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Aging effect in parent phase and martensitic transformation in Au–47.5at.%Cd alloys

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Abstract

Au–Cd alloy is one of the typical alloys which shows martensitic transformation. There are two martensites close to the 1:1 composition: one is γ_2' martensite and the other is ζ_2' martensite. When the phonon dispersion curve was measured in the composition for Au–47.5at.%Cd which produces γ_2' martensite, phonon softening was observed at the Brillouin zone boundary and at $\zeta = 0.35$ of the $[\zeta\zeta 0]TA_2$ branch and a peculiar behavior was observed. One is that the M_s temperature determined in this experiment was lower than the ordinary value. The other is the time dependence of the 1/3 elastic reflection, which was observed prior to the martensitic transformation. Electrical resistance measurements were performed in this alloy in order to clarify this peculiar behavior. A decrease of the M_s temperature was observed after aging at 393 K, in the parent phase. The lower M_s observed in neutron experiments can be explained by an aging effect in the parent phase. There are two possibilities of explaining the time-dependence of the 1/3 reflection; one is the transformation with diffusion (bainite transformation above M_s) and the other is embryo growing. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Martensitic transformation; Au–Cd; Aging effect; Neutron scattering; Electrical resistivity measurements

1. Introduction

The martensitic transformation is considered to be a diffusionless and displacive transformation and a typical first-order transformation. A first-order transformation is frequently observed in several materials and sometimes plays an important role. However, the mechanism of the transformation from a microscopic point of view was not solved completely in contrast to that for the second-order transformation. Au–Cd is one of such typical alloys which show a martensitic transformation. The parent phase has the B2 (CsCl) type structure in the proximity of the equi-atomic composition and transforms to the distinct martensitic phases called γ_2' and ζ_2'. Typically, they appear in the composition of Au–47.5at.%Cd and Au–50at.%Cd, respectively. Slight changes in the composition produce these distinct martensitic phases. Therefore, AuCd alloy is one of the most suitable and interesting systems to study the mechanism of the martensitic transformation.

Martensitic transformation is understood to be a displacive type transformation. The most direct picture of the displacive transformation is a phonon softening occurring in the parent phase. Neutron inelastic scattering techniques are the most useful methods for observing phonon softening behavior. Several attempts for observing phonon softening behavior in martensitic alloys were made [1–3]. In a few cases the observation of softening corresponding to the martensitic structure was successful, for example in NiAl and TiNi alloys [4–7].

The crystal structure of ζ_2'-AuCd martensite was solved by the ordinary crystal structure analysis technique and the microscopic picture of the transformation was presented [8]. A superposition of three transverse waves, whose polarization is $<110>$ and whose wave vector is $\langle\bar{1}10\rangle$, produces the martensite structure. Although a phonon softening was expected from the displacement waves, this was difficult to study in the neutron scattering since Au and Cd have strong absorp-

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tion coefficients for neutron. The difficulty was overcome with the use of the isotope ^{114}Cd. The absorption coefficient for ^{114}Cd is significantly small. Neutron inelastic scattering studies of Au–49.5at.%Cd were performed and revealed a softening in the [ζζ0]TA_2 branch at $\zeta = 0.35$ prior to the transformation to the crystal structure of martensite [9]. Therefore, ζ_2'-AuCd is a case of the martensitic transformation aided by phonon softening.

The crystal structure of the γ_2' phase is simpler than that of the ζ_2' phase. Atomic movements during the transformation are considered to be alternative motions of {110} planes. The motion of atoms corresponds to a softening behavior at the Brillouin zone boundary of the [ζζ0]TA_2 branch. Measurements of the neutron inelastic scattering were performed for single a crystal using the ^{114}Cd isotope. Softening behavior was observed successfully at the Brillouin zone boundary in addition to a softening at $\zeta = 0.35$ in the [ζζ0]TA_2 mode [10]. Elastic scattering measurements were performed also and a peculiar behavior was observed during the measurements. In the present paper, this peculiar behavior in Au–47.5at.%Cd is examined and reported.

2. Neutron elastic scattering experiments and their results

The results of the elastic scattering measurements performed at 316 K along $[1+\delta, 1-\delta, 0]^*$ are shown in Fig. 1. It is surprising that the intensity of the 1/3 reflection becomes stronger with time, i.e. that its time-

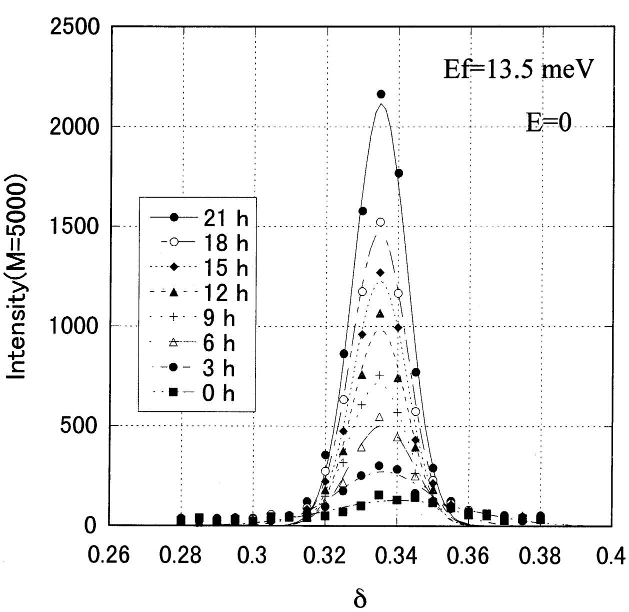

Fig. 1. Time-dependence of the 1/3 reflection in Au–47.5at.%Cd. The measurements were performed along $[1+\delta, 1-\delta, 0]^*$. The reflection becomes stronger with time.

dependence was observed. Another peculiarity was observed when we compared the M_s temperature with the reported value [8]. We noticed that M_s was lower than the reported value, that is, the $M_s = 312$ K from the neutron diffraction experiment was approximately 30 K lower than the ordinary value [10]. Suzuki et al. reported that quenching the sample of Au–47.5at.%Cd produces the mixture of γ_2' and ζ_2' martensite [11]. Consideration of the above may make us suspect that the heat-treatment of the sample was not proper. However, the heat-treatment was carefully done and differential scanning calorimetry (DSC) measurements were performed using the same single crystal. The M_s observed by DSC measurements was 348 K and it was the proper value. This means that it is difficult to ascribe the difference in M_s to an improper heat-treatment. The inhomogenity of the sample may be another cause for the discrepancy in M_s. However, DSC measurements were performed using a piece of the same single crystal of the neutron experiment. The original length of the single crystal was approximately 80 mm and was cut into a 50 mm length for the neutron experiment. The rest of the single crystal, that is, its middle part, was used for the DSC measurement. Considering this, it was also difficult to ascribe the effect to the inhomogeneity of the sample. The isotope effect may be another idea for solving the discrepancy of M_s. However, from our experience of growing a single crystal with an isotope we knew that the M_s in the previous case was almost the same as in the ordinary metal alloy [9]. Therefore, the isotope effect is rejected also.

We then followed the idea that the discrepancy may depend on the experimental method, that is, when we measured the dispersion relation, we had to keep the sample in the parent phase for several hours. There is a possibility that this experimental condition causes the decrease of the M_s temperature. In order to clarify this point, we performed electrical resistance measurements.

3. Experimental

Electrical resistance measurements were performed by a conventional DC four terminal method to examine the effect of aging in the parent phase. A 100 mA current was applied to a rectangular rod shaped specimen with $\sim 1 \times 1 \times 10$ mm^3 size. The temperature of the specimen was measured by a CA thermocouple. In order to keep thermal equilibrium, the heating and cooling was controlled at the rate of 2 K/min. The aging temperature in the parent phase was 393 K. The specimen was kept for several hours at 393 K and then was cooled down to room temperature. The measurements were repeated several times.

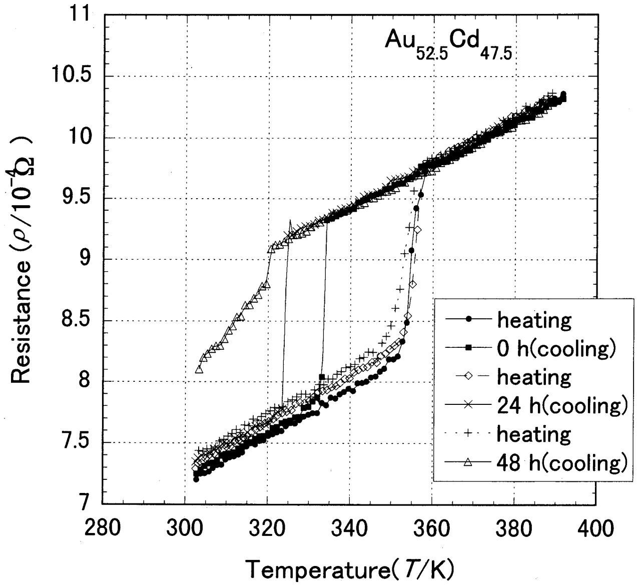

Fig. 2. Electrical resistance at various aging times.

4. Results and discussion

Fig. 2 shows the results of the resistance measurements. When we heated the sample up to 393 K and cooled it down without aging in the parent phase, we found that M_s is 334.2 K. Then we heated the sample up to 393 K, kept the temperature for 24 h and cooled down. Cross ($\times$) marks represent the resistance after 24 h aging and show that M_s is lower than for the fresh cycle, that is, M_s is 324.6 K. Further aging decreases M_s. After 48 h aging, M_s is 320.6 K (see Fig. 2). We found a decrease of 14 K in the M_s temperature. It is clear that aging in the parent phase decreases M_s in the Au–47.5at.%Cd alloy. Furthermore, it is worth noting that the resistance curve after 48 h aging showed a different behavior. M_s at various aging times is plotted in Fig. 3. A curve fitting using $A\ \exp(-t/\tau)$ was tried and it was shown that the curve describes the behavior of M_s well at $\tau = 14$ h. Therefore, the lower M_s in neutron experiments came from the aging effect of the parent phase, that is, during measurements of the inelastic neutron scattering at the parent phase, the M_s temperature decrease.

It is not easy to estimate the electrical resistance quantitatively. A qualitative interpretation is tried in this section. The resistivity is proportional to the resistance and the resistivity ρ can be expressed by $(m^*/ne^2\tau)$, where m^* is the effective mass, n is the concentration of electrons and τ is the relaxation time of electron collisions. The effective mass m^* is related to the electronic structure. Although the electrical resistivity (electron collisions) is a non-equilibrium process, a linear approximation is applied if the scattering from the impurity or the phonons is sufficiently weak. The resistivity is proportional to the temperature above the Debye temperature with the assumption [12]. The resistivity in the parent and martensitic phase is proportional to the temperature except at the transformation temperature. Since the linear coefficients of the resistance for both phases are close to each other, the relaxation time of the electron collisions will not be affected so much by the transformation. The structure change at the transformation leads to an electronic structure change. When the γ_2' phase is formed, the resistance decreases suddenly at M_s. On the other hand, when the ζ_2' phase is formed at M_s, the resistance increases suddenly as shown in the Refs. [13]. These sudden changes of ρ may be caused by the changes in electronic structure after the transformation, that is, mainly through an m^* change. Even after the aging of the Au–47.5at.%Cd, the sudden decrease of the resistance occurred at the transformation temperature, that is, the transformation temperature is defined clearly. The decrease of resistance after aging means that the γ_2' phase was produced.

The linear coefficient of the electrical resistance after 48 h aging is changed as mentioned above and shown in Fig. 2, which means that the relaxation time of collision was changed. This suggests that there is not only the γ_2' phase present but also another phase or another product after 48 h.

The decrease of M_s must be related to the time-dependence of the 1/3 reflection. If the 1/3 reflection is directly related to ζ_2' martensite, aging in the parent phase (now at 393 K) may help in the formation of ζ_2' martensite. A possible interpretation of these phenomena is the bainite transformation above M_s [14]. The detail was written in Ref. [14].

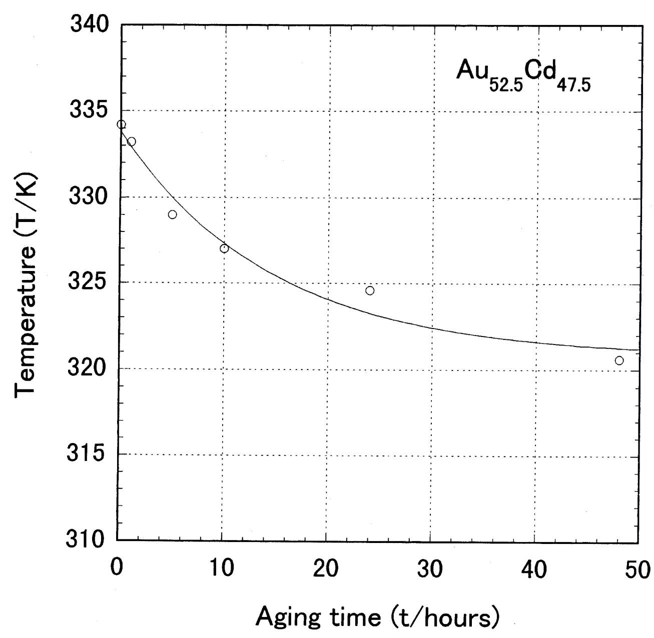

Fig. 3. M_s temperature at various aging times.

Another possibility may be that the 1/3 reflection is related to the precursor phenomenon of the transformation, that is, growing an embryo. The appearance of the 1/3 reflection indicates that something is created prior to the transformation. If an intermediate state (embryo) is created which produces internal strain fields in the parent phase and suppresses the transformation, then the transformation temperature will be lowered. Concentration fluctuations are not necessary in this case and the sharp change at the transformation, such a sudden decrease of the electrical resistance will be preserved. The idea maybe related to localized soft mode proposed by Clapp [15].

The Effect of low temperature annealing was discussed by Birnbaum [16]. He reported that the low temperature annealing produces two phases, ζ_2' and γ_2'. He suggested there are two phases at high temperature. However, two phases at high temperature cannot explain the lower M_s nor the time-dependence of the 1/3 reflection. There is some parameter which governs the amount of the M_s decrease. Although in the case of the neutron sample, a decrease of almost 30 K was observed, the resistance sample showed approximately a 15 K decrease. Changes in the degree of atomic order or the effect of vacancies may cause the difference. Mañosa et al. [17] studied the quenching effect on the shape memory alloys and reported that the shift of the transformation temperature was caused by changes of atomic order in Cu–Zn–Al and by the behavior of the vacancies in Cu–Al–Be. Furthermore, there is another problem to be solved, that is, the decrease of M_s follows an $\exp(-t/\tau)$ term. On the other hand, the intensity of the 1/3 reflection increases linearly. It is also necessary for us to interpret the relation between them. Further studies will be needed in order to clear these points.

5. Conclusions

Lower M_s and a time-dependence of the 1/3 reflection in the parent phase of Au–47.5at.%Cd was observed in neutron experiments. Electrical resistance measurements were performed after aging in the parent phase to clarify these phenomena. A decrease of M_s was observed after aging at 393 K, in the parent phase. The lower M_s in the neutron experiments was understood to be an aging effect of the parent phase. A cause of the time-dependence of the 1/3 reflection was discussed. The decrease of M_s must be related to the time-dependence of the 1/3 reflection.

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