Y-12

OAK RIDGE Y-12 PLANT

MARTIN MARIETTA

Y-12 DEVELOPMENT ORGANIZATION TECHNICAL PROGRESS REPORT

Part 5 - Ceramics/Plastics/Carbon
Materials Development (U)

Period Ending March 1, 1995

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TECHNICAL PROGRESS REPORT**

**Part 5 - Ceramics/Plastics/Carbon
Materials Development (U)**

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Period Ending March 1, 1995

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HIGHLIGHTS

The preparation of small-scale-Production crucibles by plasma-spraying of TRIBOCOR onto niobium is continuing. Microwave heat-treatment of this size crucible has been demonstrated successfully. Conventional plasma-spray coating appears to offer advantages over "vacuum" plasma-spraying for preparing the coatings.

Encapsulant/stucco "shells" for "casketing" boron carbide (B_4C) or silicon carbide (SiC) results in consistent attainment of the necessary $\geq 2100^\circ C$ processing temperatures for these nonoxide materials. Gelcasting is an excellent technique for making shapes with both B_4C and SiC . Tiles of B_4C were prepared and will be microwave sintered soon.

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CERAMICS/PLASTICS/CARBON MATERIALS DEVELOPMENT

NONGRAPHITE

C. E. Holcombe, Jr., and M. S. Morrow

Summary

A special lifting fixture for the one-piece TRIBOCOR crucible (to be evaluated for intermediate Production furnace runs) is now being made. The two-piece TRIBOCOR crucible of the same size was re-examined and considered to be usable if a new bottom section can be made.

The preparation of small-scale-Production crucibles by plasma-spraying of TRIBOCOR onto niobium is continuing. Microwave heat-treatment of this size crucible has been demonstrated successfully. Conventional plasma-spray coating appears to offer advantages over "vacuum" plasma-spraying for preparing the coatings.

Introduction

A noncarbon furnace (NCF) is desired for uranium casting technology with the following goals:

1. to allow melting and alloying without the introduction of carbon or silicon into the melt while maintaining impurity levels at or below precasting levels,
2. to allow operating temperatures $\geq 1450^{\circ}\text{C}$ in a vacuum to ensure homogeneity and eliminate prealloying, and
3. to provide a reliable and economical system that is compatible with existing induction-heating facilities.

The materials for crucibles and components should have a maximum use-temperature of at least 1600°C , excellent thermal shock resistance, minimal reactivity with uranium, and the capability of being coated with conventional paints.

Prior Work

The efforts to develop an NCF have evolved to reducing carbon in furnace systems and as a contaminant.¹⁻⁵³

Presentation of Experimental Work

TRIBOCOR/Metal Components

The condition of the two-piece intermediate-size-Production TRIBOCOR crucible was reassessed. The crucible was significantly warped during nitridation and had been deemed unusable earlier.^{52, 53} The main problem is that the bottom section is completely deformed. A replacement bottom section *could* make the crucible usable; however, the bottom section would have to be carefully designed to allow it to be loaded into the nonsymmetrical crucible housing.

Nevertheless, considering the cost of this two-piece crucible and the significant information that can be gained from comparison of its performance with the one-piece TRIBOCOR crucible of the same size, the authors think that this crucible should be retained and a new bottom section made. The new bottom section will probably be prepared of niobium metal and plasma-sprayed with un-nitrided TRIBOCOR followed by the heat-treatment/nitridation process that is being developed for the small-scale-Production crucibles (described herein).

The one-piece TRIBOCOR crucible of the same size also warped from the nitridation. The warpage necessitated a redesign of the lifting fixturing. The lifting fixture is now being built. Testing with uranium melts will be scheduled as soon as possible. The authors still plan to dye-penetrant-check the two TRIBOCOR crucibles for use in the enriched uranium foundry.

The plasma-spraying of TRIBOCOR onto niobium for crucible applications was addressed earlier.⁵⁰⁻⁵³ Two niobium crucibles for small-scale-Production usage in melting uranium were made to test this concept. These 12-in.-ID, 12-in.-inside height crucibles (shown in the as-fabricated state earlier⁵³) were designated for different plasma-spraying operations. The first crucible was "vacuum" plasma-sprayed with TRIBOCOR by Plasma Processes, Inc., Huntsville, Alabama (affiliated with Rocketdyne Division of Rockwell International Corporation). The vacuum plasma-spraying system actually propels the particles (that are initially injected into the plasma flame) into a vacuum chamber, and this process typically leads to fully dense coatings. The capability of achieving fully dense TRIBOCOR coatings by this technique was not available in the Oak Ridge area.

The vacuum plasma-sprayed coating of about 0.030 in. (0.75 mm) thickness of TRIBOCOR onto the small-scale-Production crucible was applied to the crucible bottom and to the interior sidewalls for about two-thirds of the height of the crucible. The visual appearance of the coating was that the layer was intact and dense, as applied. After the crucible sat for several days, some blistering/peeling appeared within the topmost area of the coated surfaces—such as might be expected if the coating were stress relieving. The peeling was not over the entire surface and was not considered major. Figure 1 shows the crucible interior; the roughened surface of the bottom was the result of sanding. The upper section shows the peeling area.

Microwave heat-treatment/nitridation of the coated crucible was slated, using the Advanced Manufacturing Project (AMP) unit with 2.45-GHz radiation. The interior of the crucible was loaded with zirconia fiber nearest to the plasma-spray-coated surfaces and with alumina bubbled insulation in the interior regions. The crucible exterior was boxed or "casketed" with insulation fiberboard, and the crucible was held in the upright position. A standard thermocouple was used to follow the microwave heating. However, the thermocouple was placed on the *exterior* of the crucible (to avoid bending the thermocouple); thus, the temperatures recorded are expected to be several hundreds of degrees Celsius lower than the temperatures *at* the coating. The crucible heated to $\sim 1000^{\circ}\text{C}$, as shown by the exterior thermocouple. This activity was the first heat-treatment/nitridation of a large object such as this crucible, and the ability to heat the object with controlled heat [i.e., directing the heat to the innermost surfaces of the crucible by using the zirconia (absorber) fibers] was a dramatic demonstration. Figure 2 shows the crucible after the microwave run (after the top insulation-fiberboard panel was removed). The interior packing (alumina bubbles and zirconia fiber) had shrunk away from the walls, and more peeling was evident.

After the interior packing was removed, extensive delamination of the coating obviously had occurred. Microstructural examination of a section of the spalled coating is planned to determine the changes that occurred during the heat-treatment/nitridation. The interior crucible surfaces will probably be grit-blasted and then re-plasma-sprayed, using conventional (not vacuum) plasma-spraying to achieve the new coating; then heat-treatment/nitridation will be performed.

Fig. 1. Small-scale-Production crucible of niobium as "vacuum" plasma-spray coated.

Fig. 2. Small-scale-Production crucible shown after microwave heat treatment/nitridation in the AMP unit.

Only one of the two small-scale-Production crucibles was coated by the vacuum plasma-spraying so that the process could be evaluated completely before committing the other crucible to that processing technique. Since the peeling problem occurred with the vacuum technique, the second small-scale-Production crucible will be coated by conventional (not vacuum) plasma-spraying. The high density of the vacuum plasma-spraying may worsen any tendency to delaminate and/or stress relieve on heat-treatment or nitridation. Also, on nitridation, the differences in densities of the un-nitrided TRIBOCOR (7.5 g/cm^3) in contrast to the titanium nitride (5.4 g/cm^3) that forms on the surface (and to some extent in the interior) of the coating also probably contributes to the delamination problems. The delamination problems should be lessened and/or eliminated with grading (applying a mix of the substrate material and the coating material) by using niobium plus un-nitrided TRIBOCOR for the initial 0.005 to 0.010 in. of the coating. Also, delamination should be lessened with the lower densities (typically 85% to 90%) achieved with conventional plasma-spraying.

Ceramic Noncarbon Furnace System

As was stated earlier,⁵³ the current direction is toward use of TRIBOCOR and TRIBOCOR-coated niobium. Ceramic systems can be used by foundry personnel for any casting at the small-scale-Production level. The intermediate-size casting would require assistance from the Development Organization and currently would defer to the one-piece TRIBOCOR crucible.

General Noncarbon Furnace-Related Studies and Other Efforts

In Refs. 51 through 53, the authors outlined that, as a result of reduced funding, the most appropriate direction for noncarbon furnace in H-1 Foundry (depleted uranium) is as follows:

1. to evaluate TRIBOCOR crucible/susceptors for as many small and intermediate Production furnace runs as feasible, particularly for the direct casting of U-6Nb, using foundry personnel with a minimum of direct guidance from Development Division personnel, thereby allowing Production to absorb the technology fully; and
2. to evaluate TRIBOCOR plasma-sprayed onto niobium, with either microwave or conventional nitridation, to produce more economical TRIBOCOR-like crucibles.

The goal of making a directly susceptible crucible that will perform like graphite is being pursued through Cooperative Research and Development Agreement (CRADA) No. Y-1292-0079 with Blasch Precision Ceramics, Inc., and Surface Alloys, Inc. The investigation continues to look promising. The insulation modules from Ceramic Fillers, Inc., can possibly allow improved loading and use of insulation in foundry furnaces and will be tested as soon as possible.

Future Work

TRIBOCOR/Metal Parts

After the new lifting fixture is made, it will be necessary to lift-test the fixture to prove in its capability. After the fixture is approved, tests with the one-piece TRIBOCOR crucible in the intermediate (southside) Production furnaces will be scheduled. The two-piece intermediate Production-size crucible will be made operational by construction of a new, specially fabricated bottom section.

Multipiece Ceramic Crucibles

For the small-scale-Production melting, ceramic systems can be scheduled routinely for melting tests. Larger sizes require special planning and Development assistance at this time.

Crucible/Susceptor

The metal-ceramic composite crucible (CRADA) is being evaluated to explore this alternative.

References

1. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2149-6, p. 8, Union Carbide Corp. Nuclear Div., Oak Ridge Y-12 Plant, August 1981. SECRET-RD.
2. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2303-6, p. 24, Union Carbide Corp. Nuclear Div., Oak Ridge Y-12 Plant, October 1982. SECRET-RD.
3. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2304-6, p. 21, Union Carbide Corp. Nuclear Div., Oak Ridge Y-12 Plant, October 1982. SECRET-RD.
4. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2306-6, p. 8, Union Carbide Corp. Nuclear Div., Oak Ridge Y-12 Plant, April 1983. SECRET-RD.
5. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2307-6, p. 14, Union Carbide Corp. Nuclear Div., Oak Ridge Y-12 Plant, July 1983. SECRET-RD.
6. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2308-6, p. 32, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, July 1984. SECRET-RD.
7. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2309-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, December 1984. SECRET-RD.
8. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2330-6, p. 11, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 1985. SECRET-RD.
9. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2331-6, p. 15, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 1985. SECRET-RD.

10. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2332-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 1985. SECRET-RD.

11. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2333-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 1985. SECRET-RD.

12. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2334-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, July 1985. SECRET-RD.

13. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2335-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, July 1985. SECRET-RD.

14. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2336-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 1985. SECRET-RD.

15. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2337-6, p. 13, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 1985. SECRET-RD.

16. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2338-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, December 1985. SECRET-RD.

17. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2339-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 1986. SECRET-RD.

18. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2360-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 1986. SECRET-RD.

19. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2361-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, November 1986. SECRET-RD.

20. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2362-6, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 1987. SECRET-RD.

21. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramics Fabrication (U)*, Y-2363-6, p. 21, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 1987. SECRET-RD.

22. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2364-5, p. 35, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, October 5, 1987. SECRET-RD.

23. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2365-5, p. 26, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 25, 1988. SECRET-RD.

24. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2366-5, p. 37, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 24, 1988. SECRET-RD.

25. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2367-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 2, 1988. SECRET-RD.

26. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2368-5, p. 15, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, July 22, 1988. SECRET-RD.

27. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2369-5, p. 14, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 21, 1988. SECRET-RD.

28. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2410-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 23, 1989. SECRET-RD.

29. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2411-5, p. 15, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 23, 1989. SECRET-RD.

30. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2412-5, p. 26, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 28, 1989. SECRET-RD.

31. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2413-5, p. 42, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, October 19, 1989. SECRET-RD.

32. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2414-5, p. 44, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, February 5, 1990. SECRET-RD.

33. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2415-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 10, 1990. SECRET-RD.

34. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2416-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, December 1990. SECRET-RD.

35. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2417-5, p. 19, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 29, 1991. CONFIDENTIAL-RD.

36. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2418-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 31, 1991. SECRET-RD.

37. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2419-5, p. 13, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, November 19, 1991. UNCLASSIFIED.

38. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2450-5, p. 24, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 3, 1992. SECRET-RD.

39. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2451-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 15, 1992. CONFIDENTIAL-RD.

40. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2452-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 9, 1992. CONFIDENTIAL-RD.

41. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2453-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 16, 1992. CONFIDENTIAL-RD.

42. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2454-5, p. 16, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 25, 1992. CONFIDENTIAL-RD.

43. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2455-5, p. 12, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 15, 1992. UNCLASSIFIED.

44. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2456-5, p. 20, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, November 25, 1992. CONFIDENTIAL-RD.

45. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2457-5, p. 33, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, April 1, 1993. SECRET-RD.

46. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2458-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 21, 1993. CONFIDENTIAL-RD.

47. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2459-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 8, 1993. UNCLASSIFIED.

48. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2463-5, p. 16, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 25, 1994. UNCLASSIFIED.

49. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2464-5, p. 13, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 8, 1994. UNCLASSIFIED.

50. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2465-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 21, 1994. UNCLASSIFIED.

51. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2466-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 23, 1994. UNCLASSIFIED.

52. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2467-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, February 21, 1995. UNCLASSIFIED.

53. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2468-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, in publication. UNCLASSIFIED.

MICROWAVE HEATING OF MATERIALS

C. E. Holcombe, Jr., and M. S. Morrow

Summary

Encapsulant/stucco "shells" for "casketing" boron carbide (B_4C) or silicon carbide (SiC) results in consistent attainment of the necessary $\geq 2100^\circ C$ processing temperatures for these nonoxide materials. Gelcasting is an excellent technique for making shapes with both B_4C and SiC . Tiles of B_4C were prepared and will be microwave sintered soon.

Microwave heat-treatment/nitridation of plasma-sprayed TRIBOCOR layers onto niobium and stainless steel coupons continues to look very promising for producing high-density, titanium nitride surface layers.

Introduction

The emerging technology of microwave heating and processing of high-temperature materials has been shown to provide unique properties and directions for the materials field.¹⁻⁸ The current investigations are directed primarily toward nonoxide refractories.

Prior Work

Past studies have been directed toward understanding the peculiarities of microwave processing while directing the effort toward sintering of nonoxide ceramics such as titanium diboride (TiB_2), B_4C , SiC , and lithium hydride (LiH).⁹⁻⁴⁵ Special materials, such as reaction-bonded silicon nitride (RBSN), have also been shown to be excellent materials for microwave processing;¹⁷⁻²¹ as a result of Y-12 Plant discoveries with RBSN, that material is now a primary topic of study at Oak Ridge National Laboratory (ORNL).

Presentation of Experimental Work

Boron Carbide and Silicon Carbide

Boron carbide (B_4C) and silicon carbide (SiC) shapes have been gelcast with the system described earlier.⁴⁵ The SiC pieces are still quite prone to crack on thorough drying—presumably from some interactions with the proprietary sintering agents that are mixed with the commercial "sinterable" SiC . Very slow drying and some modifications of the gelation system [using methacrylamide (MAM)/polyethylene glycol (PEG)] have reduced the problem, but tiles typically exhibit some degree of cracking. Boron carbide, however, does not have the cracking problem with the (MAM)/methylenebisacrylamide (MBAM) system.

Boron carbide tiles have been gelcast up to the 4- by 4-in. size. These thin-walled (about 0.25-in. thickness) tiles have been dried successfully and are over 50% of the theoretical density as gelled and dried. This achievement is impressive because these shapes would be very difficult to attain by normal pressing operations. Additionally, no warpage occurs with the gelling/drying operations. Small tiles will probably be used for ballistic tests when the microwave sintering operation is proven in for the tiles. Small, gelcast discs of both B_4C and SiC have been sintered to over 90% of their theoretical densities by microwaving to $2100^\circ C$ for 30 min in argon. The tiles are to be tested soon, but some casketing adjustments are likely before these tiles can be

densified successfully with microwaves; these adjustments are generally required of all new shapes and sizes. This fact was demonstrated recently when a star shape of SiC was gelcast. Microwave sintering of the piece resulted in nonuniform density regions, which will have to be overcome with casketing modifications.

The very-fine-particle-size ($\sim 0.1 \mu\text{m}$ average particle diameter) B_4C powder was investigated to determine if its use leads to better densification. Initial indications are that this finer-particle-size material is beneficial in a 50/50 blend with the normal grade of $\sim 1 \mu\text{m}$ average particle diameter. Further tests with the finer material are planned. Also, 2.5 wt % and 5.0 wt % carbon additions will be studied to determine densification benefit.

Plasma-Sprayed Coating Evaluations

The heat-treatment/nitridation of plasma-sprayed TRIBOCOR coatings was discussed earlier.⁴³⁻⁴⁵ The microwave heatability of fully dense materials was demonstrated by packing a small bar on un-nitrided TRIBOCOR metal (about $0.5 \times 0.1 \times 1$ in.) into zirconia fiber in a boron nitride crucible, subjecting the system to 2.45-GHz radiation in a nitrogen environment. This scheme allowed the TRIBOCOR metal piece to heat to a temperature of about 1300°C (as measured by optical pyrometry) for 30 min. The TRIBOCOR did not heat up further, even when more power was supplied. Visual examination of the TRIBOCOR piece indicated that it was gold colored, as is observed routinely for highly nitrided TRIBOCOR. Examination of a fracture surface of the piece (obtained by cutting partially through the piece, freezing it in liquid nitrogen, and then breaking it) by scanning electron microscopy indicated that the TRIBOCOR was indeed well nitrided—very similarly to TRIBOCOR that is normally nitrided at 1650°C to 1875°C .

The observation that un-nitrided TRIBOCOR appears to undergo accelerated nitridation with microwave radiation in a nitrogen environment implies that unusual TRIBOCOR coatings may be possible. For instance, if the nitridation can actually occur at $\leq 1300^\circ\text{C}$, then TRIBOCOR coatings on relatively low-melting, economical substrates (e.g., steel) are possible.

Therefore, several experiments were conducted to evaluate the heat-treatment/nitridation of un-nitrided TRIBOCOR plasma-spray-coated onto stainless steel. The type 440 stainless steel was chosen because it has relatively low thermal expansion for steels and was thought to give a better match to the thermal expansion of TRIBOCOR. Specimens of the type 440 stainless steel were plasma-sprayed with 0.020 to 0.040 in. of un-nitrided TRIBOCOR, placed onto zirconia fiber (microwave absorber) and heated in nitrogen. When the coatings are heated to $\sim 1300^\circ\text{C}$, the typical *nitrided* TRIBOCOR structure results—layered with titanium nitride on the outermost layer. However, the nitrided TRIBOCOR generally delaminates from the steel substrate, probably as a result of the densification and structural changes in the coating. The authors expect that using a graded layer of steel-TRIBOCOR followed by TRIBOCOR onto the steel substrate will allow the nitrided TRIBOCOR to adhere well to the steel; this arrangement will be tested soon. Note that the successful nitridation of the TRIBOCOR coatings on the steel occurs at $\leq 1300^\circ\text{C}$, without melting the steel substrate. More work in this area is planned.

Microwave heat-treatment/nitridation of TRIBOCOR coatings onto niobium substrates also indicates the accelerated nitridation of the TRIBOCOR. The delamination of the nitrided TRIBOCOR can occur even with niobium substrates, showing the need for grading the TRIBOCOR with niobium (the same as for the steel substrates).

The microwave nitridation of a small-scale-Production crucible in the Advanced Manufacturing Project (AMP) facility is discussed in the preceding section ("Nongraphite") of this report. This facility demonstrates the ability to evaluate the microwave processing of plasma-sprayed coatings for large-scale parts.

Future Work

Nonoxide pieces will be microwave sintered in the AMP unit; direction toward sintering gelcast tiles of B_4C or SiC will be pursued. Commercial B_4C tiles are being obtained to evaluate microwave heat-treatment as a possible means to improve the ballistic performance of the tiles.

The AMP system and the variable-frequency microwave unit (the two unique systems) will be evaluated further and publicized for advanced material areas. Additionally, areas in which microwave processing appears to offer significant advantages (i.e., the heat-treatment/nitridation of plasma-sprayed materials or the heat-treatment/annealing of tiles, etc.) will be explored. The gelcasting process will continue to be investigated.

References

1. A. J. Berteaud and J. C. Badot, "High-Temperature Microwave Heating in Refractory Materials," *J. Microwave Power* 11(4), 315-320 (1976).
2. J. D. Ford, "High-Temperature Chemical Processing via Microwave Absorption," *J. Microwave Power* 2(2), 61-64 (1967).
3. C. E. Holcombe, Jr., "New Microwave Coupler Material," *Am. Ceram. Soc. Bull.* 62(12), 1388 (1983).
4. M. Kamo, et al., "Diamond Synthesis from Gas Phase in Microwave Plasma," *J. Cryst. Growth* 62, 642-644 (1983).
5. T. T. Meek and R. D. Blake, "Ceramic-Glass-Metal Seal by Microwave Heating," U.S. patent 4,529,856, July 16, 1985.
6. T. T. Meek and R. D. Blake, "Ceramic-Glass-Ceramic Seal by Microwave Heating," U.S. patent 4,529,857, July 16, 1985.
7. A. J. Klein, "Processing With Microwaves," *Adv. Matls. and Proc.* 1(12), 36-39 (1985).
8. C. E. Holcombe, Jr., "Microwave Coupler and Method," U.S. patent 4,559,429, December 17, 1985.
9. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramic Fabrication (U)*, Y-2362-6, p. 27, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 20, 1987. SECRET-RD.
10. *Y-12 Development Division Technical Progress Report, Part 6 - Ceramic Fabrication (U)*, Y-2363-6, p. 13, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 13, 1987. SECRET-RD.

11. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2364-5, p. 61, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, October 5, 1987. SECRET-RD.
12. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2365-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 27, 1988. SECRET-RD.
13. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2366-5, p. 43, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 24, 1988. SECRET-RD.
14. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2367-5, p. 21, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 2, 1988. SECRET-RD.
15. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2368-5, p. 38, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, July 22, 1988. SECRET-RD.
16. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2369-5, p. 30, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 21, 1988. SECRET-RD.
17. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2410-5, p. 14, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 23, 1989. SECRET-RD.
18. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2411-5, p. 39, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 23, 1989. SECRET-RD.
19. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2412-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 28, 1989. SECRET-RD.
20. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2413-5, p. 54, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, October 19, 1989. SECRET-RD.
21. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2413-5, p. 66, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, October 19, 1989. SECRET-RD.
22. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2414-5, p. 32, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, February 5, 1990. SECRET-RD.

23. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2414-5, p. 36, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, February 5, 1990. SECRET-RD.

24. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2415-5, p. 22, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 10, 1990. SECRET-RD.

25. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2416-5, p. 19, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, December 1990. SECRET-RD.

26. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2417-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 29, 1991. CONFIDENTIAL-RD.

27. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2418-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, August 13, 1991. CONFIDENTIAL-RD.

28. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2419-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, November 19, 1991. UNCLASSIFIED.

29. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2450-5, p. 19, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 3, 1992. SECRET-RD.

30. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2451-5, p. 20, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, May 15, 1992. CONFIDENTIAL-RD.

31. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2452-5, p. 15, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 9, 1992. CONFIDENTIAL-RD.

32. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2453-5, p. 16, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 16, 1992. CONFIDENTIAL-RD.

33. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2454-5, p. 8, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 25, 1992. CONFIDENTIAL-RD.

34. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2455-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 7, 1992. UNCLASSIFIED.

35. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2456-5, p. 14, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, November 25, 1992. CONFIDENTIAL-RD.

36. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2457-5, p. 51, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, April 1, 1993. SECRET-RD.

37. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2458-5, p. 30, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 21, 1993. CONFIDENTIAL-RD.

38. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2458-5, p. 35, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 21, 1993. CONFIDENTIAL-RD.

39. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2459-5, p. 31, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 8, 1993. UNCLASSIFIED.

40. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2463-5, p. 33, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, January 25, 1994. UNCLASSIFIED.

41. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2464-5, p. 6, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, March 8, 1994. UNCLASSIFIED.

42. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2465-5, p. 41, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, June 21, 1994. UNCLASSIFIED.

43. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2466-5, p. 16, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, September 23, 1994. UNCLASSIFIED.

44. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2467-5, p. 13, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant, February 21, 1995. UNCLASSIFIED.

45. *Y-12 Development Division Technical Progress Report, Part 5 - Ceramics/Plastics/Carbon Materials Development (U)*, Y-2468-5, in publication. UNCLASSIFIED.

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