Materials Science & Engineering A 695 (2017) 74–79

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Intrinsic properties and strengthening mechanism of monocrystalline Ni-containing ternary concentrated solid solutions[☆]

K. Jin[a], Y.F. Gao[a,b], H. Bei[a,*]

[a] Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] Department of Materials Science & Engineering, University of Tennessee, Knoxville, TN 37996, USA

ARTICLE INFO

Keywords:
Solid solution alloys
Medium/high entropy alloys
Elastic constants
Nanoindentation
Solid solution strengthening

ABSTRACT

Ternary single-phase concentrated solid solution alloys (SP-CSAs), so-called "medium entropy alloys", not only possess notable mechanical and physical properties but also form a model system linking the relatively simple binary alloys to the complex high entropy alloys. The knowledge of their intrinsic properties is vital to understand the material behavior and to prompt future applications. To this end, three model alloys NiCoFe, NiCoCr, and NiFe-20Cr have been selected and grown as single crystals. Their elastic constants have been measured using an ultrasonic method, and several key materials properties, such as shear modulus, bulk modulus, elastic anisotropy, and Debye temperatures have been derived. Furthermore, nanoindentation tests have been performed on these three alloys together with Ni, NiCo and NiFe on their (100) surface, to investigate the strengthening mechanisms. NiCoCr has the highest hardness, NiFe, NiCoFe and NiFe-20Cr share a similar hardness that is apparently lower than NiCoCr; NiCo has the lowest hardness in the alloys, which is similar to elemental Ni. The Labusch-type solid solution model has been applied to interpret the nanoindentation data, with two approaches used to calculate the lattice mismatch. By adopting an interatomic spacing matrix method, the Labusch model can reasonably predict the hardening effects for the whole set of materials.

1. Introduction

The recent development of single-phase concentrated solid solution alloys (SP-CSAs), including high entropy alloys [1–4], has drawn great interest, because these alloys not only exhibit exceptional mechanical properties [5–7] and unique physical properties [8–11], but also provide intriguing new concepts for alloy development. Instead of modifying the microstructure with dilute solute species, the focus of developing those alloys is on the control of compositional complexity, i.e., the number, type, and concentration of alloying elements, while maintaining the alloys as single phase solid solutions [12]. While previous studies have shown that some of the material behaviors, e.g. sluggish diffusion, are correlated with the number of alloying elements [11], substantial experimental and theoretical evidence has shown that the type/combination of elements are more dominant in affecting their mechanical and physical properties. For example, the electrical resistivity of the ternary NiCoCr alloy is one order higher than that of another ternary NiCoFe alloy, even higher than the quaternary NiCoFeCr [8]. High electrical resistivity is attributed to the alloying of the Cr, which induces severe magnetic disorder due to the antiferromagnetic coupling of Cr atoms [8]. Regarding the mechanical properties, alloying Cr in Ni, Co, Fe, and Mn has shown very strong strengthening effects [13]. It is notable that some mechanical properties of ternary NiCoCr (e.g. strength, ductility and fracture toughness) are superior to those of the quaternary or even quinary NiCoFeCrMn alloys [6]. Recent studies have demonstrated that SP-CSAs can enhance irradiation resistance, making them promising in nuclear engineering applications [9]. Again, the combination rather than the number of elements plays the key role; for example the ternary alloy NiCoFe was reported to be more resistant to irradiation-induced swelling than the quaternary NiCoFeCr alloy [14,15].

Ternary SP-CSAs with equal or near equal atomic concentrations have been referred to as medium entropy alloys (MEAs) [6]. Besides extraordinary mechanical properties, some of them also possess unique physical properties, e.g., quantum critical behavior in NiCoCr alloy, which is surprising because such behavior usually appears in materials

---

[☆] This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

[*] Corresponding author.

E-mail addresses: jink@ornl.gov (K. Jin), ygao7@utk.edu (Y.F. Gao), beih@ornl.gov (H. Bei).

http://dx.doi.org/10.1016/j.msea.2017.04.003
Received 21 February 2017; Received in revised form 31 March 2017; Accepted 2 April 2017

with very complex structure but the NiCoCr solid solution alloy has a simple face-centered cubic (FCC) crystal structure [10]. More importantly, the ternary SP-CSAs help bridge our existing knowledge on conventional (e.g. binary) alloys to the relatively less-understood complex high entropy alloys. In other words, these medium entropy alloys are an excellent model system to study the effect of alloying elements, since they limit the number of variables, but still have a relatively high degree of chemical complexity. Ni, Co, Fe, and Cr are among the most widely considered elements in the multi-component alloys according to a recent review of 408 alloys [16]. For example, a family of FCC SP-CSAs formed with these elements, from binary NiCo and NiFe to the quaternary NiCoFeCr, which are all subsets of the well-explored high entropy NiCoFeCrMn alloy, have been experimentally identified and their mechanical properties have been systematically studied [12,13,16]. Ni-Co-Cr, Ni-Co-Fe, as well as Ni-Fe-Cr are three possible FCC medium entropy alloy systems with these four elements. While single phase equiatomic NoCoFe and NiCoCr are available, the equiatomic NiFeCr does not form a stable single phase solid solution, instead second phases have been observed previously [12]. According to the isothermal section of the ternary Ni-Fe-Cr phase diagram at 627 °C (900 K) [17], the maximum Cr concentration for single-phase FCC solid solution is ~22 at%; therefore, a composition of NiFe-20Cr is selected and its single phase nature is subjected to be experimentally confirmed in this study.

The knowledge of intrinsic physical and mechanical properties is fundamental for comprehensive studies on material behavior and potential applications. Specifically, elastic constants are important to understand a broad range of material properties, including thermodynamic properties (e.g. Debye temperature), phonon properties, and defect (e.g. dislocation) behaviors. In this study, single crystalline NiFe-20Cr, NiCoFe and NiCoCr were grown, their elastic constants as well as lattice parameters, densities, and melting temperatures were measured, and several key material properties, e.g. shear moduli, bulk moduli, elastic anisotropy, and Debye temperatures were derived. The results obtained from the single-crystalline elastic constants are compared with the values directly measured from polycrystalline samples. Furthermore, nanoindentation tests were performed on these three alloys along with Ni, NiCo, and NiFe, to reveal their slip systems and to investigate the strengthening mechanisms. The strengthening in these alloys was interpreted by using the Labusch-type solid solution model with two different methods of calculating atomic mismatch. The success and limitation of these two methods are discussed.

2. Materials and experimental methods

2.1. Material preparation and single crystal growth

Pure Ni, Co, Fe, and Cr elemental metals (> 99.9% pure) of appropriate amounts were mixed by arc-melting. Each composition (arc-melted button) was flipped and re-melted five times before drop-casting the melt into a copper mold to ensure a homogeneous well-mixed alloy. The single crystals were grown from the polycrystalline as-cast ingots using a floating-zone directional solidification method. The details of single crystal growth can be found in Ref. [18] The single crystal rods were cut with two surface normal directions, < 100 > and < 110 > , in order to measure the elastic constants.

Previous studies [12] have demonstrated that equiatomic NiCoFe and NiCoCr can form stable FCC SP-CSAs. However, equiatomic NiFeCr alloy cannot form stable single phase solid solution alloys. We show here by slightly decreasing the concentration of Cr to 20 at%, the Ni-40Fe-20Cr does form a stable single-phase FCC solid solution. Fig. 1a shows a backscattered electron image of the microstructure of the as-cast NiFe-20Cr alloys, which consists of large elongated grains extending from the edges to the center, due to the heat flux during solidification. No secondary phase is observed in the microstructure images while its XRD pattern (not shown here) exhibits only FCC peaks. Furthermore, we have carefully characterized the composition distribution and microstructure after single crystal growth, and the single crystalline NiFe-20Cr is indeed a single-phase FCC solid solution. Figs. 1b and c show the patterns of X-ray backscatter Laue diffraction of NiFe-20Cr in surfaces oriented (100) and (110), respectively, which demonstrate good single crystal quality.

2.2. Material characterizations

The lattice parameters were measured by powder X-ray diffraction with Cu-target radiation at 40 kV and 40 mA on 2.54-mm thick slices. The samples were scanned through 2θ ranging from 20 to 90° with a scan rate of 1.2°/minute. The melting temperatures were determined using a NETZSCH 404 C differential scanning calorimeter (DSC). Here, the melting (solidus) temperature was defined as the start point at which the endothermic peaks were observed on the DSC traces upon heating from room temperature. The density, ρ, was measured using an AccuPyc 1330 pycnometer.

Nanoindentation tests were performed using a Nanoindenter XP with a Berkovich triangular pyramid indenter. Tests were conducted in the continuous stiffness mode (CSM) at room temperature at a constant $\dot{P}/P = 0.05\ \mathrm{s}^{-1}$, to a maximum load of 20 mN for hardness measurements. The nanoindentations to a maximum load of 100 mN were also performed to obtain clear slip trace patterns which were imaged using a Nikon Epiphot 300 optical microscope.

For single crystals, the elastic constants c_{11}, c_{12} and c_{44}, were determined by measuring the longitudinal and transverse sound wave velocities (V_l and V_t) inside the materials along < 100 > and < 110 > directions, based on the following equations [19].

Along < 100 > ,

$$V_l = \sqrt{\frac{c_{11}}{\rho}}, \tag{1}$$

$$V_t = \sqrt{\frac{c_{44}}{\rho}}. \tag{2}$$

Along < 110 > ,

$$V_l = \sqrt{\frac{c_{11} + c_{12} + 2c_{44}}{2\rho}}. \tag{3}$$

The effective polycrystalline elastic properties such as shear modulus and Poisson's ratio were calculated using both the Voigt-Reuss (G_V-G_R) and Hashin-Shtrikman (G_H-G_S) models, as described in detail in Refs. [20] and [21].

The elastic properties were also measured directly on polycrystalline samples. To do this, the as-cast alloy was first compressed by ~60%, and then annealed at 900 °C for 3 h to produce a fully recrystallized microstructure. In the polycrystalline case [22], the shear modulus and the Poisson's ratio were determined using

$$G = V_t^2 \rho \tag{4}$$

and

$$\upsilon = \frac{1 - 2(V_t/V_l)^2}{2 - 2(V_t/V_l)^2}. \tag{5}$$

3. Results

3.1. Intrinsic physical properties and elastic constants

The lattice parameter, density and melting temperature of NiFe-20Cr are listed in Table 1; the values of NiCoCr and NiCoFe [13,23] are also shown for comparison. The lattice parameter of NiFe-20Cr is greater than that of both NiCoFe and NiCoCr, probably because the Fe and Cr have larger atomic size than Co [24]. This is similar to the case of binary alloys, in which the lattice parameter of FCC Ni-xFe and Ni-