Stress and Aging Effects on the Transformation Characteristics in Au-Cd Alloys

T.R. Finlayson¹, G.L. Kelly¹, T. Ersez² and T.F. Smith³

¹ Department of Physics, Monash University, Clayton, Vic. 3168, Australia

² Neutron Scattering Group, ANSTO, PMB 1, Menai, NSW 2234, Australia

³ Vice-Chancellor's Department, La Trobe University, Bundoora, Vic. 3083, Australia

Keywords: Gold-Cadmium Alloys, Aging Effect, Applied Stress

Abstract

The effect of martensite aging in a Au-49.5%Cd single crystal has been studied using a pushrod dilatometer with various applied stresses. The reverse transformation temperatures, A_s and A_f , are strongly influenced by the aging time and temperature. The M_s and M_f temperatures remain constant with aging time, temperature and applied stresses (0 – 0.04 MPa). A critical aging time of approximately 2-3 hours was found to exist for an alloy of this composition and appears to be dependent on the aging temperature.

Introduction

Au-Cd alloys of approximately equiatomic composition undergo martensitic phase transformations. Alloys with the compositions of approximately Au-49.5at.%Cd alloys undergo a β_2 (B2) $\rightarrow$ ζ'_2 (trigonal) phase transformation while Au-47.5at.%Cd undergoes a β_2 (B2) $\rightarrow$ γ'_2 (orthorhombic) phase transformation. A number of studies have investigated the transformation-associated, shape-memory effect and superelasticity [1,2,3] and the ζ'_2 [4] and γ'_2 crystal structures have been determined. In addition to producing the rubber-like behaviour in thermoelastic alloys such as Au-49.5at.%Cd [3], Au-47.5at.%Cd, CuZnAl [5] and AuCuZn [6], aging in the martensitic state also increases the A_s (reverse transformation start) and A_f (reverse transformation finish) temperatures. This phenomenon is referred to as the aging effect. It is generally assumed that the aging effect and superelasticity have the same physical origin [1].

Two models for the martensitic aging effect have been discussed. The “boundary effect model” depends on the pinning of martensite plate boundaries [7,8], while the “volume effect model” is related to the re-ordering of martensites [9,10]. In the first model, it is assumed that the martensite plate boundaries become less mobile with aging on account of pinning by, for example, vacancies and thus the A_s temperature is expected to increase. In the second model, the free energy change of the martensite is considered to occur by shuffling, reordering or development of short-range ordering during aging.

Kuroiwa *et al.* [11] have reported that the critical aging time is dependent on the aging temperature, with this dependence becoming stronger as the aging temperature approaches A_s . They also report significant differences in the changes of the surface martensite patterns on heating samples aged at different times and temperatures. These changes were attributed to differences in transformation dynamics.

In this study, the transformation temperatures of an Au-49.5at%Cd alloy were measured following various aging times for a constant applied stress. Also, the aging effect was investigated for various applied stresses.

Experimental Procedure

The single crystal was grown using the Bridgman method and was annealed at 530°C for 24 hours for homogenization before furnace cooling. The dimensions of the crystal were $38 \times 10 \times 2 \text{ mm}^3$ and $\langle 100 \rangle$ was the measuring direction, along the longest dimension of the specimen.

The transformation temperatures were determined by measuring strain as a function of temperature using an Adamel Lhomargy DI-24 alumina pushrod dilatometer. The measurement procedure first involved aging the sample for various periods at around 22°C in the martensite phase without an applied preload stress. Following aging, strain measurements were made as the sample was heated through the reverse transformation to 100°C ($A_f \sim 58^\circ\text{C}$). In the parent state a stress was applied and strain measurements were then made as the sample was cooled to room temperature and as it was immediately heated to 100°C and cooled while keeping the same applied stress. The stresses ranged from 0 to 0.04 MPa.

All of the experiments were carried out on the same sample and it was assumed that the previous aging effect was completely annihilated by the subsequent reverse transformation [12].

Results

The strain versus temperature curves obtained for a sample loaded at 100°C with applied stresses ranging between 0 and 0.04 MPa and then cooled (to 22°C) followed by immediate heating (to 100°C) and cooling to (22°C) are presented in Fig. 1.

In Fig. 2, the A_s and A_f obtained for various aging times at 22°C with no preload stress are presented, together with the results of Kuroiwa *et al.* [11] (for aging at 20°C) and Murakami *et al.* [12] for nominally the same composition alloy. Kuroiwa *et al.* [11] investigated the aging effect in a crystal of dimensions $\sim 2 \times 5 \times 5 \text{ mm}^3$, as a function of aging time, by observing the surface martensite bands in an optical microscope equipped with a heating/cooling stage. Murakami *et al.* [12] used a “plate-like” specimen of dimensions $0.5 \times 0.5 \times 40 \text{ mm}^3$ in their studies, employing the DSC technique. The overall trend of the reported transformation temperatures as functions of aging times is very similar for all three types of measurements in that there is a critical aging time, t_c , below which there is no aging effect on either A_s or A_f . There is, however, a significant difference in the values of A_s and A_f reported for the three sets of measurements. Kuroiwa *et al.* [11] report $M_s = 30^\circ\text{C}$ for their sample, which agrees with $M_s = 29^\circ\text{C}$ that we obtained from the dilatometer measurements. Murakami *et al.* [12] do not record M_s and M_f for their sample.

Discussion

In Fig. 1, it can be seen that, as the applied stress is increased, A_s and A_f are reduced, decreasing the size of the hysteresis loop. The application of a small stress in the parent phase initially reduces the thermal energy required to depin variant boundaries, but as the stress increases, it significantly reduces the thermal energy required to complete the reverse transformation (Fig. 1).

Figure 1: Strain versus temperature results obtained from a sequence of heating and cooling measurements (no aging) carried out at 22°C and with applied stresses ranging between 0.0 and 0.042 MPa as indicated.

Figure 2: The A_s and A_f temperatures obtained for various aging times at 22°C with no preload stress. The results of Kuroiwa *et al.* [11] and Murakami *et al.* [12] for the same composition alloy are also included.

The present measurements for the influence of aging time on the zero-applied-stress, temperature-strain cycle, show an increase in temperature hysteresis but no change in the shape of the reverse-transformation curve, resulting in the approximately constant difference, $A_r - A_s$, for different aging times (Fig. 2). In interpreting this observation, we associate A_s with the lowest thermal energy required to excite twin-boundary movement and $A_r - A_s$ with the range of values for this activation energy. It follows then, that aging, while increasing the lower limit for the thermal energy required to excite twin-boundary movement, does not change the spread of activation energies, in spite of any change that may occur in the transformation dynamics.

Conclusion

The results obtained in this investigation of an Au-49.5at%Cd alloy confirm the aging effect reported earlier with a critical aging time of 2-3 hours. It has also been found that the application of a small stress (0 - 0.04 MPa) offsets the aging effect. It is concluded that the morphology of the martensite state and through this, the reverse transformation behaviour is influenced by the application of small stresses.

Acknowledgements

The authors wish to thank Professor T. Ohba of the School of Science and Engineering, Teikyo University, Japan and Professor K. Otsuka of the Department of Materials Science and Engineering, University of Tsukuba, Japan, for the kind loan of the Au-49.5at%Cd single crystal. This work was supported by the Australian Research Council.

References

- [1] K. Otsuka and C.M. Wayman, Review on the Deformation Behaviour of Materials, Vol. 2, ed. P. Feltman (1977), p. 83.
- [2] K. Morii, S. Miyazaki and K. Otsuka, Proc. Int. Conf. on Martensitic Transformations, Monterey (1992), p. 1125.
- [3] Y. Nakajima, S. Aoki, K. Otsuka and T. Ohba, Mater. Lett. 21 (1994), p. 271.
- [4] T. Ohba, Y. Emura and K. Otsuka, Materials Trans. JIM 33 (1992), p. 29.
- [5] G. Barcelo, R. Rapacioli and M. Ahlers, Scripta Metall. 12 (1978), p. 1069.
- [6] S. Miura, S. Maeda and N. Nakanishi, Phil. Mag. 30 (1974), p. 565.
- [7] J. Jansen, J. van Humbeeck, M. Chandrasekaran, N. Mwanba and L. Delaey, J. de Phys. 12 (1982), p. C4-715.
- [8] A. Arab and M. Ahlers, J. de Phys. 12 (1982), p. C4-709.
- [9] G. Scarsbrook, J. Cook and W. M. Stobbs, J. de Phys. 12 (1982), p. C4-703.
- [10] T. Tadaki, H. Okazaki, Y. Nakata and K. Shimizu, Mater. Trans. JIM 31 (1990), p. 941.
- [11] Y. Kuroiwa, T.R. Finlayson and T.F. Smith, J. Mater. Sci. Lett. (1999) in press.
- [12] Y. Murakami, S. Morito, Y. Nakajima, K. Otsuka, T. Suzuki and T. Ohba, Mater. Lett. 21 (1994), p. 275.

Corresponding Author

Associate Professor T.R. Finlayson, E-mail: t.r.finlayson@sci.monash.edu.au, Fax: 61 3 9905 3637