On the dynamic embrittlement of copper-chromium alloys by sulphur

R. D. K MISRA*, V. S. PRASAD
Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad, India

The high temperature ductility of copper-chromium alloys has been examined in the temperature range of 25–700°C. Copper-chromium alloys exhibit severe intermediate temperature loss in ductility. The loss in ductility is associated with the ingress of sulphur along the grain boundaries under the influence of tensile stress, followed by decohesion of grain boundaries. Integranular facets of the fracture surface exhibit striations, indicative of quasi-static, step-wise crack growth process. © *2000 Kluwer Academic Publishers*

1. Introduction

We have recently made preliminary investigations on a copper-0.5 wt% Cr alloy with and without the presence of zirconium [1–3]. These studies demonstrated that zirconium-free Cu-Cr alloy is susceptible to intergranular cracking by sulphur, when tensile tested at high temperatures. In a more recent investigation, the processing of Cu-Cr alloy through electro slag crucible remelting process (ESCM), led to considerable chemical refinement of the alloy with respect to both oxygen and sulphur, compared to the conventional vacuum melted material [3]. Additionally, there was ∼45% improvement in the hot ductility, together with moderate improvement in tensile strength (from 243 MPa to 270 MPa), of the electro slag crucible melted (ESCM) material in comparison to the vacuum melting process. The processing of Cu-Cr alloy through electro slag crucible melting results in low sulphur (28 ppm) and oxygen content (21 ppm) in the alloy because of slag/metal and graphite/metal reactions respectively. The low sulphur content of 28 ppm of the ESCM processed alloy, as compared to 300 ppm of the vacuum melted alloy was suggested to be reason for the observed improvement in hot ductility of ECSM Cu-Cr alloy [3].

The zirconium-free Cu-Cr alloy (nominal composition in wt%: Cu-0.5 Cr-0.0028 S) tensile tested at low strain rates was found to exhibit intergranular cracking, whereas zirconium-containing alloy (Cu-0.5 Cr-0.04 Zr-0.0018 S), tensile tested in an identical manner showed no signs of cracking [2]. The fact that the intergranular cracking was inhibited by the presence of small amount of zirconium (0.04 wt%), it was postulated that zirconium inhibited cracking in the zirconium-containing Cu-Cr alloy. This was in concurrence with the electron microprobe observation of small particles ($<2\ \mu$m) of zirconium sulphide and with the established role of zirconium as a scavenger of sulphur [2]. It was, however, not possible to examine grain boundaries through Auger electron spectroscopy (AES), to confirm if grain boundary segregation of sulphur still occurred in the zirconium-containing alloy, because it was difficult to obtain intergranular fracture in this alloy. On the other hand, AES studies conducted on *in situ* fractured intergranular fracture of zirconium-free alloy tensile tested at elevated temperatures indicated the presence of sulphur at the grain boundaries. The phenomena of intergranular cracking alloy is further investigated here at different temperatures, considering its engineering application and for the scientific understanding of intergranular cracking of copper alloys during hot working.

2. Experimental

Copper-chromium alloys were made by electro slag crucible melting process (ESCM), developed on the well established principles of electro slag remelting. A detailed description of the ESCM process is described else where [1, 3]. The experimental set-up consisted of a 250 mm diameter graphite crucible encased in a mild steel shell lined with magnesite ramming mass and a graphite electrode of diameter 100 mm and length 1000 mm. The graphite crucible was placed on a water cooled copper base plate. The power was fed from a 350 kVA, AC, single phase transformer between the graphite electrode and the base plate.

The power was initiated by striking an arc between the electrode and the base of the crucible. The composition of the slag selected for melting was 20 CaF_2-30 CaO-20 NaF-30 SiO_2 (wt. %). After some quantity of slag was melted by arcing, the slag itself acted as the ohmic source of heat by passing heavy current through it. The process was conducted at an average voltage of 40 V and an average current of 2000 A.

After the slag had become molten and superheated, about 15 kg of copper scrap had been added through the annular gap between the electrode and the crucible. This was followed by the addition of about 300 gm of unalloyed chromium to the melt, which was then allowed to stay for about 30 minutes. The refined copper alloy

* R.D.K. Misra is presently at LTV Steel, Technology Center, Independence, OH, USA. Email: dmisra@ltusteel.com

TABLE I Chemical composition of copper-chromium alloy in wt %

Cr	0.5
Ni	0.008
Pb	0.007
Zn	0.005
S	0.0028
O	0.0021
Cu	Balance

along with the slag was transferred into another graphite crucible of 95 mm diameter, where the ingot was cast. The liquid slag was transferred into another graphite crucible of 95 mm diameter, where the ingot was cast. The liquid slag covered the molten metal during melting and transfer and protects it from atmospheric oxidation.

Chemical analysis was carried out on drillings extracted from the ingot by atomic absorption spectrometer. Oxygen was analysed by Leco oxygen and nitrogen analyser. Sulphur was analysed by Leco carbon and sulphur analyser. The chemical composition of the alloy is given in Table I.

The ingot was sectioned in the transverse direction and discs of ∼35 mm thick were cut. The discs were homogenised at 1000°C for 24 hours in a resistance furnace, followed by air cooling. The discs were covered by pieces of charcoal and titanium chips to avoid or minimise oxidation of the discs. After homogenisation the discs were then rolled to a thickness of about 15 mm. The alloy was then solutionised at 980°C for in hour and followed by rapid quenching to room temperature, and aging at 475°C for 3 hours. After heat treatment, the thin oxide layer present on the surface of plates was removed by grinding.

Tensile tests were carried out in the temperature range of 25–700°C, using Instron type testing machine, on notched specimens of gauge length 25.4 mm and gauge diameter of 4 mm from the heat treated material. The specimens were initially loaded with a cross head speed of 0.2 mm/min. to below the yield strength of the material and then the cross head speed was adjusted to the desired test cross head speed, after being allowed to equilibrate thermally at the test temperature in the environment chamber. The specimens were loaded to failure. The fracture surfaces were examined under scanning electron microscope.

3. Results and discussion

The stress-strain plots for the Cu-Cr alloy tensile tested at the displacement rate (cross head speed) of 5 mm/min and 0.01 mm/min are presented in Figs 1 and 2. It may be seen from Figs 1 and 2 that fracture occurs at approximately constant stress, soon after attaining the maxima in stress. This behaviour is more striking for the tensile test carried out at the slow displacement rate of 0.01 mm/min (Fig. 2). For both the strain rates, the total strain decreases with increase in temperature, in the temperature range of 200–550°C, beyond which the strain increases (i.e. at 700°C). This behaviour is similar to that of % reduction in area (Fig. 3) and % elongation (Fig. 4). At constant temperature, the total strain is

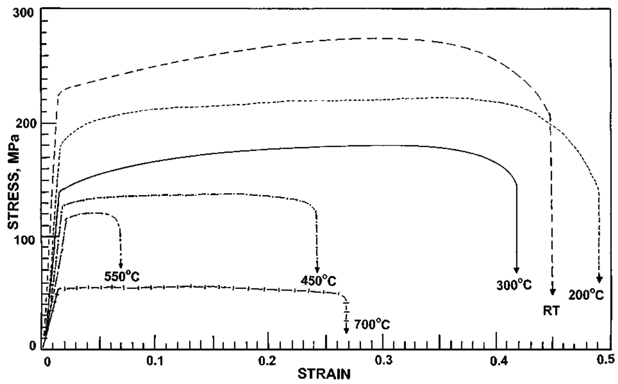

Figure 1 Stress-strain plots for the copper-chromium alloy tensile tested at a cross-head speed of 5 mm/minute at different temperatures.

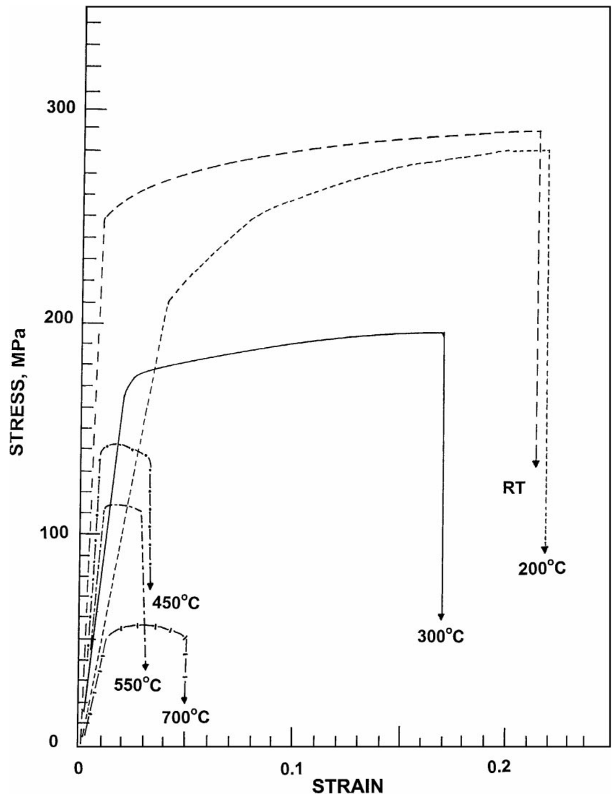

Figure 2 Stress-strain plots for the copper-chromium alloy tensile tested at a cross-head speed of 0.01 mm/minute at different temperatures.

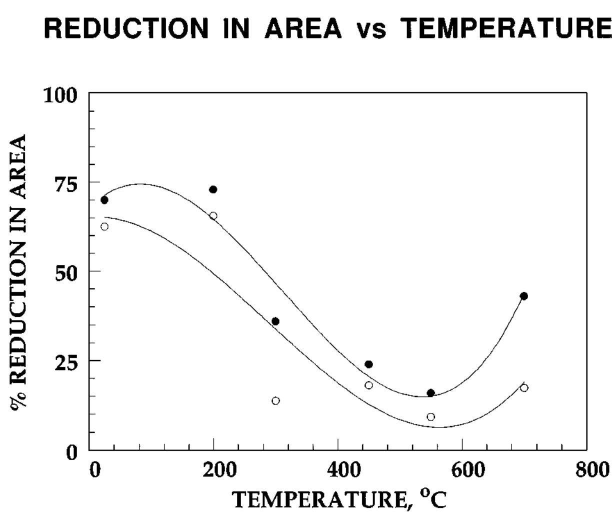

Figure 3 % reduction in area as a function of temperature for the copper-chromium alloys.

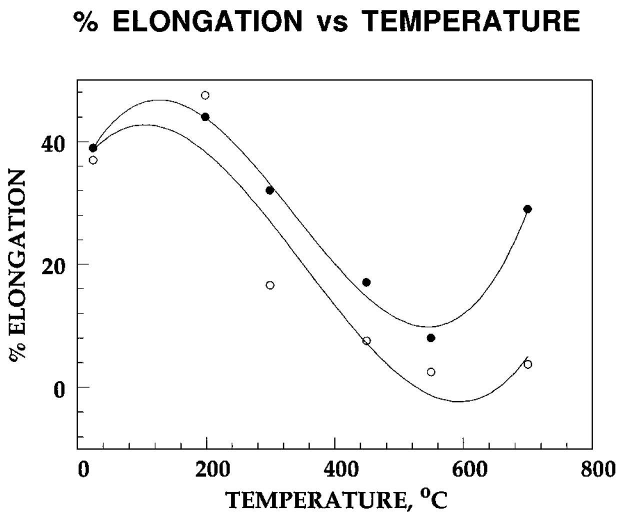

Figure 4 % elongation as a function of temperature for the copper-chromium alloys.

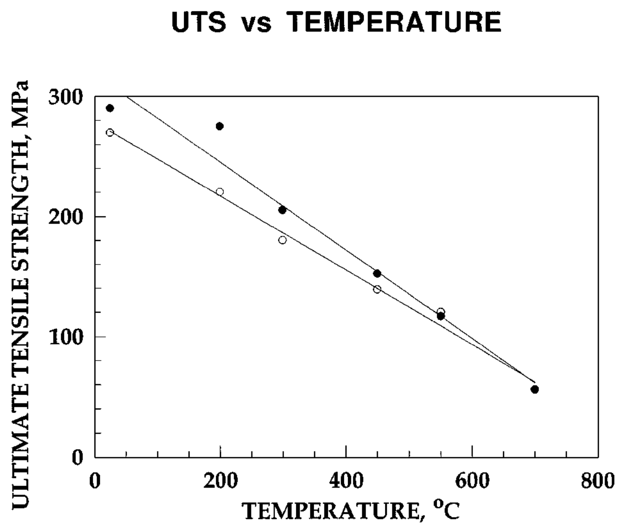

Figure 6 Ultimate tensile strength as a function of test temperature for the copper-chromium alloys.

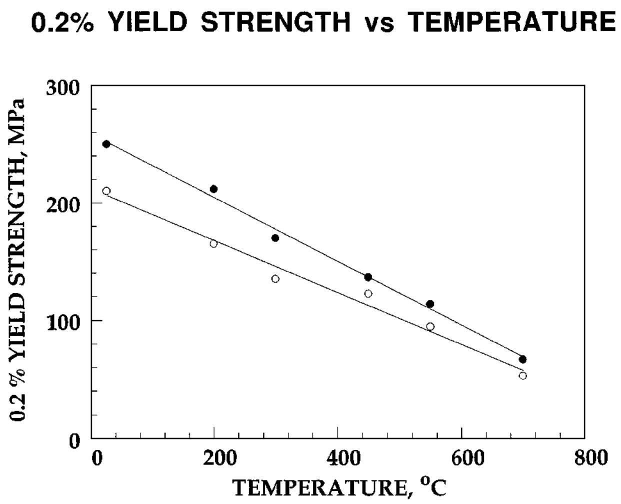

Figure 5 Yield strength as a function of test temperature for the copper-chromium alloys.

reduced by more than 50%, when the test strain rate is reduced from 5 mm/min to 0.01 mm/min. There is also a decrease in % reduction in area and % elongation with decrease in test strain rate. As regards, the yield strength (Fig. 5) and ultimate tensile strength (Fig. 6), there is a small increase in strength with decrease in test strain rate, and the effect diminishes with increase in test temperature. However, the decrease in total strain (Figs 1 and 2), % reduction in area (Fig. 3) and % elongation (Fig. 4) is comparatively greater to the small increase in tensile strength with decrease in test strain rate, up to test temperatures of up to 550°C. The aforementioned observations suggests an increase in the brittle behaviour of the alloy with decrease in the strain rate of test. It is also clear from the plots of % reduction in area and % elongation with temperature (Figs 3 and 4), that the alloy exhibits severe intermediate temperature loss in ductility; the values of % reduction in area and % elongation at 550°C being only about 10%.

The fracture surface of specimens, for either of the strain rates, were found to be predominantly intergranular, for test temperatures in the range of 200–550°C. The intergranular facets at higher magnification were found to contain striations. The spacing between striations varied from less than a micron to about 5 μm. Some examples of intergranular facets of the fracture surface displaying striations are presented in Figs 7–9. In Fig. 7 the striations are decorated with line-up of voids. Some of these striations indicated the presence of fine intergranular chromium-rich particles. The bottom right hand corner in Fig. 7 shows the presence of a ductile region adjacent to the smooth intergranular region containing striations. This ductile region is believed to be a consequence of tearing of regions connecting the intergranular facets. Fig. 8 presents a region with well-defined but widely spaced striations (3–5 μm) in the center and narrowly spaced striations (<1 μm) at the bottom right side of the fractograph. There were regions containing striations which also failed by intergranular decohesion, which probably occurred between regions where microvoids have grown and coalesced (Fig. 9). Such an area can be depicted as a band of decohesion separated by ductile regions. This experimental evidence of striations presented in Figs 7–9 is consistent with the quasi-static, step-wise crack growth, the type envisaged in a 'dynamic embrittlement' in copper-base alloys [2, 4, 5].

In dynamic embrittlement it is envisaged that any surface atom (segregated atom or externally adsorbed species) will have the tendency to penetrate mainly through the grain boundaries (grain boundaries are fast diffusion paths) under the influence of stress acting normal to the grain boundary. This ingress of surface diffusing element reduces the cohesive strength of the boundary, and at a particular threshold value of stress and concentration of the diffusing species, intergranular cracking occurs [2, 4, 5]. The presence of fine striations observed on the intergranular facets signify the discontinous nature of cracking, resulting from decohesion on a microscale [2, 4, 5].

Now considering that Auger electron spectroscopy studies conducted earlier [2] on *in situ* fractured intergranular fracture surfaces of zirconium-free Cu-Cr alloy tensile tested at elevated temperatures indicated the presence of sulphur at grain boundaries. Secondly, the

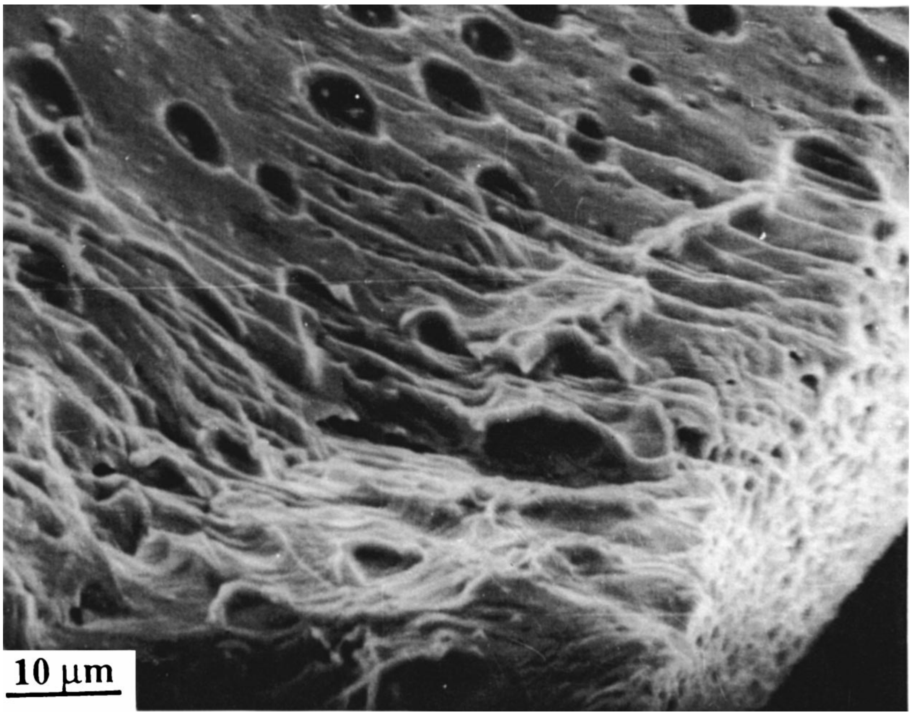

Figure 7 Intergranular fracture surface of copper-chromium alloy showing striations decorated with line-up of voids containing Cr-rich particles.

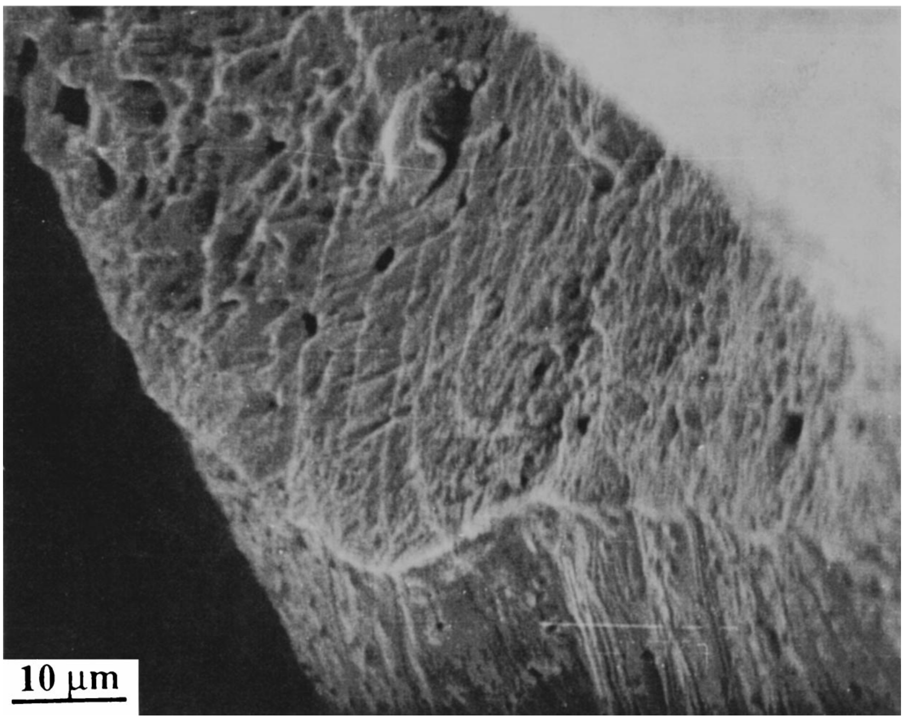

Figure 8 The presence of widely spaced striations (3 to 5 μm) (in the centre of the fractograph) and narrowly spaced striations (<1 μm) (bottom right hand corner).

grain boundary sulphur was scavenged through small additions of zirconium (0.04 wt %), leading to 100% rupture. Thirdly, with regard to the detrimental effect of sulphur, it is known that grain boundary strength is reduced by segregation of trace impurities of sulphur in ferrous alloys. It is therefore believed that the harmful effect of sulphur leading to intergranular fracture of Cu-Cr alloys is a consequence of decrease in intergranular strength, brought about by grain boundary sulphur. The harmful effect of sulphur in copper-base alloys appears to have not been seriously viewed in the past, mainly because of the fact that sulphur-content in copper-base alloys is far less than in ferrous alloys and also because intergranular fracture rarely occurs in copper-base alloys, except in situations where the alloy is subjected to elevated temperatures. Thus from the above discussion, the decrease in reduction in area (Fig. 3) and % elongation (Fig. 4) with increase in temperature (up to 550°C) is attributed to the increased diffusivity of sulphur at elevated temperatures. For similar

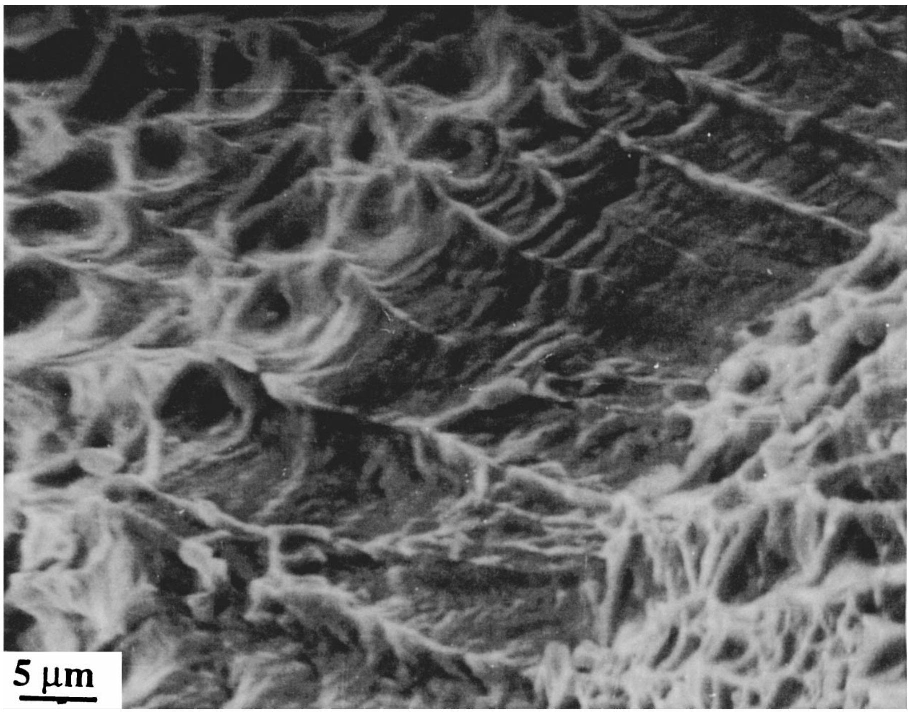

Figure 9 An intergranular region containing striations having resemblance of broad steps (in the centre of the fractograph) which appears as a band of decohesion separated by ductile regions.

reasoning, at constant temperature, the lower value of % reduction in area and % elongation observed at a relatively lower cross head speed of 0.01 mm/min, compared at of 5 mm/min, is related to increase in grain boundary sulphur with increase in test duration. As regards the increase in % reduction in area and % elongation for test temperatures greater than 550°C (i.e. at 700°C for both the test strain rates), this can be attributed to the migration of slower diffusing species (Cr) to eliminate the sulphur concentration gradient [6].

4. Conclusions

(i) Copper-chromium alloys exhibit severe intermediate temperature loss in ductility in the temperature range of 200 to 550°C.

(ii) This loss in ductility is associated with the ingress of sulphur along the grain boundaries under the influence of tensile stress, followed by decohesion of grain boundaries.

(iii) Intergranular facets of the fracture surface exhibit striations, consistent with quasi-static, step-wise crack growth process, as envisaged in dynamic embrittlement.

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