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On the role of temperature fluctuations during microstructural degradation of the Cd-Zn eutectic

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The purpose of this work was to explore the influence of various types of temperature fluctuations on the microstructural stability of the Cd–Zn eutectic which is treated as a model for certain potential high-temperature, turbine-blade materials. The main conclusion was that the holding period at the highest cycle temperature had a significant, and previously unrecognized, influence upon the rate of microstructural degradation. The mechanism of degradation is discussed and it is noted that considerably more work is needed in this area if such alloys are to fulfill their potential applicability.

1. Introduction

Certain unidirectionally solidified eutectics are good candidates for high-temperature, high-stress applications, such as turbine blades (e.g. Ni_3Al–Ni_3Nb). The microstructures of slowly solidified eutectics are known to generally exhibit good high-temperature stability with constant temperatures [1, 2]. Recent studies have shown that, with one exception [3], thermal fluctuations can degrade the structure more rapidly [4–6]. Such cyclic temperatures are a natural accompaniment to the service situations envisaged for these materials and these studies have thus highlighted a serious problem in the potential usefulness of such eutectic alloys. In studies of microstructural stability at constant temperature the major variables, apart from time, are the as-solidified structure (arrangement and spacing of the phases and the properties of the interface) and the homologous temperature. With fluctuating temperatures new variables are introduced, including the heating and cooling rates, the temperature range and the holding times at high temperature. The present work was designed to explore the effects of homologous temperature and holding time on microstructural stability for different types of temperature cycle, together with the stability during exposure at constant temperature. The system employed, Cd–Zn, is a model material with a low melting temperature (542 K). The two phases (cadmium- and zinc-rich solid solutions) have been studied in considerable detail, unlike most of the intermetallics or carbide phases which reinforce the eutectic alloys which have actual service potential. The orientation relationship of the Cd–Zn eutectic is also known [7], so that crystallographic influences on the structural changes can also be examined.

2. Experimental

Zone-refined zinc and cadmium were melted together and chill-cast into a split graphite mould to obtain eutectic rods of 9.5 mm diameter and approximately 175 mm long. Unidirectional solidification was carried out at either 10 or 25 mm h^{-1}, using a vertical travelling furnace. The initial 38 mm and final 25 mm of each rod were rejected, and sections approximately 6 mm long were cut from the remainder of the rod, using a diamond saw, for the experiments. For constant temperature

TABLE I Thermal cycles employed

Cycle	Maximum temperature (K)	Temperature range (K)	Heating and cooling rate (K min^{-1})	Time at maximum (minimum) temperature (min)
A	518	225	15	15 (1)
B	518	225	15	1 (15)
C	303	225	45	15 (0.5)
D	303	225	45	1 (1)

anneals, randomly selected specimens were enclosed individually in stainless steel foil and put into a furnace with an air atmosphere. By maintaining the furnace current at a minimum, the temperature fluctuations of the specimens were minimized (averaging ± 0.75 K).

The thermal cycling experiments employed four cycles with two maximum homologous temperatures (Table I). For the higher homologous temperature the specimens were wrapped in copper foil and alternately heated by a resistance furnace and cooled by a fan. In order to control the heating and cooling rates and the hold time at the maximum temperature, the furnace and fan currents were varied by means of a controller activated by a cam. This gave two cycles, A and B in Table I, which were identical except for hold times. A lower maximum temperature, but with the same temperature range, was achieved using liquid nitrogen (78 K) and water (303 K). For these latter cycles, C and D in Table I, the cooling and heating rates were reduced by encasing the specimens in fibre-glass insulation within a metal tube, which was immersed alternately into the two media.

The degree of anisotropy was determined by measuring the number of intercepts per unit length (N) on polished sections, making 15 measurements every 20° rotation of the measuring template. Following de Silva and Chadwick [3], the degree of anisotropy was taken as $k = 1 - (N_{\mathrm{min}}/N_{\mathrm{max}})$.

3. Results and discussion

3.1. Isothermal annealing

The eutectic structures coarsened and anisotropy was reduced when annealed at elevated temperatures, as expected from preliminary work [8]. The changes in the degree of anisotropy are shown in Figs. 1 and 2 for several annealing temperatures in specimens solidified at the two rates. The coarsening rate, and hence the degree of anisotropy, changed more rapidly at higher temperatures due to faster diffusion rates.

In his review of isothermal instability of eutectics, Weatherly [9] has shown that the rate of change of the lamellar spacing should be proportional to time if the number of lamellar defects per unit area remains constant. Measurements of the lamellar spacing and defect density during isothermal annealing at 510 K (0.94 of the melting temperature) are shown in Fig. 3 for specimens solidified at 25 mm h^{-1}. Each lamella end was counted as a defect. It can be seen that the change in spacing was proportional to time initially, but eventually the rate reduced. The defect density decreased monotonically, unlike the Al–CuAl$_2$ system in which the defect density at first increases [9]. The as-solidified eutectic contained lamellae with a large number of defects, making such lamellae appear "dotted" in transverse sections (Fig. 4a). After a short annealing time (24 h) some of these "dotted" lamellae disappeared, leaving apparent gaps with thicker adjacent lamellae (Fig. 4b). Recession from lamellar faults was also observed, with each fault comprising a number of lamellae

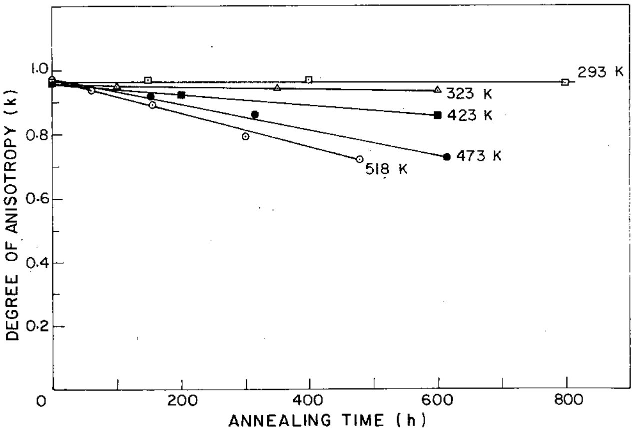

Figure 1 Degree of anisotropy versus isothermal annealing time for specimens solidified at 10 mm h^{-1}.

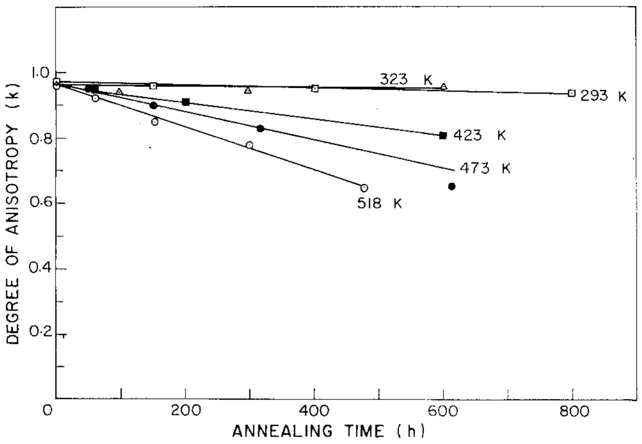

Figure 2 Degree of anisotropy versus isothermal annealing time for specimens solidified at 25 mm h^{-1}.

slightly offset at a line approximately normal to the lamellae in transverse sections. Thus the coarsening process proceeded from two locations: at fault lines and at "dotted" lamellae. Some new defects were apparently created in lamellae as annealing continued. Dotted lamellae are evident in Fig. 4b, compared to Fig. 4a, due to the recession from individual gaps in the lamellae, but other defects are apparent in which little recession has occurred. The creation of new defects might well arise through the polygonisation mechanism described by Nakagawa and Weatherly [10]. Since the total number of defects decreased with time, however, the rate of defect disappearance was greater than the rate of defect production under these isothermal conditions.

Comparison of Figs. 1 and 2 indicates that the slowly solidified specimens coarsened more slowly than those rapidly solidified, as expected. At higher temperatures, this resulted in the rapidly solidified material eventually being coarser in microstructure. Several factors contribute to this effect. Since the specimens solidified at 10 mm h^{-1} had coarser initial microstructures, both the diffusion distance and the amount of material to be diffused to cause the disappearance of one lamellae, were greater. In addition, the slowly solidified specimens had a lower defect density. Lamellar faults seem to be associated with crystallographic sub-boundaries approximately normal to the lamellae [9]. The initial dotted lamellae are probably associated with sub-boundaries parallel to the lamellae (providing dislocations for the polygonisation process) and the observation of fewer lamellar defects in more slowly solidified specimens may simply reflect a larger subgrain size. Hence, the faster solidification rate probably increases the rate of coarsening due to the smaller subgrain size within the eutectic grains, providing more paths of high diffusivity.

3.2. Thermal cycling

The changes in anisotropy for the different thermal cycles are shown in Figs. 5 and 6 for the slow and

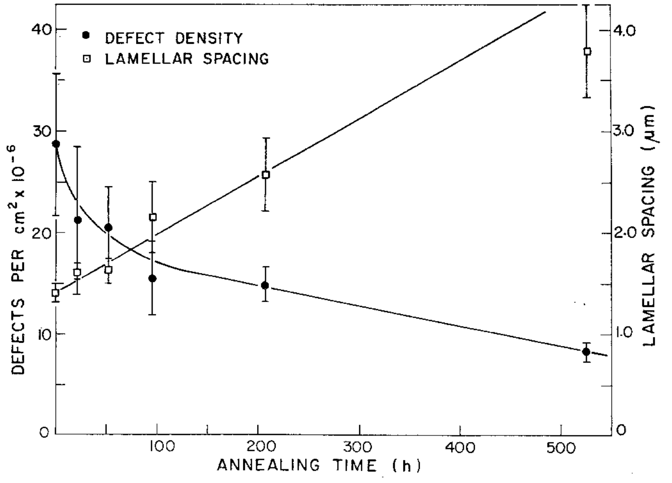

Figure 3 Defect density and lamellar spacing versus isothermal annealing time at 508 K for specimens solidified at 25 mm h^{-1}.

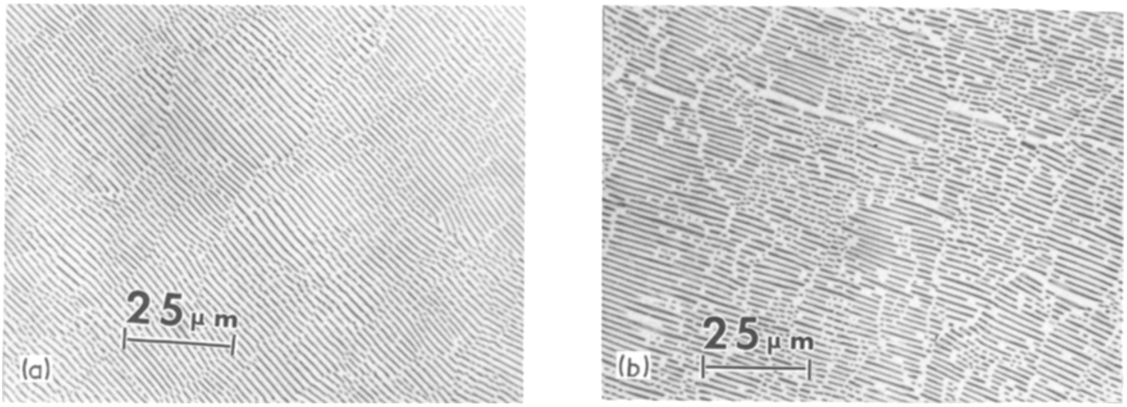

Figure 4(a) As-solidified microstructure of the Cd–Zn eutectic, using 25 mm h^{-1} solidification rate. (b) The Cd–Zn eutectic microstructure after 25 mm h^{-1} solidification rate, followed by 24 h at 508 K.

rapid solidification rates, respectively. The influence of maximum temperature and holding times are apparent. As indicated in Table I, the maximum temperature in cycles A and B was 215 K above that of cycles C and D, but all four cycles had the same temperature range. Figs. 5 and 6 show that the rate of structural degradation increased with increasing maximum temperature. Comparison of Figs. 5 and 6 shows that, as in the isothermal annealing study, more rapid solidification resulted in more rapid degradation, except in cycle D when little structural change was observed. This is shown more clearly in Fig. 7 for cycle A and for constant temperature annealing. In cycle B the structural degradation was very rapid, and occurred at approximately the same rate for specimens solidified at the two speeds. The holding time at the maximum temperature was 15 min for cycle A and 1 min for cycle B, and the reverse at the minimum temperature, giving a constant cycle length. Fig. 7 shows that anisotropy decreased more rapidly with longer holding time at the maximum temperature.

It is difficult to make a direct comparison of degradation in isothermal versus cyclic temperature conditions. Fig. 7 uses the time at maximum temperature as the basis for comparison. Since the diffusion processes involved in microstructural degradation are an exponential function of temperature, one might expect that only the time at the maximum temperature would be significant. In fact, Fig. 7 shows clearly that this is not the case. The deformation processes which take place during thermal cycling markedly enhance the rate of degradation. Since creep in both cadmium and zinc occurs by climb and prismatic glide [11, 12], dislocations transverse to the lamellae will be generated. As discussed by Nakagawa and Weatherly [10], this leads to an increased density of lamellar defects. This, in conjunction with increased diffusivity due to vacancy fluxes during thermal cycling, gives enhanced degradation and plastic

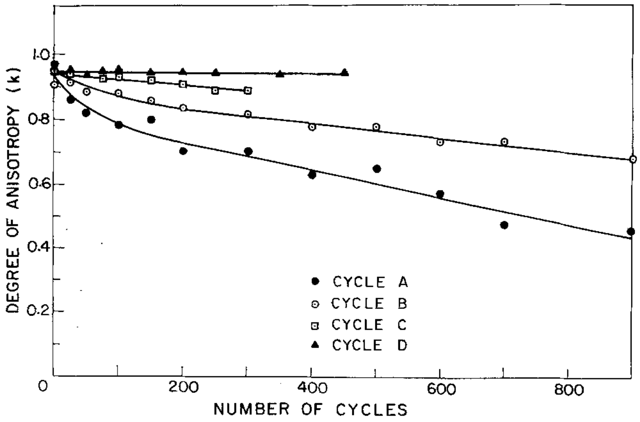

Figure 5 Degree of anisotropy versus number of cycles for specimens solidified at 10 mm h^{-1}, using the cycles in Table I.

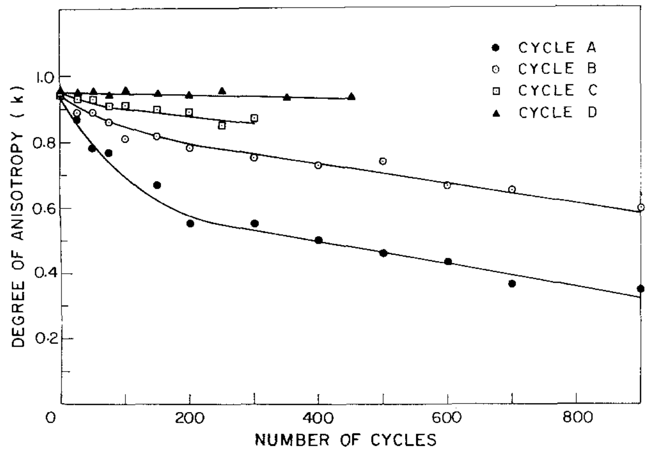

Figure 6 Degree of anisotropy versus number of cycles for specimens solidified at 25 mm h^{-1}, using the cycles in Table I.

deformation. Significantly, dimensional changes due to the deformation processes were observed with cycles A and B, similar to the warping found in thermally cycled Al–CuAl$_2$ eutectic specimens [4]. The change in circumference of a number of specimens was measured on transverse microsections. Cycle A, with a longer high temperature holding period was observed to give rise to more macroscopic plastic deformation than cycle B; after 2000 cycles the percentage changes in circumference were approximately 70% for cycle A and 40% for cycle B. In both cases the circumference increased approximately linearly with the number of cycles.

Garmong [13] has developed an elastic–plastic analysis of the effects of thermal cycling in eutectics, which has been applied to fibrous eutectics in which the fibres remain elastic. This analysis has been reformulated by Tyson [14] in differential form. The strain due to the difference in thermal expansion coefficients is considered to be made up of three terms: elastic, time-dependent plastic, and creep strain.

From calculations for fibrous eutectics, Garmong [13, 15] concluded that creep strain would generally make only a very small contribution. The dwell time during thermal cycling is accordingly predicted to have little effect. In contrast to this prediction, the present data indicate that holding time has a marked influence on stability (cycle A versus cycle B in Fig. 7). In order to calculate the contributions of elastic, plastic and creep strains, a number of material parameters must be determined. At first sight, these data are available, but difficulties arise in trying to apply them quantitatively to the Cd–Zn eutectic. The easiest mode of plastic deformation in both cadmium and zinc single crystals is basal slip, i.e. parallel to the lamellar interfaces within the eutectic alloy. Thus, in agreement with Garmong, it might be expected that plastic deformation would be easy and creep of little importance. In that case, holding time should have little effect, whereas the opposite effect was found. In the thermally cycled eutectic, the stress along the basal plane is not uniaxial, as in tensile tests, but symmetrically biaxial. This

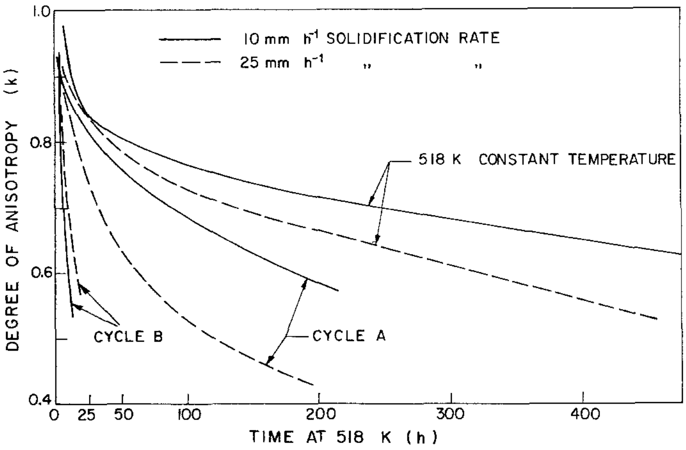

Figure 7 Degree of anisotropy versus time at 518 K for isothermally annealing and cycles A and B, after solidification at 10 and 25 mm h^{-1}.

condition is difficult to reproduce experimentally in single crystals, and neither yield stress nor work-hardening rates could be found for this situation, so that no meaningful calculation of the contributions of elastic, plastic, and creep strain could be made.

4. Conclusions

The main conclusion reached from the present work is that much more work is needed before an understanding of the influence of thermal cycling on the microstructural stability of unidirectionally solidified eutectic materials can be developed. It is apparent that thermal cycling enhances the rate of microstructural degradation in the present material. Holding period at the maximum temperature plays a significant role possibly due to creep effects. This observation is in contrast to recent analyses. The mechanism of degradation involved recession from faults and the removal of "dotted" lamellae probably formed by polygonization.

One might further add that the present work is reflective of the transformation in the focus of work on high temperature turbine materials to explore complex states of stress, complex loading spectra and complex temperature fluctuations in order to develop a realistic picture of service behaviour and provide a predictive basis for design from a materials viewpoint [16].

Acknowledgements

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