Y-12

OAK RIDGE Y-12 PLANT

MARTIN MARIETTA

Y/DV-1390

CRADA Final Report
for
CRADA Number Y-1293-0222

JOINING NZP CERAMICS

K. D. Nicklas
M. W. Richey
C.E. Holcombe Jr.
M. L. Santella

Materials Joining Center

Oak Ridge Centers
for Manufacturing Technology

Date of Issue: September 26, 1995

Prepared by the
Oak Ridge Y-12 Plant
P.O. Box 2009, Oak Ridge, Tennessee 37831-8169
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The objective of this work was to assess techniques for joining NZP ceramics, a new family of ceramic materials that have low coefficient of thermal expansion, low thermal conductivity, and excellent thermal-shock resistance. Initially, the authors evaluated laser-beam welding over volatile fluxing agents (ferric oxide, copper oxide, boric acid, and boron nitride). They also examined other laser, arc-welding, brazing, and cold joining techniques. The NZP materials were capable of sustaining the thermal stresses associated with these joining processes without substantial cracking. Of the volatile fluxes, only the copper oxide promoted weld fusion. Efforts to accomplish fusion by laser-beam welding over copper, titanium, stainless steel, yttrium barium copper oxide, fused silica glass, and mullite/alumina were unsuccessful. Gas-tungsten arc welding accompanied by porosity, irregularities, and cracking was achieved on copper sheet sandwiched between NZP tiles. Attempts at conventional oxy-acetylene welding and torch brazing were unproductive. Silica-based oxide mixtures and copper oxide-based materials show potential for development into filler materials for furnace brazing, and phosphate-based cements show promise as a means of cold joining.

INTRODUCTION

NZP is a new family of alkaline or alkaline-earth zirconium phosphate ceramic materials that have a low coefficient of thermal expansion (CTE).[1] The NZP designation is derived from the parent composition of the family, $NaZr_2P_3O_{12}$. NZP ceramics are known for their low thermal conductivity and excellent thermal-shock resistance. Specifically, NZP has potential applications in operations associated with melting materials for Department of Energy (DOE) Defense Programs (DP) weapon production activities.

The objective of this work was to assess techniques for joining NZP ceramics. Initially, the authors planned to join a full-size component. They first evaluated the feasibility of using volatile fluxing agents, which lower the melting point of ceramics to enable fusion welding. They also conducted precursory investigations of alternative fusion welding, brazing, and cold joining techniques.

EXPERIMENTAL PROCEDURE

MATERIALS AND EQUIPMENT

Two compositions of NZP tiles were provided by LoTEC, Inc., of West Valley City, Utah: barium zirconium phosphate silicate ($Ba_{1.25}Zr_4P_{5.50}Si_{0.50}O_{24}$), designated BS25, and calcium strontium zirconium phosphate ($Ca_{0.75}Sr_{0.25}Zr_4P_6O_{24}$), designated CS25. Each of the tiles measured approximately 2 X 2 X 0.25 in. thick. Fusion welding and torch brazing experiments were conducted at the Oak Ridge Y-12 Plant in the Development Division's Building 9202 Joining Laboratory using the following equipment.

1. Laser-beam welding (LBW): LBW was performed using a Raytheon Model SS550 neodymium:yttrium-aluminum-garnet (Nd:YAG) pulsed laser (1.06 -μm wavelength) with a 4-in. focal lens.

2. Gas-tungsten arc welding (GTAW): Manual GTAW was performed using a Hobart Cybertig 300 alternating current/direct current (ac/dc) constant-current power supply with a Weldcraft H-20-C torch and remote foot control.

3. Oxyacetylene welding (OAW) torch brazing (TB): Manual OAW/TB was performed using an Oxyweld torch with #4 and #6 tips

Furnace brazing experiments were performed in the Metal and Ceramic Division, Materials Joining Laboratory of the Oak Ridge National Laboratory (ORNL). Using an inert-atmosphere furnace and a induction heating system.

DESIGN OF EXPERIMENTS

Volatile Flux Assessment

Each quadrant of BS25 and CS25 tiles was painted with the following coatings: ferric oxide, copper oxide, boric acid, and boron nitride. These coatings were formulated in a water vehicle with a cellulosic binder (3 wt % Klucel, hydroxypropyl cellulose) to allow painting onto the two substrate compositions. Identical groups of BS25 and CS25 tiles were painted with a 50/50 wt % blend of coating and matching composition base-plate powder. Half of each quadrant received two coats; the other half received a single coat (one coat is ~0.0035 in.). A Nd:YAG laser beam was scanned over the quadrants at three different power settings and travel speeds. Table 1 lists the LBW parameters. After welding, the authors evaluated the tiles both visually and by scanning electron microscopy (SEM) for evidence of fusion.

Table 1 - Laser-beam welding parameters for volatile flux assessment

	SCAN		
	1	2	3
Total pulse width (ms)	2	1.0	5.0
Lead (ms)	1	1.0	1.0
Tail (ms)	1	0.0	4.0
Pulse frequency (pps)	50	100.0	50.0
Laser power (watts)	100	250.0	200.0
Sharp focus ref. (in.)	4	4.0	4.0
Weld focus (in.)	4	4.2	4.4
Travel speed (ipm)	30	100.0	30.0

Alternative Joining Techniques

Laser-beam welding. The authors attempted to introduce into the laser-beam weld additional materials that would lower the melting point of the NZP ceramic and facilitate the formation of a weld pool. Laser-beam welds were made over thin sheet titanium (0.016 and 0.011 in.), copper (0.002 in.), and stainless steel (0.012 in.) placed over BS25 and CS25 tiles both and without American Welding Society (AMS)-type FB3C flux, yttrium barium copper oxide (1-2-3 oxide, superconducting material) powder mixed with Klucel liquid and applied to the NZP ceramic tiles, and fused silica glass and a mullite/alumina thermocouple insulator. Table 2 lists LBW parameters for the thin sheet and 1-2-3 oxide welds; Table 3 lists welding parameters for the fused silica glass and mullite/alumina welds. The authors examined each weld visually for evidence of fusion.

Table 2 - Laser-beam welding parameters for thin sheets and 1-2-3 oxide welds

	Titanium	Stainless Steel	Copper
Total pulse width (ms)	2.0	2.0	2
Lead (ms)	1.0	1.0	1
Tail (ms)	1.0	1.0	1
Pulse frequency (pps)	50,100.0	100.0	50
Laser frequency (pps)	200.0	200.0	300
Sharp focus ref. (in.)	4.0	4.0	4
Weld focus (in.)	. 4.1	4.1	4
Travel speed (ipm)	50.0	50.0	30

Table 3 - Laser-beam welding parameters for thermocouple insulators

Total pulse width (ms)	2.0
Lead (ms)	1.0
Tail (ms)	1.0
Pulse frequency (pps)	50.0
Laser power (watts)	150.0
Sharp focus ref. (in.)	4.0
Weld focus (in.)	4.4
Travel speed (ipm)	6.0

Gas-tungsten arc welding. The authors sandwiched a thin strip of metal conductor (0.04 to 0.06 in.) between two pieces of the NZP ceramic tile to provide electron flow to ground. They attempted to use copper, steel, brass, Ticusil (titanium-copper-silver, an active braze alloy commonly employed to join ceramics), copper powder, and iron filings both with and without fluxes. They also evaluated both AWS-type FB3A and FB3C fluxes that were readily available for testing. They performed the welding using dc and ac operational modes.

Oxyacetylene welding/torch brazing. The authors also attempted joining by OAW using Ticusil brazing alloy as a filler metal. They sandwiched a thin strip of Ticusil brazing alloy between two pieces of the NZP ceramic tiles, then heated the assembly using a torch. They assessed the resulting joint visually, both the BS25 and the CS25 compositions. The authors also attempted to melt a 0.150-in.-diam silica glass rod onto each of the NZP ceramic tiles. They pulled apart the resulting bond and assessed the bond surface visually.

Furnace brazing. BS25 and CS25 tiles were cut into ~0.4 X by 0.4-in.-square samples. Several bonding, melting, and sessile drop experiments were made using the BS25 and CS25 ceramics with a mixture of oxide powders consisting of 62 wt % SiO_2-18 wt % Al_2O_3-20 wt % MgO and an oxide superconductor composition ($YBa_2Cu_3O_x$). Sessile drop experiments were conducted using an induction heating system under an argon inert-gas atmosphere.

Cold bonding with phosphate cements. A diamond saw was used to cut BS25 and CS25 tiles into ~0.5 X 0.5- in. samples. An intimate mixture of powdered oxide (copper oxide, NZP powder, 1-2-3 oxide, and hydrated alumina) and phosphoric acid (see Table 4) was formed and applied to two NZP ceramic tile samples.[2] With the exception of the hydrated alumina samples, all of the samples were dried for 24 h at room temperature and then for 24 h at 105°C. The hydrated alumina samples were dried for 96 h at room temperature and then for 24 h at 105°C. After drying, the samples were drop tested onto a concrete slab from a height of ~6 ft. Samples surviving the drop test were twisted apart using a torque wrench.

Table 4 - Cold bonding mixtures

Powder	Weight (g)	Phosphoric acid (ml)
Copper oxide	10.0	4.50
1-2-3 oxide	5.5	3.50
BS25	3.0	1.75
CS25	3.0	1.75
Hydrated alumina-A	2.0	5.50
Hydrated alumina-B	2.0	5.50

RESULTS AND DISCUSSION

VOLATILE FLUX ASSESSMENT

Three different LBW parameters were run across each of the volatile flux coatings. These parameters were selected to penetrate the coating completely and to produce a wide range of energy-input levels and weld widths. The NZP ceramics were able to accommodate the thermal stresses developed from LBW temperature gradients without extensive cracking.

For all test conditions both NZP ceramics vaporized readily. This behavior is typical of ceramics for fusion welding.[3] Only the copper oxide coating exhibited any evidence of fusion (see Fig. 1). Energy dispersive spectroscopy (EDS) reveals the presence of copper, phosphorus, and calcium in the weld region (see Fig. 2). The fluxes that were evaluated typically lower the melting point of ceramic materials. Overall, the volatile fluxes assessed in this investigation did not promote the formation of a weld pool and were thus ineffective at enabling fusion welding.

ALTERNATIVE JOINING TECHNIQUES

Laser-Beam Welding

LBW parameters were selected to completely penetrate the Cu, Ti and stainless steel metal sheets. Because copper is highly reflective to the Nd:YAG laser beam, only 0.002-in.-thick sheet could be penetrated completely. Attempts were made unsuccessfully to penetrate 0.005- and 0.010-in.-thick copper sheets. Complete penetration of 0.010-in-thick copper could be obtained by placing titanium or stainless steel over the copper.

Fusion was not apparent in any of the thin, metal sheet, NZP ceramic welds. Silica glass was transparent to the Nd:YAG laser beam; thus, it did not melt. Melting of the thermocouple insulator onto the BS25 ceramic was also unsuccessful. The thermocouple insulators did appear to have melted into the CS25 ceramic; however, fusion did not occur.

Gas-Tungsten Arc Welding

Direct current GTAW readily vaporized the NZP ceramics, even at low current levels. The arc deeply penetrated the NZP ceramic. To reduce the arc intensity and, therefore, the penetrating capability, ac GTAW was used with limited success. Minimal vaporization occurred because the ac welding current (~175 A) was carefully controlled and minimized. Maintaining an arc (ground) across the entire joint was difficult to achieve. Overall, the NZP ceramics were able to accommodate the thermal stresses associated with GTAW without severe cracking.

The copper and Ticusil BS25 samples exhibited some indication of metal and ceramic melting and mixing. These welds were very porous and irregular in appearance. In some cases, cracks adjacent to the joint were also evident. The CS25 ceramic vaporized and would not melt; no successful fusion was achieved.

Two of the more successful BS25 tiles that were joined using the ac GTAW process were broken apart. Only one area ~20% of the entire joint interface showed fusion to the ceramic. Visual examination of this area revealed extensive porosity and some cracking, but chemical analysis revealed that only a very small portion of copper mixed with the ceramic.

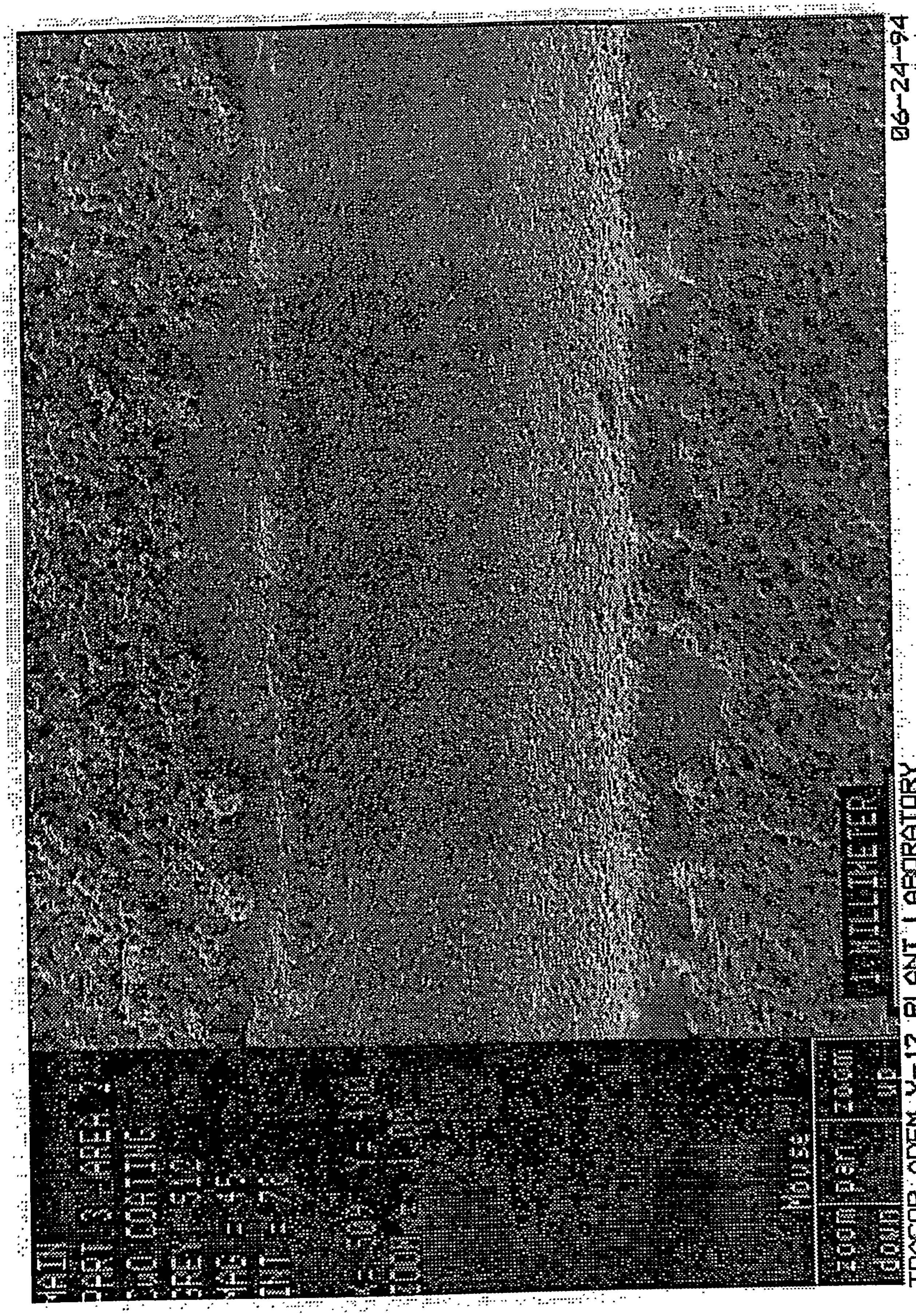

Fig.1 - SEM of laser-beam weld region, CS25, copper oxide coating.

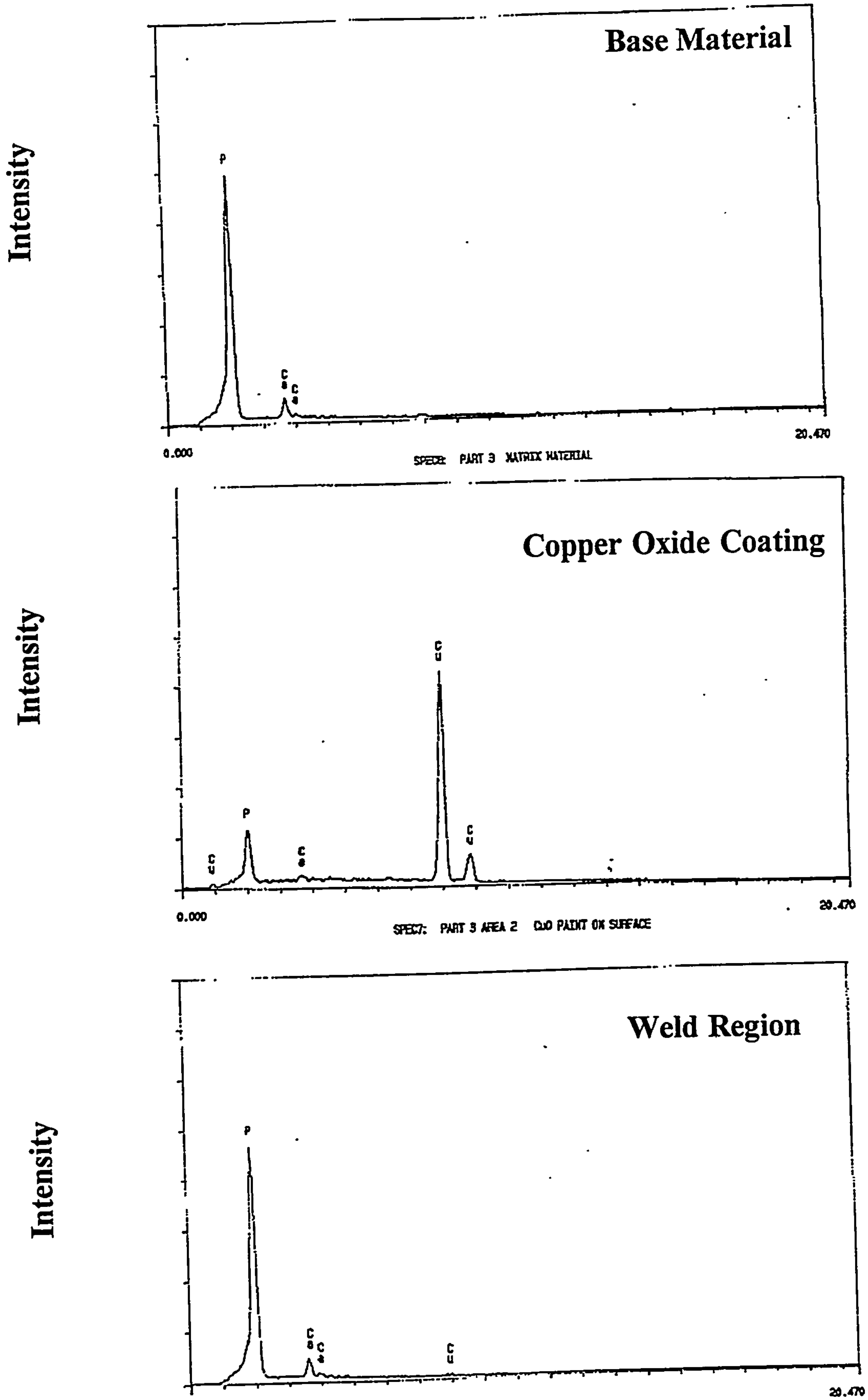

Fig. 2 - Energy-dispersive spectrometry of CS25 copper oxide laser beam weld.

Oxyacetylene Welding/Torch Brazing

Initial OAW was attempted using a neutral flame. The neutral flame, however, readily vaporized the NZP ceramics. To eliminate vaporization, a carburizing flame was used. As in the case of LBW and GTAW overall, the NZP ceramics exhibited substantial resistance to significant cracking under extreme heating and cooling conditions.

Ticusil braze alloy sheet sandwiched between two BS25 ceramic tiles did not bond to the tiles when the melting temperature of the Ticusil (850°C) was reached. Increasing the temperature to the melting point of the ceramic (>1650°C) only vaporized the braze alloy. Ticusil is not recommended for the TB process, but because of the earlier encouraging results with melting copper-based materials into NZP ceramics, the authors evaluated it.

Complete melting/flowing of a silica glass rod onto each of the ceramics was not achieved because of the higher melting temperature of the glass. Portions of a rod did appear to melt onto the BS25 ceramic. Upon cooling, the glass rod cracked transversely throughout its length and pulled away from the ceramic in some areas. No similar success was obtained using the CS25 ceramic. Complete melting may be achieved using a smaller diameter glass rod.

Furnace Brazing

The oxide powder mixture has a melting temperature near 1350°C and forms a glass. The first furnace brazing experiment consisted of using a slurry of the oxide powder to join the BS25 ceramic. The slurry was deposited first on one side of the braze joint, then the other piece was pressed onto it. This assembly was heated to 1380°C in argon and held there for 15 min. No joint was formed by this processing. Apparently, the oxide reacted somewhat with the BS25 material, but there was no indication that the powder actually melted.

Because the oxide powder is a mixture, there is some uncertainty about its melting temperature. To ensure that the mixture was melting completely, a second experiment was conducted in which a similarly prepared joint was heated inductively using a tantalum susceptor. The advantage of this system is that the specimen can be observed directly during heating. The assembled joint was heated in argon to near 1400°C when melting of the oxide mixture was observed, and it was held at temperature for 30 s. Visual examination of this specimen after cooling indicated that the oxide melted and formed a uniform fillet between the BS25 pieces. Examination of the cross-sectioned specimen confirmed that the oxide mixture melted and showed that the joint specimen contained considerable porosity. Presumably, the porosity resulted from a reaction between the oxide and the NZP material.

The last experiment conducted with the oxide mixture was simply to melt it on a flat specimen of both NZP ceramics. This sessile drop experiment was conducted in the induction system under argon. The specimens were heated individually until melting of the oxide mixture was observed directly in each case. The powder melted to form relatively uniform droplets on both ceramic materials with contact angles of ~30 degrees. After cooling, the droplets were well bonded to the ceramics, but they contained considerable porosity and some cracking. The porosity undoubtedly results from a chemical reaction between the oxide mixture and the NZP materials. The cracks result from the thermal expansion mismatch between these materials.

The superconductor powder melted and formed a relatively uniform droplet on both ceramics. The contact angles were approximately 45 degrees on BS25 and 20 degrees on CS25. Both droplets contained numerous cracks but appeared well bonded to the ceramics. These furnace brazing results suggest that both silica-bonded oxide mixture/silicate glasses and copper-oxide-based materials have potential for further development into brazing materials for the NZP ceramics

Cold Bonding With Phosphate Cements

Because all fusion welding processes vaporize the NZP ceramics readily, the authors investigated cold bonding. Set-up/hardening times varied from ~1 min for the copper oxide mixture to several days for the hydrated alumina. Except for the BS25 and CS25 powdered-cemented samples, the samples passed the drop test. Of the samples that were twisted apart, the copper oxide-cemented samples had the strongest bond (~5 ft.lbs). Additional work is needed to characterize the high-temperature performance of the cold cements.

SUMMARY

The NZP ceramics were fully capable of enduring the temperature excursions associated with the LBW, GTAW, OAW, and TB processes without significant cracking. Such behavior in ceramic materials is unique. Ferric oxide, copper oxide, boric acid, and boron nitride coatings were ineffectual in facilitating laser-beam fusion welding of NZP ceramics. Efforts to accomplish fusion by LBW over copper, titanium, stainless steel, yttrium barium copper oxide, fused silica glass, and mullite/alumina were similarly unsuccessful. The copper oxide coating was somewhat successful at promoting limited fusion. GTAW was achieved on copper sheet sandwiched between two NZP tiles. Evidence of fusion accompanied by porosity, irregularities, and cracking was observed for only the BS25 composition. The OAW and TB processes that used silica glass and Ticusil were ineffective in joining NZP. Silica-based oxide mixtures and copper oxide-based materials have potential for development into NZP filler materials for furnace brazing of NZP. Phosphate-based cements showed promise as a means of joining NZP ceramics, but additional work is needed to assess their high-temperature performance.

The results of this work were not successful enough to warrant an attempt at joining a full size component. Although the joining technologies that were investigated are not yet mature enough to have commercial applications for NZP materials, important insights were gained relative to the performance of these materials for DP applications. No inventions were made or reported as the result of this work.

CONCLUSIONS

NZP materials can sustain the thermal stresses associated with the LBW, GTAW, OAW, and TB processes without substantial cracking. Copper or copper-based coatings or filler materials show the best promise at enabling joining by the fusion or brazing processes. Phosphate-based cements should be considered as an alternative to the fusion or brazing processes.

FUTURE WORK

No additional investigations into joining NZP are planned at this time.

REFERENCES

1. J. Alamo, and R. Roy, "Ultralow-Expansion Ceramics in the System $Na_20-Zr0_2P_20_5-Si0_2$" *Communications of the American Ceramic Society*, C-78 to C-80, 1984.

2. W. D. Kingery, " Fundamental Study of Phosphate Bonding in Refractories: II, Cold-Setting Properties," *Journal of the American Ceramic Society* **33** 8, 242-250, 1950.

3. M. M. Swartz, *Ceramic Joining*, ASM International, Materials Park, Ohio, 1990.

ACRONYMS

ac	**alternating current**
AWS	**American Welding Society**
BS25	**barium zirconium phosphate silicate**
CS25	**calcium strontium zirconium phosphate**
CTE	**coefficient of thermal expansion**
dc	**direct current**
DOE	**U.S. Department of Energy**
DP	**Defense Programs**
EDS	**energy-dispersive spectroscopy**
GTAW	**gas-tungsten arc welding**
Nd:YAG	**neodymium:yttrium-aluminum-garnet (laser)**
OAW	**oxyacetylene welding**
ORNL	**Oak Ridge National Laboratory**
SEM	**scanning electron microscopy**
TB	**torch brazing**

DISTRIBUTION

Department of Energy
R. M. Poteat
FOB/3067

LoTEC, Inc.
181 West 1700 South
Salt Lake City, Utah 84119
S. Y. Limaye (6)

Y-12 Plant
Oak Ridge, TN 37831

B. B. Bovee
V. B. Campbell (3)
E. L. Epple
A. K. Lee/DOE-OSTI (2)
K. D. Nicklas
W. G. Northcutt, Jr.
M. W. Richey (RC)
M. L. Santella
Central Files