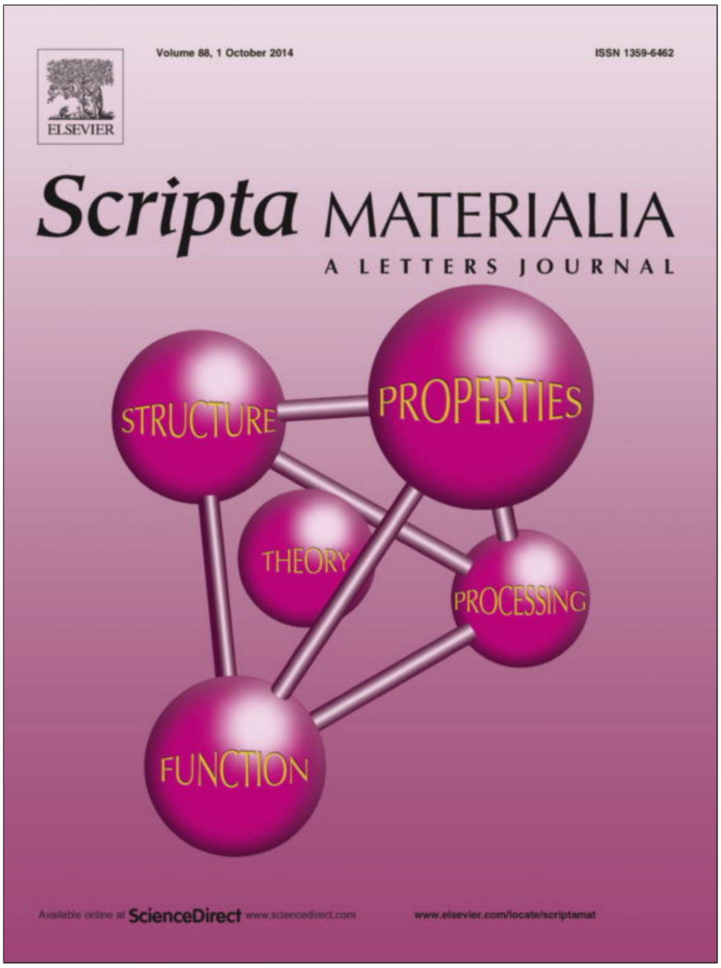
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Observation of an unusual case of triple-line instability

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Bi vapors penetrate along the triple lines in electrodeposited Ni specimens to form open channels at 800 and 900 °C. This triple-line instability can be interpreted as a case of triple-line wetting by a gas phase. Further controlled experiments using high-purity Ni specimens suggest that the presence of S impurities is essential. This unusual wetting phenomenon is related to the formation of a bilayer complexion in Ni–Bi and its occurrence can significantly affect microstructural stability and corrosion resistance.

Keywords: Grain boundary complexion; High-temperature capillary; Triple line; Microstructural stability; Wetting

It is well known in classical physical metallurgy that the ratio of the grain boundary (GB) energy (γ_{gb}) and surface energies (γ_S) is ~1/3 (in the range of 0.2–0.5) for most pure metals [1]. In multicomponent alloys, adsorption (segregation) of the solutes (or impurities) can often reduce both γ_{gb} and γ_S according to the Gibbs adsorption theory [2]. The Rice–Wang model for GB embrittlement suggests that adsorption reduces $2\gamma_S$ more than γ_{gb}, resulting in a decrease in the work of adhesion ($2\gamma_S - \gamma_{gb}$ assuming isotropic γ_S, which represents the difference in the equilibrium interfacial energies; it differs from, but is correlated with, the actual work of separation) [3]. This also implies that adsorption would likely increase the ratio of γ_{gb}/γ_S. In practice, it is uncommon (but theoretically possible) to observe cases where $\gamma_{gb}/\gamma_S > 1$. Thermodynamically, the ratio of γ_{gb}/γ_S must be <2; otherwise, a GB is no longer stable and will spontaneously separate into two free surfaces.

A series of recent Viewpoint articles emphasized the importance of understanding and controlling triple lines/junctions (a.k.a. triple-grain junctions in a polycrystal where three GBs meet) [4–6]. Thermodynamically, if $\gamma_{gb}/\gamma_S > \sqrt{3} \approx 1.73$, a triple line is no longer stable (for isotropic γ_S and ignoring torques and triple-junction line energies), as shown in Figure 1. This may be viewed as a case of triple-line wetting by a vapor phase, but it is more complex than the usual case of wetting since the triple-grain junction line is replaced with three new triple lines in addition to the formation of three new solid–gas surfaces (Fig. 1). This paper reports such a case of triple-line instability; here, the critically large ratio of γ_{gb}/γ_S is likely induced by the strong interfacial adsorption of Bi, along with S impurities, in electrodeposited Ni. The occurrence of this unusual high-temperature capillary phenomenon can significantly affect the microstructural stability and corrosion resistance.

For the first batch of experiments, electrodeposited Ni foils were prepared following a pulsed electrodeposition procedure [7] with minor modifications. Prior to electrodeposition, the Cu substrates and Pt counter-electrode were ground with SiC films (up to 800 grit), fine polished by 1.0 μm Al_2O_3 colloidal suspensions and cleaned in acetone. A bath composed of $NiSO_4 \cdot 6H_2O$ (300 g l^{-1}), $NiCl_2 \cdot 6H_2O$ (45 g l^{-1}) and H_3BO_3 (45 g l^{-1}), with additives of saccharine (5 g l^{-1}) and sodium lauryl sulfonate (0.25 g l^{-1}), was used. Each deposition was conducted for 30 min with continuous stirring, and the bath temperature was maintained at 65 ± 1 °C. The effective current density was kept at 0.1 A cm^{-2} (by using an "on" time of 5 ms with the current density of 0.4 A cm^{-2}, followed by an "off" time of 15 ms, periodically). The thickness of the electrodeposited Ni was ~40 μm (Fig. S1). The as-deposited specimens were characterized by X-ray diffraction (XRD)

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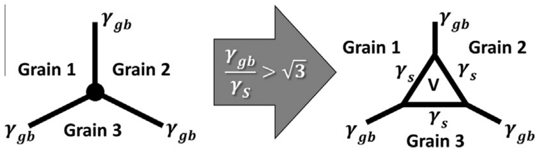

Fig. 1. A triple-grain junction line is unstable if $\gamma_{gb}/\gamma_S > \sqrt{3}$ for a simplified case of isotropic interfacial energies. This instability condition ignores the contributions of triple-junction line energies because the open channels are >100 nm in their dimensions, but the triple-junction line energies can be critically important during the nucleation stage of this instability.

using a Rigaku (Tokyo, Japan) RU-200BH diffractometer operating at 40 kV and 100 mA, which revealed no impurity phase (Fig. S1). After the electrodeposition, the Cu substrates were dissolved in aqueous solutions containing CrO_3 ($250\ g\ l^{-1}$) and sulfuric acid ($15\ cm^3\ l^{-1}$), and free-standing electrodeposited Ni foils were used in the subsequent experiments.

In the second batch of controlled experiments, two sets of high-purity Ni specimens (99.9945 at.%; purchased from Alfa Aesar), with and without pre-treatment to dope S, were used to determine the effects of impurities. The S-doped specimen was made by annealing high-purity Ni in a covered container together with S powder (without direct contact) at 400 °C for 1 h in a horizontal tube furnace flowing under Ar + 5 mol.% H_2; subsequently, surface S residuals were ground off and annealed again at 600 °C for 1 h in Ar + 5% H_2 to homogenize the S. All specimens were slightly ground, fine polished and cleaned prior to additional experiments.

Subsequently, the Ni specimens and a small amount of Bi powder were placed on the opposite sides of a covered alumina boat (without direct contact), and isothermally annealed at the desired temperature for 4 h in a flow of Ar + 5% H_2 gas. For comparison, Ni specimens were also annealed at identical conditions without Bi powder/vapor. The annealed specimens were characterized by scanning electron microscopy (SEM) with a Philips XL30 field emission microscope.

Figure 2 shows SEM images of selected representative surfaces of the electrodeposited Ni specimens annealed in the Bi vapor at various temperatures. After annealing at 700 °C, all 230 triple junctions examined were stable (i.e. free of open channels: Fig. 2a,b). After annealing at 800 °C, open channels were observed to form at 20/89 (~23%) triple junctions examined (Fig. 2c,d; Fig. S2). After annealing at 900 °C, open channels were observed to form at 85/326 (~26%) triple junctions examined (Fig. 2e,f; Fig. S3). These open channels have dimensions ranging from 200 nm to 1 μm (Fig. 2d,f); Figs. S2 and S3); further careful examination with SEM cannot determine the bottoms of the channels, indicating they are deep (beyond the SEM depth of field). They represent a case of triple-line instability at the annealing temperature, as schematically illustrated in Figure 1. Moreover, this triple-line instability is likely anisotropic since it was only observed at ~1/4 of triple junctions on the surfaces. Grooving at GBs and surface faceting were also evident (Fig. 2; Figs. S2 and S3). In contrast, all the 363 triple junctions examined were stable in the electrodeposited Ni specimens annealed at 700–900 °C without the Bi powder/vapor, as shown in Figure S4 and summarized in Table S1 in the Supplementary materials. This comparison implies that the occurrence of the triple-line instability was induced by the presence of the Bi vapor; presumably, Bi atoms adsorb/segregate at both surfaces and GBs at the annealing temperature.

It is well known that electrodeposited Ni has a low purity (~99.5%) [8,9]. Thus, a second batch of experiments using high-purity Ni was conducted. Surprisingly, SEM micrographs showed that all 75 triple junctions examined in the high-purity Ni specimens annealed at 800 and 900 °C in Bi vapors were stable (free of open channels), as shown in Figure 3 and Table S1, despite the occurrence of some grooving and faceting (Fig. 3). This result suggests that the presence of impurities in electrodeposited Ni was important for the occurrence of this triple-line instability.

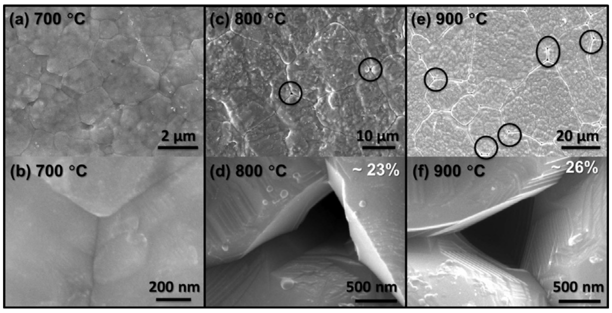

Fig. 2. Representative secondary electron SEM micrographs of electrodeposited Ni specimens annealed in Bi vapor at (a, b) 700 °C, (c, d) 800 °C and (e, f) 900 °C for 4 h. All triple junctions examined were stable at 700 °C; open channels were observed for ~1/4 of the triple junctions in specimens annealed at 800 and 900 °C.

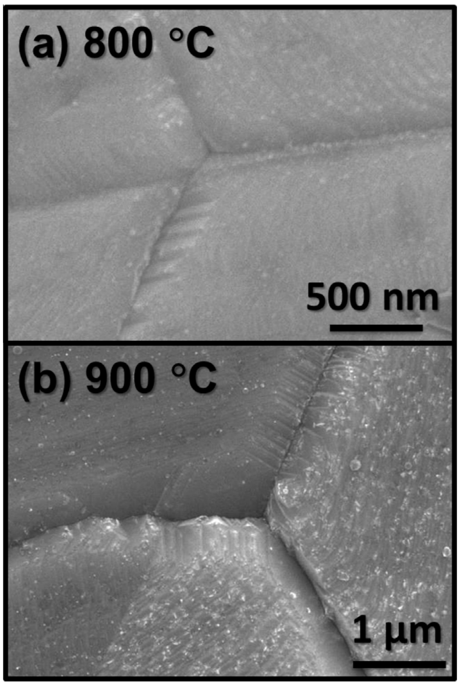

Fig. 3. SEM micrographs of typical triple junctions of high-purity Ni specimens annealed in Bi vapor at (a) 800 °C and (b) 900 °C in which all triple junctions examined were stable.

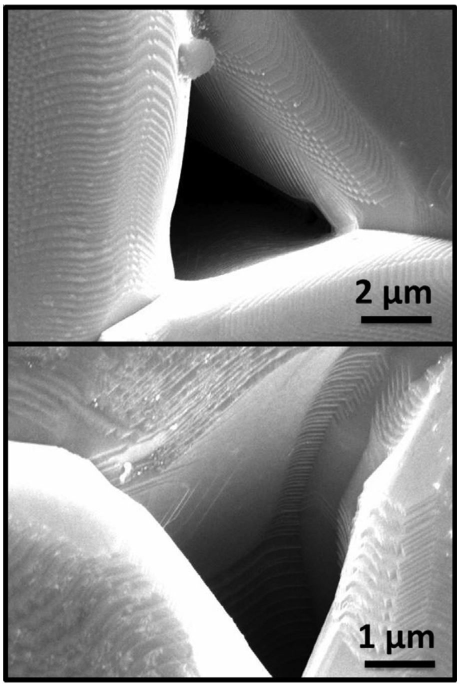

Fig. 4. SEM micrographs of triple-line instability observed in a high-purity Ni specimen that was first doped with S in a pre-treatment and subsequently annealed in the Bi vapor at 900 °C.

Since S is known as a major impurity element in electrodeposited Ni that strongly segregates to both surfaces and GBs [8,9], we hypothesize that the presence of S impurities (as a co-dopant in addition to Bi) is essential for the occurrence of this triple-line instability. Indeed, similar triple-line instability was observed in a high-purity Ni specimen that was pre-doped with S (using the procedure described above) and subsequently annealed in Bi vapor at 900 °C (Fig. 4; Fig. S5). The dimensions of these open channels was greater (>1 µm; Fig. 4), and it occurred at a smaller fraction (~7.5%) of the triple junctions; these might have resulted from the larger grain size and inhomogeneous S distribution. Nonetheless, this controlled experiment suggested that S co-doping could induce triple-line instability. Although no prior study investigated the effects of impurities on triple-line wetting/instability, a recent study did reveal that the presence of minor impurities in Ni can significantly change GB wetting and liquid metal penetration behaviors in ***Ni–Bi (the primary phases are underlined) [10].

This unusual phenomenon of triple-line instability (wetting by a gas phase) is likely related to the formation of a bilayer complexion (a type of "2-D interfacial phase" that are called "complexions" to emphasize that they are not "phases" according to the rigorous Gibbs definition [11–15]; it is important to differentiate complexions, which are interfacial chemical/structural states that are thermodynamically two-dimensional, from precipitated thin layers of secondary bulk/three-dimensional phases at GBs) that was recently observed in Ni–Bi [16], as well as in Cu–Bi [17] and Si–Au [18]. The atomic structure of this bilayer complexion in Ni–Bi is schematically illustrated in Figure S6; specifically, one monolayer of Bi adsorbs on each of the Ni grain surfaces strongly, and the two adsorbed Bi layers bonded weakly. In a phenomenological thermodynamic model that is schematically illustrated in Figure S6 [16] (the basic concepts of which were verified by quantum–mechanical calculations [19,20]), the excess free energy of a general Ni GB with bilayer adsorption of Bi can be expressed as:

$$\gamma_{gb}^{(bilayer)} = 2\gamma_S^{(mono-Bi)} - \Delta\gamma^{(Bi-Bi)} + \Delta\gamma^{(re.)}, \tag{1}$$

where $\gamma_S^{(mono-Bi)}$ is the excess free energy of a free surface with a monolayer adsorption of Bi, $\Delta\gamma^{(Bi-Bi)}$ represents the bonding energies (per unit area) between two adsorbed Bi layers, and $\Delta\gamma^{(re.)}$ represents the effects of relaxation and reconstruction. Since Ni–Bi bonds are strong and Bi–Bi bonds are weak, there is little relaxation ($\Delta\gamma^{(re.)}$ is likely relatively small and equilibrium $\gamma_S \approx \gamma_S^{(mono-Bi)}$). Thus, to the first order of approximation, we estimate:

$$\frac{\gamma_{gb}}{\gamma_S} \approx 2 - \frac{\Delta\gamma^{(Bi-Bi)}}{\gamma_S}. \tag{2}$$

Since the Bi–Bi bonds are weak, $\Delta\gamma^{(Bi-Bi)}$ is small; consequently, γ_{gb}/γ_S can be critically large.

However, no triple-line instability in the high-purity Ni specimens implies that γ_{gb}/γ_S should still be less than $\sqrt{3}$ for Bi-doped Ni (Figs. 1 and 3). Unstable triple-lines were only observed in Bi and S co-doped Ni, where both S and Bi are known to strongly segregate at surfaces and GBs. The presence of S impurities (co-dopants) can further reduce the GB and surface energy of Bi-doped Ni according to the Gibbs isotherm:

$$\frac{d\gamma}{d\mu^{(S)}} \approx -\Gamma^{(S)}, \tag{3}$$

where $\mu^{(S)}$ and $\Gamma^{(S)}$ are the chemical potential and GB excess, respectively, of S. γ can be either surface or GB energy. Analogous to the Rice–Wang model of GB embrittlement (assuming $\Gamma_{gb}^{(S)} \approx 2\Gamma_S^{(S)}$, which is an approximation here), segregation of the S co-dopants will reduce $2\gamma_S$ more than γ_{gb} because the surface segregation enthalpy is generally greater (more negative) than GB segregation enthalpy. Thus, it is possible that co-segregation of S further increases the ratio of γ_{gb}/γ_S to $>\sim\sqrt{3}$ to induce triple-line instability.

In the current case, open channels were only observed at a fraction of triple lines/junctions (Table S1), which can be explained by anisotropy in the interfacial energies (both γ_{gb} and γ_S). For an isotropic case, the value of γ_{gb}/γ_S can be measured by the dihedral angles at GB grooves. Unfortunately, the faceting and anisotropy make such quantitative measurements infeasible in the current case. Nonetheless, severe grooving was observed (Figs. S2, S3 and S5), indicating large γ_{gb}/γ_S ratios. A large γ_{gb}/γ_S ratio is correlated with a low GB cohesion and severe GB embrittlement. In fact, it is known that both S and Bi cause significant GB embrittlement of Ni [8,9,16,19–21].

In summary, an unusual high-temperature capillary phenomenon of triple-line instability (wetting by a gas phase to form open channels) was reported. While triple-line wetting by liquid phases at high temperatures was observed for a small number of systems, including AlN–Y_2O_3 [22], $SrTiO_3$–La_2O_3 [23], ZnO–Bi_2O_3 [24], W–Ni [25] and Ni–Bi [16], this is the first report of triple-line wetting by a gas phase, which is rare because it requires a critically large γ_{gb}/γ_S ratio ($\gamma_{gb}/\gamma_S > \sqrt{3}$ with an isotropic approximation, vs. $\gamma_{gb}/\gamma_S \approx 1/3$ for pure metals). This unusual triple-line instability likely results from strong interfacial segregation of both Bi and S. Specifically, it could be explained by the formation of a unique bilayer complexion in Ni–Bi and the effects of additional co-segregation of S. This phenomenon occurs concurrently with severe GB embrittlement [8,9,16,19–21], and it can significantly impact on the microstructural stability and corrosion resistance.

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