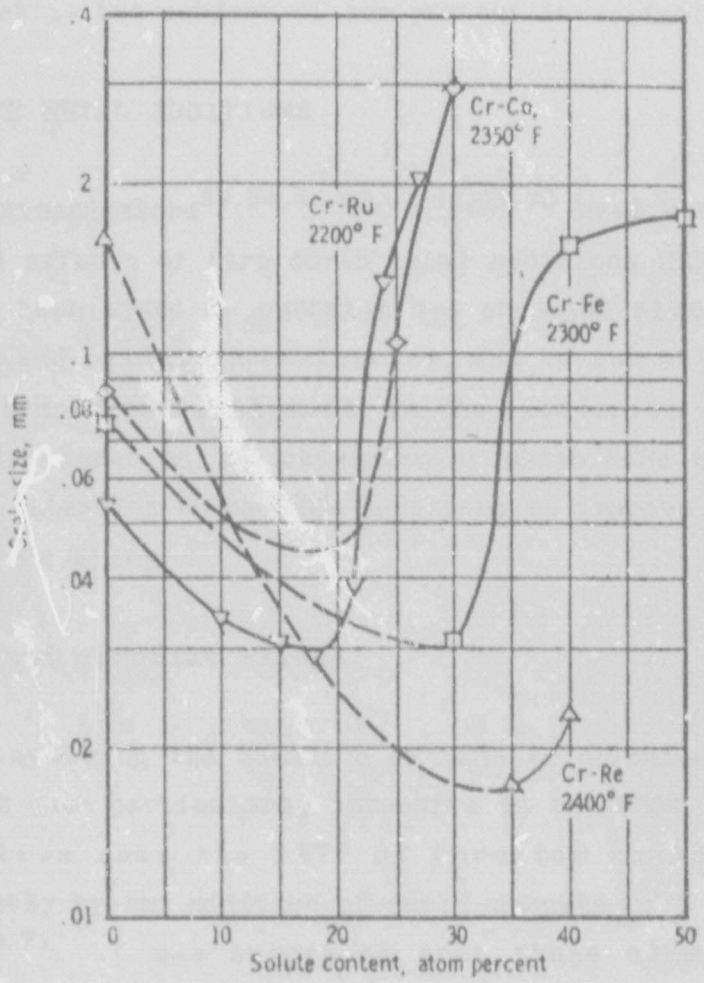


Figure 2.24 Effects of solute content on the grain size of chromium alloys annealed at the indicated temperatures[61].

example, they found that quenching the Fe-Cr alloys from a solution annealing temperature of 1260°C prevented precipitation at the grain boundaries while extensive grain boundary σ-phase was found in the furnace-cooled alloys. The DBTTs of the furnace cooled alloys were also found to be consistently higher than those of quenched specimens.

For both sets of investigators the Fe-50at%Cr (approx Fe-48Cr) had the lowest DBTT, which was -73°C for the quenched alloy. Thus, in addition to confirming the work of other investigators, Klopp and Stephens have also provided further insight into the mechanisms which control the ductilisation of high chromium stainless steels.

It should also be noted that their studies included an Fe-40Cr alloy which is the subject of the present investigation.

2.3 RARE EARTH METAL ADDITIONS

Several investigators[39,64,65,66,67,68,69,70] have demonstrated the beneficial effects of rare earth metal additions (REMs) in steels. REMs have been added to chromium and chromium alloys to improve toughness and oxidation resistance, and to low alloy steels to suppress temper embrittlement. In the discussion which follows emphasis is placed on the mechanism by which REMs modify steels, given the intention to use REM additions to improve the ductility of an Fe-40Cr alloy.

2.3.1 Chromium and chromium alloys

Research involving the addition of REMs to chromium and chromium alloys has been particularly intensive in the USSR. In the 1960's it was shown that the DBTT of chromium could be reduced significantly by the addition of small amounts of Y and REMs (La, Ce etc)[70,71]. It was suggested that these elements removed interstitial atoms from solid solution so that the precipitation of nitrides and carbides which embrittle chromium was suppressed[70].

By 1977, the nature of low temperature brittleness of chromium was reasonably well understood[69]. Metallurgists and technologists identified four factors which are primarily responsible for the transition of chromium into the brittle state:

1) the electronic structure of the metal. In BCC metals like chromium, the yield stress (σ_y) is strongly dependent on temperature because of the large values of the Peierls-Nabarro forces associated with dislocation movement[11,69];

2) the structural state of the metal, particularly the grain or cell size. The finer the grain size the lower the DBTT[69,70];

3) the rate of deformation and the stress state of the metal[68]; and

4) the concentration and form of interstitial impurity elements

in the metal[66,67,68,69,70].

To a certain degree all four factors can be manipulated and controlled. In this way it is possible to improve the low-temperature ductility of chromium, Rakitski et al[66,67,68,69,70] have shown that the most marked improvement in ductility is obtained through the removal of interstitial impurities and/or the neutralisation of these inpurities with highly active elements such as REMs. It was found that REM additions in the range 0,5 to 1,0 weight% produced markedly lower DBTTs in as-cast and work-hardened chromium alloys. For example a DBTT of -80°C was obtained for highly deformed chromium strip (ε= 75%)[66]. The REMs are effective in two ways. They react with oxygen and nitrogen to form compounds which are removed to the slag during melting, thereby refining the matrix[66]. In addition the residual quantities of these interstitials are chemically fixed in the form of oxides and nitrides[69]. However, in excess, REMs themselves form low melting point phases which usually precipitate on the grain boundaries, and this results in very poor DBTTs[69,70]. It was found that lanthanum produced the lowest DBTT at optimum levels, while cerium which forms low melting point eutectics with chromium, produced the least dramatic decrease in the DBTT. Figure 2.25 shows the effect of various REMs on the DBTT of chromium (which had been reduced by 90% by cold working).

Up to optimum levels REMs retard recrystallisation and favour the formation of a fine-grained structure during annealing. It was shown that REM additions to chromium increased the recrystallisation temperature by 50 to 75°C. After annealing at 1200°C for one hour, the grain size of an alloy containing 0,5 - 1% Y was approximately one fifth of that of unalloyed chromium[68]. At REM concentrations above the optimum, the recrystallisation rate increased and grain growth accelerated[68]. At these levels liquid films of low melting point compounds formed at the grain boundaries and promoted rapid recrystallisation and grain growth[69,70]. The variation of grain size with REM content is shown schematically in Figure 2.26.

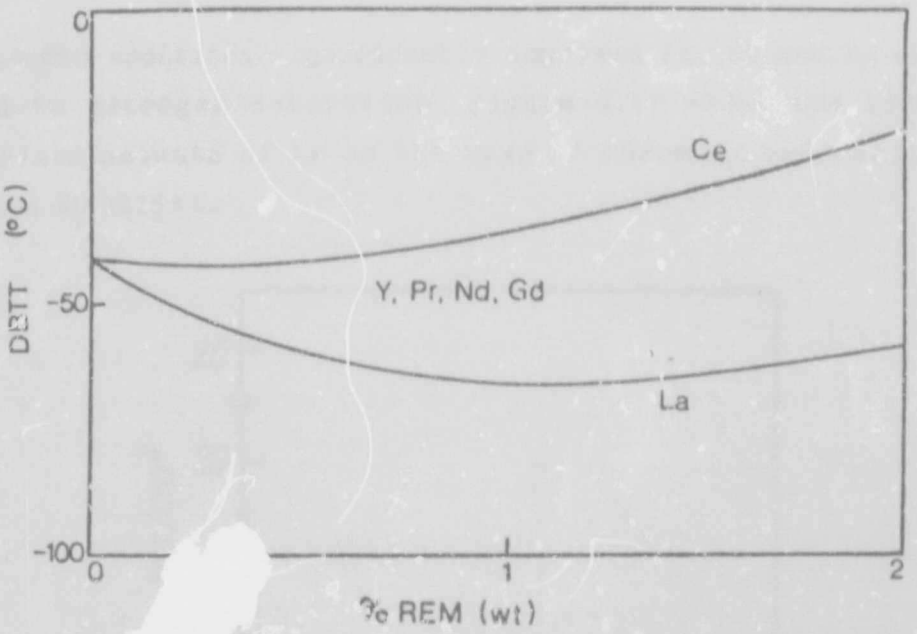


Figure 2.25 The effect of REMs on the DBTT of chromium after a 90% rolling reduction[68].

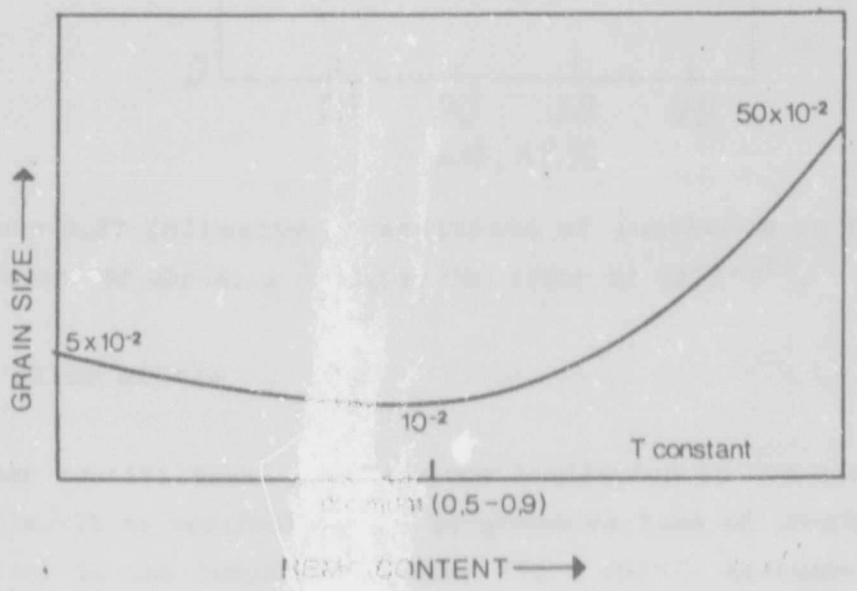


Figure 2.26 Schematic representation of the relationship between grain size after annealing and weight % REM (after 70).

Rakitskii and Trefilov[68] also demonstrated that cold-worked chromium alloyed with REMs retained its strength at higher heating and annealing temperatures. In another study the heat resistance of chromium alloyed with REMs was investigated[66]. It was found

that REM additions significantly improved resistance to oxidation and to nitrogen saturation. Figure 2.27 shows the effects of various amounts of La on the mass of chromium oxidised for 100 hours at 1225°C.

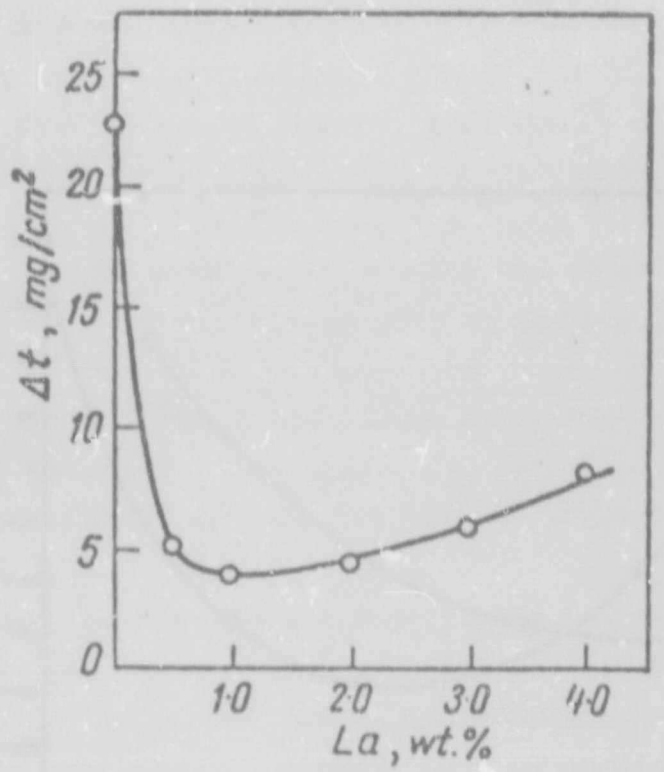


Figure 2.27 Influence of additions of lanthanum on the weight increment of chromium oxidised for 100hr at 1225°C[66].

2.3.2 Low alloy steels

Temper embrittlement is a serious limitation to the use of alloy steels. It is manifest by the progressive loss of toughness after heating in the temperature range 350 - 600°C. At temperatures in this range, metalloid impurities (P, Sn, S, Sb and As) segregate to the prior austenite grain boundaries and weaken them, thus promoting intergranular failure[64,72].

It has been shown that this segregation-induced embrittlement may, to a large extent, be removed by the addition of REMs[72]. Again, REMs reduce the amount of residuals in solid solution by removing impurities like sulphur to the slag during melting and also lower

the activity of the impurities in solution by forming sulphides, phosphides and other impurity compounds. In this way segregation and therefore embrittlement, is decreased. The resultant considerable reduction in the embrittlement susceptibility of low alloy steels is shown in Figure 2.28.

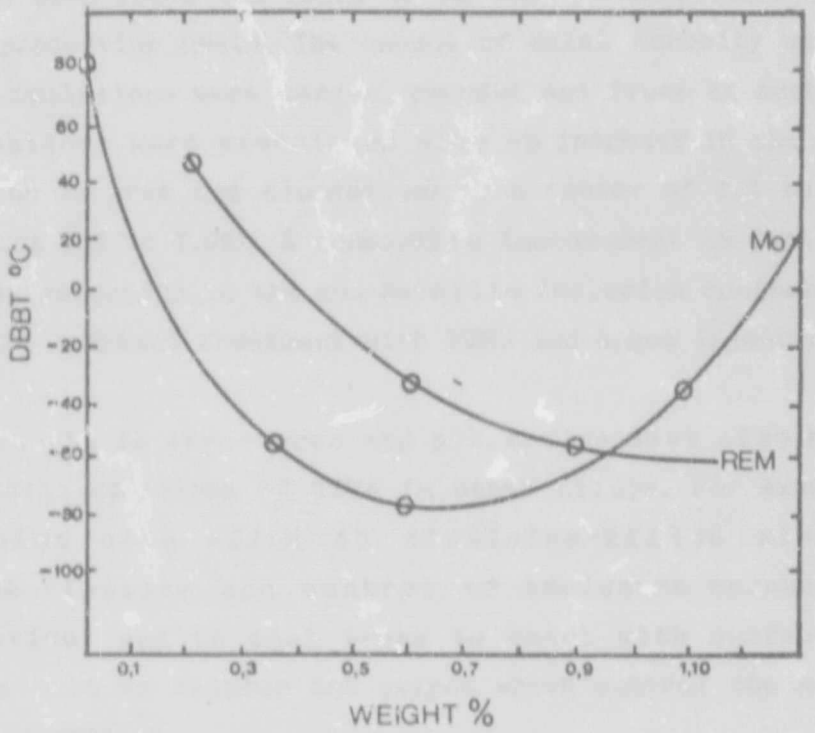


Figure 2.28 DBTT's corrected for hardness vs. wt% Mo and REM's added. Aged 96 hours at 510°C[72].

2.3.3 REM additions in ladle metallurgy

The addition of REMs to the ladle is now widely used in the USSR to achieve a considerable improvement in the structure and properties of steels and alloys[22,26].

The effectiveness of this technique can be illustrated by reference to a study in which a tool steel was subjected to trial heats using different production practices:

(i) argon purging in the ladle:
(ii) micro-additions of rare earths to ladle: and
(iii) a combined treatment - rare earth additions and argon purging[65].

When the steel was purged in argon, a sounder and less segregated alloy than the conventionally fabricated steel was produced. The structure as well as the ductility of the steel to which 0,03% REMs had been added was found to be considerably superior to the normal production heats. The amount of axial porosity was reduced and the inclusions were larger, rounded and fewer in number. These modifications were associated with an increase in the ductility (reduction in area and elongation) by a factor of 1,3 to 2,0 (i.e. from about 3,5 to 7,0%). A comparable improvement in ductility and a further reduction in the non-metallic inclusion content occurred following combined treatment with REMs and argon injection.

Improvements in structures and properties have also been made using ladle additions of REMs in other alloys. For example REMs have also been added to aluminium-killed steels for desulphurisation and control of inclusion morphology and composition: and to cast irons to react with surface active elements such as sulphur and oxygen which control the morphology of the graphite[22].

2.4 CONCLUDING REMARKS

The causes of embrittlement in ferritic steels have been identified and detailed. It has been concluded that interstitial elements (carbon, nitrogen and oxygen) are primarily responsible, since 475°C and σ phase embrittlement can be avoided by using appropriate heat treatment temperatures. In addition the rhenium-ductilising effect and the beneficial effects which REM additions have on the ductility of various alloys have been described.

The literature survey has thus indicated that an Fe-40Cr alloy with good ductility can be developed if the interstitial level is

kept low. REM additions may be used to fix oxygen and nitrogen and thus reduce the susceptibility of the alloy to high temperature embrittlement. Furthermore, the proportion of iron to chromium in the Fe-40Cr alloy, may in itself promote superior toughness properties.

3 EXPERIMENTAL PROCEDURE

3.1 ALLOY PREPARATION

3.1.1 The base materials

The alloys were prepared from relatively pure commercially available materials. The base materials were electrolytic iron flakes and electrolytic chromium in the form of angular chips. Rare earth metal (REM) additions were made using 'mischmetall'. Chemical analyses of the raw materials are given in Table 3.1.

Table 3.1 Analysis of raw materials

(a) Electrolytic iron and chromium

	%C	%O	%N
Fe	0,006	0,055	<0,001
Cr	0,016	0,1	<0,014

(b) Mischmetall

Element	Weight%
Ce	52
La	24
Nd	15
Pr	7
Sm	1
Others	1

3.1.2 The experimental alloys

Three series of alloys were prepared. The first, consisting of only LNN1 and V1, were used in a preliminary study to develop an appropriate fabrication route.

The second stage of the programme was directed at determining the optimum range of REM additions. Various amounts of REMs were added to the V2 and V3 alloys. From the results of tests on these, the

appropriate range in which REMs should be added to the Fe-40Cr base alloy was determined.

The third and final stage of the study involved the preparation of alloys (~4 series) with REM contents in the optimum range.

The results of the chemical analyses of all the alloys are reported in Table 3.2.

3.1.3 The melt procedure

The following equipment was used: a vacuum induction furnace fitted with a generator capable of delivering 60kW, cast iron moulds (with 20 and 6kg capacities) and pre-fired magnesia crucibles with alumina pouring lips. The details of the melting procedure are described below.

The crucible was charged with chromium and iron flakes and preheated for 30 minutes while the vacuum chamber was evacuated to and held at a pressure of 10Pa. During this period solid state degassing of the iron and chromium takes place. Adsorbed water and gas molecules leave the surface of the metal and gases dissolved in the metals as interstitials diffuse to the surface via vacancies, grain boundaries and dislocations[73]. Preheating of the chromium with the iron also reduces the overall melt-down time, thus limiting the exposure of the melt to the refractories which may contaminate the melt through outgassing[74].

Melting was carried out under a partial pressure of argon (15kPa). The vacuum chamber was backfilled with argon before the power was boosted to 30kW. After 20 minutes the power was reduced to 10kW and the vacuum was reduced to 90Pa. The alloy was held in the molten state at this pressure for 60 minutes to allow liquid state degassing to occur. During liquid state degassing, nitrogen and hydrogen diffuse out of the melt and oxygen is removed by reaction with carbon. The CO which forms is then outgassed.

Table 3.2 Composition of the experimental alloys

Alloy	Cr	Fe	C	O	N	REM*		P	Si	Al	S
						add	rec				
LNN1	39	60,7	0,02	0,037	0,017	–	–	NA	0,11	NA	NA
V1	38,4	61,5	0,02	0,060	0,004	–	–	0,005	0,007	NA	NA
V2/1/2	38,9	60,5	0,01	0,031	0,005	–	–	<0,005	0,035	<0,02	0,01
V3/2	39,6	60,1	0,01	0,024	0,004	0,15	0	<0,005	0,030	<0,02	<0,01
V2/2/2	39,3	59,7	0,01	0,031	0,004	0,3	0	<0,005	0,055	<0,02	0,01
V2/3	36,6	60,4	0,01	0,025	0,009	0,6	0,32	<0,005	–	<0,02	<0,01
V2/4	39,5	59,7	0,01	0,021	0,005	0,9	0,60	<0,005	–	<0,02	<0,01
V4/0	39,3	61,0	0,021	0,055	0,004	–	–	<0,003	0,17	<0,1	0,006
V4/0,05	39,6	61,1	0,023	0,060	0,004	0,05	0,04	<0,003	0,19	<0,1	0,006
V4/0,10	39,3	60,9	0,012	0,038	0,004	0,10	0,06	<0,003	0,19	<0,10	0,006
V4/0,15	39,2	60,5	0,024	0,030	0,004	0,15	0,04	<0,003	0,19	<0,1	0,003

* REM = Rare earth metals

add = added

rec = recovered

– = none added, none detected

NA = no analysis

Argon (10kPa) was reintroduced into the vacuum chamber before pouring. The power was then boosted to 40kW for tapping fluidity. After pouring into a 20kg mould, the pumps were turned on once more and the material was allowed to cool under vacuum.

This material was used as a stock bar which was then divided into four bars for remelting with appropriate REM additions During remelting shorter degassing times were used: 10 minutes for liquid state degassing and 15 minutes for solid state degassing. The remelted alloys were cast into ingots, 65mm square in section and 250mm long.

3.2 THE ADDITION OF RARE EARTH METALS

Two methods of introducing REMs into the molten Fe-40Cr alloy were investigated. The first involved placing the REM addition in the mould prior to pouring. This method proved unsuccessful because the mischmetall reacted with the atmosphere during the degassing periods and floated to the top of the melt, where it remained during pouring. The second method was more successful. The mischmetal was wrapped in a very pure (99,99%) iron foil and secured to a pure iron wire which was plunged into the melt just before pouring. All REM additions were subsequently made in this way.

3.3 ROLLING

The alloys were rolled on a two-high reversing mill with a capacity of 50 tonnes. During rolling the temperature was constantly monitored using a pyrometer linked to a digital display readout. If the ingots became bent during rolling, they were forged flat and returned to the furnace.

3.3.1 Determination of a fabrication route.

Alloy V1 was cut into two 31mm thick pieces. Each section was rolled using the same basic procedures but different rolling temperatures as shown in Table 3.3.

The alloys were quenched in water after rolling. Reductions of about 56% were achieved in each case.

Table 3.3 Rolling procedures for heat V1

Rolling route	I	II
Soaking time (950°C)	1 hour	1 hour
Rolling temperature range	950°C - 650°C	950°C - 650°C
Furnace temperature during rolling	950°C	1100°C
Number of times returned to furnace	3	3
Average time in furnace between roll periods	18 mins	18 mins

3.3.2 Rolling of heats V2 and V3

A two stage rolling procedure was employed. Route I (in Table 3.3) was followed. The alloys V2/3 and V2/4 to which 0,6 and 0,9% REM had been added respectively broke at less than 5% reduction during the first pass. The other alloys were reduced by about 60% and then water quenched. Because the grains in the centre of these ingots had not been worked sufficiently to allow recrystallisation

to take place during annealing, the ingots were reduced by a further 12% and water quenched. The final reduction of the ingot was 82% and the rolled plate thickness was about 11,5mm. It should be noted that each ingot underwent two one hour soaking periods at 950°C. The ingots were returned to the furnace four times during rolling and the average time spent in the furnace between roll periods was 20 minutes.

3.3.3 Rolling of heat V4

Again route I was followed, details are given in the Table below.

Table 3.4 Rolling procedure for heat V4

Soaking time (950°C)	1 hour
Rolling temperature range	950°C - 650°C
Furnace temperature during rolling	950°C
Number of times returned to furnace	3
Average time in furnace between roll periods	30 minutes between roll period 1 and 2 10 minutes between roll periods 2 and 3, and 3 and 4

The alloys were water quenched after rolling. The average reduction achieved was 83%.

A schematic representation of the rolling procedure followed is given in Figure 3.1.

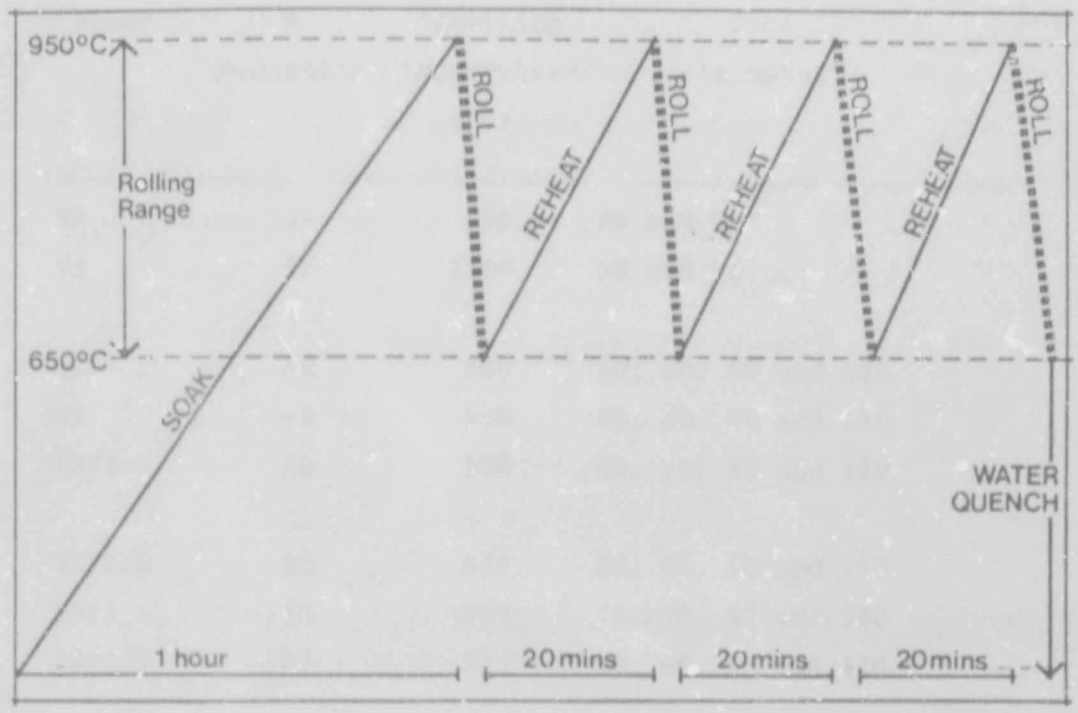


Figure 3.1 Schematic diagram for rolling procedure.

3.4 HEAT TREATMENT

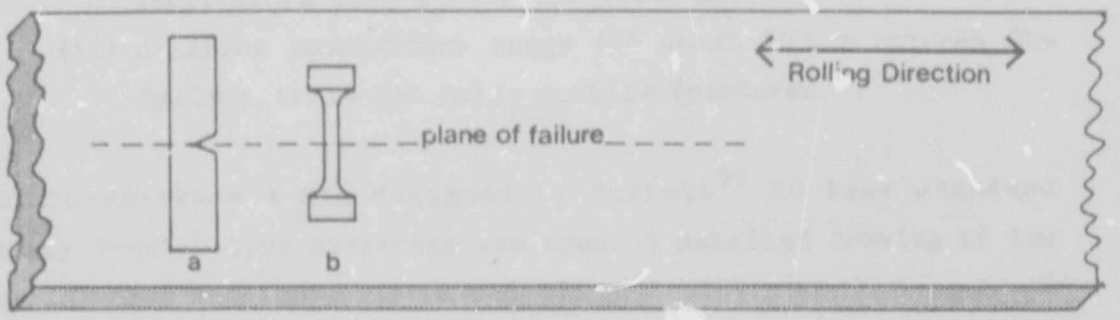
After rolling and quenching, heats V1 through to V4 were annealed for up to three and a half hours at 950, 1050, 1100 and/or 1150°C and then water quenched. The optimum annealing time and temperature for each heat was determined in annealing trials in which narrow specimens cut from the rolled plate were generally used. Once the optimum annealing time and temperature was identified, the rest of rolled plate was annealed and sampled. The annealing treatments typically involve recrystallisation of the rolled grains and the precipitation of carbides and nitrides. The heat treatments are summarised in Table 3.5.

Table 3.5 Summary of heat treatments

Alloy	% reduction	Annealing temperature (°C)	Time (minutes)
V1	56	950	30 and 60
V1	56	1100	30 and 60
V2/1	60	950	30, 60, 90 and 120
V3	60	950	30, 60, 90 and 120
V2/2	60	950	30, 60, 90 and 120
V2/1/2	82	950	30, 60, 90 and 120
V3/2	82	950	30, 60, 90 and 120
V2/2/2	82	950	30, 60, 90 and 120
V4/0	83	950	60, 90 and 120
V4/0,05	83	950	60, 90 and 120
V4/0,10	83	950	60, 90 and 120
V4/0,15	83	950	60, 90 and 120
V4/0	83	1050	60, 90 and 120
V4/0,05	83	1050	60, 90 and 120
V4/0,10	83	1050	60, 90 and 120
V4/0,15	83	1050	60, 90 and 120
V4/0	83	1150	60, 90, 120, 150 and 180
V4/0,05	83	1150	60, 90, 120, 150 and 180
V4/0,10	83	1150	60, 90, 120, 150 and 180
V4/0,15	83	1150	60, 90, 120, 150 and 180

3.5 MECHANICAL TEST SPECIMEN PREPARATION AND TESTING

Charpy, tensile and slow bend specimens were prepared from the V2, V3 and V4 heats. These were cut from the rolled plate in such a way that fracture of the specimens would occur along the rolling direction i.e. along what is theoretically the plane of lowest strength. The sampling procedure is illustrated in Figure 3.2.



a - charpy and slow bend test specimens
b - tensile specimen

Figure 3.2 Sampling procedure for mechanical test specimens.

3.5.1 Charpy impact tests

Standard Charpy V-notch impact test specimens were cut and machined from rolled plate. The specimens were machined and tested in accordance with the requirements of BS specification 131 part 2, 1972. Impact tests were performed at -40, -20, -15, -10, 0, ambient temperature, 36 and 50°C. Water and liquid nitrogen were used as the heat transfer media. The tests were performed on a Tinius Olsen machine, capable of registering absorbed impact energies up to 358J. The impact energies are indicated to within 0,5 Joules. Ductile - to - brittle transition temperatures (DBTTs) were determined by interpolation of the impact energy versus temperature data. The DBTTs are the temperatures corresponding to the energy values midway between the upper and lower shelf energies. [The 50% fibrous fracture criterion could not be used because a direct relationship between fracture mechanism (cleavage or ductile tearing) and the magnitude of fracture energy, did not appear to exist.]

3.5.2 Slow bend tests

Slow bend tests were performed on the V2 heats (82% reduction). The three-point bend test has been described as the most accurate method of comparing the DBTTs of different alloys[75]. The advantages of this technique include:

(i) very accurate temperature control, since the rig in which the specimen is mounted is submerged in a constant temperature bath during the test, and

(ii) a narrow temperature range (of about 10°C) between the fully brittle and fully ductile fractures.

For convenience a rig designed by Barrett[72] to take standard Charpy V-notch type specimens was used. A detailed drawing of the rig is shown in Figure 3.3 (a and b).

The tests were carried out on a 50kN capacity ESH universal servo-hydraulic test machine. A specimen was placed in the test rig and then put under a small tension to prevent it from shifting. The rig was then lowered into a constant temperature bath and left for 5 minutes to allow the temperature to stabilise. A thermocouple placed in contact with the specimen measured the temperature. The specimen was then loaded at a cross head displacement of 0,083 $mmsec^{-1}$. The load versus displacement data was stored on floppy disc. The data was processed by a Commodore CBC Model 8032 computer and the load versus cross head displacement curves were produced using an HP Plotter.

Edwards et al[75] identified three methods of analysing load versus displacement curves to give reproducible and identical DBTT values. These are:

(i) the area under the curve to maximum load as a function of temperature,

(ii) the total area under the curve as a function of temperature, and

(iii) the extent of rapid load drop, corresponding to the onset of brittle fracture as a function of temperature.

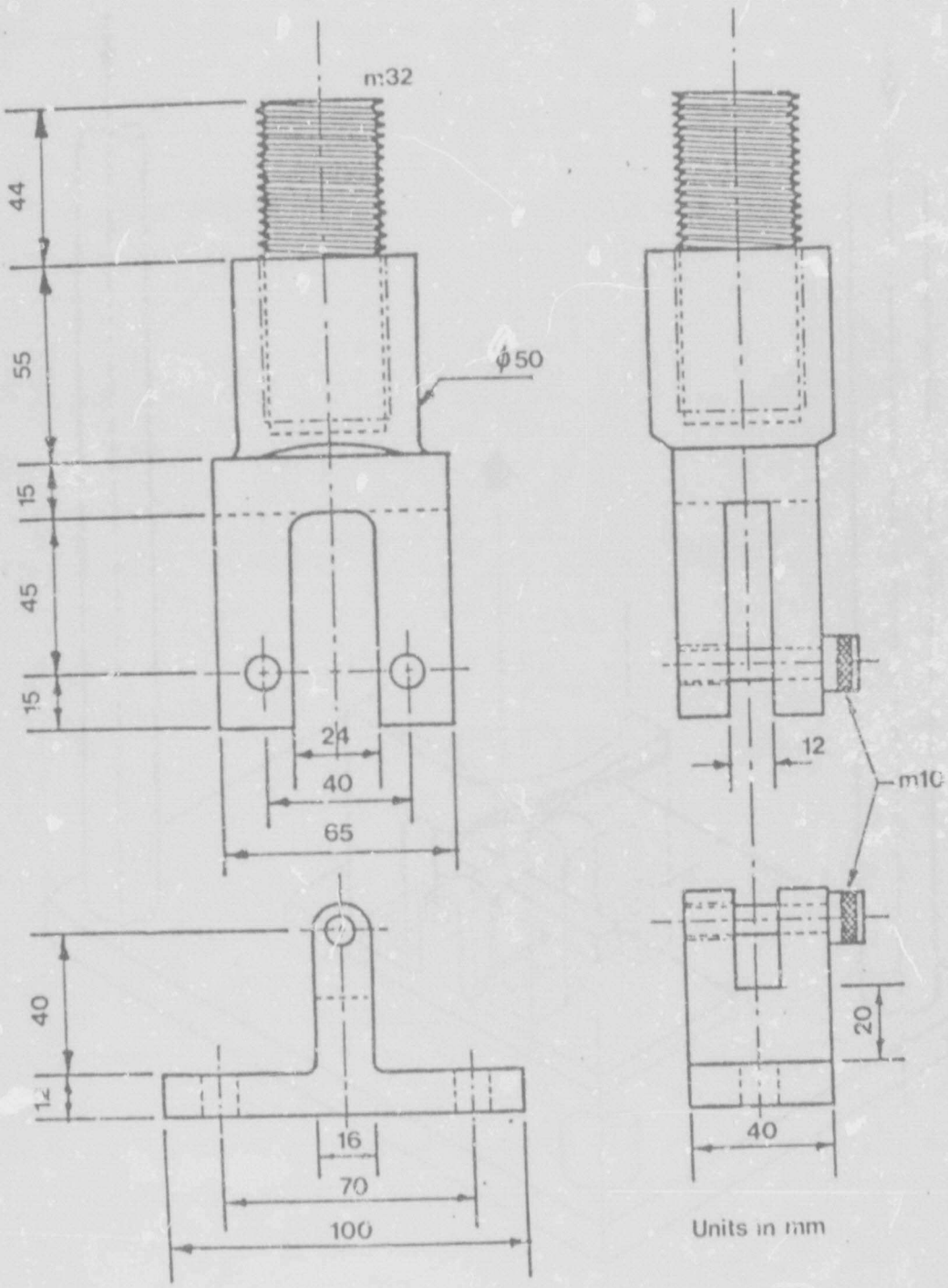


Figure 3.3a Scale drawing of the slow bend test rig. (After reference 72.)

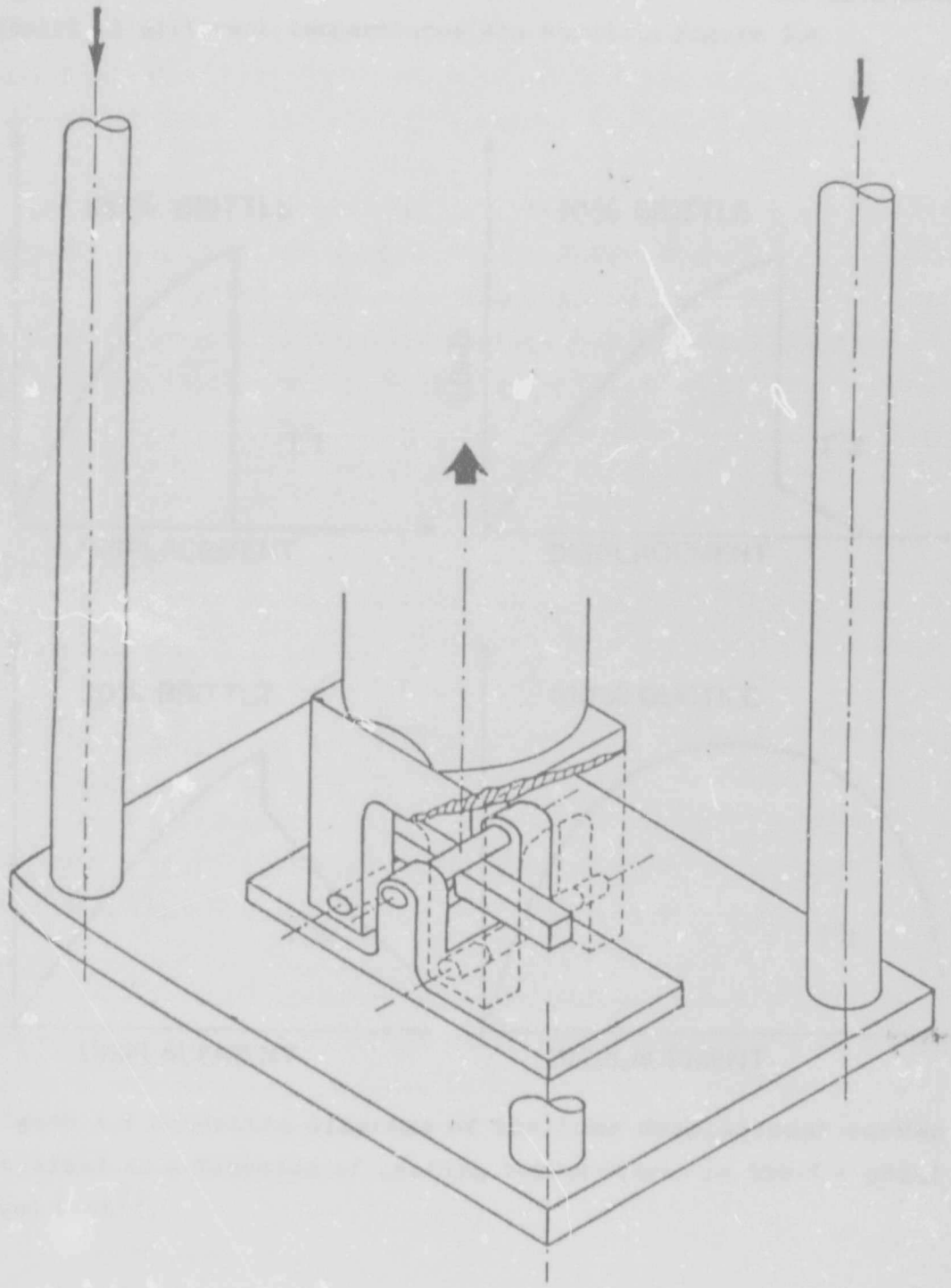


Figure 3.3b Slow bend test rig. Specimen in mounted position and general loading system. (After reference 72).

In this study methods (i) and (ii) were used and the results from each compared (see Appendix A for the computer programme). A series of typical load - displacement curves from bend specimens tested at different temperatures are shown in Figure 3.4.

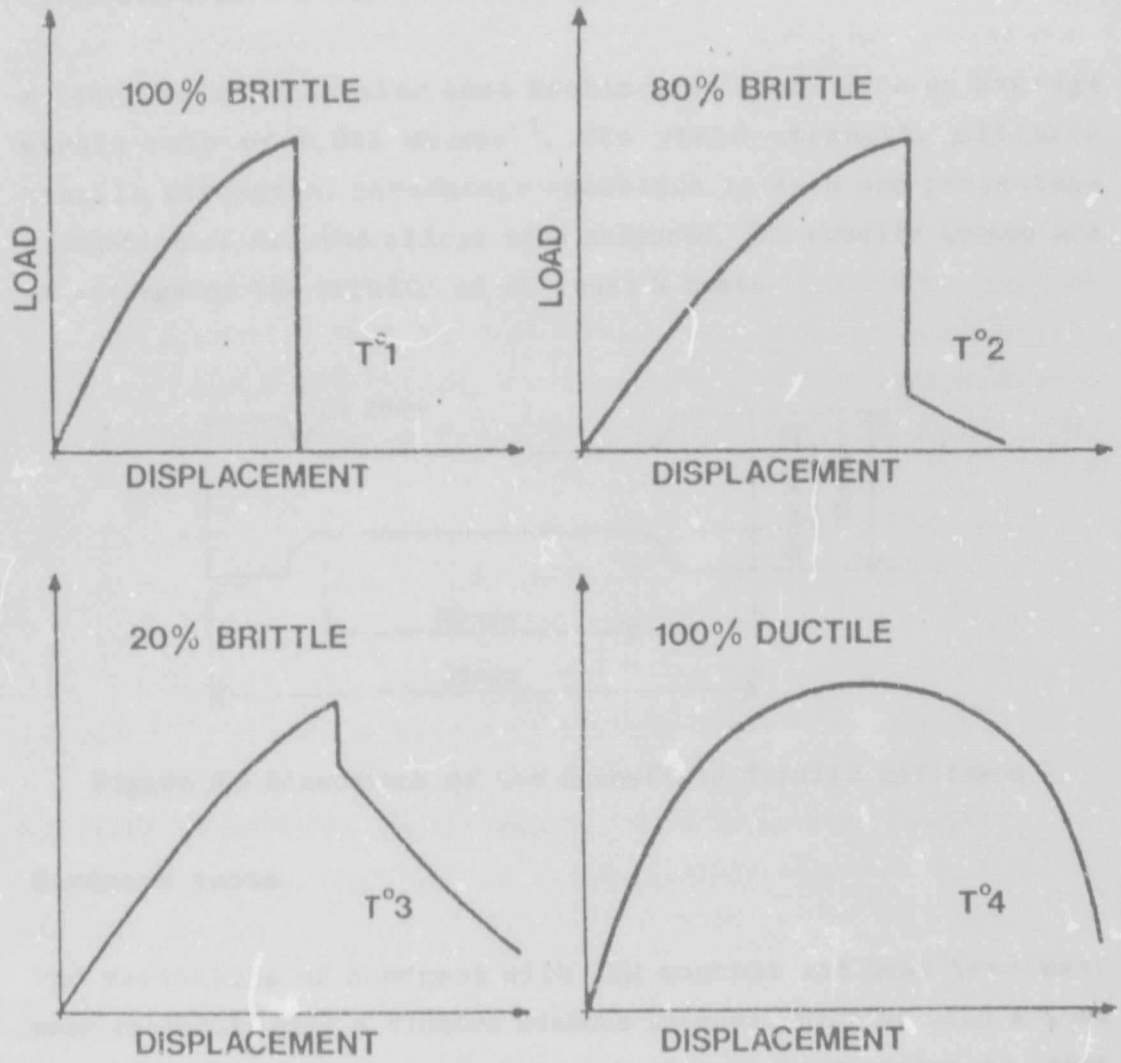


Figure 3.4 Schematic diagrams of the load displacement curves obtained as a function of testing temperature, in the 3 - point bend test[75].

3.5.3 Tensile tests

Standard Hounsfield tensile specimens (Figure 3.5) were machined from the rolled plate. Testing followed the procedure given in BS 18: PART 2: 1971. The tests were carried out at ambient temperature on the V2, V3 and V4 heats.

A Hounsfield Tensometer test machine was used, with an average strain rate of 0,083 mm.sec^{-1}. The yield strength, ultimate tensile strengths, percentage reduction in area and percentage elongation of all the alloys were measured. The results quoted are an average of the results of at least 3 tests.

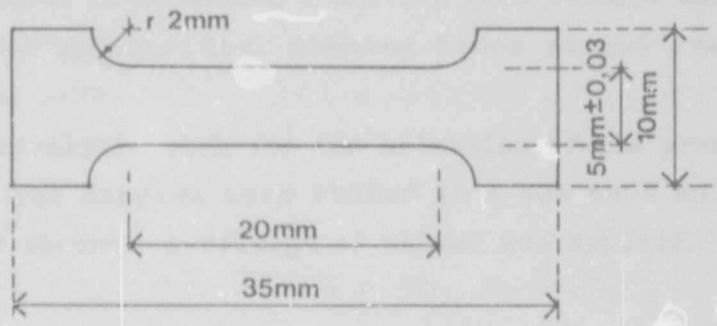


Figure 3.5 Dimensions of the Hounsfield Tensile specimens

3.5.4 Hardness tests

The variations of hardness with REM content and heat treatment were measured using a Vickers Diamond Hardness Machine with a load of 20kg. The specimen surfaces were prepared by grinding on emery paper and with diamond polish to a finish of 1 micron. The hardness values are given as an average of at least 5 impressions.

3.6 MICROSCOPY

3.6.1 Optical Microscopy

A Nikon Optiphot optical microscope with magnification up to 1000x was used. The specimens were prepared by grinding on successive grades of carbide paper up to 1200 grit. Final polishing was achieved by the use of diamond lapping compounds: 3μm and finally 1μm.

Two etchants were used:

(i) Glyceregia to reveal the grain structure. Glyceregia consists of 10ml HNO_3, 50ml HCl and 30ml glycerine. Difficulty was experienced in obtaining a uniform etch because this solution has poor wettability. Etching times ranged from 30 - 50 seconds.

(ii) An electrolytic etch for the detection of the presence of σ-phase. The samples were etched in a 40% NaOH solution for about 5 seconds. A voltage of +800mV was applied.

One side of some of the slow bend specimens was also polished to a 1μm finish. These specimens were examined optically in the as-polished condition after testing. Information relating to deformation, slip and fracture initiation was obtained from these samples.

3.6.2 Scanning electron microscopy (SEM)

The polished and fracture surfaces of slow bend and Charpy specimens were mounted for examination in a Cambridge Stereoscan scanning electron microscope and a Hitachi S45 Scanning electron microscope.

Grain boundary film thickness, precipitate distribution and their involvement in the fracture process were investigated.

Electron dispersive spectroscopy (EDS) was also used to identify