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**COMPATIBILITY OF ITER CANDIDATE STRUCTURAL MATERIALS
WITH STATIC GALLIUM**

by

P. R. Luebbbers, W. F. Michaud,
and O. K. Chopra

Energy Technology Division

December 1993

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MASTER

COMPATIBILITY OF ITER CANDIDATE STRUCTURAL MATERIALS WITH STATIC GALLIUM

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ABSTRACT

Tests were conducted on the compatibility of gallium with candidate structural materials for the International Thermonuclear Experimental Reactor, e.g., Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr alloy, as well as Armco iron, Nickel 270, and pure chromium. Type 316 stainless steel is least resistant to corrosion in static gallium and Nb-5 Mo-1 Zr alloy is most resistant. At 400°C, corrosion rates are ≈ 4.0 , 0.5, and 0.03 mm/yr for Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr alloy, respectively. The pure metals react rapidly with gallium. In contrast to findings in earlier studies, pure iron shows greater corrosion than nickel. The corrosion rates at 400°C are ≥ 88 and 18 mm/yr, respectively, for Armco iron and Nickel 270. The results indicate that at temperatures up to 400°C, corrosion occurs primarily by dissolution and is accompanied by formation of metal/gallium intermetallic compounds. The solubility data for pure metals and oxygen in gallium are reviewed. The physical, chemical, and radioactive properties of gallium are also presented. The supply and availability of gallium, as well as price predictions through the year 2020, are summarized.

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NOMENCLATURE

T	Temperature (K).
T_{mp}	Melting point (K).
T_{bp}	Boiling point (K).
Z	Atomic number.
A	Mass number.
α	Coefficient of linear thermal expansion (K^{-1}).
β	Coefficient of volumetric (cubic) thermal expansion (K^{-1}).
ρ	Mass density (g/cm^3).
H_m	Molar enthalpy (J/mol).
S_m	Molar entropy (J/K·mol).
L_f	Latent heat of fusion (J/mol).
L_v	Latent heat of vaporization (J/mol).
γ	Surface tension (N/m).
λ	Thermal conductivity (W/m·K).
μ	Dynamic viscosity (Pa·s).
c_p	Specific heat capacity at constant pressure (J/kg·K).
ρ_e	Electrical resistivity ($\Omega\cdot m$).
c_m	Concentration of metal in gallium (at.%).
c_o	Concentration of oxygen in gallium (at.%) _f
ΔG_o°	Standard free energy of solution of oxygen in gallium (kJ).
ΔG°	Standard free energy of formation (kJ).
$t_{1/2}$	Half-life of radioactive isotope (ks).
p_{Ga}	Vapor pressure of gallium (Pa).
$\sigma_{abs_{th}}$	Thermal-neutron-capture cross section ($\times 10^{-28} m^2$).
σ_{abs_f}	Fast-neutron-capture cross section ($\times 10^{-28} m^2$).

EXECUTIVE SUMMARY

Corrosion tests were conducted on Type 316 stainless steel (SS), Inconel 625, Nb-5 Mo-1 Zr, Armco Iron, Nickel 270, and pure chromium at exposure temperatures from 200°C to 400°C and exposure times up to 3,000 h. Contrary to previously reported results, iron-based Type 316 SS was found to be more susceptible to corrosion than nickel-based Inconel 625 in liquid gallium under static conditions. The niobium alloy, under the current test conditions, was not susceptible to attack by liquid gallium, except within cold-worked areas. The pure metals were severely attacked; Armco iron and pure chromium dissolved within 100 h at 400°C. Type 316 SS specimens were also oxidized in air at 350°C for 100 h and in water with 6 ppm dissolved oxygen at 290°C for 100 h. The specimens that were oxidized in water exhibited a lower corrosion rate than those oxidized in air, and both sets of oxidized specimens exhibited a lower corrosion rate than the nonoxidized Type 316 SS specimens. The corrosion rates at 400°C for Type 316 SS as-received, oxidized in air, and oxidized in water were 4.0, 2.7, and 2.2 mm/yr, respectively. The corrosion rates at 400°C for Inconel 625 and Nb-5 Mo-1 Zr were 0.46 and <0.05 mm/yr, and rates for Armco iron and Nickel 270 were ≥ 90 and 17 mm/yr, respectively. A corrosion rate was not determined for pure chromium.

Corrosion of metals in liquid gallium occurs by the dissolution of metallic elements into the melt. The dissolved elements then form binary intermetallic phases, typically of the form MGa_3 or MGa_4 , and the dissolved elements are in equilibrium with these phases. The binary intermetallic compounds form at the surface of the exposed specimen, and the reaction continues at this interface as long as dissolved metallic elements are present within the melt. Type 316 SS reacted to form FeGa_3 , whereas Inconel 625 formed CrGa_4 , instead of the expected Ni_2Ga_3 . These compounds are porous and crystalline, and thereby allow the melt to continually reach the reaction zone. It is possible that the rate-controlling parameter may be compound growth rather than dissolution rate.

Formation of the binary intermetallic compounds can be predicted from the solubility data reported by Yatsenko, which is summarized in this report. According to a general linear equation, the relative solubility of structural metals in gallium at temperatures $>300^\circ\text{C}$ are: $\text{W} < \text{Nb} < \text{Mo} < \text{Zr} < \text{V} < \text{Ti} < \text{Cr} < \text{Fe} < \text{Co} < \text{Si} < \text{Y} < \text{Ni} < \text{Mn}$. This agrees well with current corrosion data; the niobium alloy, which contains three of the four least-soluble elements listed here, experienced very little corrosion. Solubility data for the pure metals also exhibited a periodicity with atomic number, a phenomenon similar to the solubility behavior of other low-melting-point metals. The same periodicity has been reported for corrosion rates of pure metals in gallium.

Solubility data for oxygen and M_xO_y compounds in gallium are also presented. Most of the metal oxides were more stable than $\beta\text{-Ga}_2\text{O}_3$, the most stable Ga-O compound in liquid gallium that contains excess oxygen. Of the compounds presented, the exceptions are NiO , FeO , and MoO_2 . Iron [II] chromite (FeCr_2O_4) was tested experimentally and found to be unstable in gallium.

The physical, chemical, and radioisotope decay properties of gallium are reviewed. Because of its attractive thermal properties, gallium has been considered for use as a heat-transport medium in the International Thermonuclear Experimental Reactor (ITER). However,

gallium exhibits several properties that may preclude its use as a coolant, e.g., a high thermal-neutron absorption coefficient and high volumetric expansion upon solidification.

Several recent publications describe the availability, production capacity, and future cost of gallium, based on use primarily in GaAs semiconductors. Gallium constitutes $\approx 1.5 \times 10^{-3}$ mass percent of the earth's crust, but must be extracted as a byproduct from other manufacturing processes. Therefore, if the demand for gallium remains relatively low, the cost of recovering gallium from these processes will continue to remain prohibitively high for use as a heat transport medium in ITER. The current price for ultrapure gallium is $\approx \$500/\text{kg}$.

Based upon current information regarding the stability of advanced alloys in liquid gallium, two ternary alloy systems hold promise for high-temperature containment of the liquid metal. Solubility data predict that alloys of Zr-Nb-Mo and Ti-V-Cr should be stable in liquid gallium at elevated temperatures. Alloys that are susceptible to attack by liquid gallium (i.e., Inconel 625 and Type 316 SS) must be coated with a stable metal oxide to prevent severe liquid-metal corrosion of the alloy. Some alloys may be attacked in cold-worked regions, although the effect of cold-work on liquid-metal compatibility must be investigated further.

1 INTRODUCTION

Gallium is under consideration for use as a liquid-metal heat-transport medium for the International Thermonuclear Experimental Reactor (ITER) because it remains liquid over a wider temperature range than any other metal, i.e., from near room temperature (30°C) to $\approx 2300^\circ\text{C}$, and because it exhibits good thermal conductivity and very low vapor pressure at high temperatures. Its disadvantages include a relatively high thermal-neutron absorption coefficient and a 3.2% volume increase during solidification. Of all the proposed liquid-metal heat-transport media for ITER, gallium has the highest thermal-neutron-capture cross section, i.e., 2.77 barns (1 barn = 10^{-28} m^2) compared with ≈ 40 , 180, and 534 mbarns for lithium, lead, and sodium, respectively. Gallium also has a high affinity for most engineering metals and alloys. Pure metals such as aluminum, zinc, and tin disintegrate in liquid gallium at 30°C. Refractory metals and ceramics are most stable in gallium. Gallium can be contained successfully in beryllium, tantalum, stabilized ZrO_2 , or Pyrex glass at temperatures up to 450°C ; in tungsten, rhenium, or graphite, at temperatures up to 800°C ; and in refractory oxides (such as sintered BeO or Al_2O_3) and vitreous quartz, at $1,000^\circ\text{C}$ or higher.¹⁻³

A major concern regarding the use of liquid metals for heat-transport applications is their compatibility with containment materials. Compatibility of structural materials with liquid metals has a major influence on material selection and operating limitations for liquid-metal heat-transport systems. Corrosion in the form of uniform or selective dissolution, intergranular attack, and transfer of interstitial elements to and from the liquid metal can reduce the effective section thickness of structural components. Radioactive mass transfer/deposition of corrosion products may cause severe flow restrictions and excessive accumulation of radioactive material in unshielded regions. Corrosion/dissolution can reduce mechanical integrity, and mass transfer/deposition phenomena can increase pumping-power requirements, decrease the efficiency of energy conversion, and complicate system maintenance.

This report presents results of tests to determine the compatibility of gallium with candidate structural materials for ITER first-wall/blanket systems, e.g., Type 316 stainless steel (SS), Inconel 625, and Nb-5 Mo-1 Zr alloy. Armco iron, Nickel 270, and pure chromium were included in the study as reference materials. Results of preliminary tests of oxidized Type 316 SS are also presented. The world supply and physical and chemical properties of gallium are described.

2 GALLIUM SUPPLY

It has been estimated that gallium constitutes $\approx 1.5 \times 10^{-3}$ mass percent of the earth's crust, and that $5 \times 10^{-4} \text{ g/ton}$ are present in sea water.⁴ The primary supply of gallium must be derived as a byproduct from processing of other materials. Naturally occurring pure gallium has not been reported, and gallium-rich mineral ores are scarce. Table 1 lists the approximate gallium supply obtainable from the principal gallium-containing resources.

Bauxite is the most promising source of gallium, which can be extracted by the Bayer process that is used to process alumina from the raw mineral. Sphalerite (zinc ore) contains very little gallium compared with other sources, and would not be a cost-effective choice. The supply in kaolin could be accessed only when extraction of alumina from kaolin becomes

*Table 1. Gallium distribution in gallium-bearing resources
(after Katrak & Agarwal⁵)*

Resource	U.S. Resources (10 ³ metric tons)	World Resources (10 ³ metric tons)
Bauxite ^a	14	1,647
Sphalerite	1.8	6.5
Kaolin Clay ^b	56	unknown
Coal ^c	3,571	unknown
Phosphates	1,000	unknown
Total	4,643	unknown

^aU.S. bauxite reserves contain 3,000 metric tons of gallium.

World reserves contain 1.14 million tons of gallium.

^bGallium contained in kaolin clay resources in Georgia only.

^cGallium in coal ashes after combustion.

technologically and economically feasible. Gallium is concentrated in ashes from the combustion of coal, but recovery of the metal has not yet been proved economically feasible. Phosphates are an unlikely source of gallium because most phosphates are wet-processed for fertilizer production.⁵

Issues of importance to the ITER program are the worldwide availability of gallium and our capacity to produce it. ITER will require approximately ~2500 metric tons of liquid gallium for operation.⁶ Figure 1 depicts the supply and corresponding price of gallium on a worldwide basis, based on extraction of gallium from bauxite ores and 1981 statistics for the use of gallium, primarily for GaAs semiconductors. During the time frame for ITER construction, i.e.,

Figure 1. Long-range (1995–2020) supply and price of crude gallium (in 1980 U.S. dollars) from bauxite ores (after Katrak & Agarwal⁵)

2000–2020, the price to produce a large quantity (e.g., 12,000 metric ton) of crude gallium will be approximately what it currently costs to produce less than a third of that amount. However, the cost of refining crude gallium to the purity required for ITER may still be cost-prohibitive.

As of 1992, electronic components that contain GaAs semiconductors accounted for 95% of the gallium used in the U.S. The large amount of gallium needed for liquid-metal heat-transport in ITER would drastically alter the supply of and demand for gallium. Current production could not satisfy the demand that would be placed on the gallium-refining industry by ITER, while also supplying gallium for semiconductor production. The 2,500 metric tons of gallium needed for ITER far surpasses current world production capacity, which is listed in Table 2.⁷ The current price is ≈\$200/kg for 99.99%-pure gallium, ≈\$400/kg for 99.9999% pure, and ≈\$500/kg for 99.999999%-pure gallium.⁸ Considering the cost for high-purity gallium and the large amount needed by ITER, gallium may prove to be economically prohibitive as a heat-transport medium.

Table 2. Annual capacity of primary gallium-producing countries of the world (after Kramer⁷)

Country	Capacity ^a (kg)
North America: United States	<u>12,000</u>
Europe:	
Czechoslovakia (former)	3,000
France	20,000
Germany	15,000
Hungary	4,000
Norway	<u>5,000</u>
Total	<u>47,000</u>
Asia:	
China	8,000
Japan	<u>17,000</u>
Total	<u>25,000</u>
Oceania: Australia	<u>50,000</u>
World Total	<u>134,000</u>

^aAs of December 31, 1990.

3 PHYSICAL PROPERTIES OF GALLIUM

Liquid gallium offers several advantages as a possible heat-transport medium for ITER. With a high thermal conductivity, high boiling point, and the largest liquidus range of any element, gallium appears to be well-suited for this use. The disadvantages include a significant thermal-neutron absorption coefficient and a volumetric expansion of ≈3% upon solidification. The physical and chemical properties of gallium are presented in Table 3. The radioisotope decay properties⁹ of gallium are listed in Table 4.

Table 3. Physical and chemical properties of gallium^a

	Property	Value
Z	Atomic number	31
	Atomic weight (¹² C = 12)	69.717
	Atomic radius ¹⁴ (Å)	1.39
	Crystal structure	orthorhombic
ρ	Density (g/cm ³)	
	293 K	5.907
	at T _{mp} , solid	5.9037
	at T _{mp} , liquid	6.0948
	Density change on fusion ¹⁰ (%)	+ 3.4
T _{mp}	Melting point (°C)	29.7714
T _{bp}	Boiling point (°C)	≈2200
L _f	Latent heat of fusion (kJ/mol)	5.563
L _v	Latent heat of vaporization ¹⁶ (kJ/mol)	1.014
p _{Ga}	Vapor pressure (N/m ²)	
	1198 K	0.14
	1249 K	0.44
	1321 K	1.74
	1478 K	16.50
H _m	Molar enthalpy ¹⁰ at 298 K (kJ/mol)	557.70
S _m	Molar entropy ¹⁰ at 298 K (J/K·mol)	47.90
c _p	Specific heat capacity at constant pressure (J/kg·K)	
	256 K	361.4
	303 K	381.5
λ	Thermal conductivity (W/m·K)	
	axis a: 88.4	
	solid, 293 K	axis b: 16.0
	axis c: 40.8	
	liquid, 350 K	28.7
β	Coefficient of volumetric thermal expansion (K ⁻¹)	
	solid, 273–293 K	5.95 x 10 ⁻⁵
	liquid, 376 K	1.20 x 10 ⁻⁴
ρ _e	Electrical resistivity (Ω·m)	
	solid, 293 K (polycrystalline)	15.05 x 10 ⁻⁵
	liquid, 303 K	25.795 x 10 ⁻⁵
μ	Dynamic viscosity (mPa·s) at 305 K	1.810
γ	Surface tension (mN/m) at 303 K	709
σ _{absth}	Thermal-neutron absorption cross section ¹⁰ (x10 ⁻²⁸ m ²)	2.77 ± 0.12
σ _{absf}	Fast-neutron capture cross section ¹⁶ (x10 ⁻²⁸ m ²)	4

^aValues supplied by the Eagle-Picher Corp., unless noted by superscript reference number

Table 4. Description of radioisotopes of gallium (after Dymov & Savostin⁹)

Isotope	$t_{1/2}$ (ks)	Type of radiation ^a	Radiation Energy (MeV)	
			particles	γ -rays
64	2.88	β^+	–	–
65	0.90	K, e^-	–	0.54; 0.117
66	33.84	β^+	3.1	–
67	298.80	K, e^-	–	0.09; 0.18; 0.30
68	4.08	K, γ, e^-	–	–
		β^+	1.9	–
		β^+, K, γ	–	–
70	1.22	β^-, γ	1.68	–
	1.26	β^-	–	–
72	51.48	$4\beta^-, 7\gamma, 2e^-$	0.64 – 3.15	0.63 – 2.50
	51.12	β^-, γ	–	–
	50.76	β^-, γ	0.7; 1.0	0.83 ^b ; 2.50 ^b ; 0.63 ^b
73	18.00	β^-	1.4	–
74	32.40	β^-	8.0	–

^a e^- internal conversion electrons; K electron capture; β^+ positrons; β^- negatrons.

^bMixture of two or more γ -radiations.

The temperature dependence of viscosity,^{4,10,11} specific heat capacity,¹² and thermal conductivity,¹³ are shown in Figs. 2–4. The change in viscosity, specific heat capacity, and thermal conductivity as a function of temperature (measured in kelvin) are given by Eqs. 1–3.

$$\mu \text{ (N}\cdot\text{s/m}^2\text{)} = 321.5 + T^{(-0.89)} \quad (1)$$

$$c_p \text{ (J/kg}\cdot\text{K)} = -395 + 330 \log[T] \quad (0 \text{ K} \leq T \leq 200 \text{ K}) \quad (2a)$$

$$c_p \text{ (J/kg}\cdot\text{K)} = 367.8 + 0.06T \quad (200 \text{ K} \leq T \leq 1400 \text{ K}) \quad (2b)$$

$$\lambda \text{ (W/m}\cdot\text{K)} = -3.17 + 0.103T \quad (302.9 \text{ K} \leq T \leq 600 \text{ K}) \quad (3)$$

4 SOLUBILITY OF MATERIALS IN GALLIUM

4.1 PURE METALS

The solubility and corrosion of pure metals in gallium have been investigated.^{14–19} Most pure metals are highly soluble in liquid gallium. Solubility of pure metals in gallium is based on a saturated solution in equilibrium with an intermetallic compound. For most engineering metals, the intermetallic compound is of the form MGa_3 or MGa_4 . Solubility data at a given temperature, e.g., 400°C, show a periodicity with atomic number, similar to that observed in other low-melting-point metals, e.g., mercury, indium, tin, lead, bismuth, lithium, sodium, or potassium. Although the absolute value of solubility may vary for the various liquid metals, in all cases, a minimum solubility is observed for beryllium, boron, vanadium, niobium,

Figure 2.
Viscosity of gallium as a function of temperature

Figure 3.
Specific heat capacity of gallium as a function of temperature

Figure 4.
Thermal conductivity of gallium as a function of temperature

molybdenum, tantalum, tungsten, rhenium, and osmium.¹⁷⁻¹⁹ Figure 5 shows the periodicity of solubility in gallium at 400 and 600°C of metals in Periods 2–7 of the atomic chart of the elements. The metals important to the present work are in Periods 4 and 5, and are shown in more detail in Fig. 6. The elements in Groups 4–6 in Period 4 and the elements in Groups 4–7 in Period 5 exhibit a lower solubility in gallium than the remaining elements of each period. The highest solubilities occur in Groups 11–15. Similar behavior is observed in Period 6, with the lanthanides exhibiting a relatively high solubility.

Assuming that the reported solubility values for a given metal would not change much from a gallium–metal system to a gallium–ternary/quaternary–alloy system, any alloy containing low-solubility elements of Groups 4–6 would be more resistant to gallium attack than alloys composed of elements from other groups. Based upon the presented solubility data, alloys of Ti–V–Cr and Zr–Nb–Mo should be very resistant to attack by gallium at temperatures up to 600°C. Inconel alloys and austenitic SSs contain highly soluble elements, which could lead to excessive corrosion at higher temperatures.

As mentioned previously, many pure metals are highly soluble in liquid gallium. Yatsenko et al.^{14–17,20,21} have reported the variation in solubility of selected pure metals in gallium as a function of temperature; the solubilities of some of these metals are shown in Fig. 7. The discontinuities in the solubilities of manganese, nickel, and vanadium at the

Figure 5. Solubility of metals in gallium as a function of atomic number for Periods 2–7 of the atomic chart of the elements (after Guminski¹⁸ and Yatsenko^{17,19})

Figure 6. Solubility of metals as a function of atomic number for Periods 4 and 5 of the Atomic Chart of the Elements (after Guminski¹⁸ and Yatsenko^{17,19})

temperatures indicated represent reported phase changes in each gallium-metal system. Even though chromium undergoes no phase changes between 200 and 700°C, its solubility is represented by a curve. The logarithm of the solubility of titanium in gallium from 350 to 700°C increases linearly with reciprocal temperature. This behavior is observed for many of the pure metals; consequently, the solubility of pure metals in gallium can be represented¹⁹ by

$$\log[c_m] = A - \frac{B}{T}, \quad (5)$$

where c_m is concentration in atomic percent, A and B are coefficients, and T is in kelvin. Values for A and B are presented in Table 5. This equation is valid in the solubility range from 10^{-2} to 2 at.% for pure metals. In Fig. 8, the solubility curves, with concentrations converted to weight percent, are plotted as a function of reciprocal temperature. The solid phases listed in Table 5 were cross referenced with the latest published phase diagrams.²²

4.2 OXYGEN

Oxygen reacts with gallium to form three compounds: the oxide GaO , the suboxide Ga_2O , and the sesquioxide Ga_2O_3 . The allotrope $\beta\text{-Ga}_2\text{O}_3$ is the most stable. Alcock and Jacob²³ have reported the following equations for the solubility of oxygen in gallium (c_o), the standard

Figure 7. Solubility of pure metals in gallium at 200–700°C

Figure 8. Solubility of pure metals in gallium at 200–700°C as predicted by Eq. 5

Table 5. Solubility data in binary Ga-M systems (after Yatsenko¹⁹)

Pure metal	Coefficients of Equation 5		Solid phase	Phase stability range (K)
	A	B · 10 ⁻³		
Co	3.50	3.10	CoGa ₃	≤298 – 1,128
Cr	2.74	3.13	CrGa ₄	≤298 – 973
Fe	4.00	3.85	FeGa ₃	≤298 – 1097
Mn	5.40	3.90	MnGa ₆	≤298 – 683
Mo	0.86	2.80	MoGa ₃	a
Nb	2.90	5.20	NbGa ₃	a
Ni	2.52	1.85	NiGa ₄	≤298 – 525
			Ni ₂ Ga ₃	525 – 1,168
Si	4.30	3.70	Si	≤298 – 1,687 ^a
Ti	2.56	3.12	TiGa ₃	≤298 – 1,748
V	3.20	4.00	VGa ₄	a
W	4.90	8.75	WGa ₄	≤298 – 3,683 ^b
Y	3.00	2.37	YGa ₂	≤298 – 1,623
Zr	3.05	4.22	ZrGa ₃	a

^aPhase listed could not be cross referenced; therefore, the presence of this phase and the temperature stability range cannot be confirmed.

^bPhase is stable up to the melting point of pure metal; pure metal exists in solution with liquid gallium.

free energy of solution of oxygen in gallium (ΔG_o°), and the standard free energy of formation of β -Ga₂O₃ (ΔG°):

$$\log[c_o] = 4.264 - \frac{7380}{T} \quad (1048 \text{ K} \leq T \leq 1398 \text{ K}) \quad (6)$$

$$\Delta G_o^\circ = -220.73 + 0.0274T \text{ (}\pm 0.84\text{)kJ} \quad (7)$$

$$\Delta G^\circ = -1086.63 + 0.3273T \text{ (}\pm 1.26\text{)kJ} \quad (8)$$

Natesan²⁴ has compiled thermodynamic data on the free energy of formation of oxides and the solubility of oxygen in liquid-alkali metals and structural metals. This information has been adapted to the case of liquid gallium by using the above equations for oxygen in gallium. Results that are relevant for ITER applications are shown in Fig. 9.²³⁻²⁵ Based on free energy of formation alone, all of the metal oxides shown, except for MoO₂, FeO, and NiO, should be stable in the presence of Ga₂O₃. Iron[II] chromite (FeCr₂O₄) may be stable at elevated temperatures.

Figure 9 shows that oxides such as Cr₂O₃, Al₂O₃, and SiO₂ should protect coated structural alloys against corrosion in liquid gallium. Unstable compounds, such as FeO and NiO, dissociate in liquid gallium to form β -Ga₂O₃. Upon dissociation, corrosion of the substrate would occur by dissolution of metallic elements and formation of metal/gallium intermetallic compounds.

5 COMPATIBILITY OF GALLIUM WITH STRUCTURAL ALLOYS

Corrosion occurs primarily by dissolution due to the solubility of metals in gallium, which results in metal recession and weight loss, and at higher temperatures, by diffusion into the metal, which leads to formation of surface scale and weight gain. For most metals, dissolution is accompanied by formation of metal/gallium intermetallic compounds from the saturated solution.

Corrosion data correlate well with solubility, i.e., metals with high solubility show poor corrosion resistance. At 400°C, the solubility and corrosion of nickel in gallium are greater by more than one order of magnitude than the solubility and corrosion of iron.^{17,19} Various high-alloy ferritic and martensitic steels and austenitic SSs show fair resistance to corrosion in gallium at temperatures up to 400°C, i.e., a corrosion rate of ≤ 1 mm/yr.¹⁹ In general, corrosion rates of high-alloy steels decrease with increasing chromium content, whereas changes in nickel content have little or no effect on corrosion. Additions of aluminum to nickel-chromium steels increase and titanium additions decrease corrosion rates in gallium.¹⁹

This report describes an investigation of the compatibility of gallium with candidate structural materials, e.g., Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr alloy, for ITER first-

Figure 9.
Temperature dependence of minimum
oxygen concentration in gallium necessary
for oxide formation in metals

wall/blanket systems, and presents the results thereof. Pure metals such as Armco iron, Nickel 270, and chromium were included in the study as reference materials.

5.1 EXPERIMENTAL

Corrosion tests were conducted in alumina capsules (≈ 11 mm in inner diameter and 254 mm long) with a threaded metal fitting at the top end for sealing. Before the tests, the capsules were baked for 24 h at 425°C . Each capsule contained a single test specimen. The capsules were filled with $\approx 11\text{ cm}^3$ (≈ 65 g) of gallium, and an alumina rod (6.5 mm in diameter and 150 mm long) was placed in each capsule to ensure that the corrosion coupon would remain immersed in gallium and to keep the specimen in place when the capsules were inverted during cooling. The capsules were capped and sealed in a high-purity-argon environment. All components of the capsule unit are shown in Fig. 10. A sealed capsule is shown in Fig. 11. The sealed capsules were placed in an upright position during testing. Corrosion coupons ($\approx 10 \times 20 \times 0.4$ – 1.1 mm) were prepared from Type 316 SS, Inconel 625, Nb–5 Mo–1 Zr alloy, Nickel 270, Armco iron, and pure chromium. The compositions of these materials are given in Table 6. The coupons were bent into a U shape to study the effect of cold work. Dimensions and weights of the specimens were recorded after degreasing and cleaning.

Two sets of Type 316 SS specimens were prepared and oxidized; four specimens were oxidized in deionized water with 6 ppm dissolved oxygen at 290°C for 100 h, and four were oxidized in air at 350°C for 100 h. The oxide coating that formed on the Type 316 SS specimens was identified by X-ray diffraction (XRD) as the single-phase spinel compound FeCr_2O_4 (iron [II] chromite). The thickness of the oxide coatings formed in water and in air was 0.3 and $\leq 0.1\text{ }\mu\text{m}$, respectively. Corrosion tests were conducted at 400°C for up to 3,000 h for the oxidized

Figure 10. Components of test capsule

Figure 11. Sealed test capsule

Table 6. Composition of materials subjected to static gallium

Alloy	Composition (wt.%)										
	Fe	Ni	Cr	Mo	Mn	Si	C	Ti	Nb	Zr	Other
Type 316 SS	65.0	13.0	17.0	2.50	≤2.0	0.75	0.08	-	-	-	0.045 P, 0.03 S
Inconel 625	2.5	61.0	21.5	9.00	0.25	0.25	0.05	0.2	-	-	0.2 Al, 3.65 Nb + Ta
Nb - 5 Mo - 1 Zr	-	-	-	4.86	-	0.0001	-	0.0001	bal	0.81	0.0002 O, 0.0001 Ta
Nickel 270	0.0005	99.995	0.0003	-	<0.001	<0.001	0.003	-	-	-	<0.001 S, <0.001 Cu

specimens, and for up to 1076 h for as-received specimens. After testing, the capsules were inverted and the gallium drained from the specimens to prevent possible deposition of corrosion products on the specimen surface during cooling. Corrosion coupons were washed in a warm solution of soap and water to remove gallium. If needed, a rubber scrubber was used to scrape any gallium adhering to the surface. The coupons were also ultrasonically cleaned in ethanol, and then in acetone, to ensure complete cleaning. Specimen weight and dimensions were recorded after rinsing and drying. All specimens were examined metallographically to determine metal loss and thickness of the reaction layer. A schematic representation of the corrosion behavior is shown in Fig. 12. Metal loss for each surface was determined from the initial thickness of the corrosion coupon and sound metal remaining after the test.

Figure 12. Schematic diagram showing typical measurements made to determine corrosion behavior of materials

5.1.1 Formation of Gallium Whiskers

While examining mounted cross sections of specimens, an unusual phenomenon occurred. Specimens that developed an FeGa_3 surface layer during the compatibility test, e.g., Type 316 SS and Armco iron, subsequently developed what appeared to be extruded wires or whiskers of pure gallium "growing" on the surface of mounted cross sections. These wires were 0.1–0.5 mm thick and grew to varying lengths up to 50 mm. Energy dispersive spectroscopy (EDS) indicated that these wires were pure gallium. A typical wire growing out of the reaction scale on a Type 316 SS specimen is shown in Fig. 13A. A photomicrograph of the same region but with the wire removed is shown in Fig. 13B. The fine surface markings observed on all of the wires suggest that they are being extruded from the material. The fine parallel lines on the top flat surface of the gallium wire (Fig. 13A) exactly match the lamellae observed in the surrounding region. Most likely these lamellae create the parallel markings on the sides of the wires. Also, the ridges on the top surface of the wire shown in Fig. 13A are indicative of a polycrystalline structure in the wire. However, Fig. 13B shows that there are no cavities or gallium-rich regions beneath these wires. They appear to be growing from the surface of the reaction scale. Region (a) in Fig. 13B was identified by EDS as FeGa_3 . The composition of Region (b), which was at the base of the wire, was the same as that of Region (a). Only Region (c) consisted of pure gallium; most likely this region was part of the wire that remained after the bulk of the wire was removed. Photomicrographs of whiskers from other specimens are shown in Figs. 14 and 15. The whiskers in Fig. 14 appear to have curled near the tip, whereas the one shown in Fig. 15 formed a continuous spiral. The spiraling may be caused by slight temperature fluctuations during whisker growth, or by a diffusion flux gradient along the whisker's base, leading to unequal growth rates along the base.

A similar phenomenon has been reported for several metals by the electronic component manufacturing industry.^{26–33} Tin, cadmium, molybdenum, tungsten, aluminum, indium, and lead exhibit spontaneous whisker growth at room temperature and atmospheric pressure. Whisker growth can be categorized in terms of two distinct growth mechanisms: one occurring at the tip and the other occurring at the base. Growth at the tip occurs primarily by vapor deposition at the whisker tip;²⁹ base-oriented growth may occur by electromigration^{30,31} and/or to relieve internal stresses.^{27,28} The mechanism important in the growth of gallium whiskers involves the relief of internal stresses.

Figure 13. Photomicrographs of (A) a pure gallium whisker and (B) specimen surface after whisker removal. Regions a, b, and c are described in the text

Figure 14. Photomicrographs of pure gallium whiskers, one with a curled end

Figure 15. Photomicrograph of a spiral-shaped pure gallium whisker

The growth of gallium whiskers is very similar to that observed in tin. Fisher et al.²⁸ have reported three stages in the development of tin whiskers: (a) an induction/incubation stage, (b) a stage of constant growth rate, and (c) a stage of abrupt deceleration of growth rate. Current observations indicate that gallium whiskers exhibit all three growth stages. Frank²⁷ reported that the mechanism for base-oriented whisker growth is a dislocation in the substrate that travels continuously around the base of the whisker. The process is initiated by a reduction of surface energy by oxidation at the point of initial whisker growth. Fisher et al.²⁸ indicated that the free energy required for whisker initiation could be provided by another source. In the case of gallium whiskers, strains caused by possible room-temperature phase transformations may provide the necessary energy. However, this cannot be confirmed, because the room-temperature regime of the iron-gallium phase diagram is not well defined.

Assuming that the necessary energy for whisker initiation has been provided, we postulate that gallium whisker growth can be explained by the same mechanism that occurs in tin. Gallium diffuses from a high-pressure region through a pressure gradient to the whisker base, at which point the whisker is projected outward from the substrate by means of the whisker-producing dislocation mechanism. FeGa₃ is crystalline and diffusion most likely occurs along the grain boundaries. The incubation stage is defined as the time needed for phase transformation and pressure gradient formation to occur in the substrate. A constant growth rate would exist as long as the pressure gradient within the substrate provides the necessary energy for whisker growth. When pressure within the substrate is equalized, the growth slows and eventually ceases.^{27,28}

The room-temperature regime of the nickel-gallium system is not well defined, and similar conditions may exist within this system to provide for whisker growth. Whisker growth near a nickel-gallium compound, possibly Ni₂Ga₃, has been observed in the present study.

5.2 RESULTS

5.2.1 Corrosion Rates

The corrosion of metals in gallium is directly related to their solubility in gallium.^{17,19} A minimum corrosion rate at 400°C is observed for elements in Groups 4–8 of Periods 4–6; the only exceptions occur in Period 4. The corrosion trends shown in Fig. 16 closely follow the solubility trends shown in Fig. 5. High corrosion rates are observed for metals in higher numbered groups, thus, they follow the solubility trend. In the second period, beryllium, boron, and carbon are not affected by exposure to liquid gallium.

Corrosion test results for the various materials are given in Tables 7 and 8. Nearly all of the corrosion coupons gained weight after exposure; only the Nb–5 Mo–1 Zr alloy exposed at 400°C for 300 and 1,076 h lost weight. Pure metals react rapidly with gallium at 400°C. An ≈0.5-mm-thick iron specimen reacted completely within 24 h, and an ≈0.3-mm-thick chromium specimen disintegrated within 100 h. In contrast to the results of Yatsenko,^{17,19} shown in Fig. 16, pure iron shows more corrosion than nickel. The corrosion rates at 400°C were estimated to be ≥10 and 2 μm/h for Armco iron and Nickel 270, respectively. These values correspond to metal losses ≥88 and ≈18 mm/yr or mass transfer ≥7.9 and 1.8 mg/cm²·h for pure iron and nickel, respectively. A corrosion rate for chromium cannot be estimated

Figure 16. Periodicity of corrosion rate of metals in liquid gallium at 400°C (after Yatsenko^{17,19})

Table 7. Corrosion behavior of Type 316 stainless steel exposed to gallium in sealed alumina capsules

Specimen	Exposure		Before Exposure		Weight Change (mg/cm ²)	Metal Loss ^a (μm)	Reaction Layer (μm)
	Temp. (°C)	Time (h)	Mass (mg)	Thickness (mm)			
SS-4A	400	24	860.6	0.5405	31.2	21.3	90.2
SS-4F	400	48	854.1	0.5135	19.8	-3.0	37.1
SS-4B	400	100	900.1	0.5405	36.5	60.5	280.3
SS-4C	400	300	834.2	0.5675	362.6	130.0	620.2
SS-4E	400	1076	770.0	0.5675	394.5	160.1	802.2
SS-3C-D	375	300	893.9	0.5135	169.3	48.3	274.2
SS-3C-C	350	300	937.3	0.5135	30.7	3.7	68.3
SS-3C-B	320	300	899.7	0.5135	2.7	-11.6	-
SS-3B	300	100	806.7	0.5135	2.7	-11.4	-
SS-3C-A	300	300	792.5	0.5405	0.3	4.1	-
SS-3D	300	1008	845.5	0.5135	4.7	-7.4	8.9
SS-3E	300	3000	820.1	0.5405	8.4	9.6	23.3
SS-2C	200	300	743.2	0.5540	-	9.0	-
SS-2D	200	1000	870.1	0.5135	-	-13.9	-
SS-2E	200	3000	742.0	0.5675	0.1	11.5	-
SS-24C ^b	200	300	856.5	0.5540	61.5	32.8	113.0
SS-24D ^b	200	1008	928.6	0.5135	69.9	18.4	122.7
SS-24E ^b	200	3000	792.6	0.5540	59.1	34.4	122.4

^aNegative values represent an increase in thickness. Accuracy of measurements ± 10 μm.

^bSpecimens exposed at 400°C for 24 h to ensure complete wetting prior to the exposure at 200°C.

Table 8. Corrosion behavior of various materials exposed to gallium in sealed alumina capsules

Specimen	Exposure		Before Exposure		Weight Change (mg/cm ²)	Metal Loss ^a (μm)	Reaction Layer (μm)
	Temp. (°C)	Time (h)	Mass (mg)	Thickness (mm)			
Inconel 625							
IN-4A	400	24	2515.2	1.3696	17.4	-3.9	8.0
IN-4F	400	48	2465.4	1.3825	2.9	3.8	9.6
IN-4B	400	100	2441.1	1.3825	4.1	6.6	11.0
IN-4C	400	300	2471.0	1.3696	27.9	14.3	56.0
IN-4E	400	1076	2508.0	1.3567	82.9	56.5	203.4
IN-3B	300	100	2414.5	1.3825	4.6	-0.3	-
IN-3C	300	300	2447.7	1.3825	-	0.3	-
IN-3D	300	1008	2443.3	1.3825	1.8	8.8	-
IN-3E	300	3000	2427.8	1.3825	1.0	-5.8	-
Nb-5 Mo-1 Zr Alloy							
NB-4F	400	24	1560.7	0.8602	1.0	5.3	-
NB-4B	400	100	1750.2	0.8602	3.9	-1.2	-
NB-4C	400	300	1746.2	0.8736	-0.1	3.2	-
NB-4E	400	1076	1704.7	0.8602	-5.1	3.6	-
NB-3B	300	100	1550.7	0.8602	0.8	2.9	-
NB-3C	300	300	1701.7	0.8602	3.1	-0.9	-
NB-3D	300	1008	1714.2	0.8602	1.2	0.1	-
NB-3E	300	3000	1874.7	0.8602	0.6	-6.2	-
Armco Iron							
FE-4F	400	24	771.0	0.4324	reacted completely to form FeGa ₃		
FE-4B	400	100	772.0	0.4459	reacted completely to form FeGa ₃		
FE-4C	400	300	727.2	0.4324	reacted completely to form FeGa ₃		
FE-4E	400	1076	765.2	0.4459	reacted completely to form FeGa ₃		
FE-3B	300	100	765.0	0.4594	150.9	47.1	250.3
FE-3C	300	300	758.2	0.4594	346.4	129.5	713.5
FE-3D	300	1008	785.5	0.4459	reacted completely to form FeGa ₃		
FE-3E	300	3000	749.3	0.4459	reacted completely to form FeGa ₃		
Nickel 270							
NI-4B	400	100	1320.3	0.7155	277.7	201.2	663.9
Pure Chromium							
CR-4B	400	100	488.6	0.2921	disintegrated into CrGa ₄ crystals		
Type 316 SS Oxidized in Air at 350°C for 100 hours							
SSA-4B	400	100	757.5	0.5405	27.2	23.3	73.4
SSA-4C	400	300	732.2	0.5405	107.3	94.9	508.7
SSA-4D	400	1000	792.0	0.5135	b	215.6	1275.3
SSA-4E	400	3000	756.8	0.5270	b	complete reaction ^c	
Type 316 SS Oxidized in Water (6 ppm dissolved O ₂) at 290°C for 100 hours							
SSW-4B	400	100	702.4	0.5135	83.8	26.2	189.1
SSW-4C	400	300	721.3	0.5135	135.8	76.3	465.8
SSW-4D	400	1000	761.6	0.5135	b	173.6	998.6
SSW-4E	400	3000	810.6	0.5135	cb	complete reaction ^c	

^aNegative values represent an increase in thickness. Accuracy of measurements ± 10 μm.

^bPostexposure specimen could not be cleaned; therefore, final masses were not recorded.

^cComplete reaction to form intermetallic compounds FeGa₃, CrGa₄, Ni₂Ga₃, and NiGa₄.

accurately because the actual time required for the specimen to dissolve in gallium could not be established. The 100-h result yields an approximate value of ≥ 1.5 μm/h (i.e., ≥ 13 mm/yr or ≥ 1 mg/cm²·h). The corrosion rates for iron and chromium are consistent with the values reported by Yatsenko (Fig. 16), but the rate for nickel is lower by two orders of magnitude.

Elements of an alloy dissolve in liquid metals because their concentrations in the liquid are lower than their solubilities. Under isothermal conditions, this process will continue at a constant rate only when experimental conditions stay the same during the test. In capsule tests with a limited volume of liquid metal, dissolution will become slower and stop completely when the liquid metal becomes saturated. However, metallographic examination of the corrosion specimens, discussed in the next section, indicates that, at the test temperatures, corrosion of iron, chromium, and nickel occurs by dissolution and is accompanied by formation of metal-gallium intermetallic compounds. Consequently, dissolution can occur after saturation by formation of intermetallic compounds from the saturated solution of gallium. The growth of these compounds may control the overall rate of corrosion for some metals and alloys. Corrosion of metals and alloys may proceed at a constant rate when the formation of compounds is faster than dissolution of metal elements. The difference in corrosion rate for nickel observed in this study and that reported earlier¹⁹ may be attributed to a different rate-controlling process; in the present study, the corrosion rate for nickel could be controlled by the rate of formation of nickel-gallium compounds.

Metal losses for the various alloys and pure metals exposed to gallium at 300 and 400°C are plotted as a function of time in Figs. 17 and 18, respectively. Corrosion rates for the alloys are lower than those for the pure metals. The Nb-5 Mo-1 Zr alloy showed no measurable corrosion at 300 or 400°C. Type 316 SS and Inconel 625 specimens show significant corrosion at 400°C and little or no corrosion at 300°C. The iron-based Type 316 SS exhibits more corrosion than nickel-based Inconel 625. At 400°C, the corrosion rate of Type 316 SS is nearly one order of magnitude greater than that of Inconel 625.

Corrosion rates for Type 316 SS exposed at 400°C decrease with time because of the limited quantity of gallium used in the experiments, i.e., the supply of gallium is exhausted, or because of specimen geometry. For example, corrosion on the inner surface of a U-shaped coupon will stop when the space between the two sides of the specimen fills with reaction layer. This behavior was observed in the Type 316 specimen exposed at 400°C for 1,076 h, and in the oxidized specimens exposed at 400°C for 1,000 h. Consequently, only values of metal loss up to 300 h were used to determine the corrosion rate of Type 316 SS at 400°C. Short-term (300-h)

Figure 17.
Corrosion behavior of materials tested
at 300°C in static gallium

Figure 18.
Corrosion behavior of materials tested
at 400°C in static gallium

Figure 19.
Corrosion behavior of oxidized Type 316
SS tested at 400°C in static gallium

corrosion tests were conducted at 375, 350, and 320°C to better establish the temperature dependence of the corrosion rate of Type 316 SS. The results show excellent agreement with 300-h tests at 300 and 400°C. Only approximate estimates of corrosion rates could be obtained for the alloys at 300°C, because of very low metal loss; long-term (>3,000-h) corrosion data are needed for accurate estimates.

Metal losses for Type 316 SS specimens that were oxidized in air and water and then exposed to gallium at 400°C are plotted as a function of time in Fig. 19. The corrosion rates of the oxidized Type 316 SS specimens were lower than those of the as-received specimens. The estimated corrosion rates at 400°C were 0.25 and 0.31 μm/h for specimens oxidized in water and air, respectively, and 0.46 μm/h for as-received Type 316 SS. These rates, although lower than those for pure metal, would result in >2 mm/yr metal loss.

5.2.2 Metallographic Examination

After exposure to gallium, the specimens were sectioned, mounted, and polished for metallographic examination. Some of the samples were etched to reveal signs of grain boundary attack. The photomicrographs of the samples are compiled in Appendix A.

Pure Metals

Three pure metals, Armco iron, Nickel 270, and chromium, were evaluated for compatibility with liquid gallium. Armco iron showed significant corrosion even at 300°C. The specimen developed a very porous and thick reaction layer that was identified by XRD analysis as FeGa_3 , with gallium metal present in the pores. Cross-sectional photomicrographs of specimens exposed to gallium for 100 and 300 h at 300°C are shown in Figs. A42 and A43, respectively. Both specimens exhibited uniform corrosion in both cold-worked and noncold-worked regions, with no intergranular attack. Similar corrosion behavior was observed for Nickel 270, in which the reaction layer primarily consists of Ni_2Ga_3 and contains small amounts of NiGa_4 in the region in contact with gallium. Most likely, the NiGa_4 formed during cooling. XRD also revealed an unidentified phase ('X' phase), with d-spacing lines at 2.71, 2.13, and 1.92Å. We assumed that this phase was a nickel-gallium compound. Upon etching, the porous structure of the reaction layer could easily be seen to contain a large quantity of gallium in the region close to the base metal. Figure A44 shows the cross section of Nickel 270 exposed for 100 h at 400°C. Again, intergranular attack was not observed.

A somewhat different behavior was observed for chromium metal; the specimen disintegrated into small crystals. The crystals were identified as CrGa_4 by XRD analysis, indicating that the mechanism for corrosion of chromium is basically the same as that for nickel or iron, with the difference that the CrGa_4 phase in equilibrium with the saturated solution of gallium did not adhere to the metal surface.

Metallographic examination of the reaction layers indicated that at the test temperatures, corrosion of nickel, chromium, and iron occurred entirely by dissolution, accompanied by formation of metal-gallium intermetallic compounds from the saturated solution of gallium. Corrosion can occur only with the growth of intermetallic compounds. For nickel and iron, the reaction proceeds at the metal surface, and an adherent but extremely porous reaction layer grows outward into the melt. The process continues as long as gallium can reach the reaction zone.

Nb-5 Mo-1 Zr Alloy

The Nb-5 Mo-1 Zr alloy showed no measurable corrosion at 300 or 400°C, although there appeared to be significant attack of the cold-worked region. Composite photomicrographs of these specimens are shown in Figs. A34-A41. The surface of the specimens after exposure was smooth, with very little formation of intermetallic compound. XRD analysis identified the sparse surface compound formations as NbGa_3 . This compound could not be detected by EDS during examination of specimen cross sections.

All specimens exhibited significant intergranular attack in cold-worked regions. Back-scatter electron microscopy of postexposure specimens indicated that gallium was present at

the crack tip. Although a few 10–20- μm -long cracks, which were created when the U-bend was made, were observed in the cold-worked region of the specimen before exposure, cracking in this alloy was enhanced by liquid gallium. Some postexposure cracks showed significant branching, with lengths in excess of 60 μm (Figs. A37, A40). Metallographic examination indicated that the degree of attack was not significantly different at 300 and 400°C; the specimens exposed for 100 h at 300 and 400°C showed similar attack. However, intergranular attack increased with time; specimens exposed for ≥ 300 h exhibited significant crack growth and crack tip widening (Figs. A35–A37, A40, A41).

Inconel 625 Alloy

Inconel 625 specimens showed significant corrosion at 400°C, and little or no corrosion at 300°C. The specimens exposed for 24–3,000 h at 300°C exhibited no reaction layer growth; however, the metal surface was etched by the liquid metal, revealing that some attack occurred at this temperature. These specimens are shown in Figs. A27–A30. At 400°C, metal loss and reaction layer growth was evident, and increased with exposure time. The photomicrographs in Figs. A29–A33 reveal that layer growth occurred evenly on the exposed surface, without intergranular attack. There was no distinction between attack of cold-worked and noncold-worked regions. The reaction layer, identified by XRD, contained CrGa_4 and gallium across the entire thickness. XRD also identified the presence of the 'X' phase observed in the Nickel 270 specimen. It appears that the 'X' phase occurred primarily near clusters of intermetallic compounds adhering to the surface of the specimens.

Type 316 SS

The specimens exposed at 200°C exhibited minimal corrosion and formed no reaction layer. Photomicrographs of these specimens are shown in Figs. A1–A3. There are no signs of intergranular attack, and it appears that gallium did not wet the specimens during exposure. Three specimens were initially exposed for 24 h at 400°C to ensure wetting of the specimens by the liquid metal; they were then exposed at 200°C for 300, 1000, and 3000 h. The corrosion behavior of these specimens was nearly identical to that of the specimen that was only exposed for 24 h at 400°C. The reaction layer was porous and evenly distributed on the specimen surface, indicating that there was no corrosion of Type 316 SS at 200°C, even after wetting. Corrosion of the prewetted specimens occurred only during the initial 24-h exposure at 400°C. Photomicrographs of prewetted specimens are shown in Figs. A4–A6. The specimens do not exhibit intergranular attack.

Type 316 SS specimens exposed at 300°C displayed little corrosion and reaction layer formation. These specimens are shown in Figs. A7–A10. After 100- and 300-h tests, the specimens did not develop a reaction layer; however, the metal surface exposed to gallium was attacked slightly. Reaction layers formed on the entire specimen during 1008- and 3000-h exposures. Three Type 316 SS specimens were exposed for 300 h at 320°C, 350°C, and 375°C. The photomicrographs of these specimens, Figs. A11–A13, indicate that the thickness of the layer increased linearly with temperature. The reaction layer was similar to that observed after exposure for 1000 or 3000 h at 300°C.

The specimens exposed at 400°C exhibited significant corrosion and formation of a thick, porous reaction layer. Although significant corrosion occurred, the specimens were not prefer-

entially attacked along the grain boundaries. The reaction layer, shown in cross section in Figs. A14–A18, appears to be striated, with alternating light and dark regions. The larger dark regions are most likely open pores. Exposure to gallium at 400°C for extended test times (1000 h) led to separation of the specimen at the bend, resulting in accelerated corrosion at the sample ends (Fig. A18). XRD analysis confirmed that the reaction layer on Type 316 SS consisted primarily of FeGa₃ and gallium, with some CrGa₄ in the region next to the steel surface; nickel–gallium compounds were not detected. It is possible that ternary and quaternary compounds of iron, chromium, nickel, and gallium also formed. More detailed studies of the complex behavior of this four-component system are necessary to accurately identify such compounds.

Preoxidized Type 316 SS

Two sets of Type 316 SS specimens were oxidized in either water or air prior to exposure in static gallium. Both sets of specimens were heavily attacked by gallium. The specimens oxidized in air are shown in Figs. A19–A21 and those oxidized in water are shown in Figs. A22–A24. The general appearance of oxidized and as-received specimens was similar; however, the corrosion rates of the oxidized specimens were somewhat lower. Examination of the specimens exposed for 100 h at 400°C (Figs. A19, A22) revealed that the marginally lower corrosion rates of the oxidized specimens were caused by lack of wetting of the specimen and/or dissociation of the surface oxide during the initial 100-h exposure.

XRD analysis of the oxidized specimens after exposure revealed at least two phases, one nearly amorphous spinel-type phase of the form NiFeGaO₄ and another unidentified phase, with d-spacing lines at 2.67, 2.43, and 1.495Å. The results indicate that, at 400°C, an iron chromite coating does not provide protection against corrosion. The coating dissociates to form a spinel-type phase, and corrosion of the alloy proceeds by dissolution, accompanied by formation of FeGa₃ and other gallium–metal compounds. The specimens tested for 1000 h (Figs. A21, A24) were nearly identical to the as-received sample tested for 1076 h (Fig. A18), and 3000-h test specimens were heavily attacked by gallium. Both sets of specimens completely dissolved to form FeGa₃.

5.3 DISCUSSION

Corrosion of structural alloys occurs primarily by dissolution of elements in liquid gallium. After an initial incubation period to allow wetting, gallium dissolves the elements of the alloys. Intermetallic compounds, typically MGa₃ or MGa₄, form on the surface of the specimen when the gallium becomes saturated with the metals. Crystalline binary intermetallic phases grow from the melt. A photomicrograph of crystals emerging from a solidified iron–gallium solution during a test on Type 316 SS is shown in Fig. 20. Corresponding EDS spectra are also shown. Note that a crystal of CrGa₄ is present with the FeGa₃ crystals. Because a significant amount of gallium was detected in the pores of the reaction layer near the base metal, we postulate that the primary reactions and crystal formation occur at the metal surface. Fresh gallium is transported through the lattice of the reaction layer to the reaction zone. The dissolution reaction proceeds as long as fresh gallium can reach the reaction zone. Crystal growth, leading to scale formation, proceeds as more base metal is dissolved.

Figure 20. FeGa₃ (a) and CrGa₄ (b) crystals growing from gallium melt, with corresponding EDS spectra

The most complex intermetallic formation occurred on Type 316 SS. Dissolution of the primary constituent elements, iron, nickel, and chromium, led to the formation of several intermetallic compounds. XRD analysis of the reaction layer on Type 316 SS indicated the presence of FeGa₃ and CrGa₄. Nickel compounds were detected by scanning electron microscopy/EDS away from the specimen. Figure 21 shows photomicrographs and EDS spectra of iron-gallium and nickel-gallium crystals. The large, faceted crystals in Fig. 21A were identified as FeGa₃. The small platelets, shown at higher magnification in Fig. 21B, are most likely Ni₂Ga₃. Figure 22 shows a nickel-gallium compound with a somewhat different composition and morphology than that shown in Fig. 21B. The EDS spectra of the two nickel-gallium phases indicate that the large platelets in Fig. 22 contain less nickel; they may be the 'X' phase identified by XRD of the Nickel 270 and Inconel 625 specimens. The nickel-gallium phase diagram indicates that Ni₂Ga₃ was the only stable compound in contact with gallium.

Figure 23 shows photomicrographs of FeGa₃ crystals from a test on Type 316 SS. In Fig. 23A, most of the surface area of the large faceted crystal appears to be pitted. This is typical of most of the FeGa₃ crystals that were observed. The high-magnification view shown in Fig. 23B reveals that these pits are actually crystal imperfections centered upon darker regions. The EDS spectra indicate that these darker regions contain silicon.

Referring to Fig. 8 in Section 4.1, in which the solubility of pure metals is discussed, we noted that the solubilities of iron, chromium, nickel, and niobium follow the sequence Ni > Fe > Cr > Nb at temperatures above 300°C, with the solubilities of iron, nickel, and chromium greater by several orders of magnitude than the solubility of niobium at any given temperature. This explains the difference between the corrosion rates of Type 316 SS, Inconel 625, and Nb - 5 Mo - 1 Zr. The corrosion rate of Type 316 SS was greater than that of the nickel-based Inconel 625 alloy. However, XRD analysis confirmed that the major reaction layers on Type 316 SS and Inconel 625 were FeGa₃ and CrGa₄, respectively. Chromium from Inconel 625 dissolves before the highly soluble nickel, resulting in a lower corrosion rate for the

Figure 21. FeGa_3 and Ni_2Ga_3 crystals grown during exposure of Type 316 SS to liquid gallium, together with corresponding EDS spectra

Figure 22. NiGa_4 crystals grown during exposure of Type 316 SS to liquid gallium, together with corresponding EDS spectra

Figure 23. FeGa_3 crystals with silicon imperfections grown during exposure of Type 316 SS to liquid gallium, together with corresponding EDS spectra

Inconel alloy than for the stainless steel. The solubility of niobium, molybdenum, and zirconium in gallium is relatively low, and it is expected that the niobium alloy will experience little or no measurable corrosion at the present exposure times and temperatures.

An Arrhenius plot of the corrosion rates of various metals and alloys is shown in Fig. 24. In all cases, linear-rate-law for metal loss was assumed to determine the corrosion rates. These values may represent a conservative estimate of corrosion. Results of Yatsenko¹⁹ for high-alloy steels Kh18N9T (Fe-18 Cr-9 Ni-0.6 Ti) and KhN77TYu (Ni-21 Cr-2.6 Ti-0.8 Al) exposed to gallium under dynamic conditions (0.15 m/s flow velocity) at 250 and 400°C are also included in the figure. Corrosion rates of Inconel 625 and Type 316 SS at 400°C are comparable to those of Kh18N9T and KhN77TYu but show lower values at 250°C. The differences are most likely due to velocity effects.

Figure 24 can be used to establish the maximum temperature limit for gallium/structural alloy systems. A maximum corrosion rate is first defined on the basis of either the allowable change in section thickness of the component or allowable mass transfer in the liquid metal system. The maximum operating temperature corresponding to the maximum corrosion rate is then obtained from Fig. 24 for a specific alloy/gallium system. For example, the maximum

Figure 24.
Arrhenius plot of corrosion rates of
various structural metals and alloys

surface temperature of a Type 316 SS component must be $<350^{\circ}\text{C}$ to keep corrosion rates below $250 \mu\text{m/yr}$. The niobium alloy can operate at higher temperatures for the same corrosion criterion. Figure 24 does not include the effects of system variables such as velocity and ΔT on corrosion mass transfer.

6 CONCLUSIONS

Tests were conducted to determine the compatibility of gallium with candidate structural materials for ITER, i.e., Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr alloy, as well as Armco iron, Nickel 270, and pure chromium. The pure metals reacted rapidly with gallium. In contrast to earlier studies, pure iron showed greater corrosion than nickel. The corrosion rates for Armco iron and Nickel 270 at 400°C were ≥ 88 and 18 mm/yr , respectively. Corrosion of iron-based Type 316 SS was greater than that of nickel-base Inconel 625. The Nb-5 Mo-1 Zr alloy was most resistant to corrosion in static gallium. At 400°C , corrosion rates were ≈ 4.0 , 0.5 , and 0.03 mm/yr for Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr, respectively. However, intergranular attack of the cold-worked region in the niobium alloy was observed. The results indicate that, at temperatures up to 400°C , corrosion occurred primarily by dissolution, accompanied by formation of metal/gallium intermetallic compounds. The growth of intermetallic compounds may control the overall rate of corrosion. The formation of an FeCr_2O_4 compound on the surface of Type 316 SS before exposure to liquid gallium did not provide protection against corrosion. The oxide coating dissociated to form a spinel-type oxide of the form NiFeGaO_4 , and corrosion of the alloy proceeded by dissolution and formation of intermetallic compounds.

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APPENDIX A: COMPOSITE PHOTOMICROGRAPHS FROM METALLOGRAPHIC EXAMINATION

After cleaning, each specimen was sectioned, mounted in copper-filled epoxy, and polished. Some of the specimens were etched to reveal signs of grain-boundary attack. Table A1 describes the preparation methods used for each material tested. The composite photomicrographs shown in this appendix are all displayed the same way. A low-magnification view of the specimen cross section is shown at the bottom of each figure. A high-magnification view of the reaction interface in the cold-worked area of the specimen is shown in the upper left, and in the upper right is a high-magnification view of the reaction interface in a noncold-worked area. The photomicrographs are presented according to increasing exposure time within each exposure temperature. The specimen identification number (within parentheses) refers directly to the specimen number in the first column of Tables 7 and 8.

Table A1. Preparation of postexposure specimens for examination by SEM

Material	Grain-boundary etch procedure	
	Etchant	Conditions
Type 316 SS	electrolytic etch with 10% oxalic acid solution; immersed specimen	≈30 s at 15 V; Pt cathode
Inconel 625	electrolytic etch with 10% oxalic acid solution; immersed specimen	≈5 s at 5–10 V; Pt cathode
Armco Iron	solution of 1 mL HNO ₃ and 40 mL H ₂ O	immerse specimen for 15 s
Nickel 270	solution of 10 g CuSO ₄ , 50 mL HCl, 50 mL H ₂ O, ≈ 1 mL H ₂ SO ₄	immerse specimen for ≈ 5 min
Nb–5Mo–1Zr ^a	solution of 20 mL HF, 15 mL H ₂ SO ₄ , 10 mL HNO ₃ , 50 mL H ₂ O	swab on polishing cloth with ≈2 drops solution for ≈30 s

^aThe niobium-based alloy was vibratory-polished with 0.05 μm suspended alumina for 48 h after initial polishing with SiC paper.

Type 316 Stainless Steel

Figure A1. Type 316 SS exposed in gallium for 300 h at 200°C (SS-2C)

Figure A2. Type 316 SS exposed in gallium for 1000 h at 200°C (SS-2D)

Figure A3. Type 316 SS exposed in gallium for 3000 h at 200°C (SS-2E)

Figure A4. Type 316 SS exposed in gallium for 300 h at 200°C after initial exposure for 24 h at 400°C (SS-24C)

Figure A5. Type 316 SS exposed in gallium for 1008 h at 200°C after initial exposure for 24 h at 400°C (SS-24D)

Figure A6. Type 316 SS exposed in gallium for 3000 h at 200°C after initial exposure for 24 h at 400°C (SS-24E)

Figure A7. Type 316 SS exposed in gallium for 100 h at 300°C (SS-3B)

Figure A8. Type 316 SS exposed in gallium for 300 h at 300°C (SS-3C-A)

Figure A9. Type 316 SS exposed in gallium for 1008 h at 300°C (SS-3D)

Figure A10. Type 316 SS exposed in gallium for 3000 h at 300°C (SS-3E)

Figure A11. Type 316 SS exposed in gallium for 300 h at 320°C (SS-3C-B)

Figure A12. Type 316 SS exposed in gallium for 300 h at 350°C (SS-3C-C)

Figure A13. Type 316 SS exposed in gallium for 300 h at 375°C (SS-3C-D)

Figure A14. Type 316 SS exposed in gallium for 24 h at 400°C (SS-4A)

Figure A15. Type 316 SS exposed in gallium for 48 h at 400°C (SS-4F)

Figure A16. Type 316 SS exposed in gallium for 100 h at 400°C (SS-4B)

Figure A17. Type 316 SS exposed in gallium for 300 h at 400°C (SS-4C)

Figure A18. Type 316 SS exposed in gallium for 1076 h at 400°C (SS-4E)

Figure A19. Type 316 SS exposed in gallium for 100 h at 400°C after oxidation in air for 100 h at 350°C (SSA-4B)

Figure A20. Type 316 SS exposed in gallium for 300 h at 400°C after oxidation in air for 100 h at 350°C (SSA-4C)

Figure A21. Type 316 SS exposed in gallium for 1000 h at 400°C after oxidation in air for 100 h at 350°C (SSA-4D)

Figure A22. Type 316 SS exposed in gallium for 100 h at 400°C after oxidation in water for 100 h at 290°C (SSW-4B)

Figure A23. Type 316 SS exposed in gallium for 300 h at 400°C after oxidation in water for 100 h at 290°C (SSW-4C)

Figure A24. Type 316 SS exposed in gallium for 1000 h at 400°C after oxidation in water for 100 h at 290°C (SSW-4D)

Inconel 625

Figure A25. Inconel 625 exposed in gallium for 100 h at 300°C (IN-3B)

Figure A26. Inconel 625 exposed in gallium for 300 h at 300°C (IN-3C)

Figure A27. Inconel 625 exposed in gallium for 1008 h at 300°C (IN-3D)

Figure A28. Inconel 625 exposed in gallium for 3000 h at 300°C (IN-3E)

Figure A29. Inconel 625 exposed in gallium for 24 h at 400°C (IN-4A)

Figure A30. Inconel 625 exposed in gallium for 48 h at 400°C (IN-4F)

Figure A31. Inconel 625 exposed in gallium for 100 h at 400°C (IN-4B)

Figure A32. Inconel 625 exposed in gallium for 300 h at 400°C (IN-4C)

Figure A33. Inconel 625 exposed in gallium for 1076 h at 400°C (IN-4E)

Nb – 5Mo – 1Zr

Figure A34. Nb – 5Mo – 1Zr exposed in gallium for 100 h at 300°C (NB-3B)

Figure A35. Nb – 5Mo – 1Zr exposed in gallium for 300 h at 300°C (NB-3C)

Figure A36. Nb - 5Mo - 1Zr exposed in gallium for 1008 h at 300°C (NB-3D)

Figure A37. Nb - 5Mo - 1Zr exposed in gallium for 3000 h at 300°C (NB-3E)

Figure A38. Nb - 5Mo - 1Zr exposed in gallium for 24 h at 400°C (NB-4F)

Figure A39. Nb - 5Mo - 1Zr exposed in gallium for 100 h at 400°C (NB-4B)

Figure A40. Nb - 5Mo - 1Zr exposed in gallium for 300 h at 400°C (NB-4C)

Figure A41. Nb - 5Mo - 1Zr exposed in gallium for 1076 h at 400°C (NB-4E)

Armco Iron

Figure A42. Armco iron exposed in gallium for 100 h at 300°C (FE-3B)

Figure A43. Armco iron exposed in gallium for 300 h at 300°C (FE-3C)

Nickel 270

Figure A44. Nickel 270 exposed in gallium for 100 h at 400°C (NI-4B)

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