1 of 1

2

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**PROPERTIES AND POTENTIAL OF
HIGH-TEMPERATURE NIOBIUM BERYLLIDES**

S. M. Bruemmer
C. H. Henager, Jr.

J. L. Brimhall
J. P. Hirth

December 1992

Presented at the
1992 Fall Meeting of
Materials Research Society
December 1-5, 1992
Boston, Massachusetts

Prepared for
the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

CONF-921101--137

PNL-SA-21290

RECEIVED
AUG 16 1993
OSTI

MASTER

Properties and Potential of High-Temperature Niobium Beryllides

S. M. Bruemmer, J. L. Brimhall, C. H. Henager, Jr. and J. P. Hirth*
Pacific Northwest Laboratory, Richland, WA 99352
*Washington State University, Pullman, WA 99164

Abstract

Recent research on the low- and high-temperature properties of two beryllium-niobium intermetallic compounds, Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$, is reviewed and discussed. Strength (bend and compression), hardness and fracture toughness has been mapped as a function of test temperature up to 1200°C. Results for hot-isostatically-pressed Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ are highlighted illustrating the potential for reasonable strength at both low and high temperatures. Chemical compatability between Be_{12}Nb and several high-temperature materials such as SiC , Al_2O_3 , MoSi_2 and various refractory metals are evaluated. Limitations for the structural use of the beryllides are identified and discussed including low-temperature toughness, intermediate-temperature embrittlement, high-temperature creep strength and composite compatability.

Introduction

Beryllium-refractory metal intermetallic compounds, i.e. Be_{12}X , Be_{13}X and Be_{17}X_2 , exhibit excellent strength and oxidation resistance at high temperatures. Because of these properties and their very low densities, beryllides are promising candidate materials for aerospace application. The combination of properties exceeds other intermetallics such as refractory metal silicides and aluminides in most cases. Unfortunately, similar to many other intermetallics, beryllides have complex crystal structures which lead to poor low-temperature toughness.

The Be_{12}X compound is the simplest with a body-centered-tetragonal (bct) structure (I4/mmm) and 26 atoms per unit cell. Elements such as Nb, Mo, Ta, Ti, Cr, V and W all form isostructural Be_{12}X compounds with little change in the lattice dimensions. A number of metallic elements also form isostructural Be_{13}X (cubic, Fm3c) and Be_{17}X_2 (hexagonal-rhombohedral, R3m) compounds as summarized in Figure 1. Phase stability in beryllides (e.g., formation of Be_{13}X versus Be_{12}X) depends on atom size of the metal atom (X) reacting with Be and, to a lesser extent, its bonding character.¹ Face-centered-cubic (fcc) Be_{13}X is favored when the diameter of metal atom (d_X) is greater than ~0.3 nm, while Be_{12}X is stable for smaller atom sizes, $d_X = 0.25$ to 0.29 nm. Among the Be_{12}X compounds, larger (>0.28 nm) metal atoms (e.g., Nb, Ta and Ti) also form Be_{17}X_2 , but smaller ones (e.g., Cr, Mn, V, Mo and W) do not.

Recent work by the authors on Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ intermetallics is reviewed with emphasis on: (1) phase stability, (2) mechanical properties, (3) deformation mechanisms and (4) composite compatability. Specific properties of these compounds are discussed in relation to their potential for high-temperature structural applications.

until the average size of the Nb+Zr atoms reaches a critical value at which point the Be₁₃X phase forms. Relative stabilities between the various stable and metastable crystal structures is believed to play an important role in the deformation behavior and mechanical properties of Be₁₂X compounds as discussed in the following sections.

Mechanical Properties

Bend Strength and Fracture Toughness

Four-point-bend and chevron-notch-bend specimens have been used to determine strength and toughness of VHP and HIP beryllides.⁸⁻¹⁰ HIP Be₁₂Nb exhibited the best properties in bending with strengths of 210-250 MPa measured at 20°C to 650°C (Figure 2). Strength dropped sharply from 650°C to 900°C, and then increased to ~250 MPa at higher temperatures. Limited plasticity was observed below 1100°C. At low temperatures, a fine, granular fracture surface is observed consisting of intergranular (IG) facets and small cleavage regions across individual grains. The fracture surface became brittle intergranular and macroscopically flat at temperatures from 800°C to 1000°C. Temperature effects on fracture toughness closely matched the bend strength results as shown in Figure 2. Low-temperature K_{IC} ranged from 4 to 4.6 MPa√m corresponding to the highest measured bend strengths. Toughness values decreased to less than 0.5 MPa√m at intermediate temperatures before increasing above 900°C. This embrittlement occurs at temperatures where accelerated oxidation (pest) is seen in static tests, but cannot be directly linked to the fracture process.¹¹

HIP Be₁₇Nb₂ exhibited only elastic behavior in bend tests at all temperatures up to 1100°C. Slight inelastic deflection was observed at 1100°C and measurable plastic deformation was seen at 1200°C. Bend strengths increased from 100 MPa at 20°C to a maximum of 740 MPa at 1100°C (Figure 2). High-temperature strengths for Be₁₇Nb₂ at were much greater than for Be₁₂Nb. Measured K_{IC} for Be₁₇Nb₂ material was less than 2.5 MPa√m at test temperatures below 1100°C, which indicates that the measured bend strengths are limited by the toughness of the material. Be₁₇Nb₂ failed by transgranular cleavage (flat, featureless appearance) with no obvious IG features.

Compression Strength

Compression tests have been performed on various beryllide heats using small cylindrical or cube specimens.^{9,10} A maximum uniaxial compressive strength of 2750 MPa was measured for the HIP Be₁₂Nb at 20°C. Strength remained quite high (2380 MPa) at 800°C and then decreased rapidly at temperatures greater than 1000°C (Figure 3). Compression strengths at temperatures from 20°C to 800°C were significantly improved over that for Be₁₇Nb₂. Plasticity was indicated from non-linearities in the load-displacement curves for Be₁₂Nb at ~800°C, while Be₁₇Nb₂ revealed brittle behavior at temperatures up to 1000°C. Ambient temperature strength for Be₁₇Nb₂ was only 1200 MPa, less than one-half that for the HIP Be₁₂Nb. Strength increased with temperature, reaching a maximum value of 1550 MPa at 800°C (Figure 3). A very low strength of 400 MPa, below that for Be₁₂Nb, was measured at 1000°C. Compressive strength at 1200°C was identical to Be₁₂Nb (~200 MPa), in contrast to the higher strength observed in the bend tests.

Figure 2. Bend Strength and Fracture Toughness for HIP Be₁₂Nb and Be₁₇Nb₂ Compounds.

Figure 3. Compression Strength and Hot Hardness for HIP Be₁₂Nb and Be₁₇Nb₂ Compounds.

High-Temperature Microhardness and Indentation Creep Tests

High-temperature microhardness tests have been performed on VHP and HIP Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ heats^{10,12,13} and on several isostructural VHP Be_{12}X materials.¹² HIP heats showed a higher hardness than VHP heats at temperatures below 300°C, due to their finer grain size and reduced porosity. The largest difference was observed at 20°C where the HIP materials show hardness values from 12.8 GPa to 14.0 GPa, while hardness for the VHP materials range from 8.8 GPa to 9.8 GPa. Hardness results for $\text{Be}_{17}\text{Nb}_2$ were consistently above that for Be_{12}Nb (Figure 3) with a maximum difference of 3 GPa occurring at 800°C to 950°C. Test temperatures of about 1000°C were required before a significant decrease in hardness was observed, a slightly higher transition than for Be_{12}Nb (~850°C). Differences in ductile-brittle transition behavior between Be_{12}X compounds (Cr, Mn, Ti, Mo, V, Ta and Nb) were observed and related to Be_{12}X - Be_{17}X_2 phase stability. Elements such as V and Mo (which form Be_{12}X , but not Be_{17}X_2), were found to exhibit lower transition temperatures. Secondary slip systems were found to be activated in Be_{12}V at temperatures ~300°C below that for Be_{12}Nb even though both compounds have similar melting temperatures.¹³

Indentation creep tests were performed on Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ materials using the high-temperature microhardness tester and varying the indentation dwell time. This data was used to calculate creep parameters for this material.^{10,12} Power-law creep exponents of 4.3 and 4.1 were determined for the HIP Be_{12}Nb and VHP $\text{Be}_{17}\text{Nb}_2$, respectively. Activation energies for dislocation creep were about 290 kJ/mole for HIP Be_{12}Nb and 230 kJ/mol for VHP $\text{Be}_{17}\text{Nb}_2$. $\text{Be}_{17}\text{Nb}_2$ required a slightly higher temperature (950°C) for the transition to power-law creep as compared to that for Be_{12}Nb . Although individual hardness values were consistently higher for $\text{Be}_{17}\text{Nb}_2$, the rate of change with temperature was quite similar to that for Be_{12}Nb . Specific properties for Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ are summarized in Table 1.

Table 1. Selected Properties for Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ Intermetallics

Property	Be_{12}Nb	$\text{Be}_{17}\text{Nb}_2$
Crystal Structure	tetragonal	rhombic
Melting Temperature, °C	1672	1800
Density, g/cm ³	2.9	3.2
Elastic Modulus, GPa	220	320
Maximum Strength at 23°C		
• Bending, MPa	250	110
• Compression, MPa	2750	1200
• Hardness, GPa	13.7	14.9
Maximum Strength at 1200°C		
• Bending, MPa	250	390
• Compression, Mpa	295	190
• Hardness (1100°C), GPa	3.8	5.8
Ductile-Brittle Transition Temperature, °C		
• Bending	~1100	~1100
• Harness	~850	~900
Activation Energy for Dislocation Creep, kJ/mole	290	230

6. J.L. Brimhall, L.A. Charlot and S.M. Bruemmer, *High-Temperature Ordered Intermetallic Alloys*, Materials Research Society, 1991, p. 175.
7. J.L. Brimhall, L.A. Charlot and S.M. Bruemmer, *Mater. Sci. Eng.*, A152 (1992) 76.
8. C.H. Henager, Jr., R.E. Jacobson and S.M. Bruemmer, *Mater. Sci. Eng.*, A152 (1992) 416.
9. S.M. Bruemmer, B.W. Arey and C.H. Henager, Jr., *Intermetallic Matrix Composites II*, MRS Spring Meeting, Materials Research Society, 1992.
10. C.H. Henager, Jr., J.P. Hirth and S.M. Bruemmer, submitted to *Mat. Sci. Eng.*, 1992.
11. S.M. Bruemmer and L.A. Charlot, submitted to *Scripta Metall. et Mat.*, 1992.
12. R.E. Jacobson, *High Temperature Strength and Creep Resistance of Be₁₂Nb and Be₁₇Nb₂ Intermetallics*, Masters Thesis, Washington State University, 1991.
13. S.M. Bruemmer, B.W. Arey, J.L. Brimhall and J.P. Hirth, submitted to *J. Mater. Research*, 1992.
14. S.M. Bruemmer, L.A. Charlot, J.L. Brimhall, C.H. Henager, Jr., and J.P. Hirth, *Phil. Mag. A*, 65 (1992) 1083.
15. S.M. Bruemmer, L.A. Charlot, C.H. Henager, Jr., and J.P. Hirth, submitted to *Scripta Metall.*, 1992.
16. L.A. Charlot, J.L. Brimhall, L.E. Thomas, S.M. Bruemmer and J.P. Hirth, *Scripta Metall.*, 25 (1991) 99.
17. B.A. Greenberg, O.V. Antonova, V.N. Indenbom, L.E. Karkina, A.B. Notkin, M.V. Panomarev and L.V. Smirnov, *Acta Metall.*, 35 (1991) 233.
18. M.L. Kronberg, *J. Nucl. Mater.*, 1 (1959) 85.
19. S. Sondhi, R.G. Hoagland, J.P. Hirth and S.M. Bruemmer, *High-Temperature Ordered Intermetallic Alloys*, Materials Research Society, submitted 1992.
20. J.L. Brimhall and S.M. Bruemmer, *Scripta Metall.*, in press, 1992.

Acknowledgements

Contributions of R. Jacobson, S. Sondhi, L. A. Charlot and B. W. Arey, as well as critical discussions with R. G. Hoagland, are acknowledged. Work is supported by the Defense Advanced Research Projects Agency through the Office of Naval Research and under U.S. Department of Energy contract DE-AC06-76RL0 1830 with Pacific Northwest Laboratory, which is operated by Battelle Memorial Institute.

**DATE
FILMED**

10 / 20 / 93

END