Effect of surface oxidation on detwinning stress and transformation temperature of Ti–50Ni shape memory alloy

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Abstract

It was reported that the detwinning stress in martensite of Ti–Ni alloys increases with increasing annealing temperature, but the reason for such a strange behavior has remained unclear. In the present study, we made a comparative study between Ti–50Ni samples annealed in air and those in argon atmospheres. We found that samples annealed in air showed a significant increase in the detwinning stress with increasing annealing temperature, but they showed little change in M_s temperature. When the samples were annealed in argon, the detwinning stress and M_s became independent of the annealing temperature. We conclude that the increase of detwinning stress with annealing temperature results from the surface hardening of the sample due to surface oxidation; the insensitivity of M_s to oxidation is due to the fact that surface oxidation does not affect the core of the sample, where transformation takes place first. Our result shows the importance of preventing surface oxidation in obtaining proper properties for this important shape memory alloy.
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1. Introduction

Ti–Ni shape memory alloy has attracted much attention as a functional material due to its combination of excellent functional properties, such as shape memory effect and superelasticity with good mechanical properties like ductility and strength [1,2]. In martensite state, Ti–Ni alloy shows a unique soft and plastic deformation behavior called "detwinning", the microscopic process of which is a twinning process of the martensite variants under stress until the whole sample becomes a single variant of martensite (in ideal case). In the stress–strain curve, detwinning manifests itself as a stress plateau extending to a plastic strain as large as 8–9% [3,4]. The detwinning process is important as it influences the shape recovery properties [5].

Liu et al. [6] reported that for Ti–50 at% Ni (in brief Ti–50Ni hereafter) samples the critical stress for detwinning increases with increasing annealing temperature from 550 to 800 °C. This phenomenon is quite interesting but difficult to explain, as no change exists in microstructure over this temperature regime according to the phase diagram. We notice that their samples were annealed in air, thus speculate that there may be a possibility of the oxidation effect. However, Ti–Ni alloys are well known for their good corrosion and oxidation resistance below 700 °C [7–12], so such a possibility seems not self-evident.

The purpose of the present paper is thus to clarify the reason for the increase of the detwinning stress with increasing annealing temperature. We consider that such an effect may be due to the surface oxidation of Ti–Ni alloys, although the oxidation layer may not be thick. For this purpose, we designed our experiment as follows. First, solution-treated Ti–50Ni alloys were annealed in air and in Ar atmosphere (to avoid oxidation), respectively, at various temperatures from 300 to 900 °C. Second, for the samples annealed at 900 °C in air, the surface layer

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(that might be affected by oxidation) was gradually removed, followed by tensile testing and DSC measurement of the remaining portion of the sample. By comparing these results with those for the un-oxidized samples (Ar-annealed), we can identify the effect of oxidation layer on the detwinning stress and M_s (martensitic transformation start temperature). Third, for Ar-annealed Ti–50Ni samples, we changed annealing temperature and time, to check the "net" annealing effect (without oxidation) on detwinning stress and M_s. As will be shown below, oxidation layer, even very thin, has significant effect on detwinning stress for Ti–Ni alloy, but it has little effect on M_s of the alloy.

2. Experimental procedure

A solution-treated Ti–50Ni wire with a diameter of 1 mm was used in this study. In order to obtain different degree of surface oxidation, solution-treated (in Ar atmosphere) Ti–50Ni wires were air-annealed at 300–900 °C for 0.5 and 2 h, followed by quenching into room temperature water (20 °C). For comparison, we also made reference un-oxidized samples (annealed in Ar), which were also annealed and quenched under the same condition. These reference samples were made by sealing them into quartz tubes with argon gas (about 1.5×10^3 Pa), which protected the sample from oxidation during the annealing. After annealing, the tube was quenched into the water (20 °C) with the tube broken immediately. Both the air-annealed and Ar-annealed samples were chemically etched to different diameters to make the sample have different thickness of oxidation layer. The etchant was a mixture containing 10 vol% hydrofluoric acid, 40 vol% nitric acid and 50 vol% water.

The microstructure over the cross-section of the wire was characterized with an optical microscope. The tensile stress–strain curves were measured with a tensile machine of type CMT4204 from SANS. The tensile testing was performed at room temperature (20° C), which is below M_f of the Ti–50Ni alloy. All the samples were elongated to about 8% at a speed of 0.5 mm/min. The phase transformation temperatures were measured by a differential scanning calorimeter (DSC) of type 822e from METTLER TOLEDO. The cooling and heating rate was 10 °C/min.

3. Results

In order to ascertain whether or not the surface oxidation layer affects detwinning stress, one easy way is to tensile-test the air-annealed sample before and after etching off different thickness of surface layer. If the surface oxidation has strong influence on the detwinning stress, we should be able to observe a clear change of the detwinning stress as a function of the "remaining diameter". Fig. 1(a) shows the variation of the stress–strain curve with the remaining diameter of a 900 °C air-annealed (for 0.5 h) sample after etching off different thickness of the surface layer. Clear stress plateau, due to the detwinning process, is observed for the samples with all the remaining diameters. The detwinning stress of the annealed sample before etching (for $d_0 = 1.000$ mm) has a high value of 229 MPa, but it decreases rapidly to about 156 MPa at $d = 0.929$ mm; with further etching to $d < 0.929$ mm (i.e., only the "core" part is left), the detwinning stress keeps almost the same value of about 156($\pm$3) MPa, being no longer dependent on the remaining diameter.

For comparison, the stress–strain curve of a Ti–50Ni sample after annealing at 900 °C in Ar was also measured after removing the sample surface by different thickness to make different remaining diameters. The result is shown in Fig. 1(b). It is clear that the detwinning stress is independent of the
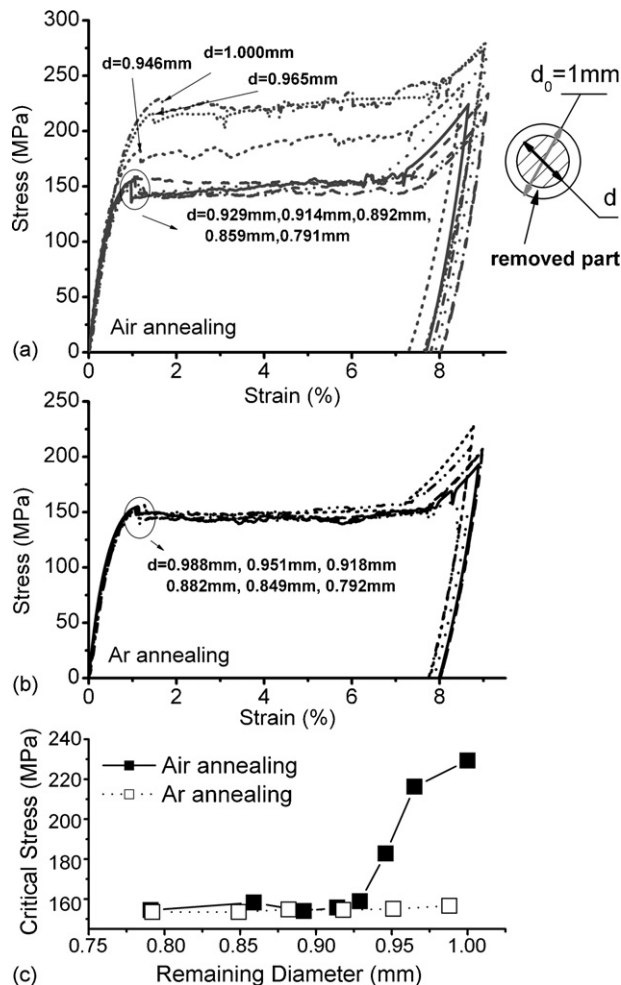

Fig. 1. (a) Variation of stress–strain curve with "remaining diameter" of a Ti–50Ni wire annealed at 900 °C for 0.5 h in air (see the inset for the relation between initial diameter d_0 and remaining diameter d). (b) Variation of stress–strain curve with "remaining diameter" for a Ti–50Ni wire annealed at 900 °C for 0.5 h in Ar. (c) Comparison of the critical detwinning stress as a function of the remaining diameter between an air-annealed sample and an Ar-annealed sample.

remaining diameter, being about 155($\pm$2) MPa, which is within experimental uncertainty the same as that of the "core" part of the air-annealed sample shown in Fig. 1(a). A comparison of the critical detwinning stress versus remaining diameter between Ar-annealed samples and air-annealed samples is made in Fig. 1(c). It is clear that the Ar-annealed sample does not show a dependence of the detwinning stress on the remaining diameter. By contrast, air-annealed sample shows a strong dependence of the detwinning stress on the remaining diameter, but the core part of the air-annealed sample behaves in the same way as that of the Ar-annealed sample. From Fig. 1(c), we can estimate that the thickness of the oxidation-affected layer for the sample after air annealing at 900 °C for 0.5 h is about $(1 - 0.929)/2 = 0.036$ mm. Fig. 1(c) shows an important result: even when the surface oxidation layer has a thickness being just a few percent of the sample diameter, it can significantly increase the detwinning stress by as much as about 50%. When the oxidation layer is removed completely (i.e., the diameter

was below 0.929 mm), the detwinning stress reduces to the true value that equals to that for the Ar-annealed samples. This clearly shows that oxidation occurs only in the surface layer.

Contrasting the significant effect of surface oxidation on detwinning stress, its effect on transformation temperature M_s is surprisingly small. All the DSC curves (showing B2–B19′ transformation) for the samples with different remaining diameters give essentially the same M_s temperature; thus, only two typical DSC curves of air-annealed Ti–50Ni samples are shown in Fig. 2(a). One is the sample with a remaining diameter of 0.979 mm, representing the Ti–Ni wire with an oxidation layer; the other is that with a remaining diameter of 0.812 mm, corresponding to the sample without oxidation layer. Both curves show similar M_s temperature. It should be noted that in our experiment the transformation heat has a large uncertainty because the wire sample has a small contact area with the DSC sample pan. For this reason, we are not able to give meaningful discussion about the change of transformation heat with the remaining diameter.

The Ar-annealed sample (as a reference) exhibits similar behavior (Fig. 2(b)), i.e., M_s temperature is independent of the remaining diameter. The behavior of Ar-annealed sample is as expected, because no surface oxidation layer exists. Fig. 2(c) shows a comparison of M_s as a function of the remaining diame-

ter between the air-annealed sample and the Ar-annealed sample. It is clear that M_s is almost independent of the thickness of oxidation layer, suggesting the insensitivity of M_s to surface oxidation.

In order to understand how the oxidation affects the property of the surface layer, it is important to characterize the transformation behavior of the oxidation-affected surface layer. However, it is difficult to do this directly, as this layer has been shown above to be very thin (e.g., about 0.04 mm even after annealing at 900 °C for 0.5 h) and it is difficult to peel it off from the sample. To circumvent this difficulty, we made a very thin sheet of Ti–50Ni with a thickness of 0.1 mm, and annealed it in air at 900 °C for 0.5 h (the same condition as that for the bulk counterpart). Under such a condition, this thin sample actually "mimics" the surface layer of the bulk sample annealed at 900 °C. This is because under such a condition the bulk sample would form an oxidation-affected layer of about 0.04 mm on each side of the sample, thus the total oxidation-affected layer would be about 0.08 mm thick. Then our 0.1 mm thick sample becomes essentially fully affected by oxidation, i.e., it mimics the oxidation-affected surface layer. We performed DSC measurement on this "mimic surface oxidation-affected layer", and found this layer showed striking transformation behavior as shown in Fig. 3: there exists no transformation peaks over the whole temperature range between 90 and −90 °C. This implies that no martensitic transition happens in the oxidation-affected layer. This is only possible when the Ni content of the oxidation layer become very high. We shall discuss how this is possible in Section 4.

Fig. 4 shows the microstructure over the cross-section of a Ti–50Ni wire after annealing for the same time (0.5 h) at: (a) 900 °C in air, (b) 900 °C in Ar and (c) 300 °C in air. The Ar-annealed sample shows almost no oxidation layer (Fig. 4(b)); by contrast, the 900 °C air-annealed sample has an oxidation layer about 0.04 mm (Fig. 4(a)). On the other hand, 300 °C air-annealed sample has a very thin oxidation layer less than 0.01 mm Fig. 4(c), suggesting that oxidation occurs at quite low temperature, though very slow.

Figs. 5(a–c) and 6(a–c) show the stress–strain curves and DSC curves of the samples annealed at 300, 600 and 900 °C
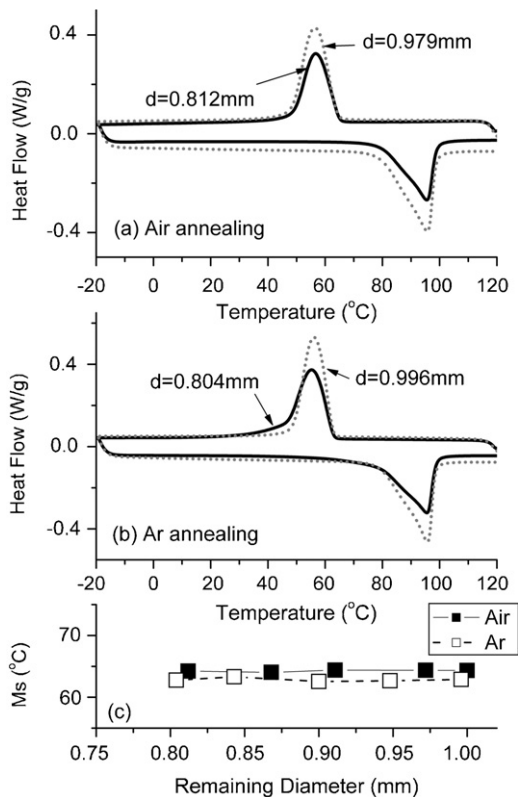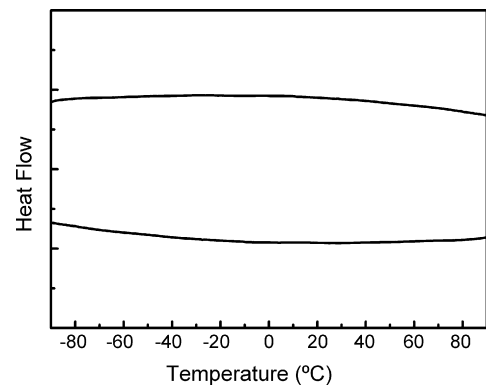

Fig. 2. (a) DSC curves of the samples annealed at 900 °C for 0.5 h in air followed by etching to 0.979 and 0.812 mm, respectively. (b) DSC curves of the samples annealed at 900 °C for 0.5 h in Ar followed by etching to 0.996 and 0.804 mm, respectively. (c) M_s temperature as a function of the remaining diameter of the sample after removing different thickness of the surface layer.

Fig. 3. DSC curve of a "mimic surface oxidation-affected layer". The sample is a 0.1-mm thick Ti–50Ni thin sheet annealed at 900 °C for 0.5 h in air after solution treatment. Such a sample "mimics" the surface oxidation-affected layer of the 1 mm Ti–50Ni wire for the same treatment.
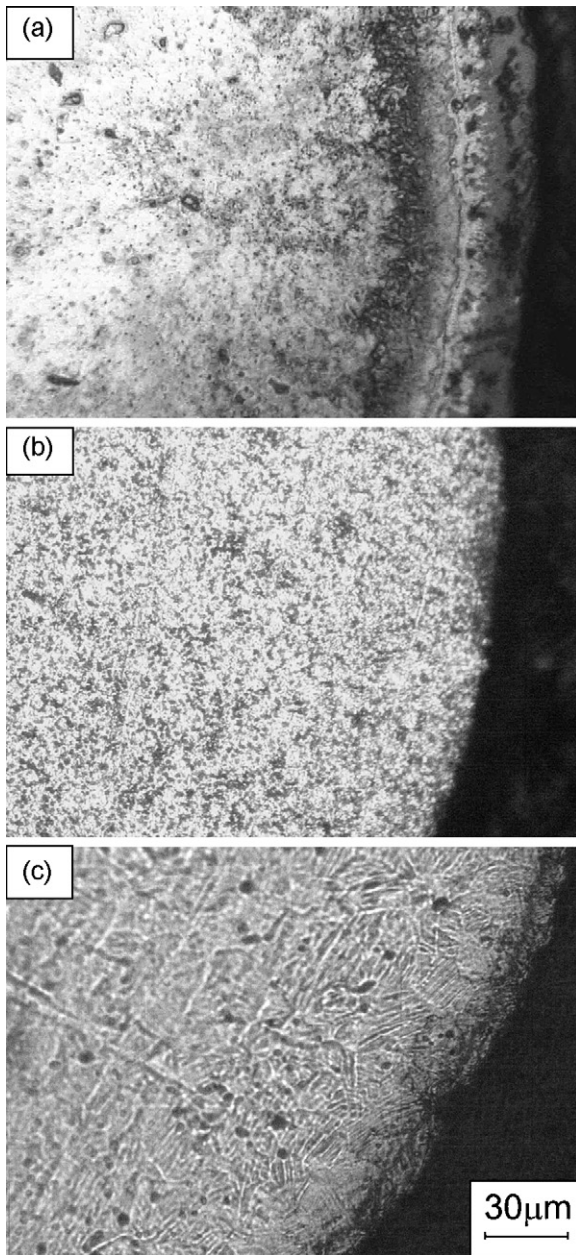
Fig. 4. The microstructure over cross-section of the sample after: (a) annealed at 900 °C for 0.5 h in air, (b) annealed at 900 °C for 0.5 h in Ar and (c) annealed at 300 °C for 0.5 h in air. There is no detectable oxidation layer in (b). The thickness of oxidation-affected layer in (a) is about 0.04 mm, and that in (c) is less than 0.01 mm.
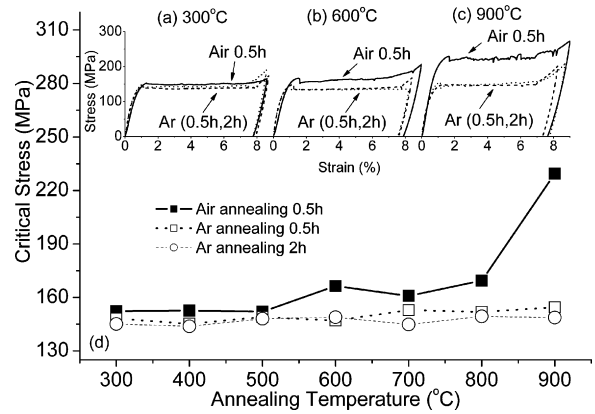

Fig. 5. Variation of stress–strain curve of Ti–50Ni with annealing condition. (a) 300 °C for 0.5 and 2 h in air and Ar, (b) 600 °C for 0.5 and 2 h in air and Ar, (c)900 °C for 0.5 and 2 h in air and Ar and (d) the annealing temperature and time effect on the detwinning stress.
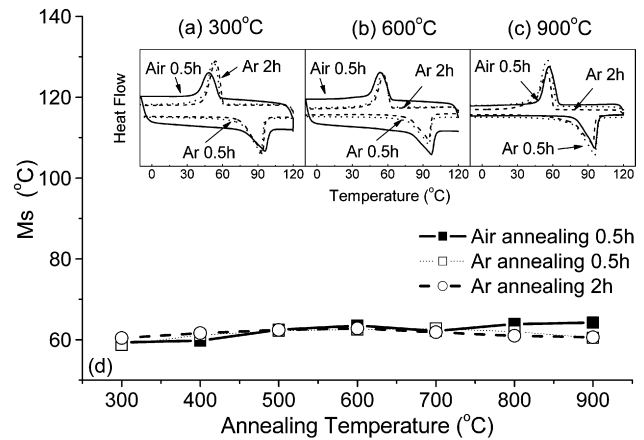

Fig. 6. Variation of DSC curve of Ti–50Ni with annealing condition. (a) 300 °C for 0.5 and 2 h, in air and Ar, respectively, (b) 600 °C for 0.5 and 2 h, in air and Ar, respectively, (c) 900 °C for 0.5 and 2 h, in air and Ar, respectively, and (d) the effect annealing temperature and time on M_s temperature.

for 0.5 and 2 h in air and Ar, respectively. Figs. 5(d) and 6(d) show the annealing temperature and annealing time effect on detwinning stress and M_s, respectively. The oxidized samples show an obvious increase in detwinning stress with increasing annealing temperature from 500 to 900 °C, being the same as that reported by Liu et al. [6]. However, for well-protected samples (annealed in Ar) the detwinning stress remains almost unchanged, regardless of the annealing temperature and time. One surprising finding is that M_s temperature keeps almost unchanged, no matter how the sample is annealed, in air or in Ar, or for different annealing temperature and time.

4. Discussion

Our results above have demonstrate clearly that the increase in the detwinning stress with increasing annealing temperature is caused by surface oxidation of the samples during annealing. A surprising finding is that such effect is significant even when the oxidation-affected layer is very thin compared with the sample diameter. Contrasting the strong effect of oxidation on the detwinning stress, its effect on M_s is negligibly small. When oxidation is avoided (i.e., annealed in Ar), annealing (at different temperature and for different time) has no effect on both detwinning stress and M_s. All these findings can be explained as follows.

When the TiNi alloy is annealed in air even at relatively low temperature, a thin oxidation layer is formed. This layer, if having different mechanical property, may strongly affect the deformation behavior. The mechanical property of this oxidation-affected layer can be deduced from its transformation behavior shown in Fig. 3. This figure shows that the oxidation-affected layer does not transform. How can an oxidation-affected layer
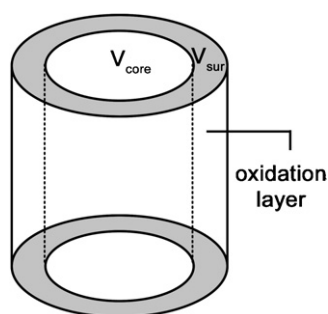
Fig. 7. A crust–core composite model for surface oxidized Ti–Ni wire. The core and the crust have different yield stress.

be non-transforming? According to the previous studies [7–12], surface oxidation produces Ti-rich oxide like TiO_2 and Ti_4Ni_2O; as a result, the matrix of the oxidation-affected layer becomes Ni-rich, which naturally keeps a B2 structure without having a B2–B19′ transformation, according to the relation between M_s and Ni content [2]. Then the deformation of this B2 layer can be accommodated only by dislocation slip, which occurs at a very high stress level about 500–700 MPa for Ni-rich Ti–Ni alloys [1,2]. Therefore, the oxidation-affected layer acts as a very "hard" crust surrounding the unaffected "soft" B19′ martensite core of the sample. Clearly, the nominal yield stress of such a "composite" should be higher than that of the soft core.

Now, we provide a quantitative evaluation of the yield strength of the "crust–core" composite shown in Fig. 7, which consists of a "soft" (unaffected) core and a "hard" (oxidation-affected) surface layer. Strictly speaking, the "crust" gradually changes into the "core", as shown in Fig. 1(c), but for simplicity, here we consider an ideal case that the change from the crust to the core is sudden so that both the crust and the core have uniform mechanical strength within their own regimes. Under such an approximation, our problem becomes a simple mechanics problem. Because the core part and the surface layer are always connected during the deformation, the surface part and the core part must have the same strain during the deformation (this is the so-called "iso-strain condition"). When such a "composite" is loaded, according to the rule of mixing [13] for iso-strain loading, we can obtain the nominal (observed) stress of the crust–core sample as:

$$\sigma = \sigma_{core}V_{core} + \sigma_{sur}V_{sur} = \sigma_{core} + (\sigma_{sur} - \sigma_{core})V_{sur} \qquad (1)$$

where σ_{core} and σ_{sur} represent the stress on the core part and on the surface oxidation-affected layer, respectively, and V_{core} and V_{sur} represent the volume fraction of the core part and the oxidation-affected layer relative to the volume of the whole sample. It is noted that $V_{core} + V_{sur} = 1$.

With Eq. (1), we can make a quantitative calculation for the effect of oxidation-affected layer on the nominal detwinning stress, i.e., the measured yield stress of a crust–core composite. We take the 900 °C, 0.5 h annealed sample as an example. For this sample, we know the yield strength (due to martensite detwinning) of the core $\sigma_{core} = 155$ MPa from Fig. 1, and we take a typical yield stress of the B2 phase $\sigma_{sur} = 600$ MPa as the yield stress of the crust (due to dislocation slip). The

total sample diameter is $d_0 = 1.000$ mm with a core diameter of $d_{core} = 0.929$ mm. It follows that

$$V_{sur} = 1 - V_{core} = 1 - \left(\frac{d_{core}}{d_0}\right)^2 = 1 - \left(\frac{0.929}{1.000}\right)^2 = 0.137 \qquad (2)$$

Substituting V_{sur}, σ_{core} and σ_{sur} values into Eq. (1), we obtain the nominal detwinning stress $\sigma = 216$ MPa. Considering the approximation in deriving Eq. (1), the calculated value is in agreement with the experimentally observed value of 229 MPa. It is clear that the true detwinning stress (of the core) does not change with surface oxidation, and the observed increase in the "nominal detwinning stress" is simply due to a hardening effect of the oxidation-affected crust.

Having explained the reason for the increase of nominal detwinning stress with oxidation, now we explain why M_s is not affected by surface oxidation. As shown in Fig. 3, the oxidation-affected layer does not undergo martensitic transformation; thus, it is natural that the B2–B19′ transformation must start from the core part, which is not affected by oxidation; thus, the M_s of the crust–core composite equals that of the unaffected core, which is always the same, no matter how thick is the crust (but it cannot be so thick that the core is also affected). This also explains why M_s of the samples annealed in air is very similar to that annealed in Ar, as the core part of the surface oxidized sample is the same as unoxidized sample (Ar-annealed sample).

Our results indicate that even at high temperature, the thickness of the oxidation-affected layer is not thick, even when annealed in air, and the core part seems completely immune from the oxidation. This seems to confirm the previous observations on the good oxidation resistance of Ti–Ni alloys [14]. It is consistent with the fact that the detwinning stress of the core part of a surface-oxidized sample is the same as that of a well-protected sample. Finally, from the insentivity of the detwinning stress to annealing temperature and time in unoxidized samples (Fig. 5), we can deduce that detwinning stress is not sensitive to grain size, as different annealing condition results in different grain size.

5. Conclusions

In order to explain why the detwinning stress of Ti–50Ni alloys increases with the increasing temperature, the role of surface oxidation during the annealing was examined. Through a comparative study between Ti–50Ni samples annealed in air and those in Ar atmosphere (avoiding oxidation), the following conclusion were obtained:

(1) When Ti–50Ni samples were annealed in air, the detwinning stress increased significantly with annealing temperature and time, but M_s was almost unaffected by the annealing. However, when Ti–Ni samples were annealed in Ar, both the detwinning stress and M_s were insensitive to annealing temperature and time.
(2) The increase of detwinning stress with annealing was identified to be due to an oxidation layer generated during

annealing. Such a layer significantly hardens the material and causes an increase in nominal detwinning stress. The insensitivity of M_s temperature to surface oxidation stems from the fact that martensitic transformation starts from the sample's core part, which is immune from the oxidation.

Acknowledgments

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