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

There are a number of points arising from the above note on which we should like to comment. In their penultimate paragraph, Williams and Edington state that we are "unable to provide an explanation" for the non-crystalline phase that we observed in our splat-quenched samples of eutectic Al–Cu alloy [1, 2]. We have, in fact, proposed [1, 2] that the non-crystalline phase was amorphous Al–17.3 at. %Cu. The crystallization of this phase was subsequently studied [3] by hot-stage electron microscopy, and the precipitation and growth of θ phase, leaving a matrix of crystalline α-solid solution phase, is shown in Fig. 1. This will be described in greater detail elsewhere [4]. The crystallization temperature was observed to be ~250° C but we believe this to be erroneously high because of poor design of the particular heating stage employed in our work.

The fracture of the diaphragm material used in our work (Mylar) was, in all cases, simple and clean and we found no evidence that carbonized Mylar became incorporated into the foils on quenching, as was observed by Williams and Edington. We observed non-crystalline phases in electron-transparent areas of splat-quenched samples of Al–Si and Al–Pd alloys also. Although we did not perform crystallization experiments on these, we are confident that they are not associated with diaphragm material either, since we did not observe an amorphous phase in samples of Al–Fe alloys quenched from similar temperatures. The time between fracture of the diaphragm and

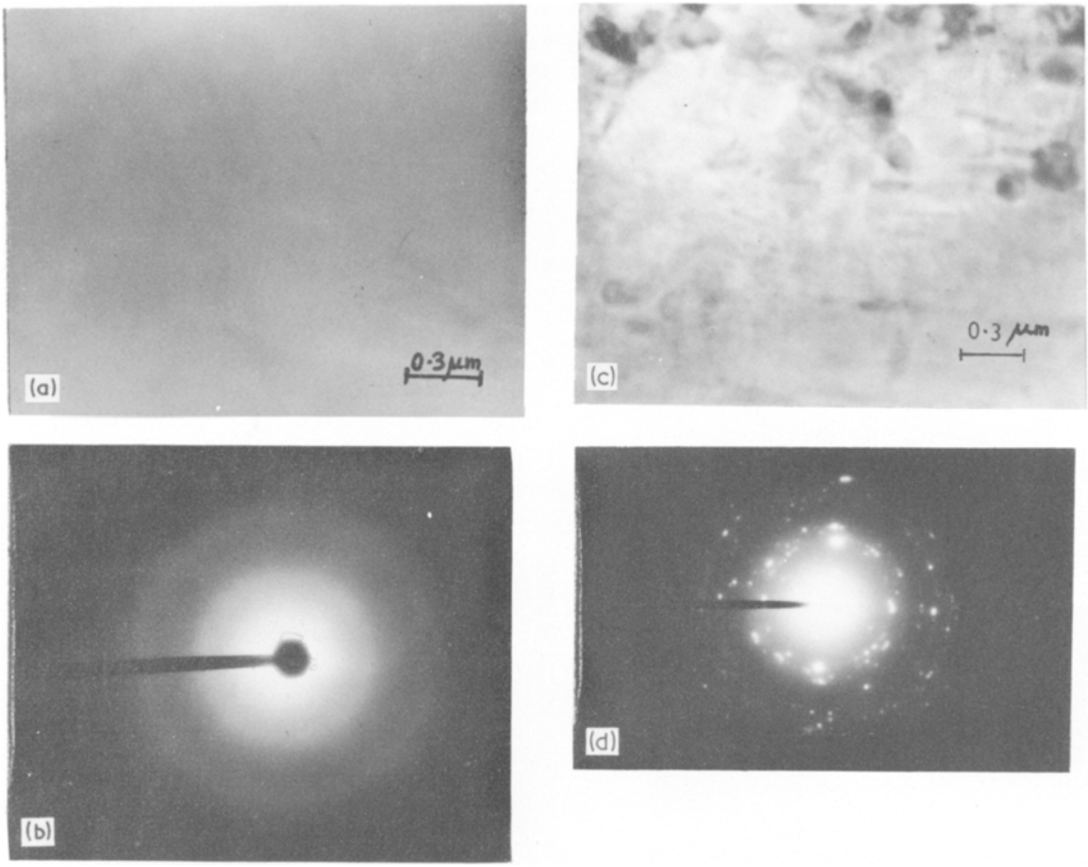

Figure 1 Electron micrographs and corresponding diffraction patterns showing the crystallization of amorphous Al–17.3 at. %Cu [3]. (a) and (b) Initial non-crystalline phase, (c) and (d) onset of crystallization, (e) and (f) final stages of transformation (dark phase – θ Al_2Cu: matrix – solid solution), (g) rapid coalescence of θ particles on slight increase of foil temperature.

TABLE I Comparison of diffraction peak positions for amorphous Al–17.3 at. % Cu with those for amorphous oxides

	$K = 4\pi \sin\theta/\lambda$ (Å^{-1})		
	First peak K_1	Second peak K_2	K_2/K_1
Amorphous Al–17.3 at. % Cu	2.70	4.93	1.82
Amorphous oxide (Williams and Edington)	1.79	4.08	2.28
Amorphous Al_2O_3 [5]	2.14	4.65	2.17
[6]	2.14	4.52	2.11

completion of quenching in the gun technique has been shown to be ~1 msec. In spite of the apparently close agreement between the diffraction patterns of the amorphous phases in quenched Al–Cu alloy and quenched Melinex observed by Williams and Edington, it is appropriate to question whether carbonization of the Melinex could occur within as short a time span of a few hundred μsec.

We had, prior to performing the *in situ* crystallization of amorphous Al–17.3 at.% Cu, considered the possibility of its being aluminium oxide. The electron diffraction peak positions, expressed in diffraction co-ordinate $K(=4\pi \sin\theta/\lambda)$, are compared with published data for amorphous alumina [5, 6] and those of the oxide phase observed by Williams and Edington in Table I. Notwithstanding the results of our crystallization studies on the amorphous Al–Cu, the possibility of confusion of the diffraction pattern with that of an oxide is small. Not only are the absolute values of the peak positions substantially different for the first two peaks but also the ratio K_2/K_1 is much smaller for the Al–Cu than for the oxides. This K_2/K_1 ratio of 1.82 falls clearly within the range 1.7 to 1.9 observed for amorphous and liquid metallic phases [7]. An error incurred in determining the microscope camera constant C should not influence the *ratios* of peak positions. With specimens normal to the beam, the uncertainty in C is generally $< \pm 2\%$. The random error associated with measuring the positions of very diffuse and low intensity diffraction peaks superimposed on a strong and steeply sloping inelastic component can, however, be significantly greater than this, unless great care is taken. The peak positions for the oxide observed by Williams and Edington are about 12% lower on average

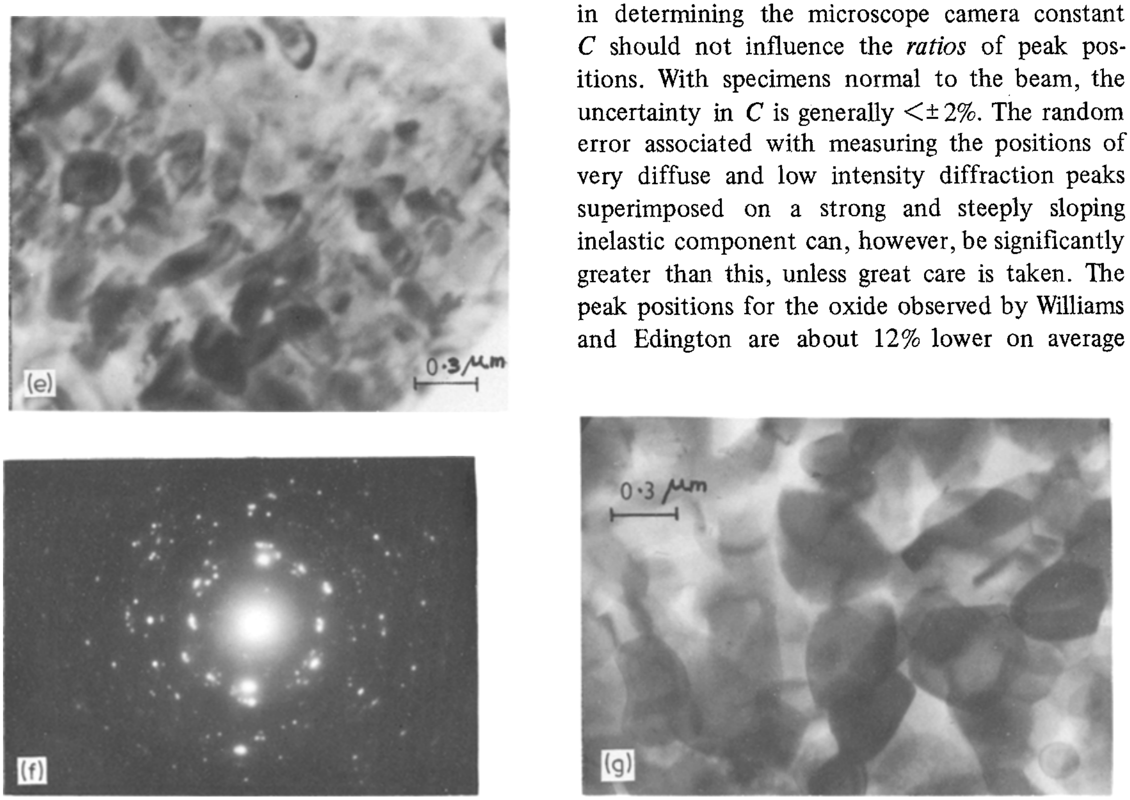

Figure 1 continued.

than the previous data for amorphous Al_2O_3 [5, 6], which were in close mutual agreement, but this may be because a mixed oxide forms on heating or ion-beam thinning of the Al–Cu foils.

Williams and Edington estimated a cooling rate of 5×10^8 K sec^{-1} from a eutectic lamellar spacing of ~20 nm, shown in their Fig. 2. This estimate is based on an assumed specimen thickness of ~150 nm whereas the area considered has been ion-beam thinned from an initially greater but unspecified thickness. We have emphasized previously [2] the need to consider the *as-solidified* specimen thickness t when estimating cooling rates $\dot{r}$ by this method since the derived $\dot{r}$ is sensitively dependent on t.

References

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The production of electron transparent areas by splat-quenching

Splat-quenching, using the gun technique [1], involves the use of a shock wave to impel molten metal droplets directly onto a cooled, inclined, copper substrate. The aim of the technique is to maximize the quench rate, thus giving rise to metastable, non-equilibrium structures. In the extreme case, areas thin enough for direct examination in the electron microscope at 100 kV are produced.

Recently, Vitek [2] proposed that the formation of such electron transparent areas was not simply due to the spreading of individual droplets upon impact with the substrate. Using combined scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM), two alternative mechanisms were proposed. These involved (a) the interaction on the substrate between a solidifying droplet and a subsequently impacting droplet that had undergone in-flight solidification, and (b) the interaction of a solidifying droplet with a flaw, or solid droplet, on the substrate. Regions arising from such droplet interactions will have undergone an unknown sequence of cooling and reheating, resulting in atypical precipitation reactions, since the specimens, in general, are highly supersaturated. It is the purpose of this communication to point out that, for comparative microstructural studies of splat-quenched specimens, it is essential that the regions observed have cooled under similar conditions. Furthermore, this situation can be approached in practice by manipulation of the experimental variables. It is possible to produce thin areas arising mainly from simple impact spreading. Such areas will have undergone a rapid, and most importantly, a relatively reproducible quench, thus permitting valid microstructural comparisons to be made between different specimens.

A thin region, similar to the type described by Vitek [2] is shown in Fig. 1. The sample of Al–17.3

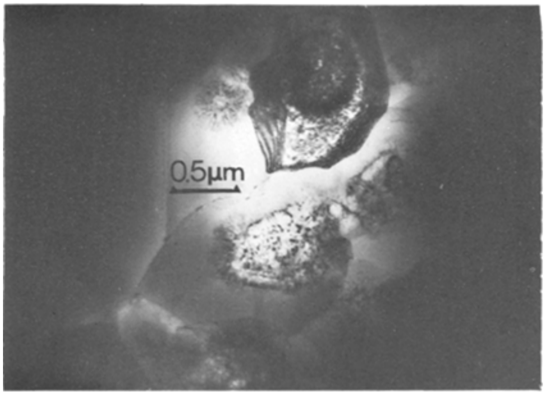

Figure 1 An electron transparent region surrounded by bulk material in a splat quenched Al–17.3 at.% Cu alloy.