

Grain boundary wetting and prewetting in Ni-doped Mo

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Grain boundary (GB) wetting and prewetting in Ni-doped Mo are systematically evaluated via characterizing well-quenched specimens and thermodynamic modeling. In contrast to prior reports, the δ -NiMo phase does not wet Mo GBs in the solid state. In the solid-liquid two-phase region, the Ni-rich liquid apparently wets Mo GBs completely. Furthermore, high-resolution transmission electron microscopy demonstrates that nanometer-thick quasiliquid films persist at GBs into the single-phase region where the bulk liquid phase is no longer stable. This is interpreted as a case of GB prewetting. An analytical thermodynamic model is developed and validated; this model can be applied to other alloys. © 2009 American Institute of Physics. [DOI: 10.1063/1.3155443]

Impurity-based intergranular films (IGFs), which are ubiquitous in ceramic materials, often control sintering, grain growth, and various mechanical and physical properties.¹ These IGFs exhibit an “equilibrium” thickness on the order of 1 nm and “quasiliquid” structures that are neither completely amorphous nor fully crystalline. Nanoscale films of similar character have been observed on oxide free surfaces² and at metal-oxide interfaces.³ In a generalized Cahn wetting model, Tang and coworkers^{4,5} proposed that subsolidus IGFs could form from coupled grain boundary (GB) prewetting and premelting transitions. An analogous first-order transition on free surfaces has indeed been observed,⁶ which can be explained as a coupled surface prewetting and premelting transition.⁷ Because van der Waals (vdW) London dispersion forces and electrostatic interactions in ceramic systems complicate interfacial behaviors, the model of Tang and coworkers^{4,5} is better applicable to binary metals. Although GB premelting and prewetting in various metallic systems have been investigated by Straumal and coworkers,⁸ high-resolution transmission electron microscopy (HRTEM) studies are rare. The only exception is a recent HRTEM study of Ni-doped W, which found stable quasiliquid IGFs in the subeutectic two-phase region.⁹ Although GB prewetting transitions in Bi–Cu and Fe–Si–Zn have been indicated by GB chemistry and diffusion measurements,⁸ direct HRTEM observation of quasiliquid IGFs in the single-phase region has not been made for any metallic system.

GB wetting and prewetting in the Mo–Ni system are practically important for understanding its sintering and embrittlement properties.¹⁰ Two prior studies found nanometer-thick layers of crystalline δ -NiMo at Mo GBs and inferred a solid state complete GB wetting.¹⁰ However, it is unknown whether these compound layers could indeed exhibit arbitrary thickness as being expected for a case of complete wetting and whether they were in fact disordered at the firing temperatures.

In this study, we derived a set of analytical equations to evaluate GB wetting and prewetting for binary transition metals and applied them to the Mo–Ni system. Subsequently, critical experiments were conducted to (1) validate the proposed model, (2) clarify the existing controversy about GB

wetting in Mo–Ni, and (3) seek direct HRTEM evidence for the stabilization of quasiliquid IGFs in the single-phase region of a binary metallic system to critically support the prewetting theories.^{4,5,8}

Ni-doped Mo specimens were prepared using a powder metallurgy method and presintered at 1100 °C for 24 h in flowing Ar–5% H₂. A special furnace system was constructed so that we could isothermally anneal a specimen in vacuum (for 2 h in this study) and drop it into a diffusion pump oil bath (in a small vacuum chamber that was immersed in a large amount of cold water) within ~ 1 s to quench the high-temperature structures. The well-quenched specimens were characterized by scanning electron microscopy (SEM) (Hitachi 4800) and HRTEM (Hitachi 9500, 300 kV).

We adopt a Miedema type model that was elaborated by Benedictus *et al.*¹¹ to evaluate relevant interfacial energies. The average excess energy for a crystal-crystal interface between Mo (bcc) and δ -NiMo is estimated as

$$\gamma_{cc} \approx \frac{\gamma_{Mo}^s + \gamma_{MoNi}^s}{6} + \frac{F_{Ni}^{Mo} \Delta H_{Mo \text{ in Ni}}^{\text{interface}}}{C_0 V_{Mo}^{2/3}} \approx 0.90 \text{ J/m}^2, \quad (1)$$

where surface energies γ_{Mo}^s and γ_{MoNi}^s are evaluated using the Miedema model [Eqs. 7 and 11b in Ref. 11, neglecting the entropic contribution], $\Delta H_{Mo \text{ in Ni}}^{\text{interface}}$ ($= -32$ kJ/mol) is the enthalpy of solution, $C_0 \approx 4.5 \times 10^8$, V is the molar volume (neglecting thermal expansion), and F_{Ni}^{Mo} is the surface fraction of Ni atoms of δ -NiMo. Furthermore, the average energy of random GBs in pure Mo is estimated as $\gamma_{GB}^{(0)} \approx 1/3 \times \gamma_{Mo}^s \approx 1.0$ J/m². In a Ni-doped specimen, the actual GB energy (γ_{GB}) is less than $\gamma_{GB}^{(0)}$, because Ni adsorption (including the formation of an IGF) reduces GB energy according to the Gibbs adsorption isothermal. Since $2\gamma_{cc} > \gamma_{GB}^{(0)} > \gamma_{GB}$, complete GB wetting cannot occur in the solid state, generally. The average dihedral angle is estimated based on the Young equation as

$$\phi = 2 \arccos\left(\frac{\gamma_{GB}}{2\gamma_{cc}}\right) > 2 \arccos\left(\frac{\gamma_{GB}^{(0)}}{2\gamma_{cc}}\right) \approx 112^\circ. \quad (2)$$

For specimens quenched from 1344 °C (with two equilibrium phases of Mo-rich bcc and δ -NiMo), the average measured dihedral angles on two-dimensional sections (which should be equal to the average true three-dimensional dihedral angle)¹² is 105° with a standard deviation of 11°. This

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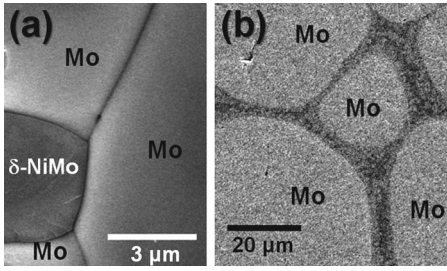


FIG. 1. (a) A SEM image of a fractured Mo +12.4 at. % Ni specimen quenched from 1344 °C shows that δ -NiMo phase does not wet Mo GBs in the solid state. (b) A cross-sectional SEM image of a Mo +12.4 at. % Ni specimen quenched from 1495 °C shows that the Ni-rich liquid phase apparently wets Mo GBs completely.

result reasonably agrees with Eq. (2), thereby supporting the validity of the equations of Benedictus *et al.*¹¹ In summary, it can be unequivocally concluded that δ -NiMo does not wet Mo GBs, which is directly shown in Fig. 1(a).

In the solid-liquid two-phase regime, the crystal-liquid interfacial energy is estimated as¹¹

$$\begin{aligned} \gamma_{cl} &\approx \frac{H_{\text{Mo}}^{\text{fuse}} + \Delta H_{\text{Mo in Ni}}^{\text{interface}} \times F_{\text{Ni}}^{\text{Mo}}}{C_0 V_{\text{Mo}}^{2/3}} + \frac{1.9RT}{C_0 V_{\text{Mo/Ni}}^{2/3}} \\ &= (0.138 - 0.160F_{\text{Ni}}^{\text{Mo}} + 8.92 \times 10^{-5}T) \text{J/m}^2, \end{aligned} \quad (3)$$

where $H_{\text{Mo}}^{\text{fuse}}$ is the fusion enthalpy, $F_{\text{Ni}}^{\text{Mo}}$ represents the fraction of Ni–Mo bonds at the interface (we calculated it using Eq. 5a in Ref. 11 and the liquidus composition, X_L), and R is the gas constant. Then, γ_{cl} is calculated to be 0.211 J/m² at 1362 °C ($=T_{\text{peritectic}}$) and 0.231 J/m² at 1495 °C. Since $2\gamma_{cl} < \gamma_{\text{GB}}^{(0)} \approx 1.0 \text{ J/m}^2$, complete wetting of Mo GBs by the Ni-rich liquid is generally expected (noting that this is neither a sufficient condition nor applicable to coincident GBs with low $\gamma_{\text{GB}}^{(0)}$). Complete GB wetting in the solid-liquid regime has been confirmed by characterizing quenched specimens, and one example is shown in Fig. 1(b). Here, we presume that the attractive vdW London dispersion force, which in principle inhibits complete wetting (or complete premelting),¹³ is negligibly small for metallic systems.

In the single-phase (Mo-rich bcc phase) region, there is a free-energy penalty (ΔG_{amorph}) for forming the metastable liquid phase. Nonetheless, a quasiliquid IGF of thickness h can be thermodynamically stable if this free-energy penalty is more than offset by the reduction in interfacial energies when a GB is replaced with two crystal-liquid interfaces,

$$\Delta G_{\text{amorph}} \times h < \gamma_{\text{GB}}^{(0)} - 2\gamma_{cl} \equiv -\Delta\gamma. \quad (4)$$

At 1495 °C, $-\Delta\gamma$ is estimated to be 0.54 J/m². Consequently, nanoscale GB wetting can occur when the (liquid) phase that does the wetting is not yet a stable bulk phase, which is a prewetting phenomenon.¹⁴

The value of ΔG_{amorph} can be quantified using calculation of phase diagram or CALPHAD method.^{15,16} Here, we propose a simpler analytical approach to estimate ΔG_{amorph} and therefore the stability of quasiliquid IGFs. In a regular solution model, the free-energy of mixing for the Mo-rich bcc phase is given by

$$\Delta G_{\text{bcc}}^{\text{mix}} = RT[X \ln X + (1-X)\ln(1-X)] + \Omega X(1-X), \quad (5)$$

where X is the Ni atomic fraction in the bcc phase, and Ω is the regular solution parameter ($\Omega \approx 46442 \text{ J/mol}$ for the

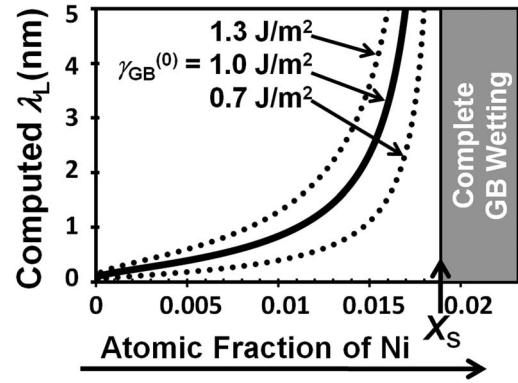


FIG. 2. Computed λ_L vs Ni atomic fraction (X) at 1495 °C. The computed λ_L value represents the maximum thickness of a stable quasiliquid IGF of liquidus composition (X_L) without considering interfacial forces, and λ_L scales the actual equilibrium IGF thickness (see Refs. 15 and 16). When the Ni content is below the bulk solidus composition ($X_S=0.0189$), the liquid phase is no longer a stable bulk phase.

Mo–Ni bcc phase¹⁷). Assuming, for simplicity, that an IGF adopts the bulk liquidus composition (X_L), ΔG_{amorph} can be estimated as

$$\Delta G_{\text{amorph}} \approx G_{\text{liq}}^f(X_L) - \left[G_{\text{bcc}}^f(X) + (X_L - X) \frac{dG_{\text{bcc}}^f}{dX} \Big|_{X} \right], \quad (6)$$

where G_{liq}^f and G_{bcc}^f are the formation free-energies of the liquid and the bcc phases, respectively. The second term in Eq. (6) represents a reference free-energy state set by the chemical potentials of the bulk bcc phase. By definition, ΔG_{amorph} vanishes if the composition of the bcc phase is on the bulk solidus line ($X=X_S$); thus

$$G_{\text{liq}}^f(X_L) = G_{\text{bcc}}^f(X_S) + (X_L - X_S) \frac{dG_{\text{bcc}}^f}{dX} \Big|_{X_S}. \quad (7)$$

Combining Eqs. (5)–(7) gives

$$\begin{aligned} \Delta G_{\text{amorph}} &= RT \left[X_L \ln \frac{X_S}{X} + (1 - X_L) \ln \frac{1 - X_S}{1 - X} \right] - \Omega(X_S - X) \\ &\quad \times (2X_L - X_S - X). \end{aligned} \quad (8)$$

Following Eq. (4), we define λ_L to represent the maximum thickness of a stable quasiliquid IGF of the liquidus composition X_L (without interfacial forces), as

$$\lambda_L \equiv -\Delta\gamma / \Delta G_{\text{amorph}}. \quad (9)$$

It should be noted that λ_L defined here is slightly different from the λ defined in Refs. 15 and 16 in that the IGF is assumed to adopt the liquidus composition. This simplification allows us to compute λ_L analytically, making this scheme easier to be implemented than the prior model.^{15,16}

Figure 2 shows computed λ_L versus bulk Ni fraction at 1495 °C ($X_S=0.0189$ and $X_L=0.5802$, calculated using the thermodynamic functions in Ref. 17). Dotted lines in Fig. 2 bound the range of computed λ_L 's for random GBs assuming $\pm 30\%$ variations in $\gamma_{\text{GB}}^{(0)}$. The actual equilibrium film thickness, which depends on the unknown interfacial forces, should be scaled by (but is typically not identical to) the computed λ_L .^{15,16} Furthermore, discrete jumps in film thickness may arise from a first-order prewetting transition⁴ or a

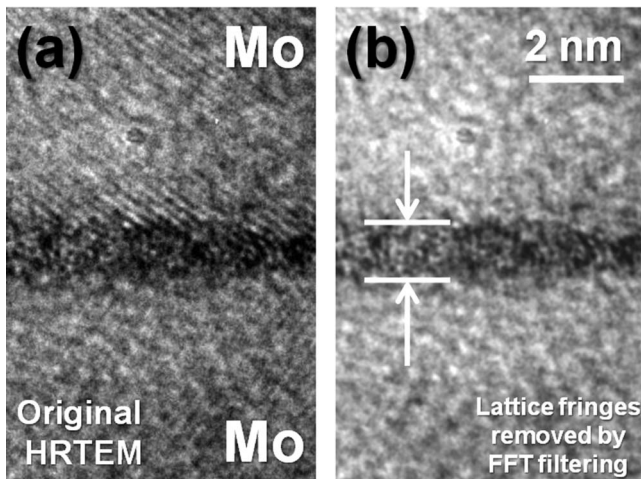


FIG. 3. (a) An original (unprocessed) HRTEM image of an IGF in a Mo +1 at. % Ni specimen quenched from 1495 °C. Since $X < X_S = 1.89$ at. %, a single bcc phase is expected from the bulk phase diagram. (b) After removing lattice fringes using a FFT filtering method that was developed for enhancing the images of thin IGFs in Ref. 19, a discrete film that exhibit high degree of structural disorder is more distinguishable.

finite atomic size effect,^{15,16} producing discrete GB complexions (phases) similar to those observed by Dillon *et al.*¹⁸

To seek the nanoscale IGFs predicted in Fig. 2 in the single-phase region, Mo +1 at. % Ni specimens were annealed at 1495 °C ($X_S = 1.89\%$) and quickly quenched. SEM examination confirmed no observable secondary phase. These well-quenched specimens were characterized by HRTEM. Nanoscale IGFs were observed at six independent GBs (among seven edge-on GBs that could be clearly imaged). The average measured thickness is 0.80 nm and the corresponding standard deviation is 0.12 nm. A representative HRTEM image is shown in Fig. 3(a), and this relatively thick IGF is presented so that the disordered structure can be clearly evident. Furthermore, a fast Fourier transform (FFT) filtering method developed by MacLaren¹⁹ was adopted to remove the lattice fringes. The filtered image shown in Fig. 3(b) clearly shows a discrete IGF that exhibits high degree of structural disorder. All six independent IGFs exhibit no discernible long-range periodicity in HRTEM (though the abut grains should impose some partial order to these IGFs).^{1,4,5} The IGF in Fig. 3(a) [and Fig. 3(b)] exhibits some random short-range order, which is a typical character of “amorphous” phases in HRTEM. Hence, the IGF is not a misaligned crystalline film (although a nanoscale IGF sandwiched between two crystalline grains cannot be fully amorphous).^{1,4,5}

It is likely that the well-known activated sintering in Ni-doped Mo is due to enhanced mass transport in nanoscale quasiliquid IGFs that form below the bulk peritectic temperature, similar to those reported for Ni-doped W (Refs. 9 and 16) and Bi₂O₃-doped ZnO.²⁰ It is possible that the GB layers of δ -NiMo observed in prior studies¹⁰ were disordered at firing temperatures but crystallized upon cooling. Alternately,

nanoscale layers of crystalline δ -NiMo could be stabilized at special GBs if there is a lattice match at one or two interface(s), where a strain effect might limit the film thickness.

In summary, both experiments and thermodynamic models show that δ -NiMo does not wet Mo GBs in the solid state, while the Ni-rich liquid apparently wets Mo GBs completely. HRTEM characterization of well-quenched specimens has directly revealed the stabilization of quasiliquid IGFs in the single-phase region in Ni-doped Mo. Such quasiliquid IGFs can critically impact materials fabrication processing and high-temperature properties. An analytical approach has been developed and validated for assessing GB wetting and prewetting. This analytical model is easier to be implemented than the previously proposed numerical analysis method,^{15,16} and it can be readily extended to subregular solutions (or the Redlich–Kister model). Further improvements of this model should consider the Langmuir–McLean adsorption and compositional gradients. This work represents an important step toward our long-range scientific goal of developing quantitative GB diagrams as a materials science tool for realizing predictable fabrication of materials by design.¹⁵

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