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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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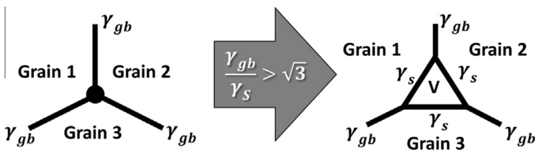

Fig. 1. A triple-grain junction line is unstable if $\gamma_{gb}/\gamma_S > \sqrt{3}$ for a simplified case of isotropic interfacial energies. This instability condition ignores the contributions of triple-junction line energies because the open channels are >100 nm in their dimensions, but the triple-junction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

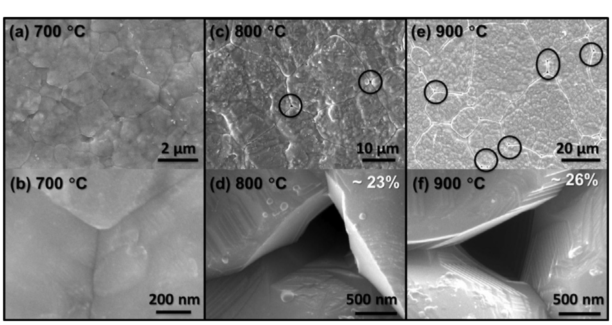

Fig. 2. Representative secondary electron SEM micrographs of electrodeposited Ni specimens annealed in Bi vapor at (a, b) 700 °C, (c, d) 800 °C and (e, f) 900 °C for 4 h. All triple junctions examined were stable at 700 °C; open channels were observed for ~1/4 of the triple junctions in specimens annealed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

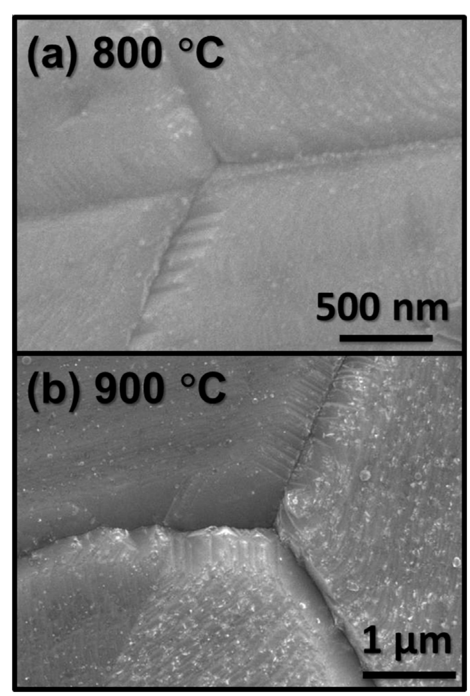

Fig. 3. SEM micrographs of typical triple junctions of high-purity Ni specimens annealed in Bi vapor at (a) 800 °C and (b) 900 °C in which all triple junctions examined were stable.