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Microstructure of precipitates and magnetic domain structure in an annealed $Co_{38}Ni_{33}Al_{29}$ shape memory alloy

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Abstract

The microstructure of a $Co_{38}Ni_{33}Al_{29}$ ferromagnetic shape memory alloy was determined by conventional transmission electron microscopy (TEM), electron diffraction studies together with advanced microscopy techniques and in situ Lorentz microscopy. Rod-like precipitates, 10–60 nm long, of hexagonal close-packed ϵ-Co were confirmed to be present by high-resolution TEM. The orientation relationship between the precipitates and B2 matrix is described by the Burgers orientation relationship. The crystal structure of the martensite obtained after cooling is tetragonal $L1_0$ with a (1–11) twinning plane. The magnetic domain structure was determined during an in situ cooling experiment using the Fresnel mode of Lorentz microscopy. While transformation proceeds from B2 austenite to $L1_0$ martensite, new domains are nucleated, leading to a decrease in domain width, with the magnetization lying predominantly along a single direction. It was possible to completely describe the relationship between magnetic domains and crystallographic directions in the austenite phase though complications existed for the martensite phase.

Keywords: CoNiAl shape memory alloys; Microstructure; Precipitates; Magnetic domains; Lorentz microscopy

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) are being intensively studied because of their potential applications as smart materials. Martensitic transformations and lattice reorientation processes in FSMAs can be triggered not only by changes in temperature and stress, as in conventional SMAs, but also by applying an external magnetic field. To date, many such systems have been investigated, including Ni_2MnGa [1–3], Ni_2MnAl [4], $Fe_{70}Pd_{30}$ [5] and Fe_3Pt [6], all of which experience large strains induced by an external magnetic field. Recently, the Co–Ni–Al system has received increased interest as a new FSMA [7–9] since these alloys have low density, high melting point, good corrosion resistance and high strength, even at temperatures as high as 573 K. Moreover, the constituent elements are cheaper compared to some other FSMAs (Fe–Pt, Fe–Pd). The Co–Ni–Al system undergoes a martensitic transformation from β-phase (B2, cubic) austenite to $L1_0$ (tetragonal) martensite at temperatures between 93 and 393 K depending on composition, with the symmetry loss being responsible for the formation of microtwinned variants in the product phase as shown in Fig. 1 [10]. It is this martensitic transformation that is responsible for the shape memory effect and pseudoelasticity. The single β-phase in polycrystalline material is extremely hard and brittle, but the presence of a secondary γ-phase, which has an Al disordered face-centered cubic (fcc) structure [8,11], significantly improves the ductility [12,13]. Furthermore, the martensitic start temperature (TM_s) and Curie temperature

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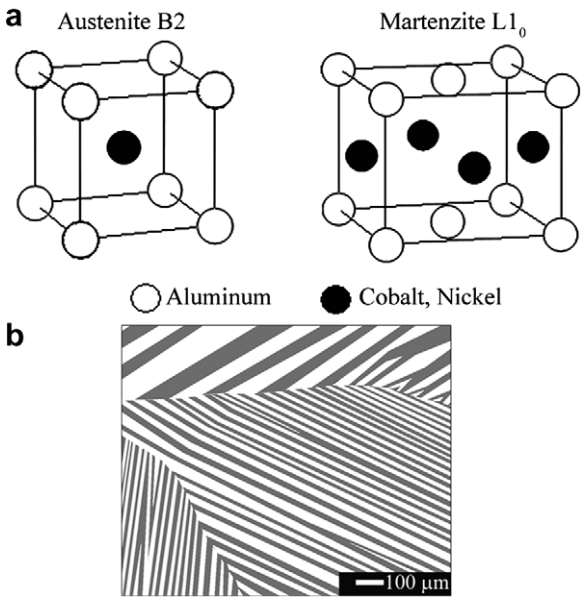

Fig. 1. Schematic drawing of (a) the unit cells of the B2 austenite and the $L1_0$ martensite. In (b) a typical morphology of the microtwinned martensite plates is depicted based on an exemplary observation by Karaca et al. [10].

(T_c) can be independently controlled by the composition. TM_s decreases with increasing content of Co and Al, whereas T_c increases with increasing Co content and decreasing amounts of Al [8]. Thus choosing the right composition, annealing conditions and desired transition temperatures is necessary to obtain a promising material for a wide range of applications.

The purpose of this work is a detailed study of the microstructure of austenite and martensite, going beyond existing work [14], and an investigation of the relation between magnetic and crystallographic structure. Since TM_s for the material studied here is below room temperature, in situ cooling experiments were performed involving conventional transmission electron microscopy (CTEM) and Lorentz microscopy [15].

2. Experimental procedures

A $Co_{38}Ni_{33}Al_{29}$ alloy was obtained from Special Metals Corporation, New Hartford, NY. The alloy was melted and single crystals were grown by the directional Bridgman technique with a pulling rate of 10 μm s^{-1} in an alumina crucible at 1803 K in a vacuum. Annealing was carried out at 1548 K for 4 h in an Ar atmosphere followed by quenching into ice water. The transformation temperatures are determined to be 231 K for TM_s and 266 K for the austenite start temperature (TA_s) as measured by differential scanning calorimetry (DSC).

The phase composition was determined by scanning electron microscopy (SEM) using a JEOL JSM 5510 microscope equipped with an INCA energy dispersive X-ray (EDX) microanalysis system. TEM specimens were prepared by twinjet electropolishing in a 20% sulfuric acid and 80% methanol electrolyte at 278 K [16]. Conventional TEM was performed on a Philips CM20, and high-resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL JEM 4000EX microscope. The spectrometer used for energy-filtered TEM (EFTEM) measurements is a post-column GATAN Imaging Filter (GIF200) mounted onto a 300 keV Philips CM30 field emission gun (FEG) microscope. EFTEM maps were obtained with the commercial software package Digital Micrograph. Diffraction pattern simulations were carried out with the commercial software package CrystalKitX.

To study the magnetic domain structure of the sample, the Fresnel mode of Lorentz microscopy was used [15]. The TEM was a modified Philips CM20 equipped with (non-immersion) Lorentz lenses, thereby allowing magnetic imaging in a field-free environment with the standard objective lens switched off [17]. All experiments involving Lorentz microscopy were performed with an untilted specimen.

3. Results and discussion

3.1. Co-rich precipitates in the austenite matrix

The morphology of the sample, following annealing and subsequent quenching, consists of the B2 matrix and a γ-phase. The experimentally obtained phase compositions are given in Table 1 with the microstructure shown in the SEM image, Fig. 2. Table 1 lists the elemental concentrations measured by EDX, averaging over seven measure-

Table 1
Chemical composition of $Co_{38}Ni_{33}Al_{29}$ alloy annealed at 1548 K/4 h measured by SEM EDX

At. (%)	Al	Co	Ni
γ-phase	17.2 ± 0.5	53.2 ± 0.7	29.6 ± 0.2
B2 matrix	29.2 ± 0.2	38.1 ± 0.2	32.4 ± 0.2

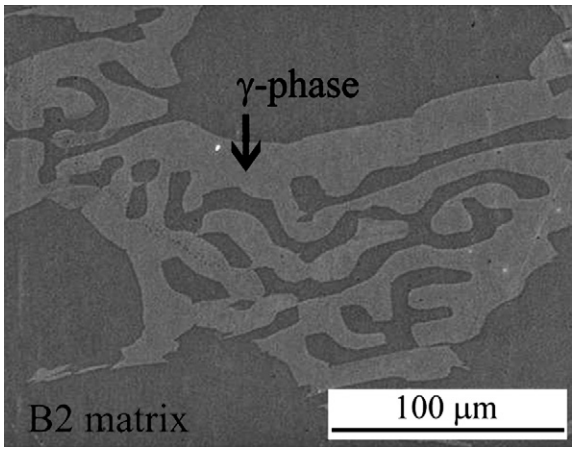

Fig. 2. SEM image of the microstructure of $Co_{38}Ni_{33}Al_{29}$ annealed alloy consisting of B2 matrix with dispersed γ-phase.