ANL/ET/CP--86690
CONF-950905--22

Compatibility of ITER Candidate Materials with Static Gallium*

P. R. Luebbers and O. K. Chopra
Energy Technology Division
Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439

RECEIVED

JAN 24 1995

OSTI

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

September 1995

For presentation at the Sixteenth Symposium on Fusion Engineering (SOFE '95), Champaign, IL Sept. 30-Oct. 5, 1995.

*This work was supported by the U.S. Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Compatibility of ITER Candidate Materials with Static Gallium

P. R. Luebbbers and O. K. Chopra
Energy Technology Division, Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439

ABSTRACT

Corrosion tests have been conducted to determine the compatibility of gallium with candidate structural materials for the International Thermonuclear Experimental Reactor (ITER) first wall/blanket systems, e.g., Type 316 stainless steel (SS), Inconel 625, and Nb-5 Mo-1 Zr. The results indicate that Type 316 SS is least resistant to corrosion in static gallium and Nb-5 Mo-1 Zr alloy is most resistant. At 400°C, corrosion rates for Type 316 SS, Inconel 625, and Nb-5 Mo-1 Zr alloy are ≈ 4.0 , 0.5, and 0.03 mm/yr, respectively. Iron, nickel, and chromium react rapidly with gallium. Iron shows greater corrosion than nickel at 400°C (≥ 88 and 18 mm/yr, respectively). The present study indicates that at temperatures up to 400°C, corrosion occurs primarily by dissolution and is accompanied by formation of metal/gallium intermetallic compounds. The growth of intermetallic compounds may control the overall rate of corrosion.

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 (2.77 barns) and a 3.2% volume increase during solidification. 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, such as tantalum, tungsten, graphite, stabilized ZrO_2 , and quartz are most stable in gallium [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 article presents results of tests to determine the compatibility of gallium with candidate structural materials for ITER first-wall/blanket systems, e.g., Type 316 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.

EXPERIMENTAL PROCEDURE

Corrosion tests were conducted in alumina capsules with a threaded metal fitting at the top end for sealing. Each capsule contained a single test specimen immersed in $\approx 11 \text{ cm}^3$ of gallium. The capsules were capped and sealed in a high-purity-argon environment. Corrosion coupons ($\approx 10 \times 20 \times 0.4\text{--}1.1 \text{ mm}$) were prepared from Type 316 SS, Inconel 625, Nb-5 Mo-1 Zr alloy, Nickel 270 (99.995 wt.% Ni), Armco iron, and pure chromium. The compositions of the alloys are given in Table 1. The coupons were bent into a U-shape to study the effect of cold work. Corrosion tests were conducted at 300 and 400°C for up to 3000 h. 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. Specimen weight and dimensions were recorded before and after testing. All specimens were examined metallographically to determine metal loss and thickness of the reaction layer. Metal loss was determined from the initial thickness of the corrosion coupon and sound metal remaining after the test.

EXPERIMENTAL RESULTS

Corrosion test results for the various materials are tabulated Ref. 4. 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 $\approx 0.5\text{-mm}$ -thick iron specimen reacted completely within 24 h, and an $\approx 0.3\text{-mm}$ -thick chromium specimen disintegrated within 100 h. The corrosion rates at 400°C were estimated to be ≥ 10 and $2 \mu\text{m/h}$ for Armco iron and Nickel 270, respectively. These values correspond to metal losses of ≥ 88 and $\approx 18 \text{ mm/yr}$, or mass transfer of ≥ 7.9 and $1.8 \text{ mg/cm}^2\text{-h}$ for pure iron and nickel, respectively. For chromium, only an approximate value of corrosion rate was obtained because the actual time required for the specimen to dissolve in gallium could not be established accurately. The 100-h result yields a corrosion rate of $\geq 1.5 \mu\text{m/h}$ (i.e., $\geq 13 \text{ mm/yr}$ or $\geq 1 \text{ mg/cm}^2\text{-h}$). The corrosion rates for iron and chromium are consistent with the values reported by Yatsenko [5,6], but the rate for nickel is lower by two orders of magnitude.

Table 1. 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

Figure 1. Corrosion behavior of materials in static gallium at 300 and 400°C

Metal losses for the various materials are plotted as a function of time in Fig. 1. Corrosion rates for the alloys are lower than those for the pure metals. The iron-based Type 316 SS exhibits more corrosion than the 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. The Nb-5 Mo-1 Zr alloy showed no measurable corrosion at 300 or 400°C. Corrosion rates for Type 316 SS exposed at 400°C decrease with time because of the limited quantity of gallium used in the experiments (the supply of gallium is exhausted) and/or because of specimen geometry (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). The latter behavior was observed in the specimen exposed for 1,076 h at 400°C. Consequently, only values of metal loss up to 300 h were used to determine the corrosion rate of Type 316 SS at 400°C.

An Arrhenius plot of the corrosion rates of various metals and alloys is shown in Fig. 2. Short-term (300-h) tests were conducted at 375, 350, and 320°C to better establish the temperature dependence of the corrosion rate of Type 316 SS. 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 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 [6]. 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.

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 results of a detailed metallographic evaluation of the samples are presented in Ref. 4. Typical photomicrographs of the specimen cross section and the reaction interface in the cold-worked and noncold-worked area of the specimen are shown in Fig. 3.

Armco iron exposed to gallium at 300°C developed a very porous and thick reaction layer that was identified by X-ray diffraction (XRD) analysis as FeGa_3 , with gallium metal present in the pores. The specimens exhibited uniform corrosion in both cold-worked and noncold-worked regions, and no intergranular attack was seen. Similar corrosion behavior was observed for Nickel 270, in which the reaction layer primarily consisted of Ni_2Ga_3 and contained 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), probably another nickel-gallium compound, with d-spacing lines at 2.71, 2.13, and 1.92 Å. A somewhat different behavior was observed for chromium metal; the specimen disintegrated into small crystals. XRD

Figure 2. Arrhenius plot of corrosion rates of various structural metals and alloys subjected to gallium exposure

Figure 3. Type 316 stainless steel exposed in static gallium for 300 h at 400°C

analysis showed the crystals to be CrGa_4 , indicating that the mechanism for corrosion of chromium is basically the same as that for nickel or iron. The difference is that the CrGa_4 phase in equilibrium with the saturated solution of gallium did not adhere to the metal surface.

Type 316 SS specimens exposed at 400°C exhibited significant corrosion and formation of a thick, porous reaction layer. Although significant corrosion occurred, the specimens were not preferentially attacked along the grain boundaries. 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. XRD analysis confirmed that the reaction layer on Type 316 SS consisted primarily of FeGa_3 and gallium, with some CrGa_4 in the region next to the steel surface. Nickel-gallium compounds were not observed, although they were detected away from the specimen. A photomicrograph of FeGa_3 and Ni_2Ga_3 crystals observed in the saturated gallium solution during a test on Type 316 SS is shown in Fig. 4. The large faceted crystals were identified as FeGa_3 , and the small platelets are Ni_2Ga_3 .

The specimens exposed at 200°C showed that gallium does not wet the surface at this temperature. Specimens exposed at 300°C displayed little corrosion and reaction layer formation. After 100- and 300-h tests, the specimens did not develop a reaction layer, although, the metal surface exposed to gallium was attacked slightly. Reaction layers formed on the entire specimen during 1000- and 3000-h exposures. Three Type 316 SS specimens were exposed for 300 h at 320, 350, and 375°C. Thickness of the reaction layer increased linearly with temperature. The reaction layer was similar to that observed after exposure for 1000 or 3000 h at 300°C.

Inconel 625 specimens showed significant corrosion at 400°C and little or no corrosion at 300°C. The Inconel 625 speci-

mens exposed at 300°C exhibited no reaction layer growth; however, the metal surface was etched by the liquid metal. At 400°C, metal loss and reaction layer growth was evident. 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 contained CrGa_4 and gallium across the entire thickness. XRD also identified the presence of the 'X' phase observed in the Nickel 270 specimen.

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. The surface of the specimens after exposure was smooth, with very little formation of intermetallic compound. XRD analysis identified the sparse sur-

Figure 4. FeGa_3 and Ni_2Ga_3 crystals grown during exposure of Type 316 stainless steel specimen to gallium at 400°C

face compound formations as NbGa_3 . In this alloy, cracking was enhanced by liquid gallium. All specimens exhibited significant intergranular attack in cold-worked regions. Some postexposure cracks showed significant branching, with lengths in excess of 60 μm .

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 because their concentrations in the liquid are lower than their solubilities. Under isothermal conditions, the dissolution 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 then stop completely when the liquid metal becomes saturated. However, in gallium, corrosion of metals and alloys 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.

Intermetallic compounds, typically MGa_3 or MGa_4 , form on the surface of the specimen when the gallium becomes saturated with the metals. Crystalline binary intermetallic phases grow from the melt. 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.

The solubilities of iron, chromium, nickel, and niobium follow the sequence $\text{Ni} > \text{Fe} > \text{Cr} > \text{Nb}$ at temperatures above 300°C, with the solubilities of iron, nickel, and chromium greater by several orders of magnitude than that of niobium at any given temperature [4]. 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. XRD analysis confirmed that the major reaction layers on Type 316 SS and Inconel 625 were FeGa_3 and CrGa_4 , respectively. Chromium from Inconel 625 dissolves before the highly soluble nickel, resulting in a lower corrosion rate for the 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 temperatures.

Figure 2 may be used to establish the maximum temperature for gallium/structural alloy systems. A maximum corrosion rate is first defined on the basis of either 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. 2 for a specific alloy/gallium system. For example, the maximum surface temperature of a Type 316 SS component must be <350°C to keep corrosion rates below 250 $\mu\text{m}/\text{yr}$. The niobium alloy can operate at higher temperatures for the same corrosion criterion. Note that the effects of system variables such as velocity and ΔT on corrosion mass transfer are not included in Fig. 2.

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 results of 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.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38. The authors thank W. Michaud, C. Reed, P. Dombrowski, and R. Clark for contributing to the experimental effort.

REFERENCES

- [1] L. R. Kelman, W. D. Wilkinson, and F. L. Yaggee, *Resistance of Materials to Attack by Liquid Metals*, Argonne National Laboratory Report ANL-4417 (July 1950).
- [2] W. D. Wilkinson, *Effects of Gallium on Materials at Elevated Temperatures*, Argonne National Laboratory Report ANL-5027 (Aug. 1953).
- [3] W. D. Wilkinson, *Effects of Gallium on Materials at Elevated Temperatures Supplementary Report*, Argonne National Laboratory Report ANL-4582 (Aug. 1953).
- [4] P. R. Luebbbers, W. F. Michaud, and O. K. Chopra, Compatibility of ITER Candidate Structural Materials with Static Gallium, Argonne National Laboratory Report ANL-93/31 (Dec. 1993).
- [5] S. P. Yatsenko, *Correlation Between the Physical Properties of Pure Solid Metals with Their Stability in Liquid Ga Metal*, Russ. J. Phys. Chem., 45, 1095-1098 (1971).
- [6] S. P. Yatsenko, *Gallium. Its Interaction With Metals*, Nauka, Moscow (1974).