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A shape memory gold alloy processed by rapid solidification

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Abstract

In the ternary system Au–Cu–Al, the β phase has a displacive transformation which can be tailored for a shape memory effect. The sequence of allotropic transformations of the β phase as a function of temperature and cooling conditions is reported in this work. The structure of the martensite (monoclinic) and the type of parent phase are identified. Rapid solidification is employed as a tool for freezing the high temperature modification and compared to quenching from the solid state. DSC analyses clearly demonstrate the thermodynamic order of transformations and the temperatures of the forward and reverse martensitic transformation. A transformation from metastable B2 to $L2_1$ has been revealed for the first time. The transformation is endothermic and irreversible.

The thin ribbon sample has been used to show the one-way shape memory effect.

Keywords: Metals and alloys; Shape memory; Rapid solidification

1. Introduction

The β phase in the ternary Au–Cu–Al system (close in composition to $Au_7Cu_5Al_4$) is known to give a displacive transformation on cooling around room temperature. The parent and martensitic phases and theirs transformation have been studied in a series of papers showing that the parent phase has very likely $L2_1$ structure whereas a modulated tetragonal structure was attributed to the martensite [1–4]. The transformation is apparently favoured by pre-annealing the alloy at temperatures above 100 °C and has been exploited to create spangling surface patterns in jewellery items. There are, however, several open points concerning this material. The reported structure of the martensite phase is not convincing if compared to other martensites originating from β phases in alloys based on both Au (Au–Cu–Ga) [5] and Cu (Cu–Au–Zn) [6–8]. Although the $L2_1$ structure was predominantly attributed to the parent austenite, the phase was in some instances reported as $D0_3$ and/or B2 [3]. Such uncertainty causes a corresponding uncertainty in the motivation for thermal treatments suited to develop the martensite structure.

In this work rapid solidification processing has been employed as a tool to obtain small samples in the form of ribbons having refined microstructure for various analyses and for showing the shape memory effect of the material [9].

2. Experimental

Batches of a Au76.0%–Cu18.0%–Al6.0% alloy (in wt.%; Au43.3%–Cu31.8%–Al24.9%; at.%) were prepared by arc melting suitable amounts of electrolytic jewellery Au and 99.999 Cu and Al under Ar. Portions of the ingots were rapidly quenched in a melt spinning apparatus under Ar to produce a ribbon some tens of micrometers thick.

Samples were analyzed on heating and cooling in DSC up to 700 °C at the rate of 4 °C/min using a heat flow TA Q100 DSC and a power compensation Perkin-Elmer DSC7. All DSC runs were performed under flowing Ar. The samples were supported by a Rh foil. Before and after each heat treatment of samples, X-ray diffraction (XRD) patterns were taken using Cu Kα radiation. Microstructures were examined by optical microscopy and scanning electron microscopy.

3. Results and discussion

3.1. Cast ingot

The Au76.%–Cu18.0%–Al6.0% ingot produced by arc melting and, therefore, cooled on the chill copper crucible of the furnace was found to be almost fully martensitic. The grains inherited from the parent austenite contain regularly spaced lamellae as already reported for this alloy. The grains are often elongated because of solidification mode (Fig. 1). Various samples of the alloy cut along different directions from the ingot were analyses by XRD. They display various reflections with

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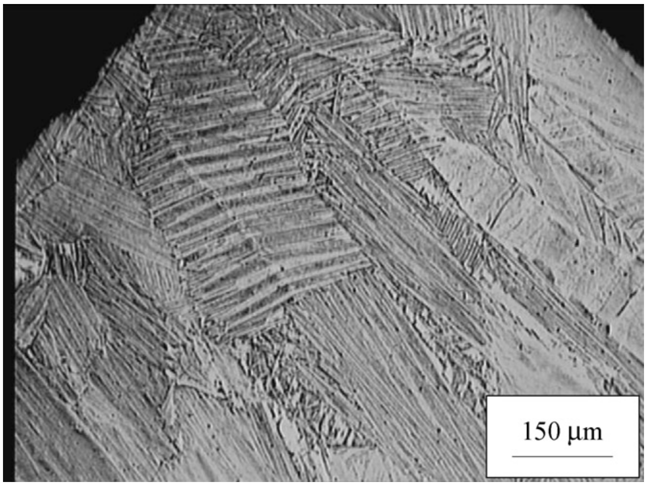

Fig. 1. The polished surface of a Au76.%–Cu18.0%–Al6.0% as cast ingot showing colonies of lamellae due to martensite originates in former austenite grains.

evident textures (Fig. 2a). From a detailed comparison with the Au–Cu–Ga martensite which was reported as orthorombic [5] and the Cu–Au–Zn martensitic phases which are demonstrated to be monoclinic, 18R type [6–8], it is suggested the present martensite is monoclinic of the latter type. The lattice parameters are $a_0 = 0.465$ nm, $b_0 = 0.556$ nm, $c_0 = 3.906$ nm and $\alpha = 87°$, as determined from lattice spacings obtained from several patterns. This is at variance with the tetragonal structure derived previously from patterns obtained with Mo Kα where various reflections could not be detected because of the short wavelength or overlap with other reflections [3]. The martensite transforms in DSC experiments to the parent austenite with two endothermic peaks: a low intensity one at 46 °C and a major one at 72 °C as shown in Fig. 3. The DSC trace displays then a tiny fluctuation on heating before a further endothermic signal at 638 °C. By heating in a high temperature DSC, the solidus of the alloy is found at 726 °C and the liquidus at 767 °C. On cooling the transformation at 638 °C is reproduced with no appreciable undercooling. The martensite start is obtained at 17 °C (inset of Fig. 3).

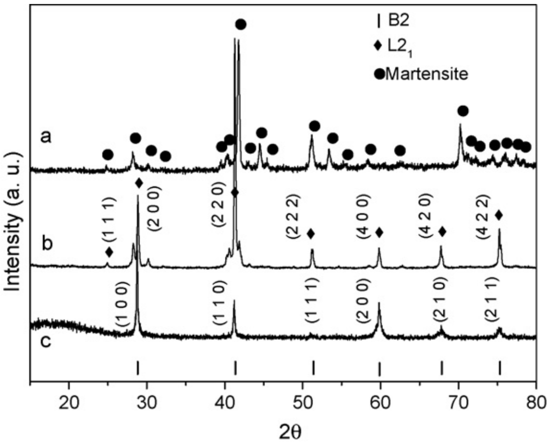

Fig. 2. XRD patterns given by samples of Au76.%–Cu18.0%–Al6.0%: (a) as cast ingot, (b) as-spun ribbon and (c) ribbon as quenched from 630 °C after annealing for 1 h.

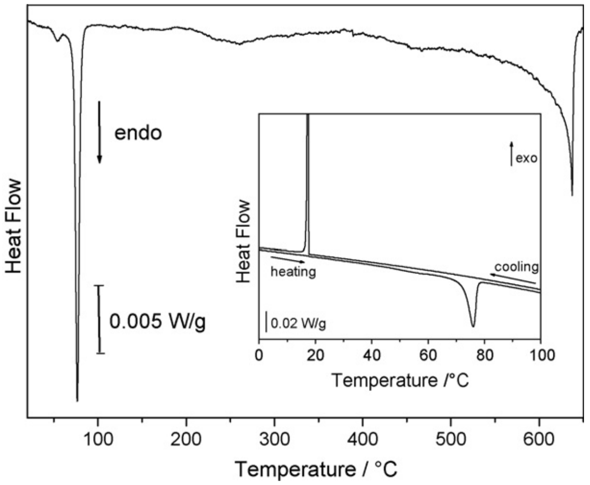

Fig. 3. DSC trace showing the transformations of a Au76.%–Cu18.0%–Al6.0% as cast ingot. The inset reports traces obtained on heating and cooling the sample through the martensite formation (cooling) and reverse transformation to austenite (heating).

3.2. Rapidly solidified samples

Since the transformation to martensite occurs close to room temperature it is difficult to retain and study the parent phase. XRD experiments at temperatures above the reverse transformation have indicated that the austenite should have a $L2_1$ structure. Quenching ingots from the temperature range 600–700 °C resulted in the formation of a mixed structure apparently constituted by a B2 phase and martensite. It has then been devised to quench rapidly the melt in order to produce a ribbon which could possibly retain the high temperature structure [9]. The quenching process is performed on a copper wheel which is not chilled. After quenching the sample was kept at temperatures above 17 °C to avoid possible transformation. The ribbon has much finer grains with respect to the ingot, mostly below 10 µm in size, equiaxed in shape (Fig. 4). The reflections in its XRD

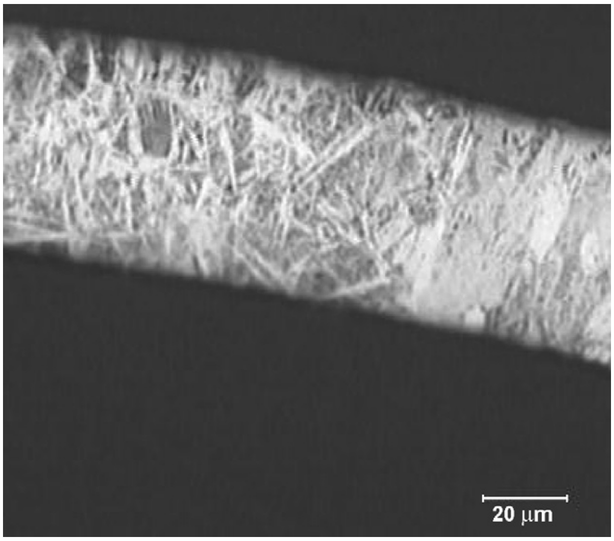

Fig. 4. Image of a cross-section of a melt spun ribbon of Au76.%–Cu18.0%–Al6.0% showing coexistence of martensitic and parent grains.

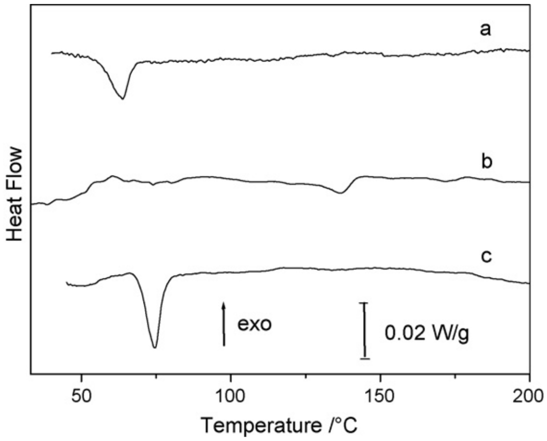

Fig. 5. DSC traces obtained with ribbon samples of the Au76.%–Cu18.0%–Al6.0% alloy: (a) as spun, (b) as quenched from 630 °C after annealing for 1 h and (c) after the DSC experiment reported in (b).

pattern can be indexed as originated by a $L2_1$ phase having lattice parameter 0.617 ± 0.001 nm. Care must be taken since distinction between $L2_1$ and B2 can be made only on the occurrence of the reflections seen at $2\theta = 25°$. The other reflections can be attributed to the martensite phase (Fig. 2b).

The DSC trace of the ribbon is shown in Fig. 5a. The reverse transformation of the small fraction of martensite it contains, gives rise to a broad signal of relatively low intensity. The area of the peak provide a value of 1.1 J/g for the heat of transformation to be compared with that of 3.4 J/g for the fully martensitic ingot.

3.3. Samples quenched from the solid state

The transition at 638 °C has the characteristics of a second order phase transformation: lambda shape in the thermal analysis curve, lack of undercooling and, therefore, no apparent barrier to nucleation. Apparently, the high temperature phase cannot be quenched without transforming. Samples of the ingot and of ribbons were annealed at 630 °C for 1 h and then quenched into iced water. The bulky samples from the ingot contained regions with lamellae marking that the transformation to martensite had occurred, next to regions where they were absent. The XRD patterns of these samples are of little help in recognizing the phase constitution due to texture effects. The DSC analysis reveals three endothermic peaks: the most intense one starts at about 38 °C, the second at 63 °C and the third one at 130 °C. The first and second peak can readily be assigned to the reverse martensitic transformation. The occurrence of a DSC signal in the temperature range of the third one was earlier signaled but its origin was not disclosed [1].

The samples of the thin ribbon contained mostly the B2 phase and a trace quantity of martensite as shown by the reflections of very low intensity in the XRD pattern of Fig. 2c, around $2\theta = 40°$, 50° and 60°. The DSC result shown in Fig. 5b, reveals that the signal due to the reverse martensitic transformation is reduced to a broad halo at low temperature and a signal at 130 °C occurs here as well.

Samples quenched from 630 °C, both from the ingot and the ribbon, were annealed for 1 h at 80 and 155 °C and then quenched in iced water. They were then observed with the microscope, used for XRD and for DSC experiments. All evidences indicate that the samples annealed at 80 °C contain a fraction of martensite and retain the B2 phase and those annealed at 155 °C are fully martensitic. This strongly suggests that the DSC signal at 130 °C is due to transformation from the B2 to $L2_1$ structure. The latter phase then transforms to martensite on cooling and the reverse transformation is revealed by DSC (Fig. 5c). In summary, the peak at 130 °C occurs when the quenched sample contains the B2 phase and is absent when the $L2_1$ phase is present.

A further confirmation has been obtained by collecting a pattern with a ribbon sample in a high temperature XRD unit at 200 °C. The $L2_1$ phase is recognized by the appearance of a reflection at 25° corresponding to its (1 1 1) line.

3.4. Phase stability

The results reported above indicate the following sequence of phase appearance as a function of temperature.

The equilibrium phase below room temperature is martensitic and reverts to austenite in the temperature range from 40 to 80 °C according to the thermal history of the sample (see differences between Fig. 5, curve c and Fig. 3). The reason for DSC signals occurring at various temperature in this range has not been investigated further. It is remarked that multiple step transformation are frequent in NiTi shape memory alloys at various stages of annealing and have been attributed to causes which might be operative also in the present alloy such as local variation in dislocation density, compositional and stress inhomogeneity of the matrix due to precipitation of an intermetallic compound [10–12]. The transformation temperatures in Ni–Ti–Cu ribbons were found to depend on processing parameters causing microstructural inhomogeneity [13]. Finally, variations of a few degrees in the peak temperature of the reverse transformation in the Au–Cu–Al alloy have been attributed to martensite stabilization induced by annealing [14].

The parent austenite is the $L2_1$ ordered phase which has earlier been described, including site occupancy by the elements, and reported to appear in XRD patterns taken after the reverse martensitic transformation in the temperature range from 100 to 550 °C [2]. The $L2_1$ phase should then transform to the B2 structure on heating. In fact, the latter phase can be quenched after annealing at 630 °C. There is no clear indication in the DSC trace of the occurrence of the transformation before the B2 phase disorders with a second order transition at 638 °C. The $B2 \rightarrow L2_1$ transformation at 130 °C is endothermic although being irreversible. This implies that the transformation is driven by the entropy difference between the two phases. The equilibrium inverse transformation should, therefore, be exothermic and occur well above 130 °C. Since a clear DSC signal is not observed, it is likely that the enthalpy and entropy differences between the two allotropes are reduced on heating, or even revert sign, because of variation in the site occupancy by the elements and the appearance of thermal vacancies. The transformation would then occur progressively in a temperature range and its thermal effect could not be detected. Note also that the enthalpy difference at 130 °C is very small and the eventual signal could be below the detection limit of the instrument. The transformation is thermally activated since it is displaced to higher temperature on increasing heating rate. It is worth remembering that a progressive character has been reported for the AuCuI to AuCuII transformation which starts in DSC at temperatures as low as 200 °C and for ordering in melt spun ribbons starting close to 130 °C, i.e. as soon as atomic mobility occurs in the time scale of the temperature rise [15,16].

The presence of the $L2_1$ phase in the rapidly solidified ribbon can be understood by considering that the liquid has been undercooled during the process of melt spinning and the $L2_1$ phase can have nucleated directly from the liquid phase.

3.5. Shape memory effect

The displacive transformation performed with polished samples produces surface faceting with attractive spangling [1]. The one-way shape memory effect has been demonstrated with ribbon samples [9]. In both cases well annealed materials are needed for optimal development of the phase transformation. The finding reported above concerning the $B2 \rightarrow L2_1$ transformation confirms that this is a pre-requisite for complete formation of the martensitic phase.

4. Conclusions

In this paper the main features of the martensitic phase transformation in the Au–Cu–Al system have been revisited and clarified where necessary:

- the structure of the martensite has been identified as monoclinic at variance to previous proposals;
- the $L2_1$ parent phase is retained at low temperature by liquid quenching probably because of direct nucleation from the undercooled melt;
- the B2 phase, on the other hand, is retained on quenching from the solid state after annealing at 630 °C;
- the $B2 \rightarrow L2_1$ transformation, needed for complete development of the martensitic phase, appears endothermic and irreversible in DSC experiments made on heating implying that it should be entropy driven.

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