Effect of annealing on cold-rolled Ni–Ti alloys

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Abstract

In this paper, we present a study on the effect of annealing a cold-rolled near-equi-atomic Ni–Ti alloy strip by transmission electron microscopy. Transmission electron microscopy of the as-received sample shows the presence of alternating amorphous and crystalline bands. The crystalline bands have widths of the order of a few microns and contain B2 nanograins of around 20 nm diameter, which are preferentially oriented along the [1,−1,−1] direction, normal to the rolling direction. As-received samples were annealed for 30 min at different temperatures up to 800 °C. With the increase in annealing temperature, crystallization starts in the amorphous bands at around 350 °C and finally ends up with the coarsening of the grains in the entire sample. The annealing of the samples at 450 °C entirely transforms the amorphous bands to crystalline bands and as off 600 °C Ni3Ti2 precipitates are formed. At 800 °C the grain size increases to 30–50 μm. Diffraction patterns from such grains reveal the presence of diffuse intensity around reciprocal lattice positions 1/3(1 1 0)∗ indicating the formation of the R-phase.

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1. Introduction

Control of the functional properties of the Ni–Ti alloys by a mere changing of the composition cannot resolve remaining problems for particular applications. An alternative way to control and improve the functional properties lies in the use of thermomechanical treatment. Especially, low temperature annealing following appropriate cold deformation is one of the effective methods for controlling shape memory alloy (SMA) properties [1,2]. A particular property of the Ni–Ti system is its ability towards solid-state amorphization. Nanocrystallization/amorphization can be accomplished in many ways like mechanical alloying [3], cold rolling [4], electron beam irradiation [5], ion beam bombardments etc. In this paper we present microstructural investigations on a severely cold-rolled and post-annealed Ni–Ti SMA.

2. Experimental procedure

A 40% cold-rolled Ni–Ti ribbon (3 mm wide and 100 μm thick) was annealed for 30 min at different temperatures (350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C and 800 °C) in an argon atmosphere and subsequently furnace cooled to room temperature. Transformation temperatures were measured by differential scanning calorimetry (DSC) with a heating and cooling rate of 10 K/min followed by an isothermal treatment for 5 min at the extreme temperatures of −50 °C and 400 °C. For transmission electron microscopy (TEM), samples were spark cut in 3 mm diameter discs which were mechanically polished with emery paper to remove the oxide layer. Mechanically polished discs were subjected to thinning by electropolishing with a twin jet polisher and an electrolyte of 90% methanol and 10% sulphuric acid. During electropolishing the electrolyte temperature was maintained at 9 °C and the potential applied was 20 V. Three different microscopes were used for TEM characterization: a Philips CM20 microscope was used for conventional microscopy and energy-dispersive X-ray (EDX) measurements, a LaB6 JEOL 4000EX microscope was used for high-resolution electron microscopy (HREM) and a CM30 microscope equipped with a field-emission gun was...
used for electron-energy-loss spectroscopy (EELS) measurements.

3. Results

Fig. 1 shows the DSC measurement on the as-received 40% cold-rolled Ni–Ti alloy. During the first heating run, it reveals an apparent change of baseline between 100°C and 150°C for which no microstructural explanation could be found, followed by a broad exothermic peak with a maximum at around 350°C. After cooling from 400°C, an exothermic peak appears around room temperature. In a second heating run, after cooling to −20°C, an endothermic peak appears around room temperature without almost any hysteresis, indicating that these peaks belong to the R-phase. The present DSC temperature range thus does not include a martensitic transformation, which could still occur below −50°C, the lowest temperature down to which the DSC measurement was performed. Further heating to 400°C reveals a flat baseline (without any shift as in the first run).

Fig. 2a shows a transmission electron micrograph of the as-received sample. The micrograph reveals the presence of alternating nanocrystalline and amorphous bands. The nanocrystalline bands (marked as ‘NC’) have widths of the order of a few micrometers and the amorphous regions (marked as ‘A’) have widths of a few tens of nanometers. These amorphous bands contain an amorphous matrix of Ni–Ti (as conformed by EELS measurements) with some residual nanograins. In the nanocrystalline regions the nanograins are surrounded by amorphous regions as confirmed by HREM (shown as inset in Fig. 2a) and have an average grain size of 20 nm. Selected area diffraction patterns (Fig. 2b) taken from the nanocrystalline bands reveal that the nanograins have the B2 structure and are preferentially oriented along the [1,−1,−1] direction, which is normal to the rolling direction. EDX measurements show that the sample contains 50.2 at.% of Ni and 49.8 at.% of Ti. In-situ cooling to liquid nitrogen temperature did not induce any martensitic transformation in the electropolished samples.

A sample annealed at 350°C for 30 min shows more or less the same kind of morphology as the as-received sample. The average grain size of the nanograins is still 20 nm with alternating amorphous and nanocrystalline bands. In samples annealed at 400°C, an increase in the grain size is observed and the average grain size as measured form bright and dark field images is 80 nm. Fig. 3a also shows the growth of nanograins in the amorphous band, which shows that the crystallization has started. The appearance of polycrystalline rings in the diffraction pattern (Fig. 3b) indicates that the sample has lost its texturing but the nanograins still preserve the parent B2 structure. On further heating to 500°C the amorphous regions have completely crystallized and still preserve the B2 structure.

Samples annealed at 600°C (Fig. 4) show coarsening of the grains and also the formation of precipitates at the grain bound-
Fig. 3. (a) Transmission electron micrograph of 400 °C annealed sample. Arrows show the crystallization of amorphous bands (b) corresponding diffraction pattern showing loss of texture.

Fig. 4. Transmission electron micrograph of 600 °C annealed sample. Arrows represent Ni$_3$Ti$_2$ precipitates. These precipitates form at the grain boundaries.

4. Discussion

The image of Fig. 2 shows that by cold rolling the Ni–Ti alloy transforms into a nanostructured material. From the DSC runs it is concluded that the martensitic transformation is suppressed due to this nanostructuring, as the Ni-concentration is only slightly above 50% thus normally expecting a martensite-start temperature $M_s$ of 13 °C [8]. The decrease in transformation temperature with the decrease in grain size can be attributed to the lack of potent internal nucleation sites [9], although this is hard to quantify in the case of nanostructures due to the increase in nucleation sites at the grain boundaries [10]. On the other hand, it has been suggested that the grain boundaries impose constraints on the martensite formation thus raising the B19’ free energy above that of the R-phase, explaining the observation of the latter at room temperature [11]. During annealing, crystallization of the amorphous regions to B2 phase occurs as of 350 °C which is lower as compared to thin amorphous Ni–Ti film [6]. It can thus be concluded that the low thermal stability of the amorphous phase as formed by cold rolling is caused by the retained nanocrystalline residues triggering crystallization by acting as heterogeneous nucleation sites leading to a high nucleation rate. As the annealing temperature increases the growth rate also increases and finally at moderately high temperature grain coarsening starts and the nanograins transform into big grains of the size of a few microns. Specific dislocation configurations such as dislocation walls or dislocation pile ups are generally considered as possible nucleation sites. However, we have not observed any kind of dislocations in our samples so we assume that grain boundaries or the residual grains act as the main nucleation sites for the crystallization. During high temperature annealing (∼600 °C) the Ni-rich (Ni$_3$Ti$_2$) precipitates start forming at the grain boundaries and the number of these precipitates increases with an increase in temperature. Nor-
Fig. 5. (a) Transmission electron micrograph of 800 °C annealed sample. Arrows represent larger Ni$_3$Ti$_2$ precipitates. (b) Two arrow heads in the diffraction pattern represents the direction along which the intensity line scan has been taken. (c) Intensity line scan showing two humps (marked by arrows) at 1/3 and 2/3 positions between the two major peaks indicating the formation of the R-phase.

5. Summary

The effect of plastic deformation and subsequent annealing on the microstructure of a Ni–Ti SMA is investigated. It has been found that the cold rolling of 40% apparently suppresses the martensitic transformation. Cold rolling introduces amorphization as well as stabilization of the B2 structure. Post-deformation annealing at or above 350 °C leads to the crystallization of amorphous regions. Formation of precipitates of Ni$_3$Ti$_2$ starts above 600 °C and at 800 °C the grain size increases to 30–50 μm with a formation of a tweed kind of morphology inside the grains as well as the R-phase.

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References