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Journal of Nuclear Materials 373 (2008) 424–428

journal of nuclear materials

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Letter to the Editors

Corrosion of ternary carbides by molten lead

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Received 16 January 2007; accepted 25 April 2007

Abstract

Two ternary carbides, Ti_2AlC and Ti_3SiC_2 were tested for corrosion in circulating molten lead at 650 °C and 800 °C for possible application as cladding or structural materials in a lead-cooled fast reactor. The extent of reaction was minimal for both materials. The only observed interaction with the lead was a result of surface cracks and strains in the Ti_2AlC produced by machining prior to exposure to the lead.

PACS: 81.05.Je

1. Introduction

Under the United States Department of Energy Generation IV Nuclear Energy Systems Initiative, preconceptual design and viability assessment are being carried out for lead-cooled fast reactor (LFR) concepts suitable for international deployment [1,2]. The concepts incorporate small-reactor proliferation-resistance features including a long core lifetime of 15–30 years, fissile self-sufficiency for efficient utilization of uranium resources, autonomous load following for deployment on small or immature grids, and a high degree of passive safety. To take advantage of higher plant efficiencies achievable with the use of supercritical carbon dioxide Brayton cycle power conversion, the LFR concepts operate at peak lead coolant/cladding temperatures exceeding 550 °C. Below that temperature existing cladding and structural materials can be used together with active control of the oxygen potential to enable the formation of protective Fe_3O_4 layers on the cladding and structures without formation of lead oxide particulates. Thus, new materials for service at temperatures above 550 °C need to be developed and tested for corrosion resistance and irradiation stability. Peak temperature goals of 650 °C and 800 °C have been identified for LFR concepts for efficient production of electricity (and optionally potable water) and process heat for hydrogen production via a Ca–Br thermochemical cycle, respectively.

Integral to the development of such a reactor is the identification or development of structural materials which can withstand the corrosive effects of lead or especially the more corrosive lead–bismuth eutectic over the proposed lifetimes of the reactor and the reactor core. To assess the viability of various candidate materials we have performed experiments on a variety of structural materials in circulating liquid metals.

In previous work [3] we found that SiC was not attacked by lead in our exposure test. Because of the difficulty of fabricating components from SiC we decided to test commercially available ternary carbides. The materials were Ti_2AlC (designated 211) and Ti_3SiC_2 (designated 312) [4]. For SiC, Ti_2AlC, and Ti_3SiC_2, the bulk densities are 3.2 g/cc [5], 4.2 g/cc, and 4.5 g/cc, and the Young's modulus of tensile elasticity are about 410 GPa [6], 280 GPa, and 330 GPa, respectively. We expected that they would show corrosion resistance and strength similar to SiC but with the advantage of being much more adaptable to fabrication. We obtained the materials through the courtesy of Tamer El-Raghy of the 3-ONE-2 LLC [7]. Both ternary

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doi:10.1016/j.jnucmat.2007.04.054

carbides are fabricated by pressureless sintering of the 211 and 211 powders.

2. Experimental

In order to assess the corrosion resistance of the samples, they were exposed to lead circulating in a convection harp for 1000 h. Our device was adopted from a design for a convection harp given by Cathcart and Manley [8]. The harp was fabricated from a 13 mm diameter quartz tube [9] as shown in Figs. 1 and 2.

The Ti_2AlC sample was prepared from a cylinder 25.4 mm long with a diameter of 6 mm. One transverse cut produced two half cylinders with a semi-circular cross-section. The original outer curved surface was maintained and the inner flat face was freshly exposed carbide. One of these segments was placed in the hot-leg and one in the cold-leg of the harp. The Ti_3SiC_2 sample was prepared from a cylinder 29.6 mm long with a diameter of 14.3 mm. The harp specimens were prepared by making three transverse cuts through the cylinder by electric discharge machining (EDM). The transverse cuts produced pie-shaped segments with a vertex angle of 60°. One of these segments was placed in the hot-leg and one in the cold-leg of the harp.

Each loop contained two samples of one test material, held in place by indentations in the quartz. Samples were placed in both the hot (800 °C) and cold (650 °C) regions of the harp during fabrication. The harp was mounted in a furnace specifically fabricated for these experiments and the assembly was purged and evacuated several times before heating was initiated. A bulb located above the loop was loaded with ~1100 g of high-purity lead and heated to about 500 °C. He–4%H_2 was bubbled through the molten lead by a simple gas-handling system (not shown in Fig. 1 or Fig. 2) to reduce its oxygen and moisture content before it was introduced to the experimental loop. A porous quartz frit at the bottom of the bulb prevented premature introduction of the lead into the loop and also served as a filter to remove any solid residues from the molten lead. When the moisture content is ~200 ppm, the molten lead is introduced by increasing the pressure of He–4%H_2 above the bulb and reducing the pressure below it. The temperature is controlled by thermocouples fixed to the

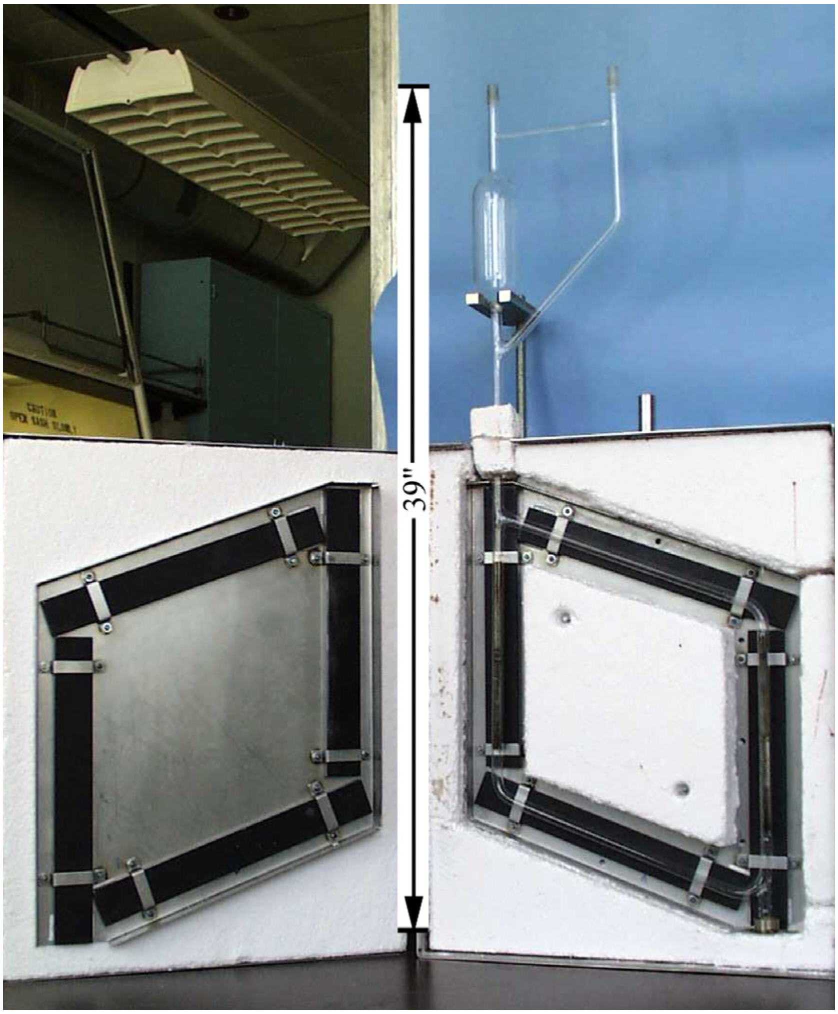

Fig. 1. Quartz harp with samples mounted in the furnace.

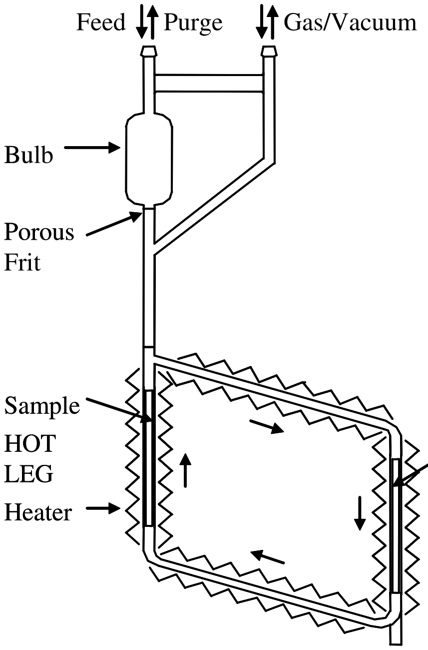

Fig. 2. A schematic of the quartz harp. The temperature gradient causes the molten lead to flow.

exterior of the quartz loop. The temperature gradient within the loop causes the molten metal to circulate. Following the 1000 h exposure, power to the furnace was stopped and the assembly allowed to cool to room temperature. The harp was removed from the furnace and the regions containing the test samples, still embedded in lead, were removed and sectioned with a low speed saw. Cross sections of the samples were prepared for scanning electron microscopy by mounting small segments of the sample in epoxy followed by grinding and polishing of the mount surface. The samples were examined in a JEOL 6400 SEM operated at 20 kV with a working distance of 25 mm. Images were obtained using backscattered electrons in order to bring out atomic number contrast.

3. Results

3.1. Ti_2AlC(211)

Both the hot and cold-leg samples of the 211 material showed similar interaction with the lead. The slight indications of lead infiltration into the 211 material are likely due to smearing of lead onto the sample during polishing rather

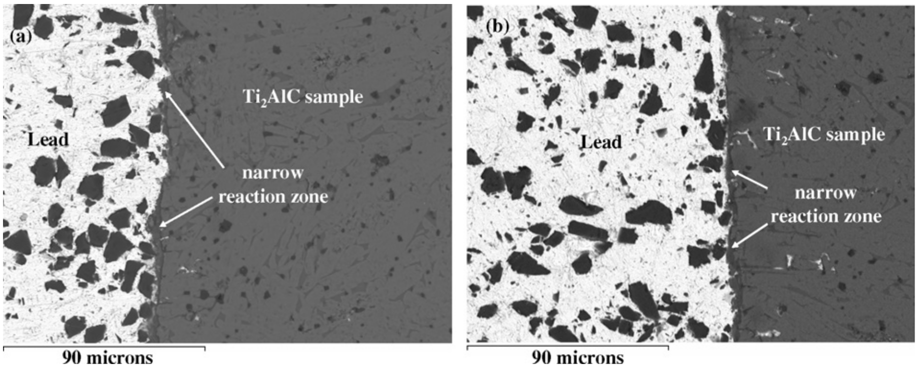

Fig. 3. Cut surface of (a) hot-leg sample and (b) cold-leg sample of Ti_2AlC sample. The sample is the dark phase on the right and the lead is the bright phase on the left. The dark spots in the lead are imbedded SiC polishing compound and the dark spots on the right show porosity. Small amounts of lead can be seen in the sample area which we believe are caused by smearing during polishing.

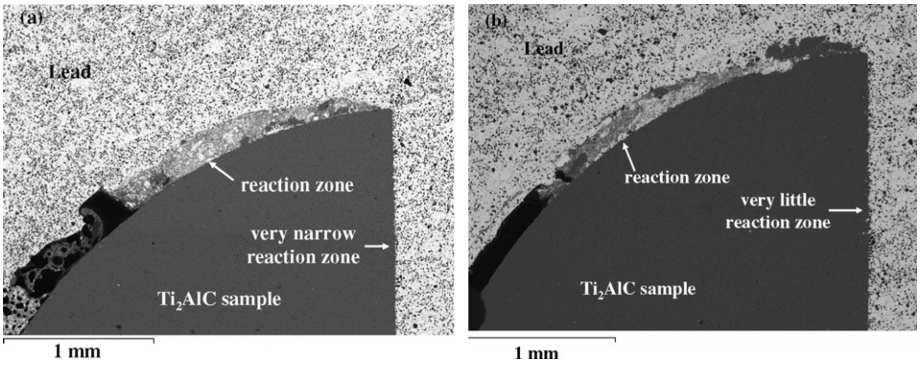

Fig. 4. Interaction zones of (a) hot-leg and (b) cold-leg samples of Ti_2AlC in lead. Pre-test cracks and strains along the curved machined surface of the sample produced a broad interaction zone containing a mixture of lead and 211 components. No interaction zone is seen on the fresh vertical face. Note: The black regions represent voids where epoxy did not infiltrate or the sample pulled away from the lead.

than actual attack. A reacted zone between the cut surface and the lead was extremely small for both the hot and cold-leg being no more than a few microns thick as shown in Fig. 3. However, along the curved surface each sample had a broad interaction zone approximately 100–250 μm thick which EDS indicated contained a mixture of lead and 211 components with no observed concentration gradients as shown in Fig. 4. The thickness of the reacted zone was about the same for both the hot and the cold samples which led us to believe that the region was present at the start of the test. The section in Fig. 4(a) shows the original curved surface with a broad reaction zone while Fig. 3 shows a small reaction zone at the transverse cut faces of the sample. A similar effect was seen in the cold-leg sample as shown in Fig. 4(b). Discussion with the supplier of these samples, Dr. El-Raghy, clarified this difference. The outer surface of the rod was machined thereby introducing numerous cracks and strain. Thus mechanical defects in the starting material appeared to be responsible for the results we observed. Dr. El-Raghy reported to us that he has observed similar phenomena in his own studies of this material. Our cutting of the sample using EDM on the other hand would not introduce such strain. Except for the reaction zone resulting from the pre-existing cracks on the outer surface, this material performed quite well in exposure to lead at 650 °C and at 800 °C.

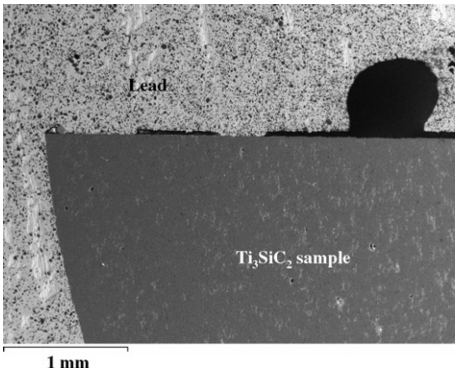

Fig. 5. Hot-leg 312 in lead.

3.2. $Ti_3SiC_2(312)$

The results of the Ti_3SiC_2 experiment show little interaction between the lead and the ceramic either along the cut or original surfaces as shown in Fig. 5. The interaction is so minimal that the lead separated cleanly from the ceramic in some places upon cooling, behaving in this respect like SiC which was not even wetted by the lead [3]. The temperature did not affect the performance of the material. At high magnification, the images show some roughness along the edge of the sample as shown in Fig. 6(a) for the hot-leg sample and (b) for the cold-leg sample, but indicate no corrosion of the materials by the lead. Unlike the Ti_2AlC sample, an interaction zone between the curved surface and lead was not present because the surface was not machined.

4. Summary and conclusions

Overall these ternary carbides appear to be quite attractive materials for this application. Extensive additional testing would be needed to verify these results. A particular advantage of these ternary carbides is that they can be machined, as confirmed by our sectioning techniques, and can even be plasma-sprayed to form coherent coatings. These materials performed better than any other material tested with the exception of pure SiC [3].

Acknowledgements

The Argonne National Laboratory's work was supported by the US Department of Energy Generation IV Nuclear Energy Systems Initiative. The authors are grateful to Dr Rob M. Versluis (US DOE), Generation IV Program Manager, and Dr James J. Sienicki (Argonne National Laboratory), Generation IV lead-cooled fast reactor co-systems integration manager. The authors wish to express their appreciation to Dr Tamer El-Raghy (3-ONE-2 LLC) for supplying the samples for this study and for his many helpful suggestions during the course of this work. They are also grateful to Joseph Gregar for his skillful fabrication of the quartz loops.

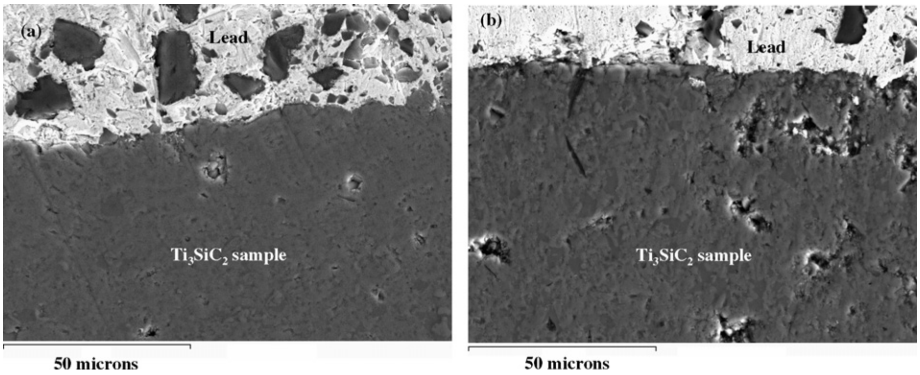

Fig. 6. High magnification micrographs of (a) hot-leg and (b) cold-leg 211 samples in lead show minimal interaction between lead and the sample.

References

[1] J.J. Sienicki, A. Moisseytsev, D.C. Wade, A. Nikiforova, in: International Congress on Advances in Nuclear Power Plants (ICAPP 2007), Nice, 13–18 May 2007.

[2] J. Sienicki, D. Wade, A. Moisseytsev, W.S. Yang, S.-J. Kim, M. Smith, G. Aliberti, R. Doctor, D. Matonis, Nuclear Engineering International, July 2005, p. 24.

[3] S.M. McDeavitt, J.M. Runge, L. Leibowitz, J.E. Indacochea, L.A. Barnes in: Proceeding of 11th International Conference on Nuclear Engineering, Tokyo, Japan, 22 April 2003.

[4] M.W. Barsoum, T. El-Raghy, Am. Sci. 89 (4) (2001) 334.

[5] R.C. Weast, M.J. Astle, W.H. Beyer, CRC Handbook of Chemistry and Physics, 67th Ed., CRC, Boca Raton, 1986.

[6] A. Wolfenden, C.P. Burris, M. Singh, J. of Mater. Sci. Lett. 18 (24) (1999) 1995.

[7] 3-ONE-2 LLC, 4 Covington Place, Voorhees, NJ 08043.

[8] J.V. Cathcart, W.D. Manly, Corrosion 10 (1954) 432.

[9] Quartz harps were fabricated by J.S. Gregar, Argonne National Laboratory.