Temperature Dependence of Pseudoelasticity and Shape Memory Effect in Fe$_3$Ga Single Crystals with D0$_3$ Structure

Hiroyuki Y. YASUDA,1,2) Kouki FUKUSHIMA,1) Mitsuhiro AOKI1) and Yukichi UMAKOSHI1)

1) Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047 Japan. 2) Division of Materials and Manufacturing Science, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871 Japan.

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Pseudoelastic behavior and shape memory effect in D0$_3$-ordered Fe–24.4at%Ga single crystals deformed at different temperatures were investigated focusing on the microstructure and dislocation configuration. High strain recovery ratios more than 80% could be obtained at temperatures between −100 and 100°C. In particular, perfect pseudoelasticity appeared in the crystals deformed at room temperature. During unloading, antiphase boundaries (ABP) left behind 1/4(111) superpartial dislocations pulled back the superpartials resulting in the pseudoelasticity. In addition, Fe$_3$Ga single crystals compressed at −150°C demonstrated shape memory effect during heating to room temperature. On the other hand, the recovery ratio decreased with increasing deformation temperature up to 300°C and remained constant at about 10%. The L1$_2$ phase precipitating during deformation, dislocation configuration associated with 1/4(111) superpartials connected by two kinds of APB and relaxation of the APB were found to strongly influence the pseudoelasticity and shape memory effect in Fe$_3$Ga single crystals.

KEY WORDS: pseudoelasticity; shape memory effect; dislocations; intermetallics; Fe$_3$Ga.

1. Introduction

Pseudoelasticity is a phenomenon by which strain is recovered during unloading and is applied to potable phone antenna and eyeglass frame.1) As typified by Ti–Ni alloys, pseudoelastic behavior is closely related to a thermoelastic martensitic transformation. However, the martensitic transformations of ferrous alloys are generally non-thermoelastic, and pseudoelasticity rarely takes place in the alloys. But recently, it was found that Fe$_3$Al2) and Fe$_3$Ga3) single crystals with the D0$_3$ structure (Fig. 1(a)) exhibited giant pseudoelasticity regardless of martensitic transformation. Their recoverable strains were as much as 5%, comparable with Ti–Ni alloys. Understanding of the mechanism of the pseudoelasticity is of great importance for their practical application in the future.

In the D0$_3$ structure, a ⟨111⟩ superlattice dislocation is dissociated into four 1/4⟨111⟩ superpartials bound by antiphase boundaries (ABP) after unloading.4)5) There are three types of dislocation configurations as shown in Fig. 1. In mode I (Fig. 1(b)), a leading 1/4⟨111⟩ superpartial move individually dragging the nearest-neighbor APB (NNAPB). In mode II (Fig. 1(c)), a paired superpartial moves dragging the next-nearest-neighbor APB (NNNAPB). In mode III (Fig. 1(d)), four superpartials bound by the NNNAPB and NNAPB move as a group. In general, mode III was selected in the D0$_3$ crystals resulting in no strain recovery.4)5) In contrast, mode I was chosen in Fe–23.0at%Al single crystals.4–12) In this case, the leading superpartials moved back due to the tension of the NNAPB, which led to giant pseudoelasticity accompanied by recoverable strain as much as 5%. On the other hand, mode II was also selected in Fe$_3$Ga; the NNNAPB and NNAPB pulled back the superpartials during unloading, resulting in giant pseudoelasticity.13) So, we called the phenomenon, “APB pseudoelasticity”. It is well known that pseudoelasticity based on martensitic transformation appears just above martensite-start temperature.1) In contrast, since APB pseudoelasticity is based on the reversible motion of dislocations, the pseudoelasticity is considered to appear in the wide temperature range. In fact, Fe–23.0at%Al single crystals showed large strain recovery in the temperature range from −50 to 200°C.12) In addition, strain recovery at and below −150°C was quite small. However, the residual strain was recovered during heating to room temperature.4,16) This means that shape memory effect appeared in Fe–23.0at%Al. At lower temperatures, frictional stress of 1/4⟨111⟩ superpartials was too large to pull back the superpartials by the APB. However,

Fig. 1. Unit cell of the D0$_3$ structure (a) and dislocation configuration in the D0$_3$ crystals. (b) Mode I, (c) mode II and (d) mode III.
3. Experimental Procedure

Master ingots of Fe₃Ga alloys were prepared by melting high purity Fe and Ga in a plasma arc furnace under an argon atmosphere, then the single crystals were grown from the ingots by the floating zone method at a rate of 5 mm/h. After homogenization at 1100°C for 48 h, the crystals were annealed at 600°C for 10 h for D₀₃ ordering. The chemical composition was determined to be Fe–24.4at%Ga by electron-probe microanalyzer. Compression specimens with [1\bar{4}9] loading axis where Schmid factor for the primary (1\bar{0}1)[1\bar{1}1] slip is 0.5, were cut from the single crystals by spark machining. After mechanical and electrolytic polishing, a gauge mark was introduced by scratching the samples to measure a residual strain. Compression tests were performed at different temperatures ranging from −150 to 600°C using a compression test machine equipped with an isothermal chamber. The test environment below and above room temperature was in air and vacuum, respectively. All the tests were conducted at a constant cross-head speed corresponding to an initial strain rate of 1.67×10⁻⁴ s⁻¹. After loading, the specimens were unloaded at the same cross-head speed. The shape recovery of the specimens during unloading was checked from the stress–strain curves and gauge marks. The quantity of strain recovery in the crystals was evaluated using recovery ratio (r) defined as follows

\[ r = \frac{\varepsilon_p - \varepsilon_r}{\varepsilon_p} \times 100 \] ...........................(3)

where \( \varepsilon_p \) and \( \varepsilon_r \) are the maximum plastic strain and the residual strain, respectively. A slip trace analysis was done using an optical microscope equipped with Nomarski interference contrast. Deformation substructure was observed by a transmission electron microscope (TEM) operated at 300 kV.

4. Results

4.1. Pseudoelastic Behavior and Shape Memory Effect

Figure 4 shows stress–strain curves of Fe–24.4at%Ga single crystals compressed to \( \varepsilon_p = 5.0\% \) at −150–600°C.
350 MPa and an applied plastic strain of 5.0% is completely recovered after unloading. On the other hand, strain recovery at \(150, 200, 400\) and \(600°C\) becomes small. Note that the yield stress at \(600°C\) is considerably small compared with that at the other temperatures. It should also be mentioned that a serration is observed in the stress–strain curves at temperatures between 400 and \(600°C\). Such serration was reported to be closely related to dynamic strain aging of APB.\(^{18}\) In contrast, a serrated flow associated with deformation twins was observed in the stress–strain curve at \(150°C\). In Fig. 5, recovery ratio is plotted against deformation temperature. High recovery ratio more than 80% can be obtained in the wide temperature range from \(-100\) to \(100°C\). On the other hand, the recovery ratio decreases with increasing temperature above \(300°C\) and becomes about 10% at and above \(400°C\). It is also noted that small strain recovery takes place at \(-150°C\) just after unloading, but recovery ratio increases during heating and reaches about 80% at room temperature. This means that not only Fe\(_3\)Al but also Fe\(_3\)Ga single crystals demonstrate shape memory effect. Figure 6 shows temperature dependence of yield stress (0.2% proof stress) of Fe–24.4at%Ga single crystals compressed at different temperatures. The yield stress decreases with increasing temperature, accompanied by a rapid drop at around \(200\) and \(500°C\), which is closely related to dislocation configuration shown in Fig. 1. The details are discussed in Sec. 5.2.

### 4.2. Microstructure before and after Deformation

From an observation by an optical microscope, primary slip system was determined to be \((\bar{1} 01) [111]\) at any test temperature. Figure 7 shows weak-beam dark-field images of the dislocations in Fe–24.4at%Ga single crystals compressed to \(\varepsilon_p=5.0%\) at different temperatures. Dislocation configuration in Fe\(_3\)Ga single crystals depends strongly on deformation temperature. At room temperature, mode I or II configuration is observed (Fig. 7(a)); \(1/4[111]\) superpartials are pulled back by the NNAPB or NNNAPB resulting in perfect pseudoelasticity at the temperature. In contrast, almost all the superpartials show mode II configuration at \(200°C\) as shown in Fig. 7(b). Furthermore, dislocation configuration changes from mode II to III at around \(500°C\) (Fig. 7(c)). If mode I and II are selected, the yield stress becomes high due to the tension of the NNAPB and NNNAPB. In contrast, no APB is left behind the superpartials in mode III resulting in low yield stress at and above \(500°C\) as shown in Fig. 6. Therefore, the change in dislocation configuration is closely related to temperature dependence of the yield stress. On the other hand, in the low magnification image shown in Fig. 8, the dislocations at \(200°C\) are observed to be strongly pinned by precipitates indicated by white arrows. The precipitates were determined to be the...
L1\textsubscript{2} phase by TEM diffraction analysis. The D0\textsubscript{3} phase and L1\textsubscript{2} phase were confirmed to satisfy the Kurdjumov–Sachs orientation relationship though the results are not shown here. The dislocations near the L1\textsubscript{2} precipitates become immobile which resulted in a decrease in recovery ratio. An optical micrograph of Fe–24.4at\%Ga single crystals compressed at $-150^\circ$C is shown in Fig. 9. In addition to the slip traces parallel to (101) primary slip, (121) traces associated with deformation twins can be observed. The deformation twins seem to be irreversible during loading and unloading, which caused a decrease in recovery ratio at the temperature.

5. Discussion

Pseudoelasticity and shape memory effect in D0\textsubscript{3}-ordered Fe\textsubscript{3}Ga single crystals showed strong temperature dependence. The origin of the temperature dependence was discussed focusing on the L1\textsubscript{2} phase formation, the dislocation configuration and the dynamic strain aging of APB.

5.1. Effect of the L1\textsubscript{2} Phase Formation on the Pseudoelasticity

As shown in the Fe–Ga equilibrium phase diagram in Fig. 2(a), the formation of the L1\textsubscript{2} phase is likely to occur depending on deformation temperature. In order to clarify the effect of the L1\textsubscript{2} phase on the pseudoelasticity, the following experiment was made. First, Fe\textsubscript{3}Ga samples were isothermally annealed at temperatures from 100 to 600°C for 3 h and then cooled down to room temperature. Therefore, these annealed samples had similar thermal history compared with the samples deformed at high temperatures. Then, the annealed crystals were deformed at room temperature. Recovery ratios of the annealed samples are plotted against annealing temperature in Fig. 10. The recovery ratio of the annealed samples starts to decrease at around 200°C and then shows a minimum at 300°C. Further increase in annealing temperature results in an increase in recovery ratio and reach 100% at 600°C. The L1\textsubscript{2} phase precipitated in the temperature range from 200 to 500°C. The formation of the L1\textsubscript{2} phase started after the degree of order of the D0\textsubscript{3} phase became high. Since the crystals were fully ordered at 600°C, the L1\textsubscript{2} phase precipitated even at 200°C after the D0\textsubscript{3} ordering treatment. The phase is considered to strongly influence the pseudoelastic behavior. For instance, the fine and coarse L1\textsubscript{2} precipitates at 200 and 500°C suppress the motion of the superpartials as shown in Figs. 11(a) and 11(b), respectively, which resulted in a decrease in recovery ratio. For comparison, recovery ratios of the crystals deformed at high temperatures are also plotted in Fig. 10. The recovery ratios of the crystals deformed at high temperatures are much smaller than those deformed at room temperature after annealing at high temperature, even at 100°C where the L1\textsubscript{2} phase hardly precipitates. Therefore, another factor should be taken into consideration to understand the temperature dependence of the pseudoelasticity.

5.2. Effect of Dislocation Configuration on the Pseudoelasticity

In D0\textsubscript{3}-ordered Fe\textsubscript{3}Ga single crystals, dislocation configuration changed depending on deformation temperature. At and below 100°C, mode I and II were selected; uncoupled or paired 1/4(111) superpartials were observed (Fig. 7(a)). In mode I and II, the NNNAPB and NNNAPB pulled back the superpartials during unloading resulting in giant pseudoelasticity. In contrast, mode II configuration was dominant in the temperature range between 200 and 400°C as shown in Fig. 7(b). The back stress of the NNNAPB was a little bit smaller than that of the NNNAPB. This was one of the reason why the recovery ratio decreased at 200–400°C. On the other hand, at and above 500°C (Fig. 7(c)), since four 1/4(111) superpartials bound by the NNNAPB and NNNAPB (mode III) moved as a group, no APB was left behind the group superpartials as shown in Fig. 7(c). Thus, since there is little driving force for APB pseudoelasticity at and above 500°C, little strain recovery occurred at those temperatures. Marcinkowski et al.\textsuperscript{10} suggested that since the activation energy for mode III configuration was higher.
5.3. Dynamic Strain Aging of APB

A serrated flow associated with dynamic strain aging of APB was observed at and above 400°C. Brinck et al.\(^{18}\) suggested that the relaxation (reordering) of APB between the coupled superpartials was associated with the serrated flow. To show serrated behavior, high diffusivity rate of constituent atoms is necessary and the relaxation time required for the diffusion should be in the order of \(10^{-1} \text{s}^{20}\) Such requirement can be satisfied at high temperatures (e.g. 400°C). But, if APB pseudoelasticity appears, the NNNAPB and NNNAPB left behind 1/4\((111)\) superpartials in mode I and II can be also relaxed (reordered) during loading. Since the loading time was more than 5 min, the APB relaxation seems to easily occur during deformation even at around 100°C. If mode II is selected at 200°C, APB tension, \(\tau_b\), is given by,

\[
\tau_b = \frac{\gamma_{\text{NNNAPB}}}{2b} \tag{4}
\]

where \(\gamma_{\text{NNNAPB}}\) is the NNNAPB energy and \(b\) is the magnitude of Burgers vector of 1/4(111). According to Eq. (4), the APB relaxation decreased the \(\gamma_{\text{NNNAPB}}\) and consequently \(\tau_b\), which resulted in a decrease in recovery ratio. In order to prove the effect of APB relaxation on the pseudoelasticity, the following relaxation test was done. First, the samples were deformed at 200°C and then a cross-head was stopped at 500 MPa during unloading for APB relaxation. Then, the cross-head moved again and then the samples were completely unloaded. The recovery-start shear stress, \(\tau_r\) in Eq. (2) is plotted against relaxation time, \(t\) in Fig. 12. The \(\tau_r\) decreases exponentially with increasing relaxation time. Lerf et al.\(^{21}\) suggested that the APB energy decreased by the relaxation as follows,

\[
\gamma_{\text{NNNAPB}} = A \exp(-Br) + C \tag{5}
\]

where \(A, B\) and \(C\) are constant. From Eqs. (2), (4) and (5), \(\tau_r\) should decrease exponentially with \(t\), if APB relaxation occurs; this was in good agreement with Fig. 12. Therefore, it is confirmed that the APB behind 1/4\((111)\) superpartials relaxed during deformation resulting in a decrease in recovery ratio.

5.4. Shape Memory Effect at Low Temperatures

At \(-150°C\), recovery ratio just after unloading was small, while recovery ratio increased to near 80% during heating to room temperature. As shown in Fig. 6, a difference in yield stress between \(-150°C\) and room temperature was about 100 MPa. It is reasonable that \(\tau_r\) in Eqs. (1) and (2) hardly changed at and below room temperature since APB relaxation never occurred in the temperature range. This suggests that \(\tau_r\) decreased by approximately 100 MPa during heating from \(-150°C\) to room temperature. So, the superpartials started to move back during heating to room temperature resulting in the shape memory effect. However, \{211\} deformation twins shown in Fig. 9 remained even after heating to room temperature, which was harmful for the pseudoelasticity and shape memory effect.

6. Conclusions

Temperature dependence of pseudoelasticity and shape memory effect in \(\text{Fe–24.4at\%Ga}\) single crystals with the \(\text{D}_0^3\) structure was examined. The following conclusions were reached.

(1) \(\text{Fe–Ga}\) single crystals with the \(\text{D}_0^3\) structure show perfect pseudoelasticity at room temperature. Uncoupled or paired 1/4\((111)\) superpartials move dragging the NNNAPB and NNNAPB, respectively. During unloading, these APBs pull back the superpartials resulting in the pseudoelasticity.

(2) The \(\text{L}_1^2\) phase precipitating during deformation at 200–500°C suppresses the reversible motion of dislocations resulting in a decrease in recovery ratio.

(3) Above room temperature, dislocation configuration depends strongly on deformation temperature. At and below 100°C, mode I and II are selected, while mode II is observed in the temperature range between 200 and 400°C. On the other hand, mode III configuration at and above 500°C results in little strain recovery since no APB is left behind 1/4\((111)\) superpartials.

(4) Relaxation of APB between 1/4\((111)\) superpartials causes a serrated flow in \(\text{Fe–Ga}\) single crystals. On the other hand, the APB left behind the superpartials relaxes easily compared with that between the superpartials. The APB relaxation decreases the tension during unloading, also leading to the decrease in strain recovery.

(5) Shape memory effect takes place in \(\text{Fe–Ga}\) single crystals deformed at \(-150°C\). Frictional stress of 1/4\((111)\) superpartials decreases during heating to room temperature and the superpartials start to move back resulting in the shape memory effect. On the other hand, \{211\} deformation twins do not contribute to the strain recovery.

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