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Anomalous hardening and microstructural evolution accompanied by reordering and restoring of plastically deformed Co_3Ti

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ABSTRACT

The anomalous hardening and microstructural evolution accompanied by the reordering and restoring of cold-rolled Co_3Ti alloy annealed at 573–773 K were investigated by hardness testing, SEM and TEM observations, XRD analysis and DSC measurements. The hardening observed in the heavily cold-rolled samples was similar to that observed in precipitation reactions, with the hardness increasing with increasing annealing time to a point and then decreasing. The hardness peak occurred more rapidly at higher annealing temperatures, and the annealing time leading to this peak was insensitive to the degree of cold-rolling reduction. The stored lattice strain evaluated from the half-width of the X-ray reflection peak steadily decreased with increasing annealing time but remained relatively high regardless of the degree of cold-rolling reduction or annealing temperature. The TEM deformation microstructures showed that a high density of dislocations was attained, even in an over-aged state. DSC measurements showed two exothermic peaks at low and high temperatures, which were attributed to the annihilation of point defects and/or reordering and to the rearrangement of dislocations, respectively. The observed anomalous hardening was discussed in association with the reordering of the mechanically disordered structure and the restoring of the plastically deformed microstructure.

1. Introduction

Co_3Ti alloy with an $L1_2$ structure (a=0.3605 nm) is stable up to its melting point and has a non-stoichiometric solid solution range in a Co-rich region [1,2]. The Co_3Ti alloy can be plastically deformed in polycrystalline form [3,4], unlike a number of intermetallic alloys, and exhibits significantly high strain hardening at ambient temperature [3,4]. Previous microstructural observation combined with isochronal hardness testing has shown that recrystallization takes place by the nucleation and growth of new grains from the deformed matrix and results in softening [3], as in ordinary disordered alloys. In the recovery stage prior to recrystallization, an anomalous hardening exceeding the hardness level of the as-rolled state has been observed at intermediate temperatures near 673 K [3]. Similar hardening behavior has also been observed in cold-rolled Ni_3Al [5] and $Ni_3(Si,Ti)$ [5,6] alloys, which plastically deformed and showed high strain hardening at room temperature.

In thermally disordered 'ordered alloy' obtained by rapid quenching from high temperature above an order–disorder temperature, *Tc*, excess vacancies are present, affecting various physical and mechanical properties. In plastically deformed 'ordered alloys' and intermetallic compounds, impaired ordered structure, dislocations and excess (athermal) vacancies are present. Accordingly, reordering of the impaired ordered structure; restoration, such as the annihilation of athermal vacancies; and the rearrangement and/or annihilation of dislocations have to proceed during annealing. During the annealing of ordinary deformed disordered alloys, consideration of the reordering process has not been necessary.

In this study, anomalous hardening at intermediate temperature is investigated by isothermal experimentation on cold-rolled Co_3Ti alloy. The observed hardening during the reordering and restoring processes of the cold-rolled Co_3Ti alloy is characterized by hardness testing, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations, differential scanning calorimetry (DSC) measurements and X-ray diffraction (XRD) analysis. The observed anomalous hardening was discussed in association with the reordering of the mechanically disordered structure and the restoring of the deformed microstructure.

2. Experimental procedures

The alloy used in this study was comprised of a nominal composition of $Co_{77}Ti_{23}$ (expressed as at%), which lies in the

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middle of the $L1_2$ solid solution range. The off-stoichiometric (i.e., excess) Co atoms have been known to behave as anti-site defects [1,2]. The purities of raw materials used were 99.99 wt% for Co and 99.9 wt% for Ti. The alloy was obtained by arc melting in an argon gas atmosphere on a copper hearth using a non-consumable tungsten electrode. The raw materials were melted more than three times to ensure chemical homogeneity and cast into a $50 \times 25 \times 15\ mm^3$ mold. After homogenization in vacuum at 1323 K for 48 h, plate-like materials (with a thickness of approximately 10 mm) sliced from the arc-melted button were rolled in air at 773 K and then annealed in vacuum at 1273 K for 5 h. This procedure was repeated several times until a sheet thickness of approximately 5 mm was obtained. The sheet material was finally annealed in vacuum at 1273 K for 5 h to prepare the starting materials for subsequent cold-rolling. By cold-rolling without intermediate annealing, sheets with thicknesses of 3, 2 and 0.5 mm were obtained, corresponding to rolling reductions of 40%, 60% and 90%, respectively. In the following, these samples are referred to as 40%, 60% and 90% cold-rolled samples, respectively.

The cold-rolled samples were isothermally annealed in a salt bath ($NaNO_2$:KNO_3=1:1) at 773 K, 673 K and 573 K for predetermined durations and then quenched in water. The salt bath was used to achieve a quick temperature response to a predetermined annealing temperature. The annealing behavior was evaluated by micro Vickers hardness testing. The annealed samples were mechanically abraded and polished on SiC paper. The hardness data for more than 12 points were collected using a load of 0.5 kgf and a holding time of 10 s and then averaged after removing the highest and lowest values for each experimental condition.

The specimens used for SEM observation were abraded on SiC paper and electrolytically polished in a mixture of 15 ml of H_2SO_4 and 85 ml of CH_3OH at 243 K for 60–90 s, followed by etching for 5 s in a mixture of 250 ml of HCl, 250 ml of H_2O and 50 g of $CuSO_4$ (Marble's reagent) at approximately 300 K. The SEM observation was performed using a JEOL JSM-7001F operated at an accelerated voltage of 10 kV. The specimens used for TEM observation were first cut normal to the rolled surface with a diameter of 3 mm and then mechanically thinned to less than 0.1 mm. They were then jet-polished in a mixture solution of 15 ml of H_2SO_4 and 85 ml of CH_3OH at 253 K. The TEM observations were carried out using a JEM-2000FX operating at 200 kV. Selected-area aperture with a diameter of 200 nm was generally used to obtain the selected-area diffraction patterns (SADPs).

The specimens used for XRD analysis were abraded parallel to the rolling surface using SiC paper and then simply rinsed in acetone. The XRD measurements were carried out to determine the relative degree of long-range order, S, and stored lattice strain using a CuKα target with an accelerated voltage of 40 kV. In this study, the relative degree of long-range order, S, was defined by the following equation:

$$S = (I'_{110}/I'_{220})/(I_{110}/I_{220}) \quad (1)$$

where I'_{110} and I'_{220} are the integrated intensities of the 110 superlattice and 220 fundamental lattice reflections of the cold-rolled samples, respectively, while I_{110} and I_{220} are the corresponding values for the samples that were fully annealed at 1323 K for 48 h. The stored lattice strain was evaluated from the X-ray half-width $\Delta\theta$ of the 220 fundamental lattice reflection of the samples.

The specimens used for DSC measurements were cut normal to the rolled surface with a diameter of 5 mm, abraded on SiC paper and then rinsed in acetone. The DSC measurement was conducted in argon gas flow at heating rates of 5, 10, 15 and 20 K/min from 298 K to 1073 K.

3. Results

3.1. Vickers hardness

Fig. 1a shows the change in Vickers hardness with increasing cold-rolling reduction. The hardness increased parabolically with increasing cold-rolling reduction from 179 HV at 0% reduction to 702 HV at 90% reduction. This result reflects the high strain hardening observed at room temperature in tensile-deformed Co_3Ti alloys [4,7].

Fig. 2 shows the changes in the Vickers hardness with annealing time for the cold-rolled samples annealed at 773 K, 673 K and 573 K. The heavily (90%) and moderately (60%) cold-rolled samples displayed anomalous hardening, while the lightly (40%) cold-rolled sample displayed monotonous softening, not anomalous hardening. Regarding the heavily and moderately cold-rolled samples, the curves were similar to the age-hardening curves observed for precipitation reactions in disordered alloys. With

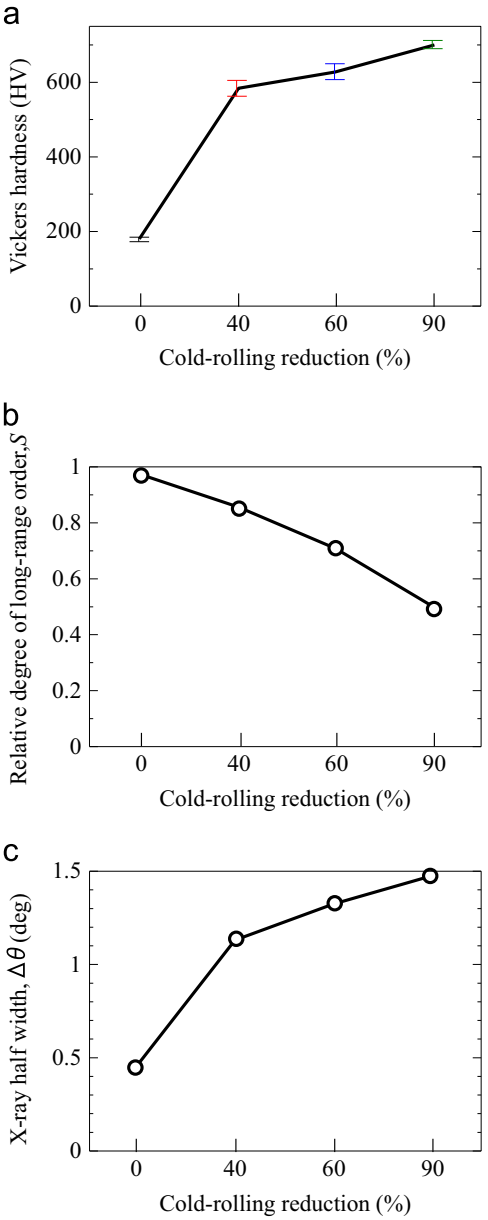

Fig. 1. Changes in (a) Vickers hardness, (b) relative degree of long-range order S and (c) X-ray half-width of the (220) reflection with increasing cold-rolling reduction.