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ScienceDirect
Acta Materialia 81 (2014) 428–441
Acta MATERIALIA
www.elsevier.com/locate/actamat

Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures

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Received 25 June 2014; received in revised form 11 August 2014; accepted 13 August 2014
Available online 3 October 2014

Abstract

Compared to decades-old theories of strengthening in dilute solid solutions, the mechanical behavior of concentrated solid solutions is relatively poorly understood. A special subset of these materials includes alloys in which the constituent elements are present in equal atomic proportions, including the high-entropy alloys of recent interest. A unique characteristic of equiatomic alloys is the absence of "solvent" and "solute" atoms, resulting in a breakdown of the textbook picture of dislocations moving through a solvent lattice and encountering discrete solute obstacles. To clarify the mechanical behavior of this interesting new class of materials, we investigate here a family of equiatomic binary, ternary and quaternary alloys based on the elements Fe, Ni, Co, Cr and Mn that were previously shown to be single-phase face-centered cubic (fcc) solid solutions. The alloys were arc-melted, drop-cast, homogenized, cold-rolled and recrystallized to produce equiaxed microstructures with comparable grain sizes. Tensile tests were performed at an engineering strain rate of 10^{-3} s^{-1} at temperatures in the range 77–673 K. Unalloyed fcc Ni was processed similarly and tested for comparison. The flow stresses depend to varying degrees on temperature, with some (e.g. NiCoCr, NiCoCrMn and FeNiCoCr) exhibiting yield and ultimate strengths that increase strongly with decreasing temperature, while others (e.g. NiCo and Ni) exhibit very weak temperature dependencies. To better understand this behavior, the temperature dependencies of the yield strength and strain hardening were analyzed separately. Lattice friction appears to be the predominant component of the temperature-dependent yield stress, possibly because the Peierls barrier height decreases with increasing temperature due to a thermally induced increase of dislocation width. In the early stages of plastic flow (5–13% strain, depending on material), the temperature dependence of strain hardening is due mainly to the temperature dependence of the shear modulus. In all the equiatomic alloys, ductility and strength increase with decreasing temperature down to 77 K.

Keywords: High entropy alloy; Face-centered cubic crystals; Solid solution strengthening; Mechanical properties; Temperature

1. Introduction

Dissolved solute atoms, to varying degrees, affect the mechanical properties of metals. Conventional treatments of solid solution strengthening assume that dislocations move through a solvent lattice of like atoms and encounter discrete unlike atoms (solutes) that can affect their mobility. The simplest case to consider is the energetics of, and the force resulting from, the elastic interaction of a dislocation with the strain field of a single solute atom (e.g. [1–7]). Both atomic size misfit and modulus mismatch between the solute and solvent atoms can contribute to this interaction. In reality, however, a dislocation interacts with multiple solute atoms simultaneously, and the net force exerted by all the solute atoms needs to be considered. For dilute solutions, early theories assumed that the interaction force between the dislocation and the solute atoms is either the

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http://dx.doi.org/10.1016/j.actamat.2014.08.026
1359-6454/

maximum value possible (strong obstacles lying exactly in the slip plane), or zero (obstacles lying above or below the slip plane) [8,9]. Taking into account the Friedel [10] separation between strong obstacles encountered by a dislocation, Fleischer developed a description in which the critical shear stress to overcome obstacles varied as the square root of the solute concentration, a result that was confirmed by early computer simulations [11,12]. For more concentrated solutions, Labusch [13–15] developed a statistical treatment of a dislocation moving through an array of obstacles with a distribution of interaction strengths, rather than the binary interaction assumed in Fleischer's treatment, and obtained a critical shear stress that varied as the two-thirds power of solute concentration. Since the development of these early theories, there have been many refinements over the years (e.g. [16–21]).

The picture of a dislocation moving through a solvent lattice and encountering discrete solute obstacles breaks down as the solute concentration and compositional complexity increase. Relatively little is known about the fundamental mechanisms of solid solution strengthening in compositionally complex alloys, i.e. alloys comprising multiple elements in high concentrations. An interesting subset of compositionally complex alloys is one in which the constituent elements are present in equal atomic concentrations. In such equiatomic alloys, there is no "solvent" or "solute" in the conventional sense. Therefore, rather than considering a dislocation moving through a solvent lattice and interacting with discrete solute atoms, it may be more appropriate to envisage the dislocation as moving through a mythical "average solvent" or "effective medium". In other words, the equiatomic alloy may not be a simple extension or extrapolation from the dilute solution limits, but rather a distinct new state akin to a stoichiometric compound with fixed atomic ratios, albeit disordered.

In order to develop accurate effective medium theories of solid solution strengthening, it is desirable to experimentally characterize the mechanical behavior of a range of equiatomic solid solution alloys. To this end, we investigate here several equiatomic binary, ternary and quaternary alloys that were previously shown to be single-phase face-centered cubic (fcc) [22]. In addition, the alloys are all subsets of an equiatomic, quinary high-entropy alloy, FeNiCoCrMn, which is known to be a fcc-structured single-phase solid solution alloy [23–28]. Tensile tests showed that the yield and ultimate strengths of this high-entropy alloy increase as the temperature is decreased [24,26].

The term high-entropy alloy (HE alloy) was coined by Yeh et al. [29] to denote alloys containing five or more elements in approximately equiatomic concentrations. These authors reasoned that the high configurational entropies of such alloys would stabilize the formation of a solid solution by counteracting the enthalpies of phase separation and compound formation. However, most of the so-called HE alloys discussed in the literature appear to be multiphase alloys (e.g. [30–39]) whose configurational entropies, as pointed out by Otto et al. [27], should in fact be low rather than high. Apparently, there are only a few multi-element equiatomic alloys that are true single-phase solid solutions with fcc (e.g. [23–28]) or body-centered cubic (bcc) crystal structures (e.g. [40–42]). The configurational entropy of these single-phase alloys is likely to be high, approaching the value of the ideal mixture assumed in the analysis of Yeh et al. [29]. The present study of equiatomic binaries, ternaries and quaternaries aims to provide an experimental basis to understand the mechanical behavior of all equiatomic alloys, including the more complex HE alloys containing five or more elements.

2. Experimental methods

2.1. Alloy preparation and characterization

The equiatomic alloys listed in Table 1 were produced by arc melting the elements Fe, Ni, Co, Cr and Mn (>99.9% pure) in a water-cooled copper hearth under Ar atmosphere. All these alloys are single-phase, fcc solid solution alloys, as shown in an earlier paper [22], and all are subsets of the quinary, single-phase, fcc-structured, high-entropy alloy, FeNiCoCrMn [23–28]. For comparison, pure Ni was produced using the same process. When Mn was added as an alloying element, special care was taken in the processing because of its high vapor pressure and tendency to oxidize rapidly, as discussed elsewhere [22,24,26,27]. The arc-melted buttons were flipped and re-melted at least five times to promote thorough mixing and then drop-cast into copper molds to produce rectangular ingots measuring 12.7 mm × 25.4 mm × 127 mm. The drop-cast ingots were homogenized for 24 h at either 1373 or 1473 K (see Table 1), followed by water quenching. They were then cold rolled along the longitudinal ingot direction to a total thickness reduction of 90–92% (Table 1) without cross-rolling or intermediate annealing. Annealing studies were conducted on the rolled sheets to determine the temperatures and times that would yield fully recrystallized microstructures and comparable grain sizes (see Table 1). In addition, the grain size of one of the alloys (FeNiCoCr) was systematically varied to investigate its influence on mechanical behavior. The annealed samples were ground (through 800-grit SiC paper), polished (through 20 nm colloidal silica suspension) and their microstructures examined in a JEOL 6500 scanning electron microscope operated in the back-scattered electron (BSE) mode.

2.2. Tensile tests

Flat dog-bone-type specimens with a gage length of 10 mm were cut from the cold-rolled sheets by electrical discharge machining (EDM) with their longitudinal axes perpendicular to the rolling direction. The specimens were annealed at the temperatures and times listed in Table 1, and all faces of their gage sections ground through 600-grit SiC paper. Nine Vickers microhardness indents spaced 1 mm apart were made along the specimen gage lengths