On the presence of amorphous regions in splat-quenched Al–Cu alloys

Splat-quenching has been commonly used to obtain amorphous films of a wide range of alloys [1]. The amorphous condition normally occurs at the highest cooling rates and is generally identified in the electron microscope by the absence of diffraction contrast and the occurrence of diffuse ring diffraction patterns. It is the purpose of this communication to point out that regions of amorphous material present in the final splat and identified in this way may be an artefact introduced during either the splatting itself or subsequent specimen thinning.

The artefacts that are described below were observed in a range of splat-quenched Al–Cu alloys up to eutectic (17.3 at.% Cu) composition. Specimens (~100 mg) were splat quenched from 850° C using a modified Duwez gun apparatus, operated under reduced pressure (400 Torr) of high purity argon after prior evacuation to 2×10^{-5} Torr. Details of the apparatus have been described elsewhere [2]. The specimens obtained were extremely porous, adhering closely to the water-cooled copper substrate. Small sections were removed using a fresh scalpel blade, and studied in a Philips E.M.301 electron microscope, either directly, or after ion-beam thinning to permit study of the thicker, slower cooled areas.

Large regions of all as-splatted alloys were transparent to 100 kV electrons, and in their thinnest regions (Fig. 1a) were crystalline and apparently single phase, as evidenced by lack of ⟨1 0 0⟩ streaking in selected-area diffraction patterns (Fig. 1b), characteristic of breakdown to G.P. zones. In thicker, slower cooled regions of the same specimen, there was diffraction evidence for G.P. zone and θ'' formation [3]. For comparative studies of splat-quenched specimens an estimate of the cooling rate is required. This has been obtained from measurements of interlamellar spacing in eutectic regions present in ion-beam thinned specimens containing more than 13 at.% Cu. Fig. 2 shows lamellae with spacing ~20 nm which was the smallest generally observed. Using the method of Burden and Jones [4], a cooling rate of 5×10^{8}° C sec^{-1} was estimated, and it is concluded that the single-phase regions in as-splatted specimens have cooled at rates significantly in excess of this figure.

In addition to such crystalline regions, amorphous structures were observed in the as-splatted specimens. A typical region, and its associated diffraction pattern is shown in Fig. 3. Table I contains

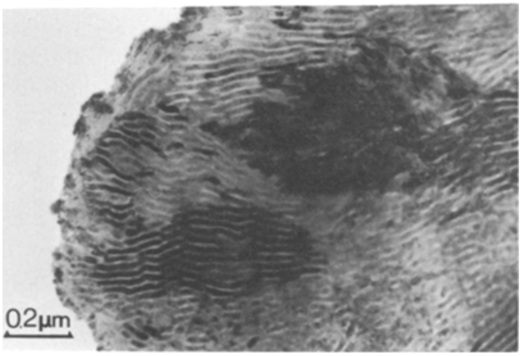

Figure 2 Al–Cu/θ lamellae in ion-beam thinned splat-quenched Al–17.3 at.% Cu with interlamellar spacing ~20 nm.

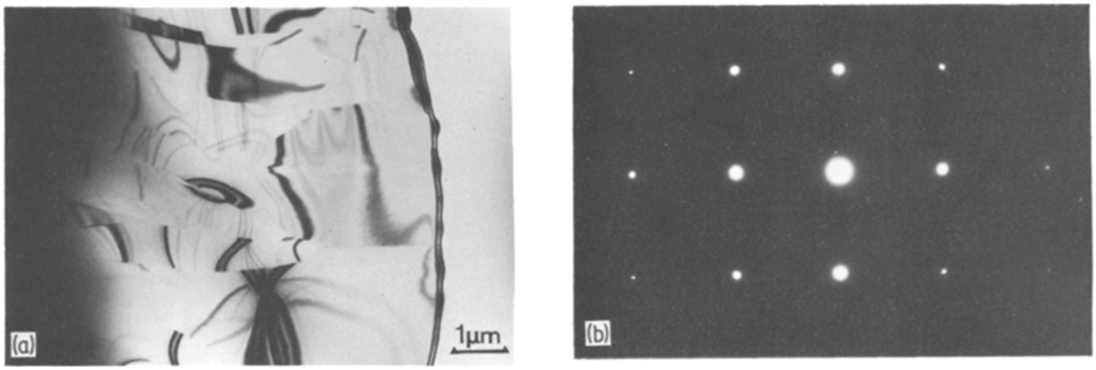

Figure 1 (a) A typical thin crystalline region in as-splatted Al–17.3 at.% Cu; (b) selected-area diffraction pattern from a single grain.

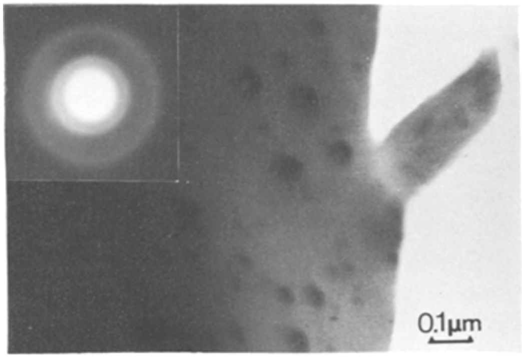

Figure 3 Amorphous region in as-splatted Al–17.3 at.% Cu with selected-area diffraction pattern.

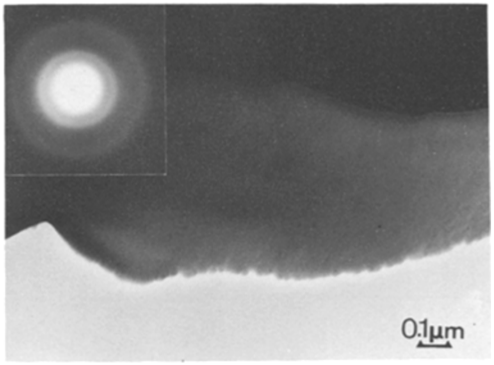

Figure 4 Amorphous material obtained by splat quenching Melinex with selected-area diffraction pattern.

TABLE I Values of $K(= 4\pi \sin\theta/\lambda)$ and associated error ΔK for the first two diffuse rings in diffraction patterns in Figs. 3 to 5.

Figure	$K_1 \pm \Delta K$ (Å^{-1})	$K_2 \pm \Delta K$ (Å^{-1})
3	2.73 ± 0.03	5.38 ± 0.05
4	2.75 ± 0.03	5.41 ± 0.05
5	2.78 ± 0.03	5.25 ± 0.05

the values of K ($4\pi \sin\theta/\lambda$, where λ is the electron wavelength and θ is the Bragg angle) obtained from microdensitometer measurements of ring radii. Regions like those in Fig. 3 were typically thicker than the crystalline areas and were, therefore, probably more slowly cooled. Thus it is unlikely that these regions were amorphous Al–Cu and an alternative explanation was sought.

The most likely external source of non-crystalline material is the polymer diaphragm which we, in common with others, use in the gun technique to develop the shock wave of high purity argon. Fragments of the ruptured diaphragm could become incorporated in the molten alloy, carbonized and subsequently splatted. To test this possibility, a small quantity of the Melinex sheet, used in the present experiments as a diaphragm material, was heated in the splat-quenching apparatus until carbonization commenced, when it was splatted in the usual manner. Small flakes were collected and observed in the electron microscope. They were electron transparent, stable under a 100 kV electron beam, were featureless and gave rise to diffuse ring diffraction patterns (see Fig. 4). Values for K from these patterns, and those from an evaporated amorphous carbon film, are included in Table I. Within the experimental errors, both values are identical to those obtained from Fig. 3. Therefore, it is concluded that carbonized diaphragm fragments can be incorporated in the splat as amorphous regions.

In the present work, amorphous regions were also observed in specimens that had been ion-beam thinned from the bulk and these did not usually correspond to amorphous carbon. A typical region, with its diffraction pattern is shown in Fig. 5, and Table II contains values of K which are clearly different from those in Table I. These regions are not amorphous Al–Cu because, on slowly heating to ~550° C (melting point of Al–Cu eutectic) *in situ* in the heating stage of an EM301 electron microscope, the region did not decompose into crystalline phases. After heating to 550° C electron diffraction patterns and oxide films remaining when

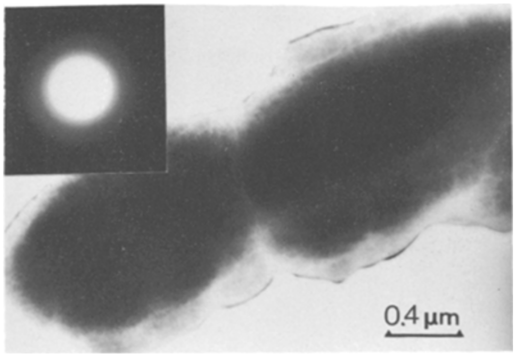

Figure 5 Amorphous region observed in an ion-beam thinned specimen of Al–17.3 at.% Cu with selected-area diffraction pattern.

TABLE II Values of K and ΔK from the first two diffraction rings observed in (a) ion-beam thinned Al–17.3 at.% Cu specimen, (b) oxide film from Al–17.3 at.% Cu, and (c) those reported by Davies and Hull [7] for amorphous Al–Cu.

	$K_1 \pm \Delta K$ (Å^{-1})	$K_2 \pm \Delta K$ (Å^{-1})
a	1.79 ± 0.02	4.08 ± 0.04
b	1.79 ± 0.02	4.08 ± 0.04
c	2.70	4.93

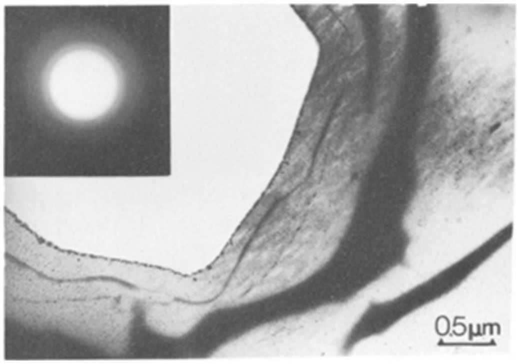

Figure 6 Amorphous oxide produced after heating splat-quenched Al–17.3 at.% Cu alloy to ~550° C in the electron microscope together with selected-area diffraction pattern.

the alloy evaporated are shown in Fig. 6 and correspond to Fig. 5. Typical values for K are also listed in Table II. Therefore, the amorphous regions in the ion-beam thinned foils are primarily oxide.

It is reasonable to assume that oxide formation does not occur during the splat-quenching because of the care taken to eliminate oxygen from the system and the complete absence of oxide films in the as-splatted condition. Accordingly, the most likely cause is the ion-beam thinning itself, during which significant specimen heating can occur [5] and contamination with oxygen is possible.

It is of interest to compare the present results with those of Davies and Hull [6, 7] who have reported the occurrence of amorphous Al–Cu eutectic. Their values of K are included in Table II. Clearly their material is not oxide. Their first ring could arise from amorphous carbon but their second clearly cannot, and neither we nor they can provide an explanation for it. However, unless the errors inherent in calibration of the camera constant in the electron microscope are minimized, using the approach outlined by Edington [8] as in this investigation, in our opinion values of K should be treated with caution, particularly where errors are not specified.

It is concluded, therefore, that the amorphous phases observed in this investigation were not amorphous Al–Cu eutectic, but can be explained either by carbonization of the diaphragm fragments or simple oxidation occurring during specimen preparation.

Acknowledgements

The authors are grateful to Dr M.G. Scott for supplying the alloys. D.B.W. is also grateful to the S.R.C. for the award of a Fellowship.

References

1. C. V. GOKULARATHNAM, *J. Mater. Sci.* 9 (1974) 673.
2. J. WOOD and I. SARE, Proceedings of the Second International Conference on Rapidly Quenched Metals, M.I.T., Boston, USA (1975).
3. D. B. WILLIAMS and J. W. EDINGTON, *J. Mater. Sci.*, to be published.
4. M. H. BURDEN and H. JONES, *J. Inst. Metals* 98 (1970) 249.
5. D. J. BARBER, *J. Mater. Sci.* 5 (1970) 1.
6. H. A. DAVIES and J. B. HULL, *Scripta Met.* 6 (1972) 241.
7. *Idem, J. Mater. Sci.* 9 (1974) 707.
8. J. W. EDINGTON, "Practical Electron Microscopy in Materials Science", (Macmillan, London, 1975).

Received 11 February
and accepted 2 March 1976

D. B. WILLIAMS
J. W. EDINGTON
Department of Metallurgy and Materials Science,
University of Cambridge,
Pembroke Street,
Cambridge, UK