# CREEP EMBRITTLEMENT OF Cu-Au ALLOY, STUDIED IN SITU BY SCANNING AUGER MICROSCOPY

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## ABSTRACT

Polycrystalline, very pure Cu-Au wires are studied under ultra high vacuum conditions in a Scanning Auger Microscope when subjected to heat treatment (0-600° C) and tensile stress ($\sigma$ = 0.98-8.3 kg/mm²). At temperatures up to 500° C and loads up to 8 kp/mm² only recrystallization and grain growth is observed, with preferential orientation relative to the stress direction, but no crack initiation occurs on the surface. Heating to ∿550° for ∿1 min leads to strong sulfur segregation and intergranular crack formation, immediately followed by fracture in an intergranular brittle mode. Auger analysis of the fracture surface shows the presence of a layer of $Cu_2S$, similar to that on the free surface. We conclude that the segregation of impurities to internal interfaces plays an important role in brittle creep rupture.

## KEYWORDS

Surface analytical methods; Cu-Au alloys; creep-embrittlement; interface segregation; surface segregation.

## INTRODUCTION

High temperature application of materials has made creep rupture an increasing field of investigation. Generally, intergranular creep controlled fracture is explained by void formation and growth due to grain boundary sliding and subsequent diffusion and power-law creep (Ashley, Gandhi, and Taplin, 1979). In spite of much evidence in the literature that residual impurities increase creep embrittlement susceptibility their role is still not well accepted and understood in detail (Briant, and Banerji, 1978). It is the purpose of this paper to get more insight in this problem.

## EXPERIMENTAL

The samples are ultra pure polycrystalline Cu(92.5)-Au(7.5) wires of 0.5 mm dia-

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meter with detailed characteristics published elsewhere (Losch, and Kirschner, 1978) (calibration standards for electron microprobes supplied by NBS). They were mechanically polished and mounted in Mo holders. A thin W-ribbon behind the specimen provided radiative heating. The temperature was measured directly on the sample surface by a Fe-Constantan thermocouple. Variable tensile stress ($0.98 \leqq \sigma \leqq 8.30$ kp/mm²) could be applied by placing a variable number of weights on a simple lever arm construction. The whole assembly was mounted on a modified carousel specimen holder of a commercial Scanning Auger Microscope (SAM) from Physical Electronics, as shown in Fig. 1.

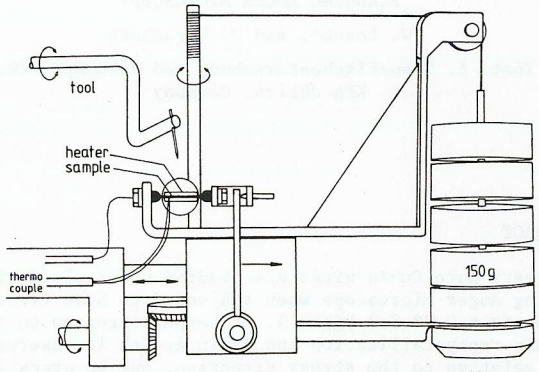


Fig. 1. Specimen mounting.

The vacuum was always better than $7 \cdot 10^{-8}$ Pa ($\cong 5 \cdot 10^{-10}$ torr). Auger spectroscopy was provided by a 0-10 keV integral scanning electron gun (resolution <3 µm) and a single pass cylindrical mirror analyser. Simple surface cleaning was performed by a differentially pumped scanning ion gun (0-5 keV).

## RESULTS

### Segregation Characteristic S = f(T,t)

The surface composition of a Cu-Au alloy is characterized by a strong Au enrichment. at elevated temperatures, however, impurity segregation is observed (Losch, and Kirschner, 1978). The characteristic features of this segregation were measured and are demonstrated in Fig. 2, where the observed elements are represented by their Auger line intensities $I_{Cu}$(59/60 eV), $I_{Au}$(66/69 eV) and $I_S$(150 eV) as a function of temperature and time. For this measurements the sample was unloaded ($\sigma \cong 0$) and heated in $\Delta t$ = 5 min intervals at different temperatures 500° C $\leqq$ T $\leqq$ 600° C. Qualitatively it is clearly seen that mild sputter cleaning during heating induces a thermal non-equilibrium of the surface composition. A short heat treatment at ∿500° C causes Au to segregate to its equilibrium level (Losch, and Kirschner, 1980) which decreases with increasing temperature as discussed in detail by Losch, and Kirschner (1978). At T $\cong$ 540° C the onset of strong S segregation is observed simultaneously with an increase in Cu- and a decrease in Au-concentration. The S segregation comes to saturation after ∿1 h heating at T = 600° C. Analysing the Auger line fine structure of the S peak we find two lines at 147 and 151 eV which indicates the formation of a $Cu_2S$ layer on the surface (Losch, 1979a). Using the method of sensitivity factors (Palmberg, 1978) the surface concentrations after S saturation are estimated: to $C_{Cu} = 0.71$; $C_{Au} = 0.04$; $C_S = 0.25$.



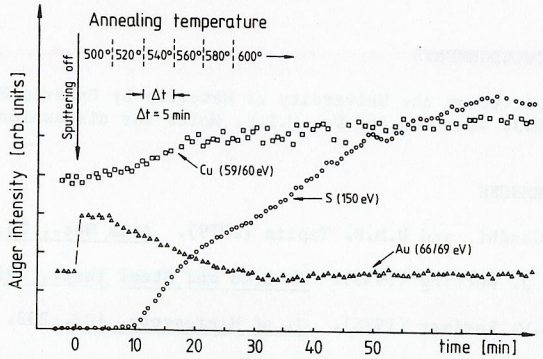


Fig. 2. Segregation characteristic for unloaded sample as obtained by Scanning Auger Microscopy.

### Intergranular Fracture

After loading the sample with $\sigma$ = 8.30 kp/mm² various heat treatments for various times were carried out. Initially the sample was polycrystalline with a grain size of ASTM n° 12. During extended stress application at 200° C $\leqq$ T $\leqq$ 450° C (i.e. far below the segregation temperature for S) we observed recrystallization and finally grain sizes of n° 4 were obtained (Losch, and Kirschner, 1980). No systematic heat treatment concerning grain growth and creep was applied but all heatings for several hours at T $\leqq$ 450° C did not lead to observable crack initiation at the surface. This was continuously controlled by taking absorbed current micrographs of the sample. Even annealing at T = 500° C for 20 minutes did not change this situation.

However, when applying a short ∿minute heating at T $\cong$ 550° C we observed immediately crack initiation at the surface grain boundaries together with S segregation as indicated by Auger analysis. These surface cracks are seen in Fig. 3.

Fig. 3. Absorbed current micrograph showing surface cracks.

This behaviour of crack initiation and its temperature dependence was completely reproducible on other samples. Further short heating (∿5 min) at 550° C caused an intergranular fracture with a well structured coarsly grained surface. Immediately

after fracture the fracture surface was turned in front of the analyser, and the chemical composition of the fracture surface was analysed. A typical Auger spectrum is shown in Fig. 4. A strong S-line is observed (4a) which also shows fine

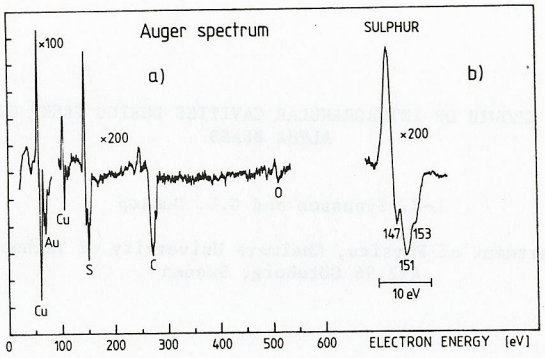


Fig. 4. a) Auger spectrum of the fracture surface.
b) Fine structure of the sulfur Auger peak.

structure (4b) indicating the formation of a $Cu_2S$ layer also on the fracture surface. Besides of S a C peak is observed the origin of which is not clear as C was not observed to segregate to the free surface. A SAM picture of S showed a quite homogeneously distributed S concentration on the fracture surface within the limits of the lateral resolution. Calculating as above the concentration we obtain $C_{Cu} = 0.63$; $C_{Au} = 0.12$; $C_S = 0.08$; $C_C = 0.17$. These concentrations are similar to those observed at the free surface for corresponding heat treatment, but cannot be compared directly due to the presence of carbon in unknown chemical state.

## Surface Boundary Orientation

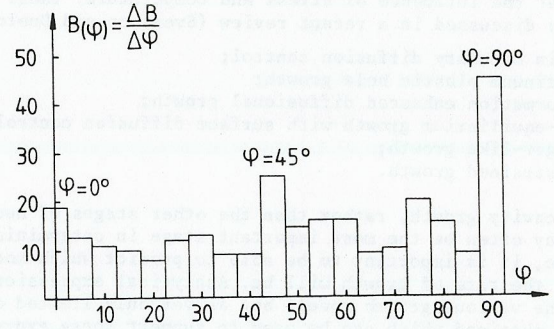


Fig. 5. Distribution of the surface grain boundary orientation relative to the direction of applied stress ($\varphi = 90°$ corresponds to grain boundary normal to stress).



From Fig. 3 we found visual evidence for a preferential orientation of the surface grain boundaries. Different parts of the sample surface were then photographed and the angular orientation $\varphi$ of the grain boundaries was analysed relative to the direction of the applied stress $\sigma$. The number of boundaries $\Delta B$ lying within the interval $[(\varphi - \Delta\varphi/2),(\varphi + \Delta\varphi/2)]$ with $\varphi$ module $\pi$ and $\Delta\varphi = 5°$, gives the distribution $B(\varphi) = \Delta B/\Delta\varphi$. This distribution is plotted as a function of $\varphi$ in Fig. 5. ($\varphi = 0°$ is parallel to $\sigma$). Most of the boundaries are oriented perpendicular to the applied stress $\sigma$.

## DISCUSSION AND CONCLUSION

We have found 2 strong arguments for the conclusion that impurity grain boundary segregation strongly influences intergranular fracture:

1. the temperature of the onset of free surface S segregation (determined by the bulk content of S impurities) exactly coincides with the temperature where brittle fracture occurs.
2. the fracture surface showed $Cu_2S$ formation in agreement with the observation on the free surface after S segretation.

These facts support the suggestions of Bruscato (1970) that creep embrittlement, like temper embrittlement, is another manifestation of impurity-induced intergranular failure (Briant, and Banerji, 1978). This also agrees well with the model of intergranular fracture recently developed by Losch (1979b).

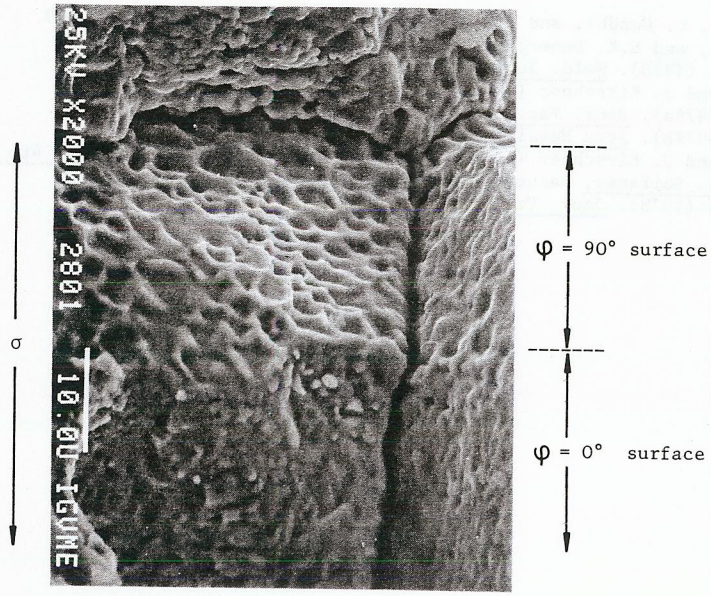


Fig. 6. Scanning Electron Microscope (SEM) picture of the fracture surface.

Two other observations seem to be of importance: The preferential orientation of the surface grain boundaries may be expected to a certain degree from texture formation during drawing of the sample wires. However, strong grain growth was observed (see Intergranular Fracture) and this necessarily is accompanied by boundary migration. Obviously many randomly distributed boundaries moved into energetically favoured orientations. This process may cause impurity dragging, a fact which also has to be considered and perhaps could explain our finding of C on the fracture surface.

A SEM picture of the fracture surface is shown in Fig. 6. It shows a $\varphi$ = 90° and a $\varphi$= 0° boundary. The surface perpendicular to $\sigma$ (90°) shows crater or void formation characteristics whereas the 0° surface contains small particles.

On summarizing our observations we have the impression that current models of intergranular creep embrittlement underestimate the contribution of impurity segregation. A detailed discussion is beyond the scope of this paper.

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