

Microbeam analysis studies of the copper–silver interface

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Copper–silver bimetallic samples have been examined by microbeam analytical techniques. Composition studies have concentrated on the interface region between the two metals. In this region two distinct phases characteristic of a eutectic structure were observed by backscatter electron imaging in the SEM. X-ray microanalysis has shown that the eutectic is composed of a copper-rich and a silver-rich phase. The crystal structure and composition of the constituent phases of the eutectic material have been confirmed by electron diffraction studies of a thinned foil of the eutectic composition. The surface structure of ion-beam etched eutectic material has been examined at high resolution. The silver-rich constituent of the eutectic is found to etch preferentially. The surface composition of the eutectic has been explained in terms of this ion-beam-induced surface structure.

1. Introduction

Bimetallic materials are routinely used in the manufacture of electronic and electrical components. High-quality composites for these applications are required to have a continuous interfacial bond with adequate strength and ductility, and to be free from porosity or inclusions. These properties are slightly less important in other areas of application, such as jewellery manufacture, but the bond must still be able to cope with deformation which would be present, for example, in a drawing process.

A controlled degree of interdiffusion between the component strips is conventionally achieved by means of a number of mechanical and thermal treatments. The number of stages involved introduces high production costs. It is clear that the ability to characterize the interfacial region is of technological interest in situations where new manufacturing processes are to be developed. The copper–silver system is of the eutectic type and exhibits only a limited degree of solid solubility.

Microbeam analytical techniques are the most appropriate techniques for examination of structure and composition at the interface between the two components of a bimetal. In an earlier investigation [1] of the copper–silver bimetallic interface composition, Auger electron spectroscopy (AES) and energy dispersive X-ray microanalysis (EDX) have been used to characterize the degree of interdiffusion between the constituent elements in a Cu/Ag bimetallic strip. In the interface region of the bimetal the eutectic composition (39.9 at % Cu) was detected by EDX extending over a distance of 0.5 mm at the copper–silver interface. Examination of the surface composition of this region by AES gave a composition of 47 at % Cu which was at variance with the eutectic composition obtained by EDX. A similar uniform surface composition has been

detected by AES by Furman [2]. A uniform surface composition was obtained by AES despite the occurrence, confirmed by EDX, of small areas ($< 1\mu\text{m}$) of distinct copper-rich and silver-rich phases in the eutectic region. Because of the degree of electron-beam spreading and the fine structure of the eutectic an accurate analysis of the composition of the constituent phases of the eutectic by EDX was not possible.

In the present investigation of the copper–silver bimetallic interface, the composition of the constituent phases in the eutectic region have been determined and the influence of ion-beam cleaning on surface composition prior to AES has been investigated.

2. Experimental procedure

The copper–silver samples investigated were prepared by punching a silver rod into a hole of similar diameter in a copper plate. The bimetal was then annealed at temperatures of the order of 800°C and quenched. This preparation differed from the previously examined samples [1] which were obtained by dispensing molten silver into a cavity in a copper strip.

Samples polished down to 0.25 μm grade diamond paste were examined in a Jeol T300 scanning electron microscope (SEM) fitted with a Link systems X-ray detector and in a VG HB100 Multilab by AES. For transmission electron microscopy (TEM), and electron diffraction samples of foil with the eutectic composition (Goodfellow Metals Ltd) were electropolished in a Bainbridge Unithin unit with 0.1 N solution of nitric acid as an electropolishing agent. Quantitative analysis by EDX in the SEM was performed using the FRAME C [3] and Magic IV [4] programs. Quantification by AES was performed using the AQUA software developed by Moir *et al.* [5].

3. Results

The compositional variations in the band of intermediate composition close to the Cu–Ag boundary are immediately apparent in the low-magnification backscattered electron image obtained in compositional contrast mode (Fig. 1).

The Cu/Ag samples examined in the investigation described here were found to have a coarser eutectic structure than observed in earlier studies of samples prepared by different techniques [1]. Large areas of the silver-rich (light) phase surrounded by the finer eutectic duplex structure (Fig. 2a) were observed. Other regions contained large areas of the copper-rich (dark) phase surrounded by this finer eutectic duplex structure (Fig. 2b). The larger areas of both the light and dark phase extended laterally over distances of the order of 5 μm and will therefore extend into the sample by a similar distance. X-ray microanalysis spectra obtained from both phases are shown in Fig. 3. The light, silver-rich phase was found to contain 85 at% silver and 15 at% copper. The dark, copper-rich phase was found to contain 90 at% copper and 10 at% silver. These compositions have been obtained with electron accelerating voltages for X-ray excitation ranging from 15–30 kV, confirming that these large inclusions extend with uniform composition into the sample.

Previous study of the Cu/Ag eutectic by AES [1] after preliminary argon ion-beam cleaning has indicated a uniform surface composition that is richer in copper than the accepted eutectic composition. Despite using the small probe size (10 nm) for AES in the HB100 Multilab, no difference in composition was recorded from the different components of the eutectic. During these AES studies of Moir and Fitzgerald [1] ion-beam cleaning was carried out at a number of different angles of incidence. In the study described here ion-beam etching has been made in the same direction and at the same angle of incidence (45°) to the sample. This has enabled the direction of ion-beam etching to be located in secondary and backscattered electron images. No obvious directional effects due to ion etching were observed.

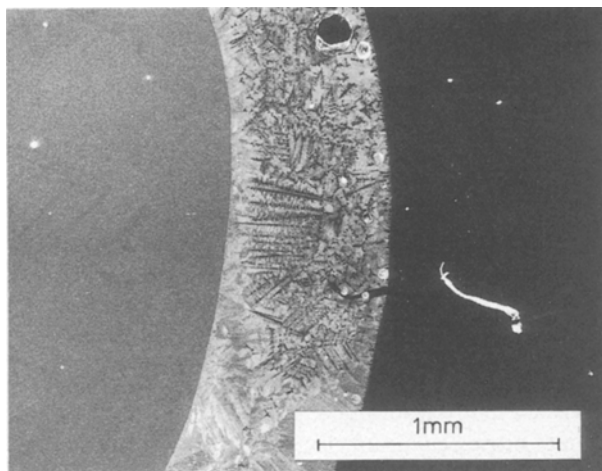


Figure 1 Backscattered electron image (atomic number contrast) from a Cu/Ag sample showing a region of intermediate composition between copper on the right and silver on the left.

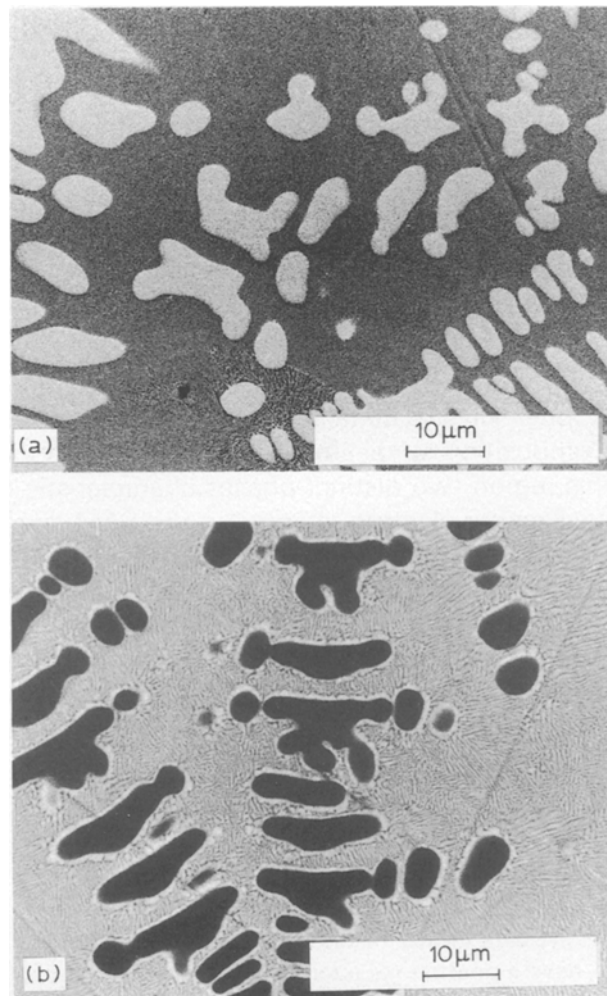


Figure 2 Backscattered electron micrographs of large areas of (a) the silver-rich component of the eutectic phase (light contrast), and (b) the copper-rich component of the eutectic phase (dark contrast).

Fig. 4a shows the secondary electron image of an area of the fine duplex region in the eutectic after ion-beam etching. Preferential sputtering of one phase of the eutectic material is evident in this micrograph with the formation of ridges and etched valleys. Fig. 4b shows the same area imaged in the backscattered electron mode. The dark contrast (copper-rich) in the backscattered image corresponds to the top of the ridges which appear bright in the secondary electron image. The backscattered electron image shows clearly that the ends of the surface ridges exhibit dark contrast and hence are of lower atomic number, and can therefore be assumed to be copper-rich. During ion-beam etching the copper regions will preserve regions of silver-rich material beneath them by shielding from the ion beam.

A consequence of this complex surface structure attained in the fine duplex structure of the eutectic, after ion-beam etching, is that, despite the use of the high-resolution spot mode, (~ 10 nm diameter) it will not be possible to obtain an accurate analysis of the surface composition by Auger electron spectroscopy of the copper-rich ridge surface. Scattered electrons produced well below the surface of a ridge will excite Auger electrons at the sidewall surface of a ridge. This surface is likely to be silver-rich at a depth of the order

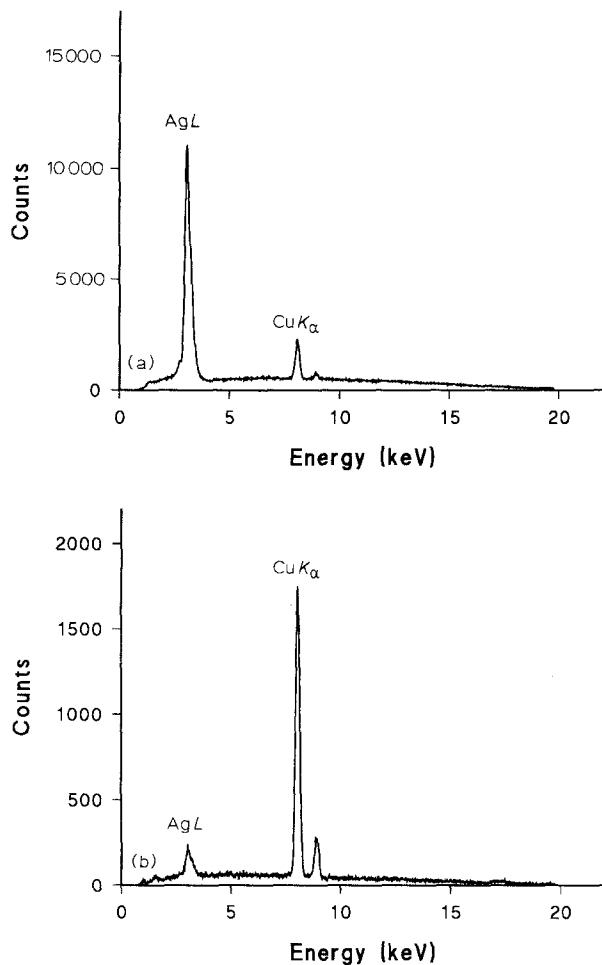


Figure 3 EDX spectra from a large area of (a) the silver-rich component of the eutectic phase, (b) the copper-rich component of the eutectic phase. Accelerating voltage 30 kV.

of 0.2 μm because this is the dimension of the eutectic phase texture shown in Fig. 4.

A schematic diagram of the sites for the origin of Auger electrons emitted from the surface structure of the eutectic, obtained by ion-beam etching, is shown in Fig. 5. The situation obtained when the primary beam is incident normal to the surface and at an angle of 45° to the surface is shown in this diagram. At a 45° angle of incidence for a regular eutectic structure, similar in form and size to the structure observed in Fig. 4, an approximately constant composition across the eutectic is likely to be detected as in the earlier work of Moir and Fitzgerald [1] where the primary incident electron beam was incident at the copper-rich ridge surface.

Composition analysis of the larger copper-rich and silver-rich areas in the coarser eutectic structure should not have the problems, discussed above, which are associated with composition analysis by Auger electron spectroscopy from the fine eutectic structure. Auger spectra from the centre of these large areas will not contain contributions from other regions as observed in fine eutectic regions. However, Auger electron spectra from the coarse eutectic structure show that the effect of ion-beam etching is more complex than the preferential etching of one component of the duplex structure. The surface composition (Table I) obtained by AES of both light (silver-rich) and dark

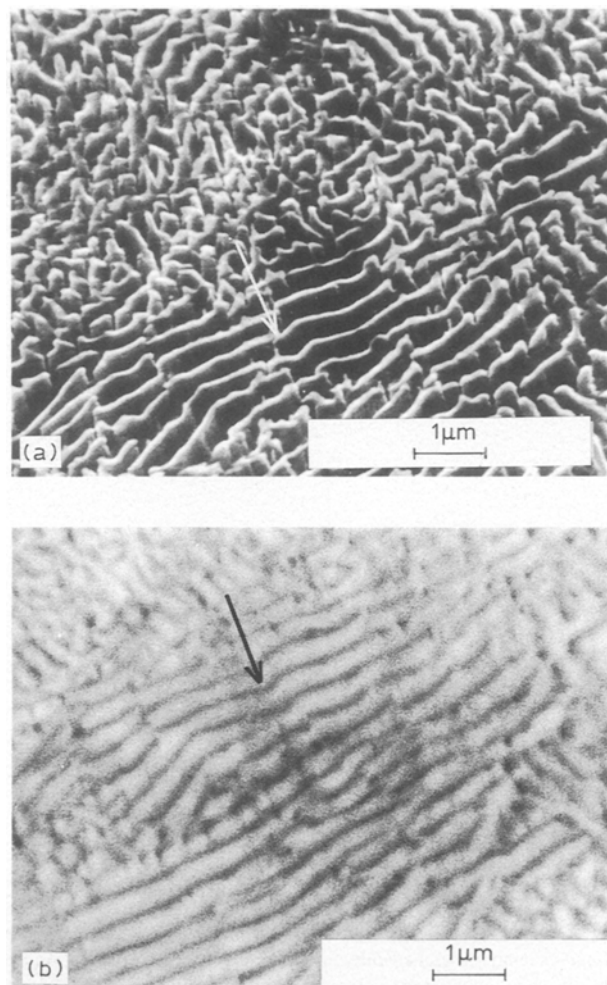


Figure 4 Area of an ion-etched surface of the copper-silver eutectic with the sample tilted 45° to the incident beam. The bottom of the micrograph corresponds to that part of the sample closest to the electron source. (a) Secondary electron image, (b) backscattered electron image. The arrow indicates equivalent areas in the two micrographs.

(copper-rich) phases differed from the bulk composition obtained by EDX.

When electropolished foils with the eutectic composition were examined by electron diffraction, electron diffraction patterns (Fig. 6) from the silver and copper crystal structures were identified and corresponded, respectively, with the silver-rich and copper-rich phases in the eutectic. These observations agree with X-ray diffraction observations [6] of the crystal structures of Cu-Ag alloys formed with small percentages of copper or silver.

4. Discussion and conclusions

The copper-silver samples investigated here were found to have a coarser eutectic structure which could be analysed by EDX in the SEM. The composition of the copper-rich constituent was found to contain 90 wt% Cu and 10 wt% Ag and the silver-rich constituent contained 85 wt% Ag and 15 wt% Cu. This high concentration of copper in the silver-rich constituent of the eutectic is slightly higher than the known limit for solubility of copper in silver [7]. Electron diffraction observations confirmed these

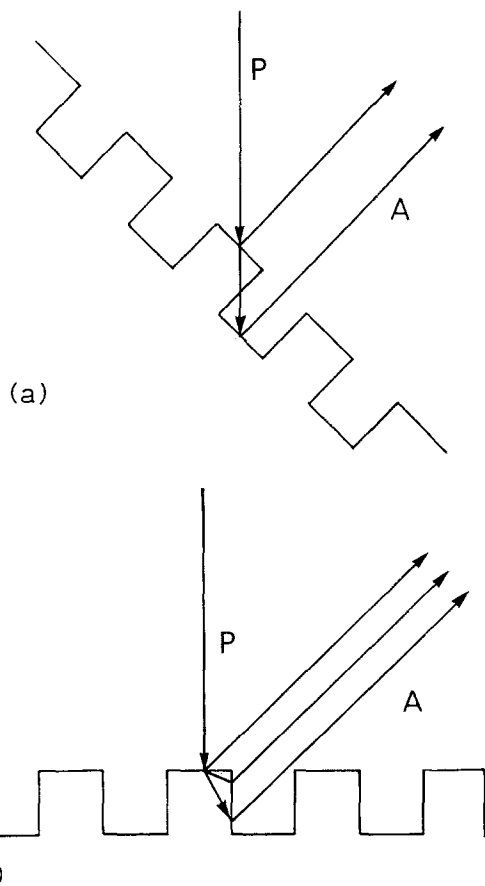


Figure 5 Diagram showing the sites of origin of Auger electrons (A) generated by the primary beam (P) at ridges, ridge walls and furrows in an ion-etched eutectic surface with a uniform distribution of the two constituent phases giving rise to an approximately constant copper-silver surface composition; (a) 45° incidence, and (b) normal incidence. Only Auger electrons directed towards the detector are shown.

TABLE I Surface composition of some large copper-rich and silver-rich areas

Inclusion	Cu (at %)	Ag (at %)
Copper-rich 1	59.5	40.5
Copper-rich 2	60.7	39.4
Copper-rich 3	62.8	37.2
Silver-rich 1	42.5	57.5
Silver-rich 2	40.3	59.7
Silver-rich 3	36.7	63.3

EDX results with crystal structures consistent with a low concentration of silver in copper and vice versa. Copper and silver crystal structures were identified from the copper-rich and silver-rich phases in the eutectic.

The effects of the ion-beam etch treatment in Cu/Ag samples, which is necessary to enable quantitative AES measurements, have been examined at high resolution in the scanning electron microscope. Correlation of secondary electron and backscattered electron images showed that silver-rich regions etch preferentially and copper-rich ridges are left at the surface. Examination of likely electron scattering paths below this copper-rich surface structure suggest that the

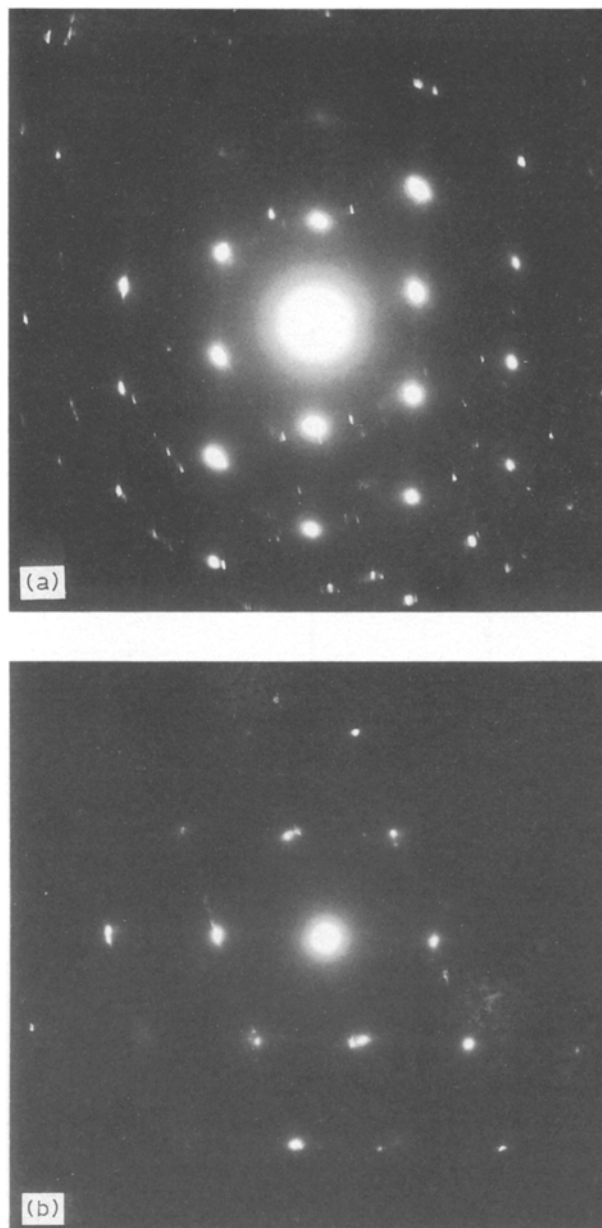


Figure 6 Electron diffraction patterns from (a) the copper-rich phase in the eutectic, copper ($\bar{3}\bar{1}9$) orientation, and (b) the silver-rich phase in the eutectic, silver ($0\bar{1}\bar{1}$) orientation.

surface composition detected by Auger electron spectroscopy has shown that silver-rich and copper-rich surfaces will be present and for the regular form of eutectic structure normally observed, an approximately constant Ag:Cu composition will be detected. Auger electron spectroscopy from the copper-rich and silver-rich components of the coarse eutectic structure has shown that the surface composition of these large silver-rich and copper-rich inclusions differs from the bulk composition obtained by EDX. The interaction of an ion beam with these large dilute alloy areas appears to differ from the interaction with the fine eutectic structure. The concentration of the minority component in the dilute alloy is found to be enhanced at the surface. It is clear that the effects of surface ion-beam cleaning are complex, and surface diffusion and surface segregation effects must be considered in interpreting the surface composition of these large dilute alloy areas.

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