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# Phase strength effects on chemical mixing in extensively deformed alloys

Zachary C. Cordero and Christopher A. Schuh*

*Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA*

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**Abstract**—Forced chemical mixing during extensive straining requires that the constituent phases co-deform, and is therefore a sensitive function of their mechanical properties, particularly strength. To develop a quantitative understanding of such phase strength effects on co-deformation and steady-state chemical mixity during severe deformation processing, we studied several tungsten–transition metal couples with a range of differences in strength during a process of mechanical alloying in a high-energy ball mill. Changes in the powders' microstructures, mechanical properties and chemical mixing revealed two distinct behaviors: alloys either chemically homogenized or remained dual phase, depending on the relative strengths of the base alloying elements. A kinetic Monte Carlo simulation of mechanical alloying that accounts for a phase strength mismatch reproduced the experimentally observed behaviors, and provides quantitative insight into the combination of material and processing parameters that control mechanical mixing.

*Keywords:* Mechanical alloying; Non-equilibrium solid solutions; Powder processing; Kinetic Monte Carlo; Alloy design

## 1. Introduction

The steady-state microstructure that evolves after the application of extensive plastic strains to alloys often comprises non-equilibrium phases or configurations [1–3]. This is generally true for most modes of severe plastic deformation [4–9], and is of particular relevance to conventional mechanical alloying [10,11]. Such non-equilibrium microstructures evolve out of a competition between recovery processes, which tend to restore the microstructure toward the equilibrium state, and deformation-related processes, which drive it away from equilibrium [12]. By adjusting the ratio of the recovery rate to the deformation rate, the steady-state microstructure can be made more or less metastable [13]. Increasing the temperature while keeping the milling intensity constant, for example, generally increases the recovery rate relative to the deformation rate, and this typically leads to microstructures closer to equilibrium [14]. Conversely, lowering the temperature so that recovery is kinetically suppressed leads to microstructures with non-equilibrium features such as supersaturated solid solutions of normally immiscible alloying elements. Such forced mechanical mixing to a non-equilibrium condition is often the explicit goal of the process.

Although there are examples of immiscible couples (e.g., Cu–Co [15] and Ag–Cu [16]) that form solid solutions during mechanical alloying, others remain phase-separated over a range of compositions despite being milled at low homologous temperatures (e.g., Cu–W [17] and Cu–Ta [18]). One reason that some couples remain dual phase is that plastic deformation occurs preferentially in the softer phase, and as a result, atoms are not sheared across the interphase interface [19,20]. Thus, alloying elements must co-deform for deformation-induced mixing to occur, and one way to encourage co-deformation is to mechanically alloy elements with "similar" mechanical properties [11]. For dual-phase metallic systems with coarse microstructures, it is also well established that the amount of co-deformation depends not just on the individual phases' mechanical properties but also on microstructure, and specifically the two phases' volume fractions and geometries [21–24]. For example, in alloys with a small volume fraction of a hard element, the softer element can flow around the hard element without the hard element deforming; however, this becomes more difficult as the volume fraction of the hard element increases [25].

Hong and Fultz [26] and others [13,27] have suggested that microstructure and mechanical properties can influence the amount of deformation-induced mixing during mechanical alloying. There have also been several recent molecular dynamics studies investigating the effect of the alloying elements' mechanical properties on the mechanisms of deformation-induced mixing [19,28–30]. But while there are many isolated data points, some empirical rules-of-thumb and qualitative discussion about the roles of the constituent phases' mechanical properties and the couple's microstructure in mechanical alloying, we are not aware of a general quantitative heuristic by which mixable couples (or conditions under which couples can become mixable)

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* Corresponding author; e-mail: schuh@mit.edu

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can be predicted. Our purpose in this paper is to provide a step towards such a view through systematic study by both experiment and simulation. Experimentally, we track the microstructure, mechanical properties and amount of co-deformation and mixing in several W–transition metal couples subjected to mechanical alloying. Computationally, we adapt a classical Bellon–Averback kinetic Monte Carlo simulation of mechanical alloying [31–33] to demonstrate how a difference in phase strength leads to multiply stable steady states. The results together point to the possibility of understanding preferred conditions for forced mechanical mixing.

## 2. Materials and methods

### 2.1. Powder processing

Elemental W, Cr and Zr as well as several equiatomic $W_{50}TM_{50}$ alloys (TM = Cr, Nb, Ni, Hf or Zr) were milled in a SPEX 8000 high-energy ball mill. The powders were acquired from Alfa Aesar, and had the following purity and sizing: W, 99.95%, −200 + 325 mesh; Cr, 99+%, −325 mesh; Zr, 99.6%, −325 mesh; Nb, −325 mesh, 99.8%; Ni, 99.996%, −120 mesh; Hf, 99.6%, −325 mesh. We selected W as the base alloying element because the maximum temperature encountered in a SPEX ball mill (~100 °C [2]) is just 10% of its melting temperature. As a result, interdiffusion in the $W_{50}TM_{50}$ couples is, to a good approximation, kinetically suppressed, and structural evolution only proceeds through plastic deformation. The alloying elements were selected because their maximum hardnesses (once refined into a nanocrystalline state) ranged from a low of 6 GPa (Zr [34]) to a high of 16 GPa (Cr), as compared to 22 GPa for W.

The $W_{50}TM_{50}$ alloys were prepared by mechanically alloying elemental feedstock powders. All of the milling runs were conducted using a steel vial and grinding media with a ball-to-powder ratio of 5:1 (10 g powder). To prevent oxidation, the milling was performed in a glovebox maintained under an ultra-high-purity Ar atmosphere. To monitor the structural evolution of the powder particles, ~0.2 g of the powder was removed periodically for subsequent characterization.

### 2.2. Microstructural and chemical characterization

The grain size and lattice parameter of the W-rich, body-centered cubic (bcc) phase was tracked with milling time using X-ray diffraction (XRD). XRD patterns were collected using a Cu $K_\alpha$ source Panalytical X'Pert Pro operated at 45 kV and 40 mA. The lattice parameter, which can be used to infer the amount of solute dissolved in the W and therefore the degree of mixing, was measured using Rietveld refinement. The grain size was calculated from the peak broadening using a Williamson–Hall analysis after correcting out the contribution from instrumental broadening using a NIST $LaB_6$ standard.

Following XRD, the powders were cold-mounted in epoxy, rough ground and polished; polishing concluded with a colloidal silica suspension. Energy dispersive spectroscopy (EDS) was performed on these mounted samples using a JEOL 6610-LV scanning electron microscope operated at 20 kV, to measure the amount of Fe contamination due to abrasion of the steel vial and media. The total amount of Fe contamination as a function of milling time for the various couples and pure W is shown in Fig. 1. We highlight the W, $W_{50}Cr_{50}$ and $W_{50}Nb_{50}$ data in red to emphasize that these powders had a similar amount of Fe contamination, which was greater than that of the $W_{50}Zr_{50}$, $W_{50}Hf_{50}$ and $W_{50}Ni_{50}$ powders, highlighted blue.

The concentration of solute, $x$, dissolved in the bcc W phase was calculated from the measured lattice parameter using Vegard's law:

$$X_{solute} = \frac{(a_{\mathrm{bcc}} - a_{\mathrm{W}})}{(a_{solute} - a_{\mathrm{W}})} - \frac{x_{\mathrm{Fe}}(a_{\mathrm{Fe}} - a_{\mathrm{W}})}{(a_{solute} - a_{\mathrm{W}})} \tag{1}$$

where $x_{\mathrm{Fe}}$ is the concentration of Fe dissolved in the W and $a_{\mathrm{W}}$, $a_{\mathrm{Fe}}$, $a_{solute}$ and $a_{\mathrm{bcc}}$ are the pure W, pure Fe, pure solute and measured lattice parameters, respectively. The first term in this expression is the standard form of Vegard's law for a binary couple, and the second term is added as a correction to account for the pickup of iron from the milling media and vial. The alloying elements' lattice parameters are given in Table 1; note that estimated bcc lattice parameters were used for the non-bcc alloying elements: Zr, Hf and Ni. We estimated $x_{\mathrm{Fe}}$ by multiplying the global concentration of Fe in the as-milled powder (Fig. 1) by the fraction of Fe dissolved in the W phase. The fraction of Fe dissolved in the W phase was calculated from a control experiment in which we milled initially pure W, and measured the global concentration of Fe using EDS and the concentration of Fe in the W lattice using Vegard's law with milling time. The ratio of these quantities gave the fraction of Fe dissolved in the W, which we assumed to be the same for pure W and the $W_{50}TM_{50}$ couples for a given milling time.

The $W_{50}Cr_{50}$ and $W_{50}Zr_{50}$ couples were down-selected for a more in-depth investigation of their microstructure using scanning electron microscopy (SEM) and dark field

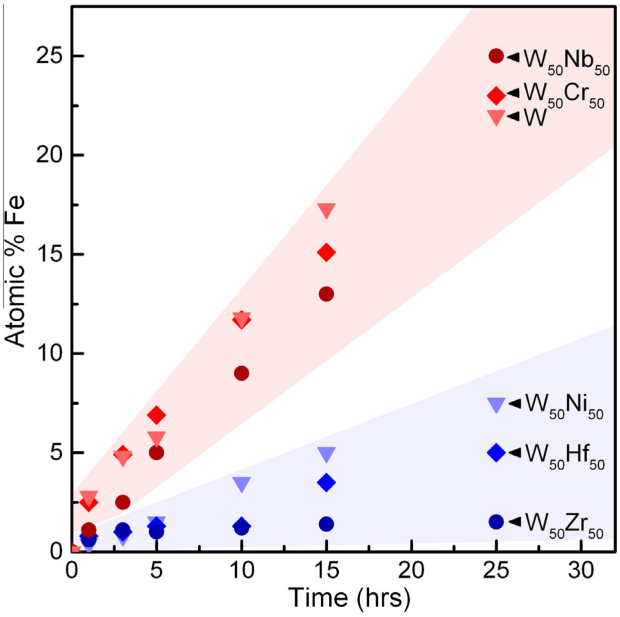

**Fig. 1.** Fe contamination as measured using EDS in the initially pure W and W–transition metal powders as a function of milling time. The W, $W_{50}Cr_{50}$ and $W_{50}Nb_{50}$ powders are harder than the $W_{50}Ni_{50}$, $W_{50}Hf_{50}$ and $W_{50}Zr_{50}$ powders, and abrade more Fe as a result.