STABILISATION OF MARTENSITE IN Cu-Zn-Si

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Introduction

In many copper based shape memory alloys, the retransformation of martensite to the parent occurs at a higher temperature, immediately after quenching through the transformation and/or ageing in the martensitic condition when compared to retransformation in continued cycles performed without any delay. This effect termed stabilisation, has been used to raise, temporarily, the retransformation temperature of the martensite in Cu-Zn-Si alloys, notably with compositions which transform to martensite well below ambient temperature. This has been achieved by heating the sample, with the martensite microstructure, very slowly, at a rate of about 0.25°/min [1]. Notwithstanding such use, stabilisation remains an unwanted problem in shape memory devices which require for proper functioning reproducible retransformation temperatures without any shifts. This accounts for the considerable interest shown in understanding the effect.

Stabilisation has been studied extensively in Cu-Zn-Al alloys [2-12]. It is evident from these studies that stabilisation is caused by a thermally activated process which is accelerated by the presence of any quenched in vacancies [5]. Moreover, changes in the lattice parameter of martensite and an evolution of the order dependent monoclinic angle of the structure towards 90° during ageing that leads to stabilisation, have been reported [6]. Correspondingly, configuration changes within the volume of the martensite have been suggested as a reason for the stabilisation [7]. This has been further corroborated by experiments on stress induced single variant martensite, where the return from the stabilised to the unstabilised state has been shown, convincingly, to be gradual as would be expected if the above mechanism was the cause for stabilisation [8]. Besides this mechanism, concurrent or alternative mechanisms for stabilisation have been proposed in the literature, which are based on certain features observed in the microstructure of the stabilised martensites [9-12]. Among them are defect pinning of martensite-martensite interfaces, relative changes in the density of basal and non-basal plane faults and the occurrence of narrow lamellae of 3R stacking sequence.

There are few reports to date on the mechanism of stabilisation of Cu-Zn-Si martensite [13,14]. These reports cite all the reasons mentioned above as possible causes for the stabilisation. Moreover, martensite boundary pinning by vacancies and narrow lamellae of 3R phase within the 9R martensite have been claimed as fairly important contributors to stabilisation. The present work was undertaken to review these earlier conclusions and has been carried out in alloys that transform nominally at sub-zero temperatures. The studies
are restricted to the first 10° or 15° of stabilisation. Another benefit from the present study, in case configuration changes have to be considered, is related to the martensite structure observed in these alloys, which is of the 9R type. Modelling, configuration changes should be easier in such 9R martensite than the 18R martensite of the Cu-Zn-Al alloys studied so far because of the reduced number of β sublattices to be considered.

Experimental procedure

Alloys of copper containing 30.7 at% Zn and 4.3 at% Si (alloy A) or 29 at% Zn and 5 at% Si (alloy B) were used in the present study. The Ms of these alloys measured in a differential scanning calorimeter (DSC) after a quench from the solution treatment temperature of 850°C into water at 20°C or 70°C did not differ by more than 1 or 2° from that measured in subsequent cycles. Thus these values -23°C and -10°C respectively for the two alloys have been taken as their nominal Ms.

The experiments were commenced by quenching the alloys after the 850°C treatment into water at 60°C. Subsequently the samples were brought to a temperature of -60°C, either by quenching into an alcohol bath at that temperature (treatment T1) or by cooling at 0.5 °/min in the DSC (treatment T2). Each sample was then heated in the DSC at a rate of 0.2°/min, which effected stabilisation of the martensite past their nominal retransformation temperatures. The heating was stopped at -10°C, after which the sample was cooled to -60°C prior to controlled heating again at a rate of 20°/min to the temperature where the retransformation could be considered as completed. With the least delay at this temperature, the sample was then cooled, at the maximum possible rate permitted by the equipment (~ 320°/min), to -60°C without recording the cooling cycle. The sample was again heated at 20°/min just to the completion of retransformation and again abruptly cooled to -60°C. This process of controlled heating and abrupt cooling was continued, till no further change in the retransformation temperature of martensite was noted. The results of the heating cycles are presented in the next section.

In some samples the martensite was stabilised past the ambient temperature. These samples were subsequently used for examination by transmission electron microscopy. They were compared with nominally transforming samples, in which martensite was induced by in-situ cooling in the microscope. The thin foils for electron microscopy were prepared by jet electropolishing at -40°C in a 2:1 HNO₃ :CH₃OH bath or at room temperature in a Struers D-2 electrolyte.

Results

Figure 1 shows the DSC heating curves of a sample subjected to treatment T1 and where the martensite to start with was stabilised without any retransformation up to -10°C, by slowly heating in the DSC at 0.2°/minute. The retransformation of this stabilised martensite, as seen in this figure, commences around -10°C and ends at around +10°C. In the subsequent retransformation following the fast cooling, the retransformation temperatures drop sharply towards the nominal values and continue to decrease in the following retransformation cycles, as can be evidenced by comparing the second and the eighth cycle results in fig.1.

The same behaviour is observed in samples with treatment T2, which were afterwards heated slowly in the DSC at 0.2°/min up to -10°C. The start and end of the retransformation of this stabilised martensite occurs at slightly higher temperatures as can be seen in fig.2, but the stepwise return towards nominal retransformation temperatures in subsequent cycles is clearly evident here as well. To ensure, that the decrease in the retransformation temperatures is not an effect of cycling, alloy A quenched to 60°C was cycled in the DSC at a rate of 20°/minute. The maximum shift in the As and Af temperatures noted after the 7th cycle was <1°C. Thus, the decrease in the retransformation temperatures is to be attributed to changes in atomic arrangement related to the return of martensite to its pre-stabilisation state.
The structure and microstructure of the stabilised martensite was compared to that of the unstabilised martensite. A quantitative comparison here, however, would not be appropriate because - (i) the stabilised martensite is obtained in a bulk sample which is later thinned for TEM examination and (ii) the unstabilised martensite is formed in a foil, already thinned for TEM examination. Yet, a qualitative comparison of certain features would be in order and is provided below. The monoclinic angle of the 9R structure of the stabilised martensite is close to 90° (as estimated after measuring the angle between 009 and 300 reflections) compared to a lesser value for the unstabilised martensite (figs. 3 and 4). Not only basal, but non-basal plane faults (so called type I defects as reported in Cu-Zn-Al alloys [15] for the 18R martensite) were observed in both stabilised and unstabilised martensite (figs. 5 and 6). This is probably the first time where direct reference and evidence for the existence of such non-basal faults related to [114] planes in 9R martensite is provided. Lamellae of 3R in a matrix of 9R martensite in Cu-Zn-Si has been reported many years back by Pops and Delaey [16]. It is believed these lamellae would be observed independent of the treatment and by them selves would not be responsible for the martensite stabilisation which sets in upon post quench ageing.

Discussion

The gradual return to nominal retransformation temperatures, in subsequent cycles following the reversion of the stabilised martensite, is to be attributed to the progressive removal of the effects responsible for the stabilisation of martensite. It can be argued that these effects are mainly configuration changes in the martensite, brought about during the slow heating in the DSC. All non-configurational effects leading only to strain energy relaxation in martensite, such as pinning of intervariant interfaces, defects within a martensite plate, viz. dislocations, basal and non-basal faults, if relevant, would give rise to raised retransformation temperatures but not a gradual return, as observed, to the nominal values. This is because, once such barriers are overcome and retransformation is complete, the barriers may be considered dissolved and there would be nothing to prevent the subsequent retransformations from taking place at nominal values. On the other hand, the gradual return of the retransformation temperatures does indicate that it is a time - temperature dependent process involving the relative stability of martensite and B phases. The latter is affected by bulk free energy changes of the phases, brought about by the configuration modifications in the martensite.

The nature of these configuration changes can be reasoned from the known superlattice of the B phase of Cu-Zn-Si and the direction in which the monoclinic angle of the 9R martensite structure changes when stabilised. The B phase is B2 ordered and the monoclinic angle of the martensitic structure tends to increase upon stabilisation towards 90°. The latter is also an indication towards formation of a regular rather than a distorted hexagonal configuration of atoms on the basal plane of the 9R structure [6], as originally inherited by the martensite from the B2 ordered phase. Stabilised martensite is thus associated with a configuration that is relatively disordered with respect to the unstabilised state inherited from the ordered B phase.

In conclusion, the tendency for Cu-Zn-Si martensite to disorder relatively with time is the primary, if not the only reason for its stabilisation. Such disordering will affect the free energy of both the martensite and the B phases. Atom relaxations around defects in martensite, commonly referred to as pinning, do not play an important role in stabilisation. It is believed that these latter barriers even if operative can be overcome rather easily, with a superheating much less than the observed shifts in retransformation temperature of martensite due to stabilisation.

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References

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Fig. 1 DSC heating curves of sample subjected to treatment T1
(See text for details)

Fig. 2
DSC heating curves of sample subjected to treatment T2
(See text for details)
Angle between the $a^*$ and $b^*$ axes as an indication of the order, fig. 3 stabilised martensite and fig. 4 unstabilised martensite.

Non-basal faults in fig. 5 stabilised martensite and fig. 6 unstabilised martensite.