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Effects of Deformation Strain and Aging Temperature on Strain Aging Behavior in a 304 Stainless Steel

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The effects of deformation strain and aging temperature on strain aging behavior in a 304 stainless steel were investigated. Age hardening of a cold-rolled 304 stainless steel was significantly influenced by the amount of α'-martensite as well as aging temperature. The similar variation of tensile strength to the amount of α'-martensite with aging temperature indicated that tensile strength of an aged steel is significantly influenced by the amount of α'-martensite formed during cold deformation. The increase of strength during aging in a 304 stainless steel cold-rolled with 40 % reduction is attributed to the additional formation of α'-martensite at 450 °C as well as to the increase of hardness in both the α'-martensite and austenite phases.

Keywords: metals aging, mechanical properties, transmission electron microscopy (TEM)

1. INTRODUCTION

The transformation of austenite to α'-martensite during deformation is the most effective way to strengthen metastable austenitic stainless steel grades [1]. Aging treatment of cold-worked metastable austenitic stainless steels containing α'-martensite results in a further increase of strength, when aging is performed in the temperature range of 200 °C to 450 °C [2-5]. The proposed mechanisms for age hardening in cold-worked metastable austenitic stainless steels are (1) hardening of α'-martensite [2,3] and (2) the formation of additional martensite [4-6].

It is well known that deformed steels can be strengthened by the diffusion of interstitial carbon (C) and nitrogen (N) solute atoms dissolved in ferrite during aging at low temperatures [7,8]. Thus, it is anticipated that cold-worked metastable austenitic steels containing the body-centered martensite (α'-martensite) phase may also be strengthened in a similar manner. Rathbun *et al.* [2] reported that neither the change in the volume fraction of α'-martensite nor the aging behavior in deformed austenite was observed during low temperature aging. The increase of tensile strength during aging is likely associated with strengthening of α'-martensite that contains a high density of dislocations. However, Mangonon and Thomas [5] reported that tensile strength increased with the thermal nucleation of α'-martensite during aging up to 400 °C. According to Mukhopadhyay *et al.* [6], the increase of tensile strength is closely related to the formation of α'-martensite occurring during cooling after aging. Since the precipitation of fine carbides causes the depletion of chromium and carbon in the surrounding matrix, a local increase of the Ms temperature in the surrounding matrix would be responsible for the formation of α'-martensite during cooling. From the above, it is concluded that age hardening of metastable stainless steels is closely related to the presence of α'-martensite phase, regardless of proposed aging mechanisms. Thus, it was expected that the degree of hardening during aging would be influenced by the amount of α'-martensite phase in cold-worked 304 stainless steels.

Thus, to investigate hardening behavior of a cold-worked 304 stainless steel during strain aging, the current study investigated the effects of deformation strain and aging temperature on strength and the amount of α'-martensite. Additionally, the kinetics of strain aging in cold-worked metastable austenitic stainless steels, were also examined with microstructural changes.

2. EXPERIMENTAL PROCEDURES

The chemical compositions of the 304 stainless steel used in this work were 0.057C, 0.376Si, 1.08Mn, 18.14Cr, 8.14Ni, 0.305Cu, 0.146Mo, and 0.033N (in wt.%). The steel was available in the form of a 3 mm thick cold-rolled and annealed sheet with an as-received austenite grain size of 36.8 μm.

To produce the different volume fractions of deformation-

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induced martensite, samples were cold-rolled by 16 % and 40 % (with 16 % reduction per pass). Aging treatment was performed on cold -rolled stainless steel sheets in a heated salt bath in a temperature range of 200 °C to 700 °C for an hour. Small rectangular specimens were cut from the cold-rolled and aged samples for X-ray diffraction analysis using Cu Ka radiation. To assess the effect of surface constraints on the transformation response, diffraction patterns were obtained on samples chemically thinned to remove specific fractions of the sheet thickness. The solution used for surface removal was a mixture of hydrochloric acid, nitric acid, and distilled water in 1:1:1 proportion.

The amount of α'-martensite was also measured using Ferritescope. Ferritescope readings were converted to the amount of α'-martensite by multiplying by a factor of 1.7 according to Talonen's work [9].

The amount of α'-martensite = 1.71 × Ferritescope reading (1)

Tensile tests were performed at room temperature with a constant displacement speed. The initial strain rate was 6.7×10^{-4}/s. For a detailed understanding of the microstructural evolution during aging, a transmission electron microscope (TEM) was used to analyze thin foils obtained from samples aged at various temperatures. Thin foils parallel to the longitudinal cross section of the sheets were prepared utilizing a conventional jet-polishing technique.

Thermal analysis was performed with a differential scanning calorimeter under a flowing Ar atmosphere. As the DSC peak position depends on the heating rate [10], the measured data from the peak positions for different heating rates of 2 °C/min to 16 °C/min were used. To obtain the activation energy, both the Kissinger [11] and Chen and Spaepen [12] methods were applied in this work. To understand the kinetics during heating, stainless steel sheets were sealed in an Al pan and heated to the desired temperatures at a rate of 4 °C/min and were then rapidly cooled in water. According to the methods [11,12], the heating rate (B), the apparent activation energy of the process (Q), and the maximum temperature of the peak T_p are related by the equation

$$\ln(\alpha) = -\frac{Q}{k_B T_p} + C \qquad (2)$$

where k_B is the Boltzmann's constant and C is an integration constant.

3. RESULTS AND DISCUSSION

3.1. The variation of mechanical properties

Figure 1 shows the effects of aging temperature and deformation strain on tensile strength and yield strength of 304 stainless steels cold-rolled and subsequently aged for 1 h. For stainless steels that received 40 % reduction, tensile strength increased continuously with aging temperature up to 450 °C, and then decreased rapidly [13]. Especially, the increment of tensile strength at the peak temperature of 450 °C reached about 140 MPa, compared with cold-rolled steels. The peak temperature of yield strength was observed around 400 °C, and subsequently decreased with aging temperature. However, in stainless steels that received 16 % reduction, the behavior of tensile strength with aging temperature was quite different from that in stainless steels that received 40 % reduction. Tensile strength and yield strength of 304 stainless steels cold-rolled with 16 % reduction did not demonstrate a noticeable variation of strength for the aging temperature range up to 600 °C.

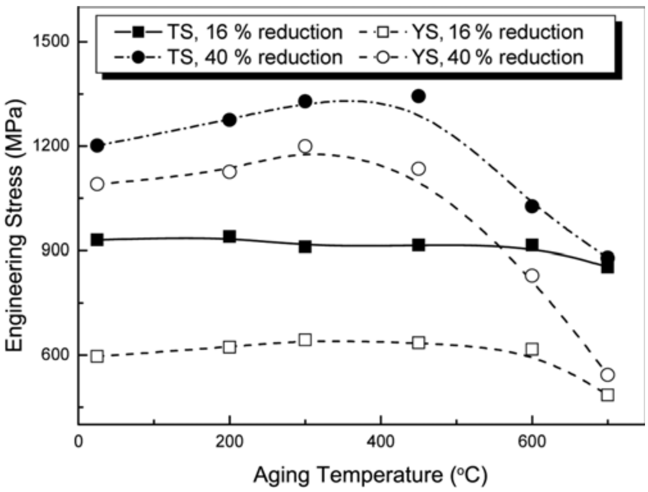

Fig. 1. Effects of aging temperature and deformation strain on tensile strength and yield strength of cold rolled 304 stainless steels received 16 % reduction and 40 % reduction, respectively. Samples were aged for an hour.

Since the larger deformation strain results in the increased amount of α'-martensite in a 304 stainless steel, it was expected that different amounts of α'-martensite would cause different strengthening behavior during aging. The amount of α'-martensite calculated from Ferritescope readings is shown in Fig. 2. The amount of α'-martensite in a sample that received 16 % reduction was as small as 4 %, compared with 45.5 % for the sample that received 40 % reduction. The amount of α'-martensite increased from 45.5 % for a cold-rolled sample to 50 % for an aged sample at 450 °C. This increase in the amount of α'-martensite with aging provides evidence for the additional formation of α'-martensite during aging [4-6], although its amount was less noticeable. Meanwhile, there was little variation in the amount of α'-martensite with aging temperature for the sample that received 16 % reduction.

The similar shapes between tensile strength and the amount of α'-martensite shown in Figs. 1 and 2 indicate that the increment of tensile strength during aging is closely related to the variation in the amount of α'-martensite. Additionally, it was found that the strain aging response was significantly

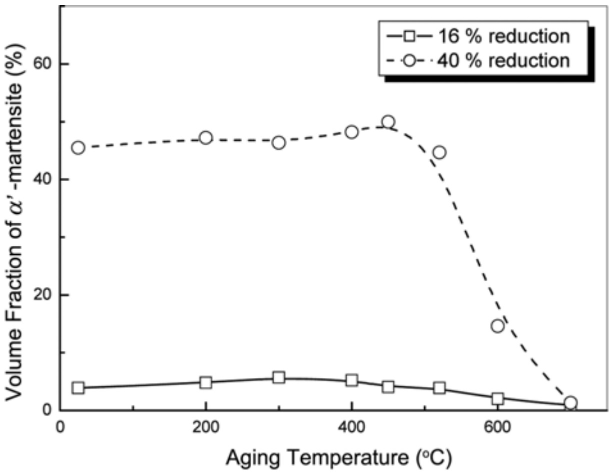

Fig. 2. Effects of aging temperature and deformation strain on the amount of α'-martensite in cold rolled 304 stainless steels.

influenced by the amount of α'-martensite produced during cold deformation. However, it is difficult to conclude that only an increase in the amount of α'-martensite contributed to the increase of strength in the aged samples. Assuming that the hardness of α'-martensite does not change during aging, the increasing amount of α'-martensite from 45.5 % (cold-rolled) to 50 % (aged at 450 °C), likely caused the increment of tensile strength, 140 MPa. This increasing rate of tensile strength with the amount of α'-martensite is too large, compared with 1200 MPa of tensile strength in a cold-rolled sample containing 45.5 % volume fractions of α'-martensite. Thus, there must be other factors that influenced the tensile strength of the aged samples.

The shapes of the stress-strain curves in Fig. 3 were significantly affected by the amount of α'-martensite. Samples that received 16 % reduction showed little variation of stress-strain curves with aging temperature. Meanwhile, aging of the samples that received 40 % reduction caused an increase of strength and a reduction of elongation, compared with the cold-rolled sample. It is significant that as aging temperature increased, not only tensile strength but also elongation increased in samples that received 40 % reduction. Generally, an increment of tensile strength results in the decrease of elongation. Han, *et al.* [14,15] reported that tensile strength and elongation of metastable austenitic steel increased as the void nucleation site during the tensile test decreased. Accordingly, if aging reduced the void nucleation sites during tensile tests in samples with the same martensitic fraction, both the tensile strength and elongation may increase.

Generally, a cold-rolled 304 stainless steel is characterized by microstructures mainly consisting of a dispersion of hard martensite in a deformed austenite matrix. Figure 4 shows the microstructures of 16 % and 40 % deformed 304 stainless steels. Deformation with 16 % reduction causes less density of micro-twins (Fig. 4(a)), resulting in a small amount of α'-martensite nuclei formed at the intersections of micro-twins (Fig. 4(b)). Meanwhile, 40 % deformed 304 stainless steel reveals deformed austenite with micro-twins (Fig. 4(c)) and α'-martensite with high density of dislocations (Fig. 4(d)). Closer examination of the XRD patterns of a 304 stainless steel deformed 40 % and aged at various temperatures reveals that phase transformation does not occur during strain aging up to 450 °C (Fig. 5).

To understand the behavior of austenite and α'-martensite during aging, the hardness of each phase was measured

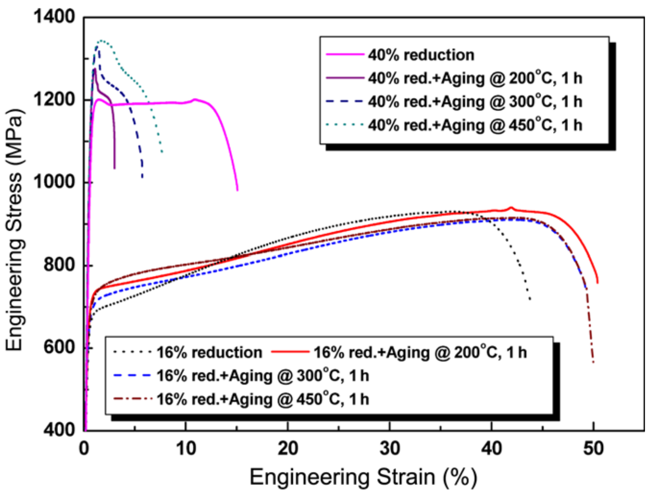

Fig. 3. Effects of aging temperature and deformation strain on engineering strain-stress curves of 304 stainless steels cold rolled with 16 % reduction and 40 % reduction, respectively.

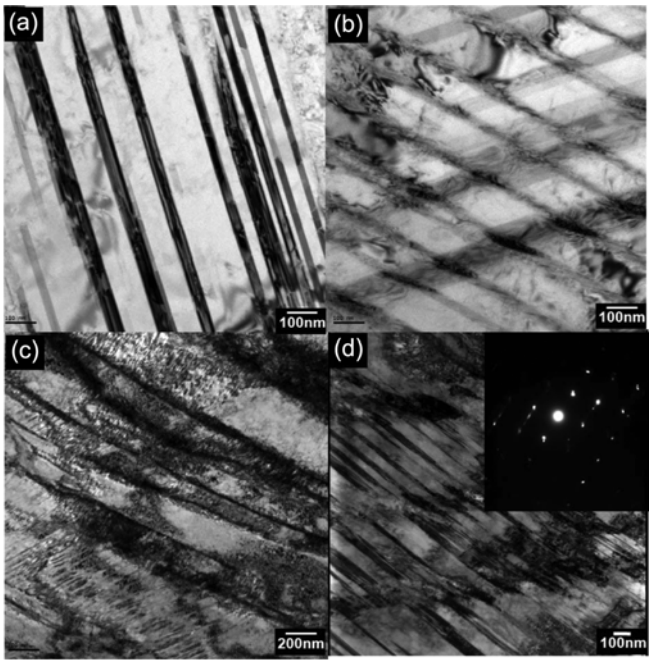

Fig. 4. TEM micrographs of 304 stainless steels deformed at room temperature (a), (b) with 16 % reduction and (c), (d) with 40 % reduction.

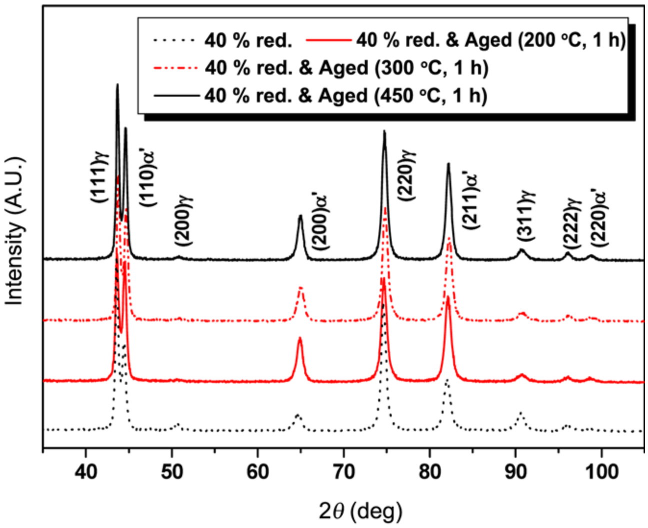

Fig. 5. X-ray diffraction scan using Cu Kα radiation of a 304 stainless steel deformed at room temperature with 40% reduction, showing the presence of α'-martensite and austenite phases.

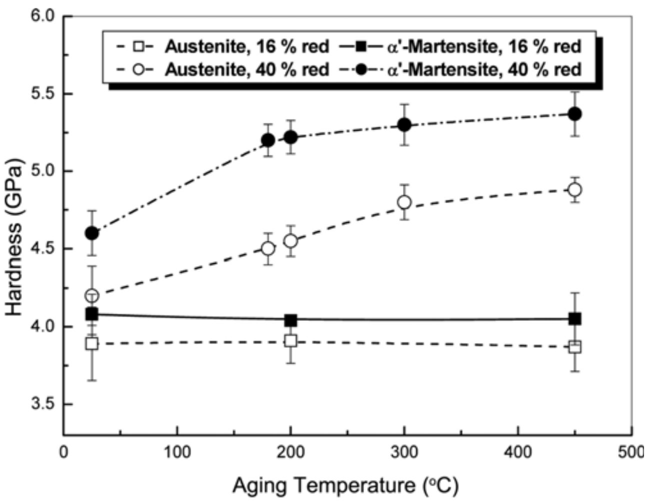

Fig. 6. The hardness of austenite and α'-martensite in 304 stainless steels cold rolled and heated to 180 °C, 200 °C, 300 °C and 450 °C with the heating rate of 2 °C/min.

using a nano-indenter (Fig. 6). For the sample that received 16% strain, there was little variation of hardness of austenite and α'-martensite with aging temperature. However, for the sample received 40 % strain, hardness of α'-martensite phase increased from 4.6 GPa (cold-rolled) to 5.4 GPa (aged at 450 °C) by 17.4 %, while that of austenite phase increased from 4.2 GPa to 4.8 GPa by 14.3 %. The rapid increase of hardness in α'-martensite for the sample heated up to 180 °C indicates that the interaction of carbon atoms with dislocations in α'-martensite is the main factor in the increase of strength during aging. However, when the heating temperature increased up to 300 °C, the hardness of α'-martensite increased only slightly, due likely to the occurrence of carbide precipitation and recovery in α'-martensite. The decrease of hardness in the sample heated to 450 °C indicates the operation of recovery in α'-martensite. Meanwhile, hardness of austenite increased steadily up to 300 °C, due possibly to the interaction of solute carbon atoms with dislocations and micro-twins in deformed austenite during aging.

Cold-rolled 304 stainless steels containing 45.5 % martensite volume fraction show more pronounced age hardening behavior than cold rolled 304 stainless steels containing 4 % martensite volume fraction for temperatures ranging from 25 °C to 450 °C. This is due to the presence of different amounts of martensite in both steels.

This suggests that the increment of strength during aging is significantly influenced by the amount of α'-martensite in cold-rolled stainless steels and that age hardening operates more effectively in α'-martensite than in deformed austenite.

3.2. Kinetics during aging

A differential scanning calorimeter (DSC) was used to investigate the kinetics of aging in cold-rolled 304 stainless steels. Both DSC curves in Fig. 7 show similar temperatures for three exothermic peaks, representing the different stages that occurred during aging of 304 stainless steels deformed with 16 % reduction and 40 % reduction. The temperature range was 100 °C to 160 °C for the first peak, 190 °C to 310 °C for the second peak, and 370 °C to 460 °C for the third peak, respectively. The apparent activation energy (Q) of the DSC peaks, obtained by analyzing the Kissinger plot shown in Fig. 8, was obtained as 67 kJ/mol to 70 kJ/mol for the first peak, 133 kJ/mol to 138 kJ/mol for the second peak, and 510 to 516 kJ/mol for the third peak.

The Q value of the first peak, 67 kJ/mol to 70 kJ/mol, corresponds to the activation energy for the diffusion of carbon atoms in ferrite, 66.9 kJ/mol [16,17], indicating that the occurrence of the first peak of aging is controlled by the migration of interstitially dissolved carbon atoms to dislocations in α'-

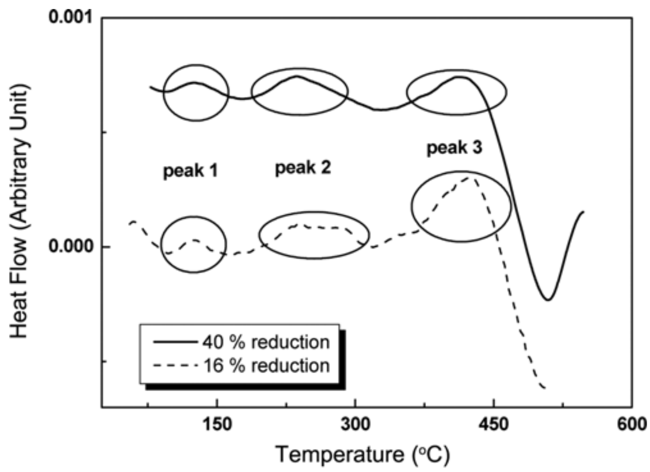

Fig. 7. DSC curves of samples cold rolled with 16 % reduction and 40 % reduction, and heated with the rate of 4 °C/min.

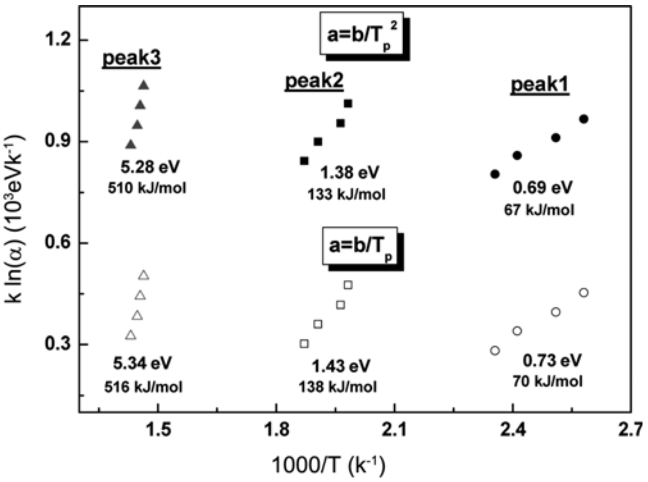

Fig. 8. Calculated apparent activation energy using Kissinger plot of the maximum peak temperatures in the DSC curves of samples cold rolled with 40 % reduction.

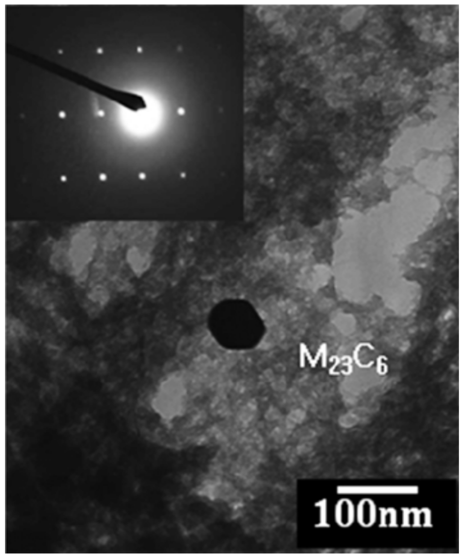

Fig. 9. A TEM micrograph, showing the presence of precipitates in a 304 stainless steel deformed with 40 % reduction and aged at 450 °C for 1 h.

martensite. At low aging temperatures, carbon atoms diffuse to neighboring dislocations and lock them in α'-martensite. The dislocations are locked by solute atmospheres and higher strain levels are required to produce free dislocations for further plastic flow. Thus, the interaction of carbon atoms with dislocations in α'-martensite would result in a rapid increase of hardness in α'-martensite when heated to 180 °C for a stainless steel that received 40 % reduction (Fig. 6). However, in the sample that received 16 % reduction, the absence of the hardness increase of α'-martensite during aging can not be readily explained. However, it seems probable that a small amount of carbon atoms dissolved in small-sized α'-martensite nuclei formed at the intersection of micro-twins (Fig. 4(b)) can not effectively hinder the movement of dislocations.

Meanwhile, the apparent activation energy of the second peak, 133 kJ/mol to 138 kJ/mol, coincides with the activation energy for carbon diffusion in austenite, 134 kJ/mol to 136 kJ/mol [18]. According to Fujita *et al*. [19], the segregation of solute atoms on the stacking fault known as the Suzuki effect can occur in both deformed and annealed 304 stainless steel. Thus, the presence of the second peak (190 °C to 310 °C) is likely related to the segregation of solute carbon atoms to dislocations and micro-twins in deformed austenite during aging. Accordingly, as shown in Fig. 6, the hardness of austenite increases steadily up to 300 °C in a sample that received 40 % reduction, while the little variation of hardness with aging temperature in a sample that received 16 % reduction might be attributed to the low density of micro-twins in deformed austenite, as shown in Fig. 4(a).

The measured activation energy of the third peak, 510 kJ/mol to 516 kJ/mol, seems significantly larger than the reported Q values available for steels, such as the Cr diffusion in an austenite phase (405 kJ/mol), the Cr diffusion in a ferrite phase (343 kJ/mol) [20], and the self-diffusion of deformed ferrite (239.7 kJ/mol) [21]. There is no clear explanation regarding the mechanism of the third peak. The occurrence of the third peak in the temperature range of 370 °C to 460 °C might be related to one or more of microstructural evolutions that occurred at high temperatures, such as recovery of α'-martensite, the precipitation of carbides, or the additional formation of α'-martensite during aging. The activation energy of the third peak, 510 kJ/mol to 516 kJ/mol, has the order of magnitude of the sum of the apparent activation energy for carbon diffusion in austenite and for Cr diffusion in austenite, 538 kJ/mol to 543 kJ/mol. Additionally, the presence of carbide precipitates at dislocations (Fig. 9) and the increased volume fraction of α'-martensite at 450 °C (Fig. 2) is most likely closely related to the occurrence of the third peak shown in Fig. 7. Thus, although the current authors do not have exact physical insight at this stage of their investigations, the diffusion of carbon and Cr atoms in austenite, which is related to the depletion of carbon and Cr in the surrounding matrix caused by the precipitation of fine carbides [6], is the likely candidate for the mechanism of the third peak.

4. CONCLUSION

The effects of deformation strain and aging temperature on strength and the amount of α'-martensite in cold-rolled 304 stainless steels were investigated.

Age hardening of a cold-rolled 304 stainless steel was significantly influenced by the amount of α'-martensite as well as aging temperature. Tensile strength increased continuously up to 1344MPa at an aging temperature of 450 °C, and then decreased in a steel that received 40 % reduction, while tensile strength did not demonstrate a noticeable variation of strength for the whole aging temperature range up to 600 °C in the steel that received 16 % reduction.

The increased amount of α'-martensite during aging at 450 °C provides the evidence for the additional formation of α'-martensite in the steel that received 40 % reduction. For a deformed 304 stainless steel that received 40 % reduction, the hardness values of both the α'-martensite and austenite phases increased in accordance with the aging temperature. Thus, the increase of strength during aging in a cold-rolled 304 stainless steel with 40 % reduction is attributed to the additional formation of α'-martensite at 450 °C as well as to the increase in hardness in both the α'-martensite and austenite phases.

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