

New Shape-Memory Compositions in the $\text{Au}_{2-x}\text{Cu}_{1+x}\text{Al}$ ($0 < x < 2$) β -Phase

V.K. Bhatia, C.S. Kealley, A. Dowd and M.B. Cortie

Institute for Nanoscale Technology, University of Technology Sydney, NSW 2007, Australia.

Two stoichiometries of the $\text{Au}_{2-x}\text{Cu}_{1+x}\text{Al}$ β -phase are known to exhibit reversible displacive phase transformations and hence shape memory properties. These are $\text{Au}_7\text{Cu}_5\text{Al}_4$ ($x=0.25$, also known as ‘Spangold’) and Cu_3Al ($x=2.0$, a well-known shape memory alloy). Here we show that some intermediate compositions, in the vicinity of AuCu_2Al ($x=1$), are also stable and that they too have transformations suitable for potential use in shape memory applications.

1. Introduction

Although Al, Au and Cu each has the face centred cubic (fcc) structure in their elemental solid forms, they do not readily alloy with one another. Instead Al and Au, and Cu and Al, form a series of binary intermetallic compounds with one another, while the (Au,Cu) solid solution is stable only at elevated temperatures, transforming to a series of ordered superstructures at lower temperatures. A ternary intermetallic compound, $\text{Au}_7\text{Cu}_5\text{Al}_4$, is also known. This is an eighteen-carat, shape memory, electron compound and is sometimes called ‘Spangold’ [1]. Although at first misidentified as being related to the $L1_0$ phase (*Strukturbericht* notation) formed from (Au,Cu) [2], it was later shown that the Spangold composition is a Hume-Rothery style β -electron compound [3, 4] with a high temperature phase in the $L2_1$ ordered body-centred cubic packing arrangement and a low temperature martensitic phase of lower symmetry. Like many of the other intermetallic β -phase electron compounds, these two crystal structures are related by a reversible displacive phase transformation. The phenomenon can be exploited to produce a ‘shape memory effect’ (SME) in terms of which a device or actuator made from the shape memory alloy (SMA) can alternate between two shapes.

The martensite phase of $\text{Au}_7\text{Cu}_5\text{Al}_4$ was at first reported to be tetragonal with some additional modulation or distortion [5]. Later it was shown that it might be more accurate to describe it as having a hexagonal-type packing arrangement on the B19 model, although with a unit cell of double size to account for the ternary ordering [6]. In contrast, the martensite in other samples has been identified as monoclinic [7], by analogy to the heavily faulted structures determined for many Cu-base martensites. Levey *et al.* mapped the phase boundaries of the Au-Cu-Al β field at 500°C , and noted that, at that temperature, it existed only between the stoichiometries approximately corresponding to Au_2CuAl through to AuCu_2Al . This phase field was not contiguous with the Au_4Al and Cu_3Al β -phases on the binary edges of the phase diagram but it was suggested that it might possibly link up with them at higher temperatures [1].

Not much further was known, however, regarding the full nature or extent of the ternary β -phase field in the Au-Cu-Al system, or its properties. In the present work, we examine the properties of alloys in the vicinity of AuCu_2Al , i.e. $x=1$. In particular we were interested to know whether these compositions are stable with respect to decomposition and aging at lower temperatures, and whether they might exhibit a reversible displacive phase transformation.



2. Sample preparation

The nominal target composition was AuCu₂Al (electron-to-atom (e/a) ratio 1.50) but since better SME and mechanical properties in β -phase SMAs are generally obtained for e/a ratios between 1.35 to 1.48, a range of target compositions with slightly reduced Al contents was actually weighed out. The samples to be considered further here were 27%Au-55%Cu-18%Al (designated “A”, $e/a=1.36$), 30%Au-49%Cu-21%Al (“B”, $e/a=1.42$) and 29%Au-47%Cu-24%Al (“C”, $e/a=1.48$). All compositions are in atomic percent and are plotted in Fig. 1 on top of the 500°C isothermal section proposed in 2002 by Levey *et al.* [1]. High purity forms of the elements were weighed out and melted in an alumina crucible under a protective atmosphere. The Au was melted first, then the Cu and Al stirred in. The samples were then annealed at 750°C to convert them into β -phase, following which they were quenched into iced brine. This was expected to freeze in any β -phase that formed during the annealing, by analogy with the situation pertaining to Cu₃Al, Cu_xSn, Cu_xZn, and other SMAs. Of course, if the martensite start temperature (M_s) of the sample had been above room temperature then the sample would be in the martensitic form after this treatment.

Samples were cut up using a low speed Leco saw, taking care to avoid over-heating. Differential scanning calorimetry (DSC) analyses were performed using a Thermal Analysis DSC 2920. A ramp rate of 10 °C/min was used. A Zeiss Supra 55 VP scanning electron microscope (SEM) was used at 20 keV on high current mode with a 120 μ m aperture in back-scatter mode to verify the composition and phase relationships. A Cu standard was used to calibrate the electron dispersive spectroscopy (EDS). The EDS analysis mentioned are each the average of five measurements and are likely to be accurate to within 0.5%. Optical microscopy on an Olympus BH2 equipped with a JVC TK-1280E digital camera was used to examine polished and etched samples using ordinary light and polished samples using Nomarski interference contrast (the latter is very sensitive to surface relief). Ferric chloride solution was found to be a suitable etchant.

3. Results

Up to 2% variation in composition was found in Sample A by EDS, indicating either that coring had occurred during solidification and/or that there was a miscibility gap of only about 2 at.% between the α - and β -phase fields in this region of the phase diagram. Furthermore, the microstructure was acicular in the as-cast condition, becoming duplex after annealing; compare Fig. 2(a) and Fig. 2(b). The application of XRD revealed that this sample consisted of α -phase, i.e. fcc (Au,Cu), after annealing, with some proportion of a minor second phase. However, the as-cast structure was β -phase, which subsequently transformed to martensite on further rapid cooling in the as-cast samples. This would occur if the $\alpha+\beta$ phase field had a similar shape to that in Cu-Zn, for example. In this case annealing at 750°C would convert the β -phase microstructure substantially into the α -phase, as observed. Sample B was single phase in both the as-cast and annealed states, with an analysed composition of about 28.4%Au, 50.2% Cu and 21.4% Al. It consisted of an acicular microstructure, very similar in nature to that of Spangold, other β -phase SMAs, and the as-cast A. On the other hand, EDS

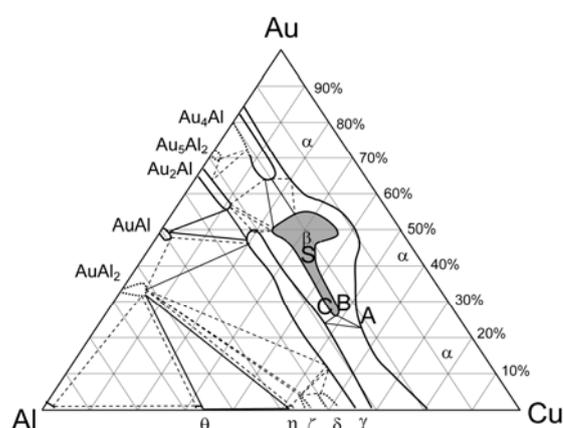


Fig. 1. Isothermal section of Au-Cu-Al phase diagram after Levey *et al.* [1], showing extent of β -phase at 500°C (shaded grey here) and the location of the present experimental Samples A, B and C. The stoichiometry of the ‘Spangold’ alloy is shown with the symbol S.



analysis and microstructural examination of Sample C indicated that it contained a substantial fraction of a second phase with 27% Al, Fig. 2(c) to (f). This can be matched by its composition to the ternary γ -phase $\text{Au}_4\text{Cu}_{9-x}\text{Au}_x$ [1]. The feathery intragranular morphology in some parts of the microstructure suggest, by analogy to the known behaviour of other Cu-containing β -phases (e.g. Cu-Sn [8] or CuAlMn [9]), that a proportion of the γ formed by intragranular precipitation from the β parent phase at a relatively low temperature. This would very likely have occurred during the cooling of the casting to room temperature, and indicates that the $\beta/(\beta+\gamma)$ surface in this system slopes down towards the Au-Cu binary edge, i.e. the β -phase field is restricted in extent as the temperature is decreased. A V-shaped narrowing of the β -phase field as temperature decreases is very typical of coinage metal systems although, oddly, apparently not of Spangold [10].

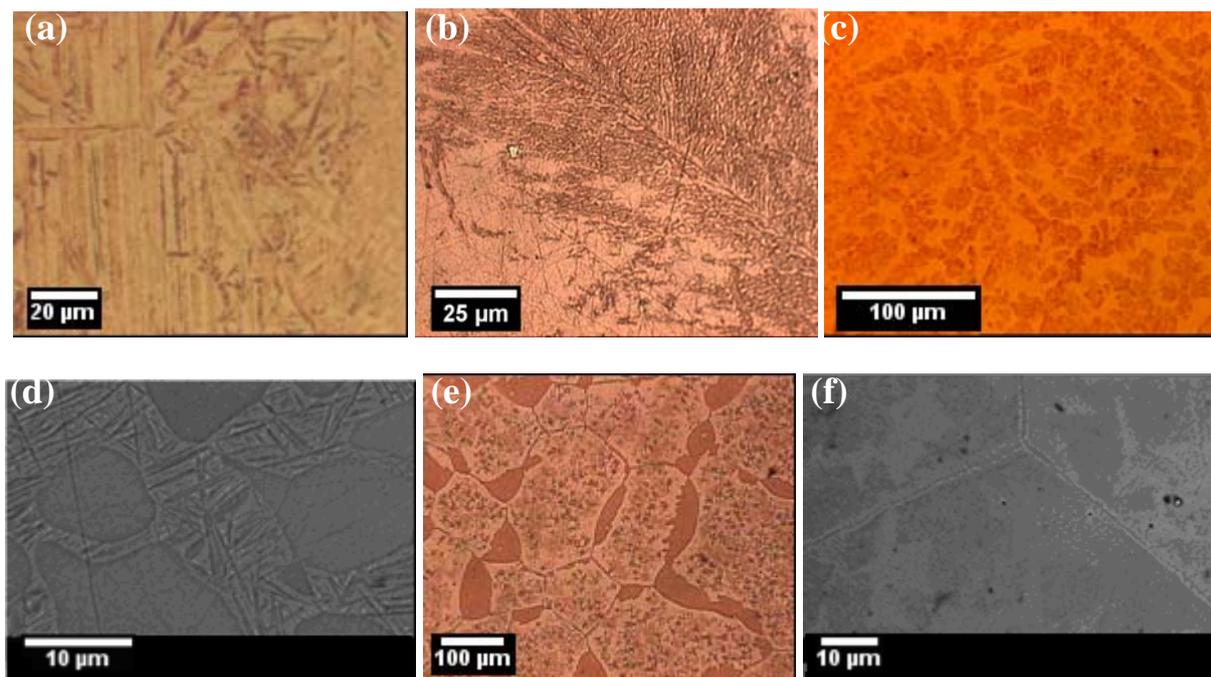


Fig. 2. (a) Sample A in the as-cast condition showing laths and needles of martensite formed in the as-cast sample. (b) Sample A after annealing showing duplex microstructure of α and β -phases. (c) Two-phase microstructure in as-cast Sample B before annealing, showing inter- and intra-granular γ -phase. (d) As for (c) but with SEM, showing islands of γ -phase surrounded by a matrix of β -phase that has transformed to martensite. (e) Two-phase microstructure in as-cast Sample C after annealing, showing intergranular islands of γ -phase and fine intragranular precipitates of γ . (f) As for (e) but with SEM, showing inter- and intragranular precipitates of γ .

Differential scanning calorimetry indicated the onset of melting at about 811°C and complete melting at about 851°C in Sample C, increasing to 824 and 858°C in B and 868°C and 899°C respectively in A. The values are significantly higher than those for Spangold (which melts over the range 715 to 770°C depending on stoichiometry [2]) although lower than those for Cu_3Al ($\sim 1050^\circ\text{C}$), or for the Au-Cu solid solution ($\sim 920^\circ\text{C}$ at 50 at%Cu). Therefore, the data indicate that the liquidus surface slopes upwards from $\sim 750^\circ\text{C}$ to $\sim 1050^\circ\text{C}$ as x goes from 0 to 2 in $\text{Au}_{2-x}\text{Cu}_{1+x}\text{Al}$, and also upwards to $\sim 920^\circ\text{C}$ as the binary Au-Cu edge is approached. DSC also indicated some reversible solid state transformations, one at about $612 \pm 5^\circ\text{C}$ in B and C, and another in the range of 300 to 370°C , depending on e/a ratio. The lower temperature reactions exhibited a clear hysteresis implying that they were first-order in nature. Examination of the XRD and metallographic data of Samples B and C indicated that the transformation at $\sim 360^\circ\text{C}$ was due to the austenite/martensite transition. Transformed samples contained laths of martensite and, if they had been previously polished prior to a heat



treatment over this temperature range, then examination using Nomarski interference microscopy revealed that their surfaces displayed the characteristic surface morphology generated by a displacive phase transformation. A more detailed view of the transformation enthalpies in Samples B and C is provided in Fig. 3. The A_s (austenite start) and M_s (martensite start) temperatures for these displacively transforming couples were $365 \leftrightarrow 325^\circ\text{C}$ and $357 \leftrightarrow 300^\circ\text{C}$ respectively.

The thermal analysis of Sample A was more complex, as expected. It also displayed another signal on its DSC trace, this time associated with a phase transformation at $\sim 410^\circ\text{C}$. This sample was expected to contain a substantial proportion of α -phase (i) on the basis of the existing isothermal phase diagram, (ii) by analogy to CuZn, and (iii) from its XRD pattern. Therefore one of the remaining the DSC signals could be due to a possible reversible order/disorder transformation to AuCu_3 , which has a eutectoid temperature of about 300 to 310°C in pure Au-Cu, while the other could be due to transformation of the small proportion of β -phase present. Further work is required to resolve this puzzle.

4. Conclusion

These experiments have shown that the shape memory effect will also be found in β -phase alloys at the lean-Au end of the ternary phase field identified by Levey *et al.* The new shape memory alloys are based around AuCu_2Al , and possess many similar properties to those of Spangold and the better-known Cu-base shape memory alloys. However, Sample A was not stable with respect to decomposition to α -phase, and Sample C contained too much brittle γ -phase to be viable. Sample B seemed optimum. The displacive transformation temperatures of all samples are relatively high, at 300 to 350°C , a range that is very difficult to achieve with other Cu-base SMAs due to their rapid decomposition or aging at these temperatures. This suggests that the Sample B composition might find some niche industrial applications. Furthermore, there is scope to customise the transition temperature by adjusting both the Au content and the *e/a* ratio of the compounds.

Acknowledgments

The authors thank Drs Richard Wuhner and Norman Booth, of the University of Technology Sydney, for technical assistance, and Drs Fiona Levey and Ira Wolff (both formerly of Mintek, South Africa) for earlier contributions and discussions.

References

- [1] Wolff I M and Cortie M B 1994 *Gold Bulletin* **27** 44
- [2] Levey F C, Cortie M B, and Cornish L A 2002 *Metall. Mater. Trans. A.* **33A** 987
- [3] Levey F C, et al. 1998 *Proc. Microscopy Society of Southern Africa* **28** 18
- [4] Cortie M B and Levey F C 2000 *Intermetallics* **8** 793
- [5] Levey F C and Cortie M B 2001 *Mater. Sci. Eng. A* **303** 1
- [6] Cortie M B and Levey F C 2002 *Intermetallics* **10** 23
- [7] Battezzati L, Fiore G, and Massazza M 2007 *J. Alloys and Compounds* **434/435** 264
- [8] Cortie M B and Mavrocordatos C E 1991 *Metallurgical Transactions A* **22A** 11
- [9] Sutou Y, Kainuma R, and Ishida K 1999 *Mater Sci Eng A* **273-275** 375
- [10] Levey F C, Cortie M B, and Cornish L A 2003 *J. Alloys and Compounds* **354** 171

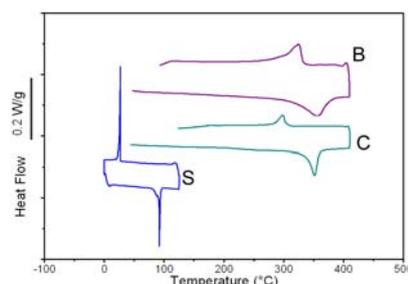


Fig. 3. DSC signals of Samples B and C compared to those of Spangold (S).

