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THE PREPARATION AND PROPERTIES OF
THREE REFRACTORY BERYLLIDES

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THE PREPARATION AND PROPERTIES OF THREE REFRACTORY BERYLLIDES

Walston Chubb and Ronald F. Dickerson

The beryllium compounds NbBe₁₂, YBe₁₃, and ZrBe₁₂ were prepared by arc melting. Some beryllium was lost in this operation but sound ingots were obtained. The hardness, density, metallographic structure, X-ray structure, and oxidation resistance in air of each ingot were determined.

The zirconium compound apparently had a tetragonal structure corresponding to ZrBe₁₂ and a hardness of 790 Knoop and a density of 2.94 g per cm³. The yttrium compound had a cubic structure corresponding to YBe₁₃ and a hardness of 870 Knoop and a density of 2.57 g per cm³. The niobium compound had a tetragonal structure corresponding to NbBe₁₂ and a hardness of 1100 Knoop and a density of 3.14 g per cm³.

The zirconium alloy was most difficult to prepare and crumbled at 700 C during oxidation testing. The niobium and yttrium alloys were both relatively easy to prepare and both were highly resistant to oxidation at 1300 C. The niobium alloy had the most satisfactory behavior in all respects and appears most promising for further development.

INTRODUCTION

Beryllium is an extremely oxidation-resistant metal, and it may reasonably be expected that some beryllium-rich alloys and compounds share this oxidation resistance to some degree. In addition, beryllium-rich alloys and intermetallic compounds may be expected to have beryllium densities and thermal conductivities near that of beryllium. A few beryllium-rich intermetallic compounds are also known to have melting points above that of pure beryllium. In this research only the more refractory beryllium-rich compounds having low thermal neutron capture cross sections, having high boiling points, and containing more than 91 a/o beryllium were considered.

A survey of the literature on beryllium compounds⁽¹⁻¹³⁾ disclosed two distinct types of beryllium compounds containing more than 91 a/o beryllium. The first type has the general formula MBe₁₃ and a face-centered-cubic structure of the D₂₃ type (NaZn₁₃). This type of beryllium compound is formed only with the elements of Groups 2A and 3A of the periodic chart, including the lanthanide and actinide series elements. According to the literature, zirconium may also form a compound, ZrBe₁₃; but, if so, this is the only such compound found outside of Groups 2A and 3A. The second type of beryllium compound containing more than 91 a/o beryllium has the general formula MBe₁₂, and usually has a body-centered-tetragonal structure of the ThMn₁₂ and NbBe₁₂ type. This type of beryllium compound is formed with many of the elements of Groups 4A, 5A, 6A, 7A, and 8 of the periodic chart.

(1) References at end.

The literature mentions six beryllium-rich compounds of elements having low thermal-neutron capture cross sections. These compounds are CaBe_{13} , CeBe_{13} , MgBe_{13} , NbBe_{12} , YBe_{13} , and ZrBe_{13} . Calcium, cerium, and magnesium have low boiling points relative to the melting point of beryllium; and, therefore, these compounds probably cannot be prepared by standard melting techniques. The preparation and properties of the compounds NbBe_{12} , YBe_{13} , and ZrBe_{13} is the subject of this investigation.

EXPERIMENTAL WORK

Melting Studies

The materials used for these studies were sintered beryllium (about 98 per cent metallic beryllium), sintered niobium metal (over 99 per cent niobium), cast and hot-rolled yttrium metal (over 99 per cent yttrium), and cast and wrought iodide zirconium (over 99.5 per cent zirconium). The major impurity in the beryllium, yttrium, and zirconium was oxygen. The major impurity in the niobium was zirconium.

Charges weighing 25 g were melted in an inert-electrode flip-type arc-melting furnace which does not need to be opened to turn the ingot over for remelting. Melting was accomplished using 2/3 atm absolute pressure of helium gas in the furnace. The zirconium-beryllium alloy was melted at 25 to 35 v and 400 to 600 amp with considerable difficulty. The first four melting operations resulted in a porous ball of clinker which split into several fragments on cooling. On subsequent melts the porosity gradually decreased until on the eighth melt the coherent button shown in Figure 1 was obtained. Considerable beryllium was volatilized and condensed on the inner walls of the melting furnace during the course of the eight melting operations. The ingot shown in Figure 1 analyzed 53 w/o zirconium and weighed 20 g, whereas the charge weighed 25 g and contained only 43 w/o zirconium. The refractory behavior of this alloy during melting suggested that it had a melting point well above the melting points of the constituent elements, perhaps $2000\text{ C} \pm 300\text{ C}$.

Two ingots of yttrium-beryllium alloys were prepared. The first ingot was melted at 25 to 35 v and 400 to 600 amp. Like the zirconium alloy, the yttrium alloy formed a porous ball on the first meltdown, but some solid metal formed around the circumference of the porous mass even on the first melt. After three melts, the melting behavior of the yttrium-beryllium alloy became quiet, and gas evolution was confined to the final stages of solidification. After six melts the button shown in Figure 2 was obtained. Some beryllium was volatilized during the melting of this ingot. It weighed 23 g and analyzed 46 w/o yttrium, as compared with a charge of 25 g containing only 43 w/o yttrium. The melting behavior of this ingot suggested that it had a melting point near or only slightly above the melting points of the constituent elements, perhaps $1600\text{ C} \pm 300\text{ C}$. The favorable melting behavior of this first ingot suggested that better analytical results could be obtained, and a second ingot was prepared. A portion of the first ingot was used as a starter charge in the second ingot, and as a result the second ingot melted with very little gas evolution. Unfortunately for the analytical results, an

2X

RM11411

FIGURE 1. ARC-MELTED INGOT OF THE 53 w/o ZIRCONIUM-47 w/o BERYLLIUM ALLOY

Photograph shows the ingot after the eighth melt. Original charge contained 43 w/o zirconium.

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FIGURE 2. ARC-MELTED INGOT OF THE 46 w/o YTTRIUM-54 w/o BERYLLIUM ALLOY

Photograph shows the ingot after the sixth remelt. Original charge of yttrium was 43 w/o.

attempt was made to cast this second ingot into the form of a slab by the inert arc drop-casting technique. A tenacious film on the surface of the molten metal frustrated all attempts to cause the metal to flow into the mold opening, and the mold became overheated in the attempt, and alloyed with the button to a limited extent. This accident occurred during the eighth melt of this ingot and only 22 g of the original 25-g charge were recovered. This material contained 49 w/o yttrium and 0.4 w/o copper.

An ingot of niobium-beryllium alloy was melted at 25 to 35 v and approximately 400 amp. No puffiness or gas evolution was observed during the melting of this alloy, although considerable beryllium was vaporized and condensed on the walls of the melting furnace. It is believed that much of this beryllium was evolved during the first few remelts before all of the niobium was dissolved. Prealloying the niobium with perhaps 10 w/o beryllium might reduce this tendency to volatilize beryllium. The niobium-beryllium ingot was recovered as a sound button containing no serious defects after six melts. However, two additional remelts were made in an attempt to make a drop casting of this alloy. The product of the eighth melt was cracked into five pieces, as shown in Figure 3. The photograph shows the bottom of the ingot, and the slight mound running from left center to lower right across the button illustrates the extent to which the molten metal entered the slab mold. This ingot weighed 22 g and analyzed 52 w/o niobium, as compared to a charge weight of 25 g containing 46 w/o niobium. The relative ease with which this alloy melted suggested that it had a melting point near that of beryllium, perhaps $1500\text{ C} \pm 300\text{ C}$.

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FIGURE 3. ARC-MELTED INGOT OF THE 52 w/o NIOBIUM-48 w/o BERYLLIUM ALLOY

Photograph shows the bottom of the ingot following an attempt to make a drop casting in a slab mold. The original charge contained 46 w/o niobium. The ingot is shown after the eighth melt.

According to the analyses obtained above, only beryllium was lost from the charges during arc melting. This metal was vaporized during melting and condensed on the walls of the furnace as an extremely fine (apparently amorphous) metal powder. The deposit was pyrophoric and tended to smear like graphite during cleanup so as to present a considerable potential fire and consequent health hazard. A furnace designed to melt beryllium alloys exclusively could be operated in an inert atmosphere so as to eliminate the fire hazard, and most of the vapor-deposited beryllium could be collected and reused. Under such conditions the health hazard would be negligible.

Density measurements were obtained on fragments of each ingot by weighing the fragments by means of an analytical balance, first in air and then in water. The densities were as follows: beryllium-53 w/o zirconium, 2.94 g per cm³; beryllium-46 w/o yttrium, 2.57 g per cm³; beryllium-52 w/o niobium, 3.14 g per cm³.

X-Ray Diffraction Studies

X-ray diffraction patterns were obtained on powdered samples of each alloy (except the copper-contaminated yttrium alloy) using a Debye-Scherrer camera and manganese-filtered iron radiation. The powdered samples were not homogenized or heat treated in any way, so that the patterns obtained represent the alloys in their as-cast condition. This procedure was intended to and, in some cases, undoubtedly has caused the suppression of equilibrium phases which form by sluggish reactions at low temperatures. It is believed that the phases which have been detected are those phases in each system which have congruent melting points; i.e., their melting points coincide with the liquidus.

The zirconium alloy produced a pattern containing at least two crystal structures. One of these was the body-centered-tetragonal structure found for the isotypes ThMn₁₂ and NbBe₁₂. The compound producing this X-ray pattern in this alloy is presumed to be ZrBe₁₂. The pattern and lattice parameters associated with this compound are shown in Table 1. The second structure was neither the face-centered-cubic (NaZn₁₃) type structure nor the hexagonal (AlB₂) type structure⁽¹⁴⁾, and it must be concluded that this unknown pattern derives from one of the compounds intermediate to ZrBe₁₂ and ZrBe₂.

The yttrium alloy produced a pattern showing one predominant crystal structure. This structure was face-centered cubic of the NaZn₁₃ (D₂₃) type; and the compound producing this X-ray pattern is presumed to be YBe₁₃. The pattern and lattice parameter associated with this compound are shown in Table 2.

The niobium alloy produced a pattern showing one predominant crystal structure. This was the body-centered tetragonal structure found for the isotypes ThMn₁₂ and NbBe₁₂. The compound producing this X-ray pattern in this alloy is presumed to be NbBe₁₂. The pattern and lattice parameters associated with this compound are shown in Table 3. It should be noted that this pattern and the pattern produced by the zirconium compound do not index precisely on a tetragonal net. This finding suggests that perhaps the structure has been incorrectly described as tetragonal or that perhaps impurities or nonequilibrium conditions have distorted the structure. The compounds NbBe₁₂ and ZrBe₁₂ found in these alloys are certainly isostructural, however.

TABLE 1. STANDARD X-RAY POWDER PATTERN OF ZrBe_{12}

d	I_0 (a)	d	I_0
3.76	0.8	1.318	0.5
3.13	0.3	1.260	0.15
2.63	1.0	1.190	0.5
2.18	0.5	1.164	0.5
1.88	0.8	1.147	0.1 (diff.)
1.795	0.2	1.126	0.6
1.68	0.3	1.087	0.4
1.65	0.3	1.067	0.6
1.46 (?)	0.05	1.045	0.5
1.425	0.3	1.037	0.4
1.405	0.4	1.027	0.3
1.39 (?)	0.1	1.0065	0.8
1.33	0.6		

Body-centered tetragonal: $a_0 = 7.48 \pm 0.03 \text{ \AA}$, $c_0 = 4.35 \pm 0.03 \text{ \AA}$.

(a) An intensity of 1.0 indicates a line of very strong or high intensity in the pattern; "diff." indicates a diffuse line.

TABLE 2. STANDARD X-RAY POWDER PATTERN OF YBe_{13}

d	I_0 (a)	d	I_0
5.12	0.8	1.37	0.8
3.62	1.0	1.280	0.1
2.96	0.6	1.242	0.8
2.56	0.4	1.204	0.6
2.29	1.0	1.172	0.5
2.09	1.0	1.144	0.4
1.81	0.2	1.117	0.6
1.70	0.5	1.091	0.5
1.61	0.7	1.045	0.8
1.54	0.5	1.024	0.3
1.48	0.4	1.004	1.0
1.42	0.6	0.985	0.8

Face-centered cubic: $a = 10.237 \pm 0.003 \text{ \AA}$.

(a) An intensity of 1.0 indicates a line of very strong or high intensity in the pattern.

TABLE 3. STANDARD X-RAY POWDER PATTERN OF NbBe₁₂

d	I ₀ (a)	d	I ₀
3.67	0.8	1.190	0.05
2.59	1.0	1.164	0.6
2.32	0.1	1.143	0.3 (diff.)
2.13	0.5	1.103	0.5
1.98	0.05	1.085	0.05 (diff.)
1.84	1.0	1.067	0.5
1.73	0.05	1.059	0.1
1.64	0.3	1.048	0.5 (diff.)
1.61	0.3	1.037	0.05
1.43	0.1	1.025	0.4
1.392	0.4	1.024	0.5
1.372	0.5	1.0185	0.5
1.301	0.6	1.008	0.08
1.288	0.5	0.9865	0.6
1.230	0.25		

Body-centered tetragonal: $a_0 = 7.34 \pm 0.02$ Å, $c_0 = 4.26 \pm 0.02$ Å.

(a) An intensity of 1.0 indicates a line of very strong or high intensity in the pattern; diffuse lines are indicated by "diff.".

FIGURE 4. AS-CAST STRUCTURE OF THE 53 w/o ZIRCONIUM-47 w/o BERYLLIUM ALLOY

Major phase present is believed to be $ZrBe_{12}$. Knoop hardness: 790 kg per mm^2 .

FIGURE 5. AS-CAST STRUCTURE OF THE 46 w/o YTTRIUM-54 w/o BERYLLIUM ALLOY

Major phase present is YBe_{13} . Grain-boundary phase is probably yttrium. Knoop hardness: 870 kg per mm^2 .

FIGURE 6. AS-CAST STRUCTURE OF THE 52 w/o NIOBIUM-48 w/o BERYLLIUM ALLOY

Major phase present is $NbBe_{12}$. The secondary phase is also a compound, possibly $NbBe_2$. Knoop hardness: 1100 kg per mm^2 .

Metallography and Hardness

Samples of each alloy in the as-cast condition were prepared for metallographic examination by grinding and polishing by standard techniques. Etching was accomplished using a solution consisting of lactic acid-50 volume per cent nitric acid, plus 5 drops of hydrofluoric acid per 100 cm³ of solution.

Photomicrographs of a typical section of each of the alloys are shown in Figures 4, 5, and 6. In no case does the secondary constituent present in each of these alloys appear to amount to more than 5 volume per cent of the alloy. The photomicrograph of the zirconium alloy shows many discontinuous hairline cracks which undoubtedly contributed to its rapid disintegration during subsequent oxidation tests. The major phase shown in Figure 4 is believed to be the beryllium-rich compound (probably ZrBe₁₂). The Knoop hardness (500-g load) of this zirconium alloy was 790 kg per mm². The yttrium alloy shows a rapid-etching grain-boundary phase, and, since there is probably only one compound, YBe₁₃, containing 43 w/o yttrium, in this system and the alloy contains 46 w/o yttrium, this grain-boundary phase probably is largely yttrium metal. The matrix is presumed to be YBe₁₃, and this had a Knoop hardness of 870 kg per mm². The niobium alloy, Figure 6, shows a few cracks which appear to be associated with the secondary phase. The lack of penetration of these cracks into the matrix suggests that the second phase is much more brittle than the primary phase. The major phase shown in Figure 6 is presumed to be NbBe₁₂. By analogy with the iron-beryllium system, the secondary phase in this alloy is also an intermetallic compound, possibly NbBe₂. This specimen had a Knoop hardness of 1100 kg per mm². None of the alloys showed any crushing or cracking under the Knoop indenter at the 500-g load. This behavior suggests that the alloys are not totally brittle in compression.

Oxidation Tests

Small, apparently solid and uncracked chunks of the as-cast ingots were placed in separate porcelain crucibles. These were covered and heated to successively higher temperatures in air. After 1 hr at each temperature, the crucibles were cooled, weighed, and then reheated to the next higher temperature in steps of 200 C starting at 300 C. The results of these tests are shown in Table 4. It is quite evident from these data that the niobium-beryllium alloy and the yttrium-beryllium alloy are very resistant to oxidation at temperatures up to 1300 C. The niobium alloy appears to be slightly more resistant to oxidation at 1300 C than the yttrium alloy. The zirconium alloy is relatively soft and friable, and because of its friability, it does not appear to have satisfactory oxidation resistance at temperatures over 700 C. The friability of the zirconium alloy is probably associated with the cracks observed in its microstructure.

TABLE 4. OXIDATION TESTS OF BERYLLIUM-RICH ALLOYS

Alloy Composition (Balance Beryllium), w/o	Initial Sample Weight, g	Temperature of 1-Hr Test, C	Total Weight Gain		Appearance
			G	Per Cent	
53 Zr	1.6318	500	0	0	Metallic
		700	0.0930	5.7	Some oxide; specimen crumbled
		900	0.2616	16	Specimen reduced to powder
46 Y	0.4673	500	0.0001	0.02	Metallic
		700	0.0005	0.1	Metallic
		900	0.0019	0.4	Metallic
		1100	0.0049	1.0	Slight oxide visible
		1300	0.0166	3.6	Flaking oxide over sound metal
49Y-0.4 Cu	0.9697	500	0.0009	0.09	Metallic
		700	0.0013	0.13	Metallic
		900	0.0075	0.8	Slight oxide visible
		1100	0.0295	3.0	Oxide visible
		1300	0.0915	9.4	Adherent oxide; specimen fragmented
52 Nb	1.5897	500	0.0008	0.05	Metallic
		700	--	--	Metallic
		900	0.0055	0.35	Metallic
		1100	0.0083	0.52	Metallic
		1300	0.0149	0.94	Metallic; flaking oxide

DISCUSSION

The properties of each of the alloys prepared are listed in Table 5. While the X-ray data leave some doubt as to the correct crystal structure of the niobium and zirconium compounds NbBe_{12} and ZrBe_{12} , it is quite clear that these compounds are isostructural with ThMn_{12} and the other MBe_{12} compounds and that, if these compounds have been correctly described as body-centered tetragonal, the niobium and zirconium compounds are likewise tetragonal. The zirconium compound can be prepared by arc melting, but it appears that castings prepared by melting may contain microcracks which will prevent the use of such castings at elevated temperatures.

Both the niobium alloy and the yttrium alloy demonstrated good behavior during melting, but the niobium alloy had the lowest rate of oxidation in air at 1300 C. The data obtained suggest that beryllium-yttrium alloys and beryllium-niobium alloys should be investigated in greater detail.

Hypothetical phase diagrams for the systems investigated are shown in Figures 7, 8, and 9. These diagrams have been drawn by taking into consideration all the data available from the literature and from this investigation. The resultant diagrams are believed to be consistent with almost all of the data available.

ACKNOWLEDGMENT

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TABLE 5. TABULATED PROPERTIES OF BERYLLIUM ALLOYS

	Beryllium-53 w/o Zirconium	Beryllium-46 w/o Yttrium	Beryllium-52 w/o Niobium
Major Constituent	ZrBe ₁₂	YBe ₁₃	NbBe ₁₂
Minor Constituent, volume per cent	~3	~5 Y	~5 NbBe ₂ (?)
Approximate Melting Point, C	2000	1600	1500
Density, g per cm ³	2.94	2.57	3.14
Knoop Hardness (500-G Load), kg per mm ²	790	870	1100
Oxidation Behavior in Air	Crumbled at 700 C	Good at 1300 C	Excellent at 1300 C
Crystallographic Isotype	ThMn ₁₂	NaZn ₁₃	ThMn ₁₂
Crystal Structure	Body-centered tetragonal	Face-centered cubic	Body-centered tetragonal
Lattice Constant, A			
a	7.48	10.237	7.34
c	4.35	--	4.26
X-Ray Density, g per cm ³	2.70	2.53	2.89

FIGURE 7. HYPOTHETICAL BERYLLIUM-NIOBIUM CONSTITUTION DIAGRAM

FIGURE 8. HYPOTHETICAL BERYLLIUM-YTTRIUM CONSTITUTION DIAGRAM

FIGURE 9. HYPOTHETICAL BERYLLIUM-ZIRCONIUM CONSTITUTION DIAGRAM

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