2. LITERATURE REVIEW

2.1 WC-Co sintered alloys

Cemented carbides were developed in the 1920’s for the production of wire drawing dies [1-4]. WC based cemented carbides are hard and brittle materials used mainly for cutting tools, structural components, rock drilling inserts and wear parts and are the most widely used composite material [1-4].

2.1.1 Manufacture of WC-Co

WC-Co alloys are produced by powder metallurgy techniques. This involves a sequence of manufacturing activities, which are all important to the final product [1]. The final product consists of hard and abrasion resistant particles of tungsten carbide cemented by tough metallic cobalt [1,4]. Figure 2.1 shows a typical microstructure of the final product of a WC-12wt%Co grade. WC is produced by mixing tungsten metal and carbon black, which is then carburized at temperatures between 1400 and 2650ºC [1,2,4]. The cobalt powder must be very fine to allow excellent dispersion in the tungsten carbides. The last stage of the manufacturing process is sintering which is done at high temperatures; from around 1350ºC for alloys containing around 30 percent cobalt to around 1650ºC for less cobalt content alloys [1]. Particles of tungsten carbides partly dissolve in the molten cobalt during sintering [1]. During sintering porosity must be eliminated as this affects the mechanical and physical properties of the alloy. Figure 2.2 is a schematic flow chart of how WC-Co cemented carbides is produced.

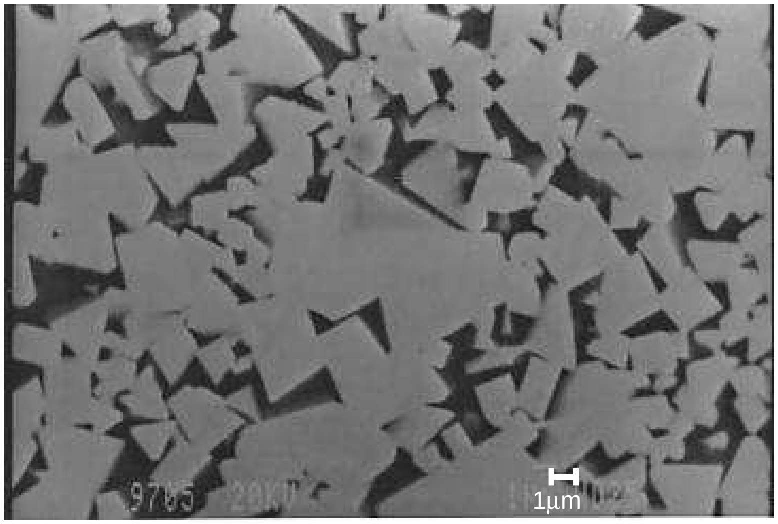


Figure 2.1: Typical microstructure of WC-12wt%Co. The grey angular particles are hard WC grains and the dark material between the WC grains is Co.

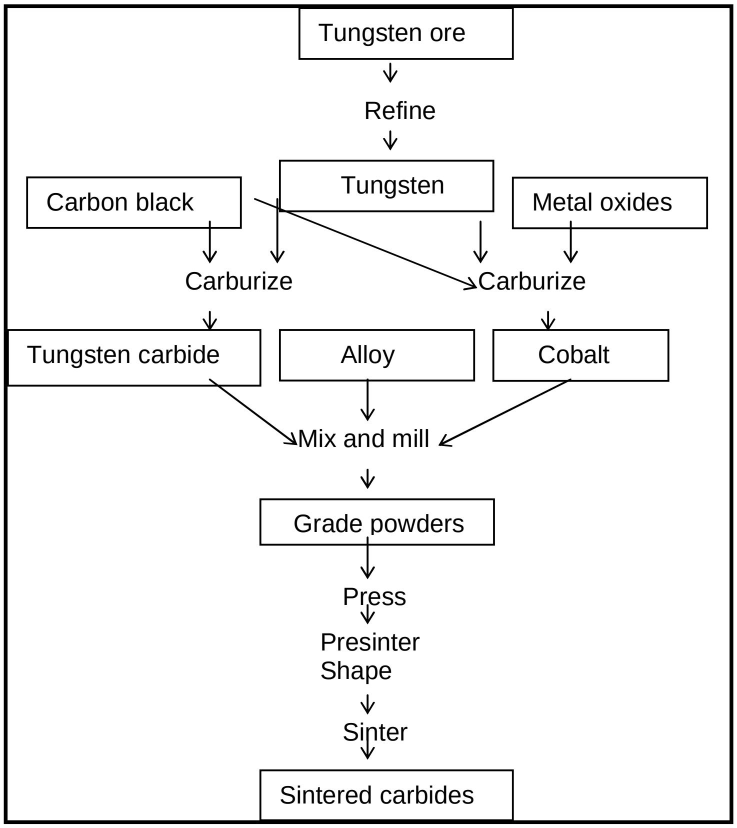


Figure 2.2: Schematic flow chart for the manufacture of WC-Co alloys [1].

2.1.2 Properties of WC-Co

The properties of WC-Co cemented carbides depend mainly on the WC grain size, Co weight percent and ability of Co to wet WC. They have, amongst others, excellent properties of high hardness with good toughness and wear resistance [1-5]. This section summarizes the properties and how they are affected by the composition and microstructure.

2.1.2.1 Cobalt binder phase and mean free path

The cobalt structure is closed-packed hexagonal (ε) at temperatures below approximately 400°C and face-centered cubic (α) at temperatures above 400°C [3,5]. The cobalt in the WC-Co components is commonly found at its low temperature phase (hcp - brittle). The ε-Co phase is more brittle and more susceptible to crack formation [3]. Other binder phases can be used with WC but cobalt is usually preferred mainly because of its excellent wetting of WC and its ductility that so allows some plastic deformation in the structure [3,5].

The mean free path is known as the measure of the mean distance between WC grains i.e. mean thickness of cobalt layers between the WC grains [6,7]. The mean free path increases with the cobalt content. Increasing both the cobalt content and the mean free path lowers the hardness of the WC-Co alloys but improves the fracture toughness [4,6-9]. The relationship between the mean free path, mean WC grain size and the hardness is given in the equations below:

$\mathrm{H}_{WC-Co} = 4100[22.3(\lambda / 2d^{1/2} + 1]^{-1} - 130$ [10],

H_{WC-Co} = Hardness of WC-Co

λ = Mean free path in Co,

d = Mean WC grain size

2.1.2.2 Tungsten carbide

WC grains in WC-Co are single crystals with a closed-packed hexagonal structure [3,4,5]. WC is a hard phase with high young modulus [3]. The hardness of the WC-Co alloys varies from below 1300HV to above 2300HV, which depends mainly on the WC grain size, which may range from ultra fine (<0.5µm) to extra coarse (>5.0µm) [1,2]. The hardness of WC varies from 1300HV to 2300HV depending on the crystal orientation. The finer the grains, the harder the alloy. Another phase that may form in cemented carbides is W_2C, which is harder than WC [3, 11]. The W_2C phase is formed during sintering at high temperatures if the material is carbon deficient and can easily be produced by decarburization of tungsten [3].

2.1.2.3 General properties

Figure 2.3 by Mills [12] is a schematic ternary diagram of how different phases contribute to the properties of cemented carbides. Some cemented carbide grades can contain other carbides like TiC, NbC and TaC, which are mainly used for cutting steels. The metal binder contributes with its ductile behavior to improve the toughness of cemented carbides while hardness of the WC contributes to the high wear resistance [4].

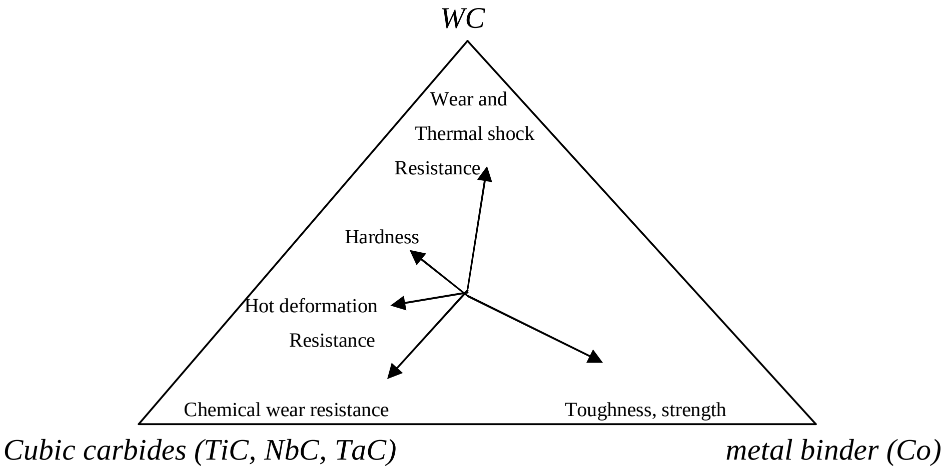


Figure 2.3: Ternary diagram showing effect of composition on mechanical, chemical and thermal properties of cemented carbides [12].

Fracture toughness is another important property of materials, which depends on the microstructure. It is established that fracture toughness increases with increasing cobalt content, increasing WC grain size and increasing mean free path [6,9,11]. In general high wear resistance is achieved by increasing the hardness of the alloy [7,13,14].

2.1.2.4 Thermal properties of WC-Co alloys.

WC-Co hardmetals have good thermal conductivity, which is approximately twice that of unalloyed steel [3]. Thermal conductivity of unalloyed steel ranges from 20 to 48 W/mK. Thermal properties directly influence the thermal shock characteristics of the material. Their thermal properties vary based on their composition and structure. In general thermal properties of cemented carbides vary according to the Co content and WC grain size. Grades with large WC grain size are known to have a higher thermal conductivity than grades with fine grain size [3]. Typical values of thermal conductivity range from 50 to 120 W/m.K for WC-Co alloys. Figure 2.4 is a graph of thermal conductivity versus Co content; the values are scattered because thermal conductivity does not depend only on Co content but also with the WC grain size [1]. Thermal expansion is another important property, which increases when increasing Co content and temperature (see Figure 2.5).

Table 2.1 lists thermal properties of WC, Co and hardmetal grades that differ in cobalt content and WC grain size [2]. The rock drilling grade has a higher thermal conductivity than the other 2 grades, implying that heat travels faster through this grade.

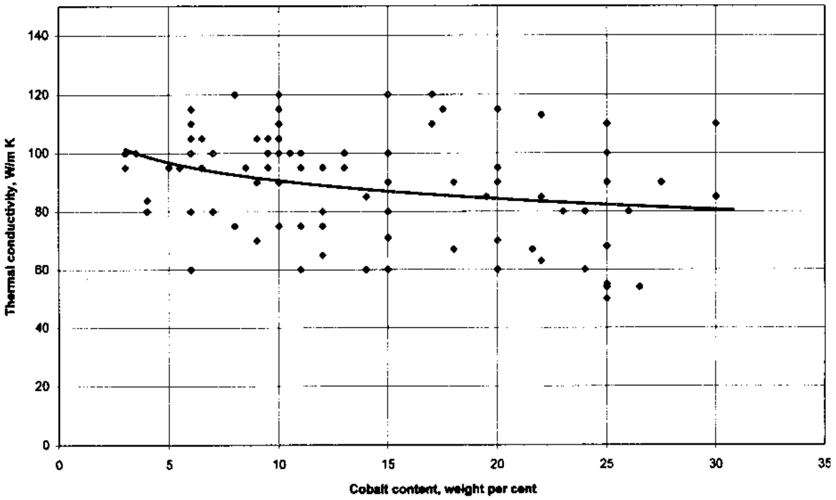
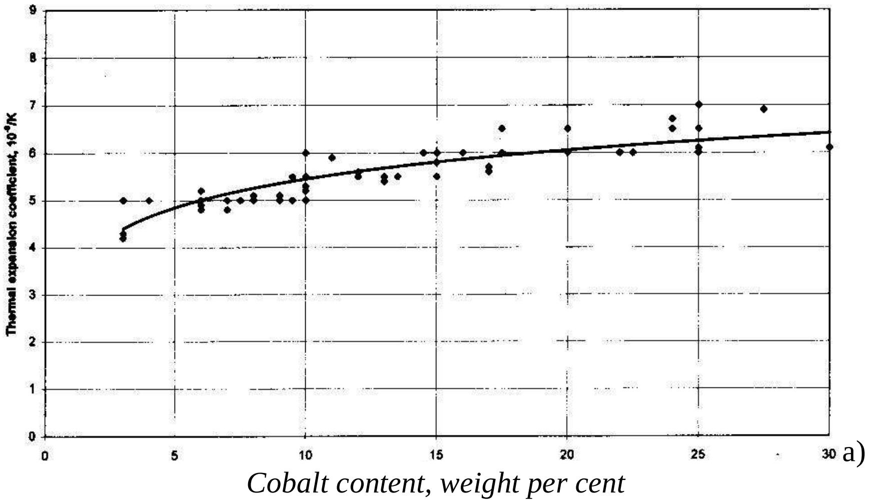


Figure 2.4: Thermal conductivity of WC-Co hardmetals [1].



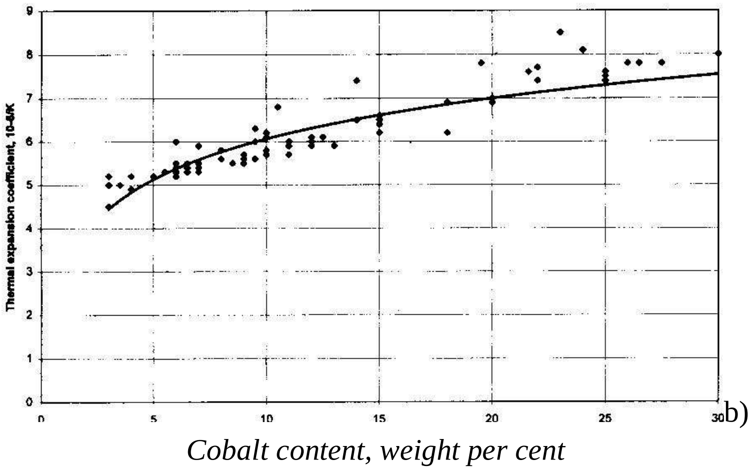


Figure 2.5: Thermal expansion coefficient of WC-Co hardmetals. a) at room temperature and b) at 20-800℃. Typical values ranges from 4.5 to 8.5 $\times 10^{-6}$/K between 0 and 800° [1].

Table 2.1: Thermal properties of WC, Co and different WC-Co grades. i) rock drill grade has 6wt%Co and 5µm WC, ii) hot rolling grade has 15wt%Co and 4µm WC, and iii) a multi purpose grade with 11wt%Co and 2,5µm WC [2].

	Density g/cm^{-3}	**Thermal expansion coefficient (1x10e-6/K)**	**Thermal conductivity (W/mK)**	**Heat capacity (J/gK)**
Pure WC	15.7	3.8	170	0.18
Pure Co	8.9	12.5	100	0.42
i) Rock drill grade	14.8	4.9	122	0.22
ii) Hot rolling grade	13.9	5.8	106	0.24
iii) Multi purpose grade	14.4	5.6	95	

Table 2.1 confirms that the thermal expansion coefficient increases with increasing Co content and that the thermal conductivity does not depend only on Co content.

2.2 Abrasive wear of WC-Co alloys

The abrasive wear of WC-Co alloys has been studied for many years. Abrasive wear may involve plastic flow and/or brittle fracture [2,14]. Plastic flow implies removal of material by plastic deformation, which can be defined as ploughing [14]. Plastic deformation is usually followed by severe fragmentation of WC grains that is accompanied by gradual extrusion of the cobalt binder [15,16]. During wear by brittle fracture the abrasives slide over the WC-Co sample without severe indentation of the surface [17].

In a study by Larsen-Basse [16] on the sliding wear of WC-Co alloys it was suggested that Co binder extrusion is an important mechanism in abrasive wear of cemented carbides. The author explained that binder extrusion weakens the surface layer since it results in micro-cracking of the WC. During cooling from the high sintering temperatures Co contracts more than WC which puts WC in compression in the WC-Co alloys; this lowers the possibility of crack formation in the WC grains [14,16]. During abrasive wear, the compressive stresses on the WC grains are reduced as the Co binder is extruded from the surface which makes WC vulnerable to crack formation followed by fragmentation. WC-Co alloys have high abrasion resistance due to their hardness, caused by the hard WC phase. Below are some of the factors affecting the abrasion resistance of WC-Co alloys; which are: microstructure, hardness and surface roughness.

Microstructure and composition

The microstructure and composition which include the Co mean free path, WC grain size, cobalt content and porosity, affects the wear rate of the hardmetals. Figure 2.6 shows the relationship between abrasion resistance and cobalt content and mean free path for hardmetal grades with various WC grain sizes. Abrasion resistance decreases with increasing cobalt content and increasing mean free path and increases with decreasing WC grain size. This is because cobalt is less hard than WC and therefore more prone to removal during wear.

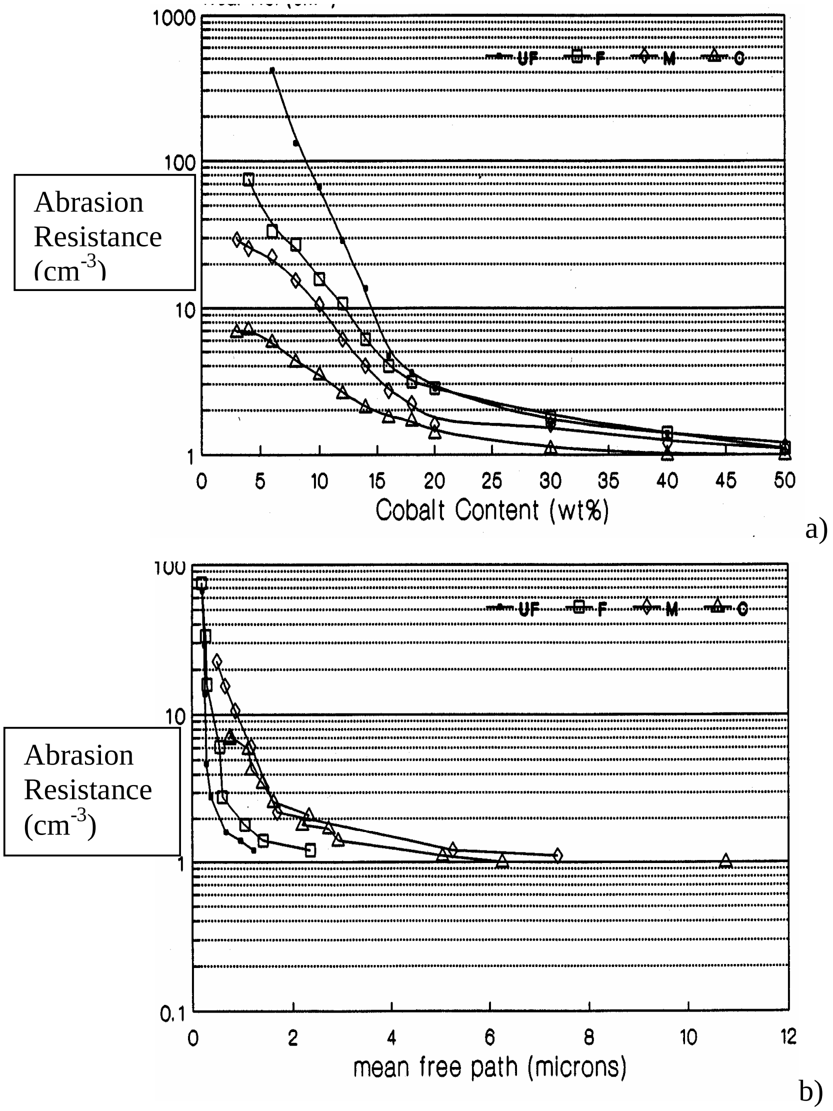


Figure 2.6: Graphs of abrasion resistance versus (a) cobalt content and (b) mean free path for different grain sized alloys. The WC grain size is designated by UF (0.6 μm), F(1.1μm), M (3μm) and C (5.1μm) [6].

Hardness

Hardness is the resistance to indentation or resistance to plastic deformation [4,6,18]. Hardness of WC-Co alloys depends mainly on cobalt content, WC grain size and mean free path as mentioned in Section 2.1.2.1 and 2.1.2.2. Figure 2.7 shows a graph of abrasion resistance versus hardness for different WC grain sized alloys, and it show that abrasion resistance increases with increasing hardness.

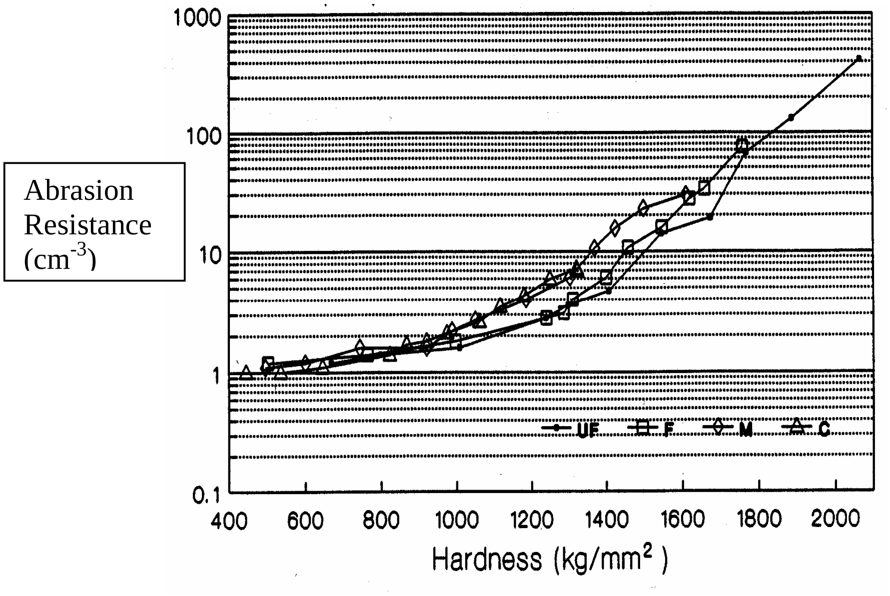


Figure 2.7: Graph of abrasion resistance versus hardness of different grain sized alloys [6].

Surface roughness

Surface roughness causes mechanical interlocking between the specimen and the abrasive body. Therefore the wear rate increases with increasing surface roughness. Unevenness of the material due to poor surface finish during manufacturing, sample preparation or anything that can alter the surface of the specimen can lead to increase in the wear rate [19].

2.3 Thermal shock

Thermal shock is due to a sudden change in temperature, which may result in the formation of surface cracks [20-25]. Due to its ability to generate surface cracks some authors refer to it as *crack induction* [23]. Cracks may be generated by the combination of high temperature and rapid cooling by water or other fluids. Surface cracks are caused by differences in thermal expansion and contraction between the interior and the surface of the material [23-25]. The resistance of metals to thermal shock depends mainly on their thermal conductivity and on the strain due to thermal expansion [2,21]. High Young’s modulus materials can withstand small strains and are susceptible to thermal shock; low Young’s modulus materials that can withstand larger strains are more able to absorb thermal shock [2]. WC-Co alloys have a high Young’s modulus and therefore they are susceptible to thermal cracks. As WC-Co alloys are highly wear resistant materials the effect of thermal cracks on the wear response is important. Table 2.2 lists some of the properties that influence thermal shock of WC-Co alloys.

Some of the thermal surface cracks generated by thermal shock are also referred to as snake skin or reptile skin cracks. They are fine cracks that can easily propagate through a material [2,22]. These cracks generally occur on cemented carbide rock drill bit inserts, hot rolls and seal rings [2,22,26,27]. They may be avoided by increasing both the WC grain size and the Co content but this can lead to a high wear rate as the hardness will be decreased [2, 4].

Table 2.2: Thermal and mechanical properties for WC and Co binder that influences the thermal shock [24].

	Coefficient of thermal linear expansion (K^{-1})	Young's modulus (GPa)	Poisson's ratio	Tensile strength	Thermal conductivity (W/mK)
Hard phase (WC)	3.84×10^{-6}	696	0.22	392	170
Cobalt	12.3×10^{-6}	206	0.31	256	100

2.3.1 Thermal stresses caused by thermal shock

Thermal stresses are induced by thermal shock [24,25]. Thermal stresses occur when a material is subjected to heat and different regions of the material have different coefficients of thermal expansion [23-25,28]. High thermal stresses may cause surface cracks in some materials like WC-Co alloys [24,25].

Figure 2.8 [25] shows the relationship between thermal stresses induced by thermal shock and distance from the cooled surface when a specimen is quenched in water. This graph confirms that high thermal stresses are caused by thermal shock at zero distance i.e. at the surface of the specimen. The thermal stresses then decrease gradually in magnitude as the distance from the cooled surface to the core increases. The figure shows negative thermal stress implying contraction at the core, unlike tension occurring at the surface of the specimen indicated by positive thermal stress.

Thermal stresses due to thermal shock increase as the heating temperature gradient is increased [25]. The stresses decrease with increasing distance from the surface (see Figure 2.8). Ishihara et.al [25] investigated thermal stresses at different specimen height and different cooling media (room temperature-water and silicon oil, see Figure 2.9) [25]. The increase in thermal stresses resulted in more damage or cracks on the surface of the specimen and this will result in high wear rate during abrasion applications. Tokomoto et.al [23], who investigated the thermal shock resistance of cemented carbides, found that thermal shock resistance increases with the thermal stress resistance i.e. higher thermal stresses in the material will result in lower thermal shock resistance (see Figure 2.10) [23].

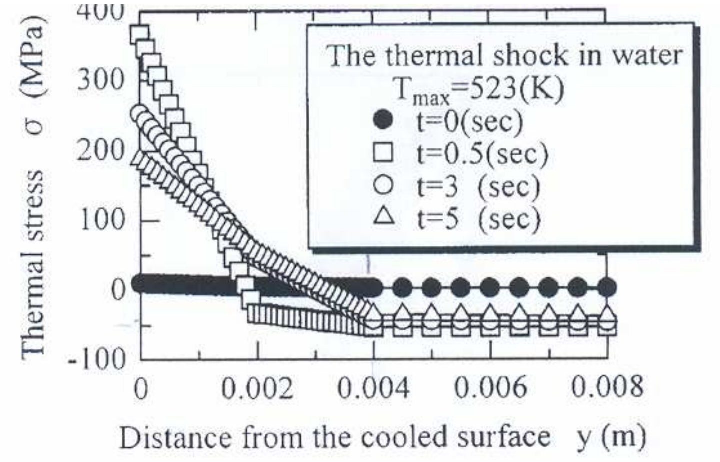


Figure 2.8: Distribution of thermal stresses induced by thermal shock near the cooled surface with time when the specimen is quenched in water, the material tested had 8.5μm WC grain size and 10wt% Co [25].

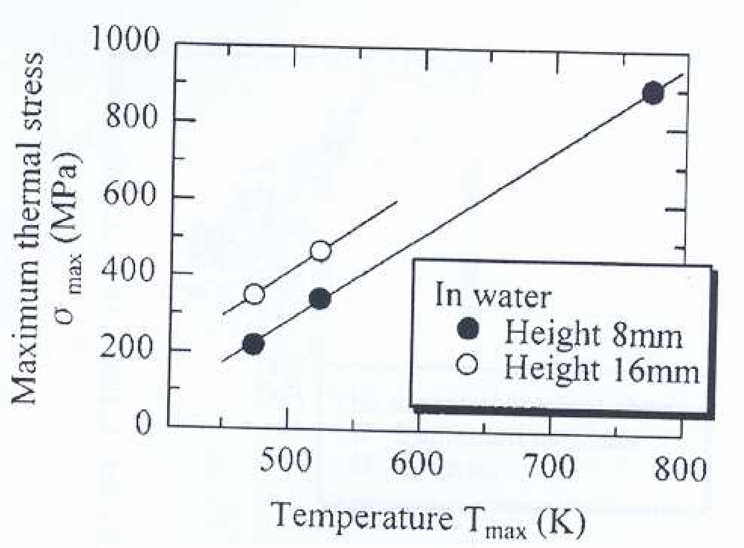


Figure 2.9: Maximum thermal stresses during thermal shock as a function of the heating temperature. The specimen tested had a 8.5μm WC grain size and 10wt% Co [25].

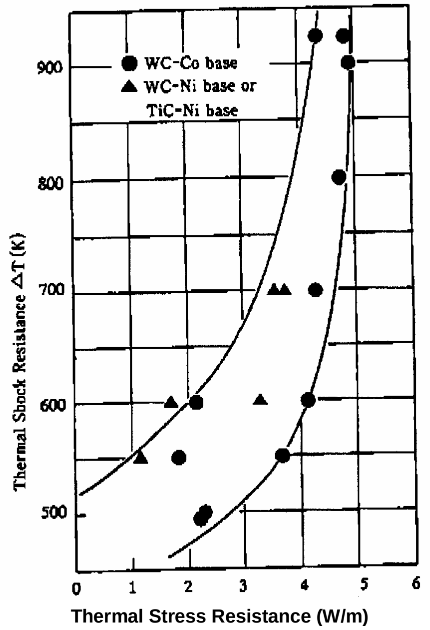


Figure 2.10: The relationship between thermal stress resistance and thermal shock resistance [23].

It was reviewed above that thermal stresses in the material increase as the heating temperature gradient increases, thus damage on the surface of the material increase [25]. Here the effect of increasing the number of thermal shock cycles on thermal stresses in a material is reviewed. Repeated thermal shock is common in the operation of rock drilling [1, 2]. This is because the cooling is not continuous during drilling operations.

It has been observed by Ishihara et.al [25] that the crack density (number of micro cracks per unit area) increases as the number of thermal shocks increase which suggest that higher thermal stresses are induced as the thermal shock cycles increase [24]. The crack density is measured by drawing lines on micrographs of the samples having micro-cracks on the surface and counting the cracks that intersect the lines [24,27]. Figure 2.11 shows a relationship between crack density and number of thermal shocks.

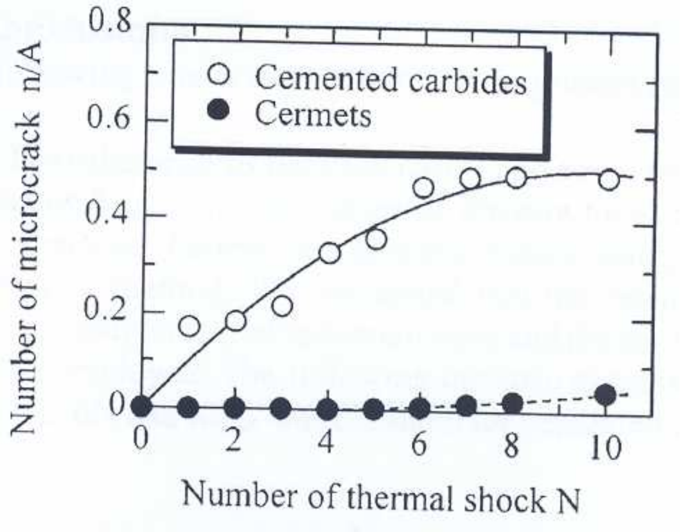


Figure 2.11: Number of cracks per area with increasing number of thermal shocks [25].

2.4 Thermal shock fracture and wear

No publications have been found on the direct relationship between thermal shock and abrasive wear of WC-Co alloys. Many authors studied observed thermal shock effects during rock drilling with cemented carbide [2,20-22,29,30]. High temperatures could be generated by friction during rock drilling. It is difficult to study the effect of thermal shocks during drilling as this is combined with wear, and so it is difficult to study the synergy between thermal shock and wear.

The following section reviews the failure mechanisms observed during rock drilling since thermal shock is one of the factors contributing to the failure of rock drilling buttons. This is followed by a general review of the wear of WC-Co alloys during rock drilling.

2.4.1 Failure mechanisms during rock drilling

The life of WC-Co drill bits depend on how much material is lost during rock drilling by wear or fracture [2,20,21]. Thus the contact in this case is between two hard materials with WC-Co having superior hardness.

Figure 2.12 shows typical rock drill faces with failure of buttons in B shown schematically in Figure 2.13. The drill bits are embedded with WC-Co buttons (or inserts) of different grades depending on the type of rock to be drilled. The steel crown shown in Figure 2.12 is used to support or hold up the drill face.

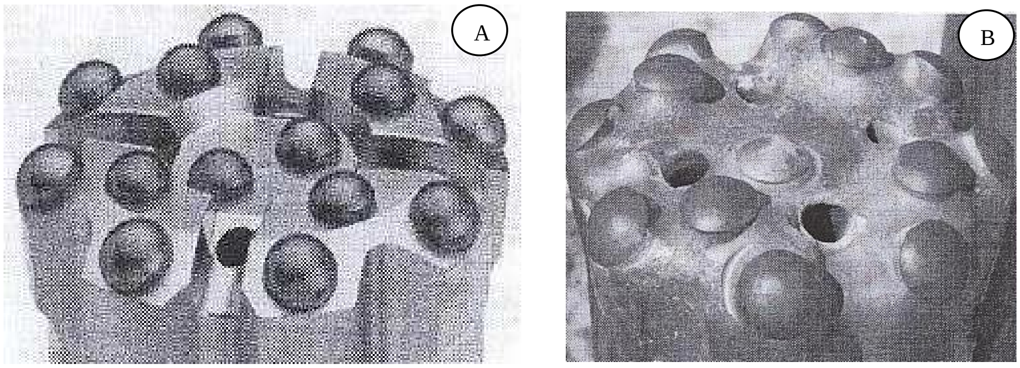


Figure 2.12: Typical rock drill face embedded with WC-Co buttons. A is unused and B is used. Some of the buttons in B are fractured or worn [2].

Figure 2.13 is a schematic of the macroscopic life limiting factors of inserts during rock drilling [2]. The first button (A) is unworn, B is worn as a result of drilling on hard rocks and C lost a large portion of material by catastrophic fracture, which may be generated by inclusions, defects, stress concentrations or micro-cracks in the material. Button D is partly worn; the change of shape introduces stress concentrations as shown by two arrows in Figure 2.13. These stress concentrations can lead to catastrophic fracture. Button E shows surface cracks that are the result of thermal stresses. These cracks can also lead to catastrophic fracture and can propagate through the material unnoticed. These thermal cracks are mainly a result of thermal shock, which induces thermal stresses as explained in Section 2.3.

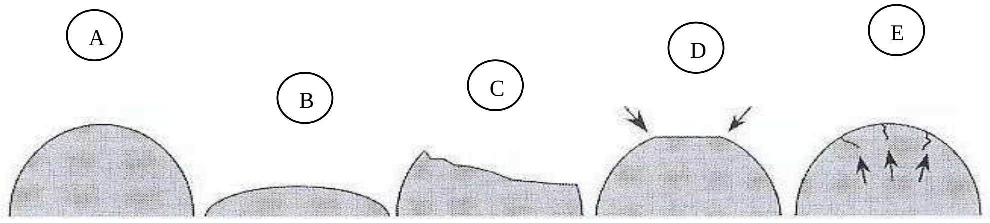


Figure 2.13: Schematic of a life limiting processes of drill buttons where A ~ Unworn, B ~ Worn, C ~ catastrophic fracture, D ~ Gradual wear, E ~ Snake skin cracks [2].

2.4.2 Wear of WC-Co in rock drilling

There are general rock drilling types used in mining industries such as percussive drilling, rotary drilling, percussive-rotary drilling and cutting. All these are used selectively depending on the nature of the rock [2,17]. Normally, rock drilling WC-Co grades are manufactured to have a large WC grain size and a high Co binder content depending on the rock type [2]. As reviewed previously in section 2.2, binder extrusion is considered to be one of the wear rate controlling factors during rock drilling [2,15,16].

Beste [2] carried out the most comprehensive investigation into the wear of rock drills and found that the main wear mechanisms are the following:

1. Crushing of WC grains and release of fragments; this occurs from buttons exposed to hard rocks. Crushing occurs as the button impacts the rock repeatedly with less indentation.
2. Detachment of WC grains. May occur when the drill bits scratches the rock

3. Crushing of drill bits inserts may occur due to impacts against the rock
4. Scrapping and pounding off of corroded or oxidized layers on the WC. Occurs from less hard rocks that leave a polished appearance on the buttons after wear.
5. Detachment of fragments occurring from buttons exposed to repeated high loads. This behavior occurs due to the formation of surface cracks or inter-granular cracking.

Crushing of WC grains and then removal of fragments can happen when there are voids between the WC grains caused by binder extrusion, which exposes the WC grains to abrasive wear. Jonsson [22] observed that areas of binder phase could be lost from the surface during drilling either by erosion or being hollowed out. Detachment of whole grains and composite-scale fragments result from repeated loading [16].

2.5 Oxidation behavior of WC-Co

When WC-Co is used for rock drilling and high-speed cutting, temperatures at the interface with the work-piece or the rock can easily reach as high as 1000°C [31-33]. Thus, oxidation of the cemented carbide can easily happen because it is reported that the oxidation of WC-Co starts at temperatures as low as 500°C [31]. This section reviews the oxidation of WC-Co, the effect of temperature and the swelling due to oxidation. The oxidation behavior is reviewed since the hardmetals in this project have been exposed to temperatures between 600°C and 1000°C prior to quenching.

2.5.1 Effect of cobalt content

Cobalt in WC-Co alloys accounts for the high oxidation resistance of the material i.e. increasing the cobalt content of the material will lead to a decrease in oxidation [31,32]. Figure 2.14 shows the effect of binder phase on the oxidation behavior of WC-Co.

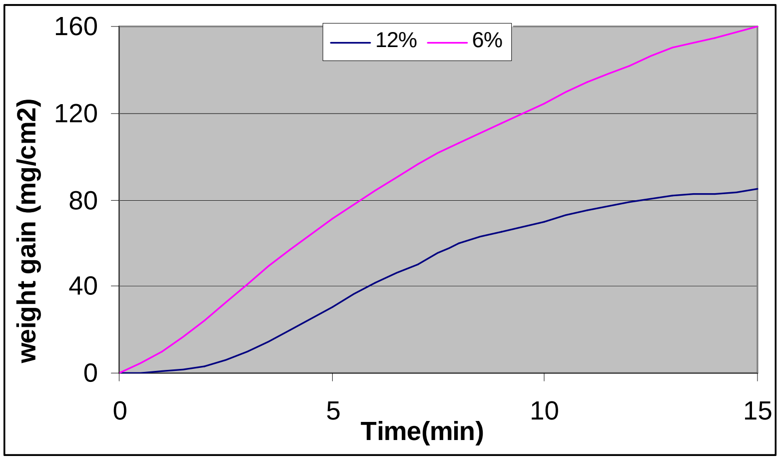


Figure 2.14: Weight gain per unit area vs. time graphs for 6% and 12%Co WC-Co samples oxidized at 800°C in 50O_2/50Ar for 15 min [31].

2.5.2 Effect of temperature and oxygen

Basu et.al. [31] investigated the oxidation behavior of WC-Co under various oxygen atmospheres. They observed an increase in the rate of oxidation as the oxygen content of the atmosphere increased as shown by Figure 2.15. The surface showed an oxide layer of WO_3, which was highly porous and cracked. Cracking was due to the generation of CO and CO_2 during oxidation. Apart from WC peaks the only peaks observed by the XRD in Figure 2.16 are WO_3 and $CoWO_4$ [31].

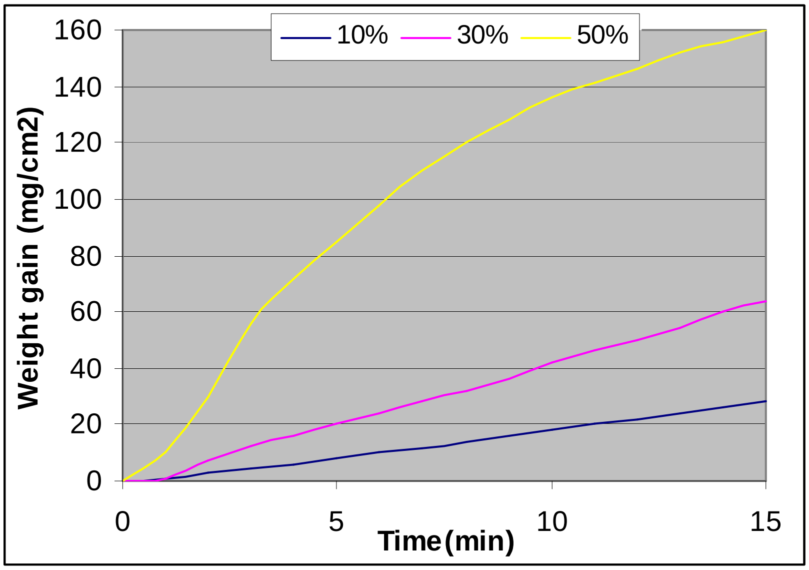


Figure 2.15: Weight gain per unit area vs. time plots for WC-6%Co oxidized at 800°C in Ar-O_2 mixtures of varying oxygen contents of 10%, 30% and 50% at a total flow rate of 1.1 min^{-1}[31].

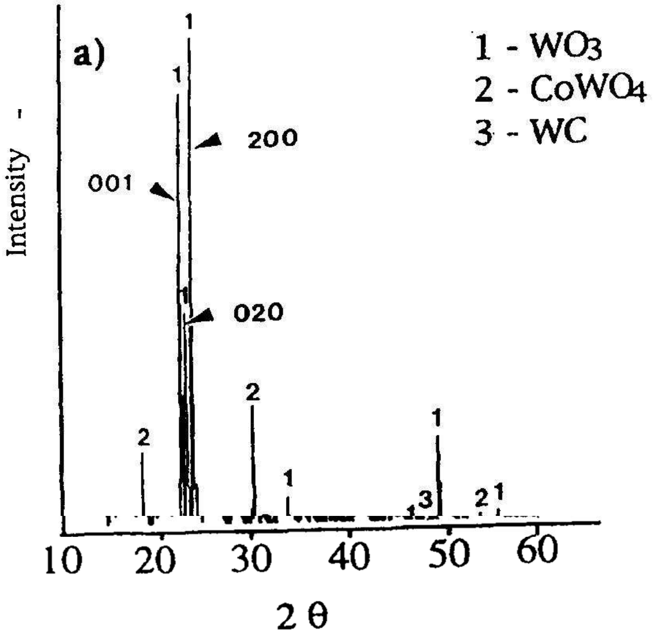


Figure 2.16: XRD pattern from a WC-12wt%Co sample oxidized for 15 min at 800°C in 50O_2/50Ar. It shows the formation of WO_3 and $CoWO_4$ [31].

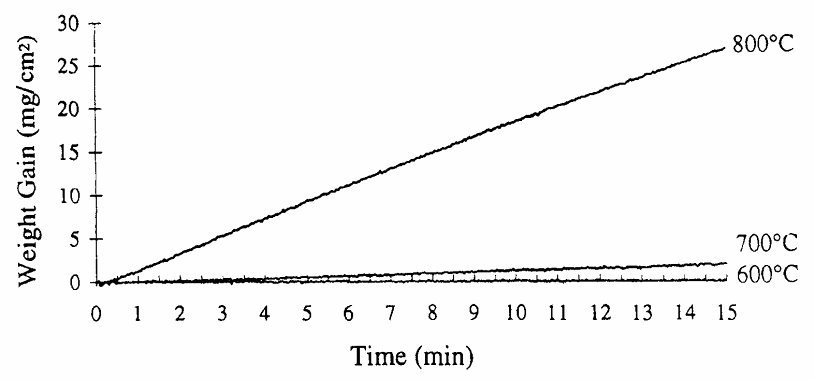


Figure 2.17: Effect of heating temperature on the oxidation of a sample of WC-6wt%Co [31].

Figure 2.17 shows a weight gain versus time graph for a 6wt%Co grade oxidized at 600°C, 700°C and 800°C in $10O_2/90Ar$ for 15 minutes [31]. The figure shows a rapid increase in weight gain at 800°C, implying a higher amount of oxidation at 800°C than at 700°C and 600°C.

Another possible result of oxidation beside the formation of oxides is the decarburization of WC which happens when oxygen reacts with C in WC and forms a volatile carbon oxide, which is then lost leaving WC poor of C to form W_2C [32]. Below are some of the reactions that can occur as a result of oxidation of WC [32]:

$WC + 2O_2 \rightarrow WO_3 + CO$
$WC + O_2 \rightarrow WO_2 + C$
$2WC + O_2 \rightarrow W_2C + CO_2$

There is a significant strength loss, which is accompanied by swelling after oxidation of WC-Co alloys [34-36]. WC oxidizes immediately in oxygen forming WO_3 which is brittle and porous. Then the oxygen diffuses through the WO_3 to form carbon dioxide at the interface of $WC(WO_3)/Co$ which then forms cavities which grow until the formation of open porosity (see Figure 2.18) [34]. This cause changes in the specimen shape as seen in Figure 2.19.

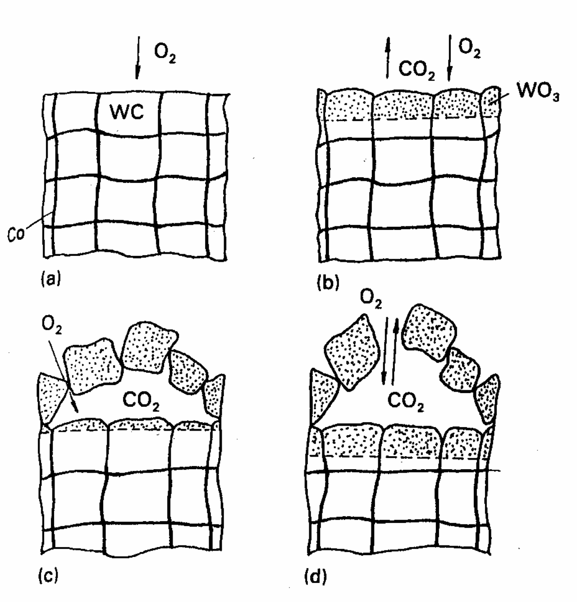


Figure 2.18: Schematic model of the oxidation of WC-Co alloys accompanied by swelling [34].

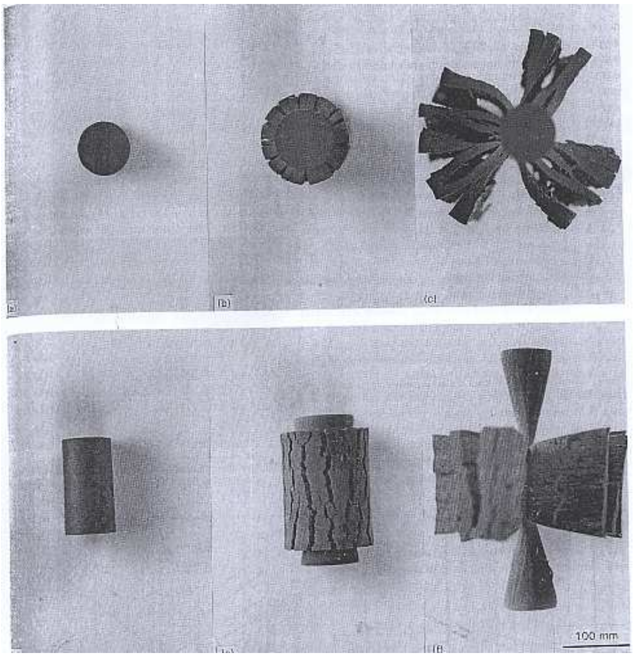


Figure 2.19: Swelling of WC-6wt%Co after exposure to oxidation at 700°C for 570 minutes [34].