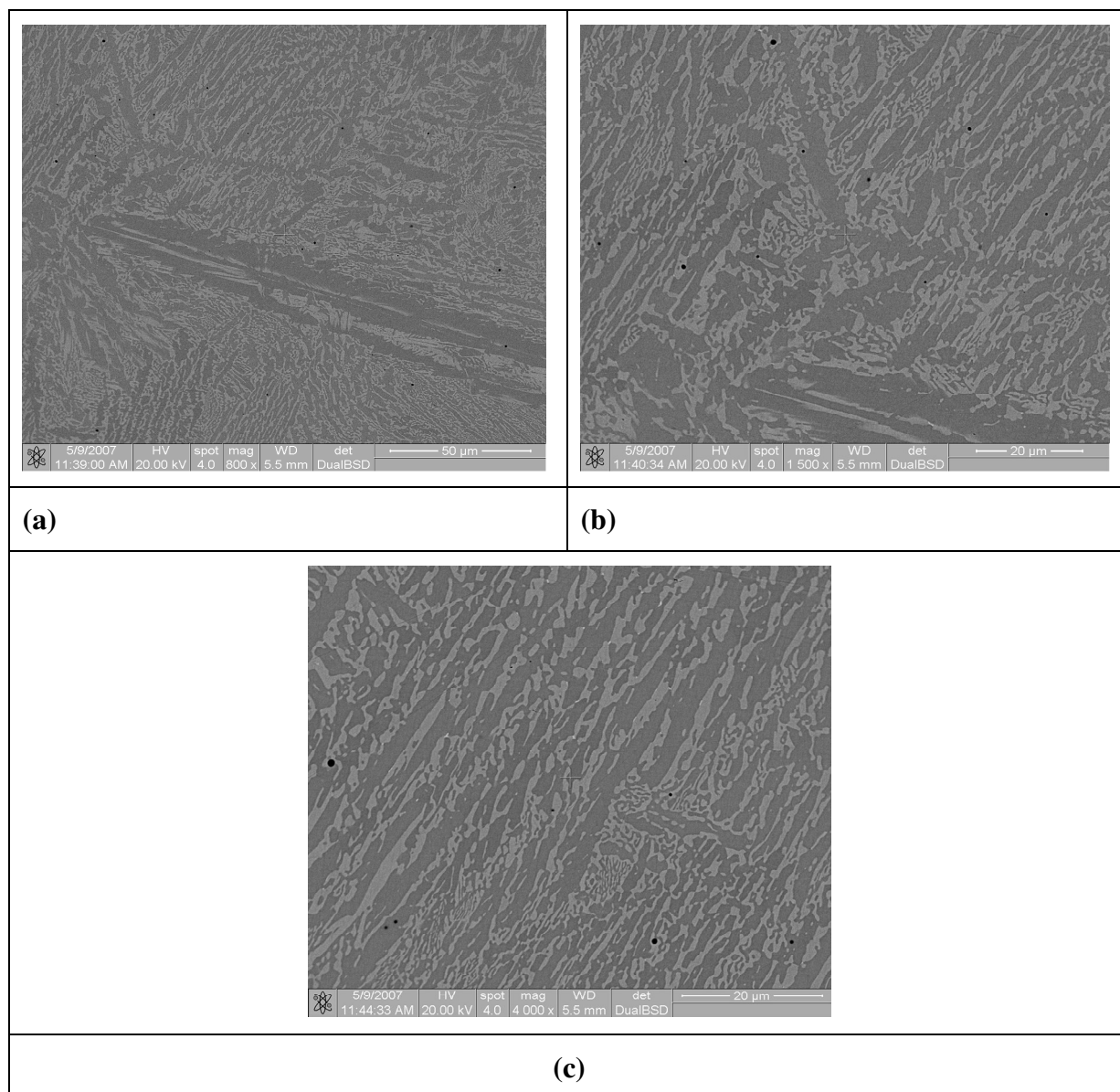


Figure 4.126. BSE-SEM image for the nominal 53.5 at.% Pt in the arc-melted condition, showing the dark PtAl needles surrounded by the eutectic mixture of light Pt₅Al₃ + dark PtAl.

Table 4.39. Phase analysis for the as-cast nominal 53.5 at.% Pt sample.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Arc-melted	Overall	53.7 ± 1.0	46.3 ± 1.0	-
	Light	60.2 ± 1.2	39.8 ± 1.2	Pt ₅ Al ₃
	Dark	50.0 ± 0.2	50.0 ± 0.2	PtAl
	Eutectic	56.3 ± 0.5	43.7 ± 0.5	Pt ₅ Al ₃ + PtAl

Table 4.40. XRD database [2005ICD] information for the nominal 53.5 at.% Pt sample in the arc-melted condition.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) PtAl	I (%) Pt₅Al₃
10.7	3.8	120	5	-	38
11.8	3.4	110	26	64	-
14.5/14.9	2.8/2.7	111/121	15	33	49
16.8/17.2	2.4/2.4	200/131	5	6	13
18.3	2.2	201	28	-	55
18.4	2.2	041	-	-	99
18.8/18.7	2.2/2.2	210/211	100	99	56
18.9	2.2	230	-	-	28
20.5/20.7	2.0/2.0	211/002	49	42	38
21.5	1.9	240	11	-	27
25.3	1.6	221	7	5	-
26.7	1.5	013	15	11	-
28.0/27.9	1.5/1.5	311/170	8	9	3
29.2/29.4	1.4/1.4	222/341	8	8	2
29.8	1.4	171	7	-	20
30.4	1.3	320	29	12	-
31.7/31.9	1.3/1.3	123/322	24	21	2
33.9/34.3	1.2/1.2	400/133	6	5	10
34.9/35.1	1.2/1.2	410/213	8	3	7
36.0/36.0	1.1/1.1	411/281	9	4	5
39.0	1.1	421	10	10	-
41.8/42.1	1.0/1.0	422/343	7	3	-
43.6	1.0	134	10	6	-
44.5	0.9	511	9	5	-
46.2	0.9	025	14	10	-

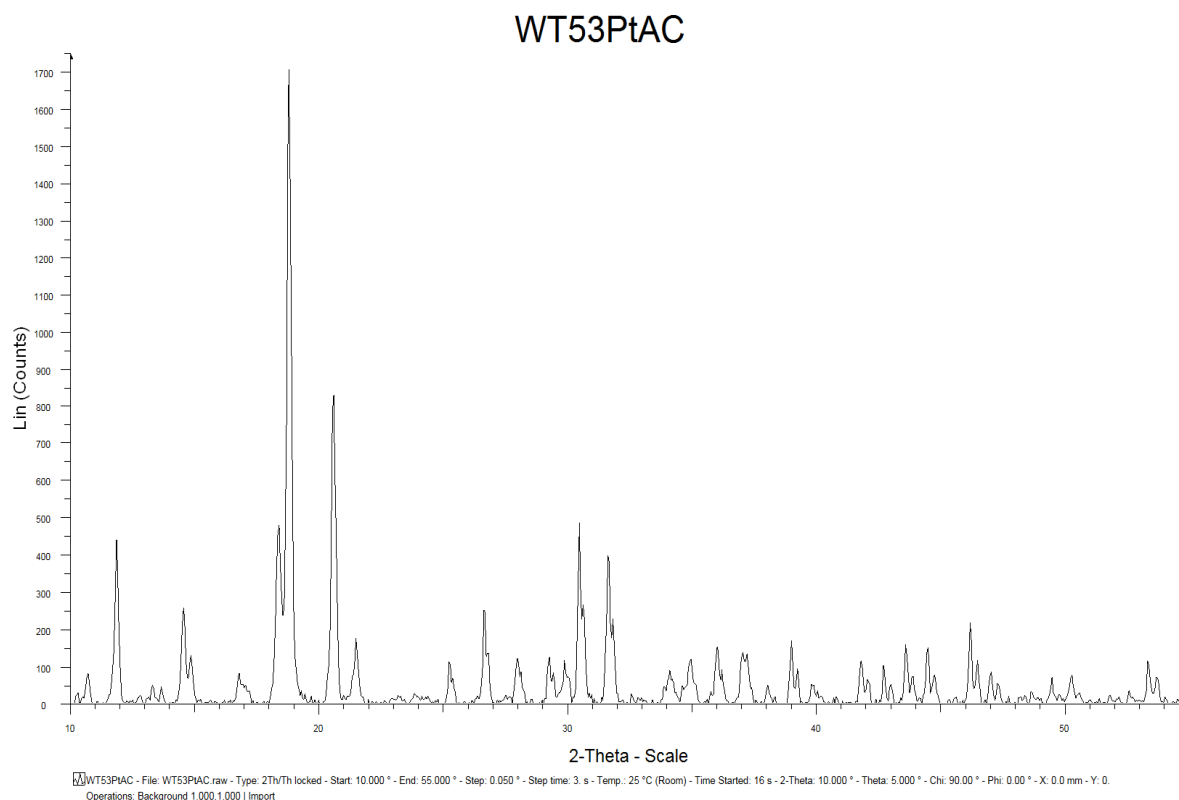


Figure 4.127. Raw XRD spectrum for the arc-melted 53.5 at.% Pt sample.

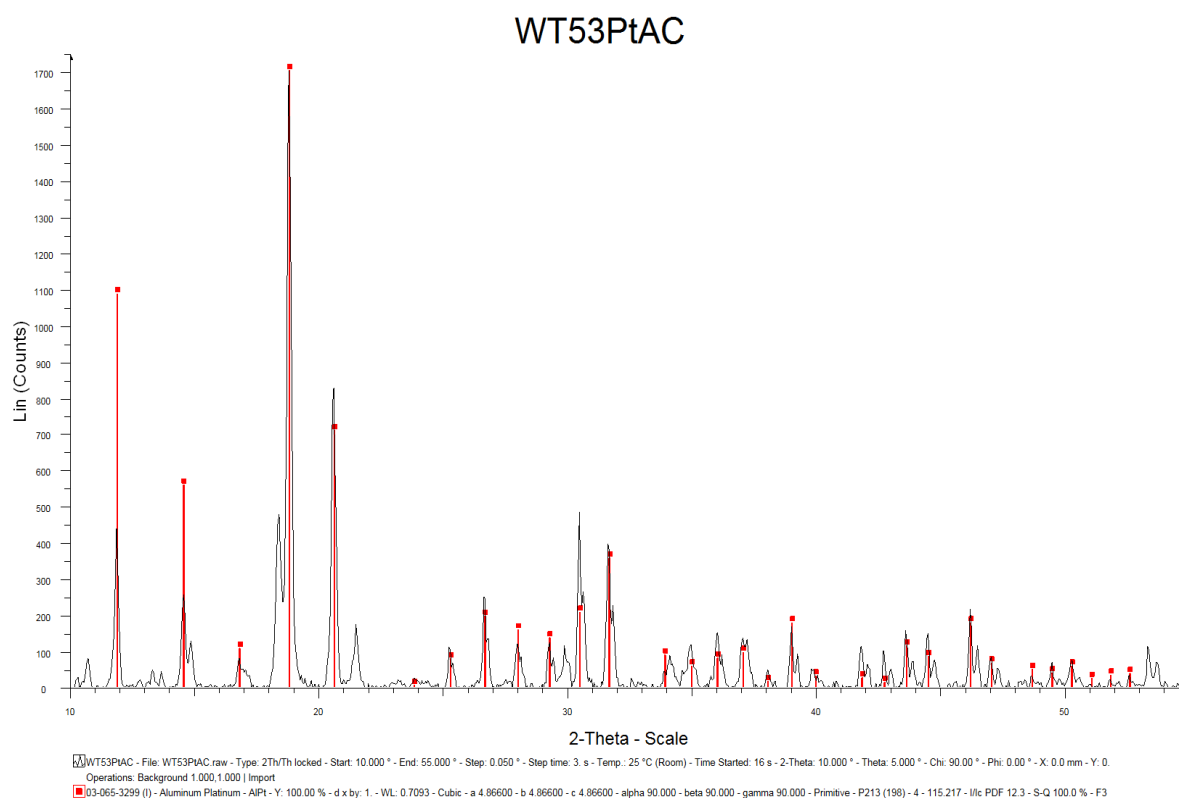


Figure 4.128. XRD trace showing peaks for the PtAl phase in the arc-melted 53.5 at.% Pt sample.

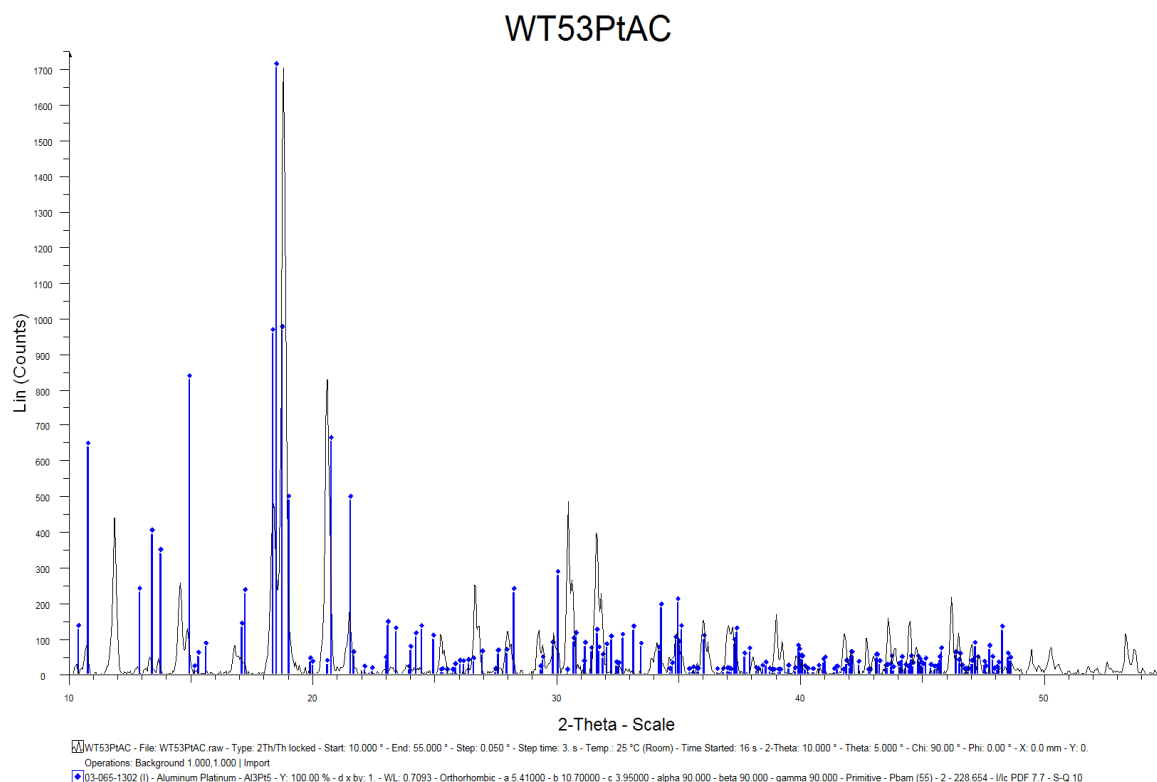


Figure 4.129. XRD trace showing peaks for the Pt_5Al_3 phase in the arc-melted 53.5 at.% Pt sample.

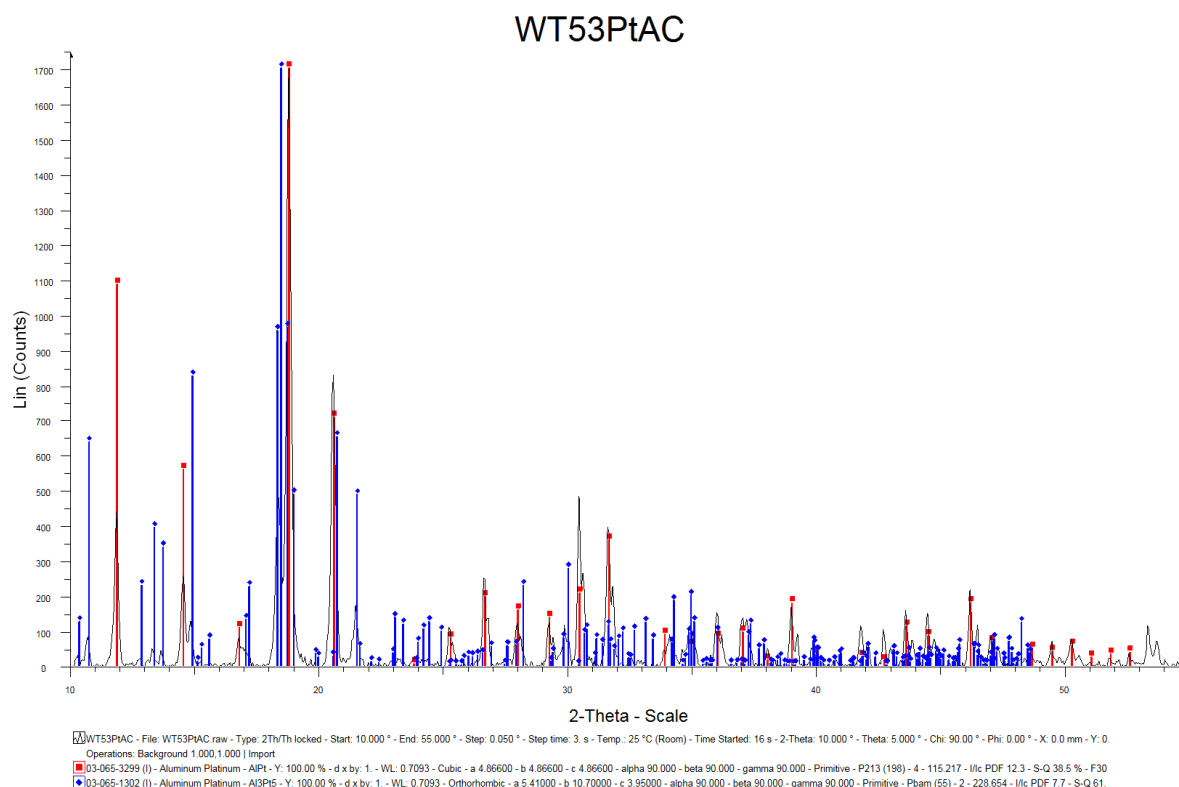
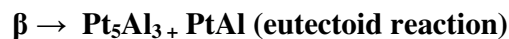
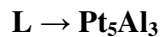


Figure 4.130. XRD trace showing peaks for the PtAl and Pt_5Al_3 phases for the arc-melted 53.3 at.% Pt sample.

The XRD spectrum had well defined peaks with high counts and high signal to background noise (Figure 4.127). The XRD spectrum shows a precise match of PtAl at $2\theta = \sim 12^\circ, \sim 15^\circ, \sim 17^\circ, 18.5^\circ, \sim 21^\circ, \sim 25^\circ, \sim 27^\circ, \sim 28^\circ, \sim 29^\circ, \sim 31^\circ, \sim 32^\circ, \sim 34^\circ, \sim 35^\circ, \sim 36^\circ, \sim 37^\circ, \sim 38^\circ, \sim 39^\circ, \sim 40^\circ, \sim 42^\circ, \sim 43^\circ, \sim 44^\circ, \sim 45^\circ, \sim 46^\circ$ (and the smaller peaks at higher 2θ values, which were: $\sim 47^\circ, 48.5^\circ, 49.5^\circ, \sim 50^\circ, \sim 51^\circ, \sim 52^\circ, \sim 53^\circ$ (Figure 4.128)). In Figure 4.129, a good match of peaks for Pt_5Al_3 was observed at $2\theta = 10.5^\circ, \sim 13^\circ, 13.5^\circ, \sim 14^\circ, \sim 17^\circ, 18.5^\circ, \sim 21^\circ, 21.5^\circ, \sim 23^\circ, \sim 24^\circ, \sim 27^\circ, \sim 28^\circ, \sim 30^\circ, \sim 32^\circ, \sim 34^\circ, \sim 34^\circ, \sim 36^\circ, \sim 37^\circ, \sim 40^\circ, \sim 42^\circ, \sim 43^\circ, \sim 44^\circ, \sim 45^\circ, \sim 46^\circ, \sim 47^\circ$ and $\sim 49^\circ$. The strongest peak was at $2\theta = 18.5^\circ$, and the intensities of both phases matched the intensity of the peak. Thus, the PtAl and Pt_5Al_3 phases were clearly shown to be present.

4.7.2 Nominal 53.5 at.% Pt sample annealed at 1400°C

On heat treatment at 1400°C, the sample partially melted, as shown by the primary phase which is different from that in the as-cast sample. The microstructure revealed light needles, surrounded by a eutectic mixture (Figure 4.131). The outside of the needles appeared ragged, which showed there was a peritectic reaction. The phases were fine and very close to each other, therefore the phase analyses may not be accurate. The overall composition of the alloy was within the target of the original composition (Table 4.41). The EDS composition of the light phase was in the Pt_5Al_3 phase region, whereas the EDS composition of the dark phase which also collected X-rays from the small areas of the light phase was in the β -phase region [1986McA], and is thought to be decomposed β . The solidification sequence according to the microstructure was:



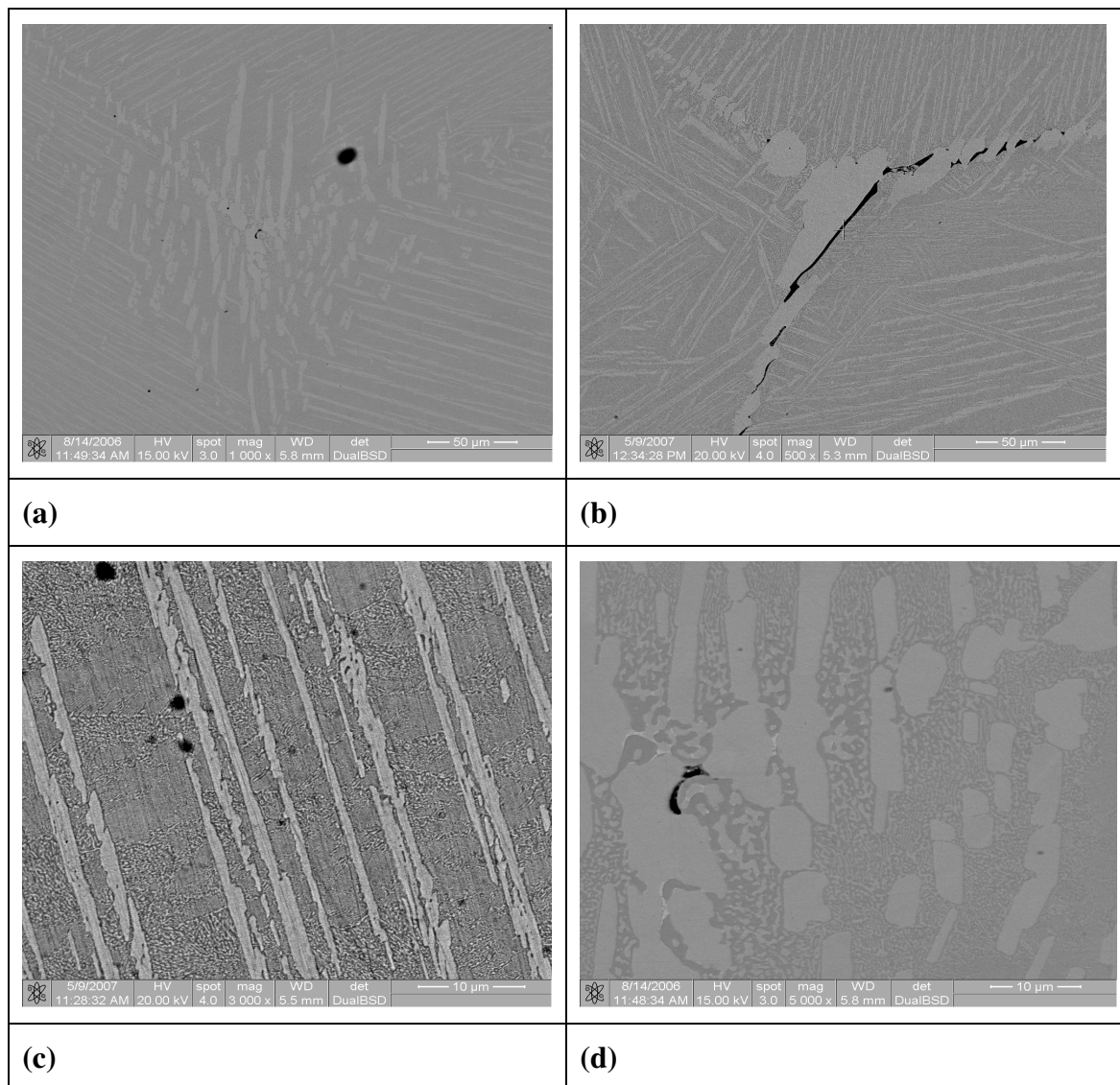


Figure 4.131. BSE-SEM image of the nominal 53.5 at.% Pt sample annealed at 1400°C, showing the light Pt₅Al₃ needles surrounded by the eutectic mixture of Pt₅Al₃ + dark PtAl.

Table 4.41. EDS analysis for the nominal 53.5 at.% Pt sample annealed at 1400°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
Annealed at 1400°C	Overall	55.9 ± 0.3	44.1 ± 0.3	-
	Light	62.1 ± 0.8	37.9 ± 0.8	Pt ₅ Al ₃
	Dark	54.2 ± 0.6	45.8 ± 0.6	PtAl
	Eutectic	56.4 ± 0.3	43.6 ± 0.3	Pt ₅ Al ₃ + PtAl

Table 4.42. XRD database [2005ICD] information for the nominal 53.5 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) PtAl	I (%) Pt ₅ Al ₃
10.3	3.4	001	4	-	7
10.7	3.8	120	6	-	38
11.8	3.4	110	20	64	-
12.8	3.2	021	6		13
13.3	3.1	111	6		23
14.5/14.9	2.8/2.7	111/121	11	33	49
16.8/17.2	2.4/2.4	200/131	4	6	13
18.3	2.2	201	100	-	55
18.4	2.2	041	-	-	99
18.8/18.7	2.2/2.2	210/211	66	99	56
18.9	2.2	230	-	-	28
20.5/20.7	2.0/2.0	211/002	70	42	38
21.5	1.9	240	11	-	27
23.0	1.8	151	3	-	8
24.9	1.6	132	4	-	5
25.3	1.6	221	8	5	-
26.7	1.5	013	8	11	-
28.0/27.9	1.5/1.5	311/170	10	9	3
29.2/29.4	1.4/1.4	222/341	6	8	2
29.8	1.4	171	12	-	20
30.4	1.3	320	13	12	-
31.7/31.9	1.3/1.3	123/322	19	21	2
33.9/34.3	1.2/1.2	400/133	5	5	10
34.9/35.1	1.2/1.2	410/213	6	3	7
36.0/36.0	1.1/1.1	411/281	7	4	5
37.0/37.3	1.1/1.1	331/082	13	5	7
39.0	1.1	421	11	10	-
41.8/42.1	1.0/1.0	422/343	8	3	-
43.6	1.0	134	4	6	-
44.5	0.9	511	6	5	-
46.2	0.9	025	7	10	-
47.0	0.9	521	9	4	-

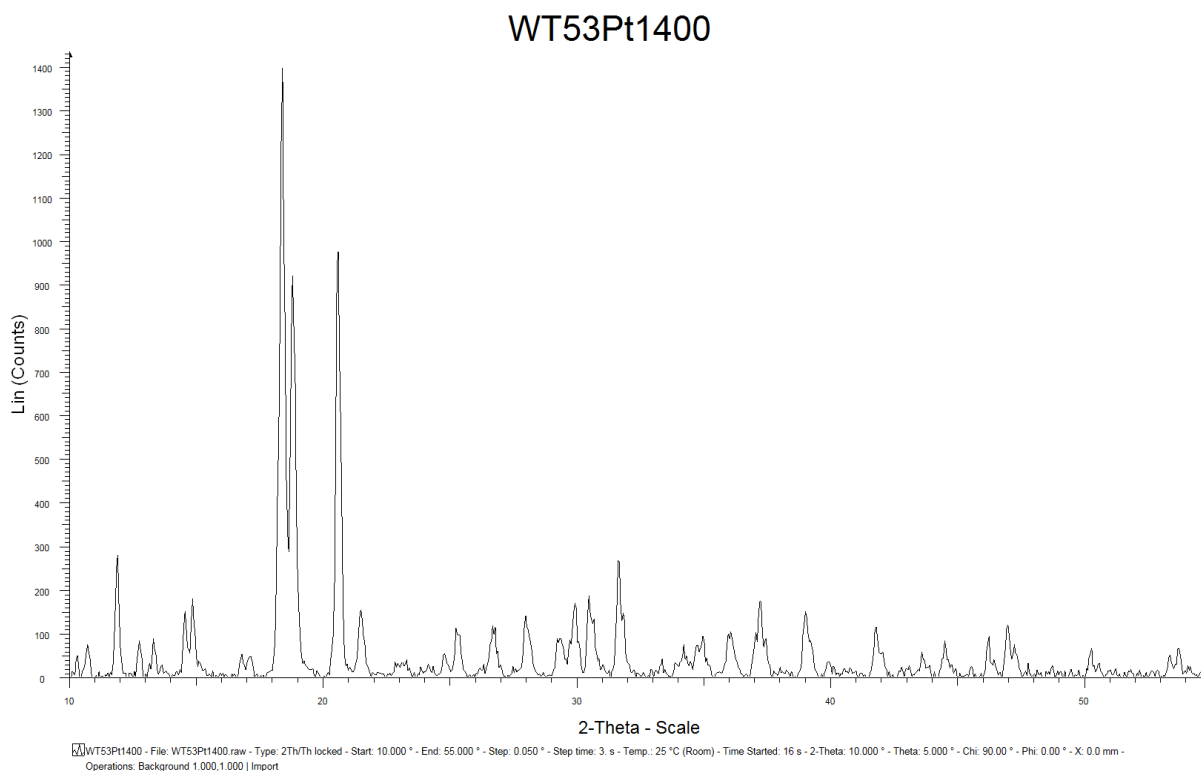


Figure 4.132. Raw XRD spectrum for the nominal 53.5 at.% Pt sample annealed at 1400°C.

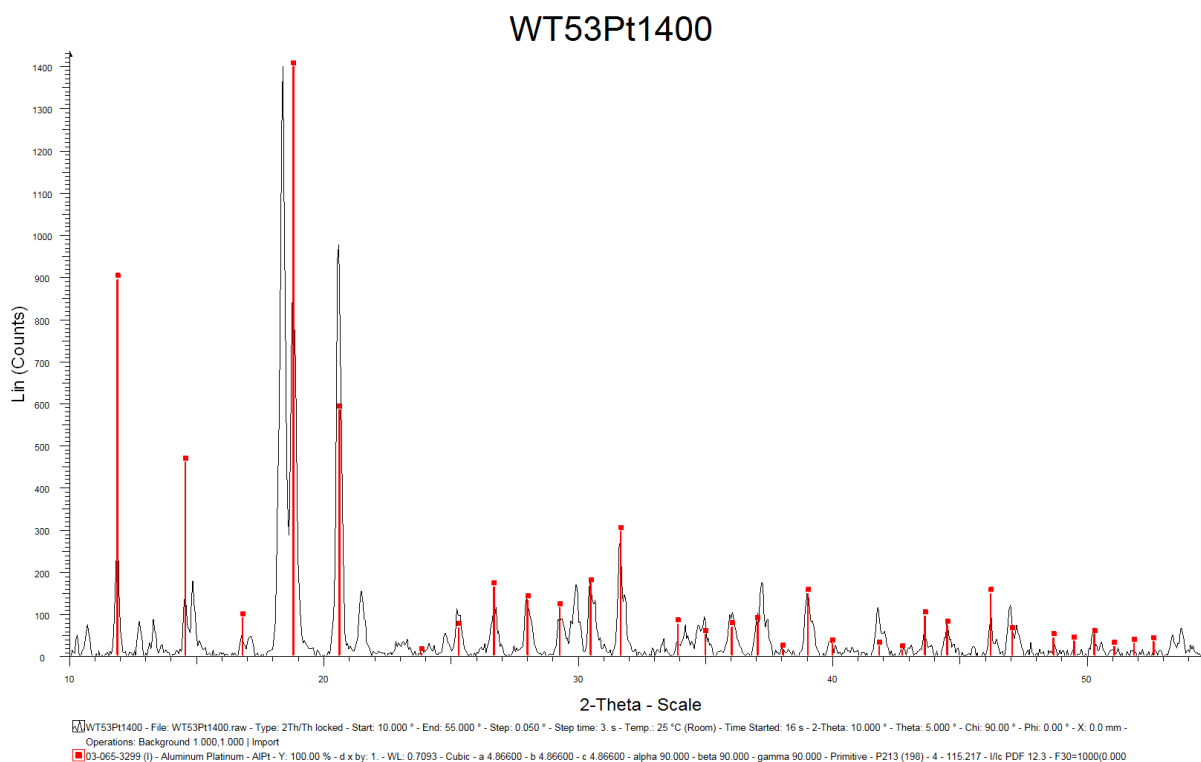


Figure 4.133. XRD trace showing peaks for the PtAl phase for the nominal 53.5 at.% Pt sample annealed at 1400°C.

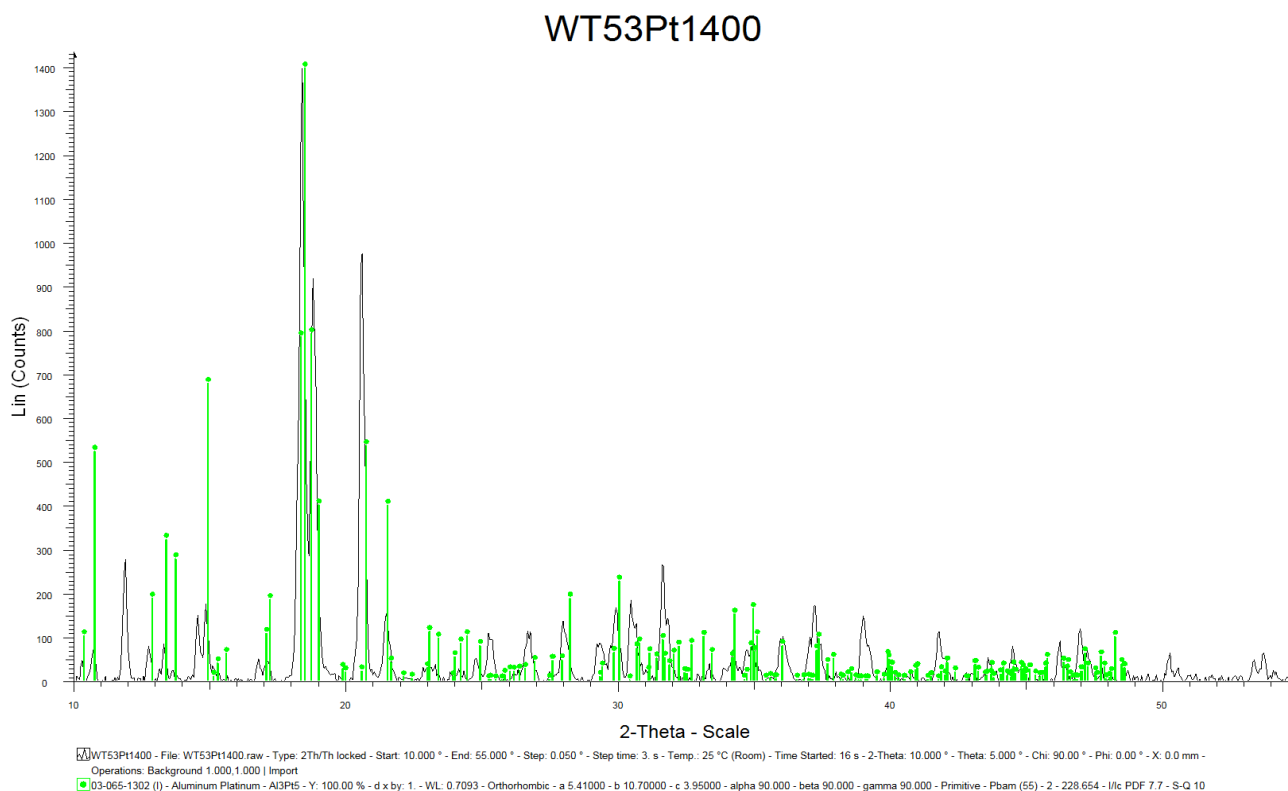


Figure 4.134. XRD trace showing peaks for the Pt_5Al_3 phase for the nominal 53.5 at.% Pt sample annealed at 1400°C.

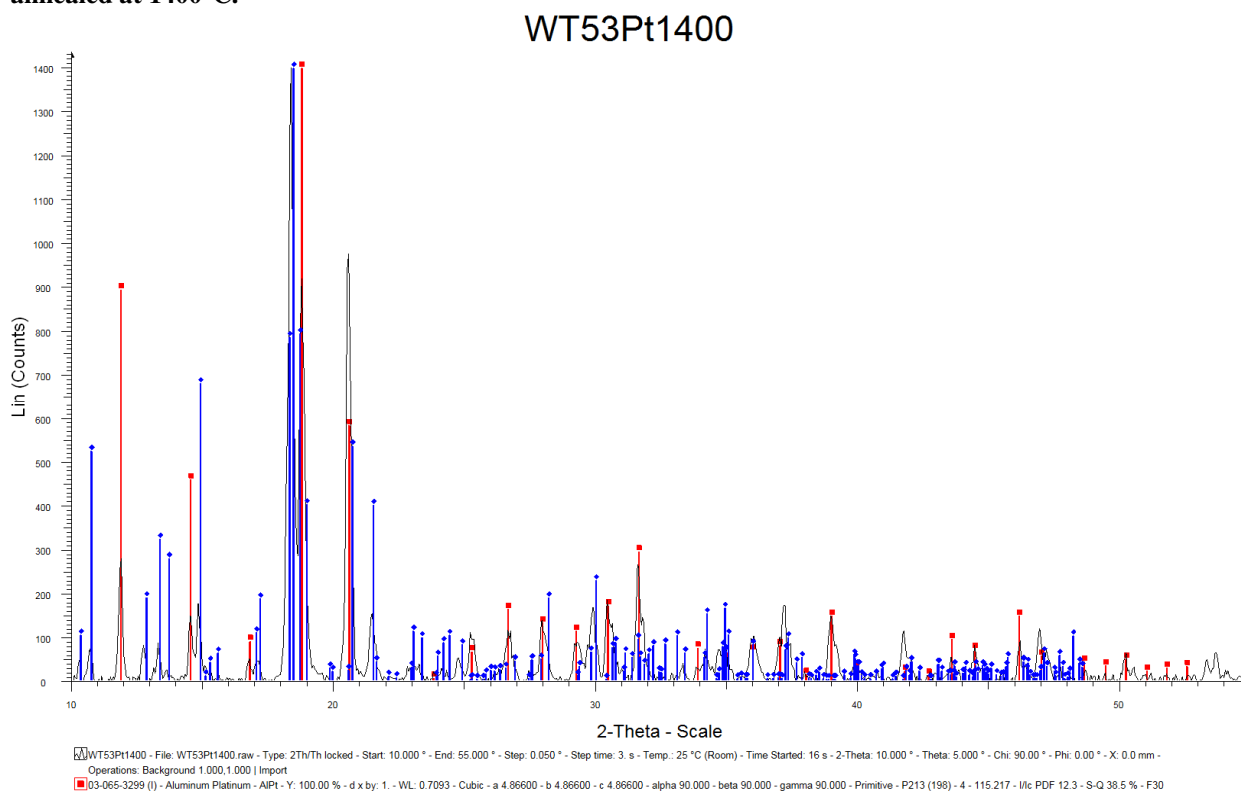


Figure 4.135. XRD trace showing peaks for the PtAl and Pt_5Al_3 phases for the nominal 53.5 at.% Pt sample annealed at 1400°C.

The XRD spectrum was fairly complex, with high counts, broad peaks and high background to noise ratio (Figure 4.132). There was a good match with PtAl with minimal shift (Figure 4.133) and the Pt₅Al₃ peaks matched well also (Figure 4.134). Therefore, the sample was shown to contain both PtAl and Pt₅Al₃ phases. Relative to the as-cast alloy, the peaks followed a similar pattern. Both have the highest peak at around $2\theta = \sim 19^\circ$, as well as similar peaks at $2\theta = \sim 12^\circ$, $\sim 15^\circ$ and $\sim 21^\circ$.

4.8 Phase analyses for 51 at.% Pt samples

4.8.1 Nominal 51 at.% Pt sample in the arc-melted condition

The microstructure of the as-cast 51 at.% Pt had dark dendrites, surrounded by the eutectic mixture comprising light needles and the dark phase (Figure 4.136a). Between the interdendritic light phase (Figure 4.136b), a very light phase was observed (Figure 4.136c). EDS analyses (Table 4.43) showed that the dendrites were β without obvious signs of decomposition, except at high magnification. The microstructure further cooled to form a eutectic mixture of $\beta + \text{Pt}_5\text{Al}_3$. The very light phase was shown by the EDS to be gold contamination (Figure 4.137), although it was too small to be analysed accurately without collecting X-rays from the surrounding phases (mainly Pt₅Al₃). The overall composition was in the eutectic region, but not exactly at the eutectic composition [1986McA], although the eutectic here is actually a ternary eutectic, having three phases. The light phase was in the Pt₅Al₃ phase region and the dark phase was in the β -phase region [1986McA].

The solidification sequence according to the microstructure was:

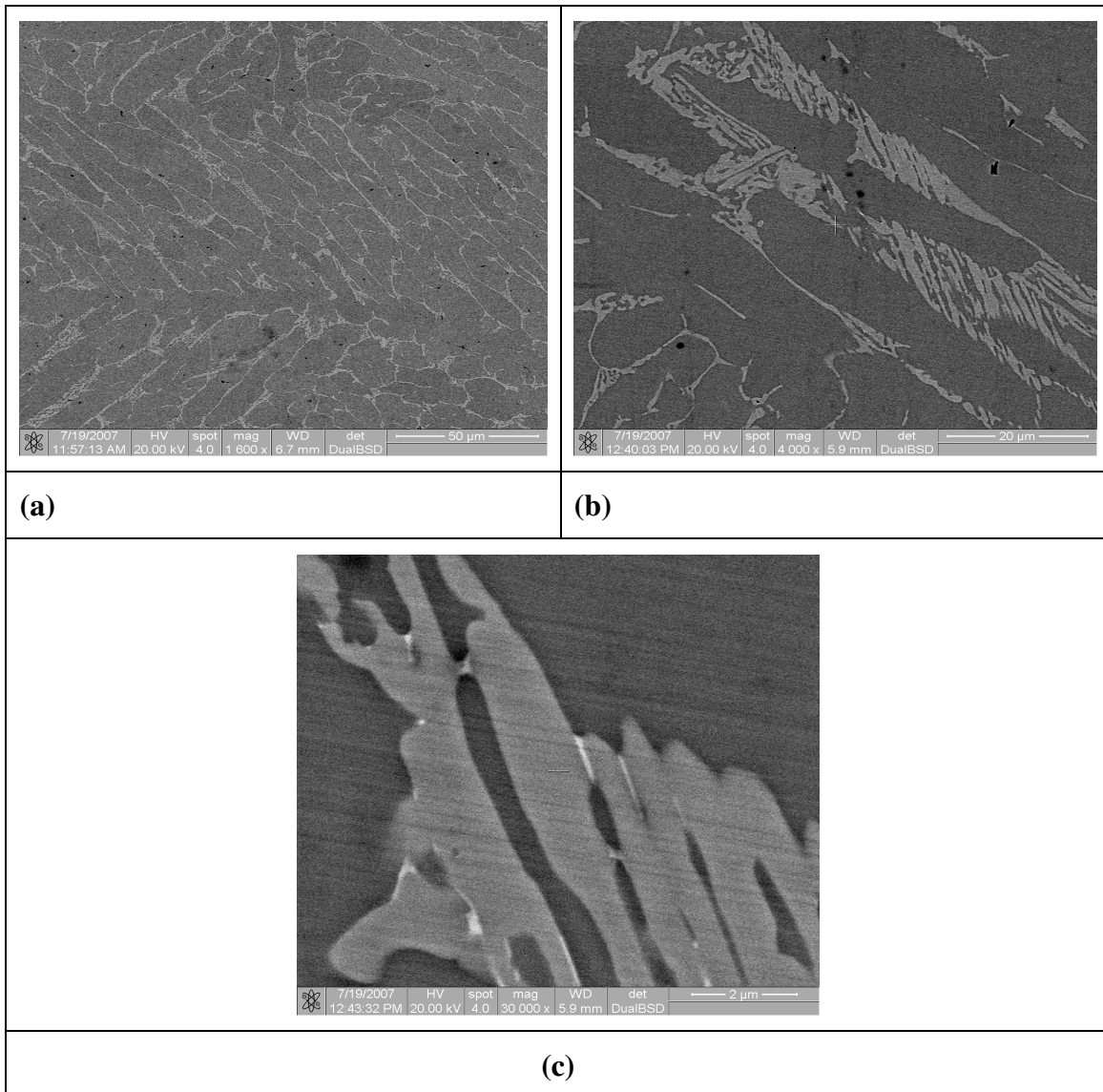
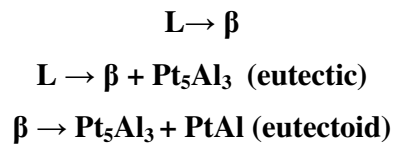


Figure 4.136. BSE-SEM image for nominal 51 at.% Pt in the arc-melted condition, showing dark PtAl dendrites surrounded by the eutectic mixture of light $\text{Pt}_5\text{Al}_3 + \text{PtAl}$, and a very light phase of gold between the Pt_5Al_3 .

Table 4.43. EDS analysis for the arc-melted nominal 51 at. % Pt sample.

Condition	Description	Pt (at. %)	Al (at. %)	Au (at. %)	Phase
Arc-melted 51 at. % Pt sample	Overall	56.0 ± 3.6	44.0 ± 3.6	-	-
	Light	62.3 ± 1.6	37.7 ± 1.6	-	Pt ₅ Al ₃
	Dark	54.1 ± 0.6	45.9 ± 0.6	-	β
	Very light	42.2	25.3	32.5	gold
	Eutectic	59.6 ± 0.9	40.4 ± 0.9	-	β + Pt ₅ Al ₃ + gold

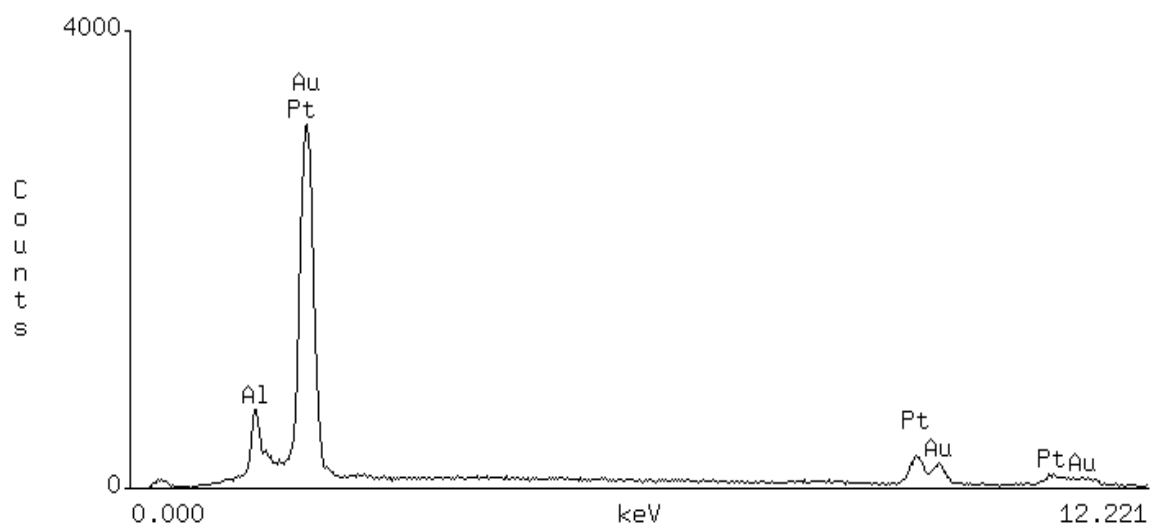


Figure 4.137. EDS spectrum for the arc-melted nominal 51 at. % Pt sample, showing the presence of gold (very light phase) in the alloy.

Table 4.44. XRD database [2005ICD] information for the nominal 51 at.% Pt sample in the arc-melted condition.

2 θ	d (Å)	h k l	I (%) raw spectrum	I (%) PtAl	I (%) Pt ₅ Al ₃
10.7	3.8	120	4	-	38
11.8	3.4	110	100	64	-
13.3	3.1	111	3	-	23
14.5/14.9	2.8/2.7	111/121	26	33	49
16.8/17.2	2.4/2.4	200/131	8	6	13
18.3	2.2	201	20	-	55
18.4	2.2	041	-	-	99
18.8/18.7	2.2/2.2	210/211	84	99	56
18.9	2.2	230	-	-	28
20.5/20.7	2.0/2.0	211/002	90	42	38
21.5	1.9	240	12	-	27
25.3	1.6	221	14	5	-
26.7	1.5	013	28	11	-
28.0	1.5	311	22	9	-
29.2/29.4	1.4/1.4	222/341	21	8	2
29.8	1.4	171	5	-	20
30.4	1.3	320	53	12	-
31.7/31.9	1.3/1.3	123/322	119	21	2
33.9	1.2	400	7	5	-
34.9/35.1	1.2/1.2	410/213	18	3	7
36.0/36.0	1.1/1.1	411/281	11	4	5
37.0/37.3	1.1/1.1	331/082	25	5	7
39.0	1.1	421	29	10	-
41.8/42.1	1.0/1.0	422/343	20	3	-
43.6	1.0	134	32	6	-
44.5	0.9	511	22	5	-
46.2	0.9	025	33	10	-
47.0	0.9	521	6	4	-

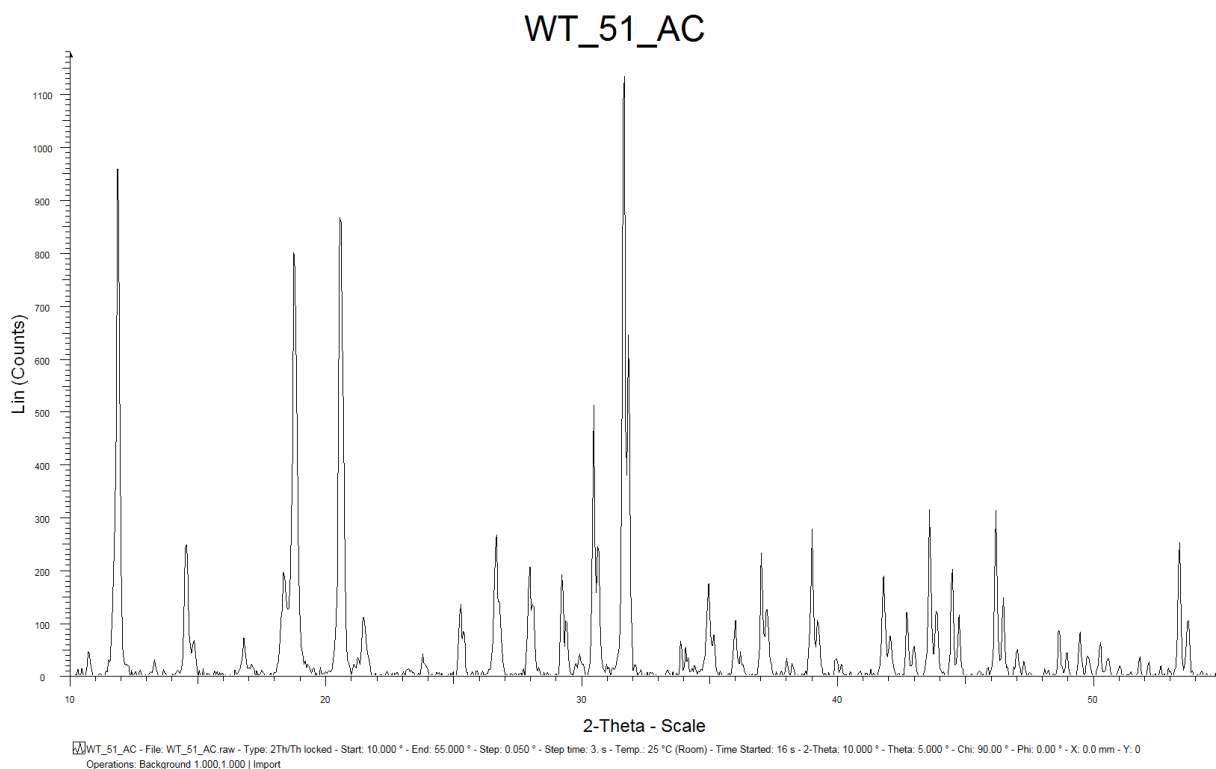


Figure 4.138. XRD spectrum for the arc-melted nominal 51 at.% Pt sample.

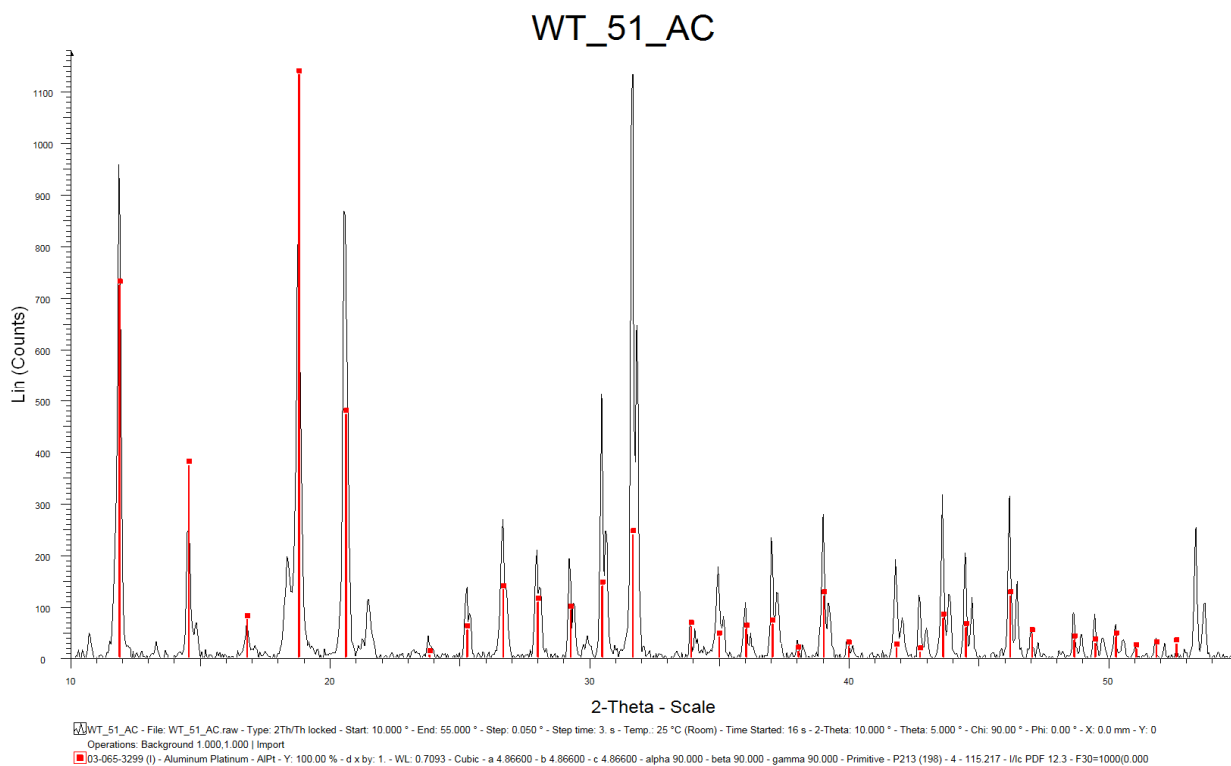


Figure 4.139. XRD trace showing peaks for the PtAl phase in the arc-melted nominal 51 at.% Pt sample.

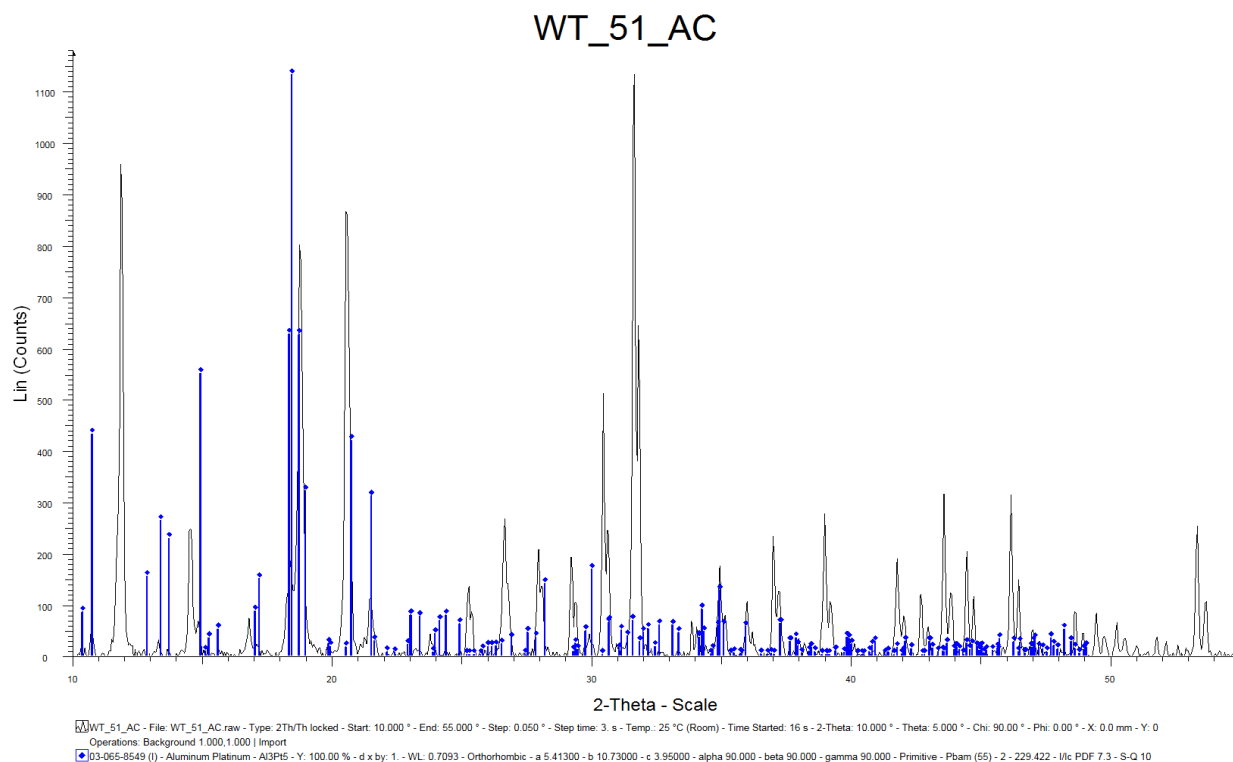


Figure 4.140. XRD trace showing peaks for the Pt_5Al_3 phase in the arc-melted nominal 51 at. % Pt sample.

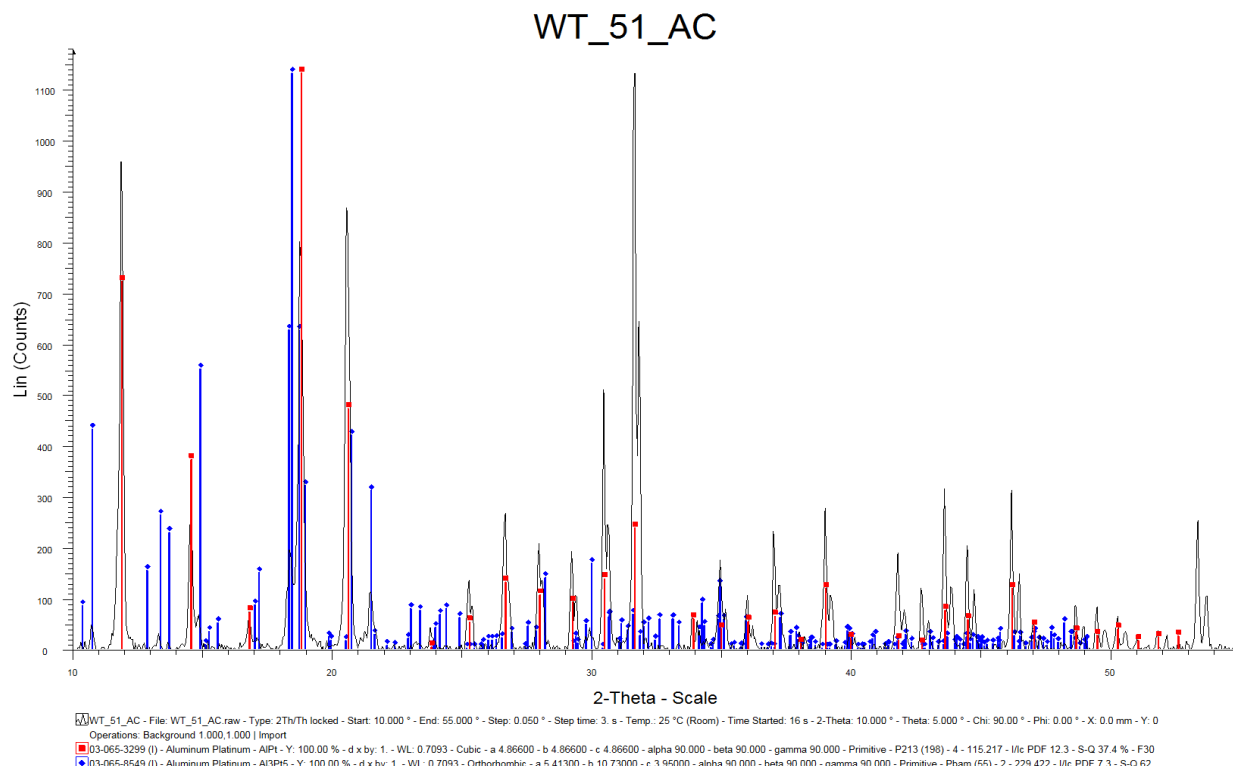


Figure 4.141. XRD trace showing peaks for the PtAl and Pt_5Al_3 structures for the arc-melted nominal 51 at. % Pt sample.

The XRD spectrum showed good peaks, high counts and a high signal to background ratio (Figure 4.138). In Figure 4.139, there was a match for PtAl in peaks at $2\theta = 11.8^\circ, 14.5^\circ, 16.8^\circ, 18.8^\circ, 20.5^\circ, \sim 24^\circ, 25.5^\circ, 26.5^\circ, \sim 28^\circ, \sim 29^\circ, 30.5^\circ, 31.5^\circ, \sim 34^\circ, \sim 35^\circ, \sim 36^\circ, \sim 37^\circ, \sim 38^\circ, \sim 39^\circ, \sim 40^\circ, \sim 42^\circ, 42.5^\circ, 43.5^\circ, 44.5^\circ, 46.2^\circ, \sim 47^\circ, 48.5^\circ, 49.5^\circ, 50.2^\circ, \sim 51^\circ, 51.8^\circ$ and 52.5° . In Figure 4.140, a match was observed for Pt₅Al₃ at $2\theta = 10.5^\circ, 13.4^\circ, 13.6^\circ, \sim 15^\circ, 15.5^\circ, \sim 17^\circ, \sim 18^\circ, \sim 20^\circ, 20.5^\circ, 21.5^\circ, \sim 24^\circ, 28.2^\circ, \sim 30^\circ, 30.6^\circ, \sim 31^\circ, \sim 35^\circ, \sim 36^\circ$ and 37.4° . The highest peak was at $2\theta = \sim 32^\circ$, but the intensities of the phases in this peak were very low, because of texture effects. All peaks were identified, showing that the β phase must have decomposed, even though this was not very obvious in the microstructure.

4.8.2 Nominal 51 at.% Pt sample annealed at 1400°C

Heat treatment at 1400°C gave a microstructure with light needles, surrounded by a eutectic mixture (Figure 4.142(a)). The sample must have melted, because it had a different primary phase from the as-cast sample (Figure 4.136). The overall composition of the sample was at the eutectic composition, and it had higher platinum content than targeted. The light phase composition was in the Pt₅Al₃ phase region, and the dark phase was unable to be analysed, because the phases were too fine and too close together, and eutectic overalls were analysed. The dark phase could actually be two-phase with a very fine structure, suggesting decomposed β . The EDS compositions for the phases had large errors as shown in Table 4.45, which is due to analysing small phase areas.

The solidification sequence according to the microstructure was:

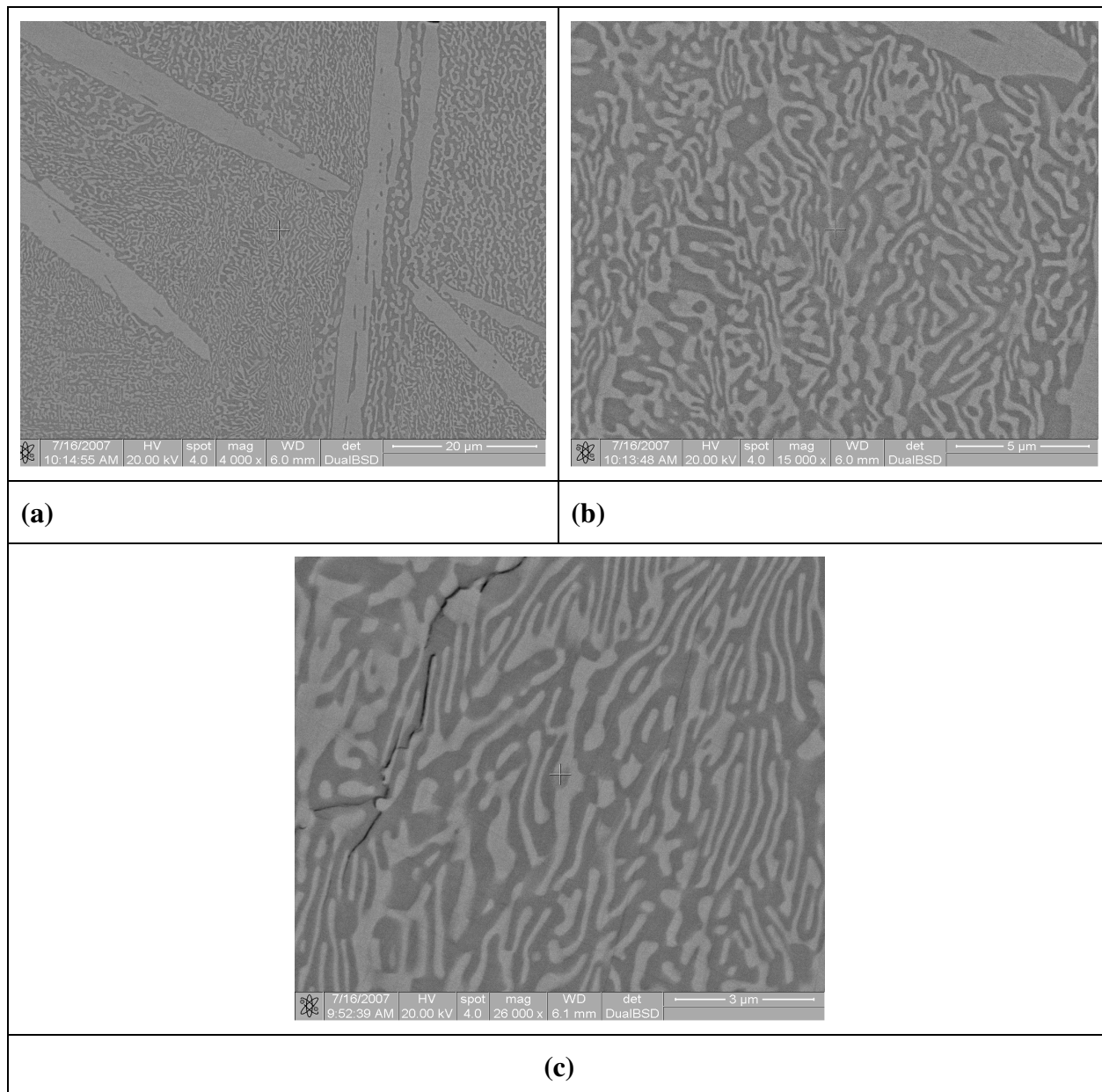
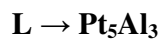


Figure 4.142. BSE-SEM image of the nominal 51 at.% Pt sample annealed at 1400°C, showing the light Pt_5Al_3 needles surrounded by the eutectic mixture of $\text{Pt}_5\text{Al}_3 + \text{PtAl}$

Table 4.45. EDS analysis for the nominal 51 at.% Pt sample annealed at 1400°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
51 at.% Pt annealed at 1400°C	Overall	59.3 ± 1.3	40.7 ± 1.3	-
	Light	63.0 ± 1.5	37.0 ± 1.5	Pt ₅ Al ₃
	Eutectic	59.3 ± 1.3	40.7 ± 1.3	β + Pt ₅ Al ₃

Table 4.46. XRD database [2005ICD] information for the nominal 51 at.% Pt sample annealed at 1400°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) PtAl	I (%) Pt ₅ Al ₃
10.7	3.8	120	8	-	38
11.8	3.4	110	37	64	-
12.8	3.2	021	6	-	13
13.3	3.1	111	4	-	23
13.7	3.0	130	5	-	20
14.5/14.9	2.8/2.7	111/121	27	33	49
16.8/17.2	2.4/2.4	200/131	7	6	13
18.3	2.2	201	41	-	55
18.4	2.2	041	-	-	99
18.8/18.7	2.2/2.2	210/211	100	99	56
18.9	2.2	230	-	-	28
20.5/20.7	2.0/2.0	211/002	51	42	38
21.5	1.9	240	16	-	27
23.0	1.8	151	5	-	8
24.2	1.7	160	3	-	6
24.9	1.6	132	5	-	5
25.3	1.6	221	10	5	-
26.7	1.5	013	27	11	-
28.0/27.9	1.5/1.5	311/170	13	9	3
29.2/29.4	1.4/1.4	222/341	12	8	2
29.8	1.4	171	17	-	20
30.4	1.3	320	27	12	-
31.7/31.9	1.3/1.3	123/322	39	21	2
33.9/34.3	1.2/1.2	400/133	4	5	10
34.9/35.1	1.2/1.2	410/213	18	3	7
36.0/36.0	1.1/1.1	411/281	8	4	5
37.0/37.3	1.1/1.1	331/082	10	5	7
39.0	1.1	421	12	10	-
41.8/42.1	1.0/1.0	422/343	5	3	-
43.6	1.0	134	13	6	-
44.5	0.9	511	11	5	-
46.2	0.9	025	15	10	-
47.0	0.9	521	-	4	-

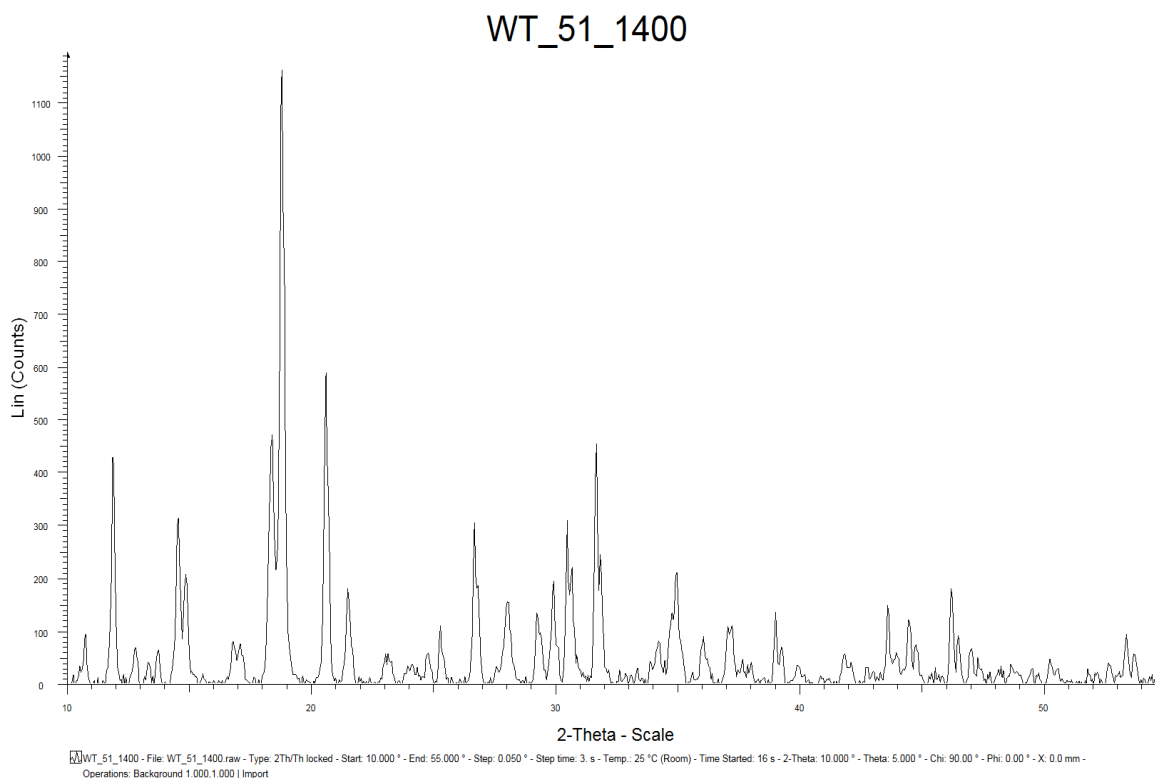


Figure 4.143. Raw XRD spectrum for the nominal 51 at.% Pt sample annealed at 1400°C.

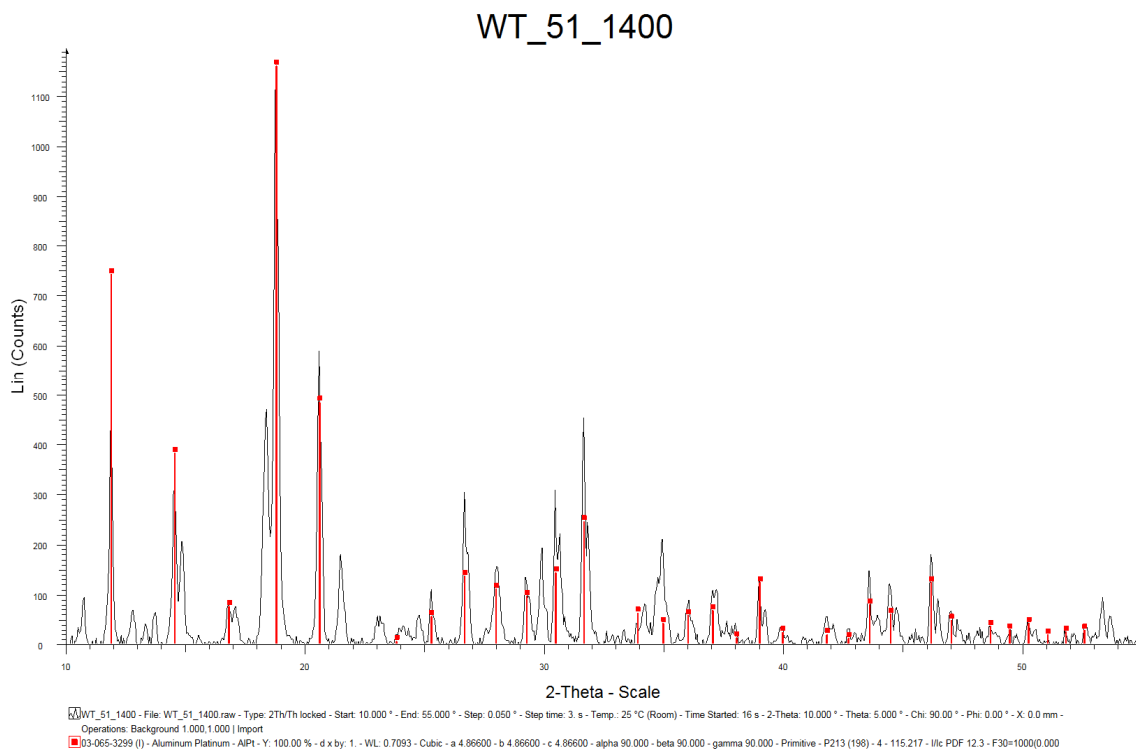


Figure 4.144. XRD trace showing peaks for the PtAl phase for the nominal 51 at.% Pt sample annealed at 1400°C.

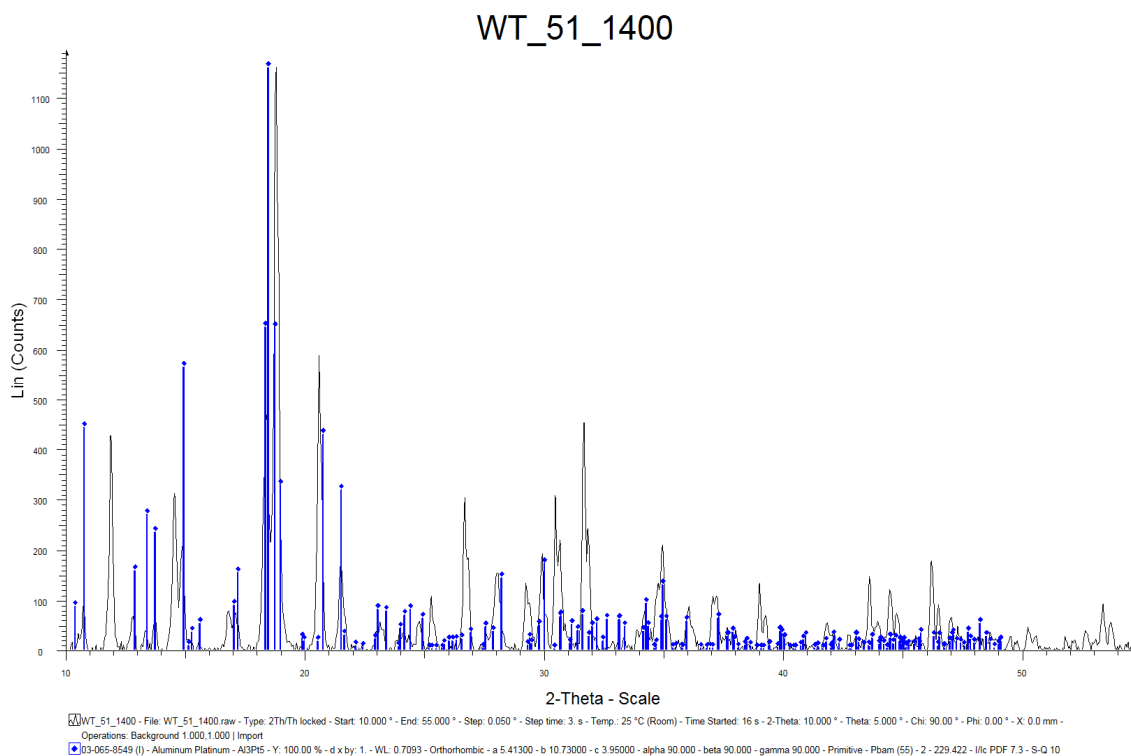


Figure 4.145. XRD trace showing peaks for the Pt_5Al_3 phase for the nominal 51 at.% Pt sample annealed at 1400°C.

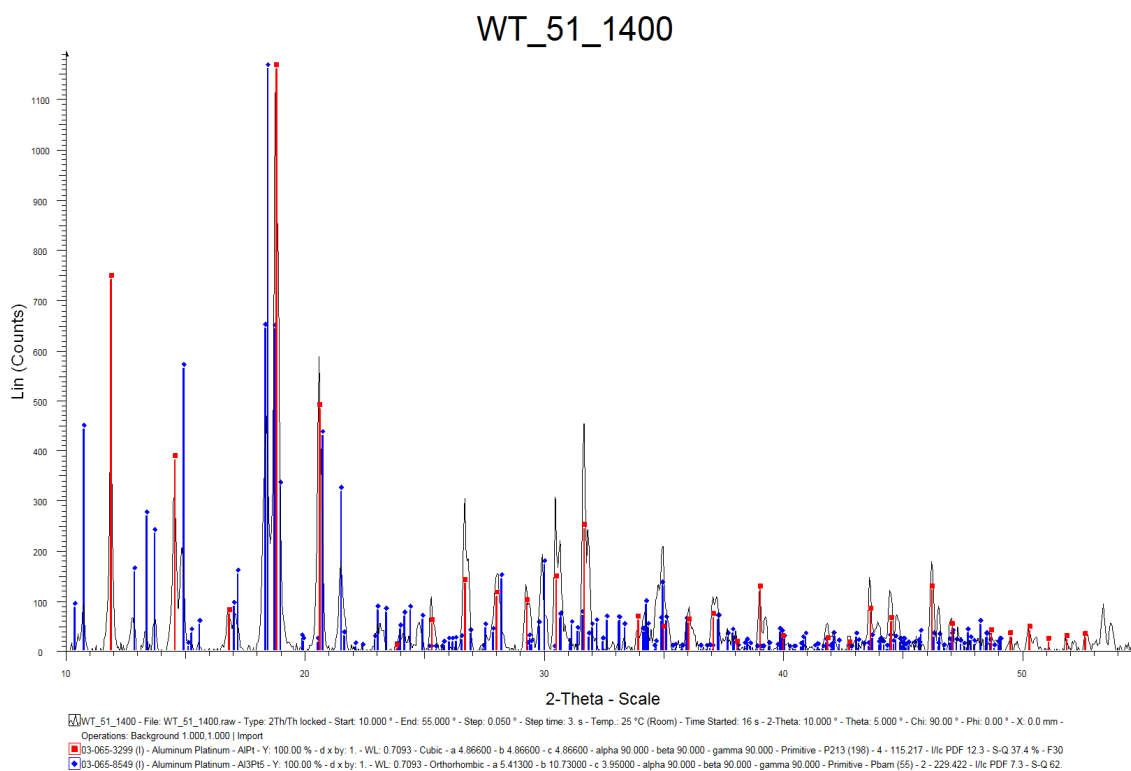


Figure 4.146. XRD trace showing peaks for the PtAl and Pt_5Al_3 structures for the nominal 51 at.% Pt sample annealed at 1400°C.

The XRD spectrum showed fairly narrow peaks, high counts and high signal to background ratio (Figure 4.143). The PtAl phase peaks matched well with the database peaks [2005ICD], (Figure 4.144), and the Pt_5Al_3 peaks were also observed to match well with the database peaks (Figure 4.145). The strongest peak was at $2\theta = \sim 18^\circ$ and it was constituted by both phases with matched intensities (Figure 4.146). The spectrum was very similar to the as-cast spectrum, except for the intensities of the peaks, which may have been due to texture effects.

4.9 Phase analyses for the 24 at.% Pt sample

4.9.1 Nominal 24 at.% Pt sample in the as-cast condition

The sample was brittle, and disintegrated on preparation for metallographic characterisation, although XRD analyses were undertaken. The XRD spectrum was complex, with many broad peaks, high counts and a high signal to background ratio (Figure 4.147). According to the database [2005ICD], $\text{Pt}_8\text{Al}_{21}$, $\text{Pt}_6\text{Al}_{21}$ and (Al) phases were present (Table 4.47). A good match for $\text{Pt}_8\text{Al}_{21}$ at $2\theta = \sim 12^\circ, 12.5^\circ, 13.5^\circ, 14.8^\circ, \sim 16^\circ, 17.2^\circ, \sim 19^\circ, \sim 20^\circ, 20.5^\circ, 21.5^\circ, 22.5^\circ, \sim 23^\circ, \sim 24^\circ, \sim 27^\circ, \sim 29^\circ$ and $\sim 32^\circ$ was observed with a slight shift to the right (Figure 4.148). The presence of $\text{Pt}_6\text{Al}_{21}$ was shown by a match at $2\theta = \sim 11^\circ, 13.8^\circ, \sim 17^\circ, 17.9^\circ, \sim 20^\circ, 20.5^\circ, 21.9^\circ, \sim 23^\circ, \sim 25^\circ, \sim 28^\circ, \sim 29^\circ, \sim 30^\circ, \sim 34^\circ, \sim 36^\circ, \sim 37^\circ$ and 38.2° with a slight shift to the right (Figure 4.149). No data were found for $\text{Pt}_5\text{Al}_{21}$ [2005ICD]. All the remaining spectrum peaks were matched for $\text{Pt}_8\text{Al}_{21}$, $\text{Pt}_6\text{Al}_{21}$, although all the peaks were well matched by the intermetallic phases, only the peak at $2\theta = \sim 20^\circ$, which is the strongest peak, showed that (Al) could be present (Figure 4.150).

Table 4.47. XRD database [2005ICD] information for the nominal 24 at.% Pt sample in the as-cast condition.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Al	I (%) Pt ₈ Al ₂₁	I (%) Pt ₆ Al ₂₁
10.8	3.8	300	45	-	-	65
11.9	3.4	321	60	-	99	-
12.5	3.3	312	28	-	40	-
13.5/13.8	3.0/3.0	411/302	75	-	22	100
14.8	2.7	303	4	-	5	-
16.1	2.5	323	5	-	5	-
17.3/17.0	2.3/2.4	413/004	14	-	8	16
17.9	2.3	223	16	-	-	10
18.9	2.2	600	49	-	14	-
19.9/20.2	2.0/2.0	620/200	35	46	15	-
20.1	2.0	502	96	-	-	18
20.5/20.6	2.0/2.0	523/332	100	-	11	60
21.5/21.7	1.9/1.9	631/600	21	-	6	14
22.4	1.8	613	9	-	5	-
23.1/23.3	1.8/1.8	415/215	44	-	4	16
24.0	1.7	642	17	-	5	-
25.4	1.6	334	23	-	-	6
27.2	1.5	822	11	-	5	-
28.0	1.5	434	32	-	-	5
29.6/28.8	1.4/1.4	734/630	8	-	4	4
30.1	1.4	632	37	-	-	45
32.1	1.3	745	14	-	12	-
34.3	1.2	008	27	-	-	7
36.1	1.1	635	12	-	-	10

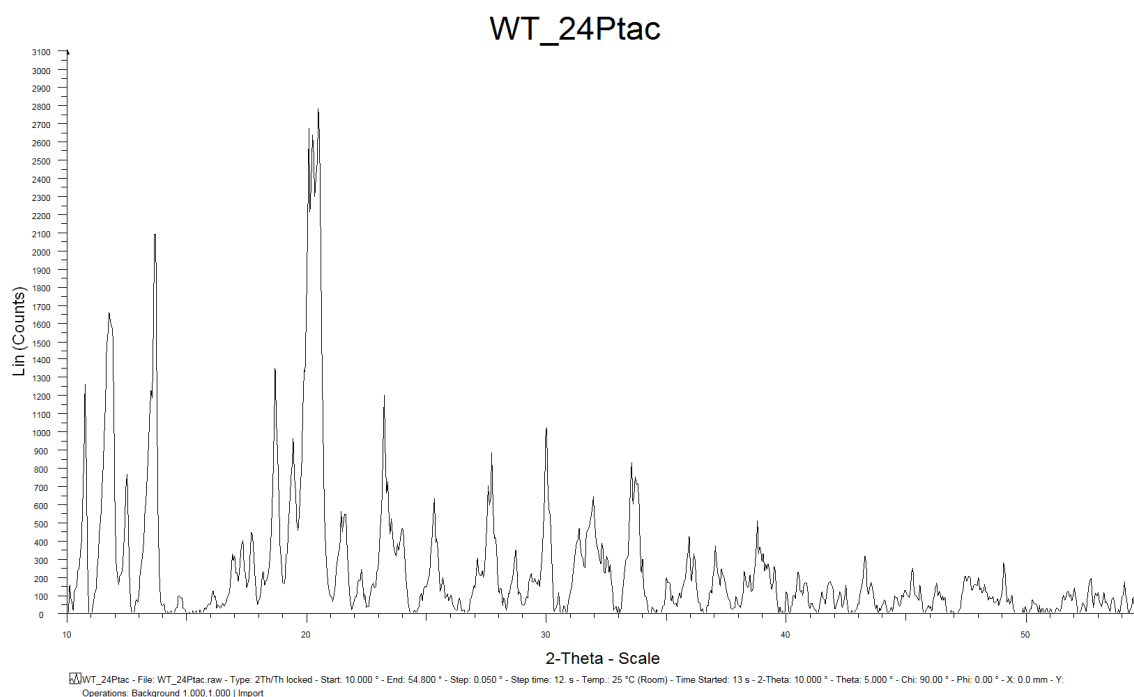


Figure 4.147. XRD spectrum for the arc-melted 24 at.% Pt sample.

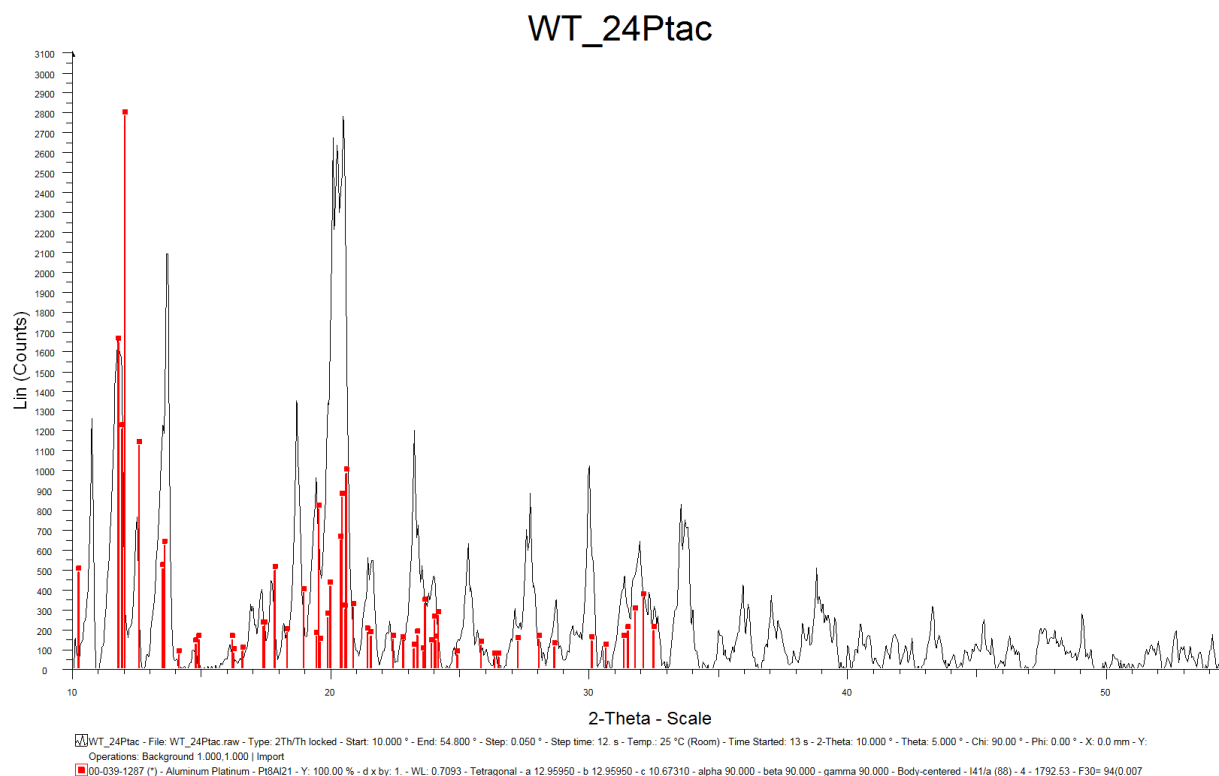


Figure 4.148. XRD trace showing peaks for the $\text{Pt}_8\text{Al}_{21}$ phase for the arc-melted 24 at. % Pt sample.

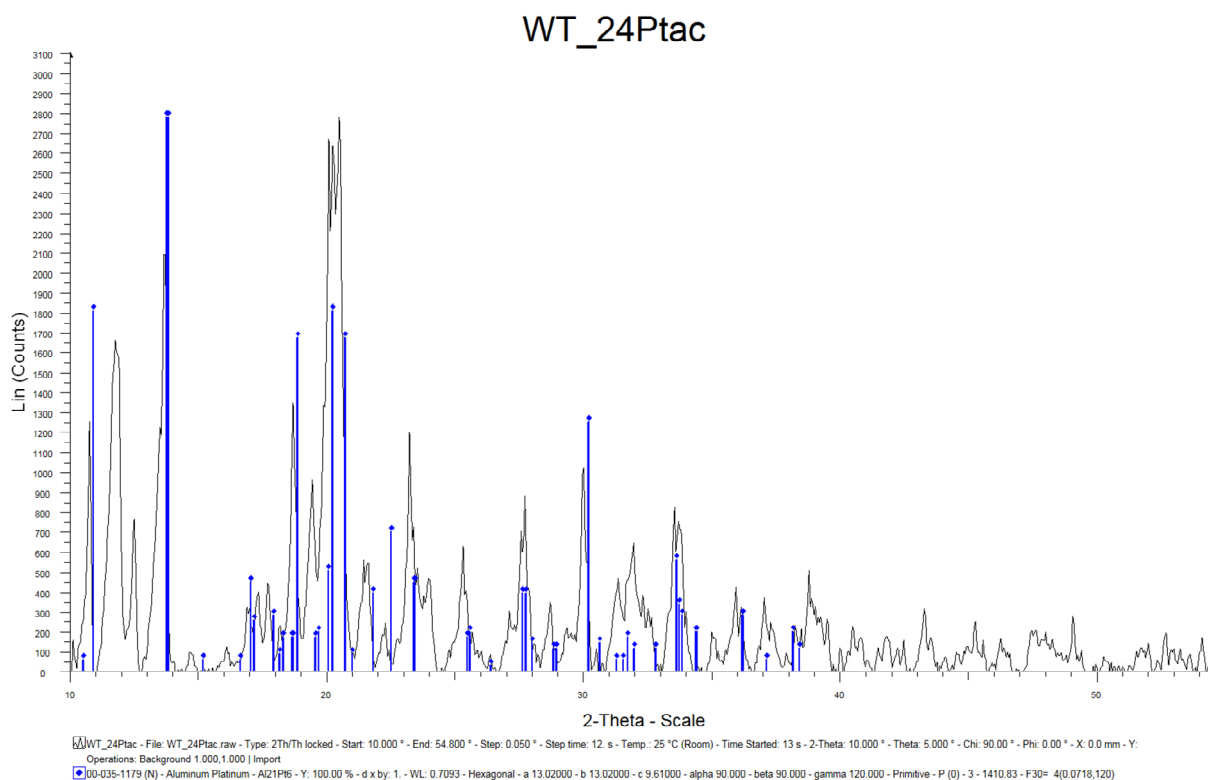


Figure 4.149. XRD trace showing peaks for the $\text{Pt}_6\text{Al}_{21}$ phase for the arc-melted 24 at. % Pt sample

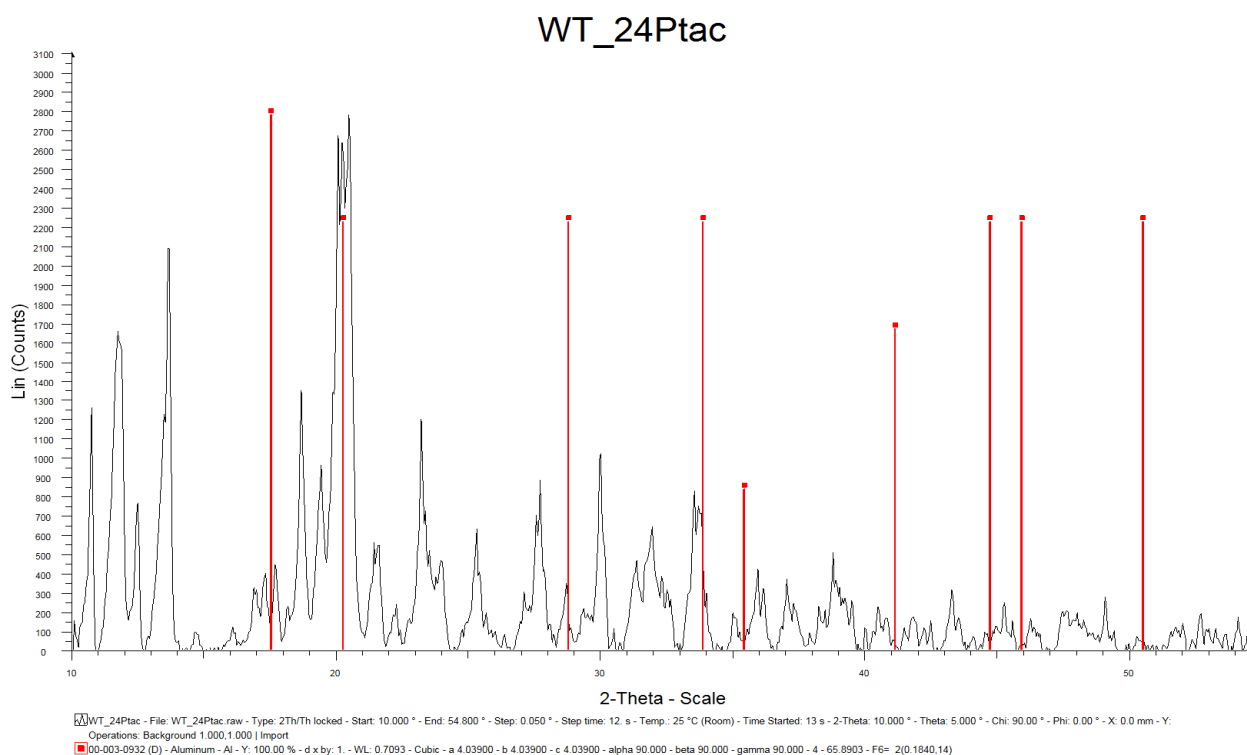


Figure 4.150. XRD trace showing peaks for Al for the arc-melted 24 at.% Pt sample.

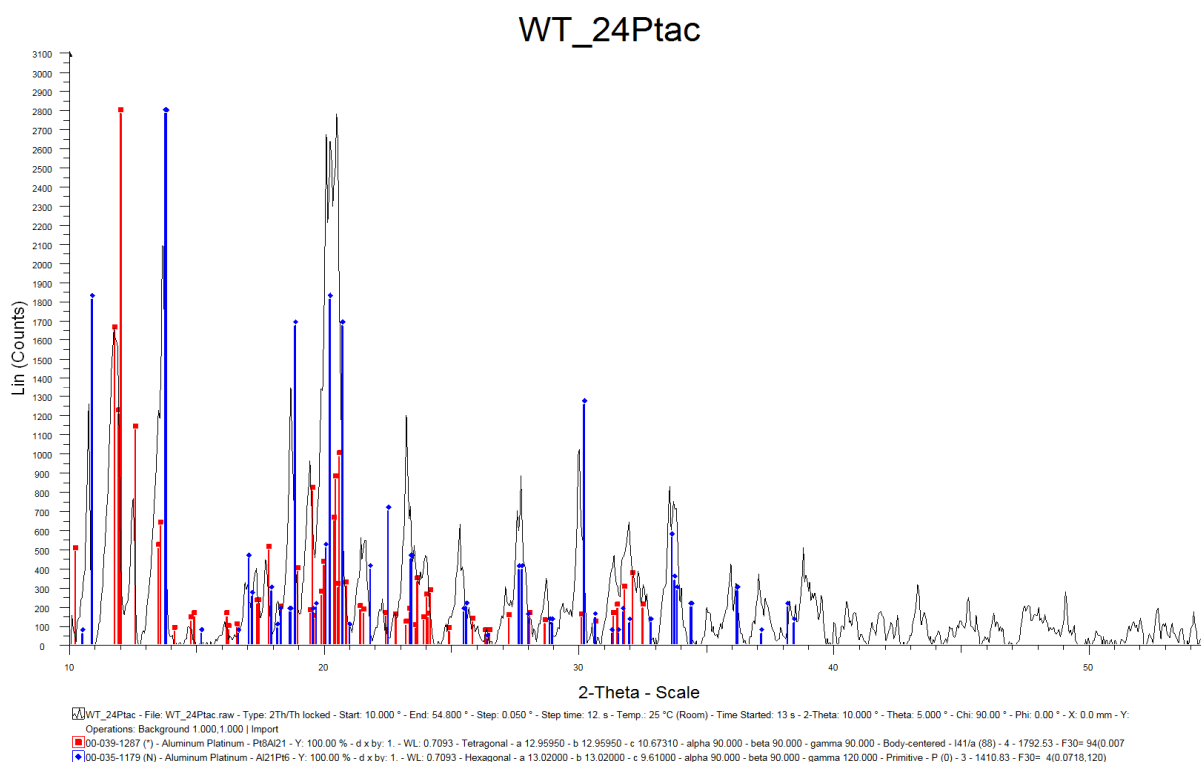


Figure 4.151. XRD trace showing peaks for the $\text{Pt}_8\text{Al}_{21}$ and $\text{Pt}_6\text{Al}_{21}$ phases for the arc-melted 24 at.% Pt sample.

4.10 Phase analyses for the nominal 16 at.% Pt samples

4.10.1 Nominal 16 at.% Pt sample in the as-cast condition

The sample did not melt properly, and the Pt-rich region solidified first, to form light dendrites, surrounded by a eutectic mixture (Figure 4.152a, 4.152b). Upon solidification, the microstructure formed three main regions: Pt-rich region, a layered region and a coarse region (Figure 4.152). Around the Pt-rich region were platinum-rich layers, with decreasing platinum contents moving outwards (from Layer 4 to Layer 1) (Figure 4.152d). Layer 4 was very close to the Pt-rich region, and had a too small area for accurate analysis. Layer 3 also had a too small area for accurate analysis and was very close to Layer 4, therefore the resulting analyses may be imprecise (Table 4.48). The coarse region was very porous and formed of: a light phase with platinum content of about ~22 at.% Pt, a dark phase highly rich in aluminium (~99.6 at.% Al), and a eutectic mixture (Figure 4.152). The coarse region appeared brittle. The compositions of the phases had high errors, and were not exactly in agreement with the phase diagram [1986McA].

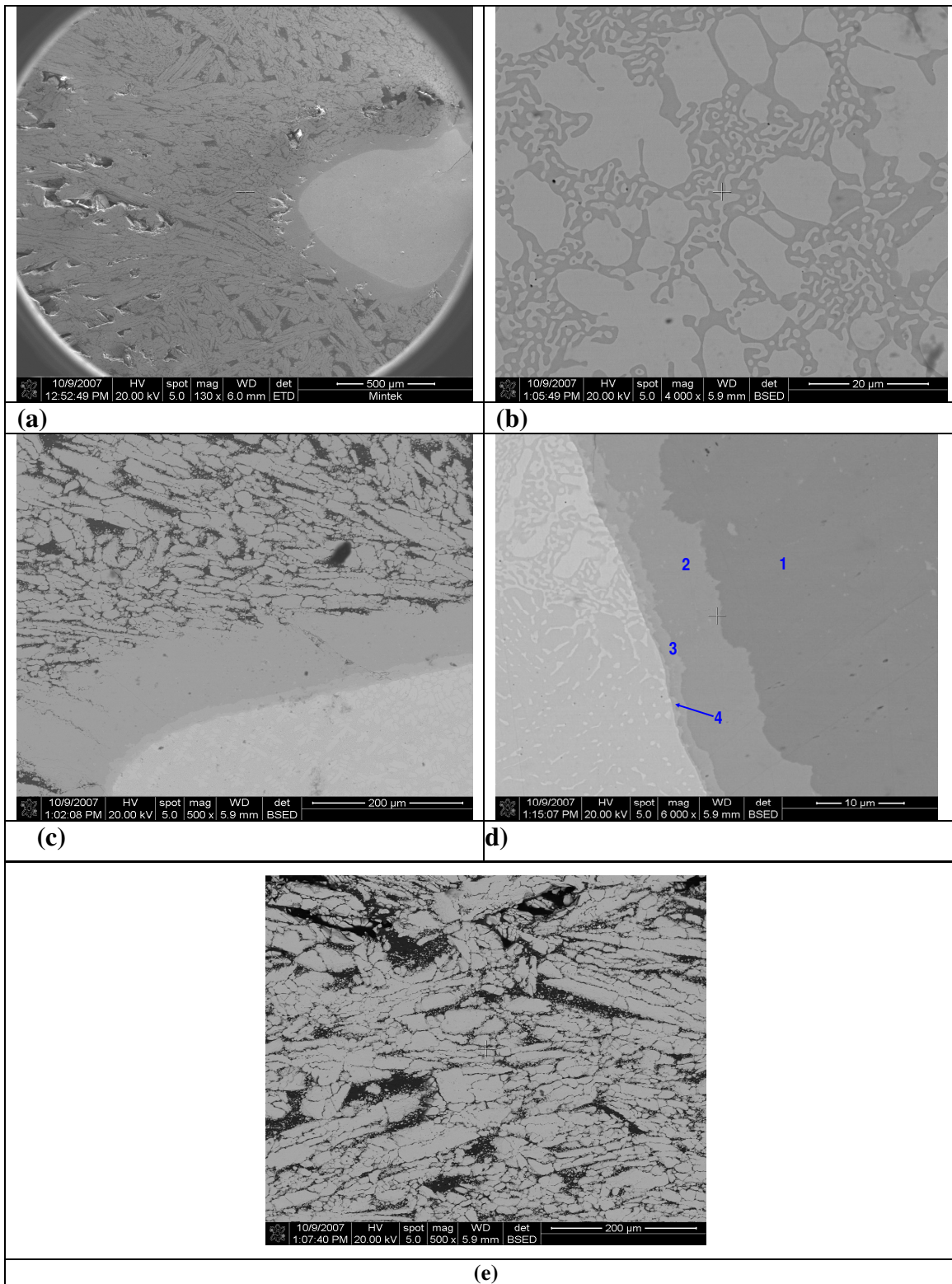


Figure 4.152. BSE-SEM image for the 16 at.% Pt sample in the arc-melted condition, showing (a) the different regions, with the Pt-rich region having the lightest contrast, (b) dendrites in a eutectic mixture in the Pt-rich part, (c) a boundary between the coarse and the fine region, (d) the layered region with decreasing Pt-content in the outer layers, from Layer 4 to Layer 1, and (e) the coarse region.

Table 4.48. Phase analyses for the as-cast 16 at. % Pt sample.

Condition	Description	Pt (at. %)	Al (at. %)	Phase
As-cast 16 at. % Pt sample	Overall (Pt-rich region)	52.6 ± 0.4	47.4 ± 0.4	-
	Light phase (Pt-rich region)	52.4 ± 0.5	47.6 ± 0.5	PtAl
	Dark phase (Pt-rich region)	43.9 ± 0.3	56.1 ± 0.3	Pt ₂ Al ₃
	Eutectic mixture (Pt-rich region)	49.1 ± 1.0	51.0 ± 1.0	Pt ₂ Al ₃ + PtAl
	Overall (Layer 4)	37.3 ± 1.2	62.7 ± 1.2	Pt ₂ Al ₃
	Overall (Layer 3)	35.3 ± 0.8	64.8 ± 0.8	PtAl ₂
	Overall (Layer 2)	29.3 ± 0.1	70.7 ± 0.1	Pt ₈ Al ₂₁
	Overall (Layer 1)	22.9 ± 0.1	77.1 ± 0.1	Pt ₅ Al ₂₁
	Overall (coarse region)	11.6 ± 2.1	88.4 ± 2.1	-
	Light phase (Coarse region)	22.1 ± 0.1	77.9 ± 0.1	Pt ₅ Al ₂₁
	Dark phase (Coarse region)	0.4 ± 0.6	99.6 ± 0.6	(Al)
	Overall eutectic mixture (Coarse region)	1.58 ± 0.7	98.4 ± 0.7	(Al) + Pt ₅ Al ₂₁

Table 4.49. XRD database [2005ICD] information for Pt₆Al₂₁ and Pt₈Al₂₁ for the nominal 16 at. % Pt sample in the as-cast condition.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₆ Al ₂₁	I (%) Pt ₈ Al ₂₁
10.8/11.9	3.8/3.4	300/321	73	65	100
13.8/13.5	3.0/3.0	302/411	96	100	22
17.0	2.4	004	21	16	-
18.8/18.9	2.2/2.2	330/600	100	60	14
19.5/19.5	2.1/2.1	214/433	6	6	29
20.1/19.9	2.0/2.0	502/620	88	18	15
20.9/20.6	2.0/2.0	413/541	83	3	35
21.7/21.4	1.9/1.9	622	20	14	7
23.3/23.3	1.8/1.8	602/721	38	16	6
25.4	1.6	334	27	6	-
27.7	1.5	622	44	14	-
28.8/29.6	1.4/1.4	316/734	17	4	4
30.1/30.1	1.4/1.4	632/725	41	45	5
31.4/31.5	1.3/1.3	506/763	5	2	7
32.0/32.1	1.3/1.3	336/745	8	4	13
32.8/32.5	1.3/1.3	552/318	6	4	7
34.0	1.2	606	38	10	-
34.3	1.2	008	7	7	-
36.1	1.1	635	15	10	-

Table 4.50. XRD database [2005ICD] information for PtAl₂, Pt₂Al₃ and PtAl for the nominal 16 at. % Pt sample in the as-cast condition.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) PtAl ₂	I (%) Pt ₂ Al ₃	I (%) PtAl
11.9	3.4	111	4	99	-	-
13.8/13.7	3.0/3.0	200/102	96	24	100	-
16.8	2.4	200	21	-	-	6
19.5/19.4/18.8	2.1/2.1/2.2	220/110/210	6	55	78	99
20.6	2.0	211	83	-	-	42
23.0	1.8	311	38	36	-	-
27.8/27.5	1.5/1.5	400/204	44	7	14	-
30.3/30.5	1.4/1.3	331/320	41	12	-	12
31.1/31.7	1.3/1.3	420/123	13	5	-	21
34.2/33.9/33.9	1.2/1.2/1.2	422/124/400	38	12	16	5
36.3/36.0	1.1/1.1	511/411	15	8	-	5
37.0	1.1	331	10	-	-	6
38.0	1.1	420	6	-	-	0.9
39.7/39.0	1.0/1.1	440/421	11	3	-	10
42.2	1.0	600	8	2	-	-
43.6	0.9	134	9	-	-	7
46.2	0.9	025	5	-	-	10
51.9	0.8	600	5	-	-	2
52.6	0.8	610	6	-	-	2

WT 16 AC

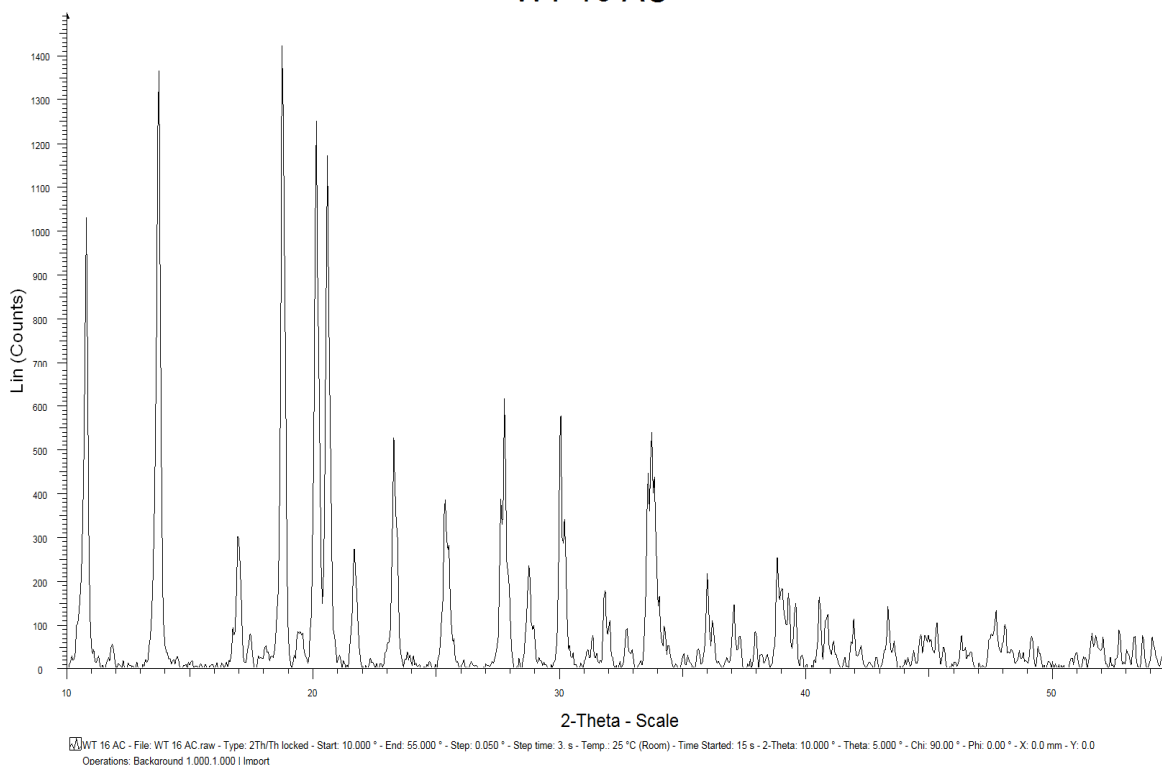


Figure 4.153. Raw XRD spectrum for the arc-melted 16 at. % Pt sample.

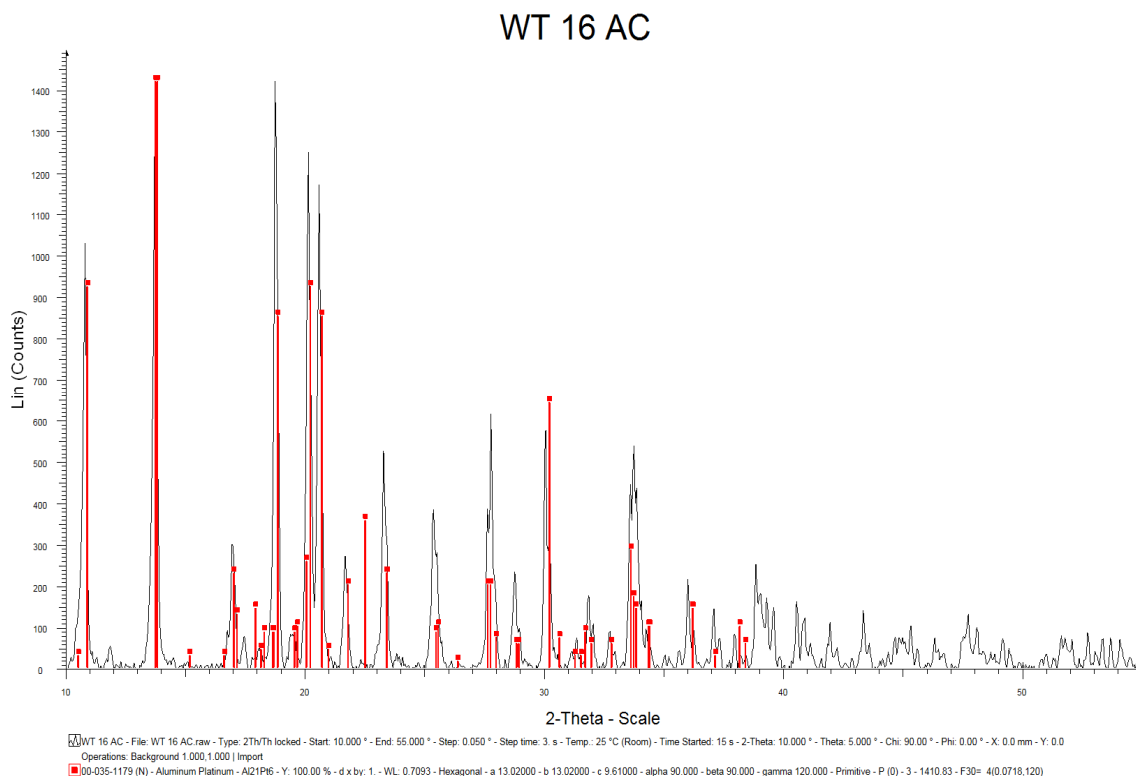


Figure 4.154. XRD trace showing peaks for the $\text{Pt}_6\text{Al}_{21}$ phase for the arc-melted 16 at. % Pt sample.

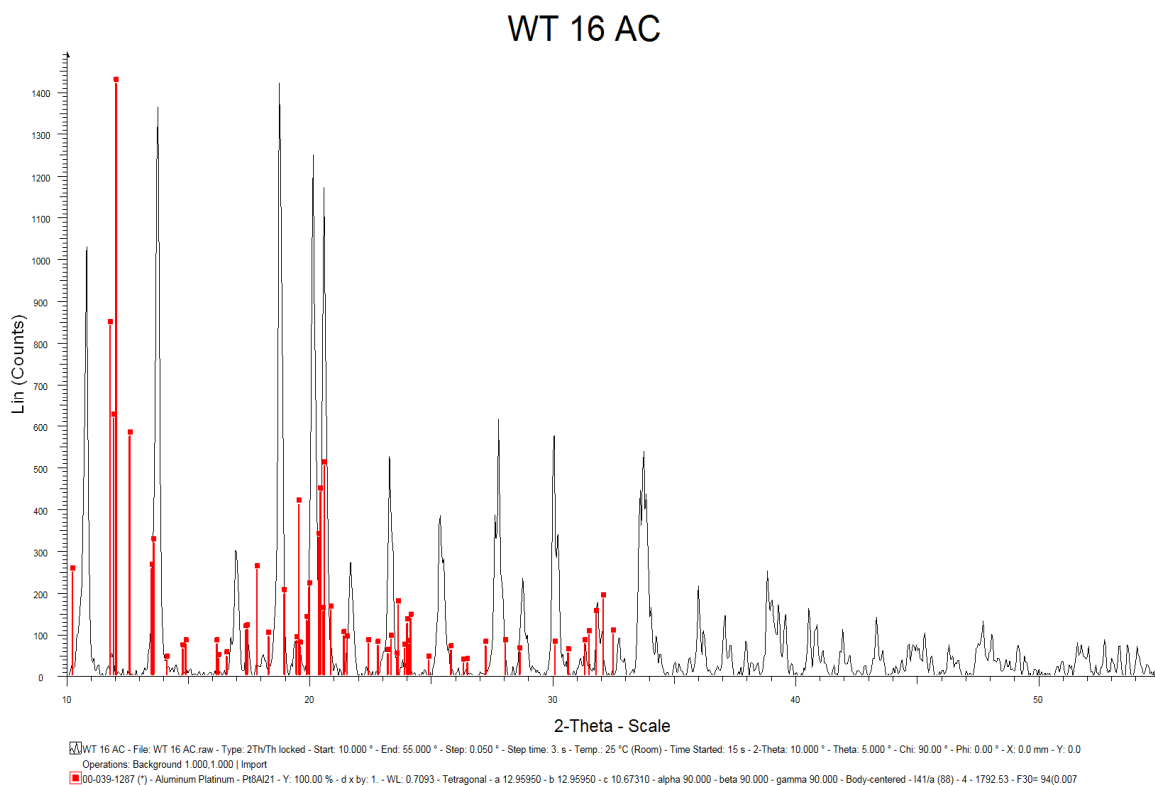


Figure 4.155. XRD trace showing peaks for the $\text{Pt}_8\text{Al}_{21}$ phase for the arc-melted 16 at. % Pt sample.

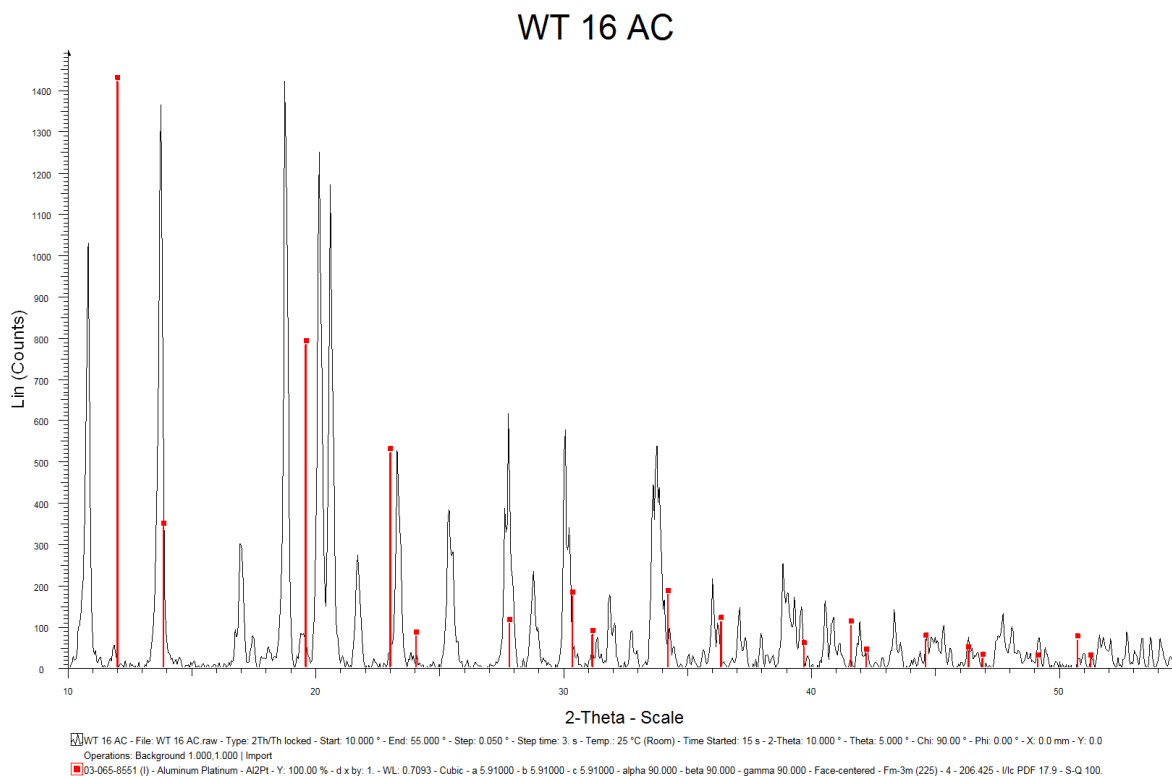


Figure 4.156. XRD trace showing peaks for the PtAl_2 phase for the arc-melted 16 at.% Pt sample.

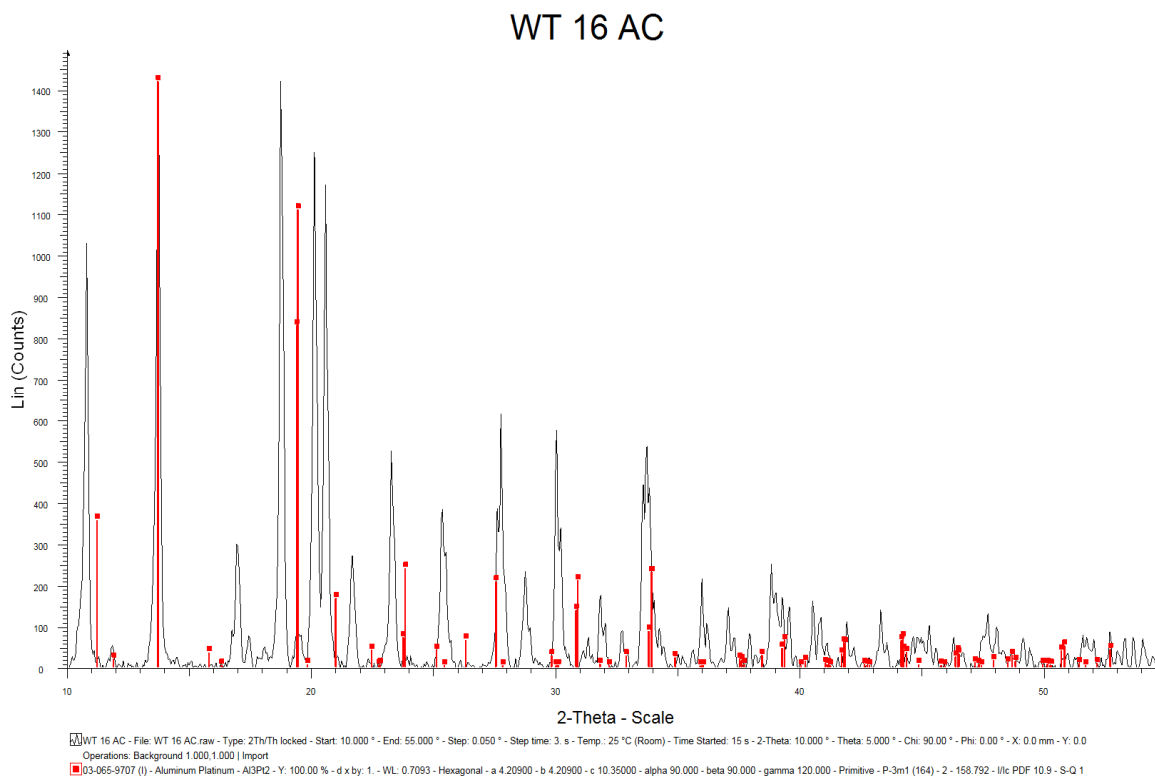


Figure 4.157. XRD trace showing peaks for the Pt_2Al_3 phase for the arc-melted 16 at.% Pt sample.

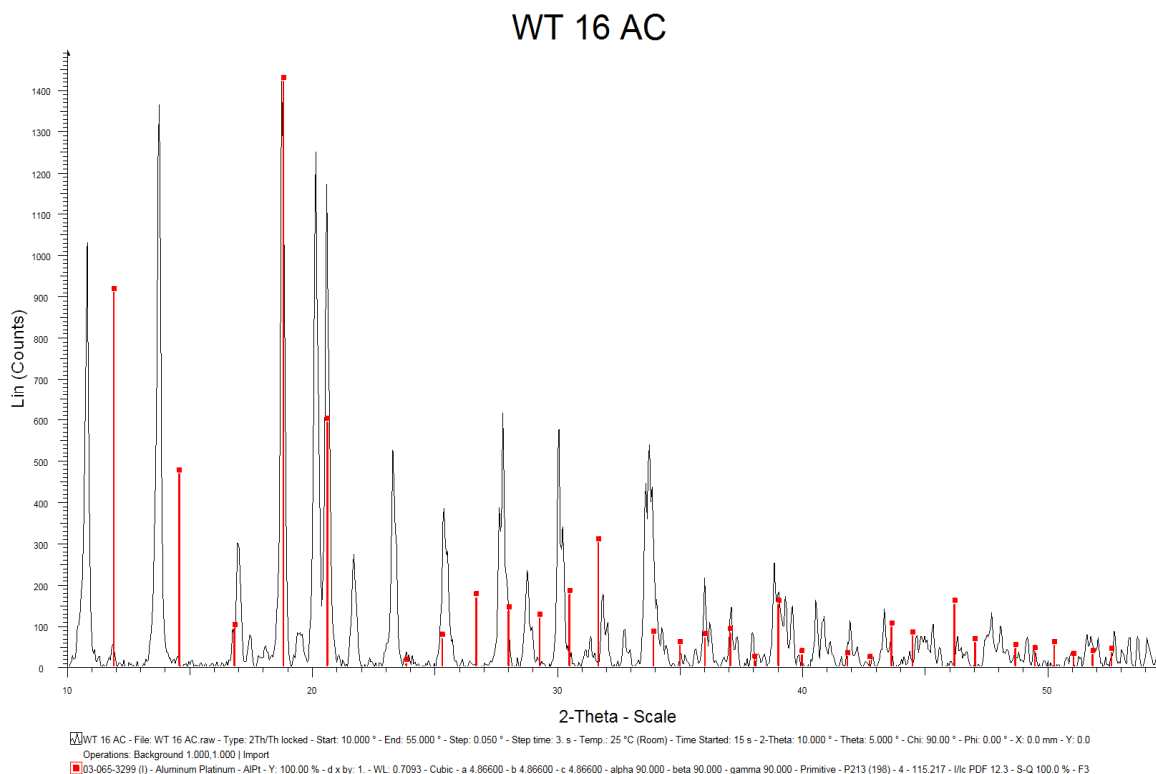


Figure 4.158. XRD trace showing peaks for the PtAl phase for the arc-melted 16 at.% Pt sample.

The spectrum had broad peaks, high counts and high signal to background ratio (Figure 4.153). A good match was observed for $\text{Pt}_6\text{Al}_{21}$ phase at $2\theta = 10.9^\circ, 13.9^\circ, \sim 17^\circ, 18.9^\circ, 19.5^\circ, \sim 20^\circ, 20.8^\circ, 21.9^\circ, 23.5^\circ, 25.5^\circ, 27.8^\circ, \sim 29^\circ, \sim 30^\circ, 31.5^\circ, \sim 32^\circ, 32.9^\circ, \sim 34^\circ, 34.5^\circ, \sim 36^\circ, \sim 37^\circ$ and $\sim 38^\circ$ with a slight shift to the right (Figure 4.154). A less good match was observed for $\text{Pt}_8\text{Al}_{21}$ at $2\theta = 13.5^\circ, \sim 19^\circ, \sim 20^\circ, 20.5^\circ, 21.5^\circ, \sim 29^\circ, \sim 30^\circ$ and 32.5° with a slight shift to the left (Figure 4.155), although peaks at $2\theta = \sim 12^\circ, 19.5^\circ, 23.5^\circ, 31.5^\circ$ and $\sim 32^\circ$ were good matches. The presence of PtAl_2 was shown by a less good match at $2\theta = \sim 12^\circ, \sim 14^\circ, 19.5^\circ, \sim 23^\circ, \sim 28^\circ, 30.5^\circ, \sim 31^\circ, \sim 34^\circ, 36.5^\circ, 39.6^\circ, \sim 42^\circ$ and 44.5° slightly shifted to the right, although the major peaks of the phase did not match the major peaks of the database (Figure 4.156). The presence of Pt_2Al_3 was shown by a less good match at $2\theta = 13.8^\circ, 19.5^\circ, 27.5^\circ, \sim 34^\circ$, and the smaller peaks at the higher 2θ scale (Figure 4.157). The presence of PtAl was shown by a less good match at $2\theta = \sim 17^\circ, \sim 19^\circ, 20.6^\circ, 30.5^\circ, 31.6^\circ, \sim 34^\circ, \sim 36^\circ, \sim 37^\circ, \sim 38^\circ, \sim 39^\circ$, and smaller peaks at the higher 2θ values and these were: $2\theta = 43.8^\circ, 46.2^\circ, \sim 52^\circ$ and 52.5° , with a negligible shift (Figure 4.158). XRD showed the definite presence of $\text{Pt}_6\text{Al}_{21}$ and likely presence of $\text{Pt}_8\text{Al}_{21}$. Thus, all the peaks were identified, showing that the $\text{Pt}_5\text{Al}_{21}$

phase was not in the alloy. However, there were no available database peaks to match for $\text{Pt}_5\text{Al}_{21}$.

4.10.2 Nominal 16 at.% Pt annealed at 600°C

After heat treatment at 600°C, the microstructure was coarse and porous throughout (Figure 4.159a). The sample was homogeneous, and there was no sign of the Pt-rich parts. The light phase formed as needles, with large holes between them, where a eutectic mixture was observed in the smaller spaces (Figure 4.159c). The sample was annealed near the melting point; therefore, it partially melted, and lost some aluminium, probably by vaporisation. The overall composition of the sample was in the two-phase region ((Al) and $\text{Pt}_5\text{Al}_{21}$) [1986McA], the dark phase was very rich in aluminium (aluminium solid solution) (Table 4.51).

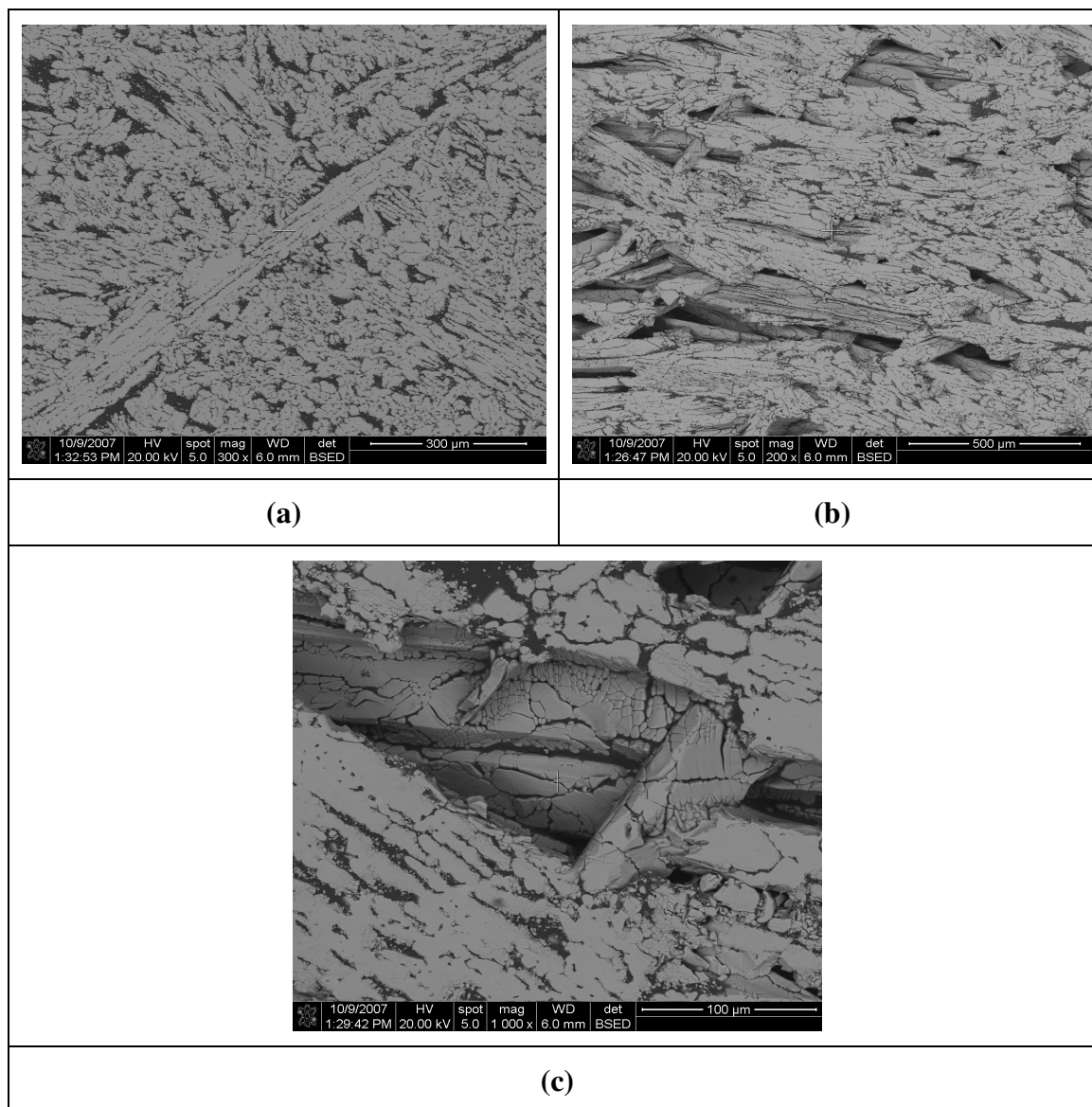


Figure 4.159. (a) BSE-SEM image of nominal 16 at.% Pt annealed at 600°C, showing a two-phase region of a coarse microstructure, (b) needles (light), with large holes between and (c) a dark phase as part of a eutectic mixture between the light needles.

Table 4.51. Phase analysis for nominal 16 at.% Pt annealed at 600°C.

Condition	Description	Pt (at.%)	Al (at.%)	Phase
16 at.% Pt sample annealed at 600°C	Overall (coarse)	17.0 ± 0.3	83.0 ± 0.3	-
	Light phase	21.9 ± 0.05	78.1 ± 0.05	Pt ₅ Al ₂₁
	Dark	0.03 ± 0.02	99.9 ± 0.02	(Al)
	eutectic	15.2 ± 1.0	84.8 ± 1.0	(Al) + Pt ₅ Al ₂₁

Table 4.52. XRD database [2005ICD] information for the nominal 16 at.% Pt sample annealed at 600°C.

2θ	d (Å)	h k l	I (%) raw spectrum	I (%) Pt ₆ Al ₂₁	I (%) Al
10.8	3.8	300	55	65	-
13.8	3.0	302	100	100	-
17.0	2.4	004	18	16	-
17.5	2.3	111	13		99
18.8	2.2	330	51	60	-
20.1/20.2	2.0/2.0	510/200	97	65	46
20.6	2.0	332	78	60	-
21.7	1.9	600	18	14	-
23.3	1.8	602	34	16	-
25.6	1.6	433	28	7	-
28.0	1.5	434	35	5	-
28.7	1.4	220	17		23
30.1	1.4	632	40	45	-
32.0	1.3	336	15	4	-
33.8/33.9	1.2/1.2	311/606	38	10	23
36.1	1.1	635	12	10	-

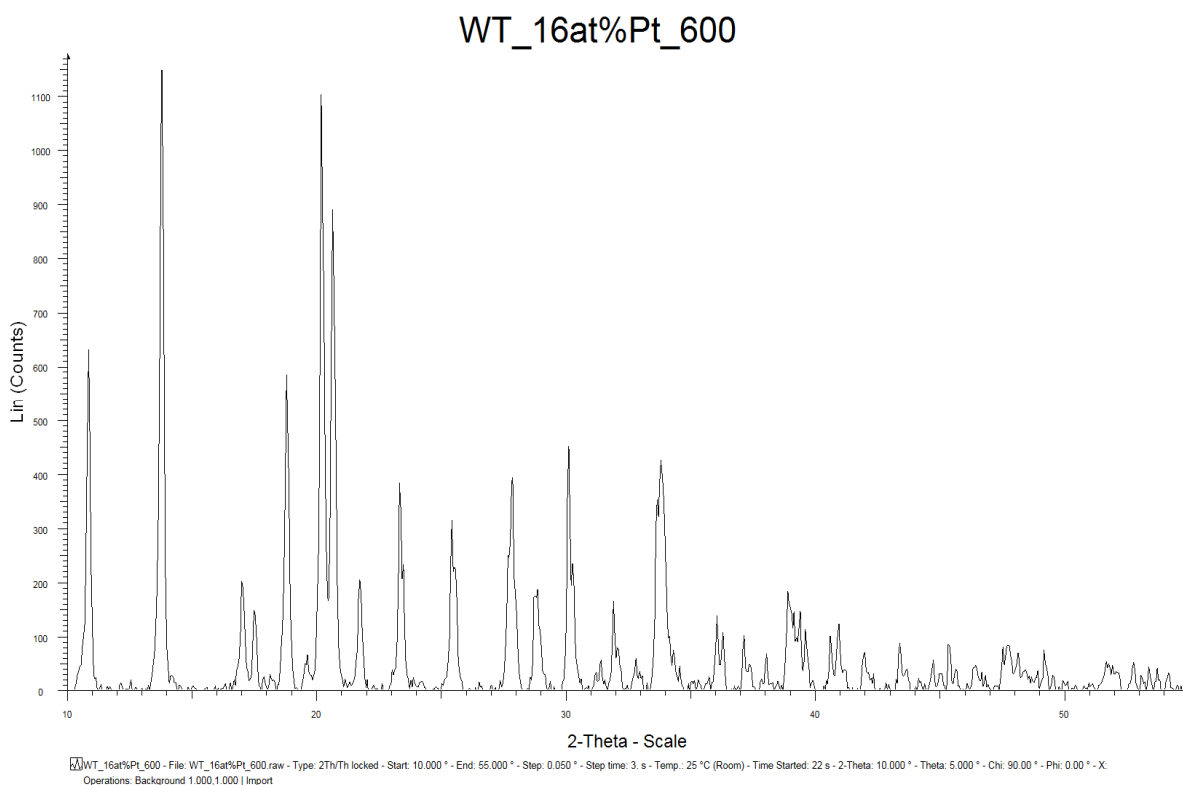


Figure 4.160. Raw XRD spectrum for the nominal 16 at.% Pt sample annealed at 600°C.

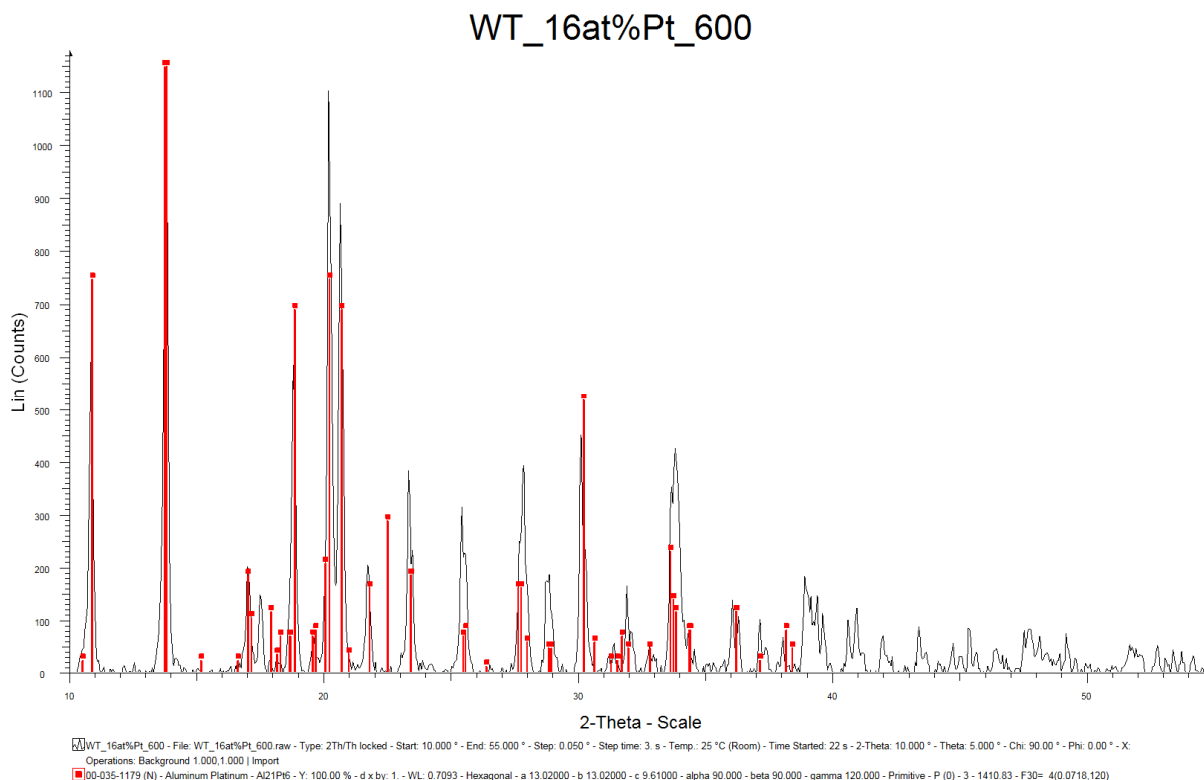


Figure 4.161. XRD trace showing peaks for the Pt₆Al₂₁ phase for the nominal 16 at.% Pt sample annealed at 600°C.

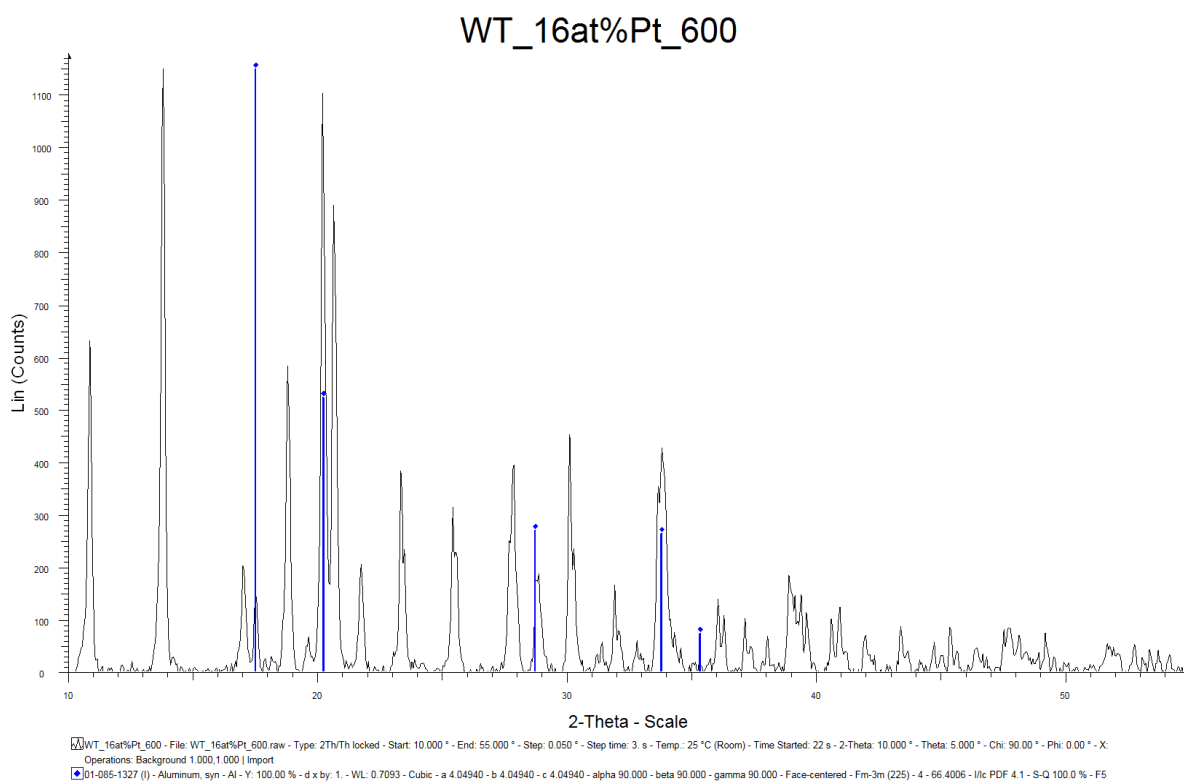


Figure 4.162. XRD trace showing peaks for Al for the nominal 16 at.% Pt sample annealed at 600°C.

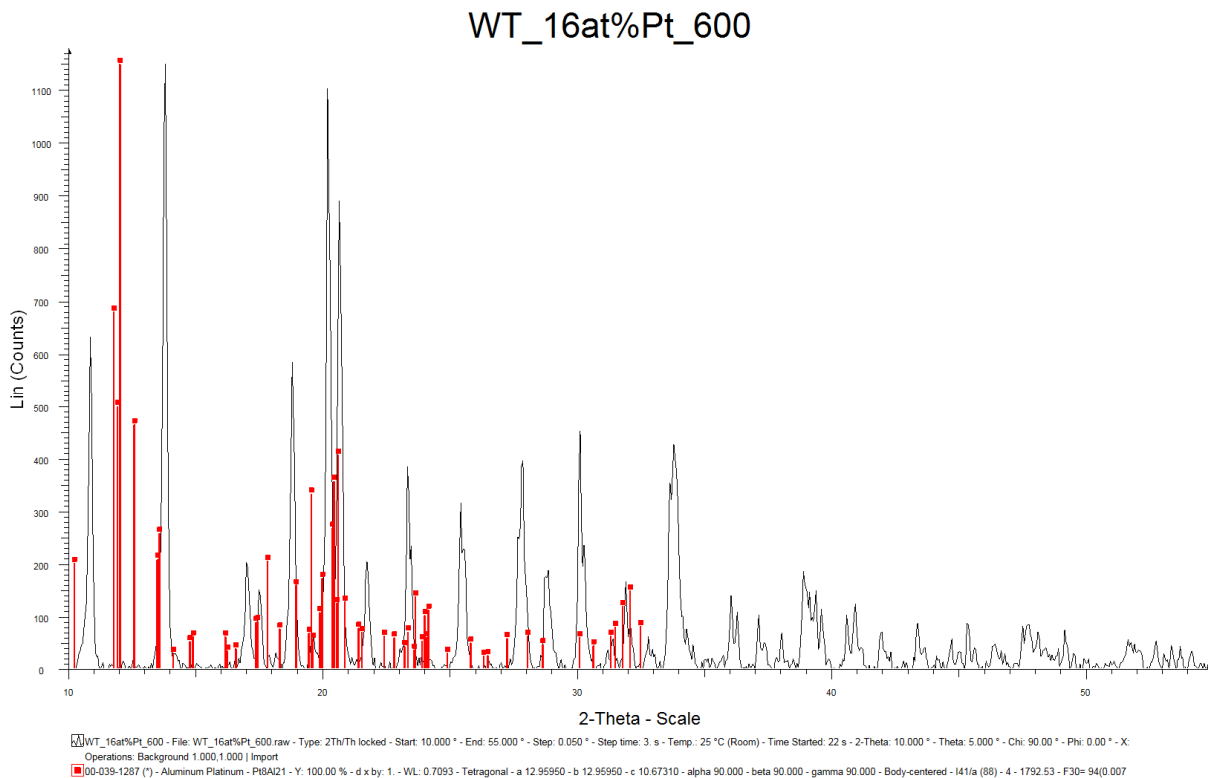


Figure 4.163. XRD trace showing peaks for the $\text{Pt}_8\text{Al}_{21}$ phase for the nominal 16 at. % Pt sample annealed at 600°C.

The spectrum had fairly narrow peaks, high counts and high signal to background ratio (Figure 4.160). The spectrum was similar to the as-cast spectrum, except that the annealed sample had fewer peaks (Figure 4.153). The presence of $\text{Pt}_6\text{Al}_{21}$ was shown by the match of peaks at $2\theta = \sim 11^\circ, 13.9^\circ, \sim 17^\circ, \sim 19^\circ, \sim 20^\circ, 20.8^\circ, 21.9^\circ, 23.5^\circ, 25.5^\circ, \sim 28^\circ, \sim 30^\circ, \sim 32^\circ, \sim 34^\circ, 36.2^\circ, 37.1^\circ$ and 38.2° (Figure 4.161). According to the XRD database [2005ICD], there was a match of the peaks for (Al) at $2\theta = 17.5^\circ, 20.1^\circ, 28.6^\circ$ and 33.9° , with a slight shift to the right (Figure 4.162). The $\text{Pt}_8\text{Al}_{21}$ phase did not show a good match (Figure 4.163).

4.11 Hardness measurements on the samples

No hardness measurements could be made on the 24 and 67 at. % Pt samples because they disintegrated. The 24 at. % Pt sample disintegrated during casting, and the 67 at. % Pt sample disintegrated on removal of the resin in preparation for XRD analysis. The results of the Vickers hardness measurements on the as-cast and heat treated samples are given in Table

4.53, and are plotted against measured composition in Figure 4.164. The alloys which were above 50 at.% Pt had hardnesses more than 300HV including the Pt-rich region of the ~16 at.% Pt alloy, while the Al-rich region of the ~16 at.% Pt alloy had a hardness of less than 300HV. Three alloys stood out, having higher hardness (>500HV) compared to the rest. These were: as-cast 53.5 at.% Pt (~583HV) containing ~PtAl and ~Pt₅Al₃; 51 at.% Pt annealed at 1400°C (~774HV), containing ~PtAl and ~Pt₅Al₃; and the Pt-rich region of as-cast ~16 at.% Pt (~570HV), containing ~PtAl and ~Pt₅Al₃. Thus, the ~PtAl and ~Pt₅Al₃ phases were very hard intermetallic phases. The other sample with high hardness was the 81.5 at.% Pt alloy, with hardness of ~458HV, which had (Pt) and both forms of the ~Pt₃Al phases.

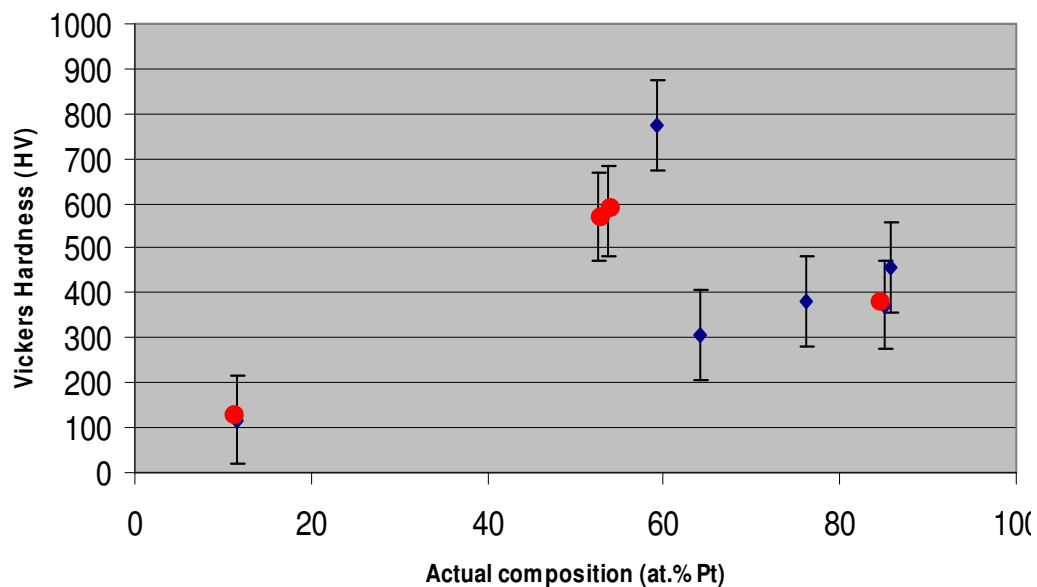


Figure 4.164. Hardness measurements of the Pt-Al alloys under a 5kg load.

Key:
● As-cast
● Heat treated

Table 4.53. Hardness values of as-cast and annealed Pt-Al alloys (HV5).

Nominal Composition (at.% Pt)	Condition	Actual composition (at.% Pt)	Phases	Comments	Hardness	Indentation description
16	as-cast	11.6	(Al), ~Pt ₅ Al ₂₁	Al-rich region	118 ± 35	distorted
16	as-cast	52.6	~PtAl, ~Pt ₂ Al ₃	Pt-rich region	570 ± 95	cracks
51	annealed at 1400°C	59.3	~PtAl, ~Pt ₅ Al ₃	-	774 ± 55	cracks
53.5	as-cast	53.5	~PtAl, ~Pt ₅ Al ₃	-	583 ± 72	cracks
64	annealed at 1200°C	64.2	~Pt ₃ Al(HT), ~Pt ₂ Al(HT)	-	307 ± 54	cracks
72	annealed at 1200°C	76.1	~Pt ₃ Al(HT), ~Pt ₃ Al(LT)	-	382 ± 18	cracks
75	as-cast	85.1	(Pt), ~Pt ₃ Al(HT), ~Pt ₃ Al(LT)	-	374 ± 54	cracks
81.5	annealed at 1400°C	85.8	(Pt), ~Pt ₃ Al(HT), ~Pt ₃ Al(LT)	-	458 ± 18	cracks

5 DISCUSSION

Originally, seven alloys were manufactured and studied (81.5, 75, 72, 67, 64, 53.5 and 51 at.% Pt), and subsequently extra alloys were made to clarify the $\text{Pt}_5\text{Al}_{21}$ phase boundary (16 and 24 at.% Pt) from the Pt-Al phase diagram [1986McA].

The results from all the alloys in the as-cast state were plotted on the solidus of Massalski's diagram [1986McA]. The as-cast alloys showed the primary phases that solidified and the subsequent solidification reactions. Additionally, the phases were confirmed by X-ray diffraction. In general, there was good agreement between the experimental EDS and XRD results in identifying the phases, although the peaks of the $\sim\text{Pt}_3\text{Al}$ and $\sim\text{Pt}_2\text{Al}$ phases were difficult to distinguish.

Figure 5.1 shows a comparison between the as-cast results of this work and the Pt-Al binary system of McAlister and Kahan [1986McA]. A good agreement was found between the as-cast compositions and the solidus line [1986McA]. The analysis for the as-cast eutectic was 56.3 ± 0.5 at.% Pt which is slightly lower than Massalski's value of 57.9 at.% Pt, and the annealed results were 56.4 ± 0.3 at.% Pt at 1400°C, which was very close. Analyses for the Pt-rich β boundary and the Pt_5Al_3 phases were in very good agreement with Massalski [1986McA].

Similarly, Figure 5.2 [1987Oya] shows the plot of the as-cast samples compared with Oya and Mishima's phase diagram [1987Oya]. A good agreement between the solidus line and the as-cast compositions was observed.

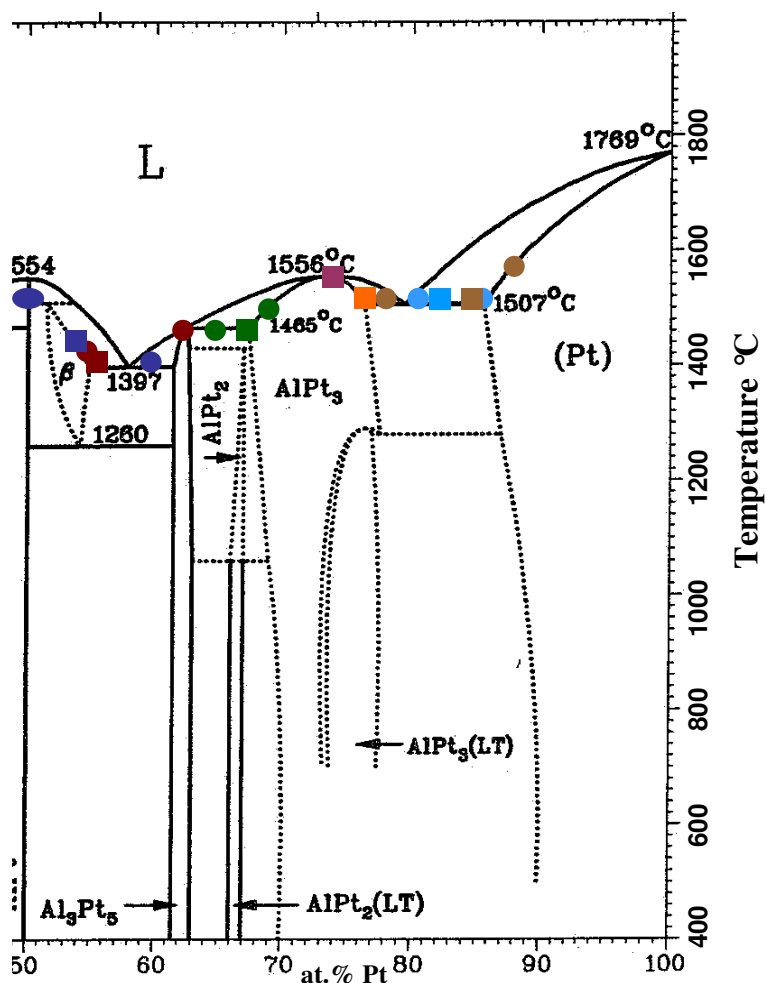


Figure 5.1. Partial (Pt-rich side) Pt-Al phase diagram [1986McA], showing comparison with the as-cast results of this work. The square (■) symbol indicates the overall compositions, and the round (●) symbol indicates the composition of the phases.

Key: ● 81.5 at.% Pt alloys

● 75 at.% Pt alloys

● 72 at.% Pt alloys

● 67 at.% Pt alloys

● 64 at.% Pt alloys

● 53.5 at.% Pt alloy in as-cast condition

● 51 at.% Pt alloys

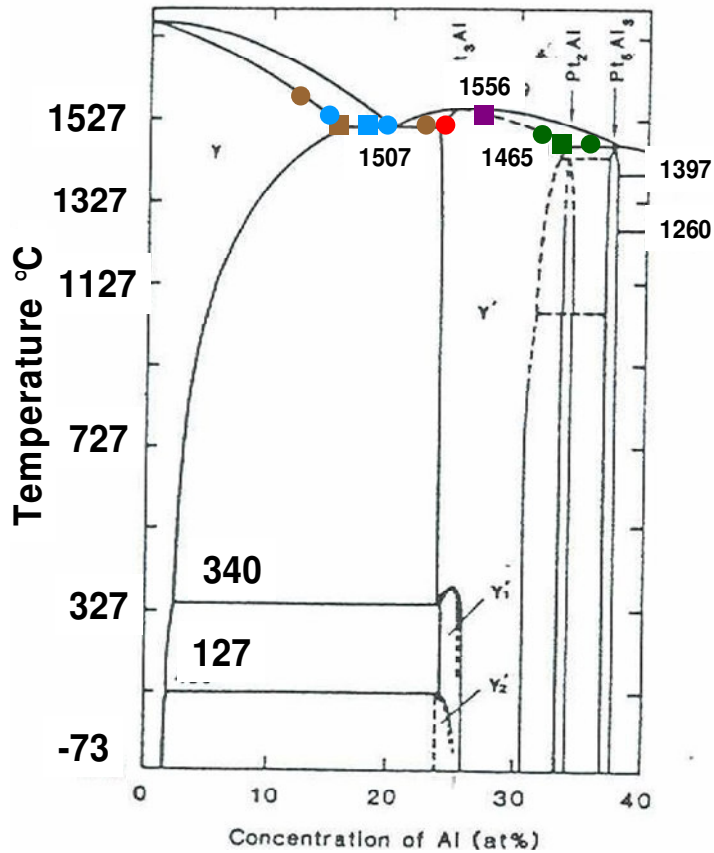


Figure 5.2. Partial Pt-Al phase diagram [1987Oya], showing comparison with the as-cast results of this work. The square (■) symbol indicates the overall composition, and the round (●) symbol indicates the compositions of the phases.

- Key:**
- 81.5 at.% Pt alloys
 - 75 at.% Pt alloys
 - 72 at.% Pt alloys
 - 67 at.% Pt alloys
 - 64 at.% Pt alloys

The results of the annealed samples were compared with McAlister and Kahan's phase diagram [1986McA] in Figure 5.3. A good agreement was found, and most of the phase compositions matched the phase boundaries from McAlister and Kahan's phase diagram [1986McA] as shown in Figure 5.3.

The annealed samples, which were from the Pt-rich side (81.5, 75 and 72 at.% Pt), were compared with Oya and Mishima's phase diagram [1986Oya] as shown in Figure 5.4. The results from the annealed samples did not fit well with the phase boundaries, especially for the (Pt) phase, and instead the (Pt) phase compositions were in the two-phase region. Oya and Mishima's phase diagram [1986Oya] has a wider (Pt) + Pt₃Al two-phase region than McAlister and Kahan's phase diagram [1986McA]. All the tetragonal Pt₃Al phase analyses did not fit well with Oya and Mishima's phase diagram, since the tetragonal phase is only found there at temperatures lower than 340°C.

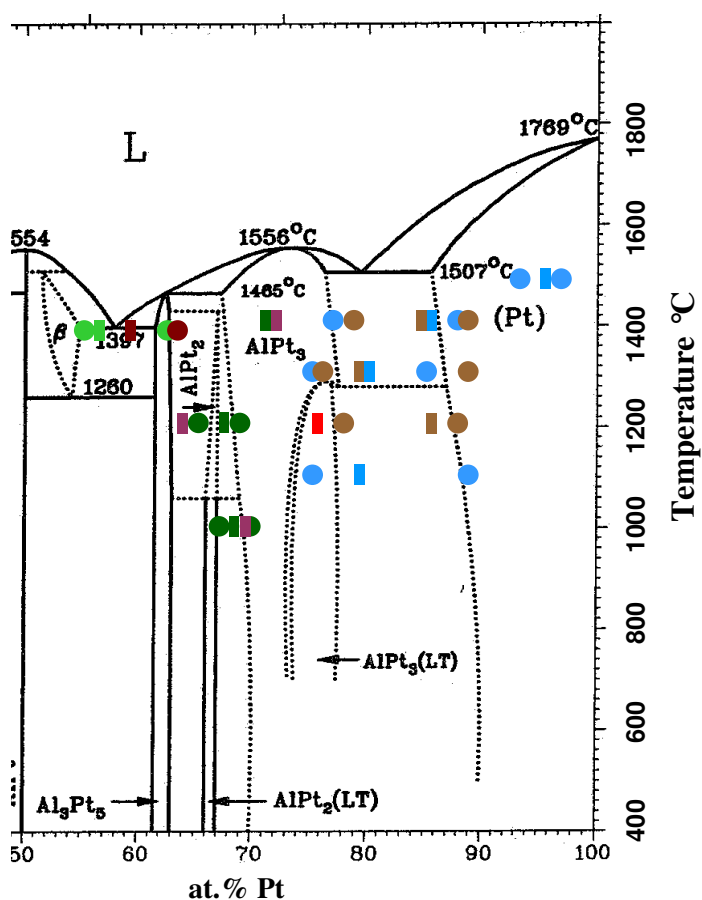


Figure 5.3. Partial (Pt-rich side) Pt-Al phase diagram [1986McA], showing a comparison with the annealed results of this work. The square (■) symbol indicates the overall compositions, and the round (●) symbol indicates the compositions of the phases.

- Key:**
- 81.5 at.% Pt alloys
 - 75 at.% Pt alloys
 - 72 at.% Pt alloys
 - 67 at.% Pt alloys
 - 64 at.% Pt alloys
 - 53.5 at.% Pt annealed at 1400°C
 - 51 at.% Pt alloys

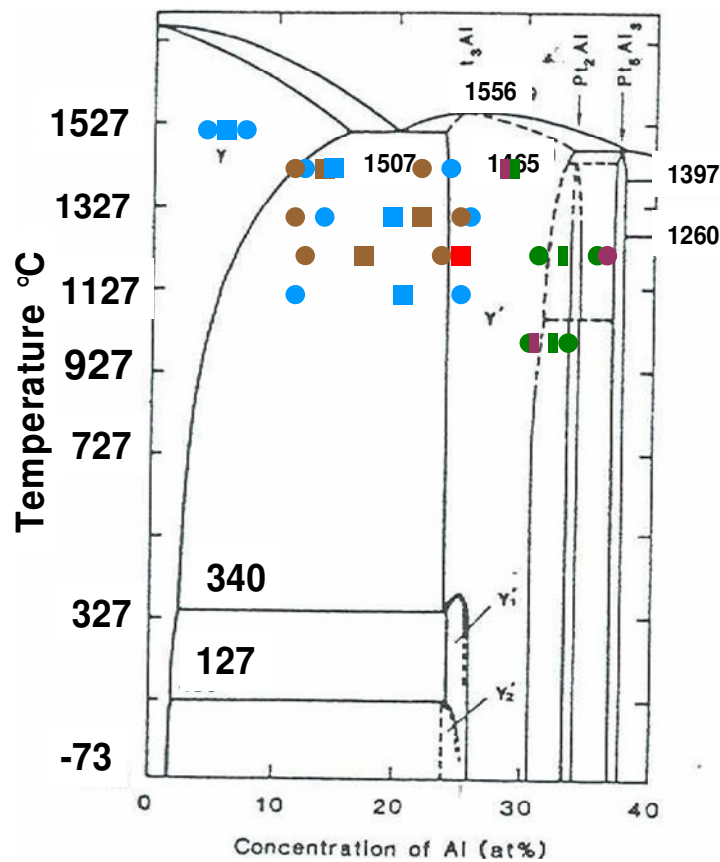


Figure 5.4. Partial Pt-Al phase diagram [1987Oya], showing comparison with the annealed samples of this work. The square (■) symbol indicates the overall composition, and the round (●) symbol indicates the compositions of the phases.

Key:

- 81.5 at.% Pt alloys
- 75 at.% Pt alloys
- 72 at.% Pt alloys
- 67 at.% Pt alloys
- 64 at.% Pt alloys

The 81.5, 75 and 72 at.% Pt alloys were manufactured to clarify the (Pt), cubic and tetragonal $\sim$ Pt₃Al phases and their phase boundaries at selected temperatures (1500°C, 1400°C, 1300°C and 1100°C), as shown in Table 5.1. The as-cast sample contained (Pt) and the cubic and tetragonal forms of $\sim$ Pt₃Al, according to the XRD results, which was consistent with Massalki's phase diagram [1986McA], although there were no twins observed in the microstructure. Twinning would be expected from a martensitic-like transformation, in which

a high temperature phase, which is $\sim\text{Pt}_3\text{Al}_{\text{HT}}$ in this sample, transforms to a low temperature phase which is $\sim\text{Pt}_3\text{Al}_{\text{LT}}$. Thus, twinning is an indication of the tetragonal phase. The compositions for (Pt) and $\sim\text{Pt}_3\text{Al}$ were in the two-phase region of Massalski's phase diagram [1986McA]. The low platinum content in (Pt) was because the light (Pt) phase had dark $\sim\text{Pt}_3\text{Al}$ precipitates within it. The dark phase formed part of the eutectic mixture between the dendrites and analyses included both eutectic phases. This was confirmed by the analysis, which was very close to the eutectic ($\text{L} \rightarrow (\text{Pt}) + \sim\text{Pt}_3\text{Al}$) composition as shown in Figure 6.1. Although both phase analyses included a second component, the errors were apparently acceptable (± 0.9 at.% Pt for (Pt) and ± 0.8 at.% Pt for $\sim\text{Pt}_3\text{Al}$) because the microstructure was homogeneous (Table 5.1).

On the basis of microstructural evidence, it was difficult to distinguish between the eutectic and the eutectoid reactions, although the eutectoid products should be finer, and according to the phase diagram [1986McA], the presence of the tetragonal $\sim\text{Pt}_3\text{Al}$ indicated that there had been a eutectoid reaction.

The microstructure of the 81.5 at.% Pt sample annealed at 1500°C showed partial melting, either because the furnace reached a higher temperature than planned, or that Massalski's [1986McA] temperature is incorrect. However, it is more likely that the furnace reached a higher temperature than planned, especially as the eutectic temperature is only 7°C higher than the targeted temperature. The overall analyses of the sample showed major losses of Al (~ 15 at.%), which placed the composition in the (Pt) phase region of Massalski's phase diagram [1986McA]. According to XRD, the alloy contained (Pt) and both forms of the $\sim\text{Pt}_3\text{Al}$ phases. The (Pt) phase composition had increased by ~ 9.9 at.% Pt, and the $\sim\text{Pt}_3\text{Al}$ phase had increased by ~ 13.8 at.% Pt, with an error of ± 1.5 at.% Pt as shown in Table 6.1, which placed both phases in the (Pt) phase region. The XRD results also possibly indicated some Al_2O_3 . Since the sample had partially melted and lost Al, it could not be used to define the phase boundaries using the EDS compositions, as all the compositions were in the (Pt) phase field as indicated in Figure 5.2.

Table 5.1. EDS analyses of the alloys and their phases.

Alloy	Nominal comp (at.% Pt) and alloy condition	Overall	(Al)	Pt ₅ Al ₂₁	Pt ₈ Al ₂₁	PtAl ₂	Pt ₂ Al ₃	PtAl	Pt ₅ Al ₃	Pt ₂ Al	Pt ₃ Al	(Pt)
Pt: Al:	81.5 As-cast	81.7 ± 1.2 18.3 ± 1.2	-	-	-	-	-	-	-	-	80.2 ± 0.8 19.8 ± 0.8	85.5 ± 0.9 14.5 ± 0.9
Pt: Al:	81.5 1500°C	95.4 ± 1.7 4.6 ± 1.7	-	-	-	-	-	-	-	-	94.0 ± 1.5 6.0 ± 1.5	96.7 ± 0.4 3.3 ± 0.4
Pt: Al:	81.5 1400°C	85.8 ± 1.0 14.2 ± 1.0	-	-	-	-	-	-	-	-	77.1 ± 1.7 22.9 ± 1.7	88.3 ± 0.6 11.7 ± 0.6
Pt: Al:	81.5 1300°C	80.9 ± 5.4 19.1 ± 5.4	-	-	-	-	-	-	-	-	75.9 ± 0.9 24.1 ± 0.9	85.9 ± 0.6 14.1 ± 0.6
Pt: Al:	81.5 1100°C	79.2 ± 2.0 20.8 ± 2.0	-	-	-	-	-	-	-	-	75.8 ± 0.5 24.2 ± 0.5	89.0 ± 0.2 11.0 ± 0.2
Pt: Al:	75 As-cast	85.1 ± 2.5 14.9 ± 2.5	-	-	-	-	-	-	-	-	77.7 ± 1.2 22.3 ± 1.2	87.9 ± 0.1 12.1 ± 0.1
Pt: Al	75 1400°C	86.1 ± 0.8 13.9 ± 0.8	-	-	-	-	-	-	-	-	79.0 ± 1.0 21.0 ± 1.0	88.8 ± 0.8 11.2 ± 0.8

Table 5.1. EDS analyses of the alloys and their phases. (continued)

Alloy	Nominal comp (at.% Pt) and alloy condition	Overall	(Al)	Pt ₅ Al ₂₁	Pt ₈ Al ₂₁	PtAl ₂	Pt ₂ Al ₃	PtAl	Pt ₅ Al ₃	Pt ₂ Al	Pt ₃ Al	(Pt)
Pt: Al:	75 1300°C	79.1 ± 0.01 20.9 ± 0.01	-	-	-	-	-	-	-	-	76.5 ± 0.6 23.5 ± 0.6	89.0 ± 1.8 11.0 ± 1.8
Pt: Al:	75 1200°C	84.6 ± 0.8 15.4 ± 0.8	-	-	-	-	-	-	-	-	77.8 ± 0.3 22.2 ± 0.3	87.9 ± 1.8 12.1 ± 1.8
Pt: Al:	72 As-cast	76.4 ± 0.8 23.6 ± 0.8	-	-	-	-	-	-	-	-	-	-
Pt: Al:	72 1200°C	76.1 ± 0.2 23.9 ± 0.2	-	-	-	-	-	-	-	-	-	-
Pt: Al:	67 As-cast	67.7 ± 0.5 32.3 ± 0.5	-	-	-	-	-	-	65.2 ± 1.7 34.8 ± 1.7	65.2 ± 1.7 34.8 ± 1.7	68.7 ± 0.5 31.3 ± 0.5	-
Pt: Al:	67 1400°C	71.0 ± 0.5 29.0 ± 0.5	-	-	-	-	-	-	-	-	-	-
Pt: Al:	67 1200°C	67.2 ± 1.0 32.9 ± 1.0	-	-	-	-	-	-	-	64.9 ± 4.8 35.1 ± 4.8	68.8 ± 0.2 31.2 ± 0.2	-

Table 5.1. EDS analyses of the alloys and their phases. (continued)

Alloy	Nominal comp (at.% Pt) and alloy condition	Overall	(Al)	Pt ₅ Al ₂₁	Pt ₈ Al ₂₁	PtAl ₂	Pt ₂ Al ₃	PtAl	Pt ₅ Al ₃	Pt ₂ Al	Pt ₃ Al	(Pt)
Pt: Al:	67 1000°C	67.5 ± 0.5 32.5 ± 0.5	-	-	-	-	-	-	-	67.2 ± 0.8 32.8 ± 0.8	69.7 ± 1.2 30.3 ± 1.2	-
Pt: Al:	64 As-cast	73.8 ± 0.6 26.2 ± 0.6	-	-	-	-	-	-	-	-	-	-
Pt: Al:	64 1400°C	71.6 ± 0.4 28.4 ± 0.4	-	-	-	-	-	-	-	-	-	-
Pt: Al:	64 1200°C	64.2 ± 4.0 35.8 ± 4.0	-	-	-	-	-	-	-	-	-	-
Pt: Al:	64 1000°C	69.7 ± 0.1 30.3 ± 0.1	-	-	-	-	-	-	-	-	-	-
Pt: Al:	53.5 As-cast	53.7 ± 1.0 46.3 ± 1.0	-	-	-	-	-	50.0 ± 0.2 50.0 ± 0.2	60.2 ± 1.2 39.8 ± 1.2	-	-	-
Pt: Al:	53.5 1400°C	55.9 ± 0.3 44.1 ± 0.3	-	-	-	-	-	54.2 ± 0.6 45.8 ± 0.6	62.1 ± 0.8 37.9 ± 0.8	-	-	-

Table 5.1. EDS analyses of the alloys and their phases. (continued)

Alloy	Nominal comp (at.% Pt) and alloy condition	Overall	(Al)	Pt ₅ Al ₂₁	Pt ₈ Al ₂₁	PtAl ₂	Pt ₂ Al ₃	PtAl	Pt ₅ Al ₃	Pt ₂ Al	Pt ₃ Al	(Pt)
Pt: Al:	51 As-cast	56.0 ± 3.6 44.0 ± 3.6	-	-	-	-	-	54.1 ± 0.6 45.9 ± 0.6	62.3 ± 1.6 37.7 ± 1.6	-	-	-
Pt: Al:	51 1400°C	59.3 ± 1.3 40.7 ± 1.3	-	-	-	-	-	too small to analyse	63.0 ± 1.5 37.0 ± 1.5	-	-	-
Pt: Al:	16(Pt-rich region) As-cast	52.6 ± 0.6 47.4 ± 0.4	-	-	-	-	43.9 ± 0.3 56.1 ± 0.3	52.4 ± 0.5 47.6 ± 0.5	-	-	-	-
Pt: Al:	16(Al-rich region) As-cast	11.6 ± 2.1 88.4 ± 2.1	0.4 ± 0.6 99.6 ± 0.6	22.1 ± 0.1 77.9 ± 0.1	-	-	-	-	-	-	-	-
Pt: Al:	16 (Layers) As-cast	59.3 ± 1.3 40.7 ± 1.3	-	22.9 ± 0.1 77.1 ± 0.1	29.3 ± 0.1 70.7 ± 0.1	35.2 ± 0.8 64.8 ± 0.8	37.3 ± 1.2 62.7 ± 1.2	-	-	-	-	-
Pt: Al:	16 600°C	17.0 ± 0.1 83.0 ± 0.1	0.0 ± 0.02 100 ± 0.02	21.9 ± 0.1 78.1 ± 0.1	-	-	-	-	-	-	-	-

The 81.5 at.% Pt sample annealed at 1400°C consisted of (Pt) and both forms of $\sim\text{Pt}_3\text{Al}$ according to the XRD results, although no twinning was observed in the microstructure which would be expected from the tetragonal phase. The microstructure had precipitates in the (Pt) dendrites, thus the analyses would have had more Al. The overall composition had increased by 4.1 at.% Pt, and the (Pt) phase composition had increased by ~ 2.8 at.% Pt as shown in Table 5.1. The $\sim\text{Pt}_3\text{Al}$ phase had decreased by ~ 3.1 at.% Pt, with an uncertainty of ± 1.7 at.% Pt, and was at the $\sim\text{Pt}_3\text{Al}$ phase boundary of Massalski [1986McA]. XRD results also possibly showed the presence of aluminium oxide in the sample.

After annealing the 81.5 at.% Pt sample at 1300°C, a similar microstructure to the sample annealed at 1400°C was observed. Relative to the as-cast sample, the overall composition had slightly decreased in Pt (~ 0.8 at.% Pt) with a high error of ± 5.4 at.% Pt, and the (Pt) phase slightly increased by ~ 0.4 at.% Pt, as shown in Table 5.1, and thus was in the two-phase region, with an error of ± 0.6 at.% Pt (Figure 5.3). The dark phase decreased in Pt by ~ 4.3 at.%, with an error of ± 0.9 at.% Pt, which placed it close to the eutectoid composition (Figure 6.3). The very light phase (rim) was too fine for accurate analysis with EDS, but was assumed to be the (Pt) phase. No twinning to indicate a solid state transformation at this temperature was observed in the microstructure.

The 81.5 at.% Pt sample annealed at 1100°C did not show twinning in the microstructure, although the XRD results showed both forms of $\sim\text{Pt}_3\text{Al}$ phases. There were no precipitates in the dendrites, therefore a good analysis was obtained. The overall composition of the sample was in the two-phase region of the phase diagram [1986McA] as expected (Figure 5.3), with an error of ± 2.0 at.% Pt (Table 5.1). The (Pt) had increased by ~ 3.5 at.% Pt with an error of ± 0.2 at.% Pt as shown in Table 5.1. The $\sim\text{Pt}_3\text{Al}$ phase decreased in Pt content by ~ 4.4 at.%, with an error of ± 0.5 at.% Pt, and the composition was in the tetragonal $\sim\text{Pt}_3\text{Al}$ phase field, as shown in Figure 5.2.

Taking all of the 81.5 at.% Pt samples into account, some were useful in defining the phase boundaries, whereas others were not. Analyses of the 81.5 at.% Pt sample annealed at 1500°C were inside the (Pt) phase field, because the sample had partially melted, then lost Al, and so these could not be used to define the phase boundaries. The analyses of (Pt) in 1400°C and 1300°C samples were compromised by the small $\sim$ Pt₃Al precipitates, giving them a higher Al content, whereas those in the sample annealed at 1100°C had no precipitates, giving a good analysis. The latter analysis agreed with Massalski [1986McA]. The analyses of the as-cast and 1100°C samples showed the (Pt) phase boundary to narrow as temperature decreased, and thus agreed with Huch and Klemm [1964Huc], Darling *et al.* [190Dar] and Guex and Feschotte [1976Geu].

The overall analyses for the as-cast nominal 75 at.% Pt sample showed apparent major losses of Al ($\sim$ 10 at.%), and was therefore in the (Pt) and $\sim$ Pt₃Al two-phase region. Since all sample compositions for nominal 75 at.% Pt were incorrect, it is likely that mistakes on weighing had occurred. Based on the microstructure (Figure 4.41), a eutectic of Pt₃Al + (Pt) formed along the grain boundaries, and its composition was in the (Pt) phase region. The $\sim$ Pt₃Al matrix composition was fairly close to the eutectic composition in the two-phase region ((Pt) and $\sim$ Pt₃Al) with a high uncertainty of ± 1.2 at.% Pt (Table 5.1). Although there were no precipitates observed in the microstructure, the contrasts were so close that any second phase was very difficult to distinguish. It is possible that there were precipitates which could not be resolved and gave a higher Pt content. The XRD results confirmed the presence of (Pt) and both forms of $\sim$ Pt₃Al.

Annealing the nominal 75 at.% Pt sample at 1400°C, resulted in only (Pt) and cubic $\sim$ Pt₃Al phases, without tetragonal $\sim$ Pt₃Al, and no twinning was observed in the microstructure. The overall composition was in the two-phase region of Massalski's phase diagram [1986McA]. The (Pt) phase increased by ~ 0.9 at.% Pt, and it was in the (Pt) phase region, and the $\sim$ Pt₃Al increased by ~ 1.3 at.% Pt as indicated in Table 5.1, and was in the two-phase region with an error of ± 1.0 at.% Pt, because the phase was too small to analyse accurately.

After annealing the nominal 75 at.% Pt sample at 1300°C, the sample lost aluminium, and this was evident from the microstructure, since there was a thin outer layer of (Pt) + $\sim$ Pt₃Al around an inner region of $\sim$ Pt₃Al (Figure 4.55) i.e. the outer layer was Al-poor compared to the inner layer. Relative to the as-cast sample, the (Pt) phase in the outer layer had increased by $\sim$ 1.1 at.% Pt, with a high error of $\pm$ 1.8 at.% Pt as shown in Table 5.1, which originated from the $\sim$ Pt₃Al precipitates within it. For the $\sim$ Pt₃Al phase, the Pt content had decreased by 1.2 at.%, with an error of $\pm$ 0.6 at.% Pt (Table 5.1). Thus, the light phase was in the (Pt) phase field and the dark phase was fairly close to the eutectoid composition of Massalski [1986McA] as indicated in Figure 5.3. The XRD showed that the sample contained the (Pt) phase and both forms of the Pt₃Al phases.

A similar microstructure to the sample annealed at 1400°C was observed after annealing the 75 at.% Pt sample at 1200°C, and XRD confirmed that the same phases, (Pt) and cubic $\sim$ Pt₃Al, were present. Relative to the as-cast alloy, there was less than $\sim$ 1.0 at.% Pt composition difference between the overall compositions, and there were negligible differences ($\sim$ 0.1 at.% Pt) between the as-cast and annealed (Pt) and $\sim$ Pt₃Al phase compositions (Table 5.1). The $\sim$ Pt₃Al composition was at the tetragonal $\sim$ Pt₃Al phase boundary of Massalski [1986McA], with an error of $\pm$ 0.3 at.% Pt as shown in Table 5.2, although there was no XRD evidence for the tetragonal $\sim$ Pt₃Al phase, and no twinning. Both phase compositions were at the phase boundaries of the Pt-Al phase diagram [1986McA].

The as-cast 72 at.% Pt sample composition was in the $\sim$ Pt₃Al phase field, within the experimental error of $\sim$ 0.8 at.% Pt as shown in Figure 5.1 [1986McA]. According to the XRD results, there were both high and low temperature $\sim$ Pt₃Al forms, although no twinning was observed in the microstructure.

Comparing as-cast and annealed samples at 1200°C for 72 at.% Pt, the annealed sample lost $\sim$ 0.3 at.% Pt (Table 5.1), and contained both forms of $\sim$ Pt₃Al, which was consistent with the as-cast sample. There was no twinning observed in the microstructure. The overall

composition of the sample was in the tetragonal $\sim\text{Pt}_3\text{Al}$ phase field of Massalski's phase diagram [1986McA] as shown in Figure 5.3, with an error of ± 0.2 at.% Pt.

The 75 at.% Pt sample annealed at 1300°C showed a solid state transformation from cubic to tetragonal $\sim\text{Pt}_3\text{Al}$, since only cubic $\sim\text{Pt}_3\text{Al}$ was found in the sample annealed at higher temperatures ($\sim 1400^\circ\text{C}$), which agreed with the solid state transformation at $\sim 1280^\circ\text{C}$ of McAlister and Kahan [1986McA], and disagreed with that of Oya *et al.* [1987Oya] and Douglas [2006Dou] at 340°C . However, all the 81.5 at.% Pt and 72 at.% Pt samples had tetragonal $\sim\text{Pt}_3\text{Al}$ phase at all selected temperatures. The samples in the Pt-rich side of the Pt-Al system had dark precipitates within the light phase, and this caused inaccurate analyses of the phases. Alternatively, the transformation could have occurred after quenching, if the quenching was not severe enough to retain the higher temperature phases.

The 67 and 64 at.% Pt alloys were selected to clarify the $\sim\text{Pt}_2\text{Al}$ phases and phase boundaries, as well as the transformation temperatures of these phases. The phases were very difficult to distinguish and analyse in this sample, because the contrasts were so similar.

The overall composition of the arc-melted 67 at.% Pt sample was near the $\sim\text{Pt}_3\text{Al}$ boundary as shown in Figure 5.1. The composition of the light phase was in $\sim\text{Pt}_3\text{Al}$ phase region, and the dark phase was in the two-phase region of $\sim\text{Pt}_2\text{Al}$ and $\sim\text{Pt}_5\text{Al}_3$, but with large errors of ± 1.7 at.% Pt, as shown in Table 5.1. The microstructure indicates the formation of $\sim\text{Pt}_2\text{Al}$ (medium contrast phase) by the peritectoid reaction between $\sim\text{Pt}_3\text{Al}$ and $\sim\text{Pt}_5\text{Al}_3$. According to the XRD results, the phases were: $\sim\text{Pt}_3\text{Al}_{\text{HT}}$, $\sim\text{Pt}_2\text{Al}_{\text{HT}}$ and $\sim\text{Pt}_5\text{Al}_3$, which is consistent with Massalski [1986McA].

Annealing the 67 at.% Pt alloy at 1400°C resulted in a slight increase of the overall composition by ~ 3.3 at.% Pt as shown in Table 5.1. XRD showed that the cubic $\sim\text{Pt}_3\text{Al}$ and possibly the tetragonal $\sim\text{Pt}_3\text{Al}$ phases were present.

The 67 at.% Pt sample annealed at 1200°C had laths, which indicated a solid state transformation to a low temperature phase. According to the XRD results, the sample consisted of cubic $\sim\text{Pt}_3\text{Al}$, with high and low temperature $\sim\text{Pt}_2\text{Al}$ phases. These results indicate that the phase transformation occurred at higher temperatures than the 1060°C reported [1986McA]. Alternatively, the transformation could have occurred on quenching. Comparing the as-cast and the annealed samples, there was a negligible difference between the overall compositions (~ 0.6 at.% Pt) of the samples, as shown in Table 5.1. The light phase increased by ~ 0.1 at.% Pt, and was in the $\sim\text{Pt}_3\text{Al}$ phase boundary, and the dark phase decreased by ~ 0.3 at.% Pt, and was in the $\sim\text{Pt}_2\text{Al}$ phase boundary as shown in Figure 5.3.

The microstructure of the 67 at.% Pt sample annealed at 1000°C showed three different contrasts and only two different phase analyses. The light and the medium contrast phases had similar chemical compositions, and the difference in contrast could be a consequence of different orientations. EDS and XRD identified the phases as cubic Pt_3Al and high temperature Pt_2Al . The cubic Pt_3Al phase was consistent between the 1000°C and 1200°C temperatures. Therefore, the results showed that the transformation phase boundary from high temperature Pt_2Al to low temperature Pt_2Al is possibly a slope passing through $\sim 1200^\circ\text{C}$, instead of a horizontal line at $\sim 1000^\circ\text{C}$. The Pt_2Al phase analysis was at the Pt_2Al phase boundary and the Pt_3Al phase analysis was at the Pt_3Al phase boundary as shown in Figure 5.3.

For the 67 at.% Pt samples, the as-cast sample had $\text{Pt}_2\text{Al}_{\text{HT}}$, which was also found at 1000°C, whereas $\text{Pt}_2\text{Al}_{\text{LT}}$ was found at 1200°C. The overall composition of the 1000°C and 1200°C samples were similar ($\sim 67.5 \pm 0.5$ and $\sim 67.2 \pm 1.0$ respectively), although the errors were different, as shown in Table 5.1. To agree with these results, the boundary between the two forms have to be very steep, possibly too steep to be real.

The overall analyses of the as-cast 64 at.% Pt sample showed major losses of Al (~9.8 at.%), as shown in Table 5.1. Due to an increased Pt content, the sample contained $\sim\text{Pt}_3\text{Al}$, and the XRD confirmed the presence of cubic $\sim\text{Pt}_3\text{Al}$ phase (single phase) (Figure 5.1).

After annealing the 64 at.% Pt sample at 1400°C, cubic $\sim\text{Pt}_3\text{Al}$ was present, but the XRD spectrum was of poor quality and it could not be definitely determined that tetragonal $\sim\text{Pt}_3\text{Al}$ was absent. However, both the high temperature $\sim\text{Pt}_2\text{Al}$ and $\sim\text{Pt}_5\text{Al}_3$ phases could also give the “shoulder” to the XRD peaks at $2\theta = \sim 18^\circ$, $\sim 21^\circ$, $\sim 30^\circ$ and $\sim 35^\circ$, and these phases are more likely.

The EDS results for the 64 at.% Pt sample annealed at 1200°C showed major Pt-losses (~9.6 at.%) compared to the as-cast sample, although there were high errors associated with the overall analyses (~4 at.% Pt) as indicated in Table 5.1, which originated from inhomogeneity of the sample. The phases within the sample were difficult to resolve, and so there were also problems in distinguishing the phases to analyse. The XRD results showed that the sample consisted of cubic Pt_3Al and high temperature Pt_2Al phases, but these phases were not identified from the EDS analyses because the sample was difficult to resolve, although the high error implied that the sample was inhomogeneous.

The 64 at.% Pt sample annealed at 1000°C had lost some aluminium, and XRD possibly showed some Al_2O_3 . The overall composition had increased by ~4.1 at.% Pt as shown in Table 5.1. The sample constituted both high and low temperature Pt_2Al phases, although the EDS composition was in the Pt_2Al and Pt_3Al two-phase region, nearer to Pt_3Al with a negligible error (± 0.1 at.% Pt) as shown in Figure 5.3. However, since the XRD spectrum was so complex, it is difficult to state accurately that Pt_3Al phases were not present.

The phases of the alloys with Pt contents of above 60 at.% Pt are given in Table 5.2. The $\text{Pt}_3\text{Al}_{\text{HT}}$ phase was seen in all the samples with suitable compositions, whereas the

Pt₃Al_{LT} phase was only seen in a few samples. Most of this could be explained by the nominal 75 at.% Pt samples having higher Pt contents, probably due to weighing errors

The aim of the 51 and 53.5 at.% Pt alloys was to clarify the presence and the phase boundaries of the β -phase. Additionally, verification of the formation temperature and its eutectoid decomposition was sought. Massalski [1986McA] gave a decomposition temperature of 1260°C.

The XRD results showed the presence of both $\sim$ PtAl and Pt₅Al₃ phases in the as-cast 53.5 at.% Pt sample. These phases confirmed the existence of the β -phase, because they are the eutectoid decomposition products of the β -phase but the β -phase itself was not observed in the as-cast sample, as it had already decomposed.

The microstructure of the 53.5 at.% Pt sample annealed at 1400°C was complex because of the solid state transformation of $\beta \rightarrow \text{PtAl} + \text{Pt}_5\text{Al}_3$ which occurred at lower temperatures. According to the solidification sequence interpreted from the microstructure, the β -phase formed peritectically from $L + \text{PtAl} \rightarrow \beta$, and subsequently decomposed to $\sim$ PtAl and $\sim$ Pt₅Al₃.

The as-cast 51 at.% Pt sample lost $\sim$ 5 at.% Al. The dark primary phase had a composition of $\sim$ 54.1 at.% Pt which would be β rather than $\sim$ PtAl, although the XRD results only showed the presence of the $\sim$ PtAl and $\sim$ Pt₅Al₃ phases. This indicated that the β -phase decomposed, and close inspection of the dark phase suggested that there were two fine phases, which was an indication of decomposed β . Gold had been observed in the eutectic as pure gold, but its presence did not appear to alter the phases which were expected from the sample.

Table 5.2. Possible phases found in the selected compositions of this work.

Nominal Composition (at.% Pt)	Actual composition (at.% Pt)	Phases
81.5 as-cast	81.7 ± 1.2	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
81.5 at 1500°C	95.4 ± 1.7	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
81.5 at 1400°C	85.8 ± 1.0	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
81.5 at 1300°C	80.9 ± 5.4	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
81.5 at 1100°C	79.2 ± 2.0	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
75 as-cast	85.1 ± 2.5	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
75 at 1400°C	86.1 ± 0.8	(Pt), Pt ₃ Al _{HT}
75 at 1300°C	79.1 ± 0.01	(Pt), Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
75 at 1200°C	84.6 ± 0.8	(Pt), Pt ₃ Al _{HT}
72 as-cast	76.4 ± 0.8	Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
72 at 1200°C	76.1 ± 0.2	Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
67 as-cast	67.7 ± 0.5	Pt ₃ Al _{HT} , Pt ₂ Al _{HT} , Pt ₅ Al ₃
67 at 1400°C	71.0 ± 0.5	Pt ₃ Al _{HT} , Pt ₃ Al _{LT}
67 at 1200°C	67.2 ± 1.0	Pt ₃ Al _{HT} , Pt ₂ Al _{HT} , Pt ₂ Al _{LT}
67 at 1000°C	67.5 ± 0.5	Pt ₃ Al _{HT} , Pt ₂ Al _{HT}
64 as-cast	73.8 ± 0.6	Pt ₃ Al _{HT}
64 at 1400°C	71.6 ± 0.4	Pt ₃ Al _{HT} , possibility of Pt ₃ Al _{LT} , Pt ₂ Al, Pt ₅ Al ₃
64 at 1200°C	64.2 ± 4.0	Pt ₃ Al _{HT} , Pt ₂ Al _{HT} ,
64 at 1000°C	69.7 ± 0.1	Pt ₂ Al _{HT} , Pt ₂ Al _{LT}

After annealing 51 at.% Pt at 1400°C, the sample had partially melted, and re-solidified with a different primary phase from the as-cast sample, and there was a eutectic of $\sim$ PtAl and $\sim$ Pt₅Al₃. Again, close inspection of the dark phase showed that it comprised two fine phases, and the β -phase was assumed to have decomposed eutectoidally to form $\sim$ PtAl and $\sim$ Pt₅Al₃ at a lower temperature.

The 53.5 and 51 at.% Pt samples illustrated that the β -phase formed from a liquid-reaction and then decomposed eutectoidally on cooling, which confirms the latest work by Prins *et al.* [2005Pri]. The β -phase could not be retained, and decomposed at lower temperatures to form very fine $\sim$ PtAl + $\sim$ Pt₅Al₃.

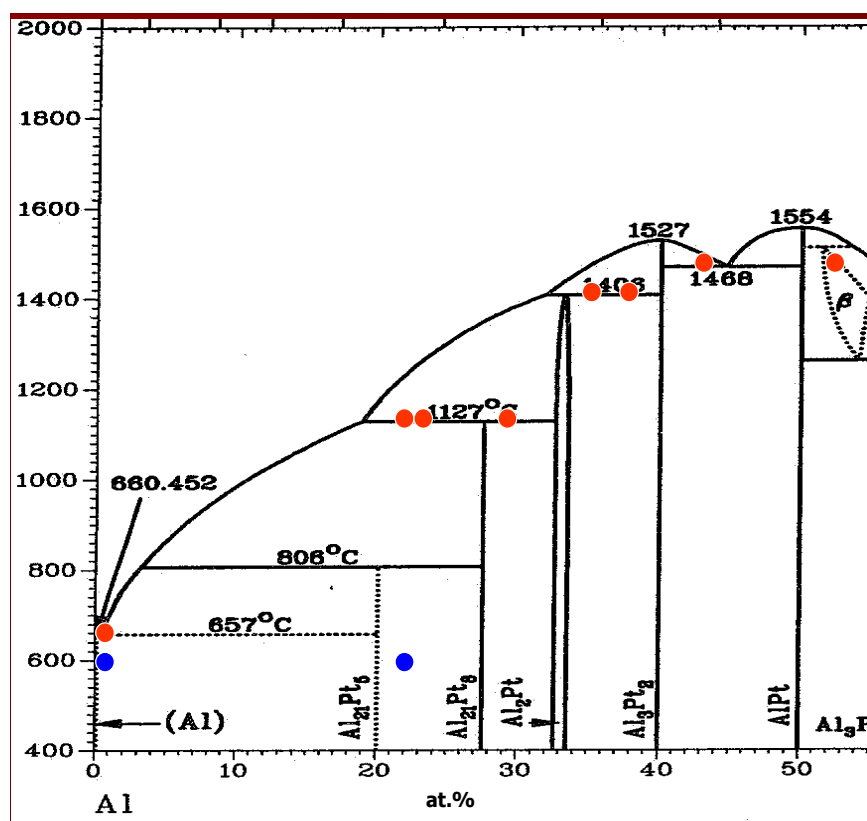


Figure 5.5. Partial (Al-rich side) Pt-Al phase diagram [1986McA], showing comparison with the as-cast and annealed results of this work.

Key: ● As cast 16 at.% Pt

● Heat treated 16 at.% Pt

The aim of the 16 and 24 at.% Pt alloys was to determine the $\sim\text{Pt}_5\text{Al}_{21}$ phase boundaries, since the phase had been shown as a line compound with uncertainty [1986McA].

The 24 at.% Pt sample disintegrated during casting. X-ray diffraction showed the presence of the $\sim\text{Pt}_6\text{Al}_{21}$, $\sim\text{Pt}_8\text{Al}_{21}$ and (Al) phases. There was no $\sim\text{Pt}_5\text{Al}_{21}$ phase in the XRD database [2005ICD], and all the peaks were well matched by the present phases. Thus, $\sim\text{Pt}_6\text{Al}_{21}$ and $\sim\text{Pt}_5\text{Al}_{21}$ are possible different interpretations of the same phase. However, Piatti and Pellegrini [1980Pia] reported that $\text{Pt}_6\text{Al}_{21}$ was metastable, and slowly transformed to $\text{Pt}_5\text{Al}_{21}$. Thus, the phase observed was probably the metastable phase.

The microstructure of the as-cast 16 at.% Pt sample was very complex, with local differences in composition which resulted in different solidification paths. A cascade of peritectic reactions was observed from the microstructure and the phases were confirmed by XRD, and the observed phases were: $\sim\text{PtAl}$, $\sim\text{Pt}_2\text{Al}_3$, $\sim\text{PtAl}_2$, $\sim\text{Pt}_8\text{Al}_{21}$, $\sim\text{Pt}_6\text{Al}_{21}$ and (Al). However, the compositions of the phases had high errors (Table 6.1), and were not exactly in agreement with the phase diagram [1986McA], and this was because small phases were analysed, and the analyses included surrounding phases. However, the $\sim\text{Pt}_5\text{Al}_{21}$ was not observed in the sample, but instead the $\sim\text{Pt}_6\text{Al}_{21}$ phase was found, which was previously reported by Piatti and Pellegrini [1980Pia] as a metastable phase. Thus, the line compound, previously reported to be $\sim\text{Pt}_5\text{Al}_{21}$ was shown to be the reported metastable $\sim\text{Pt}_6\text{Al}_{21}$ instead.

6 CONCLUSIONS

There were difficulties in interpreting the high Pt content phases due to similar contrasts in BSE in the SEM and overlapping peaks in the XRD. The results in the Pt-rich side, were generally consistent with Massalski's Pt-Al phase diagram [1986McA], and disagreed with Oya's phase diagram [1987Oya]. The samples had the tetragonal Pt_3Al phase (by a solid phase transformation) at higher temperatures than reported by Oya and Mishima's phase diagram [1987Oya], since they reported the tetragonal Pt_3Al phase to be below 340°C , although the quenching rates might not have been enough.

Samples in the region 75 to 81.5 at.% Pt consisted of (Pt) and both forms of $\sim\text{Pt}_3\text{Al}$ phases, and the samples in the region around 72 at.% Pt consisted of cubic and tetragonal $\sim\text{Pt}_3\text{Al}$ phases, therefore a displacive or martensite-type transformation had occurred. The (Pt) phase boundary, which was drawn from the as-cast and the sample annealed at 1100°C , narrowed as temperature decreased, thus the (Pt) phase field width decreased as temperature decreased which agreed with Huch and Klemm [1964Huc], Darling *et al.* [190Dar] and Guex and Feschotte [1976Geu]. The $\sim\text{Pt}_3\text{Al}$ phase boundary, which was drawn from the samples annealed at 1400°C , 1300°C and 1100°C became narrower as temperature decreased, thus increasing the two-phase field width ((Pt) and $\sim\text{Pt}_3\text{Al}$) and decreasing the tetragonal $\sim\text{Pt}_3\text{Al}$ phase field width.

The $\sim\text{Pt}_2\text{Al}$ phase was observed in the 64 to 67 at.% Pt region. A displacive or martensite-type transformation occurred at 1200°C , which was at higher temperatures than the previously reported 1060°C [1986McA], and the resulting microstructure was twinned, with the twins observed in the dendrites. The phase boundary between the high and the low temperature forms was a very steep slope. A peritectoid reaction ($\sim\text{Pt}_5\text{Al}_3 + \sim\text{Pt}_3\text{Al} \rightarrow \sim\text{Pt}_2\text{Al}$) was confirmed from the as-cast 67 at.% Pt results. Phase boundaries for $\sim\text{Pt}_2\text{Al}$ were drawn from the 67 at.% Pt sample, and the results agreed with Massalski [1986McA].

The 51 and 53.5 at.% Pt alloys had microstructural evidence of the β -phase which decomposed eutectoidally to form the $\sim\text{PtAl}$ and $\sim\text{Pt}_5\text{Al}_3$ phases. The peritectic reaction ($\text{L} + \sim\text{PtAl} \rightarrow \beta$) was identified from the 53.5 at.% Pt sample annealed at 1400°C, which partially melted.

The $\sim\text{Pt}_5\text{Al}_{21}$ phase was not present in the XRD database [2005ICD], and instead the $\sim\text{Pt}_6\text{Al}_{21}$ phase at similar phase composition was observed. However, $\sim\text{Pt}_6\text{Al}_{21}$ has been reported as metastable, which slowly transforms to $\sim\text{Pt}_5\text{Al}_{21}$ [1980Pia].

Through hardness measurements, $\sim\text{PtAl}$ and $\sim\text{Pt}_5\text{Al}_3$ were identified as hard phases (>500HV), and the Pt_3Al phase had a hardness >400HV.

7 RECOMMENDATIONS FOR FUTUREWORK

- ❖ A better technique is required to distinguish between the different Pt_3Al and Pt_2Al phases. This could be TEM, a high-resolution imaging technique capable of directly viewing crystal defects such as dislocations, stacking faults or grain boundaries. It can also obtain the structures of selected areas by selected area diffraction, which would aid the identification of the finer phases. TEM can image microstructural features to the atomic level and can be used to obtain crystallographic information of submicron-sized regions with resolutions of 0.1 to 0.2 nm. An important requirement for TEM analyses is that the specimen must be thinned to $\sim 0.3 \mu\text{m}$ to allow electrons to transmit, to enable features to be seen. The TEM analyses will therefore assist to confirm the existence of the phase crystal structures present, and identify defects which were not picked up by the HRSEM imaging technique, such as twinning. Analyses will further clarify the crystallographic information given by the X-ray diffraction technique.

- ❖ It was planned that high temperature DTA would be undertaken as part of this investigation, but there were problems in installing the machine. During Differential Thermal Analyses (DTA), temperature differences between the sample and the thermally inert material are measured during heating or cooling conditions. The DTA curve records these differences during reactions in the sample, showing thermal effects as deviations from the zero line. Changes in the sample where a reaction requires heat (endothermic) which include:
 - Structural decomposition
 - Melting, evaporation and sublimation
 - Structural transformations (heating)

can be detected relative to the inert reference.

Changes in the sample where a reaction releases heat (exothermic) which include:

- Oxidation
- Reconstruction of the crystal structure
- Structural transformation (cooling)

can be detected relative to the inert reference.

Therefore, the DTA can assist to confirm the phase transformation temperatures, and indicate if the transformation reactions are exothermic or endothermic.

- ❖ In order to compare the quenched β -phase with β -phase that had time to decompose, samples should be annealed below that transformation temperature.

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APPENDIX A (Publications during the course of this M.Sc. dissertation)

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A STUDY OF THE Pt_3Al , Pt_2Al and β PHASES IN THE Pt-Al SYSTEM

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Mintek is developing Pt-based alloys for applications in high temperature and corrosive environments¹. Simultaneously, a thermodynamic database is also being developed, based on the Pt-Al-Cr-Ru system¹. There are two versions of the Pt-Al phase diagram concerning the transformation temperatures of the Pt_3Al phase^{2,3}. The (Pt) and Pt_3Al phase widths are also reported differently^{2,3}. Additionally, more information on the high temperature form of the Pt_2Al and β is needed.

The alloy compositions were selected to lie in the (Pt) + Pt_3Al (~81.5 at.% Pt), Pt_3Al + Pt_2Al (~67 at.% Pt), and the high temperature β phase (~53.5 at.% Pt) fields. Samples were made from elements of at least 99% purity, and were arc-melted under argon. One alloy of each composition was studied in the as-cast condition and the rest were annealed at different temperatures, for phase boundary studies at different temperatures. Samples were prepared metallographically using OPS polishing and studied in a JEOL 840A SEM and FEI Nova NanoSEM, with EDS. XRD studies are underway.

For the (Pt) + Pt_3Al samples, the as-cast and 1400°C samples were difficult to resolve due to the fine nature of the microstructures arising from the eutectoid reaction. However, a two-phase structure was clearly seen after annealing at 1100°C (Fig. 1a), although the analyses might be inaccurate because of the phase's fineness. The (Pt) phase boundary agrees with McAlister and Kahan², whereas the Pt-rich Pt_3Al boundary is less Pt-rich, and indicates that both phases become narrower at lower temperatures, which would be expected (Table 1).

In the Pt_3Al + Pt_2Al region, the as-cast sample was two-phase, but barely resolvable, as was the sample annealed at 1400°C. The 1000°C sample had a clearer microstructure (Fig. 1b). The phase analyses show that the Pt_3Al phase narrows with decreasing temperature, whereas the Pt_2Al phase boundary is constant.

None of the ~53.5 at.% Pt alloys retained high temperature β , and the as-cast sample had a two-phase structure indicative of a eutectic or eutectoid transformation (Fig. 2a). The sample annealed at 1400°C had a higher Pt content, and the microstructure was different (Fig. 2b). The light phase was a primary one, and the dark region (54.2 ± 0.6 at.% Pt) was actually $PtAl$ + Pt_5Al_3 , the same as decomposed β . Thus, the annealed sample had been partially liquid on annealing (which might have allowed for Al loss) and on cooling formed primary Pt_5Al_3 and eutectic Pt_5Al_3 + β . The latter would have then decomposed subsequently. Therefore, the eutectic reaction is above 55.9 ± 0.3 at.% Pt, and at a lower Pt content than reported².

Mintek, NRF/DST and the PDI are thanked for their support.

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Table 1. Phase analyses for the ~81.5 at.% Pt alloys.

Condition	Phase	Pt (at.%)	Al (at.%)
As-cast	(Pt)	85.5 ± 0.9	14.5 ± 0.9
	Pt_3Al	80.2 ± 0.8	19.8 ± 0.8
1100°C	(Pt)	89.0 ± 0.2	11.0 ± 0.2
	Pt_3Al	75.9 ± 0.5	24.2 ± 0.5

Table 2. Phase analyses for the ~67 at.% Pt alloys.

Condition	Description	Pt (at.%)	Al (at.%)
1200°C	Pt_3Al	68.8 ± 0.2	31.2 ± 0.2
	Pt_2Al	67.2 ± 1.1	33.0 ± 1.1
1000°C	Pt_3Al	69.7 ± 1.2	30.3 ± 1.2
	Pt_2Al	67.2 ± 0.8	32.8 ± 0.8

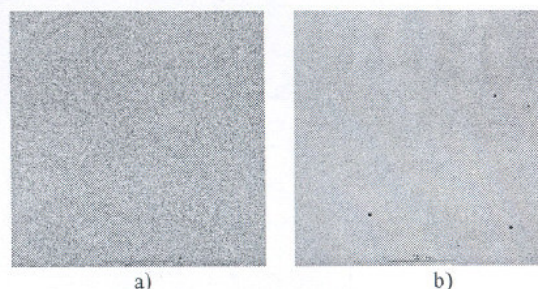


Fig. 1. SEM BSE images a) ~81.5 at.% Pt showing light (Pt) with darker Pt_3Al ; and b) (~67 at.% Pt showing light Pt_3Al with darker Pt_2Al .

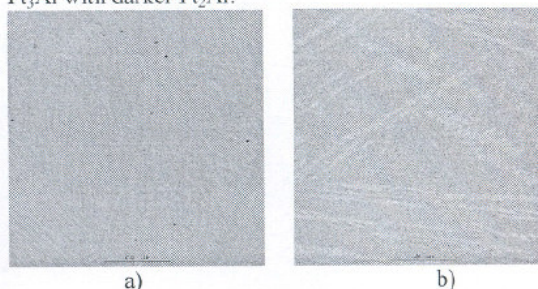


Fig. 2. SEM BSE images of ~53.5 at.% Pt with Pt_5Al_3 (light) and $PtAl$ (dark): a) As-cast and b) after annealing at 1400°C.

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ANOMALIES AND PITFALLS IN PHASE ANALYSES USING BSE

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Backscattered electron imaging (BSE) is widely used in characterising different phases in samples because the contrast depends on the average atomic number. However, what is less known is that the backscatter coefficient versus atomic number is not a smooth curve¹, but is irregular. As the atomic number increases, the curve levels off giving reduced differences in intensity, so that it becomes increasingly difficult to distinguish between phases of alloys with high atomic number components¹. This can be seen working with PGMs². The object of this work is to demonstrate some examples where the contrasts in BSE were not sufficiently different, leading to difficulties in interpretation.

There are many examples where orientation affects the contrast in BSE. This was clearly shown by Biggs et al in alloys containing the Pt₃Al phase³. A martensitic transformation had sheared the resulting phase, without changing the composition, and the twinning of the martensitic phase was clearly seen by the different contrasts in BSE. A similar example is shown in Fig. 1 in a Pt-Al alloy, where the Pt₃Al phase (analysed at 67.1±1.0 at.% Pt) is twinned and shows two different contrasts, and the Pt₃Al (analysed at 68.8±0.2 at.% Pt) was not twinned. The effect is deduced to arise from a surface relief and/or channelling.

Another pitfall is where phases have been pulled out on sample preparation leaving a hole with some or none of the original phase in the hole to lull the unwary worker into interpreting the hole as an actual phase. This emphasises the advantage of utilizing both SEI and BSE imaging. Fig. 2 shows a situation where brittle oxides have been mostly removed on sample preparation, leaving holes in a Ni₃₈:Ru₄₂:Y₂₀ (at.%) alloy. A similar trap for the uninitiated originates from underlying holes or pores yielding different contrasts to the material above. This phenomenon is shown in Fig. 3 for a Ni₁₆:Ru₄₈:Y₃₆ alloy (at.%) where the two darkest phases are actually artefacts due to the holes.

Thus it must be realised that although BSE imaging is a powerful tool, there are pitfalls, especially for higher atomic number samples and those with uneven surfaces.

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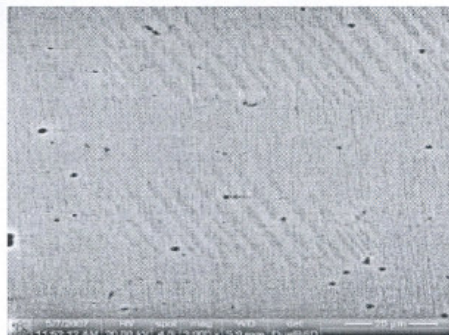


Fig. 1.



Fig. 2.

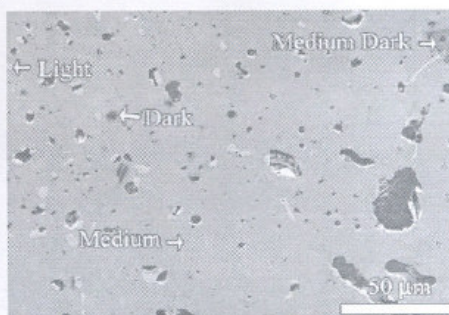


Fig. 3.

Fig. 1. BSE image of nominal 67 at.% Pt-Al alloy heat treated at 1200°C for 1000h, water quenched: twinned Pt₃Al and non twinned Pt₃Al.

Fig. 2. BSE image of Ni₃₈:Ru₄₂:Y₂₀ in the as-cast condition: (Ru) (light); ~YNi₃ (medium); YNi₄ (medium dark 1); YNi₅ (medium dark 2), and pulled-out Y₂O₃ (dark).

Fig. 2. BSE image of Ni₁₆:Ru₄₈:Y₃₆ annealed at 1200°C for 1000h: (Ru) (light); ~YNi₂ (medium); apparent phases medium dark and dark caused by holes under and at the surface.

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