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Precipitation behavior and mechanical properties of Ti-Ni-Nb-Co alloys

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ABSTRACT

The $Ti_{44.5}Ni_{46.5-x}Nb_9Co_x$ (x = 0.5, 1, 2, 4) alloys were designated to investigate the effect of Co content and annealing treatment on the precipitation behavior and mechanical properties. The formation of nanoscale precipitates was being reported here for the first time in the Ti-Ni-Nb alloys due to the Co addition. For the $Ti_{44.5}Ni_{45.5}Nb_9Co_1$ and $Ti_{44.5}Ni_{44.5}Nb_9Co_2$ alloys, homogeneous GP zones and precipitates were observed at the lower annealing temperature. Additionally, the yield strength was enhanced by the higher strain field produced by the nano coherent precipitates. The effect of precipitation strengthening was weakened because of coarsened and clustered precipitates as annealing temperature increased. As a result, the highest yield strength of 520 MPa and the highest recovery stress of 482 MPa could be realized in the $Ti_{44.5}Ni_{44.5}Nb_9Co_2$ alloy annealed at 550 °C.

1. Introduction

Ti-Ni-based shape memory alloys (SMAs) with unique shape memory effect and pseudoelasticity have been widely used in the numerous fields [1,2], such as actuators [3], automobiles [4], aerospace and biomedical applications [5,6]. In particular, SMAs have been successfully applied in the pipe joint for hydraulic lines because of the simple installation and high fastening force. So far, Ti-Ni-Nb alloys gather much greater interest as the promising candidate on the aerospace couplings, which are characterized by wide hysteresis to bring more convenience for the practical engineering applications [7]. However, the main obstacle for becoming high recovery applications lies in the lower yield strength. Therefore, plenty of researches have focused on the improvement of the yield strength for Ti-Ni-Nb shape memory alloys.

As known, the introduction of dislocations by cold deformation is an effective method to improve the yield strength [8]. Recently, Tong et al. has found that ultra-fine grains and high density dislocations in Ti-Ni-Nb alloys, introduced via Equal Channel Angular Pressing processing, resulting in the increased yield strength, the maximum value as high as 450 MPa [9]. The proper addition of the quandary element into Ti-Ni-Nb alloys has also improved the yield strength by the solid solution strengthening effect [10,11]. In addition, The Ti-Ni-Nb alloys with low Nb contents exhibits the higher yield strength via controlling the eutectic structure of B2 parent phase and β-Nb phase [12–14].

Although the above-mentioned approaches can improve yield strength to a certain extent in the Ti-Ni-Nb alloys, the related mechanical properties fail to reach the engineering requirements as shape memory pipe couplings. Therefore, new methods or strategies to substantially enhance yield strength needs to be further figured out. The precipitation strengthening has been reported as an effective method to significantly improve the mechanical and recovery properties of other Ti-Ni-based alloys [15–18], whereas this method has never been applied in Ti-Ni-Nb alloys. H. Hosoda et al. previously reported the mechanical properties of ternary Ti-Ni alloys [19], where the alloy with minor addition of Co element possessed apparently excellent performance in comparison with all the previous studies via the solid solution strengthening effect. Additionally, the addition of Co contributed to promote precipitation in the Ti-Ni alloys that finally displayed outstanding mechanical and recovery properties by the precipitation strengthening [20,21]. Thus, it is highly expected that precipitation strengthening in the Ti-Ni-Nb alloys could be applicable to improve yield strength as well. Considering the two above advantages, Co is chosen as the alloying element to substitute Ni partially in the Ti-Ni-Nb alloys, which exhibits precipitation strengthening of yield strength. The effect of Co content and annealing treatment on the precipitation behavior and the mechanical properties of $Ti_{44.5}Ni_{46.5-x}Nb_9Co_x$ (x = 0.5, 1, 2, 4) alloys have been systematically investigated. It is demonstrated that the alloy with the proper Co content and annealing temperature can achieve the highest yield strength and best recovery properties. The related mechanism on the improved properties has also been clarified.

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2. Materials and methods

The initially as-cast $Ti_{44.5}Ni_{46.5\text{-}x}Nb_9Co_x$ (x = 0.5, 1, 2, 4) alloys (nominal composition) were fabricated on a non-consumable arc-melting furnace under Ar atmosphere using water-cooled crucible. Hereafter, each alloy was labeled as its Co content such as 0.5Co, 1Co, 2Co and 4Co. The raw materials were high purity of 99.9% Ti, 99.9% Ni, 99.95% Nb, 99.95% Co. The as-cast buttons were re-melted six times to ensure the homogeneity of the composition. Then the ingots were cut into different shapes for the different tests via electrical discharge machine. Afterwards, the samples with different Co content were annealed for 2 h in the temperature range from 550 °C to 750 °C. All the annealing treatment was done in the vacuum quartz tubes and then the annealed samples were quenched into the ice water.

The phase structure of all the samples was measured by X-ray diffraction (XRD) measurements with Cu K_α radiation. The microstructure was observed by Transmission Electron Microscopy (TEM). TEM observation was performed on FEI TECNAI G^2F30 STWIN equipped with a double-tilt cooling stage at the room temperature. The thin foils for TEM observation were first mechanically polished to about 100 μm and then double-jet electropolished in the electrolyte of methanol and sulfuric acid, 4:1 in volume, at around −30 °C. The phase transformation temperature was measured on a PerkineElmer Diamond differential scanning calorimeter (DSC) with constant heating/cooling rate of 20 °C/min. The mechanical properties were carried out on ThermoMechanical Analyzer at the room temperature and $M_s + 30$ °C. The dimensions of samples for tension and recovery tests were 20 mm × 1 mm × 1 mm and the strain rate is $4.0 \times 10^{-4} s^{-1}$. Afterwards, the $Ti_{44.5}Ni_{44.5}Nb_9Co_2$ sample annealed at 550 °C was loaded to the different pre-strain and also unloaded at $M_s + 30$ °C. The recovery strain and stress of all the samples were measured after heating over the temperature of A_f'.

3. Results and discussions

Fig. 1 shows room temperature XRD profiles of the as-cast and annealed $Ti_{44.5}Ni_{46.5\text{-}x}Nb_9Co_x$ (x = 0.5, 1, 2, 4) alloys. Totally, all the XRD profiles of as-cast alloys can be indexed as the diffraction peaks of B2 parent phase and β-Nb phase. This indicates that the no other phase is appeared in the as-cast Ti-Ni-Nb-Co alloys. Similar to the as-cast alloys as shown in Fig. 1a, no other peak can be detected in the 0.5Co alloys with different annealing temperature, either. However, when the 1Co and 2Co samples annealed at 650 °C and the 4Co sample annealed at 550 °C, a new diffraction peak can be clearly observed beside the main diffraction peak of B2 parent phase. Meanwhile, it can be noticed that the relative peak intensity of new diffraction peak increases with the increase of Co content and annealing temperature, which means the increasing quantities of new phase. It can preliminarily be indexed this new phase as the Ti-Co compound. The new phase will be further identified later in detail.

Fig. 2a shows the TEM bright field images and corresponding selected area electron diffraction (SAED) patterns of the as-cast 0.5 alloy. It can be seen that the microstructure consists of white and dark regions. The SAED pattern of white region can be indexed as Ti-Ni phase with lattice parameter of 0.3015 nm and body-center-cubic structure. Meanwhile, the SAED pattern of dark region can be indexed as β-Nb phase with lattice parameter of 0.3303 nm and body-center-cubic structure. Our indexed results are consistent with previous report [22]. As shown in Fig. 2b, c and d, except for Ti-Ni matrix and β-Nb phase, no precipitate and dislocation can be observed at the various annealing temperatures, which is in accordance with the XRD results.

Fig. 3 shows the TEM images and corresponding SAED patterns of the 1Co alloys annealed at different temperature. The contrast can be obviously observed in the grain interiors (Fig. 3a). But the contrast does not arise from the precipitates. From Fig. 3b, the corresponding diffraction pattern of Fig. 3a is in accordance with B2 parent phase taken from [001] zone. No extra diffraction spot can be observed, while there are diffuse diffraction streaks along $<010>_{B2}$ and $<100>_{B2}$

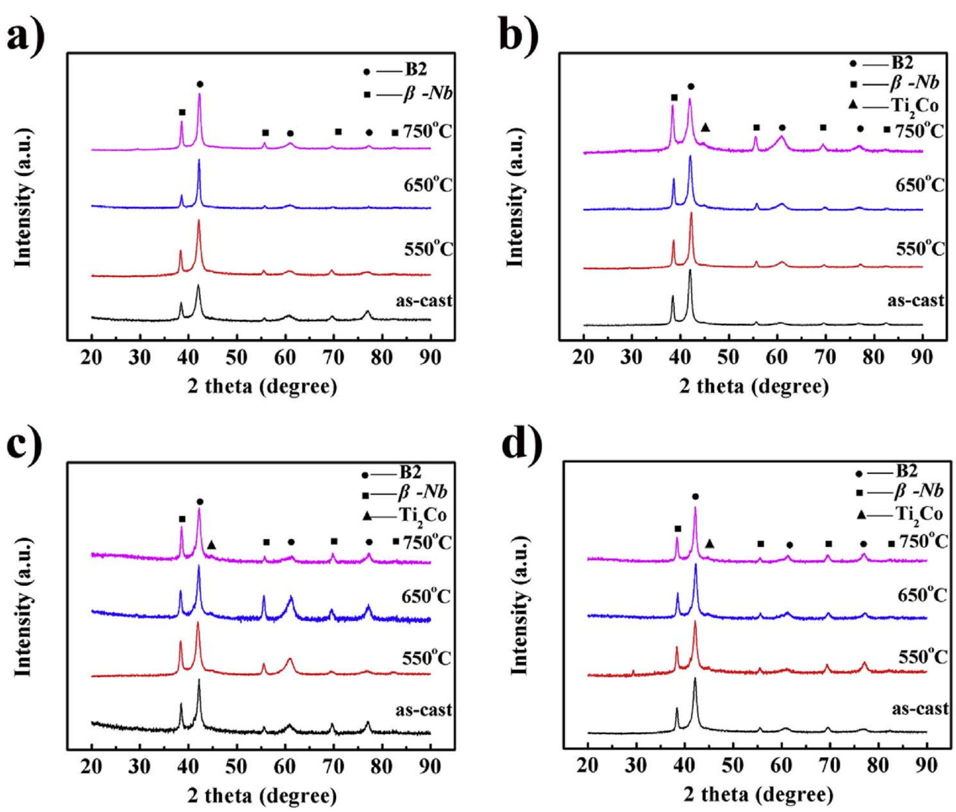

Fig. 1. Room temperature XRD profiles of the as-cast and annealed $Ti_{44.5}Ni_{46.5\text{-}x}Nb_9Co_x$ (x = 0.5, 1, 2, 4) alloys, (a) 0.5Co, (b) 1Co, (c) 2Co, (d) 4Co.