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Structure and magnetic properties of a multi-principal element Ni–Fe–Cr–Co–Zn–Mn alloy

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ABSTRACT

A nanocrystalline alloy with a nominal composition of $Ni_{20}Fe_{20}Cr_{20}Co_{20}Zn_{15}Mn_5$ was produced by mechanical alloying and processed using annealing treatments between 450 and 600 °C for lengths from 0.5 to 4 h. Analysis was conducted using x-ray diffraction, transmission electron microscopy, magnetometry, and first-principles calculations. Despite designing the alloy using empirical high-entropy alloy guidelines, it was found to precipitate numerous phases after annealing. These precipitates included a magnetic phase, α-FeCo, which, after the optimal heat treatment conditions of 1 h at 500 °C, resulted in an alloy with reasonably good hard magnetic properties. The effect of annealing temperature and time on the microstructure and magnetic properties are discussed, as well as the likely mechanisms that cause the microstructure development.

1. Introduction

Conventional alloys are generally based on a single principal element with additional elements added to affect specific properties. Even complex alloys such as Alnico [1] and Inconel [2] alloys contain no more than 2 elements in concentrations above 20%. Over the past several years, significant attention has been given to alloys containing five or more elements in equal, or nearly equal atomic ratios [3]. Alloys of this type can be difficult to design, as phase equilibria data is often unavailable for high-concentration multi-component mixtures beyond binary systems and common ternaries. Most focus is on solid solution alloys, called "high-entropy" alloys (HEAs) due to their high configurational entropy [4]. However, limiting to solid solutions also limits the potential properties and applications, as the controlled formation of secondary phases can result in properties difficult or impossible to achieve in a single-phase material. Many engineering metals used today contain multiple phases. Therefore, some research has also been conducted on multi-principal element alloys that may not meet the strict HEA definition but have interesting properties. Several alloys have been developed with age-hardening capabilities [5,6] while others have been alloyed with non-metal elements such as boron to form phases that aid in wear-resistance and high-temperature strength [7].

To date there has been little research on the magnetic properties of HEAs or other multi-principal element alloys. The single-phase NiFeCrCo alloy has been shown to be ferromagnetic, with properties dependent on short-range chemical ordering. However, the magnetic properties of the ball-milled alloy at room temperature are poor and when produced by casting it has a Curie temperature near 100 K [8]. A BiFeCoNiMn thin film was found to have hard magnetic behavior after annealing [9] and hard magnetic behavior has been observed in an AlCoCrCuFeNi alloy [10].

In this study, we describe a nanostructured NiFeCrCoZnMn alloy prepared by mechanical alloying. This alloy is based on the previously described NiFeCrCoMn system, which has been widely studied for its mechanical properties and tendency for forming solid solution alloys [11,12]. We characterize the magnetic properties and microstructure as a function of heat treatment time and temperature, and describe how the magnetic properties relate to the microstructure. Empirical HEA design guidelines predict the alloy to form a stable solid solution, but we show from experimental and first-principles computational methods that formation of a multiphase alloy is energetically preferred.

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2. Methods

Alloy powders were prepared by mechanical alloying elemental powders in a SPEX 8000 mixer mill. Powders of at least 99% purity were loaded into a stainless steel vial in a high-purity argon atmosphere with approximately 0.7 wt% dodecane as a process control agent (PCA). A 10:1 ball-to-powder weight ratio was used, with stainless steel balls. The sample was milled at room temperature for 24 h. Before any analysis, the sample powder was put in a vacuum chamber for 18 h to evaporate any dodecane remaining on the surface.

Samples of ~0.09 g were compacted into 3 mm diameter cylinders using cold uniaxial pressing. Samples were then annealed at 450, 500, 550, and 600 °C for 0.5, 1, 2, and 4 h in an Ar-2%H_2 atmosphere. Hardness tests were conducted using a Buehler microhardness tester with a 100 g load.

X-ray diffraction (XRD) analysis was conducted on the as-milled powders as well as the samples annealed at 500 °C for 1 and 4 h using a Rigaku SmartLab diffractometer with Cu Kα radiation. Phase analysis was done using Pananalytical HighScore Plus software with the ICDD PDF-4+ database [13]. Further analysis for lattice parameter determination was done using the PM2K Whole Powder Pattern Modeling program [14]. Compositional analysis of the as-milled and 2 h/500 °C samples were done using a Hitachi S3200N scanning electron microscope (SEM) equipped with an Oxford energy dispersive x-ray spectroscopy (SEM/EDS) detector, using an accelerating voltage of 30 kV.

Magnetization versus field (M vs. H) curves were measured using a Quantum Design MPMS SQUID-VSM at 1.8 K and 300 K with an applied field between ±20 kOe.

The 1 h/500 °C sample was prepared for transmission electron microscopy (TEM) sample using an FEI Quanta 3D FEG dual-beam focused ion beam (FIB)/SEM with the in-situ lift-out technique. Energy dispersive X-ray spectroscopy (STEM/EDS) analysis was performed using a probe-corrected FEI Titan G2 60–300 kV S/TEM equipped with an X-FEG source operated at 200 kV. Bruker Esprit was used for post-processing with a 3-pixel smoothing filter to reduce noise. Standardless quantification was performed for all EDS spectra using the Q-map function. All EDS maps were formed using X-ray K-lines.

First principles calculations were performed by the exact muffin-tin orbital method combined with coherent potential approximation (EMTO-CPA) [15]. The Perdew-Burke-Ernzerhof version of generalized gradient approximation (GGA-PBE) of exchange-correlation functionals was used [16,17]. The Kohn–Sham equations were solved within the so-called soft-core approximation, which let the code recalculate core states after each iteration. The Green's function was calculated for 16 complex energy points. The basis set of EMTO included s, p, d, and f states. A 13 × 13 × 13 k-point mesh was used; the total energy converged within 1 meV/atom. The screened impurity model parameter of 0.902 was applied for electrostatic correction to the single-site CPA. Equilibrium lattice parameters were obtained by fitting volume-energy data to the Vinet equation of state [18]. Similar calculations have proven to agree well with experiments [8,11].

3. Results and discussion

3.1. Alloy structure

The NiFeCrCoZnMn alloy forms a single-phase fcc solid solution after ball milling as shown in Fig. 1a. The nominal composition of the alloy is $Ni_{20}Fe_{20}Cr_{20}Co_{20}Zn_{15}Mn_5$. As the atomic radius of Zn is significantly larger than the other components, its concentration was reduced from the equiatomic condition and balanced with Mn, to reduce the average atomic size difference. SEM/EDS measurements of the as-milled alloy showed a higher Fe concentration (~23 at%) and reduced Ni and Co content, as is common with ball milling using steel media. The formation of a solid solution is predicted by the empirical HEA solid solution formation rules [19–21].

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \tag{1}$$

T_m is the weighted average melting point of the constant elements, ΔS_{mix} is calculated for an ideal mixture, and ΔH_{mix} is calculated from the binary systems.

$$\delta = \sqrt{\sum_{i=1}^{N} c_i \left(1 - \frac{r_i}{\bar{r}}\right)} \tag{2}$$

c_i and r_i are the concentration and atomic radius, respectively, of element i and $\bar{r}$ is the weighted average atomic radius. Alloys that have high values of Ω (>1.1) and low values of δ (<6.6%) are likely to form solid solutions [3]. For this alloy, Ω = 7.18 and δ = 4.31%. Additionally, the largest $|\Delta H_{mix}|$ value for the binary systems in the alloy using Miedema's model is only 9 kJ/mol [22]. These values suggest that the system should form a stable solid solution.

However, after annealing at 500 °C for 1 h, numerous additional peaks can be seen in the XRD results, shown in Fig. 1b. Due to the complex nature of the alloy and large numbers of the elements, STEM/EDS analysis was used in conjunction with conventional automated XRD phase analysis. The presence of various phases can be observed in the EDS maps presented in Fig. 2. Using this data, the phases in the alloy can be identified based on XRD results. Table 1 shows the phases identified in the 1 h/500 °C sample, their lattice parameters, the lattice parameters of the phase reported in the PDF-4+ database [13], and the average composition of 12–21 particles from the EDS maps. Due to the high degree of peak overlap, quantitative XRD phase analysis was not attempted. The carbon in the carbide phase was likely incorporated into the powder during milling from the organic PCA. The PDF entries referred to are 04-004-6329 (NiZn), 04-003-5514 (FeCo), and 01-089-2724 ($Cr_{23}C_6$). No significant change in overall composition was observed by SEM/EDS after 2 h at 500 °C.

While the annealing temperatures used in this work are all below the FeCo order-disorder transition temperature, due to the highly non-equilibrium starting material and substantial amount (17.6%) of impurity atoms in the phase, we assume the FeCo is the disordered α phase. In practice, the α and α′ phases are difficult to distinguish experimentally and have similar magnetic moments [23].

After the 1 h/500 °C anneal, the lattice parameter of FeCo is larger than the reported value, which agrees with the quantitative EDS results that show an enrichment in Fe and an average of 5% Zn in the FeCo particles. The lattice parameter of $Cr_{23}C_6$ is slightly smaller than expected, likely due to substitution of Fe for Cr. The largest difference is seen in NiZn, which has a cell volume 0.45% smaller than the reference with the **c** vector having the largest difference from its expected value. EDS measurements suggest that Zn is below the stoichiometric ratio, with Mn being the largest impurity. As Zn is in the center of the cell, substituting the much smaller Mn atom would substantially decrease the cell height. As Ni is the smallest metallic element in the system, any substitutional impurities in the Ni sites would increase the **a** vector, as is also observed. The lattice parameter of the solid solution phase decreases by 1.1% compared to the as-milled alloy due to the loss of Zn to the NiZn phase. For reference, the close-packed atomic radii reported by Pearson [24] are also provided in Table 2.