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Site occupation of Nb atoms in ternary Ni–Ti–Nb shape memory alloys

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Abstract

Nb occupancy in the austenite B2-NiTi matrix and Ti_2Ni phase in Ni–Ti–Nb shape memory alloys was investigated by aberration-corrected scanning transmission electron microscopy and precession electron diffraction. In both cases, Nb atoms were found to prefer to occupy the Ti rather than Ni sites. A projector augmented wave method within density functional theory was used to calculate the atomic and electronic structures of the austenitic B2-NiTi matrix phase and the Ti_2Ni precipitates both with and without addition of Nb. The obtained formation energies and analysis of structural and electronic characteristics explain the preference for Ti sites for Nb over Ni sites.

Keywords: Shape memory alloys; Transmission electron microscopy; Scanning transmission electron microscopy; Precession electron diffraction; Occupancy

1. Introduction

Shape memory alloys (SMAs) have been widely used for a variety of applications in a number of different fields from thermomechanical couplings to medical stents, because of their two unique properties: pseudo-elasticity and the shape memory effect. Among SMAs, the binary Ni–Ti systems provide the majority of commercially relevant materials [1,2]. Although this system has excellent shape memory and mechanical properties, which are based on the underlying B2 to B19′ martensitic transformation, its use is limited by its particular hysteresis and the appearance of the transformation at temperatures close to RT or even below [3]. In order to extend the application of SMAs for different transformation temperatures, many investigations have been performed to determine the factors that can influence the transformation temperature and hysteresis [4–9]. In 1997, Tang [4] pointed out that the martensite start temperature M_s of binary Ni–Ti decreases along with the increase in the Ni/Ti atomic ratio for Ni-rich material, while no effect is observed in Ti-rich material. Afterwards, this empirical rule was extensively accepted and adopted by many researchers on both binary and ternary SMAs [10,11]. Recently, Zarinejad and Liu [5,6] tried to find the relationship between the transformation temperatures of NiTi-based SMAs and the concentration of valence electrons. They concluded that ternary and quaternary alloying elements influence the number and concentration of valence electrons of NiTi-based SMAs and, therefore, change the transformation temperatures. The valence electron concentration c_v is found to be an

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important parameter influencing the transformation temperatures, since M_s as well as the austenite start temperature A_s both decrease with increasing c_v.

The need to adjust the transformation temperatures and the resulting hysteresis for use in a larger variety of different applications has led to extensive research to find suitable ternary or quaternary alloying elements [12]. In this respect, the site occupancy of the ternary or quaternary alloying atoms becomes a very important parameter, because the addition of the ternary or quaternary atoms will significantly change both the Ni/Ti atom ratio and the electronic state of all atoms, thus resulting in changing transformation temperatures and thermal hysteresis. In earlier work, electron channelling enhanced microanalysis (ALCHEMI) as well as the discrete variational-X_α cluster method were applied in order to determine the location of the extra alloying elements [13–15]. More recently, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was also applied for the investigation of minority elements in various alloy system. For example, HAADF was used in 2009 by Rosenauer et al. [16] to determine the composition of $Al_xGa_{1-x}N/GaN$ with low values of x, while in 2013 Radtke et al. [17] measured Ge diffusion in strained Si. The model-based technique [17], also applied in the present work, was used by Van Aert et al. [18] to reliably count the number of Ag atoms in a binary alloy consisting of Al with 3 at.% Ag and by Martinez et al. [19], in order to quantify the concentration of Pb in a complex $Pb_{1.2}Sr_{0.8}Fe_2O_5$ compound.

The present work focuses on Ni–Ti–Nb SMAs, which have been widely used for pipe couplings. It was found that Nb additions to Ni–Ti increase the hysteresis after the correct thermo-mechanical treatment, which is useful for thermal couplings, since the coupling parts can then be expanded and stored at ambient temperature [20–23]. The most popular hypothesis for the enlarged hysteresis is that the plastic deformation of Nb-rich precipitates appearing in the material relaxes the elastic strain energy stored in the austenite–martensite and martensite–martensite interfaces during thermo-mechanical treatment [22,24,25]. However, no experimental microstructural evidence to support this mechanism has been provided so far. In earlier work using in situ cooling and heating transmission electron microscopy (TEM) nanoscale Nb-rich precipitates were also shown to induce a "stop-and-go" process of the martensitic transformation, which could be another reason for the increased hysteresis [26,27]. Also, based on differential scanning calorimetry (DSC) results and electron probe micro analysis, it is concluded that the solute Nb atoms in the matrix lower the transformation temperatures when compared with the corresponding binary concentration [11]. One hypothesis to explain this observation is that the Nb atoms substitute for the Ti atoms in the Ni–Ti matrix, which will increase the Ni/Ti atom ratio, thus yielding lower transformation temperatures according to the rules for the binary system. The aim of the present work is to determine experimentally for the first time the preferential substitutional sites for Nb in both the austenite matrix and in Ti_2Ni particles appearing during further heat treatments.

Although HAADF-HRSTEM combined with precession electron diffraction (PED) has been used before for structure solution and refinement [28,29], the analysis for finding the minority alloying element in alloys has not yet benefited much from the combination of these advanced techniques.

2. Materials and methods

2.1. Sample preparation

An as-cast ternary Ni–Ti–Nb SMA with nominal composition $Ni_{45.5}Ti_{45.5}Nb_9$ was used for the austenite work in the present study. The alloy was produced by arc melting under a protective atmosphere and then remelted 12 times before drop casting for rapid solidification and cooling [7]. A ternary $Ni_{45.8}Ti_{45.8}Nb_{8.4}$ alloy, annealed at 1140 °C for 2 h and then water quenched, was used to investigate the Ti_2Ni phase. A homogenized and quenched binary Ni–Ti SMA containing 51.7 at.% Ni was used for comparison. In the following, the ternary alloys are referred to as Nb9 and Nb8.4, respectively. For the scanning electron microscopy (SEM) studies, slabs 1 mm thick were cut from the original alloys by diamond saw and subsequently mechanically polished. TEM samples were prepared by focused ion beam (FIB) thinning and electropolishing. For FIB, samples were prepared by the same method as SEM samples, completed by a lift-out method in an FEI Helios Nanolab 650 SEM/FIB instrument. The latter method was applied to avoid preferential thinning during electropolishing in the ternary samples containing multiple phases and to ensure the inclusion of the Ti_2Ni phase in the thinned region. The binary reference samples for the quantitative comparison of the HAADF-HRSTEM images were made by electropolishing from slabs 1 mm thick cut from the original alloys by low-speed diamond saw cooled by water. Discs 3 mm in diameter were subsequently spark-cut from these slabs, mechanically polished to 200 μm or less and finally electropolished to perforation in a Tenupol 3 operated at 25 V, 0.12 A, −20 °C with an electrolyte of 80% CH_3OH and 20% H_2SO_4.

2.2. HAADF-HRSTEM

Aberration-corrected HAADF-HRSTEM images were obtained with an FEI TITAN 80–300 microscope (QuAnt-EM) equipped with image and probe aberration correctors. The working high tension was 300 kV. For the quantification of the binary and ternary matrices, the HAADF detector inner acceptance angle used was 56 mrad, while for the Ti_2Ni phase it was 45 mrad. Both values are larger than twice the convergence angle of 20.2 mrad, and it is thus assumed that the remaining elastic