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Abstract

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Full Text

Corrosion Behavior of Pure Metals (Ni and Ti) and Alloys (316H SS and GH3535) in Liquid GaInSn

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Abstract

This study investigated the interactions between a Ga-based liquid metal, GaInSn, and several metallic materials—including pure metals (Ni and Ti) and alloys (316H stainless steel (SS) and GH3535)—at 650 °C. The objective was to evaluate corrosion performance and select a suitable candidate material for use as a molten salt manometer diaphragm in thermal energy storage systems. The results demonstrated that the alloys (316H SS and GH3535) exhibited significantly less corrosion than the pure metals (Ni and Ti) in liquid GaInSn. Ga-rich binary intermetallic compounds formed on the surfaces of all tested materials exposed to liquid GaInSn, resulting from the decomposition of the liquid metal and its reaction with the constituent elements of the metallic materials. A corrosion mechanism for all tested materials exposed to liquid GaInSn was proposed, which may aid in selecting optimal candidate materials when liquid GaInSn is employed as the pressure-sensing medium.

Keywords: Metal materials, Liquid GaInSn, Corrosion, Intermetallic compounds, Thermal energy storage systems

1. Introduction

In recent years, Ga-based liquid metals (GLMs) have attracted widespread attention due to emerging applications in soft robotics [1], magnetically active solid–liquid transformation machines [2], and wearable, flexible electronic devices for medical applications [3]. This novel class of multifunctional materials possesses metallic conductivity combined with liquid fluidity at room temperature, making them a popular subject of investigation [4–9].

GaInSn, a specific GLM material, is considered a key candidate for sensors in wearable and stretchable electronic devices due to its advantageous properties, including low toxicity, low melting point, high electrical and thermal conductivity, ultralow vapor pressure, and excellent fluidity [10-12]. Several research groups have investigated the development and application of GaInSn-based devices. Matsuzaki et al. fabricated a GaInSn sensor electrode for wearable devices capable of simultaneously sensing dispersed local and global strains. Li et al. [13, 14] and Zhang et al. [15] produced Ga_2O_3-, GaN-, In_2O-, and SnO-based devices and other electronic components using room-temperature liquid metal printing of electronics and semiconductors, injecting new vitality into the semiconductor manufacturing industry. He et al. [16] reported an elastic composite consisting of lightweight liquid metal foam spheres (LMSs) with lenticular contacts and polydimethylsiloxane, systematically studying the interface contact conduction mechanism and strain sensitivity between LMSs with different melting points. Their results demonstrated the composite's potential applications in biomedicine and industry. So et al. [17] reported a method for manufacturing reversible and adjustable fluid antennas from GLMs with radiation efficiency reaching 90% in far-field measurements. Shirzadi et al. [18] reported that Ga could be used to remove the native oxide layer during grinding of the jointing faces of 304 SS and Ti prior to diffusion bonding experiments.

Recently, GaInSn has been selected as the pressure-conducting medium in molten salt manometers for thermal energy storage (TES) systems. However, the optimal material for the pressure-sensing diaphragm remains unselected. A critical issue that must be addressed for pressure-sensing diaphragms is the possibility of corrosion hardening or embrittlement caused by long-term contact between liquid GaInSn and metallic elements such as Ni, Fe, Cr, and Mo, which could result in pressure conduction failure. The mechanisms of corrosion and failure may involve elemental dissolution from the pressure-sensing diaphragm when directly exposed to a GLM environment or the simultaneous formation of Ga-rich intermetallic compounds (IMCs). Therefore, the most crucial characteristic for a pressure-sensing diaphragm material is excellent corrosion resistance to GLMs, ensuring the safe operation of the molten salt pressure gauge.

316H SS is a widely used Fe-based structural material in the petroleum, chemical, electric power, aerospace, transportation, and energy industries due to its favorable comprehensive performance, including high-temperature resistance, corrosion resistance, oxidation resistance, high strength, ease of processing, and cost-effectiveness. Consequently, 316H SS is a leading candidate structural material for TES systems [19, 20]. According to the literature [21–23], corrosion of 316H SS in chloride salts—the heat storage medium used in TES systems—primarily manifests as oxidation or dissolution of Fe. The GH3535 alloy, which is the Chinese version of the UNS N10003 alloy [24], is a solid-solution-strengthened nickel-based alloy selected as the primary candidate structural material for molten salt reactors (MSRs). MSRs are among the six most promising Generation IV nuclear reactors worldwide [25]. Previous studies have shown that the UNS N10003 alloy exhibits superior corrosion resistance in molten fluoride salts [26–29], with corrosion generally caused by dissolution of Cr from the alloy into fluoride salts. However, material corrosion resistance and stability are affected by various factors, including impurities in the corrosive solvent [26–28] and factors such as coatings [29], elemental additives [30], and segregation of impurities on grain boundaries (GBs) [31].

Because liquid metal corrosion (LMC) involves numerous factors such as element dissolution, diffusion, and chemical reactions, it is more complex than molten salt corrosion. Consequently, very few systematic studies have investigated the corrosion behavior of various metallic materials in liquid metals. Barbier et al. [32] and Shin et al. [33] reported that 316L austenitic stainless steel experienced severe corrosion in GLMs. However, they did not compare the corrosion properties of various materials in GLMs or propose candidate materials with superior corrosion resistance. Guo et al. [34] studied the corrosion behavior of T91 steel in liquid GaInSn and found that an $FeGa_3$ reaction film formed at

400 °C could provide better boundary lubrication performance. As previously reported, Ti exhibits minimal corrosion when exposed to Ga in air at 220 °C [35]. Moreover, pure Ni is widely acknowledged as an optimal corrosion-resistant coating material in molten salt environments [26, 29]. Nevertheless, pure Ni is susceptible to severe corrosion in GLMs [32]. Thus, we investigated the corrosion behaviors of pure Ti and Ni, providing a valuable reference for our study. It is necessary to evaluate the corrosion behavior of metals and alloys in liquid GaInSn and select a suitable pressure-sensing diaphragm before employing it in molten salt manometers for TES systems.

In this study, the interactions between liquid GaInSn and various materials, including pure metals (Ni and Ti) and alloys (316H SS and GH3535 alloy), were investigated through static immersion tests at 650 °C for 5 h. After LMC, changes in mass, phase structure, and morphology of the metals and alloys were characterized using gravimetric analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Based on the corrosion behavior of the tested materials in GaInSn, the corresponding corrosion mechanism was investigated and proposed.

2. Experimental Procedures

2.1 Materials

The chemical compositions of the pure metals (Ni and Ti) and alloys (316H SS and GH3535) used in this study are listed in Table 1 , as provided by the metal suppliers. All sample surfaces were mechanically ground with silicon carbide (SiC) paper to 2000 grit. After polishing, all samples were ultrasonically cleaned with ethanol and dried prior to corrosion testing. The composition of the GaInSn used in the corrosion experiments is shown in Table 2 .

2.2 Static Corrosion Test

A schematic of the corrosion test setup is shown in Fig. 1 [Figure 1: see original paper]. Specimens of Ni (8.0 mm × 8.0 mm × 2.0 mm), Ti (10.0 mm × 8.0 mm × 1.2 mm), 316H SS (10.0 mm × 8.0 mm × 2.0 mm), and GH3535 alloy (9.0 mm × 9.0 mm × 2.0 mm) were placed into quartz tubes measuring 250 mm (length) × 20 mm (diameter). An equal amount of liquid GaInSn was then introduced into each quartz tube using a syringe to ensure complete coverage of the metallic materials. Before vacuum sealing, the quartz tubes were preheated with a flame spray gun for several seconds to remove internal moisture. They were then evacuated to approximately 10^{-4} Pa and sealed with a flame spray gun.

After vacuum sealing, the sealed quartz tubes containing the various metallic specimens and GaInSn were placed vertically inside a furnace to ensure complete submersion of the specimens in liquid GaInSn during testing. The specimens were heated at 650 °C for 5 h. After heating, the quartz tubes were cooled to 23 °C and broken to remove the specimens. The corroded samples were then ultrasonically cleaned with ethanol to remove residual GaInSn from their surfaces.

2.3 Characterization Methods

The mass of all samples was measured using an analytical balance (METTLER TOLEDO MS105DU) with an accuracy of 0.01 mg before and after corrosion testing. The weight gain ratio γ for each sample was calculated using the following equation: $\gamma = (W_1\text{-}W_0)/W_0$, where W_0 and W_1 represent the mass of each sample before and after corrosion, respectively.

The crystal structure of the samples before and after corrosion was characterized using an XRD spectrometer (Bruker D8) with a Cu Kα_1 radiation source (λ = 0.154 nm). The surface morphologies and elemental distributions of the samples before and after corrosion were analyzed using SEM (LEO 1530 VP) and EDS.

3. Results

Figs. 1(b) and (c) show the specimens after exposure to GaInSn, revealing strong adhesion of GaInSn to the metallic material surfaces following the corrosion test. After cleaning, the corrosion phenomena and degrees of corrosion among the materials exposed to GaInSn at 650 °C for 5 h were distinct and are analyzed separately below.

To directly compare the corrosion degrees of the four materials, the weight gain ratio γ of each material after exposure to GaInSn was calculated, as shown in Fig. 2 [Figure 2: see original paper]. The weights of all specimens immersed in GaInSn increased after corrosion, indicating reactions between GaInSn and the metallic materials during immersion. Furthermore, the average weight gain ratios of the pure metals (Ni: 62.17% and Ti: 150.00%) were significantly larger than those of the alloys (316H SS: 13.71% and GH3535: 12.68%), reflecting considerably more severe corrosion of the pure metals compared to the alloys in liquid GaInSn.

3.1 Corrosion Behavior of Ni in GaInSn

Pure Ni metal exhibited significant corrosion, forming a thick reaction layer (Fig. 1(c)) even after a short immersion time of 5 h, indicating strong interaction between Ni and GaInSn. The reaction layer displayed a regular cruciform pattern on the initial square Ni substrate. A similar corrosion morphology was observed by Barbier et al. [32] when immersing pure Ni in Ga at a lower temperature of 400 °C for 49 h.

The XRD patterns of the Ni sample immersed in liquid GaInSn at 650 °C for 5 h are shown in Fig. 3 [Figure 3: see original paper]. The main Ni peaks disappeared after corrosion, but peaks corresponding to Ni_2Ga_3 IMC with a small quantity of Ni_3Ga_4 were detected near the surface, indicating that the

Ni matrix surface was completely covered by Ni_2Ga_3 due to the reaction between Ni and Ga at 650 °C. The formation of this reaction layer may explain the weight gain observed after corrosion. Moreover, no significant Ga, In, or Sn signals were detected via XRD, suggesting that GaInSn was completely removed from the sample during cleaning. According to the Ni–Ga binary phase diagram [36], Ni_2Ga_3 is the most stable phase at 650 °C. Hence, the reaction layer consisted primarily of stable Ni_2Ga_3 accompanied by a small quantity of metastable Ni_3Ga_4 due to the short 5-h corrosion duration.

The surface morphology and elemental distribution of the Ni sample after corrosion in liquid GaInSn at 650 °C for 5 h are illustrated in Figs. 4(a)–(i). The thickness of the reaction layer with a regular cruciform pattern formed on the corroded Ni specimen surface was approximately 995–998 m, corresponding to a dimensional change ratio of 24.8%. These results demonstrate that Ni was significantly corroded by liquid GaInSn. Barbier et al. [32] reported that reaction layer morphology directly depends on the properties of diffusing elements during growth, and that thickness is influenced by specimen size. Figs. 4(d) and (g) show the surface morphologies of the reaction layer and matrix, respectively. The layer surface was densely distributed with large cylindrical particles, whereas cylindrical particles on the Ni matrix were sparsely distributed, though many fine acicular particles were observed.

Elemental mapping results (Figs. 4(e)–(f) and (h)–(i)) and EDS point analyses (Table 3) indicated that both the cylindrical particles on the reaction layer (marked as Point 1 in Fig. 4 Figure 4: see original paper) and the acicular particles on the Ni matrix (marked as Point 2 in Fig. 4(c)) after corrosion were rich in Ni and Ga, confirming that the reaction layer and substrate after corrosion consisted primarily of Ni_2Ga_3 IMC, consistent with the XRD analysis.

3.2 Corrosion Behavior of Ti in GaInSn

Pure Ti metal exhibited the most severe corrosion after immersion in liquid GaInSn, as confirmed by its highest weight gain ratio among all materials (Fig. 2). In contrast to pure Ni, no noticeable cruciform pattern was observed on the Ti surface. Instead, bending deformation and even fracture occurred at the Ti specimen edges after LMC, indicating that severe corrosion in GaInSn leads to Ti embrittlement or failure.

The XRD patterns of the Ti sample before and after corrosion in liquid GaInSn at 650 °C for 5 h are shown in Fig. 5 [Figure 5: see original paper]. For the corroded Ti sample, only a new binary $TiGa_3$ IMC was detected on the Ti matrix surface via XRD, indicating complete coverage by the $TiGa_3$ corrosion product.

The surface morphology and elemental distribution of the Ti sample after corrosion in liquid GaInSn at 650 °C for 5 h are shown in Figs. 6(a)–(d). The surface was curled with evident cracking, indicating significant corrosion by liquid GaInSn. A surface tomography image of the cracked region is shown in

Fig. 6 Figure 6: see original paper, with corresponding elemental mapping in Figs. 6(c) and (d). After corrosion, the Ti sample surface was covered with large polyhedral particles and numerous smaller particles, both consisting of Ga and Ti. Many polyhedral particles were distributed at crack edges. SEM-EDS point analysis was conducted on a large polyhedral particle and several smaller particles (marked as Points 1 and 2 in Fig. 6(b), respectively), with results presented in Table 4 . Both particle types exhibited an almost identical Ga:Ti atomic ratio (3:1), further confirming $TiGa_3$ IMC formation on the Ti surface during corrosion.

3.3 Corrosion Behavior of 316H SS in GaInSn

316H SS exhibited better corrosion resistance than pure Ni and Ti metals, as shown in Figs. 1(c) and 2. A relatively thinner reaction layer with a cruciform pattern was observed on the 316H SS surface after corrosion.

The XRD patterns of the 316H SS sample before and after corrosion in liquid GaInSn at 650 °C for 5 h are shown in Fig. 7 [Figure 7: see original paper]. After corrosion, the intrinsic 316H SS peaks disappeared, and binary IMCs ($FeGa_3$ and $CrGa_4$) were detected, indicating formation of new corrosion products. Analysis of the Fe-Ga [37] and Cr-Ga binary phase diagrams [38] revealed that Fe and Cr solubilities in liquid Ga are very similar; therefore, either Fe or Cr in the 316H SS matrix could react with Ga to form the corresponding binary IMCs $FeGa_3$ and $CrGa_4$, respectively.

The surface morphology and elemental distribution of 316H SS after corrosion in liquid GaInSn at 650 °C for 5 h are shown in Figs. 8(a)-(f). As shown in Fig. 8 Figure 8: see original paper, a reaction layer formed on the corroded 316H SS. Similar to Ni, the layer formed on 316H SS exhibited a regular cruciform pattern. The layer formed from the short side (501.4 m) of the original rectangular 316H SS substrate was similar to that formed from the long side (496.8 m), resulting in a dimensional change ratio of only approximately 9.8% for 316H SS—less than that of Ni (24.8%). Magnified surface morphologies and corresponding elemental distributions of the 316H SS matrix after corrosion are shown in Figs. 8(d)-(f). Numerous corrosion products of varying sizes were distributed on the corroded 316H SS surface, which could be classified into three types. The first comprised fine particles (marked as Point 1 in Fig. 8(b)) that adhered to the substrate and contained Fe and Ga according to EDS results. Second, polyhedral particles with regular shapes stacked atop the fine particles could be further classified into two types. The first type (marked as Point 2 in Fig. 8(b)) was rich in Fe and Ga, whereas the second type (marked as Point 3 in Fig. 8(b)) was rich in Cr and Ga. Combined with the XRD results in Fig. 7, these two polyhedral particle types were identified as $FeGa_3$ and $CrGa_4$ IMCs, respectively. As shown in Table 1, the Fe content of 316H SS was considerably higher than that of Cr. Hence, Fe atoms in the matrix were prone to diffuse to the sample surface and react with Ga, resulting in more $FeGa_3$ formation than $CrGa_4$. Based on these results, the wetting properties of metal bonds may lead to formation of a dense corrosion layer consisting of irregular $FeGa_3$ particles that becomes strongly bound to the steel surface [39].

3.4 Corrosion Behavior of GH3535 Alloy in GaInSn

The GH3535 alloy exhibited better corrosion resistance than the other three materials, as evidenced by the absence of cruciform morphology, deformation, or cracks on the sample surface. Although several scattered corrosion particles were observed (Fig. 1(c)), they were negligible compared to other materials. Additionally, the lowest weight gain ratio observed in Fig. 2 further confirmed the excellent corrosion resistance of the GH3535 alloy, suggesting it is a highly viable and promising material for harsh environment applications.

The XRD patterns in Fig. 9 [Figure 9: see original paper] reveal that the GH3535 alloy underwent corrosion in liquid GaInSn at 650 °C for 5 h. After corrosion, the characteristic diffraction peaks of the GH3535 alloy were completely suppressed, and new features identified as $FeGa_3$ and Mo_6Ga_{31} IMCs were observed. The XRD results indicated that the GH3535 alloy sample surface was entirely covered by these two corrosion products after LMC.

The surface morphologies and corresponding elemental distribution of the GH3535 alloy after corrosion in liquid GaInSn at 650 °C for 5 h are shown in Figs. 10(a)-(f). The corroded GH3535 alloy surface was primarily covered with three types of IMCs. The bottom of the surface was densely packed with fine particles (marked as Point 1 in Fig. 10 Figure 10: see original paper), which were primarily composed of Mo and Ga according to EDS analyses. The top was dotted with several larger polyhedral particles (marked as Point 2 in Fig. 10(b)), which had regular shapes and were rich in Fe and Ga. Strip-shaped particles (marked as Point 3 in Fig. 10(b)) were also observed on the surface adjacent to the fine particles, and EDS results showed they were rich in Ni and Ga. Based on the XRD results in Fig. 9, the densely distributed fine particles at the bottom of the surface were identified as the Mo_6Ga_{31} IMC, whereas the large, regularly shaped polyhedral particles at the top were the $FeGa_3$ IMC. However, the strip-shaped particles rich in Ni and Ga could not be identified via XRD, possibly due to their low concentration. EDS mapping showed that the corroded GH3535 alloy surface was rich in Mo, Fe, and Ga but poor in Ni, further indicating that the GH3535 substrate was covered with newly generated $FeGa_3$ and Mo_6Ga_{31} IMCs, consistent with the XRD results.

Figs. 11(a)-(g) show cross-sectional SEM images and corresponding elemental distributions of the GH3535 alloy sample corroded in liquid GaInSn. The GH3535 alloy corrosion layer consisted mainly of two layers. The outer layer was severely depleted in Ni, Cr, and Fe but rich in Mo and Ga, indicating massive dissolution of metallic elements (Ni, Fe, and Cr) from the matrix into liquid GaInSn, as well as inward diffusion of Ga into the matrix. The XRD patterns in Fig. 9 and SEM images in Fig. 10 confirmed the existence of Mo-Ga and Fe-Ga IMCs on the GH3535 alloy surface after corrosion. However, no remarkable Ni-

Ga IMC was detected in the XRD analysis of the corroded GH3535 alloy (Fig. 9). Only a few strip-shaped particles corresponding to the Ni_2Ga_3 IMC were embedded in the Mo-rich layer, as observed via SEM (Fig. 10). It is speculated that the Ni_2Ga_3 IMC has very weak adhesion to the GH3535 matrix and likely peels off due to stress occurring during solid-liquid phase interaction or differences in thermal expansion coefficients between the Ni_2Ga_3 IMC and the alloy during cooling. The outer Mo-rich layer consisting of the Mo_6Ga_{31} IMC had a thickness of approximately 153 m. An inner corrosion layer with a thickness of approximately 45 m was visible between the outer Mo-rich layer and the matrix. The total corrosion layer thickness for GH3535 was approximately 197 m. The Ni, Cr, Mo, and Fe contents were higher in the inner corrosion layer than in the outer Mo-rich layer but lower than those in the matrix. However, the Ga content was relatively lower in the inner corrosion layer than in the outer Mo-rich layer and decreased to zero in the matrix. This implies that the outer Mo-rich layer prevented Ga diffusion into the GH3535 matrix and metallic element (Ni, Cr, and Fe) diffusion to the alloy surface. Therefore, formation of this outer Mo-rich layer may alleviate LMC of the GH3535 alloy in GaInSn. This is reasonable because Mo exhibits lower solubility and reactivity than Ni, Fe, and Cr in liquid Ga according to previous reports [40]. Miyakawa et al. [41] also reported formation of Mo-rich and Cr-rich layers on the Hastelloy C276 matrix surface in liquid Sn, which beneficially influenced corrosion mitigation.

4. Discussion

After exposure to liquid GaInSn at 650 °C for 5 h, all materials experienced corrosion and exhibited weight gain due to reactions between their metallic components and Ga, leading to formation of various binary Ga-rich IMCs on their surfaces. XRD analyses indicated that each sample surface was covered with newly generated IMCs.

It should be noted that only Ga-rich binary IMCs were detected on the surfaces of Ni, Ti, 316H SS, and GH3535 after corrosion in liquid GaInSn, with few In or Sn compounds detected via XRD. This occurred because Ga has lower activation energy than Sn or In, causing Ga atoms to preferentially diffuse toward and adhere to these material surfaces. According to literature results, the diffusion activation energies of Ga, In, and Sn adsorbed on W surfaces, as revealed by Nishikawa et al. [42], are 0.29 eV, 0.35 eV, and 0.71 eV, respectively. Additionally, Saadat et al. [43] calculated the activation energies of Ga, In, and Sn on Mo surfaces to be 0.25 eV, 0.3 eV, and 0.5 eV, respectively. Therefore, it can be inferred that Ga was selectively deposited onto these material surfaces and reacted with metallic elements such as Fe, Ni, Cr, Ti, and Mo to form the corresponding binary $FeGa_3$, Ni_2Ga_3, $CrGa_4$, $TiGa_3$, and Mo_6Ga_{31} IMCs, respectively.

An important factor in determining material compatibility with GaInSn is the solubility of different elements in Ga. According to the literature [40, 44], the solubility of Ni, Fe, Cr, Ti, and Mo in liquid Ga at 400 °C is 0.59 at.%, 1.9 ×

10^{-2} at.%, 1.2×10^{-2} at.%, 9.5×10^{-3} at.%, and 5.0×10^{-3} at.%, respectively. At 500 °C, solubility increases for certain elements, with Ni, Fe, Cr, Ti, and Mo exhibiting solubilities of 1.35 at.%, 0.11 at.%, 4.9×10^{-2} at.%, 3.9×10^{-2} at.%, and 1.9×10^{-2} at.% in liquid Ga, respectively. It should be noted that element solubility in liquid Ga typically increases with temperature. Therefore, it can be inferred that at 650 °C, the elements in descending order of solubility in liquid Ga are Ni, Fe, Cr, Ti, and Mo. This is important for predicting potential material corrosion behavior in GaInSn.

Based on the corrosion results, pure metals (Ni and Ti) are more prone to corrosion in liquid GaInSn than alloys (316H SS and GH3535). Specifically, Ti exhibited the largest weight gain ratio among all four materials, and its surface was completely distorted (Fig. 1(c)), presumably due to $TiGa_3$ IMC formation after LMC. In contrast, the reaction layer consisting of Ni_2Ga_3 IMC with a small quantity of Ni_3Ga_4 that formed on the Ni surface exhibited a cruciform pattern along substrate edges. The growth mechanism of the reaction layer formed on Ni is illustrated in Fig. 12 [Figure 12: see original paper]. In the binary Ni–Ga system, dominant Ga diffusion into the Ni matrix led to reaction layer formation on the Ni matrix surface. As immersion time increased, the Ni substrate was partially peeled off by the reaction layer, beginning at the four edges of the initial square Ni substrate and gradually forming a cross-shaped pattern. These newly formed reaction layers caused severe substrate deformation, with a corresponding dimensional change ratio of up to 24.8% after only 5 h of corrosion. The embrittlement and deformation observed after LMC imply that neither Ti nor Ni is suitable for use as a molten salt manometer diaphragm material, as corrosion-induced hardening or embrittlement would degrade mechanical properties.

Compared to pure metals (Ni and Ti), the alloys (316H SS and GH3535) exhibited relatively better corrosion resistance to liquid GaInSn. However, a high density of $FeGa_3$ IMC and a small quantity of $CrGa_4$ were observed on the 316H SS surface, which could potentially cause corrosion hardening and material failure in a liquid metal environment during long-term service. Furthermore, a thin new reaction layer formed on the four edges of 316H SS, with thickness only half that of pure Ni, indicating a more severe reaction of Ni than Fe with liquid GaInSn. The reaction layer formed on 316H SS had a regular cruciform pattern similar to that of Ni (Fig. 8(a)). Barbier et al. [32] reported the transition from a linear growth pattern with sharp corners to a parabolic pattern with rounded edges at layer corners on 316L SS with increasing immersion time, indicating that kinetic regimes during the corrosion process changed from an initial interface-controlled mechanism to a later diffusion-controlled mechanism. During the 5-h corrosion experiment, Ga diffusion into the 316H SS matrix was dominant, leading to formation of a reaction layer with a cross-shaped pattern on the 316H SS matrix surface.

Guo et al. [45] found that the microhardness of the resulting $FeGa_3$ corrosion layer (7.63 ± 0.31 GPa) was significantly higher than that of the matrix (4.11 ±

0.41 GPa) during reaction of T91 steel with liquid GaInSn at 600 °C. Therefore, it is plausible to hypothesize that $FeGa_3$ IMC formation on the 316H SS surface after corrosion in GaInSn may contribute to increased hardness of 316H SS, though further studies are needed to confirm this hypothesis.

On the GH3535 alloy surface, many Mo_6Ga_{31} and several $FeGa_3$ and Ni_2Ga_3 IMCs were observed. As shown in Table 1, although the constituent elements of 316H SS and GH3535 alloys are similar, different types of binary Ga-rich IMCs formed. This difference may be attributed to element content in the matrix and the solubility or reactivity of elements in liquid Ga. The reaction of Ni with liquid Ga was the most active among all constituent elements. However, very few Ni–Ga IMCs were found on the GH3535 alloy surface, possibly due to peeling of the Ni–Ga IMC formed on the surface during cooling or cleaning. Additionally, after immersion in liquid GaInSn, the surface $FeGa_3$ IMC, outer Mo-rich layer, inner corrosion layer, and matrix were clearly observed in the GH3535 alloy. Miyakawa [41] compared corrosion behaviors of iron-based and nickel-based alloys in liquid Sn. Their results showed that elements with low reactivity easily formed enrichment layers on alloy surfaces, which prevented elements with high reactivity in the matrix from diffusing to the surface to a certain extent, thus alleviating corrosion. Therefore, it is inferred that an enrichment layer of some elements formed in both Fe- and Ni-based alloys to alleviate corrosion. The corrosion resistances of 316H SS and GH3535 alloys to GLMs were significantly better than those of pure metals (Ni and Ti). However, a reaction layer formed on the 316H SS surface after corrosion, which is detrimental to material integrity and mechanical properties during application. In comparison, the GH3535 alloy is more suitable as a candidate material for a pressure-sensing diaphragm because it does not exhibit such a reaction layer. However, it should be noted that because the corrosion duration in this experiment was only 5 h, further investigation is necessary to evaluate GH3535 alloy corrosion behavior in liquid GaInSn for longer durations.

5. Conclusion

In this study, the corrosion behavior of pure metals (Ni and Ti) and alloys (316H SS and GH3535) in liquid GaInSn was investigated via static immersion tests at 650 °C for 5 h. After corrosion, mass changes, phase structures, and morphologies of all specimens were analyzed using gravimetric analysis, XRD, and SEM-EDS characterization methods, leading to the following conclusions:

1. All specimens exhibited weight increases after immersion in GaInSn at 650 °C for 5 h, indicating that GaInSn decomposition and reactions between metallic materials and GaInSn occurred during immersion. The corrosion resistance of the alloys (316H SS and GH3535) was significantly better than that of pure metals (Ni and Ti) in GaInSn.
2. After corrosion in GaInSn, various types of binary Ga-rich IMCs formed on metal and alloy surfaces. On the Ni surface, Ni_2Ga_3 IMC and a small

quantity of Ni_3Ga_4 formed, whereas $TiGa_3$ IMC formed on the Ti surface. On the 316H SS surface, $FeGa_3$ IMC with a small quantity of $CrGa_4$ was detected, which is known to cause material hardening after long-term service. On the GH3535 alloy surface, a small quantity of $FeGa_3$ and a Mo-rich layer consisting of Mo_6Ga_{31} IMC were found. Notably, reaction layers with a cruciform pattern formed on the surfaces of Ni and 316H SS.

3. Given that reaction layer formation on the 316H SS surface after corrosion is detrimental to its integrity and mechanical properties, the GH3535 alloy is a more favorable choice for a pressure conduction diaphragm. However, the corrosion duration in this experiment was only 5 h, and further investigation is needed to examine GH3535 alloy corrosion behavior under extended durations.

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Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Jianhui Yu and Hongxia Xu. The first draft of the manuscript was written by Jianhui Yu. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Note: Figure translations are in progress. See original paper for figures.