

Gallium-Induced Oxidation of Selected Pure Metals and Alloys at 1200°C

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BACKGROUND

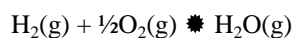
The processing of Pu compounds, which involves the intentional or unintentional separation of Ga or Ga₂O₃ from Pu or PuO₂, has adverse consequences with respect to furnace materials. Common materials of construction, such as iron- and nickel-base alloys, have failed in service following processing of PuO₂ containing Ga₂O₃. It was hypothesized that failures were attributable to Ga₂O, given its very high volatility as compared to Ga₂O₃ or Ga. There have been few studies of the behavior of Ga₂O₃ under expected furnace conditions. Research by Besmann detailed the Ga-O system.¹ Work by Butt *et al.*² examined the thermodynamics of Ga₂O evolution. Two primary pathways for Ga₂O formation were identified. The first involves reaction of Ga₂O₃ with a reducing species, such as hydrogen:



A second pathway involves Ga₂O production via Ga₂O₃ disproportionation:



The partial pressure of Ga₂O, produced by the above two reactions, is related to the water-to-hydrogen ratio by the reaction:

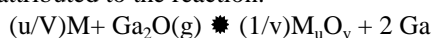


Butt *et al.* analyzed the oxidation state of Ga in downstream deposits after heating Ga₂O₃ in hydrogen. They found that deposits contained a combination of Ga, Ga₂O₃, and a Ga oxide having an intermediate oxidation state, possibly Ga₂O. These deposits were rapidly oxidized to Ga₂O₃ upon exposure to air.

None of the prior research has examined the reaction of materials with Ga₂O / Ga₂O₃. This research seeks to detail the reactivity of various metals and alloys with Ga₂O₃, understand the failure mechanisms and determine metals or alloys suitable for use in the environments of interest.

RESULTS

Following exposure to Ga₂O₃ in 800 to 1200°C Ar - 6% H₂, 304 SS, 316 SS, and Hastelloy C-276 (Ni-Cr-Mo alloy) were examined using micro X-ray fluorescence (MXRF), proton-induced X-ray emission (PIXE), Rutherford backscattering spectroscopy (RBS), and X-ray photoelectron spectroscopy (XPS). All three alloys were attacked following exposure to Ga₂O / Ga₂O₃ at 800 to 1200°C. Significant oxidation and Ga uptake were observed following exposure of the three alloys. The simultaneous Ga₂O reduction and alloy oxidation were initially attributed to the reaction:



It was hypothesized that Ga metal was available for diffusion into the alloy following reaction. Ga₂O was found to be primarily responsible for iron- and nickel-base

alloy oxidation although Ga₂O₃ alone was shown to be capable of attack during elevated temperature processing. Oxidation and subsequent Ga uptake were attributed to the presence of Cr, Mn, Si, and V within the alloys. These elements are susceptible to oxidation by Ga₂O, as shown by their enrichment in surface oxides and by thermodynamic calculations. Ga uptake was shown to severely degrade the mechanical properties of 304 SS. Uniform Ga concentrations of 20 wt.% promoted a low-energy, brittle fracture. Both field and laboratory experience indicate that common materials of construction (iron- and nickel-base alloys) are unsuitable for containment of Pu-Ga compounds during processing. Materials of construction must be resistant to melting, creep, oxidation, Ga uptake, and hydriding. The above constraints dramatically reduce the types of materials that can be used for furnace construction. Further constraints require that the materials be introduced into and assembled within the confines of a preexisting, plutonium-contaminated glovebox, that they are amenable to machining, and that they have good mechanical properties. Therefore, metals are considered preferable to ceramics. Chromium-, cobalt-, tungsten-, and molybdenum-base materials were believed to be suitable candidates based on the above criteria. Therefore, the behavior of these materials in the presence of Ar-6% H₂ and Ga₂O / Ga₂O₃ was examined.

Alloys Haynes 25 (Co - 20Cr - 15W - 10Ni), 52Mo - 48Re, 62W - 38Cu, and commercially pure Cr, Co, Mo, W, and alumina were exposed to Ar-6% H₂ at 1200°C in an effort to screen the materials. As predicted by thermodynamic calculations, only Haynes 25 and Cr appreciably oxidized, albeit to a lesser extent than iron- and nickel-base alloys. The fact that these materials also contained less Ga than the iron- and nickel-based alloys suggests that the extent of attack (oxidation, Ga uptake, and elemental redistribution) cannot be predicted based on a simple rule of elemental mixtures. Earlier work assumed that reduction of Ga₂O was inextricably linked to alloy oxidation and Ga uptake. However, Ga uptake in Mo, Co, and W-Cu occurred in the absence of oxidation, suggesting that an alternate pathway for Ga uptake must exist. Based on thermodynamic calculations, it was shown that Ga alloying can occur in the absence of alloy oxidation for materials which do not contain Cr, Mn, V, Si or Al. An apparent link between Ga solubility and Ga uptake was noted, although kinetic factors may limit Ga uptake. Preliminary results suggest that W, Mo-Re, and alumina are all suitable for furnace construction based on their resistance to Ga₂O. None of these materials experienced significant oxidation or Ga uptake.

REFERENCES

- 1) T. M. Besmann, *J. Amer. Ceram. Soc.* **81**, 3071 (1998).
- 2) D. P. Butt, Y. Park, and T. N. Taylor, *J. Nucl. Mater.* **264**, 71 (1999).