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The mechanical behaviour of cerium-modified alpha-beta brass at high temperatures

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The mechanical behaviour of a fine-grained Cu–38.6% Zn alloy with and without 0.07% Ce was studied at 475 to 675° C. It was found that the addition of Ce lowered the flow stress by a factor of three. It was concluded that this arose from a decrease in the volume fraction of the harder alpha phase due to the reduced zinc solubility.

1. Introduction

The concentration of lead and bismuth in copper alloys must generally be kept low to ensure good high temperature mechanical behaviour both during fabrication and service [1]. This is because these elements increase the likelihood of both hot shortness or intergranular cavitation. A method of countering the presence of these impurities is to dope the alloys with an element known to form with them high melting point intermetallic compounds. For example, lead will combine with uranium [2] to form UPb_3, which melts at 1220° C, and bismuth reacts with lithium to form Li_3Bi [2, 3], which also melts above 940° C. Similarly, improved hot workability in 70/30 brass, aluminium bronze and cupro-nickel alloys has been obtained by the addition of zirconium, chromium and boron [2–4]. Recently, the effect of cerium addition on the hot ductility of alpha brass has been investigated by Sunter and Burman [5]. They found that hot-cracking in alpha brass is reduced considerably in the presence of cerium, although the effect was not explained in detail. In the present work the basic material is a fine grained alpha-beta brass which exhibits intergranular and interphase cavitation during superplastic flow [6]. The nature of cavitation in this alloy has been studied by Sagat and Taplin [7] and Chandra [8] in some detail with the object of limiting cavity formation so that the super-plastic potential of the alloy may be further developed. The present paper describes work on the influence of a small addition of cerium on the high temperature mechanical behaviour. The idea was to develop an understanding of the cavitation behaviour of the alloy and provide a practical means of improving hot workability.

2. Experimental procedure

Binary alpha-beta brass alloys with and without trace amounts of cerium were prepared by Imperial Metal Industries, Birmingham (UK). The compositions of these alloys are given in Table I. The

TABLE I Compositions and grain size of α/β brasses

Alloy	Composition (wt %)					Average grain size, d (μm)
	Zn	Pb	Bi	Ce	Cu	
A	38.7	0.003	0.03	–	balance	32.2
B	38.6	0.004	0.03	0.07	balance	31.7

alloys were prepared by quenching first from the β phase field to yield a shear transformation product and then by extruding at 500° C to produce a fine dispersion of the α phase. Structures with similar average grain sizes of $\simeq 32\,\mu$m were produced by annealing in argon at 700° C. Compression tests were carried out on cylindrical specimens at constant true strain-rates in the range 2.3×10^{-2} to 7.7×10^{-5} sec^{-1} and in the temperature interval 475 to 675° C. The tests were conducted under an argon atmosphere using a floor model Instron testing machine equipped with a variable speed drive and a three zone split furnace. This apparatus has been described in more detail elsewhere [7]. The specimens were given a 1 h soak at the test temperature to ensure that a stable microstructure was present prior to deformation. In order to promote conditions of homogeneous flow at high temperatures, powdered glass lubricant was used to decrease the effect of friction on ends and barrelling. The end faces of the compression specimens were grooved by a modified 56 tooth/inch thread chaser to retain the glass lubricant at elevated temperatures similar to those used earlier by other investigators [9].

All specimens were deformed by compression well into the steady state regime of behaviour to maximum true strains of 0.8. During each compression cycle, three deformation variables; load, contraction and temperature were recorded simultaneously. Loads were measured by means of the standard 20000 lb Instron load cell and displacements by means of an LVDT position transducer which monitored the cross-head displacement. The automatic data acquisition was performed by means of a remote GE/PAC 4020 computer through two voltage lines connecting the load and displacement output to a VIDAR 610 low level scanner in series with an ohm converter and a 521 VIDAR integrating digital voltmeter. The maximum scanning rate used in the present experiments was 300 readings per minute. Within the strain-rate range considered here, each stress/strain curve was made up of from 50 to 150 scanned points. A higher scanning rate was used during the early part of the deformation in order to improve curve definition around the yield stress. The load/contraction data were stored on tape for further data processing.

The true stresses and true strains were abstracted from the data on tape and were drawn by a Calcomp plotter on line with the GE/PAC computer. Two types of curves were produced in this way. First, complete true stress–true strain plot

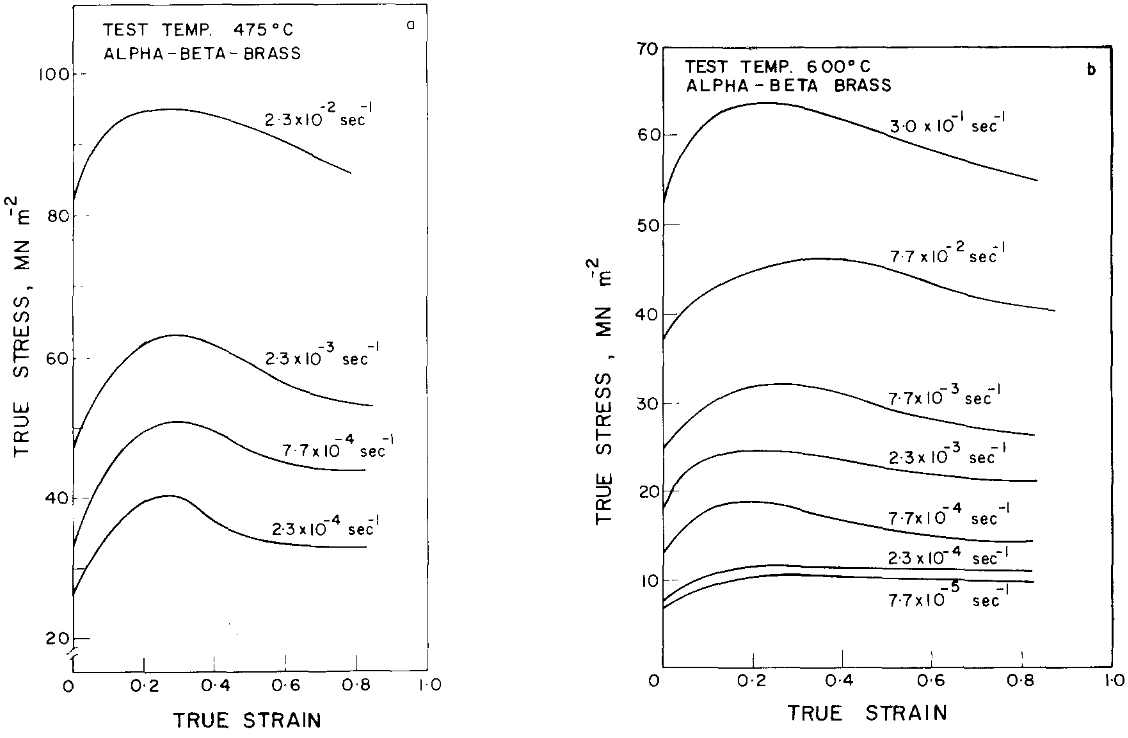

Figure 1 True stress–true strain curves for the cerium-free alloy (A) tested in compression at various true strain-rates at (a) 475° C and (b) 600° C.

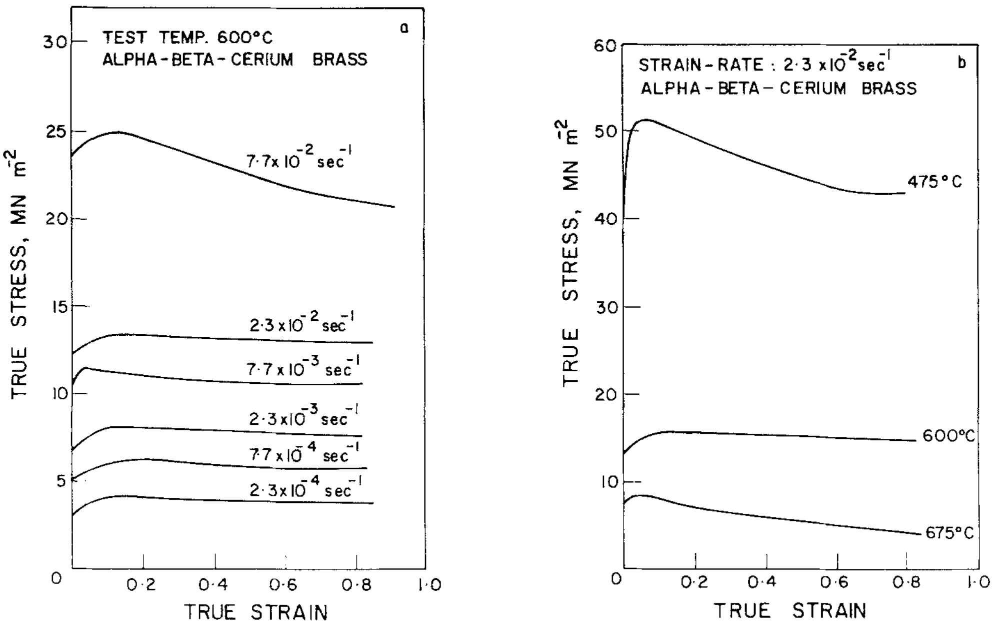

Figure 2 True stress–true strain curves for the cerium-modified alloy (B) tested in compression (a) at various true strain-rates at 600° C and (b) at various temperatures at 2.3×10^{-2} sec^{-1}.

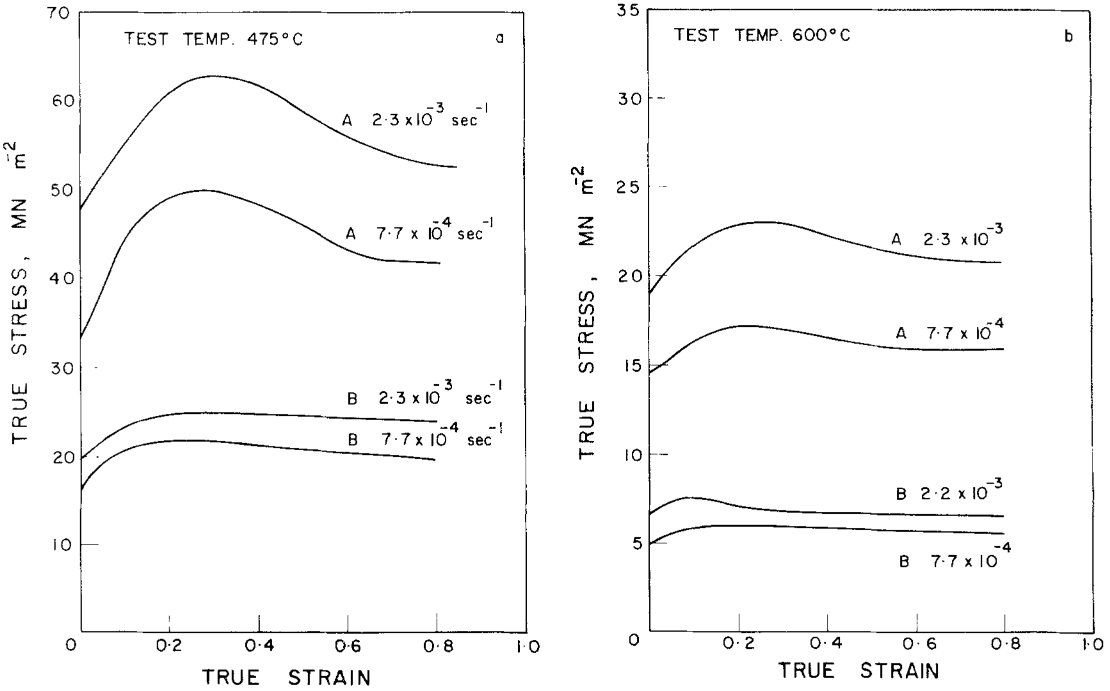

Figure 3 Comparison of flow stresses of the cerium-free alloy (A) and the cerium-doped alloy (B) deformed in compression at 2.3×10^{-2} and 7.7×10^{-4} sec^{-1} at (a) 475° C and (b) 600° C.

covering the entire strain of 0.8 range and second, an expanded strain scale plot covering the first true strain of 0.1 of the deformation in order to determine the yield stress.

3. Experimental results

Selected flow curves for alpha/beta brass without cerium are shown in Fig. 1. Equivalent flow curves indicating the influence of strain-rate and temperature for the cerium modified alloy are shown in Fig. 2. It seems evident that the addition of cerium lowers the flow stress of the material considerably. This decrease varies with strain-rate and temperature of testing and a flow stress comparison is recorded in Fig. 3. Here it can be seen that the cerium addition lowers the flow stress by a factor of three. This decrease is important practically, both in lowering forming loads and reducing cavitation which is stress dependent.

The decrease in the flow stress due to cerium could arise from one or more of the following causes:

(i) the cerium may act as a scavenger and deoxidizer thereby for example eliminating hardening particles from the boundaries and matrix;

(ii) the cerium may soften either the alpha or beta phases by increasing the stacking fault energy thereby making dislocation processes such as node-unpinning, cross-slip and climb much easier;

(iii) the cerium may alter the relative volume fraction of the alpha and beta phases – the beta phase is b c c and considerably softer than the f c c alpha phase at the test temperature so that any change in the equilibrium phase proportions can be expected to alter the flow stress.

These alternatives will now be considered in turn.

Transmission electron microscopy of the alloys could detect no difference in precipitate distributions: indeed the alloys were virtually two phase with few impurity particles at all. Hence it is unlikely that the cause can be due to alternative (i) and this is discounted.

4. X-ray line broadening measurements

The technique of X-ray line broadening analysis was employed to determine whether the addition of cerium does indeed increase the stacking fault energy of the α- and β-phases in the present alloys. This technique is applicable because the presence of stacking faults on $\{1\,1\,1\}$ planes in f c c crystals produces an angular shift in the diffraction peaks in addition to broadening them [10]. A stacking probability of 0.01 signifies that 1 out of every 100 planes in the stacking sequence is likely to be faulted. A determination of the stacking fault probability η can in turn be made from a knowledge of the peak shift [11]. The quantity η is inversely related to the stacking fault energy γ.

The (1 1 1) and (2 0 0) reflections from cold-worked filings (–325 mesh size) were recorded in a Philips X-ray diffractometer fitted with a vertical goniometer. Copper $K\alpha$ radiation was used in conjunction with a scanning speed of $1/8^\circ$ min^{-1} in 2θ and a time constant of 8 sec. For purposes of comparison, X-ray line profiles for (1 1 1) and (2 0 0) reflections were also recorded from briquettes which had been annealed for 2 h at 475° C in argon. The $K\alpha_1$ peak position in each case was located after subtracting the $K\alpha_2$ component from the observed composite profile by the Rachinger method [12]. The stacking-fault probabilities were computed from the differences in the (1 1 1) and (2 0 0) peak positions associated with the annealed and deformed states. The following equation [10] was used for this calculation;

$$\eta = \frac{2\pi^2 \Delta(2\theta_{200} - 2\theta_{111})}{45\sqrt{3}(2\tan\theta_{200} + \tan\theta_{111})} \qquad (1)$$

where θ is the Bragg angle, and the combined peak shift $\Delta(2\theta_{200} - 2\theta_{111})$ represents the difference between the angular displacements associated with the (2 0 0) and (1 1 1) reflections in the annealed and cold-worked conditions.

The peak shifts and the deformation fault probabilities η with and without cerium are presented in Table II. The (1 1 1) and (1 1 0) reflections associated with the α- and β-phases respectively occur at nearly the same Bragg angle. However, the presence of deformation faults in polycrystals of the b c c materials do not lead to peak shifts; the measured peak shift was, therefore, attributed entirely to the α phase. It should be added that the fault probability obtained from the (2 0 0) peak shift alone was comparable to that

TABLE II X-ray diffraction peak shifts, stacking fault probability and volume proportion of α and β phases in α/β brasses

Alloy	$\Delta(2\theta_{200} - \Delta 2\theta_{111})$ (deg)	Stacking fault probability, η	Volume proportion (%)	
			$V\alpha$	$V\beta$
A	0.162	3.1×10^{-2}	70	30
B	0.086	1.7×10^{-2}	55	45

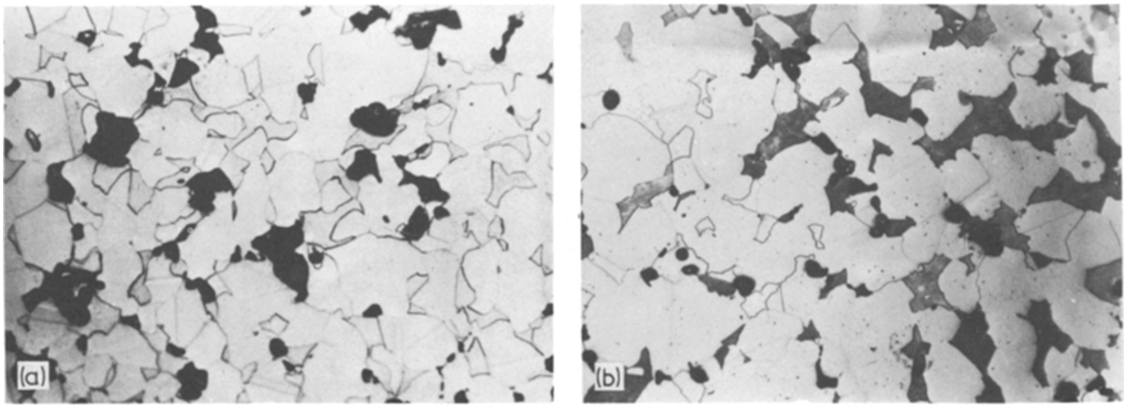

Figure 4 Optical micrographs of gauge length of the (a) Ce-free alloy (A) and the (b) cerium-doped alloy (B) strained to 80% at 600° C and $\dot{\epsilon} = 7.7 \times 10^{-4}$ sec^{-1}. Tensile axis is horizontal (× 450).

obtained from the composite shift. The results indicate that the stacking fault probability η in the α-phase is decreased by a factor of about two in the presence of cerium. Such a probability decrease can take its origin from a fault energy increase of similar properties. This change in fault energy can in turn lead to softening at high temperatures by making it easier for both recovery and glide processes to occur. The observed change in fault probability is unlikely, however, to be the principal cause of the considerable softening observed in the present work, as will be shown in more detail below.

Alternative (iii) was investigated by the relatively simple technique of determining volume fractions of the alpha and beta phases after equilibration at 600° C and fast water quenching. This was achieved with the aid of a Quantimet image analysing computer (QTM) and the data are recorded in Table II. It is evident that the alloy with the lower flow stress also has the lower volume fraction of the harder alpha phase. Optical micrographs showing the difference in cavitation behaviour for the alloys are recorded in Fig. 4. Cerium doping lowers the level of cavitation in the material, probably by lowering the flow stress; the nucleation, growth and linkage stages of cavitation are all stress dependent.

5. Discussion

Several reports [11–13] support the contention that alloying usually decreases the stacking fault energy (SFE) in an f c c matrix. Although instances where alloying had led to an increase in the stacking fault energy can be cited [14] an addition as small as 0.07% Ce can hardly be expected to directly increase the SFE of the alpha phase by a factor of nearly two (Table II). The observation of a change in the volume fraction of the two phases is clearly linked to this observation. The change in phase proportions is clearly a reflection of the shift in the $\alpha/\alpha + \beta$ and $\alpha + \beta/\beta$ phase boundaries in the Cu–Zn phase diagram brought about by the addition of cerium. In particular, the increased volume fraction of β in the Ce-modified brass can be interpreted in terms of a shift of the $\alpha/\alpha + \beta$ boundary towards a lower zinc content. This shift in the phase boundary is easily understood due to low solid solubility of Ce in copper, as showh schematically in Fig. 5. Thus, the "effective zinc concentration" of the α-phase in the cerium-modified brass is lower than that given by the

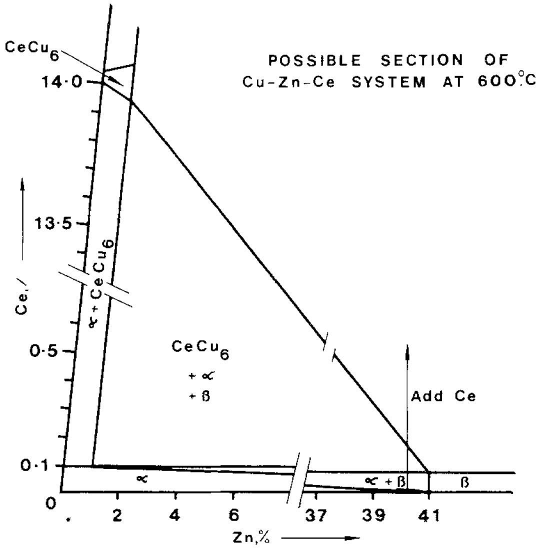

Figure 5 Schematic representation of a possible section of the Cu–Zn–Ce ternary system up to 14 wt % Ce at 600° C.

Cu–Zn phase diagram. Since it is well known that the SFE of α-brass decreases with increase in zinc concentration [11], the observed increase in the SFE of the α-phase in the Ce-modified alloy is only to be expected. Thus cerium appears to have affected the SFE of the α-phase only indirectly, by altering the effective zinc concentration, rather than by direct means, such as changes in the segregation to stacking faults or stability of the f c c phase.

Possible changes in the SFE of the β-phase by the addition of cerium could not be investigated, as the disordered phase present at the testing temperature cannot be retained at room temperature by quenching. The present results are, however, indicative of a probably increase in the SFE of the α-phase by Ce addition. This behaviour could in turn be attributed to changes in the phase boundary compositions accompanying the cerium addition.

As discussed in an earlier publication [17] the ductility as well as the flow stress of the brass is significantly affected by the addition of cerium. The ductility is improved from 80% to 230% by the addition of 0.07% Ce to the Cu–38.6% Zn under the present test conditions. According to the Crane phenomenon [17], an optimum ductility in microduplex, superplastic alloys is obtained at equal volume proportions of the two phases. By the addition of 0.07% Ce the α:β ratio is changed from 70:30 to 55:45 so that the observations pertaining to ductility can be explained essentially in terms of the Crane phenomenon rather than a change in the cavitation behaviour.

6. Conclusions

The following conclusions can be reached from this work:

(1) in the present alloy the addition of cerium serves to modify the alpha/beta by decreasing the solubility of zinc in the f c c phase;

(2) The addition of cerium only indirectly modifies the mechanical properties mainly through decreasing the proportion of the harder f c c phase;

(3) The decrease in flow stress by a factor of 3 through the addition of 0.07% cerium is remarkable but of no practical significance here.

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