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Letter Report

Fabrication of Intermetallic Compounds by Solid State Reaction of Roll-Bonded Materials

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Prepared for:

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Quarterly Progress Report (#18)
(MCR-85-721)

1.0 **Contract Number:**
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2.0 **Reporting Period:**
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3.0 **ONR Scientific Officer:**
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4.0 **Work Performed At:**
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5.0 **Principal Investigator:**
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6.0 **Project Title:**
Fabrication of Intermetallic Compounds by Solid State Reaction of Roll-Bonded Materials

7.0 **Description of Research:**

7.1 Objectives of Present Research

- Intermetallic compounds offer very high specific material properties and property retention at elevated temperatures. However, reliable processing techniques to fabricate these materials have not been developed. This program will investigate the use of a novel, low cost fabrication technique involving a deformation-solid state reaction bonding process to form titanium beryllides. The objectives of this investigation are to:

  — Establish reaction kinetics for the formation of Ti beryllide intermetallic compounds,

  — Establish processing parameters needed to reproducibly fabricate these materials,

  — Characterize the properties of Ti beryllides fabricated using a deformation-solid state reaction bonding process,

  — Investigate the effects of alloying additions on the crystal structure of Ti beryllides and determine how these changes impact mechanical properties.

7.2 Summary of Work Accomplished During Previous Reporting Period

- Analysis of Sputter Deposited Foils

  Transmission electron microscopy of the sputtered foils was initiated during the previous period. Analysis of an as-deposited foil containing approximately 93% Be showed that the grain size of the material was approximately 200-300 nm, the interior of grains contained a high defect concentration, and the structure was $TiBe_{12}$, as indicated by selected area diffraction. Heat treatment studies were also initiated to determine the optimum annealing conditions for the foils.

- Roll Bonding of Ti-Be laminants

Ti-Be foils were roll bonded at 650°C in a steel can to make a laminated foil approximately 0.2-mm-thick. A heat treatment study was initiated to determine the optimum conditions that were necessary to completely react the material in less than eight hours.

7.3 Progress During the Reporting Period

- Characterization of Sputtered Foils

Foils were characterized to determine chemical composition using inductively coupled plasma (ICP), density, fracture toughness, and microstructure. Foil chemistry measured by ICP was found to vary similarly to the concentration measured previously by wavelength dispersive spectroscopy (WDS). However, the Be concentrations was slightly higher for the ICP samples. The change is believed to be due to the difference in the detected volume, with ICP measuring the bulk concentration and WDS measuring several microns into the foil. Foil concentrations will be reported using the ICP results.

A heat treatment study was conducted at several temperatures to determine a temperature at which the foils could be annealed prior to testing at high temperatures. Annealing was performed by placing the beryllides between two flat ceramic tiles and heat treating the assembly in flowing Ar at 1000°C for 0.5 h. The ceramic restrained the foils during annealing and kept them flat. This procedure will be used to anneal the high temperature test samples next quarter prior to testing.

Early work on fracture strength showed that the strength was a function of the Be concentration. Density measurements were made to determine the density of the foils, to assess whether density had an impact on strength, i.e., lower strength correlating with lower density. Foil density, measured using a displacement method in methanol with the results shown in Table 1, was very close to the theoretical density for each composition, indicating that the foils are highly dense, and variations in foil density can not explain the fracture strength behavior.

Fracture toughness of the foils were characterized using hardness indents. The sputtered foils, which where approximately 50-μm-thick, where mounted on their edges so that hard-

Table 1. ICP-Measured Be Concentration and Density Compared to the Calculated Theoretical Density

Sample Number	Be (at.%)	Density (g/cc)	Theoretical Density
6	0.943	2.106	0.984
7	0.946	2.145	1.01
8	0.949	2.097	0.996
9	0.950	2.058	0.980
10	0.953	2.081	1.00
11	0.913	2.274	0.980
12	0.924	---	---
13	0.932	2.220	0.995
14	0.935	2.201	1.00

ness measurements could be performed on the edge of the foil. Fracture toughness, K_{IC}, can be calculated by the length of a crack, c in mm, emanating from the edge of a Vicker's hardness indent using the following equation:

$$K_{IC} = \chi P c^{-\frac{3}{2}} \left(\frac{E}{H_v}\right)^{\frac{1}{2}}$$

where P is the load in kg, H_v is the Vicker's Hardness in kg/mm^2, E is Young's Modulus in MPa, and χ is a calibration constant for the material. Young's modulus and χ are not expected to change significantly over the range of Be concentration in the foils that were tested, so that $P/(c^3H_v)^{0.5}$ should be proportional to the fracture toughness. Hardness measurements were made on as-deposited and heat treated samples. Results of these tests are listed in Table 2, which clearly shows a trend of increasing fracture toughness with Be concentration. Fracture toughness values were taken on all samples at 75 g, except for sample 9, which could not be crack, even at loads as high as 600 g where the diagonal of the indent barely fit within the sample thickness. Figure 1 shows an indent on samples 9 in the heat treated and as-deposited conditions. In the case of heat treated sample, cracks can be seen emanating from the corners of the indent impression made at 75 g, whereas no cracks can be detected in the as-deposited foil with an indent made at a 600 g load. In addition, the edge of sample 9 has clearly deformed to accommodate the hardness indent.

The correlation between fracture toughness and fracture strength, shown in Figure 2, appears to be very good. As the fracture toughness increases, the fracture strength also increases, indicating that the fracture strength that was measured is controlled by a critical flaw size rather that the material's inherent strength. Even more promising is the variation of fracture toughness with Be concentration. Although the deformation made on sample 9 was in the compressive state during the hardness test, it does suggest that the material can be toughened by alloy variations. At this time, the mechanism that is toughening the beryllide is not clear, and this area will be a focus of study in the next quarter.

The same trend of improved fracture toughness with increased Be concentration is also valid after the annealing cycle, although the resistance to crack growth decreased for sample 9, and improved for sample 11.

TEM analysis of the foils show that the grain size of all of these samples is very fine, on the order of 0.2-0.5 μm. The grain size decreases at higher Be concentrations, and the microstructure of as-deposited foils has a high density of defects. It is not clear at this time how the microstructure plays a role in toughening the material, although reduced grain size

Table 2. Hardness and Crack Length Measurements on $TiBe_{12}$ Foils

SAMPLE NO.	H_v (kg/mm)		Crack Length* (mm)	
	Mean	± σ	Mean	± σ
9 As Deposited**	955	180	---	---
9 Heat Treated	1438	180	7.7	0.7
11 As Deposited	1520	75	82.6	18
11 Heat Treated	1350	200	29.4	2.1
14 As Deposited	1625	65	27.3	5.5
14 Heat Treated	1340	215	17.1	6.8

* - Crack length measured at 75 g load
** - As-Deposited Sample #9 did not crack at maximum load of 600

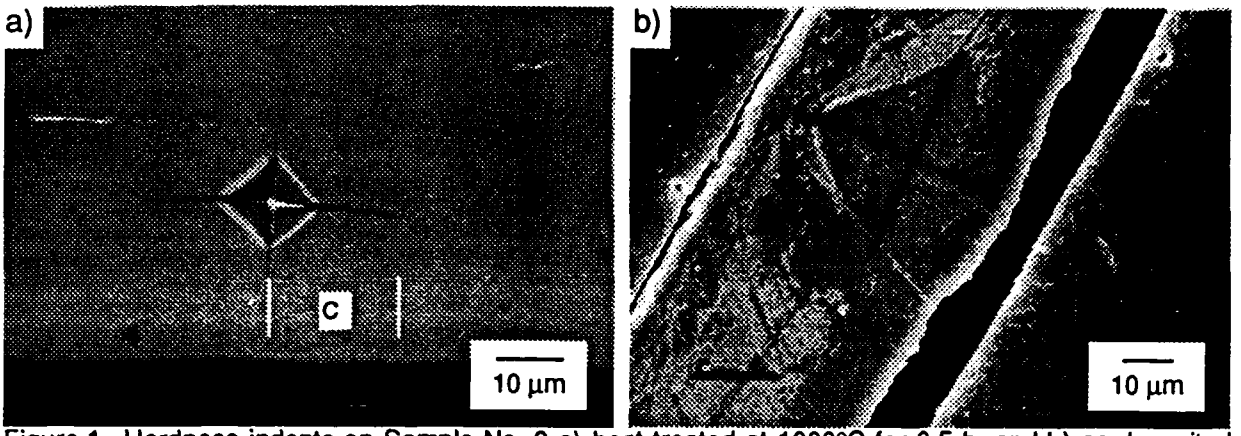

Figure 1. Hardness indents on Sample No. 9 a) heat treated at 1000°C for 0.5 h, and b) as-deposited. Cracks are emanating from the corners of the indent at 100 g for the heat treated sample, whereas the as-deposited sample shows no indication of cracking. and the material is deformed around the indent.

may be beneficial. Figures 3-5 show the grain size for each sample 9, 14, and 11 in the as-deposited condition and heat treated conditions. Heat treating the foil resulted in their decomposition to the structures expected from the phase diagram, and the dense defect structure in the original $TiBe_{12}$ grains has been reduced.

- Analysis of Roll Bonded Material

A second set of Ti-Be foils were rolled to provide starting material to make either $TiBe_{12}$ of $TiBe_2$. HIP'ing the Ti-Be laminants was performed at 1000°C for 8 h, which resulted in the complete conversion of the laminant to a monolithic beryllide foil. Figure 6 shows the a $TiBe_2$ laminant precursor before and after the heat treatment, revealing the extent of the reaction between the Ti and Be to form the beryllide. In the case of these samples, the can

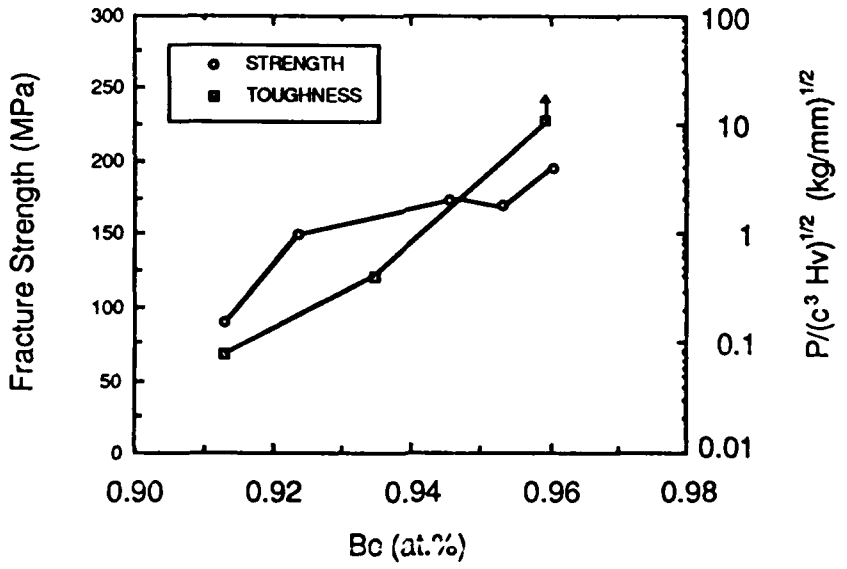

Figure 2. Tensile fracture strength of the beryllide foils as a function of composition, compared to a measure of fracture toughness. As the material becomes more resistant to fracture, the fracture strength increases. Note that the toughness value at 95.3 at.% Be is actually the minimum possible toughness.

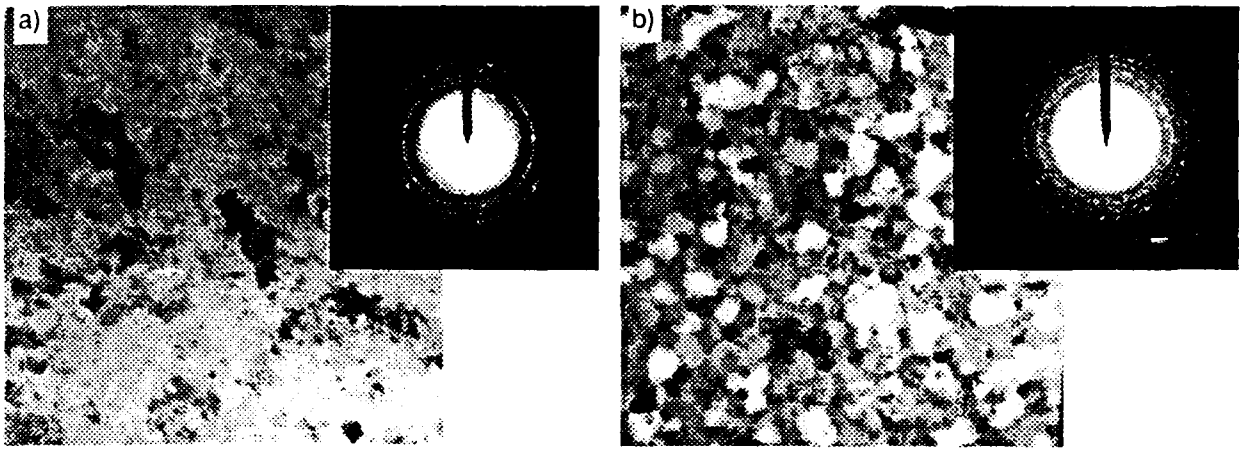

Figure 3. Bright field images and selected area diffraction patterns of sample 9 (95.0 a/o Be) in the a) as-deposited, and b) after heat treated at 1000°C for 0.5 h. The as-deposited sample has grains on the order of 0.1 μm, and only $TiBe_{12}$ is present in the foil. After heat treatment, the grain size has not grown significantly, but Be, as well as $TiBe_{12}$, is now present.

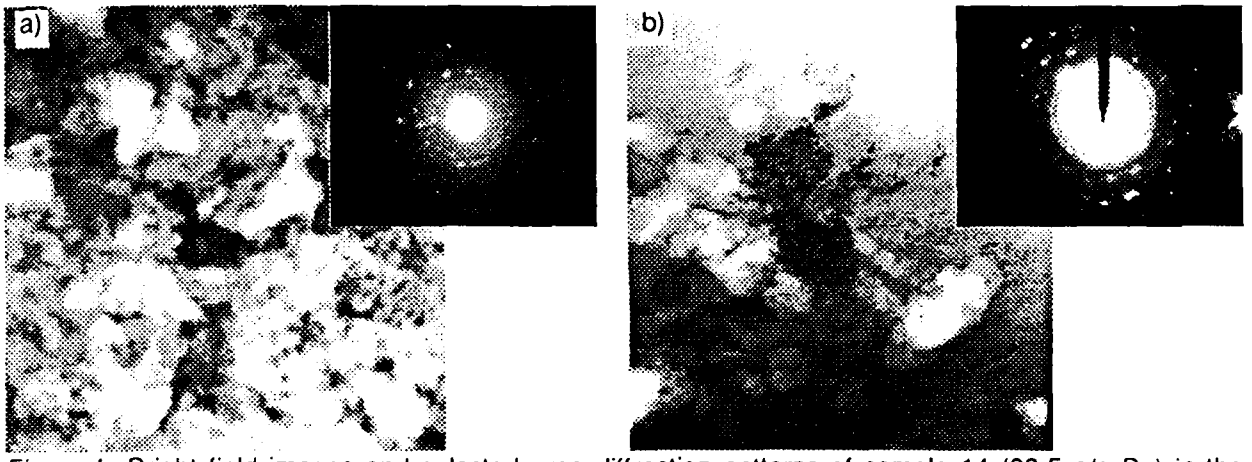

Figure 4. Bright field images and selected area diffraction patterns of sample 14 (93.5 a/o Be) in the a) as-deposited, and b) after heat treatment at 1000°C for 0.5 h. The microstructure of has not changed significantly with heat treatment, and only $TiBe_{12}$ is present in the foil.

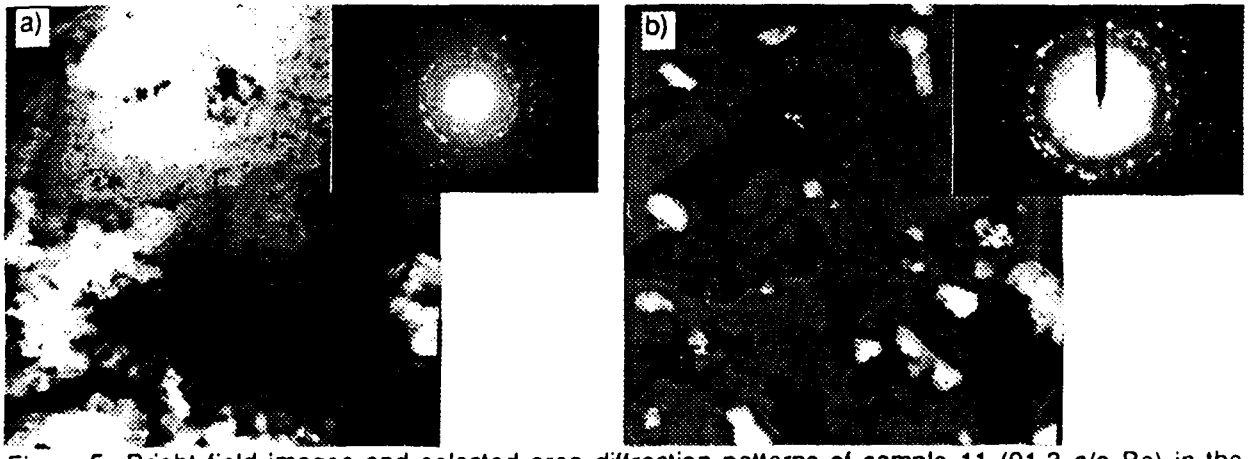

Figure 5 Bright field images and selected area diffraction patterns of sample 11 (91.3 a/o Be) in the a) as-deposited, and b) after heat treatment at 1000°C for 0.5 h. Although $TiBe_{12}$ is still present in the foil, the heat treatment has led to the formation of Ti_2Be_{17}

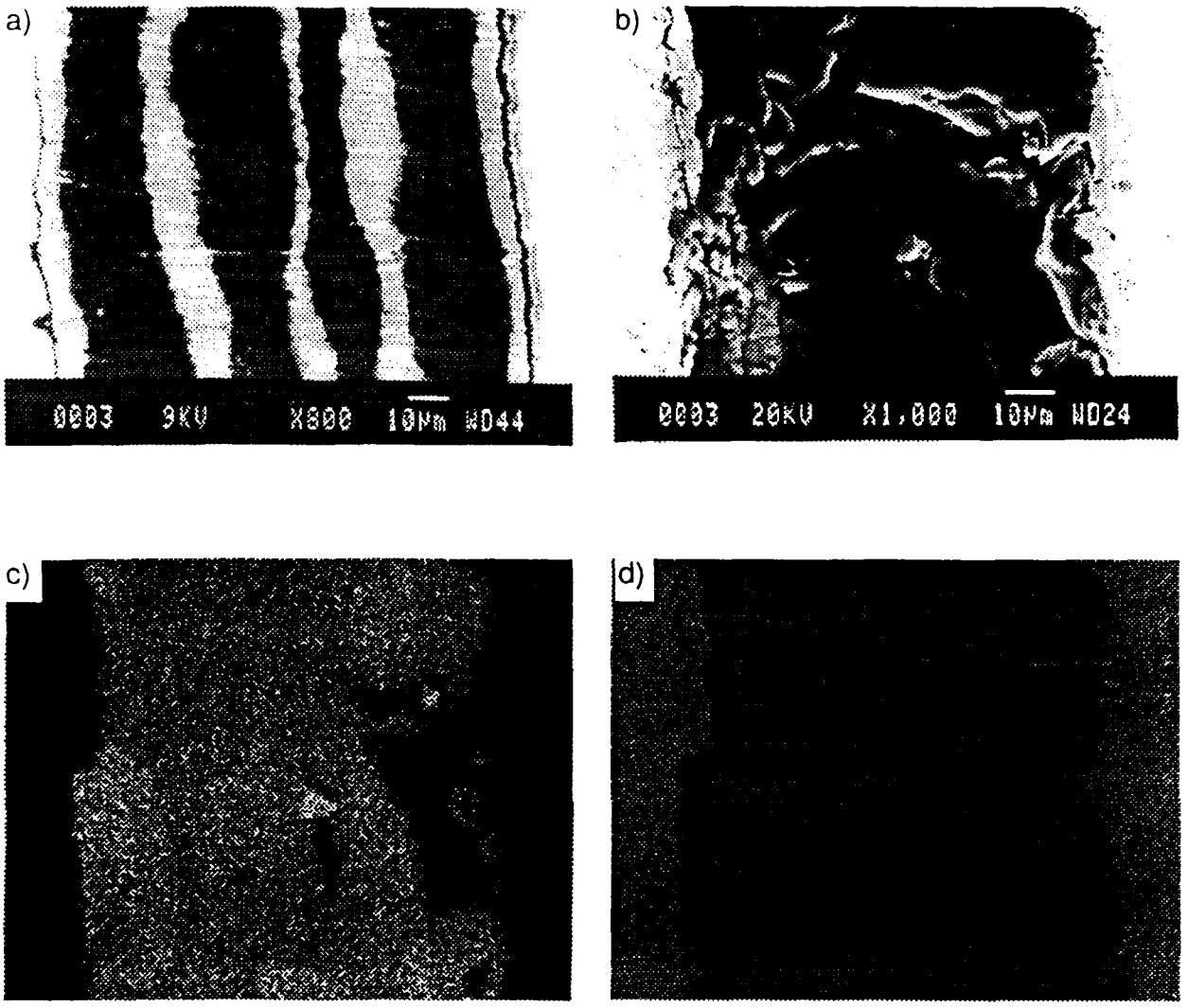

Figure 6 Ti-Be roll bonded laminant a) after reduction and compaction of foils to make laminant, b) after reaction at 1000°C for 8 h and 138 MPa, c) Ti map, and d) Ta map. A Ta liner was used to separate the steel can from the beryllide, and no interaction between the two is evident from the elemental maps. CTE mismatch between the can and the laminant resulted in the fracture of the beryllide during cooling.

material consisted of a Ta foil encased in a steel can. The large CTE difference between the can and the beryllide resulted in the fracture of the beryllide. Several new can designs were fabricated and are now being used to HIP beryllide samples. Test results for these samples will be available in the next quarter.

7.4 Tasks for the Next Period

- High Temperature Mechanical Testing and Structure Evaluation of Sputtered Material

High temperature testing will be conducted on beryllide samples that have been deposited onto a Molybdenum substrate. The samples will be chemically milled to remove the substrate from the gauge length, and tested at elevated temperatures. In addition to the mechanical testing, microstructure characterization will continue in the next quarter. Efforts

will be made to relate the improvement in fracture toughness to microstructure.

- Evaluation of Roll Bonded Material

  HIP'ing studies in thin wall Molybdenum cans (0.127-mm-thick) are in progress to determine whether thin beryllide foil (0.4-mm-thick) can be successfully fabricated without cracking during the solid state reaction bonding process. Laminants to make either $TiBe_2$ or $TiBe_{12}$ monolithic foils are being HIP'ed for evaluation and are expected to be completed by early March.

7.5 Participants On The Program (Last Quarter)

Name	Task
Nuclear Metals Inc., Concord, MA.	Extrusion & Specimen Preparation
EG&G, Rocky Flats, Golden, CO	Sputter-deposit Ti-Be foils
Manufacturing Sciences Corp, Oak Ridge, TN	Roll Bonding Ti-Be laminant
LANL, Los Alamos, NM	TEM of Ti beryllide foils