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High temperature stress relief cavitation of an Al-bearing α-brass

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High temperature stress relief intergranular cavitation and subsequent room temperature embrittlement of an aluminium-bearing α-brass has been studied metallographically. The behaviour of a cast susceptible to cavitation has been compared to one which does not exhibit intergranular cavitation during stress relief, and which is subsequently more ductile at room temperature. A number of micro-analytical techniques (SIMS and EDX) failed to reveal any difference in the grain boundary chemistry between a cast susceptible to intergranular cavitation and one which was not, but it is suspected that the combined action of dissolved gases (e.g. hydrogen) and trace element impurities plays a major role in cavitation. The cavities formed during stress relief were often polyhedral in shape and it is considered that this occurs by the diffusion of matter around the cavity surface to attain a lower energy surface configuration. Second phase particles were found to play only a minor role in the nucleation of cavities. Room temperature intergranular fracture surfaces of material, in which cavities had formed during stress relief, were interpreted in terms of high temperature cavity formation and coalescence combined with low temperature plastic void growth and interlinkage.

1. Introduction

A serious and often unpredictable problem which sometimes arises during the thermo-mechanical treatment of metals and alloys, is the embrittlement of the product due to intergranular cavitation. The formation of cavities can lead to premature fracture during working operations or during subsequent service under load.

The phenomenon of high temperature intergranular cavitation has been most extensively studied in relation to creep fracture (for review articles see [1, 2]). As is often the case for low temperature fracture (e.g. the temper embrittlement of steels), impurity elements can have a strong influence on the susceptibility of a material to intergranular cavitation. This is because segregated impurities at grain boundaries can weaken interatomic bonding across grain boundaries and decrease the energy required to create fresh surfaces. In copper alloys, some elements which are known to be harmful in this regard are Bi, Sb, Pb, S, Se, Te and As [3, 4]. The presence of these elements can sometimes be detrimental at concentrations as low as several parts per million.

The present investigation was undertaken as a result of a problem which occasionally arises during the fabrication of pipe flanges (see Fig. 1)

Figure 1 A pipe flange of aluminium brass made by welding together the two ends of an extruded "L" profile.

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from an Al-bearing alpha brass. The flanges are fabricated from "L-profiles" (extruded at ~800° C) by bending the profiles at room temperature and welding the ends together. The flanges are then subjected to a stress relief annealing treatment at 550° C for 3 min. Subsequently the diameters and shape of the flanges are adjusted slightly to their correct values in a "calibration" operation at room temperature. During this latter operation, intergranular cracking and sometimes fracture can occur away from the weldment in certain casts of material of the same nominal composition despite the fact that the strain during calibration is considerably less than that which occurs during the initial bending of the profile to form the flange. Preliminary investigations have shown that the intergranular embrittlement is associated with the formation of intergranular cavities during the stress relief annealing treatment.

This type of embrittlement of brass and especially aluminium brass by high temperature cavitation has been studied for many years. Some important factors which can affect the amount of cavitation, and subsequent embrittlement are: grain size, the rate of heating in the temperature range 250 to 400° C and the amount of residual stress prior to the annealing or stress relief operation [4, 5]. Embrittlement has often been found during the production of condensor tubes and showed up as cracks when the tubes were flattened or, in severe cases, as cracking during annealing. Brittleness has also been found in tensile testing at elevated temperatures with the ductility minimum occurring at around 300° C. Through an addition of 0.1% Zr to brass it has been shown that the ductility can be improved [6]. Wilson [7] has provided evidence that intergranular cavitation may be a result of the precipitation at grain boundaries of hydrogen previously present in supersaturated solid solution. Hydrogen precipitation may take place during cooling from hot working temperatures or during a stress relief annealing. A reason for this is that the solubility of hydrogen in alpha-brass is strongly temperature dependent and decreases to approximately 0.01 p.p.m. at 500° C [8]. The strong interaction between zirconium and hydrogen or other trace impurities can be one explanation of the effect of zirconium. The occurrence of annealing brittlenes in oxygen-free copper is further evidence of the importance of hydrogen when grain boundary cavities are formed. Here the brittleness occurs when lightly cold-worked material is annealed. Cavities are formed in the old grain boundaries when the hydrogen content is high, the grain size is large and when residual stresses are present [9, 10]. The similarity with cavitation and embrittlement of aluminium brass is evident.

The investigation has concentrated largely upon the metallography of the intergranular fracture process in material subject to embrittlement. Two casts of material have been investigated (see Table I): one of which was not susceptible to intergranular embrittlement (cast number 1) and the other which was highly prone to embrittlement (cast number 2). A variety of metallographic and microanalytical techniques were used to study the fracture behaviour of these two casts.

2. Experimental

Two casts of material of the compositions shown in Table I were made available in the form of "L-profiles" which had been extruded at approximately 800° C and as pipe flanges which had been subjected to the treatments outlined in the introduction.

Metallographic sections which had been mechanically polished and carefully etched in a dilute solution of ammonium persulphate in water were examined by optical metallography and scanning electron microscopy (SEM). Thin foil specimens prepared by jet electropolishing at 14 to 18 V in Struers D2 electrolyte were examined in a 100 kV transmission electron microscope (TEM) and also in a 200 kV scanning transmission electron microscope (STEM). Microanalysis was

TABLE I Bulk compositions (wt%) of the two experimental casts

Cast	Cu	Al	Sn	Pb	Fe	Ni	Mn	P
Cast 1	76.5	1.8	0.0025	0.007	0.010	0.005	0.0024	0.004
Cast 2	77.2	1.9	0.013	0.023	0.011	0.006	0.057	0.003

Cast	Ag	As	Si	Sb	H	Cd, Cr, S, Se, Bi, Te	Zn
Cast 1	0.0012	0.023	0.002	<0.003	1.3 p.p.m.	<0.001	Balance
Cast 2	<0.001	0.031	0.019	0.003	1.4 p.p.m.	<0.001	Balance

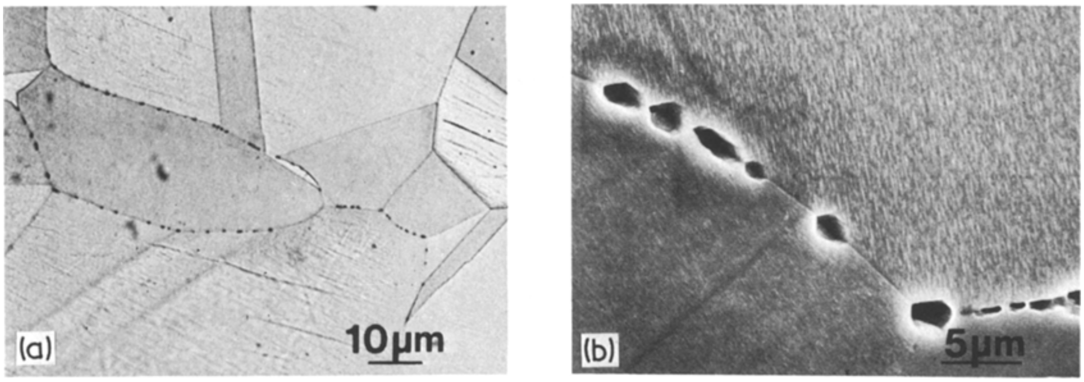

Figure 2 Grain boundary cavitation in a stress relieved flange of cast No. 2. (a) Optical micrograph; (b) SEM showing the regular polyhedral shape of the cavities.

performed using energy dispersive X-ray (EDX) spectrometers attached to the SEM and STEM instruments and also using a secondary ion microanalyser (SIMS). Some thin foils taken from material crept in tension at 400° C were examined in a 1 MeV electron microscope.

Tensile specimens were cut from flange material and deformed in tension to fracture at room temperature. Fracture surfaces from these specimens and also the free surfaces parallel to the tensile axis were examined by SEM with EDX analysis facilities.

3. Results

Optical metallography and SEM of polished and etched sections taken from flanges revealed the presence of small intergranular cavities in cast No. 2 (Fig. 2). Similar cavities could not be detected in flanges from cast No. 1. As can be seen in Fig. 2a the cavities were densely arranged on some grain boundaries and absent on others. No preferred orientation of the cavitated boundaries with respect to the geometry of the flanges was observed. In general, the density of cavities on boundaries which were prone to cavitation was high and very few boundaries contained intermediate cavity densities.

As can be seen in Fig. 2b the metallographic preparation technique closely preserved the shape of the cavities so that it could be observed that a high proportion of cavities had a regular polyhedral shape. In general, all polyhedral cavities on the same grain boundary segment contained the same number of surface facets and each facet was parallel to the equivalent facets in the adjoining cavities. The slightly streaked contrast, on the polished surfaces observed by SEM, results from the slight etching used primarily to reveal the grain boundaries. A few of the grain boundary cavities contained second phase particles (Fig. 3) and these were most frequently found by EDX to contain Mn and S suggesting their composition to be MnS

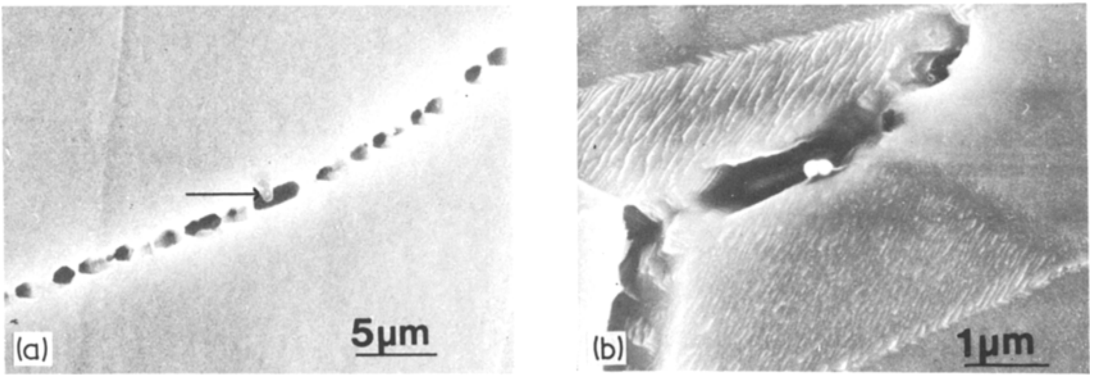

Figure 3 Second phase particles associated with cavities. (a) An MnS particle (arrowed) in one of a row of cavities. (b) An elongated Pb particle in a cavity (the white spots are contamination marks following EDX analysis).

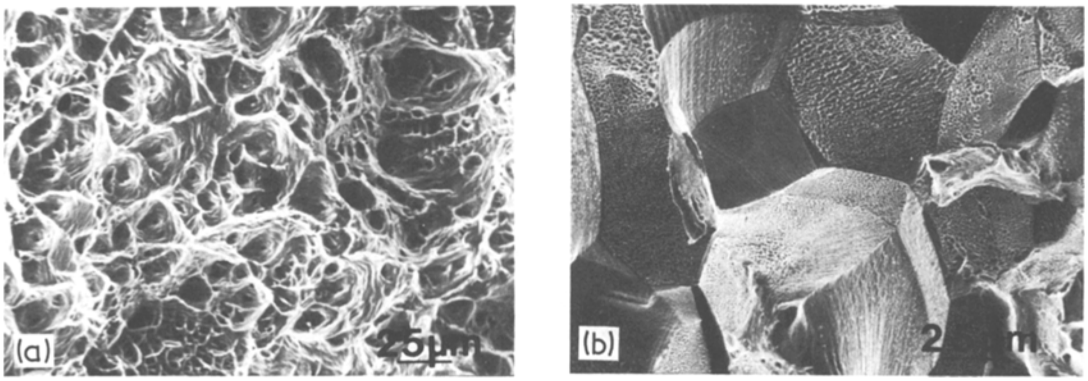

Figure 4 Fracture surfaces of tensile specimens taken from stress relieved flanges and strained to fracture at room temperature. (a) Cast No. 1, transgranular ductile fracture. (b) Cast No. 2, intergranular fracture.

(Fig. 3a). Occasionally elongated particles were observed in cavities and these were identified as containing substantial quantities of Pb (Fig. 3b).

Stringers of inclusions independent of the grain boundaries and sometimes with associated voids, were observed occasionally in cast No. 2. Such stringers contained either Pb or Al. SIMS analysis showed that the Al-containing inclusions also contained O suggesting that they were aluminium oxide. No preferential association of either Pb or Al_2O_3 particles with grain boundaries was observed. Occasional particles, identified as MnS, were also observed in the matrix.

TEM and STEM microscopy largely confirmed the above findings. Stringers of Pb inclusions were observed in extruded profiles of both casts of material traversing a number of grains. Occasional grain boundary particles of MnS were observed and in one instance in cast No. 2 elongated particles which had "*d*" spacings corresponding to Pb were observed at a grain boundary. In no case was the density of grain boundary particles comparable with the density of intergranular cavities observed in flanges from cast No. 2. Detailed microanalyses of grain boundaries without the presence of grain boundary particles by both STEM with EDX and SIMS techniques did not reveal any variation from the bulk composition.

The room temperature fracture surfaces of tensile specimens taken from flanges of both casts are shown in Fig. 4. Cast No. 1 exhibited typical transgranular dimpled fracture surfaces while the fractures in cast No. 2 were mainly intergranular and macroscopically brittle. Close examination of the fractures from cast No. 2 revealed that the intergranular fracture surfaces were essentially of three types (Fig. 5):

(1) micro-dimpled;
(2) irregularly patterned;
(3) relatively smooth and featureless.

Detailed examination of the micro-dimpled surfaces showed that some of the dimples contained particles which were analysed as containing both

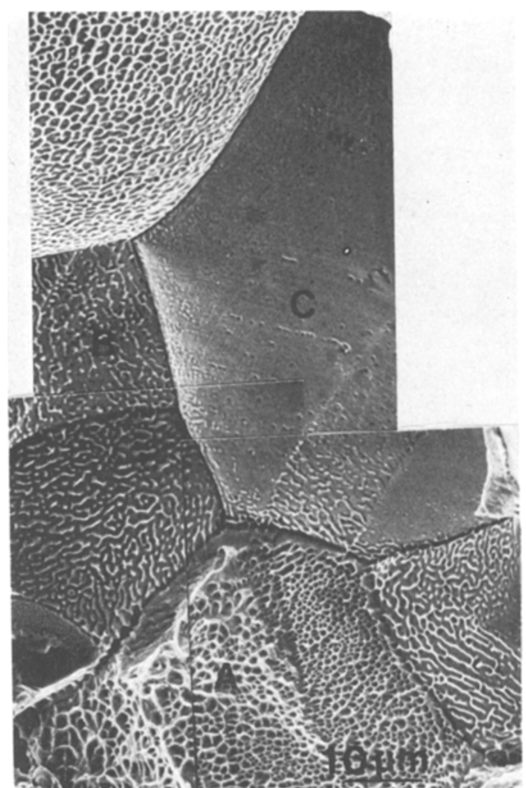

Figure 5 Intergranular fracture surface of tensile specimen taken from stress relieved flange, cast No. 2, showing the three types of fracture surface feature: A, micro-dimpled; B, irregularly patterned; C, relatively smooth and featureless.

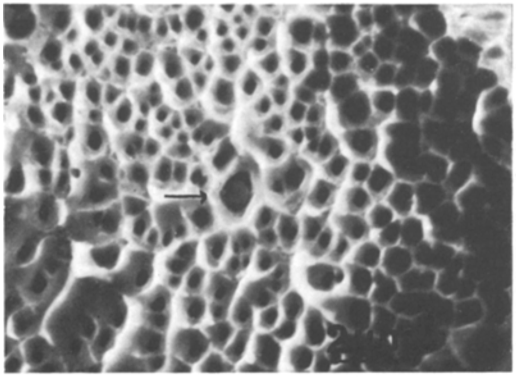

Figure 6 Micro-dimpled room temperature intergranular fracture surface with arrowed particle identified by EDX as MnS.

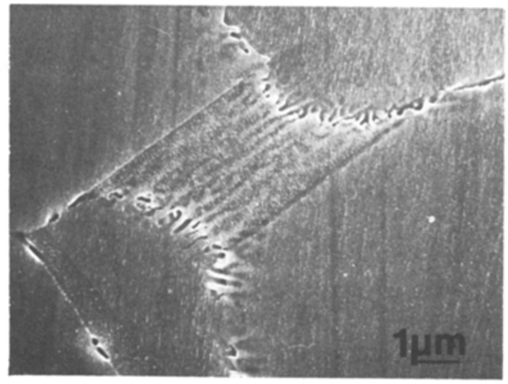

Figure 8 Elongated cavities in a grain boundary intersecting the polished section at a shallow angle. Specimen taken after stress relief of cast No. 2.

Mn and S (Fig. 6). Microanalysis at random on the dimpled and irregularly patterned surfaces did not reveal any variation from the bulk composition of the alloy. It was observed that more than one of the separate types of intergranular fracture surface could occur on a grain boundary facet of the same grain. For example, in Fig. 5 can be seen a straight band of irregularly patterned surface which traverses an otherwise relatively smooth and featureless grain boundary facet. It is very likely that the straight band corresponds to the intersection of an annealing twin with the grain boundary.

The manner in which cavities can interlink at high temperatures to form larger intergranular voids and cracks is shown clearly in Fig. 7 taken from flange material. Of particular interest is that cavities can maintain their polyhedral shape up to the point of coalescence. The lack of influence of adjacent cavities on each other's shape and growth morphology is striking in this micrograph. After coalescence the lip between adjacent cavities appears to smooth out (see point marked B in Fig. 7), probably due to the influence of surface diffusion.

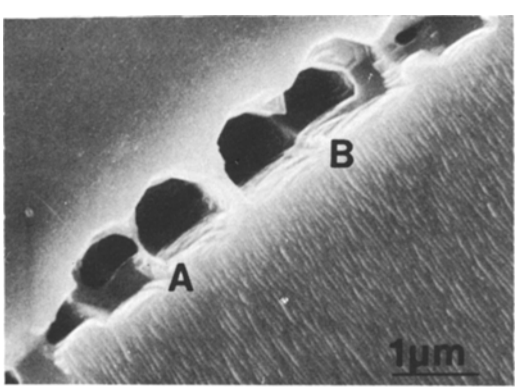

Figure 7 Interlinkage of cavities during high temperature stress relief, showing two cavities just prior to coalescene at A and after coalescence B.

Fig. 8 is a polished section taken from a flange of cast No. 2 and contains features which can be associated with the irregularly patterned fracture surfaces seen in certain areas of Fig. 5. Apparently a grain boundary surface lies just under and almost parallel to the polished section. Bands of dark contrast run from one trace of the grain boundary on the free surface to the other trace and these dark bands coincide with the visible cavities. The dark contrast probably arises because cavities lie just under the free surface and the material above them was depressed during mechanical polishing. If this explanation for the contrast effect is accepted then it can be seen that the cavities are interlinked in a complex way and are considerably elongated in the plane of the boundary. Fig. 9 is taken from the polished free surfaces of tensile specimens taken from cast No. 2 flange material and which were deformed in tension until fractured at room temperature. The low temperature interlinkage of cavities to form a crack by shear deformation in the plane of the cavitated boundary can be seen in Fig. 9a. The interlinkage of large intergranular voids, themselves produced by coalesced cavities, by a combination of internal necking and plastic tearing is seen in Fig. 9b.

4. Discussion

The regular polyhedral shape of the vast majority of intergranular cavities observed in flanges from

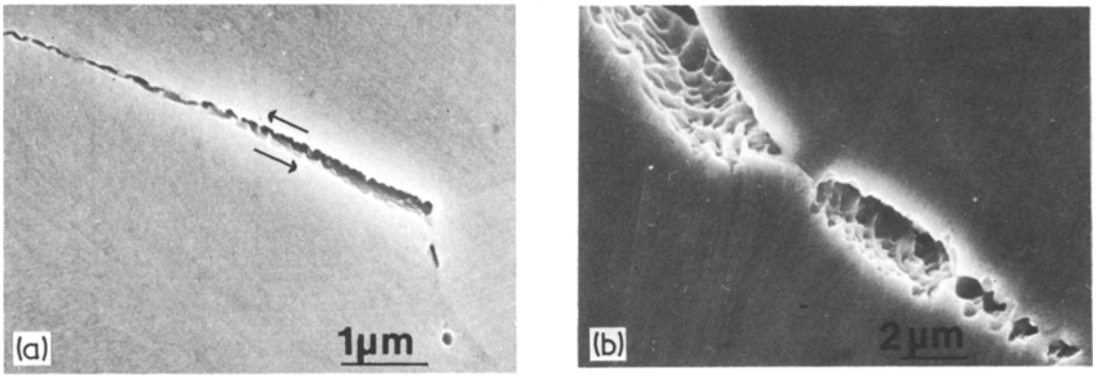

Figure 9 The formation of intergranular cracks by the plastic coalescence of stress relief cavities during subsequent room temperature straining: (a) interlinkage by a final shear movement along a cavitated boundary, the arrows show the direction of intergranular shear; (b) interlinkage by a combination of internal necking and plastic tearing.

cast No. 2 suggests that the cavities assume a shape which is influenced by the crystallographic dependence of interfacial energy and that this shape can be maintained to a late stage in their development, i.e. until their coalescence during high temperature stress relief (Fig. 7). As also suggested by other authors [11, 12], the attainment and maintenance of this shape is no doubt brought about by interfacial diffusion in the surface of the cavity. In order to maintain the polyhedral shape the rate of surface diffusion must considerably exceed the rate of increase of cavity volume (i.e. the cavity growth rate) towards the end of the stress relief operation.

From the SEM results, the occurrence of cavitation would not seem to be necessarily associated with the presence of second phase particles at grain boundaries. That some cavities nucleated at particles is almost certain, but the number of particles observed in either SEM or TEM does not at all correspond with the frequency of cavitation. Also, a significant number of grain boundary particles was observed in cast No. 1 where the incidence of cavitation was virtually nil. As can be seen from Table I, the cast susceptible to intergranular cavitation (No. 2) had a considerably higher content of impurity elements than cast No. 1. In particular, the Mn content was 20 times greater while the contents of Si, Sn, As, P and Pb were also much greater.

The presence of tramp elements which could possibly segregate to grain boundaries suggests the importance of segregation but use of such highly sensitive techniques as STEM with EDX and SIMS (where the chemical resolution is of the order of a few p.p.m.) failed to reveal the presence of any segregated species. It is however important to note here that it was not possible to analyse in any detail for Pb using SIMS because of the presence of overlapping ionic signals from other elements present.

The presence of three types of intergranular fracture surface in specimens from flanges of cast No. 2 drawn to fracture at room temperature is of some interest (see Fig. 5). The micro-dimpled regions are similar to surfaces produced by intergranular micro-void coalescence in overheated steels [13, 14]. In the present case, the micro-voids responsible were almost certainly high temperature intergranular cavities which had not grown to the stage where they could coalesce during stress relief annealing. Coalescence instead took place by plastic interlinkage during room temperature deformation. The manner in which this can occur can be seen in Fig. 9. It should be noted that the observations in Fig. 9 were made on the free surfaces of tensile specimens where the rate of void growth and coalescence are somewhat accelerated in comparison to the same processes occurring internally in tensile specimens [15].

It is suggested that the irregularly patterned intergranular fracture surfaces reflect the shape of high temperature cavities on these grain boundaries which subsequently coalesced during room temperature deformation. Thus the light contrast relief on these surfaces is considered to be the walls of high temperature cavities which fractured during room temperature straining. This viewpoint is supported by Fig. 8 where the shape of these cavities, prior to room temperature straining, can

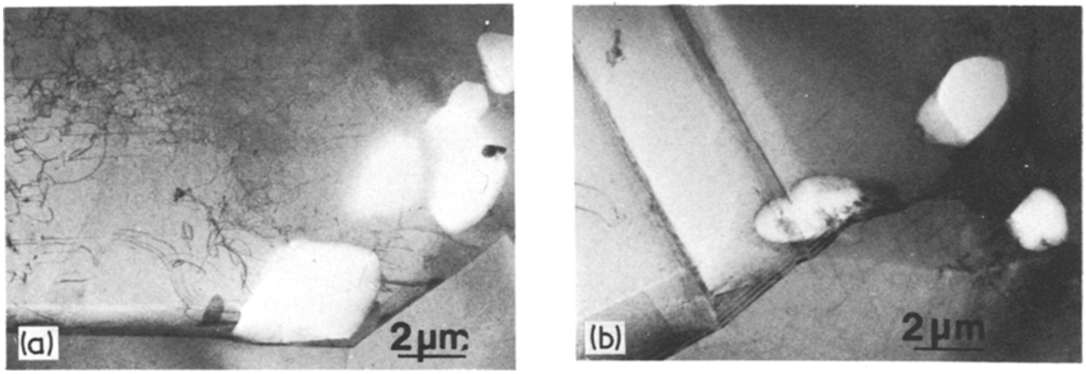

Figure 10 1 MeV electron micrographs showing cavities within the foil thickness of creep tested material.

be seen. The irregular and sometimes elongated shape of these cavities would seem to arise because they were formed by interlinkage of smaller cavities at high temperatures. This would appear to have taken place in certain areas of Fig. 5 and it can be seen clearly at B in Fig. 7 that the lip between coalesced cavities tends to disappear at high temperatures.

The relatively smooth and featureless intergranular surfaces visible in the room temperature fracture surfaces (Figs. 4b and 5) probably arise through elevated temperature interlinkage of cavities to form cracks covering whole grain boundary facets. It has been shown previously that such featureless surfaces can arise by smoothing of the previously cavitated surface by surface self-diffusion [16].

As a result of the interesting effects of intergranular cavitation reported here, a transmission electron microscope study has been begun on intergranular cavitation in creep deformed aluminium brass. Examples of creep cavities observed using 1 MeV microscopy where the cavities lie within the volume of thin foils, are given in Fig. 10. Preliminary results show that cavities are seldom associated with second phase particles but they are often associated with the intersections of twin boundaries with grain boundaries and also with grain boundary triple junctions. Creep cavities are observed to be often polyhedral in shape but without the sharp apices that were often observed in stress-relieved material. This suggests that surface diffusion could adjust the shape of cavities, in keeping with the rate of individual cavity volume increase, much more readily in the latter stages of stress relief annealing than during steady state creep.

The 1 MeV microscopy has also shown that creep cavities have little influence on the three dimensional dislocation network present during steady state creep. This is at variance to a recent model of Dyson and McLean [17] who suggest that accelerated recovery of the network may arise in the vicinity of intergranular cavities. This investigation is continuing and will be reported more fully at a later date.

5. Conclusions

(1) Room temperature intergranular brittleness in aluminium brass can result from the formation of intergranular cavites during stress relief heat treatment.

(2) The cavities formed during stress relief are often polyhedral in shape suggesting that the rate of diffusion of matter around the cavity surface is more than commensurate with the rate of cavity volume increase.

(3) Second phase particles only play a minor role in the nucleation of cavities in this material.

(4) The room temperature intergranular fracture surfaces of material susceptible to cavity formation can be interpreted in terms of high temperature cavity formation and coalescence combined with low temperature plastic void growth and interlinkage.

(5) Further investigation is required in order to isolate the factors which result in some casts being susceptible to intergranular brittleness while others are not.

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