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Structural transformations in (CoFeNi)/Ti nanocomposite systems during prolonged heating

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ABSTRACT

A complex CoFeNi/Ti nanocomposite system with an average grain size of about 8 nm was fabricated on a Ti sheet under ball collisions. Heating experiments were performed at 400, 500, and 600 °C with hold times of up to 100 h at each temperature. The as-fabricated (CoFeNi)/Ti nanocomposite system demonstrated high thermal stability upon heating to 400 and 500 °C. Growth of the CoFeNi phases was retarded by closely spaced Ti particles. After heating to 600 °C, the system exhibited a bimodal nanograin structure due to coursing of the body-centered cubic (bcc) CoFeNi grains, which occurred more rapidly than with the face-centered cubic (fcc) CoFeNi grains. Upon heating, the diffusion that occurred between the phases tended to equilibrate the composition. Pairwise atomic interactions between the Co, Fe, and Ni components arose as chemical interactions in the corresponding binary alloy. The diffusive flux of elements in the system was outlined as Co from the fcc phase diffused into the bcc phase, Ni from the bcc phase diffused into the fcc phase, and Fe from the fcc phase diffused into the bcc phase. The activation energy for the reaction was calculated using time dependence curves of saturation magnetization. The activation energy coincided very closely with the value for the grain boundary diffusion activation energy for the Co, Fe, and Ni binary systems.

1. Introduction

Multicomponent material systems have attracted considerable attention from design engineers due to the unique property profiles exhibited by these systems [1–11]. It is believed that multicomponent nanocomposite systems and multicomponent alloys such as high-entropy alloys will replace conventional industrial materials that have begun to approach their performance limits. However, thermal stability and structural transformation reactions upon heating of multicomponent systems are still not fully understood [12–19]. For example, it is unclear why the face-centered cubic (fcc) phase sometimes forms in high-entropy alloys, while formation of the body-centered cubic (bcc) phase occurs in other cases [20–23]. High-entropy alloys typically contain Co, Ni, and Fe; atomic reactions between these elements are likely to be a key point in understanding structural formations in these multicomponent alloys. A model describing pairwise interactions in multicomponent alloys was recently suggested, according to which chemical interactions between dissimilar atoms (existing within each of the diffusion couples of a multicomponent alloy) occurred as chemical interactions in a corresponding binary alloy [24]. A change in the sign of the chemical interaction between dissimilar atoms would alter the direction of diffusion between the atoms, affecting a change in the microstructure type. In order to understand the nature of transformation phenomena in multicomponent systems and to design new metallic materials, physical metallurgists and engineers should explore the mechanisms of microstructural development from atomic to microscopic levels for various multicomponent systems in order to determine the effects of various alloying components on structural formation and design of transformation diagrams.

Recently, we presented a deformation-induced surface alloying technique and the fabrication of multicomponent nanocomposite structures on metallic sheets, integrating principles of severe plastic deformation and mechanical alloying [25]. We fabricated a

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complex CoFeNi/Ti nanocomposite system on a Ti sheet with an average grain size of about 8 nm (Fig. 1). The as-fabricated surface alloyed layer exhibited magnetic properties representative of soft-magnetic materials. The alloyed layer was extremely hard, much harder than many industrial alloys and steels. Furthermore, the as-fabricated lightweight structure should exhibit enhanced corrosion and heat resistance since cobalt-based alloys are generally described as wear resistant, corrosion resistant, and heat resistant (strong even at high temperatures) [26]. Obviously, the as-fabricated metallic nanocomposites processed via extreme deformation were preserved as non-equilibrium structures. The main issues that arose here are the stability of this nanocomposite structure during heating and evaluation of this non-equilibrium multicomponent system at elevated temperatures. In general, the thermal stability of nanocrystalline materials is lower than desired [27]. In the present work, we studied the microstructural development of a (CoFeNi)/Ti nanocomposite system after prolonged heating.

2. Experimental details

The detailed processing parameters have been reported in our previous work [25]. For the treatment process, a special vibration vial composed of SKD 11 steel was designed (Fig. 1a). Ti (99.95%), Ni (99.95%), and Co (99.95%) sheets with a thickness of 3 mm (Nilaco Corp., Japan) were used in the present experiments. Disks with a diameter of 50 mm were cut from the as-received sheets. Ti disks were used as a substrate, and the Co and Ni disks were used as targets for the alloying components. A Ti disk was affixed to one side of the vial, while Ni or Co disks were affixed to the opposite side. Eighty grams of steel balls (7 mm diameter) were loaded into the vial to produce the desired impacts. The vial was sealed within an argon glove box using silicone rubber "O" rings to prevent exposure to the outside atmosphere and to ensure that interstitial contamination was kept to a minimum during the milling process. The vial was mechanically vibrated with a Spex high-energy mill. In the present study, a Ti disk was treated with Ni for 1 h, at which point the Ni disc was replaced with Co. The Ni-processed Ti disk and the Co disk were then subjected to 1 h of ball milling. A cross-sectional image of the as-fabricated surface alloyed layer is shown in Fig. 1b.

After processing, the Ti disk was cut into 7 mm × 3 mm specimens for heating experiments. Heating experiments were performed using a Physical Property Measurement System (PPMS, Quantum Design Inc., USA) equipped with a vibrating sample magnetometer oven. This oven used a heater and a thermocouple integrated into a vibrating sample rod. The temperature precision and accuracy were 0.5 K and 2%, respectively. The heating experiments were performed under a 10^{-4} Pa vacuum at 400, 500, and 600 °C with hold times up to 100 h at each temperature. The heating rate was 10 °C/min. After heating for 1, 5, 10, 20, and 50 h, magnetic properties were measured by the registration of hysteresis loops at room temperature in maximum fields up to 30 kOe, upon which heating was continued. In this work, a normalized saturation magnetization value, $\sigma/\sigma_{initial}$ was calculated, where $\sigma_{initial}$ is the saturation magnetization of the as-fabricated specimen measured prior to heating.

After heating at each temperature for 50 and 100 h, structures of the specimens were analyzed via X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with CoKα radiation. Analysis of the XRD data was performed via the Rietveld method. After heating for 100 h, specimens for transmission electron microscopy (TEM) analysis were prepared over copper TEM grids using a focused ion beam instrument (FIB: FEI Helios NanoLab DualBeam). Specimen structures and chemical compositions were studied with an atomic-resolution analytical electron microscope (JEOL JEM-

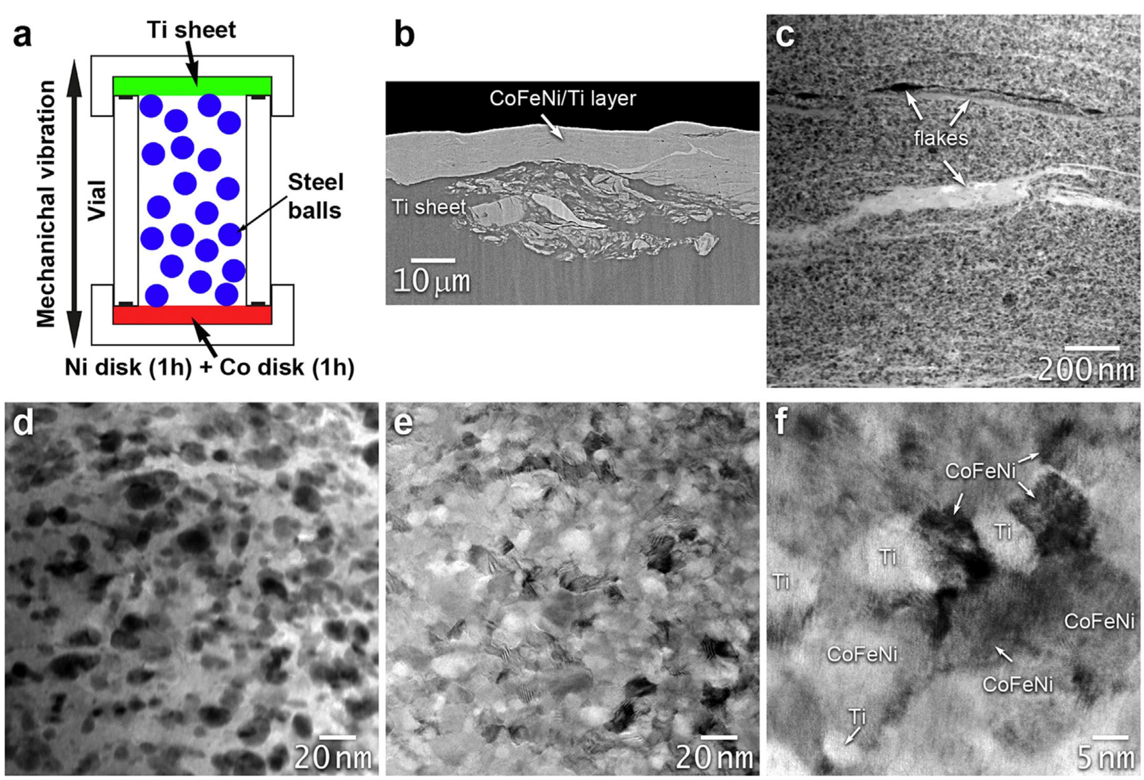

Fig. 1. The as-fabricated alloyed layer: (a) schematic illustration of the processing procedure, (b) cross-sectional SEM view of the layer, (c) HAADF STEM image showing the typical structure at low magnification, (d) HAADF STEM image, and (e) BF STEM image showing the matrix structure, (f) BF STEM image showing nanocrystalline matrix grains.