Stress Induced R→B2 Transformation and Pseudoelasticity Associated with Twinning in a Ti-Ni Alloy Including Aligned Particles of Ti₃Ni₄†

Takashi Fukuda, Akiyoshi Deguchi††, Tomoyuki Kakeshita and Toshio Saburi

Department of Materials Science and Engineering, Faculty of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565, Japan

A Ti-51 at%Ni alloy including aligned particles of Ti₃Ni₄ precipitate formed by aging under an applied stress exhibits an anomalous transformation, i.e., stress induced R(martensite)→B2(parent) transformation. Confirmation of this transformation was made by tensile tests combined with simultaneous resistance measurements. This alloy also exhibits pseudoelasticity associated with twinning when tensile test is made at a temperature sufficiently below its transformation temperature, i.e., in the R-phase state. The stress induced R→B2 transformation and the pseudoelasticity in the R-phase state are due to the internal stress field formed by the aligned particles of Ti₃Ni₄.

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I. Introduction

In many materials exhibiting a martensitic transformation, an applied stress generally assists the formation of specific variants of the martensite. Consequently, the martensitic transformation start temperature (Mₐ) increases as the externally applied stress increases as illustrated in Fig. 1(a). In our previous investigation, however, we observed an anomalous behavior that Mₐ decreases as externally applied stress increases as illustrated in Fig. 1(b). This occurs in the B2(parent)→R(martensite) transformation of a Ti-51 at%Ni alloy which includes aligned particles of Ti₃Ni₄ precipitate formed by aging under an applied stress.

In the former case, when an external stress is applied to a specimen kept at a temperature slightly above Mₐ (under no applied stress), stress induced martensitic transformation occurs. This process is indicated by the arrow in Fig. 1(a). This type of stress induced martensitic transformation is widely observed in alloys exhibiting thermoelastic martensitic transformation. In the latter case, however, when an external stress is applied to the specimen kept at a temperature slightly below Mₐ (under no applied stress), stress induced R→B2 transformation is expected as indicated by the arrow in Fig. 1(b).

The purpose of the present paper is to demonstrate that the stress induced R→B2 transformation really occurs and to explain this transformation thermodynamically. A pseudoelasticity associated with twinning in the R-phase state is also discussed.

II. Experimental Procedure

A Ti-51 at%Ni alloy was prepared by induction melting and then hot rolled to a plate 1.3 mm in thickness. A tensile test specimen 30 mm in gauge length, 3 mm in width and 0.5 mm in thickness were cut from the rolled plate so as the tensile axis orientates to the rolling direction. The specimen was solution treated at 1123 K for 3.6 ks, and then aged at 773 K for 6 ks under an external tensile stress of 300 MPa. By this treatment, particles of Ti₃Ni₄ precipitate are preferentially aligned so as their habit plane normal becomes perpendicular to the tensile axis. We are able to detect the stress induced phase

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†† Graduate Student, Osaka University.
transformation by electrical resistance measurements, since the resistance varies significantly in association with the B2→R and reverse transformations.

Tensile tests were made with a strain rate of \( \dot{\varepsilon} = 2.5 \times 10^{-4} \text{s}^{-1} \). The specimen was immersed in a bath of 3M's Fluorinert FC-77 kept at constant temperatures during tensile test. Electrical resistance measurements were made by the direct current four-probe method with a constant current of 500 mA. For comparison, the same tests were made on a solution treated Ti-48.5Ni-1.5Fe at% alloy, which exhibits the B2→R transformation but does not include Ti2Ni.

### III. Results

In electrical resistivity measurements of metals and alloys, the shape change of the specimen during the measurement is usually ignored. However, in the present study, we should not do so, since the resistance change due to the shape change is in the same order of the resistance change due to the phase transformation. To obtain the “true” resistivity of the specimen, we must know the accurate shape of the specimen at a specific temperature and external stress. Since the accurate shape is not easily obtained, instead of the “true” resistivity, we employed the “nominal” resistivity \( \rho_n \), which is expressed as:

\[
\rho_n = R \frac{t_0 \cdot w_0}{l_0}.
\]

Thereby, \( t_0, w_0 \) and \( l_0 \) are the thickness, width and length between voltage probes of the specimen measured at room temperature under no external stress; \( R \) is the resistance of the specimen.

Figure 2 shows temperature dependence of \( \rho_n \) of the Ti-51 at%Ni alloy aged under a stress of 300 MPa. The measurement was made in the heating process starting from 240 K, which is higher than the R→B19 transformation start temperature. The value of \( \rho_n \) is almost constant at temperatures below 295 K and above 315 K. It decreases rapidly in the temperature range between 295 K and 315 K due to thermally induced R→B2 transformation. We notice that \( \rho_n \) of the B2-phase is about 10% smaller than that of the R-phase. Now we consider how \( \rho_n \) changes when external stress is applied at the temperature indicated by B. It is expected that \( \rho_n \) decreases if the R→B2 transformation occurs and \( \rho_n \) increases if the B2→R transformation occurs.

Prior to describing the experimental results of the change in \( \rho_n \) during tensile tests, we consider the change in \( \rho_n \) due to the shape change. Let \( \rho_{no} \) be the “nominal” resistivity of the specimen at a temperature under no applied stress. If the “true” resistivity does not change but the specimen shape changes due to the applied stress, the “nominal” resistivity at this temperature may be expressed as:

\[
\rho_n = \rho_{no}(1 + (1 + 2\nu)\varepsilon)
\]

where \( \nu \) is Poisson’s ratio and \( \varepsilon \) is the strain in the direction of the tensile axis. In this equation, we assumed \( \varepsilon \ll 1 \). The eq. (2) shows that \( \rho_n \) increases linearly as \( \varepsilon \) increases if the “true” resistivity does not change.

Tensile tests combined with simultaneous resistance measurements were made at various temperatures in the heating process on the Ti-51 at%Ni alloy aged under a stress of 300 MPa. Figure 3 shows the results obtained by testing at 270, 305 and 336 K (these temperatures are indicated as A, B and C in Fig. 2). Figures 3(a), (b) and (c) are stress vs strain curves and Figs. 3(a’), (b’) and (c’) are the corresponding \( \rho_n \) vs strain curves. The solid curves show the measured \( \rho_n \) values, and the dashed lines show the \( \rho_n \) values calculated by using eq. (2), where \( \nu \) is assumed to be 1/3.

The specimen of the aged Ti-51 at%Ni alloy is in the R-phase state before applying tensile stress at 270 K, which is far below its R→B2 transformation start temperature. The stress vs strain curve obtained at this temperature (Fig. 3(a)) exhibits a hysteresis between loading and unloading processes, which will be discussed later. As seen in its corresponding \( \rho_n \) vs strain curve (Fig. 3(a’)), \( \rho_n \) increases as strain increases. The fact that the measured values and the calculated ones (dashed line) are close indicates that the change in \( \rho_n \) is mainly due to the shape change of the specimen.

At 305 K, the specimen is in a mixed state composed of the B2-phase and the R-phase. The stress vs strain curve at 305 K (Fig. 3(b)) exhibits a small hysteresis. The corresponding \( \rho_n \) vs strain curve (Fig. 3(b’)) shows that the \( \rho_n \) decreases as strain increases (as stress increases). The decrease of \( \rho_n \) should be due to stress induced R→B2 transformation.

At 336 K, which is sufficiently higher than its R→B2 transformation finish temperature, the specimen is in the B2-phase state. The stress vs strain relation at 336 K (Fig. 3(c)) is linear, which is a typical elastic behavior. Its corresponding \( \rho_n \) vs strain relation (Fig. 3(c’)) is also nearly
linear and agree with the calculated one (dashed line).

In order to confirm that the decrease in $\rho_n$ in Fig. 3(b) is due to the stress induced $R \rightarrow B2$ transformation, we made similar tests for a solution treated Ti–48.5Ni–1.5Fe at% alloy. We selected this alloy because this alloy shows clear $B2 \leftrightarrow R$ transformation, but does not include Ti$_3$Ni$_4$ precipitates.

Figure 4 is the $\rho_n$ vs $T$ curve of the Ti–48.5Ni–1.5Fe at% alloy. Measurement was made during heating from 270 K. The sharp decrease in resistivity at 290 K is due to the thermally induced $R \rightarrow B2$ transformation.

Tensile tests combined with simultaneous resistance measurements were made at several temperatures by successively increasing the test temperature. The results at 281, 286 and 320 K (these temperatures are marked as A, B and C in Fig. 4) are shown in Fig. 5.

At 281 K, the Ti–48.5Ni–1.5Fe at% alloy is in almost the R-phase state. In the stress vs strain curve at this temperature (Fig. 5(a)), there is a residual strain. It is seen in the corresponding $\rho_n$ vs strain curve (Fig. 5(a')) that $\rho_n$ increases with increasing strain. This behavior is quite similar to that of the aged Ti–51 at%Ni alloy in the same R-phase state (Fig. 3(a')).

At 286 K, the specimen is in a mixed state composed of the B2-phase and the R-phase. The stress vs strain curve at this temperature (Fig. 5(b)) is similar to that of the aged Ti–51 at%Ni alloy shown in Fig. 3(b), although a small residual strain remains. However, the corresponding $\rho_n$ vs strain curve (Fig. 5(b')) is completely different from that of the aged Ti–51 at%Ni alloy shown in Fig. 3(b'). That is, $\rho_n$ increases as strain increases in this alloy, but it decreases in the aged Ti–51 at%Ni alloy. The increase of $\rho_n$ is much larger than that expected from the shape change (dashed line). This large increase of $\rho_n$ should be due to the stress-induced $B2 \rightarrow R$ transformation.

At 320 K, which is sufficiently higher than its $R \rightarrow B2$ transformation finish temperature, the specimen is in the B2-phase state. The stress vs strain relation (Fig. 5(c)) and its corresponding $\rho_n$ vs strain relation (Fig. 5(c')) are linear at this temperature. This result is quite similar to that of the aged Ti–51 at%Ni alloy tested at 336 K (Fig. 3(c) and (c')).

By comparing all the results of tensile tests shown in
Figs. 3 and 5, there is no doubt that the decrease of $\rho_n$ seen in Fig. 3(b') is due to the stress induced R $\rightarrow$ B2 transformation.

IV. Discussion

1. Thermodynamical explanation of stress induced R $\rightarrow$ B2 transformation

Stress induced R $\rightarrow$ B2 transformation is experimentally demonstrated in the previous section. In this subsection we make a thermodynamical explanation of the stress induced R $\rightarrow$ B2 transformation.

For simplicity, we treat the transformation process as quasi-reversible. This treatment will be adequate for the B2+$\gamma$R transformation because the hysteresis of this transformation is very small (below 5 K). Thus, instead of $M_\gamma$ or $A_\gamma$, we refer to the equilibrium temperature $T_0$. Thereby, Gibbs free energy difference $\Delta G = (G_m - G_p)$ between the parent ($G_p$) and the martensite ($G_m$) equals to zero, i.e.,

$$\Delta G(T_0) = 0.$$  \hspace{1cm} (3)

We divide the total $\Delta G$ into three terms, i.e.,

$$\Delta G = \Delta G_\text{el} + \Delta G_\text{ex} + \Delta G_\text{ef}.$$  \hspace{1cm} (4)

$\Delta G_\text{el}$ is the elastic free energy difference due to internal stress, $\Delta G_\text{ex}$ is that due to external stress, and $\Delta G_\text{ef}$ is the free energy difference due to all the other generalized forces. The term $\Delta G_\text{ef}$ equals to zero if external stress is not applied.

We discuss the effect of the external stress for two cases.

Firstly, we consider the case that the matrix (parent) does not include any fine particles or the effect of the particles is relatively small. In this case, we may treat $\Delta G_\text{el}$ and $\Delta G_\text{ef}$ to be identical for all the variants in the early stage of transformation. The $\Delta G$ vs temperature ($T$) relation under no applied stress may be drawn as $A$ in Fig. 6(a) for all the variants. Under an external stress, each martensite variant has a unique value of $\Delta G_\text{ex}$; the variant preferable for the external stress takes a negative value, and the variant not preferable for it takes a positive value. Therefore, the $\Delta G$ vs $T$ relation under an external stress may be drawn as $B_1$ and $B_2$ for the preferable variant and the not preferable variant, respectively. Thus, in the cooling process under the external stress, transformation occurs at $T_1$ which is higher than $T_0$. In this way the transformation temperature increases as the external stress increases. When the external stress is applied at $T_1$ which is slightly above $T_0$, $\Delta G$ changes from a positive value indicated by $P$ to a negative value indicated by $Q$, and stress induced martensitic transformation occurs.

Secondly, we consider the case that fine particles form a specific stress field in the matrix of the parent. An aged Ni-rich Ti-Ni alloy including preferentially aligned particles of Ti$_3$Ni$_4$ as illustrated schematically in Fig. 7 is the case. We assume that $\Delta G_\text{ef}$ is identical for all the variants as we did in the previous case. We consider a hypothetical situation where there is no internal stress. Thereby, $\Delta G$ vs $T$ relation under no external stress is drawn as $A_0$ in Fig. 6(b). The hypothetical equilibrium temperature is marked as $T_0$. In this case, each variant has a unique value of $\Delta G_\text{el}$ because the particles of Ti$_3$Ni$_4$ form a characteristic internal stress field around them$^{[60]}$. This internal stress field is preferable for the variants that expand to the direction of the habit plane normal of the aligned particles (one of these variants is termed as "variant 1"):
Fig. 6 Schematic illustrations of $\Delta G$ vs $T$ relations. The arrow from P to Q in (a) is the path of stress induced martensitic (B2 $\rightarrow$ R) transformation. The arrow from P$^*$ to Q$^*$ in (b) is the path of stress induced reverse (R $\rightarrow$ B2) transformation.

Fig. 7 Schematic illustrations showing aligned particles of Ti$_3$Ni$_4$ and shape change due to B2 $\rightarrow$ R transformation. The shape of the B2-phase shown by dashed rectangle changes to that of the R-phase shown by solid rectangle. In (a), the R-phase expands to the habit plane normal of the Ti$_3$Ni$_4$ and contracts to the direction of tensile axis. In (b), the R-phase contracts to the habit plane normal of the Ti$_3$Ni$_4$ and expands to the direction of tensile axis.

...it is not preferable for the variants contracting to the direction (one of them is termed as "variant 2"). Under this internal stress field, $\Delta G^t_u$ is negative for "variant 1" and is positive for "variant 2". Thus, the $\Delta G$ vs $T$ relation under no external stress is drawn as curves A$_1$ and A$_2$ for "variant 1" and "variant 2", respectively. The B2 $\rightarrow$ R transformation occurs at $T^*_0$ if external stress is not applied.

Under an external tensile stress, $\Delta G^t_o$ is positive for "variant 1" and is negative for "variant 2", because "variant 1" contracts and "variant 2" expands to the direction of the tensile axis as illustrated in Fig. 7. Thus the $\Delta G$ vs $T$ relation under the external stress is drawn as curves B$_1$ and B$_2$ in Fig. 6(b) for "variant 1" and "variant 2", respectively. Thus in the cooling process under the external stress, transformation starts at $T^*_0$ which is lower than $T^*_0$. In this way, transformation temperature decreases as external stress increases. When the external stress is applied at $T_2$ which is slightly lower than $T^*_0$, $\Delta G$ changes from a negative value indicated by P$^*$ to a positive value indicated by Q$^*$. Consequently, stress induced reverse transformation occurs. The curve B$_1$ shifts upward and the curve B$_2$ shifts downward as the external tensile stress increases. If $\Delta G$ of B$_2$ at $T_2$ become negative by increasing external stress, previously mentioned stress induced parent phase may again transform to the martensite (R-phase) of "variant 2". Thus, the stress induced transformation sequence may be written as R(variant 1) $\rightarrow$ B2 $\rightarrow$ R(variant 2), if the external stress required for the transformation does not exceeds the yield stress.

2. Pseudoelasticity associated with twinning in the R-phase state

The stress vs strain curves shown in Figs. 3(a) and 5(a) are of the R-phase (martensite). Both curves exhibit a hysteresis, but they are completely different each other. While the stress vs strain curve shown in Fig. 3(a) does not exhibit residual strain, that shown in Fig. 5(a) does. The residual strain of the latter vanishes when the specimen is heated above its $A_f$ temperature. This feature is
characteristic of shape memory alloys. The former is pseudoelasticity. This pseudoelasticity is not associated with stress induced martensitic transformation, nor with stress induced reverse transformation, since the test is made sufficiently below the transformation temperature. This pseudoelasticity should be associated with twinning.

Pseudoelasticity associated with twinning is known to occur in copper based shape memory alloys and Au–Cd alloys, and is referred as rubber-like behavior. The rubber-like behavior in copper based alloys and Au–Cd alloys arises when the specimens are aged in the martensitic state, and its origin has been explained by local change in structure through aging in the martensitic state.

However, in the present case shown in Fig. 3(a), the pseudoelasticity associated with twinning arises without aging in martensitic state, and its origin is completely different. In the present case, the pseudoelasticity arises due to the stress field around particles of Ti<sub>3</sub>Ni<sub>4</sub>. Before applying an external stress, the specimen is composed of variants which are preferable for the internal stress. When the external stress is applied, some amount of these variants is converted to other variants which are preferable for the applied stress. But the latter variants are not preferable for the internal stress. Thus, when the external stress is removed, the once converted these variants return to the original variants which are preferable for the internal stress.

The above discussion is for the case that Ti<sub>3</sub>Ni<sub>4</sub> is preferentially aligned. If the aging is made under no applied stress, preferential alignment of Ti<sub>3</sub>Ni<sub>4</sub> does not occur and the fraction of each variant of Ti<sub>3</sub>Ni<sub>4</sub> obtained is identical, i.e., one fourth. In this case, the recoverable strain due to variant conversion should be only one fourth of the case that Ti<sub>3</sub>Ni<sub>4</sub> is preferentially aligned.

3. Hysteresis in \( \rho_n \)

In the \( \rho_n \) vs strain curves shown in Figs. 3 and 5, we notice the following. While the \( \rho_n \) vs strain curve does not exhibit any hysteresis when tested in the B2-phase state (Figs. 3(c') and 5(c')), it exhibits a hysteresis when tested in the R-phase state (Figs. 3(a') and 5(a')) and in the two-phase region (Figs. 3(b') and 5(b')). This hysteresis may be due to the anisotropy in resistivity of the R-phase. That is, if the R-phase is anisotropic in resistivity and arrangement of the R-phase variants is different between the loading and unloading processes, the \( \rho_n \) at a specific strain is different between loading and unloading processes. Another explanation of the hysteresis could be made if we take the failure of isothermal condition into account. That is, if the isothermal condition is not kept strictly, there could be a hysteresis in \( \rho_n \) between loading and unloading processes. The destruction of isothermal condition may arise because of the enthalpy change of the specimen due to transformation.

V. Conclusions

Stress induced transformation of a Ti–51 at%Ni alloy including aligned particles of Ti<sub>3</sub>Ni<sub>4</sub> formed by aging under an applied tensile stress was investigated by tensile tests and simultaneous resistance measurement. The following conclusions were derived.

1) Stress induced R→B2 transformation occurs in this alloy.

2) This transformation occurs because thermally induced R-phase variants are preferable for the stress field formed by the aligned particles, but these variants are not preferable for the applied stress.

3) This alloy exhibits pseudoelasticity associated with twinning in the R-phase state.

4) This behavior arises because the R-phase variants once converted by the external stress return to the original variants which are preferable for the internal stress formed by the aligned particles.

REFERENCES


