Enhanced solid solution effects on the strength of nanocrystalline alloys

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Abstract

Solid solution strengthening in nanocrystalline alloys is studied using sputtered Ni–W as a model system. In the composition range of 0–20 at.% W, the sputtered alloys have a nanocrystalline structure with a grain size that is independent of composition. Nanoindentation of these alloys shows that solute addition increases strength to very high levels, almost in proportion to the solute content. This behavior is not expected based on traditional solid solution strengthening mechanistic models of local dislocation pinning at solute atoms, but can be explained by further considering a global effect of solute on the average properties of the Ni lattice. The new strengthening term arises by considering grain boundaries as pinning points for dislocation motion in nanocrystalline materials and incorporating the effect of solutes on such a mechanism. Our discussion surrounding Ni–W also provides insights into other solid solution nanocrystalline systems, a variety of which we show can be accurately described using the same concept. These developments also explain the origin of solid solution softening in some nanocrystalline alloys.
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1. Introduction

Nanocrystalline metals have been the focus of intense research efforts in recent years due to their novel deformation physics. As grain size reaches the nanometer range, traditional intragranular dislocation mechanisms for plasticity are suppressed and deformation becomes dominated by grain boundary processes such as grain boundary dislocation emission [1–3], grain boundary sliding [4,5], and grain boundary migration [6–8]. The emergence of these novel mechanisms is not only scientifically interesting, but also has a profound effect on engineering properties; for example, improved strength [9,10], fatigue resistance [11], and wear resistance [12–14] have all been reported for grain sizes below about 100 nm where the mechanisms begin to shift, as has an increased rate dependence [15,16] and pressure dependence [17,18] of strength.

In practice, nanocrystalline systems with significant alloying additions are more useful than their pure metal counterparts, due to the increased thermal stability and grain size control that can be realized with alloying additions. A number of pure nanocrystalline metals experience room temperature grain growth [19,20], with a corresponding degradation of their properties. Others have been reported to coarsen under load or in service conditions [21,22], limiting the possibility of prolonged use in application. On the other hand, recent work has shown that the addition of alloying elements can produce stabilized nanocrystalline metals, either through classical kinetic constraints on coarsening or through thermodynamic reduction of the driving forces for coarsening [23,24]. For example, electrodeposited Ni–W alloys have nanocrystalline grain structures that do not coarsen appreciably when heated to temperatures up to ~500 °C [25]. In these Ni–W alloys, W additions exhibit a subtle tendency to segregate to grain boundaries, where they lower the grain boundary energy and bring the system closer to thermodynamic equilibrium [26]. As a result of this segregation tendency, alloy-

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ing additions also allow grain size to be precisely controlled during a process of electrodeposition, with W promoting grain refinement [27].

In light of these considerations, we view alloying elements as a key ingredient for almost any commercializable nanocrystalline metal. Therefore, a more complete understanding of alloying effects on the novel deformation mechanisms that dominate at the finest grain sizes is needed. What complicates this task is that when an alloying addition and a nanoscale grain size are present, both have potentially significant effects on properties and the two are difficult to decouple systematically because composition affects structure. For example, in the electrodeposited Ni–W alloys mentioned above, grain size is intimately tied to composition [27], and changing one of these variables tends to cause changes in the other (at least in the as-deposited state). A number of other nanocrystalline alloys, such as Ni–P [28], Pd–Zr [29], and Ni–Fe [30], exhibit a similar dependence of grain size on composition. Detailed studies that isolate the effects of grain size and composition for various systems (solid solution, phase separating, etc.) are needed.

There have been a number of papers that have addressed alloying effects on the mechanical properties of nanocrystalline metals [31–33]. These are for the most part somewhat speculative, again because they are generally unable to separate the effects of composition and grain size. At the same time, it is only relatively recently that detailed understanding of the deformation mechanisms of nanocrystalline pure metals has emerged [3,34–37], and many early studies of alloying effects could not benefit from the insights of those works. We suggest that the understanding of deformation mechanisms in pure metals with nanoscale grain sizes is now sufficiently mature that it may be possible to begin to specifically isolate the effects of alloying additions upon those mechanisms. In the present paper, we provide some initial steps towards this goal, by developing a set of idealized solid solution nanocrystalline specimens of Ni–W. After exploring the processing space for these alloys by magnetron sputtering, we prepare a set of samples that all have the same grain size (~20 nm), but contain solid solution additions spanning a broad range of 0–20 at.% W. The mechanical properties of these alloys are investigated to provide insight into solid solution strengthening of nanocrystalline metals, at a grain size where deformation is dominated by grain boundary processes. The results are then generalized to other solid solutions, and broad conclusions about the role of solution alloying on the strength of nanocrystalline alloys are developed.

2. Materials and methods

As noted above, Ni–W is a well-studied nanocrystalline system, especially in electrodeposited form. However, the grain size and composition of Ni–W electrodeposits are linked monotonically; in fact, composition is used to control grain size [27]. Here, we seek an alternative route for

producing nanocrystalline Ni–W alloys where grain size is not controlled purely by composition. Specifically, we employ sputter deposition, since this highly energetic deposition process leads to kinetic limitations on grain size. The existing literature on sputter deposited Ni–W suggests that face-centered-cubic (fcc), amorphous, or body-centered-cubic (bcc) phases can be produced [38–43], although detailed microstructural characterization spanning a wide range of compositions does not appear to exist. Alloys with a broad range of compositions were deposited using an ATC magnetron sputtering system (AJA International, Scituate, MA). Prior to deposition, the chamber was evacuated to $<10^{-6}$ torr and then backfilled with Ar to 4 m torr, which was maintained throughout deposition. Direct current magnetron sputtering was used; to vary the W content in the alloys, the relative currents to the W and Ni targets were adjusted. To identify a composition range where grain size is constant, alloys for transmission electron microscopy (TEM) were directly deposited onto Ni TEM grids with a carbon-stabilized resin backing (Ted Pella Inc., Redding, CA) to a thickness of ~50 nm so that no subsequent sample preparation was necessary; these will be referred to throughout as the "thin" samples. Thicker coatings (thickness ~1 μm) were deposited onto Si wafers for structural characterization by X-ray diffraction (XRD) and for mechanical testing by nanoindentation; these will be referred to as "thick" samples.

The thin specimens were examined using a JEOL 2010 TEM operated at 200 kV. The phases present in each sample were determined using bright field images and electron diffraction patterns. Grain size (d) was measured by manually tracing individual grains and determining the circular equivalent diameter. XRD of the thick specimens was performed on a PANalytical X'Pert Pro diffractometer with a Cu Kα radiation source operated at 45 kV and 40 mA. XRD profiles were used for phase determination, to measure lattice parameter, and to estimate the average grain size to within ±15% by applying the Scherrer equation [44] to the (1 1 1) peak after subtracting instrumental broadening. The composition of each alloy was measured by energy dispersive spectroscopy (EDS) in a Leo 438VP scanning electron microscope (SEM) operated at 20 kV.

Mechanical properties were measured by instrumented nanoindentation using a Hysitron Ubi1 with a diamond Berkovich tip. The Oliver–Pharr method [45] was used to extract hardness and reduced modulus from load–displacement curves, using a tip area function which was carefully calibrated on fused silica. All tests were carried out at constant indentation strain rates, $\dot{\varepsilon}$, given by [46]:

$$\dot{\varepsilon} = \frac{1}{h}\frac{\partial h}{\partial t} = \frac{1}{2}\left(\frac{1}{P}\frac{\partial P}{\partial t}\right) \tag{1}$$

where h is indentation depth, t is time, and P is applied load. After loading at the strain rate of interest, the sample was unloaded to 20% of the maximum load and a 10 s hold was used to characterize instrumental drift. A maximum load of 2 mN was used, corresponding to indentation