STRUCTURE OF SPATIO-TEMPORAL FLUCTUATIONS IN SHAPE MEMORY ALLOY $Au_{50.5}Cd_{49.5}$ REVEALED BY X-RAY DIFFRACTION

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Structural variation of shape memory alloy $Au_{50.5}Cd_{49.5}$ with different temporal scale is investigated by X-ray diffraction. We found that once the crystal undergoes the Martensitic transformation, several spontaneous variations in crystal structure simultaneously occur. A $1/f$ type spectrum is observed in structural fluctuations of (112) surface in the frequency range of 1/100 Hz to 1 Hz. Structural fluctuations with the period of ca. 200 seconds are recognized more than 100 hours after the phase transformation. An ultraslow structural change over 53,000 hours (six years) is found, indicating a novel structural relaxation beyond the well-known slow relaxation referred to as rubber-like-behavior.

Introduction

Martensitic transformation is a diffusionless transformation which is considered to serve a substantial role for both of the shape memory effect and superelasticity in shape memory alloys (SMA). $Au_{50.5}Cd_{49.5}$ is one of the most intensively studied SMAs, which also exhibits the superelasticity. The parent phase of CsCl-type structure is stable above 309K. Under cooling, it undergoes a transformation to a trigonal phase (ζ'_2 phase) at 303K. The ζ'_2 phase consists of a multi-domain structure called variant [1]. In spite of a lot of experimental and theoretical studies, information on spatial-temporal development in domain structure in bulk as well as in the surface region seems to be highly limited. However, not a few studies are dedicated to clarify the resemblance to the development of domain structure of SMA and self-organized criticality (SOC) [2-5]. In the present study, we investigate temporal variations of $Au_{50.5}Cd_{49.5}$ single crystal at surface and bulk by using X-ray diffraction.

Experimental

A single crystal of $Au_{50.5}Cd_{49.5}$ with 5 mm X 5 mm X 3 mm in dimension was prepared in 2001. The (112) surface with 5 mm X 5 mm in area was electro-chemically polished to measure the (112) Bragg reflection and X-ray reflectivity (XR). A high resolution diffractometer with a rotating-anode X-ray generator was used for XR measurements (SLX2000+UltraX,

Rigaku Co.), and a diffractometer TTR-450 (Rigaku Co.) was exploited for the measurements of Bragg reflection. We also used a multi-circle diffractometer at BL13XU of SPring-8 to detect the temporal variations. Sample temperature was controlled between the room temperature and 350K within a precision of 0.4K. The (112) reflection was collected by transverse scans, usually referred to as ω scans. XR is measured with a very shallow angle of incidence close to the critical angle of total reflection. Temporal fluctuation in (112) Bragg reflection enables us to get information on structural fluctuations in bulk, whereas temporal fluctuation in XR can be an excellent tool to investigate those in the surface region.

Results and Discussion

Figure 1 shows profiles of XR obtained by transverse scans. In the parent phase, X-ray is reflected by (112) planes. In the ζ'_2 phase, incident X-ray is reflected by several equivalent crystallographic planes (e.g. (142) planes) which correspond to the (112) plane in the parent phase. Therefore, the peak of XR would be split in the ζ'_2 phase reflecting the multi-domain structure in the low symmetry phase. However, the peak is more diffusive in the parent phase as shown in the middle curve in Fig. 1, since the surface initially had been polished at room temperature (ζ'_2 phase). Several peaks in XR profile indicate that the surface consists of several domains of which crystallographic directions are slightly different with each other, usually referred to as

"variants". In Fig. 1, it is remarkable that the upper profile collected at 303K is different with the lower profile measured at 303K, indicating that the variant structure formed in ζ'_2 phase differs after each transformation.
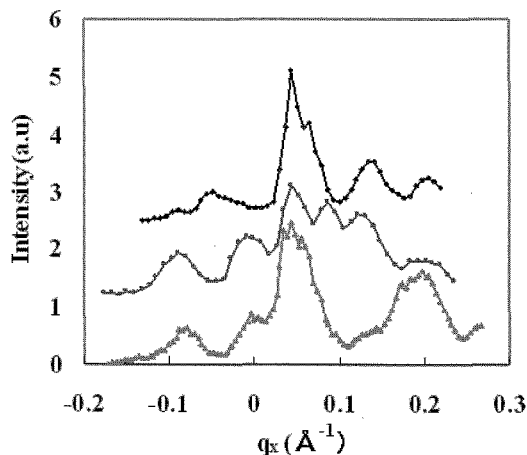

Fig. 1 X-ray reflectivity profiles around its critical angle. Upper profile is obtained at 303K (in ζ'_2 phase), middle is at 313K (in parent phase), and lower one is at 303K (in ζ'_2 phase) just after a cooling from 313K. For clarity, each curve is shifted vertically.

Figure 2 indicates (112) Bragg reflection obtained in the parent phase and corresponding Bragg reflections obtained in the ζ'_2 phase, which should be some of the 48 reflections indexed as (-512), (142), (114) reflections, and so on. An irreproducible character seen in the surface region (Fig. 1) is also recognized in the bulk region.
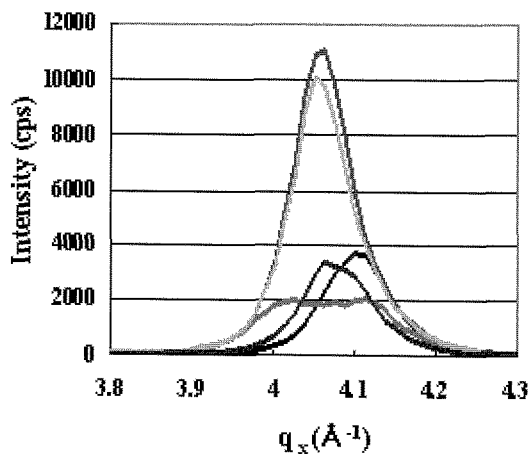

Fig. 2 (112) Bragg reflections in parent phase and corresponding Bragg reflections in the ζ'_2 phase.

Diffraction profile in the parent phase is almost independent on the thermal cycles as indicated by two profiles with stronger intensity. However, situation is different in the ζ'_2 phase in which each diffraction profile is different after cooling from the parent phase (the three curves with weaker intensity).

In Fig. 2, Bragg reflections in the ζ'_2 phase are slightly split i.e. Bragg peak consists of more than one peak. Since the ζ'_2 phase does not have a center of symmetry, there is a possibility that this sample has inversion domain boundaries. These domain boundaries would introduce an unpredictable stacking fault or some other faults in the crystal and those faults may introduce slightly split peaks of Bragg peaks of which shape is slightly different in each transformation to the ζ'_2 phase [6]. Therefore, formation of variant structure of $Au_{50.5}Cd_{49.5}$ can be regarded as a stochastic process inherent in many systems revealing the SOC.
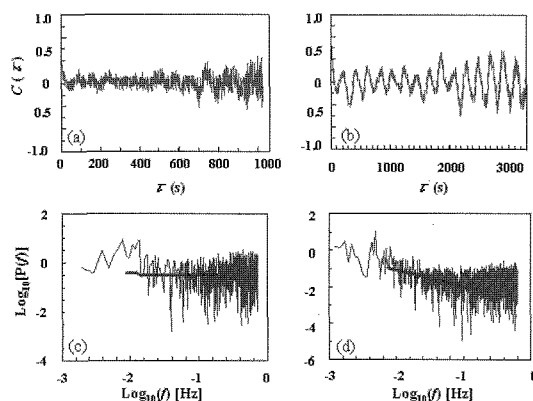

Fig.3 Auto-correlation function ((a), (b)), and power spectrum ((c), (d)) obtained by fluctuations in XR intensity. (a) and (c) are in the parent phase, and (b) and (d) are the corresponding ones in the ζ'_2 phase, respectively. Solid line in (c) and that in (d) are fitted lines by assuming $P(f) \propto 1/f^{\alpha}$. The value of α in (d) is 0.9, indicating the SOC behavior in the surface region of the ζ'_2 phase.

Figures 3(a) and 3(b) show auto-correlation functions of temporal fluctuation obtained by XR under total reflection condition in the parent phase and that in the ζ'_2 phase, respectively. Intensity data were collected at the peak position of X-ray reflectivity with the resolution of 0.12 nm^{-1} along the circumferential direction. Intensity data in the ζ'_2 phase were collected just after the rapid cooling from 350K to room temperature. No distinct structure is seen in Fig. 3(a), whereas a clear oscillatory fluctuation is indicated in Fig. 3(b). Power spectrum $P(f)$ in the parent phase and that in the ζ'_2 phase were numerically calculated from the auto-correlation functions (Figs. 3(c) and 3(d)).

Although both spectra are rather noisy, $P(f)$ in the parent phase (Fig. 3(c)) is more structureless (white noise like pattern) than that in the ζ'_2 phase in which a long monotonous tail described as $P(f) \propto 1/f^{\alpha}$ is seen in the frequency range between 1/100 Hz and 1 Hz: The solid line in Fig. 3(d) is a fitted line yielding the exponent $\alpha = 0.9$. The result shown in Fig. 3(d) reveals that the SOC behavior of $Au_{50.5}Cd_{49.5}$ is more dominant in the surface region, just after the Martensitic transformation.

We also observed the temporal fluctuations of the ζ'_2 phase 120 hours (five days) after an annealing (Fig. 4). Auto-correlation function obtained by (112) Bragg reflection shows some residual periodic fluctuation with the period of 200 seconds in bulk, whereas that in surface region ceases to fluctuate in 120 hours. It would indicate that a characteristic time for stochastic evolution of multi-domain structure in bulk differs from that in the surface region.
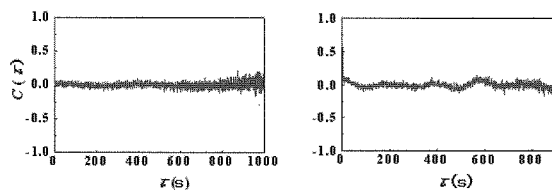

Fig. 4 Auto-correlation function of the ζ'_2 phase 120 hours after the Martensitic transformation. Left is calculated by fluctuation in XR and right is the one obtained by that in (112) Bragg reflection, respectively.
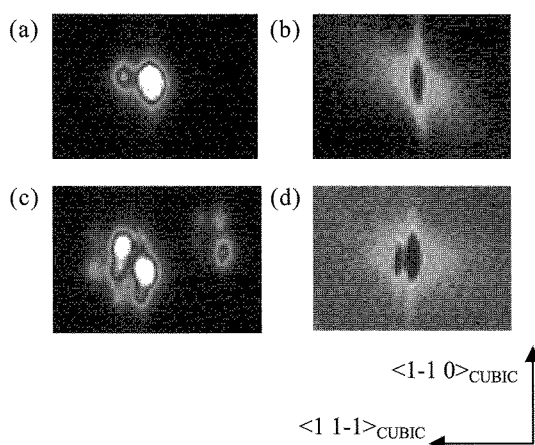

Fig. 5 Oscillation photographs of (112) Bragg reflection recorded by an imaging plate detector. (a) parent phase (309K), (b) parent phase (313K) measured 53,000 hours later, (c) ζ'_2 phase (room temperature), and (d) ζ'_2 phase (room temperature) measured 53,000 hours later.

Finally, we compare oscillation photographs of (112) Bragg reflection recorded by an imaging plate detector with those measured about 53,000 hours (about 6 years) later (Fig. 5). In Fig. 5(a) two (112) peaks are seen even in the parent phase, although they look merged during the 53,000 hours (Fig. 5(b)). As for the diffraction pattern in the ζ'_2 phase, the variation is much more distinct: many (112) Bragg reflections diffracted from many variants are seen in the first observation (Fig. 5(c)), whereas only two major reflections are recognized 53,000 hours later (Fig. 5(d)). The origin of such a long-term variation remains unclear, but it certainly manifests that there is an ultraslow relaxation in $Au_{50.5}Cd_{49.5}$ of which relaxation time is much longer than that of the rubber-like behaviour of this substance [7].

Conclusion

In conclusion, we confirm the irreproducibility in distribution of variants in bulk as well as in the surface. Temporal fluctuation in the surface region is characterized by a power law, although such a SOC character is not indicated in the bulk region. The origin of SOC might be in boundaries, e.g. surface, domain walls, and grain boundaries. The $1/f$ fluctuation ceases within 120 hours, but some structural relaxation accompanying periodicity still remains. A very long term fluctuation over 50,000 hours has been observed, presumably showing a novel relaxation of which relaxation time is much longer than the time for developing the rubber-like-behavior.

References
[1] T. Ohba and K. Otsuka, Jpn. J. Appl. Phys., **37** (1998) L64-66.
[2] P. Diodati, F. Mrchesoni and S. Piazza, Phys. Rev. Lett., **67** (1991) 2239-2242.
[3] M. Rao, S. Sengupta and H. K. Sahu, Phys. Rev. Lett., **75** (1995) 2164-2167.
[4] E. Vives, J. Ortin, L. Manosa, I. Rafols, R. Perez-Magrane and A. Planes, Phys. Rev. Lett., **72** (1994) 1694-1697.
[5] G. Ananthakrishna, S. J. Noronha, C. Fressengeas and L. P. Kubin, Phys. Rev. E**60** (1999) 5455-5462.
[6] T. Ohba and K. Otsuka, Materials Transactions, JIM, **33** (1992) 29-37.
[7] Y. Nakajima and T. Ohba, Mat. Lett., **2** (1994) 271-274.