

**METASTABLE PHASE FORMATION IN Be-Nb
INTERMETALLIC COMPOUNDS**

J. L. Brimhall
L. A. Charlot
S. M. Bruemmer

November 1990

For publication in the proceedings of the 1990
Fall Meeting of the Materials Research Society
Symposium on High-Temperature Ordered
Intermetallic Alloys

Work Supported by the Defense
Advanced Research Projects Agency
through the Office of Naval Research
and by the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

lower Nb contents than expected from the equilibrium concentration. The reported compositions, in at.%, have been corrected for this slight discrepancy. Microstructural analysis was performed on selected samples using transmission electron microscopy (TEM) and selected area electron diffraction. The extremely fine grain size precluded phase identification from single grains.

RESULTS

The structure of deposits made at ambient temperature was completely amorphous, as confirmed by both X-ray diffraction and TEM analysis. An example of the microstructure and electron diffraction pattern is shown in Figure 1. Deposits with >5.5 at.% Nb were completely amorphous, whereas compositions <5.5 at.% Nb were two-phase and contained crystalline Be. Crystallization occurred at temperatures $>500^\circ\text{C}$.

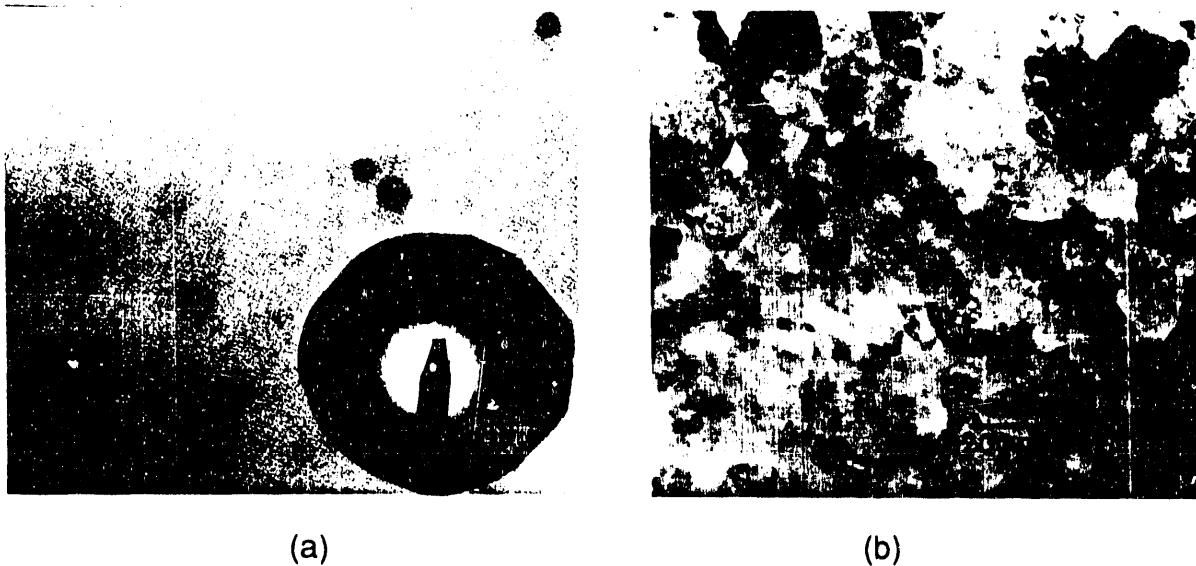


Figure 1. TEM micrographs of low temperature deposit. (a) as-deposited (b) annealed at 650°C for one hour.

Annealing the low temperature deposits at 650°C for one hour produced the X-ray patterns shown in Table 1. Also shown is the pattern for Be_{12}Nb given in the JCPDS file. The pattern from the annealed deposit is almost identical to that from Be_{12}Nb , with the $(hk0)$ lines absent. The (110) line in the Debye-Scherrer pattern actually appeared as a broad diffuse band. Both diffractometer scans and Debye-Scherrer patterns gave the same basic pattern, so the lack of the $(hk0)$ lines is not just a result of preferred orientation. This same type of pattern was also observed in the selected area diffraction pattern obtained in TEM. The pattern from the annealed deposit can also be indexed to a bcc lattice with $a_0 = .521$ nm. This a_0 is equivalent to $(\sqrt{2}/2)a_0$ of the bct Be_{12}Nb phase. This phase, referred to as $\text{Be}_{12}\text{Nb}'$, is a metastable, and probably, disordered form of Be_{12}Nb .

Annealing at temperatures $>800^\circ\text{C}$ produced the ordered Be_{12}Nb pattern indicated in Table 1. No free Be was detected in compositions >5.5 at.% Nb annealed to 1000°C . This was shown by the lack of a diffraction line at $.179$ nm. The other Be peaks overlap with lines of the Be_{12}Nb phase. In a deposit with 4 at.% Nb annealed at 800°C , the Be line at $.179$ nm was clearly resolved. If Be_{12}Nb is a line compound, an

Table 1. Observed X-Ray Patterns for Annealed, Low-Temperature Deposit

Measured Values (nm)			Calculated (nm)	Card File
<u>3.5%Nb</u> (650°C)	<u>5.5%Nb</u> (650°C)	<u>5.5%Nb</u> (1000°C)	<u>bcc(a₀=0.521)</u>	<u>Be₁₂Nb (hkl)</u>
		.522		.520 (110)
.3668	.369	.3683	.3676 (100)	.369 (101)(200)
.2603	.262	.2600	.2600 (200)	.2608 (211)(200)
		.2331		.2327 (310)
.214	.213	.2133	.2123 (211)	.2127 (002)(301)
.1975*		.1988		.1971 (112)
.1833	.185	.1849	.1839 (220)	.1842 (202)(402)
.1797				
.1730		.1740		.1736 (330)
	.1661	.1655	.1644 (310)	.1648 (222)(411)
		.1577		.1573 (312)
	.1402	.1399	.1390 (321)	.1445 (510)
		.1309	.1300 (400)	.1393 (103)(402)
				.1344
	.1228		.1226 (411)	.1302 (213)(422)
				.1226

*Bold figures indicate Be lines.

alloy of 5.5 at.% Nb would have about 30 at.% Be, which should be readily identified.

For the high temperature deposit, Nb strips were placed at opposite edges of the target, which produced a minimum in Nb concentration at the center of the deposit and maximum at the edge. Analysis of the center region (4-5.5 at.% Nb) indicated a mixture of Be and the Be₁₂Nb' phase from X-ray diffraction patterns essentially identical to those shown in Table 1 for the 3.5 at.% Nb alloy. The region extending from about 5.5 to 7.7 at.% Nb indicated a single phase Be₁₂Nb' pattern also identical to that shown for the 5.5 at.% Nb alloy in Table 1.

Beyond 7.7 at.% Nb, the structure in the high temperature deposit was again two phase with Be₁₂Nb' and a different metastable phase (x). This phase could be indexed to a bcc lattice with a₀ = 1.208 nm as shown by the comparison in Table 2.

Annealing the region with single phase Be₁₂Nb' at 1100°C for one hour produced the equilibrium Be₁₂Nb X-ray pattern. However, there was still no evidence of free Be after the high temperature annealing.

The metastable phase transformed to the Be₁₇Nb₂ phase after high temperature annealing. In alloys with >10.5% Nb, a mixture of Be₁₇Nb₂ and Be₃Nb was identified. After annealing up to 1200°C, only these two phases were present; i.e. there was no evidence of a Be₅Nb phase.

DISCUSSION

The results show that both amorphous and metastable crystalline phases form in sputter-deposited Be-Nb alloys. The equilibrium phases that eventually form

Table 2. Comparison of Observed Pattern of Unknown Phase with Calculated bcc Pattern

<u>Measured Values</u>	<u>Calculated Values</u> ($a_0 = 1.208 \text{ nm}$)		<u>Be₁₇Nb₂ Card File</u>
d	d	(hkl)	
.4902	.4927	(211)	.550
.424	.4267	(220)	.414
.3798	.3816	(310)	
.366*	-	-	.370
.3500	.3484	(222)	.362
.3217	.3225	(321)	
.302	.3017	(400)	.308
.280	.2845	(411)	.276
-	.2699	(420)	
.2571	.2573	(322)	.259
.246	.2463	(422)	.250
.363	.2367	(431)(510)	.237
.2268	-	-	
.202	.2204	(521)	.221
.2121*	.2133	(440)	.214
.2067	.2069	(433)	.206
-	.2012	(442)(600)	
.1957	.1958	(532)	
.1910	.1908	(620)	
.1862	.1862	(541)	.185
.1837*	-	-	.184
-	.1819	(622)	.180
.1780	.1780	(631)	
.1742	.1742	(444)	.176
.1708	.1707	(550)(710)	

*Possible Be₁₂Nb' lines

are Be₁₂Nb, Be₁₇Nb₂ and Be₃Nb. A range of stoichiometry is indicated for the Be₁₂Nb phase.

The formation of an amorphous phase during rapid liquid or vapor quenching has been widely observed [3-6]. The amount of alloying element required to cause the amorphous structure, 5.5 at.% Nb, is quite low compared to most other investigations. Tanner [4] has observed amorphous structures in liquid quenched Be alloys with higher alloy content. In general, alloy contents of around 15 to 20 at.% are required to stabilize the amorphous structure.

Several factors can account for amorphous phase formation in an alloy of only 5.5 at.% Nb alloys. The composition is near that of an intermetallic compound. Wang [7] has developed an empirical relationship which shows the stability of the amorphous structure to increase with complexity of the crystalline counterpart. Qualitatively, it takes very little shuffling of the atoms in a complex crystal structure to produce an amorphous phase. Secondl, the solubility of Nb is extremely small. Johnson et al. [8] have used the concept of limited solubility to explain the creation of an amorphous structure during ion implantation and ion mixing. The analysis can be applied to sputter deposition where atoms are condensing in a random fashion at an

extremely rapid rate. Finally, for low substrate temperature, diffusion of the atoms is very slow compared to the deposition rate. In essence, the atoms do not have time to rearrange into a stable crystalline configuration during the deposition process.

If the material is deposited as amorphous at low temperature, there appears to be a high probability of creating metastable crystalline phases or allotropic forms of the phases when depositing at higher temperatures. For the high temperature deposit, $T_{\text{sub}}/T_{\text{melt}}$ is about 0.33. With some atomic mobility, the atoms can position themselves into a lower-energy, crystalline configuration which may not be the thermodynamic equilibrium phase. The difference in free energy between the metastable and stable phases can be slight. A metastable phase with a less complex structure would require less atomic motion during deposition to attain its crystalline structure than a stable but more complex phase. Metastable phase formation prior to the equilibrium phases in rapidly quenched alloys has been widely reported [9-11].

The structural relation between the metastable phases and equilibrium phases is not obvious. No simple structural transformation has been found between the $\text{Be}_{12}\text{Nb}'$ and the tetragonal Be_{12}Nb phase, even though a_0 of the bcc is equal to $(\sqrt{2}/2) a_0$ of the bct. For compositions up to about 10.5 at.% Nb ($\text{Be}_{17}\text{Nb}_2$), the pattern of the $\text{Be}_{12}\text{Nb}'$ phase always appeared in the initial stages of annealing the amorphous structure. This $\text{Be}_{12}\text{Nb}'$ could be a precursor phase to the formation of both Be_{12}Nb and $\text{Be}_{17}\text{Nb}_2$ during crystallization of the amorphous phase. Similarities in structure of the two phases and a possible transformation process from the Be_{12}Nb to $\text{Be}_{17}\text{Nb}_2$ have been described [12].

The results, in particular the high temperature deposit, show the Be_{12}Nb phase to have a small but measurable range of solubility. In a recent work, Fleischer and Field have shown free Be particles in an alloy of about 7 at.% Ti [13]. In an earlier work, Kirby observed free Be in an alloy with 7.2% Nb which would indicate a near line compound [14]. However, in this same work 9 (which used electron probe microanalysis), a composition gradient was reported in Be_{12}Nb particles with Nb concentrations as low as 5.9% near the interface with the Be matrix. It would seem that Be_{12}Nb may not be a true line compound, but the magnitude of the stoichiometry range is still a question. The sputter deposition process introduces considerable defects in the structure and therefore the magnitude of the deviation from ideal stoichiometry could be larger for this case compared to material prepared from the melt.

Vacancies at the Nb sites most likely account for the observed range of solubility in the Be_{12}Nb phase. This is analogous to the situation in NiAl, where vacancies occur on the Ni sublattice to account for the apparent increase in Al concentration [15]. These beryllide structures can be represented as cages of Be atoms surrounding the large refractory metal atom, i.e., Nb [16]. The stability of this cage can probably be maintained even with the removal of a certain fraction of the Nb atoms. A $\text{Re}_{0.92}\text{Be}_{16}$ phase in which up to seven of the eight Re sites are claimed to be unoccupied has been reported [17]. The Nb concentration in Be_{12}Nb does not extend beyond the equilibrium concentration, as it would be very difficult to incorporate the large Nb atoms into the dense Be sublattice.

CONCLUSIONS

Metastable amorphous and crystalline phases are produced during sputter deposition of Be-Nb alloys. Metastable crystalline phases also form upon low temperature annealing of the amorphous phase. Temperatures $>800^\circ\text{C}$ are required

to transform to the stable phases. The Be₁₂Nb phase indicates a stoichiometric range of 5.5 to 7.7 % Nb, which probably results from Nb vacancies in the lattice. There was no evidence of the Be₅Nb phase. The phase formation agreed with the phase diagram published in reference 2.

ACKNOWLEDGMENTS

This work is supported by the Defense Advanced Research Projects Agency through the Office of Naval Research and by the U.S. Department of Energy (DOE) under contract DE-AC06-76RLO-1830. Pacific Northwest Laboratory is operated for DOE by Batelle Memorial Institute.

REFERENCES

1. Phase Diagrams of Binary Beryllium Alloys, ed. by H. Okamoto and L. Tanner, ASM International, Metals Park, OH, 1987.
2. Binary Alloy Phase Diagrams, ed. by T. B. Massalski, ASM International, Metals Park, OH 1986.
3. J. L. Brimhall, H. E. Kissinger and R. Wang, J. Mat. Sci., 16, 994-1000, 1981.
4. L. E. Tanner and R. Ray, Acta Met., 27, 1727-1747, 1979.
5. H. F. Rizzo, L. E. Tanner, M. A. Mall, E. D. McClanahan and T. B. Massalski, in "Fundamentals of Beam-Solid Interactions and Transient Thermal Processing", MRS, vol. 100, 81-86, 1988.
6. T. W. Barbee, Jr. and D. L. Keith, in "Synthesis and Properties of Metastable Phases", ed. by E. S. Machlin and T. J. Rowland, TMS, Warrendale, PA, 93-114, 1980.
7. R. Wang, in "Theory of Alloy Phase Formation", ed. by L. H. Bennett, Metallurgical Soc. of AIME, Warrendale, PA, pp. 472-475, 1980.
8. W. L. Johnson, Y. T. Cheng, M. Van Russum and M-A. Nicolet, Nucl. Instr. & Meth., B7/8, 657-685, 1985.
9. H. Fujita, K. Hashimoto and T. Tabata, Mat.Sci. and Engr., 45, 221-228, 1980.
10. Z. Altounian, Tu Guo-hua and J. O. Strom-Olsen, J. Appl. Phys., 54, 3111-3118, 1983.
11. O. T. Inal, L. Keller and F. G. Yost, J. Mat. Sci., 15, 1947-1961 1980.
12. E. Gillam and H. P. Rooksby, Acta Cryst., 17, 762-763, 1964.
13. R. L. Fleischer and R. D. Field, Development Potential of Advanced Intermetallic Materials, WRDC-TR-90-4046, 1990.
14. R. F. Kirby, Development of the Columbium Beryllides for High-Temperature Applications, University Microfilms, Inc., Ann Arbor, Mi, 69-14, 187, 1969.
15. A. J. Bradley and A. Taylor, Proc. Roy. Soc., 159, 56, 1937.
16. D. M. Collins and M. C. Mahar, Acta Cryst., C40, 914-915, 1984.
17. M. C. Mahar and D. M. Collins, Acta Cryst., C40, 912-913, 1984.

END

DATE FILMED

02 / 14 / 91

