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SOME POSSIBLE FILLER ALLOYS WITH LOW VAPOR PRESSURES FOR REFRACTORY-METAL BRAZING

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SUMMARY

This is a compilation of eutectics and melting-point minima for binary combinations of metals having vapor pressures below 10^{-10} torr at 1500 K and 10^{-5} torr at 2000 K. These compositions and others near them on their phase diagrams are potential special brazing fillers for refractory metals. The discussion indicates some possible problems and advantages for fusion bonds of such mixtures. It also touches briefly on evaluations of brazing fillers containing refractory metals. Primarily, though, the intent is to provide the tabulation of low-vapor-pressure eutectics and melting-point minima for the consideration and convenience of those working with high-temperature, low-pressure hardware.

THE NEED FOR REFRACTORY-METAL BRAZING FILLERS

In nuclear thermionics assemblies of refractory metals and insulators are commonplace. Yet joining parts made of such materials while maintaining their effectiveness is a major problem. As a subsequent discussion indicates, just mounting simple electrode disks in a plane thermionic diode involves unusual bonding requirements. In fact fixing thermionic emitters and collectors on their bases provided the impetus for obtaining the information presented here: The primary contribution of this report is a compilation of data suggesting possible refractory-metal brazing fillers. But comments on fusion bonding with refractory-metal mixtures - as well as on metallides, which occur in many brazes, and on the Kirkendall effect (appendix) - also appear.

Often fabrication with refractory metals requires bonds made at temperatures well below the melting points of the pieces being joined. And because the designs call for refractory metals, ordinary brazing fillers are seldom acceptable. Thermally inferior bonding materials introduce high vapor pressures and low melting points - with possible formations of mixtures that liquefy at even lower temperatures. Brazing fillers are needed with vapor pressures comparable with those of the refractory metals but with relatively low fusion points and higher remelt temperatures.

Eutectics and melting-point minima for selected refractory-metal combinations offer such advantages. Even with apparent problems, which a later section treats, these compositions and their near neighbors on phase diagrams deserve some attention as special brazing fillers for refractory metals. To facilitate their consideration the present memorandum tabulates eutectics and melting-point minima for binary combinations of metals having vapor pressures below 10^{-10} torr at 1500 K and 10^{-5} torr at 2000 K. These elements in atomic-number order with their symbols, melting and boiling points, and 1500- and 2000-K vapor pressures make up table I (refs. 1 to 4).

REFRACTORY-METAL BINARY ALLOYS WITH RELATIVELY LOW MELTING POINTS

Excellent surveys on phase relationships for binary alloys appear in references 5 to 7. Taken from those references the selections in table II emphasize local low-melting-point combinations involving only the low-vapor-pressure metals of table I. The resulting tabulation lists specific elements, compounds and local maxima - but not phase-diagram fine structures. Where notes on particular mixtures are either absent or indicate "no entries," references 5 to 7 may still present information but not of the type described in the preceding two sentences.

In general table II suggests composition ranges that may yield effective brazing fillers for refractory metals. In detail table II comprises major divisions each labeled for an element of table I in atomic-number order. These primary sections in turn have subdivisions for references 5 to 7. And the secondary groupings contain respective citations for the metal given in the main title in binary combinations with the other elements of table I. The final page of table II is a brief summary of the previously described eutectics and melting-point minima, this time in fusion-temperature order.

Table II reveals that Th is very effective generally in producing possible refractory-metal brazing fillers with low melting points and low vapor pressures. Table III lists those Th-containing eutectics melting below 1500° C (from table II). Large nuclei and mild radioactivity may deter certain applications of such Th-bearing brazing fillers. But the unusual capability of Th to form potential low-melting-point, low-vapor-pressure refractory-metal brazing fillers seems worth mentioning.

Other bimetallic eutectics with fusion temperatures considerably below those of their constituents also appear in table II and merit special attention. Some of the non-Th-containing eutectics make up table IV. And the following section contains a brief discussion of the Ta, 44.5 a/o-Ir eutectic (table IV) used as a brazing filler between Ta and W and of a near-future application for the Zr, 21 a/o-Ru eutectic.

EXPERIENCE WITH BRAZES CONTAINING REFRACTORY METALS

Because few references exist on brazing with mixtures of the metals listed in table I, table II includes no evaluations. But local interest in this application began with the fusion-bond mounting of thermionic electrodes (essentially 0.64 cm in diameter and 0.32 cm thick) in the production of miniature cesium diodes (diminiodes, ref. 8). In the diminiode the base (approximately 2 cm in diameter and 3 cm long) comprises a central rod and two concentric annuli of Nb, 1%-Zr alloy pressure-bonded together at high temperatures with intervening cermet layers composed of tiny Al_2O_3-coated Nb spheres (refs. 8 and 9). The Nb, 1%-Zr; Al_2O_3-cermet base carries a conservative thermal safety factor: 1400 K is the limit for prolonged operation; short-term heating can exceed that temperature somewhat. For this reason Cu served initially as the high-temperature brazing filler to fix collector, guard assemblies on diminiode bases. As the collectors reach 1100 K, though, the vapor pressure of Cu approaches 10^{-6} torr and becomes a problem in thermionic diodes.

To obviate this difficulty the Nb, 48.2%-Ni eutectic (ref. 7) seemed a good prospect for bonding Nb collectors and guards on the Nb, 1%-Zr elements of the diminiode base. This brazing-filler composition lies between the intermetallic compounds NbNi and $NbNi_3$ (intermetallides, appendix) and melts at 1443 K compared with 1356 K for Cu, 1726 K for Ni, and 2740 K for Nb. The vapor pressure of Ni is approximately 10^{-4} times that of Cu at 1000 K. And with dilution (ref. 10) and chemical association (ref. 7) of Ni in Nb the vapor pressure of the eutectic should be considerably lower than that of Ni alone.

W. D. Klopp, Chief of the Refractory Metals and Corrosion Branch at Lewis, provided this Nb, 48.2%-Ni brazing filler in bulk and powder forms. Between the Nb pieces it joins together, this eutectic wets well upon fusing and remelts at higher temperatures. Although intermetallide brittleness and thermal-expansion differences caused some concern, the mixture containing NbNi and $NbNi_3$ apparently presents no problems when used in thin interfacial films for the diminiode application. In fact brazes with the Nb,Ni eutectic are performing more than satisfactorily.

As a result of this success and the present survey the Ta, 46%-Ir eutectic (tables II and IV) became the brazing filler selected to bypass a diffusion-bonding impasse encountered in mounting some CVD-W (chemically vapor-deposited-tungsten) diminiode emitters on their Ta holders. This eutectic between the intermetallides $TaIr_3$ and Ta_3Ir fuses at ~2220 K compared with Ir at ~2630 K, $TaIr_3$ at ~2720 K, and Ta at ~3270 K. And, of course, the dilution and chemical association of Ir in Ta should make the vapor pressure of the eutectic considerably lower than that of Ir alone, which is approximately 10^{-8} torr at 1850 K. Since that temperature is near the operating maximum for the CVD-W, Nb diode, the new brazing filler should serve well.

Upon fusing, the Ta,Ir eutectic wets the Ta and CVD-W pieces well. But the absence of a complete Ta, W, Ir phase diagram precludes an estimate of the remelt temperature. The boundaries of the ternary system appear in the Ta, W; the Ta, Ir; and the W, Ir binary phase diagrams (refs. in table II). However, the Ta,Ir and the W,Ir data indicate enough complexities to prevent even the prediction of either increasing or decreasing remelt temperatures. If the Ta,Ir eutectic brazed together only Ta pieces, the remelt temperatures would rise, of course, as for the Nb,Ni eutectic joining Nb pieces.

Again the brittleness and thermal-expansion differences for the braze containing intermetallic compounds (intermetallides, appendix) appear to cause no difficulties. To this point in the diminiode-emitter application the thin film of Ta,Ir eutectic between the Ta and CVD-W appears to be performing at least adequately.

Another eutectic revealed by the present survey may replace the Nb, 48.2%-Ni brazing filler for diminiode collector, guard assemblies. Although the latter is certainly an improvement over the originally used Cu, the great differences in the Nb and the Ni vapor pressures cause some difficulties: At its fusion point (1726 K) Ni has a vapor pressure ($\sim 10^{2.5}$ torr) over 10^8 times that of Nb. This imbalance militates against composition maintenance while producing the eutectic because Ni vaporizes far more rapidly than Nb during the melting. And, of course, any shift in concentration from that of the eutectic means an abrupt increase in the effective melting point, which is the liquidus temperature for the noneutectic compositions. Then too the Ni not the Nb dictates the low-vapor-pressure service capability in that brazing filler.

For these reasons the Zr, 22.8%-Ru eutectic melting at 1240° C (tables II and IV) is on order for evaluation as a diminiode collector brazing filler. As table I shows, Zr (melting at ~2130 K) and Ru (~2700 K) have almost identical vapor pressures, which are very low compared with those of Ni. In fact at 1500 K the vapor pressure of this Zr,Ru eutectic is less than 10^{-11} torr as opposed to somewhat below 5×10^{-5} torr for its Nb, 48.2%-Ni counterpart. These observations mean that the Zr, 22.8%-Ru eutectic should process more easily with inherently better composition control because Zr and Ru vaporize at quite similar rates which are very small relative to those of Ni. Furthermore, the phase diagrams reveal nothing to predict failure for the use of this Zr,Ru brazing filler with the Nb parts in the diminiode collector, guard assembly: The lowest melting point for Zr in Nb is a 1740° C minimum at 22% Nb; for Ru in Nb, a 1774° C eutectic at 65% Nb. These temperatures are well above the Zr, 22.8%-Ru fusion point which is considerably higher than the maxima that the brazing filler would encounter in diminiode operation. So all advance data and the experiences with the Nb,Ni and the Ta,Ir eutectics indicate probable success for Zr, 22.8% Ru in brazing diminiode collector guard, assemblies.

BRAZE POSSIBILITIES FOR HOT, VACUUM SERVICE

The present compilation of eutectics and melting-point minima for binary metallic mixtures suggests some potential brazing fillers for high-temperature, low-pressure applications. Such conditions typify environments often encountered by components of nuclear thermionic systems. And in this vein the preceding discussion of two diminiode brazes containing refractory metals indicates limited success - even for fusion bonds involving intermetallides. Because metallides occur in many brazes, more information about them appears in the appendix; there the emphasis is on thermionic-electrode problems like conduction, electron emission and reception, and the Kirkendall effect. But as stated earlier, the intended primary contribution of this report is a convenient listing of some compositions to consider for brazing refractory metal parts while maintaining their effectiveness.

Note Added in Proof

The Zr, 22.8%-Ru brazing filler (discussed in the paragraph prior to the preceding one) arrived during a time lapse in processing the present report. Initial applications of this eutectic in bonding the diminiode collector, guard configuration to its base indicate success. Molten Zr, 22.8%-Ru wets Nb well and remains machinable after subsequent solidification. And as previously stated, this new eutectic brazing filler offers substantial advantages in diminiode processing and quality over its Nb, 48.2%-Ni predecessor.

APPENDIX - PROBLEMS AND POTENTIALS OF METALLIDES

Many eutectics listed in this report involve chemical compounds comprising metals only, an important class of metallides. These intermetallides often exhibit rather nonmetallic properties that provoke questions about their effects in brazes. But the previously discussed diminiode electrode bonds indicate limited success: Certainly in thin films under little or compressive stress those two brazing fillers containing intermetallic compounds show definite promise. Perhaps intermetallides in particular and metallides in general deserve more attention. This is the tone of some excerpts taken from the introduction of "Metallides - A New Basis for Refractory Materials" (ref. 11):

> "Yet another method of strengthening metals is based on the formation of metallides, i.e., of compounds of metals with other elements /3/ (ref. 12). In the general system of inorganic compounds metallides occupy a particular position. They have a specific electron structure and may have different chemical bonds such as metallic, ionic, metallic - covalent, and covalent - ionic, etc. Because of the great variety of chemical bonds and crystal structures, metallides have also different physicochemical, mechanical, and other properties. The characteristic properties of metallides can be summarized as follows /3/:
>
> 1) they are usually more heat resistant than their components;
>
> 2) they are very hard and strong at low and elevated temperatures, but brittle at low temperatures;
>
> 3) they are considerably less weakened by heating than pure metals, solid solutions, or alloys with a heterogeneous structure;
>
> 4) they exhibit low-temperature brittleness, but the ductility of metallides tends to increase at temperatures above 0.5 to 0.7 T^{o}_{mp};
>
> 5) it has recently been found that some metallides are sufficiently ductile to be cold worked as well as hot worked;
>
> 6) they are chemically less active than their components, and are highly resistant to corrosion and oxidation at elevated temperatures;
>
> 7) metallides, like all chemical compounds, can react with one another and with other elements to form continuous and limited solid solutions, as well as ternary or more complex compounds.
>
> Many of these properties of metallides and their reactions are discussed in a special monograph /3/ (ref. 12). The mechanical and other properties of intermetallic compounds at both low and elevated temperatures are reported in /3,4/ (refs. 12 and 13) and they were discussed at the International Symposium in the USA (in 1959), and compiled in the form of a book edited by Westbrook, which has been translated into Russian /5/ (ref. 14).

Refractory metallides formed by transition metals with elements of groups IIA and IIB-VIB of the second and third short periods are of the greatest interest from the point of view of the thermal resistance of materials.

The most important heat-resistant materials are aluminides, beryllides, borides, carbides, and silicides /6,7/ (refs. 15 and 16).

Some metallides are also found in metallic systems, and as already mentioned these are ductile to a certain extent. The problem of the ductility of such compounds needs special study.

These compounds are found in the Ni-Al, Ni-Ti, Ti-Al, Ti-Ag, and other systems /8/ (ref. 5)."

In addition to these generalizations on metallides several specific comments relative to space power and to nuclear thermionic applications in particular seem apropos.

Many metallides are not only refractory but also good electrically and electronically: Metallic borides, carbides, nitrides, and silicides often have melting points comparable with those of the refractory metals and bulk conductivities that range from one to one-tenth times those of the refractory metals (ref. 4). For example, TiB_2 melts at 3250 K and conducts electric current 1.8 to 2.9 times as well on a weight basis as W between 300 and 2500 K. Common aluminides and beryllides fuse at temperatures as high as 2500 K (ref. 4), and a few of the intermetallides in table II have melting points well over 3000 K. Additional engineering data on such compounds are generally sparse and sometimes vary widely with small composition changes. But work-function values are available and run from 2.9 to 3.7 eV for aluminides, from 2.7 to 4.9 for borides, from 2.0 to 4.8 for carbides, from 3 to 4 for nitrides, and from 2.5 to 4.3 for silicides (refs. 17 and 18). Such ranges are similar to the work-function span including all metals, not just the refractory ones.

For this reason some investigators evaluated metallides as electrodes in Cs thermionic converters in the early 1960's (refs. 19 and 20, for example). But these are very complex materials compared with a metal; their phases and compositions often alter considerably with large temperature changes. So the quickest path to predictability and quality control in Cs diodes led toward high-purity refractory metals.

Specific metallides, though, still look too good to forget for thermionic applications. In this category LaB_6, which melts near 2800 K (ref. 4), serves as an excellent electron emitter in vacuum (work functions from 2.4 to 3.2 eV, refs. 17, 18, 21, 22) and gives work functions as low as 0.8 eV with adsorbed cesium. Such results imply more current, higher output voltages, and smaller plasma losses for Cs diodes with lower emitter and collector temperatures.

Closer to the specific application described in the present memorandum is the use of special refractory-metal brazes, which often contain metallides, to reduce the Kirkendall effect (ref. 23). In a simple view of that phenomenon, diffusion of the more mobile atoms in a segregated bimetallic system is compensated by a flow of vacancies in the opposite direction. So long-term, high-temperature service of a joint with abrupt concentration gradients often produces voids near the interface. For example, a thermionic emitter diffusion (or pressure) bonded to a support made of a different metal can readily develop Kirkendall symptoms during normal high-temperature diode operation. As this condition extrapolates, the growing voids decrease the transport area, reducing heat transfer and electric conduction toward a terminal state for the converter - and perhaps for the whole power-generating system.

If a bimetallic joint must be hot for a long time, lowering the concentration gradients diminishes the Kirkendall effect. As an illustration, joining Re to Nb, Mo, Ta, or W might be accomplished with a eutectic brazing filler containing Re and the other refractory metal, rather than with diffusion bonding. This approach guarantees smaller concentration gradients of compositions that occur at the interfaces in any event: If, for instance, the eutectic contains brittle intermetallides, so does a diffusion bond of the two metals. And at temperatures below the melting points of the joining metals but above those of their eutectic fillers, brazing interactions shrink the effective thicknesses of the eutectic layers while the regions of concentration changes spread and reduce Kirkendall tendencies.

That example works well, but what technique can mitigate Kirkendall effects in joints of metals that fail to form either eutectics or melting-point minima? This is an important category that contains any pair from Nb, Mo, Ta, and W except Nb in Mo. When no binary eutectic or melting-point minimum exists, one from a ternary system involving the two joining metals might serve appropriately. For pairs from Nb, Mo, Ta, and W, ternaries with Re (refs. 22 to 25), Os, or Ir look promising. But this is merely a suggestion not a prescription.

Of course, ternary alloys often contain intermetallides too, as the Ta, Ir, Nb system almost assuredly does (see table II, binary data). So these wholly metallic compounds with their unusual properties occur not uncommonly in refractory-metal fabrication - even though they are not always recognized. And they certainly deserve more attention.

These few points of interest came from background material for work initiated in the Thermionic Branch at the NASA Lewis Research Center. But undoubtedly potentialities for improvements through the use or recognition of metallides exist in many areas. For example, other developments may benefit from joining refractory metals with fusion bonds of special compositions involving metallides - similar to the intermetallide eutectics that show promise as high-temperature, low-vapor-pressure brazing fillers for diminiode emitters and collectors. The present memorandum encourages and facilitates consideration of such possibilities.

REFERENCES

1. Anon.: Advanced Materials. Materials Research Corp., Oct. 1969.

2. Gray, Dwight E., ed.: American Institute of Physics Handbook. Second ed., McGraw-Hill Book Co., Inc., 1963.

3. Anon.: Vapor-Pressure Charts. RCA, Sept. 1962.

4. Touloukian, Y. S., ed.: Thermophysical Properties of High Temperature Solid Materials. Macmillan Co., 1967.

5. Hansen, Max: Constitution of Binary Alloys. Second ed., McGraw-Hill Book Co., Inc., 1958.

6. Elliott, Rodney B.: Constitution of Binary Alloys. Second ed., First Supplement. McGraw-Hill Book Co., Inc., 1965.

7. Shunk, F. A.: Constitution of Binary Alloys. Second ed., Second Supplement. McGraw-Hill Book Co., Inc., 1969.

8. Morris, James F.: The Diminiode: A Research and Development Tool for Nuclear Thermionics. NASA TM X-2586, 1972.

9. Kaufman, Warner B.; Tischler, Richard F.; and Breitwieser, Roland: A High-Temperature, Electrically Insulating Cermet Seal Having High Strength and Thermal Conductance. Proceedings of the Thermionic Conversion Specialist Conference. IEEE, 1967, pp. 260-270.

10. Singhal, Subhash C.: High Temperature Thermodynamic Properties of Solid Refractory Metal Alloys: The Tantalum-Molybdenum, Tantalum-Tungsten and Niobium-Molybdenum Binary Systems. Ph.D. Thesis, Pennsylvania Univ., 1969.

11. Kornilov, I. I.: Metallides--A New Basis for Refractory Materials. Structure and Properties of Heat-Resistant Metals and Alloys. NASA TT F-557, 1970, pp. 40-50.

12. Kornilov, I. I.: Metallides and Reactions Among Them. Rep. JPRS-34774, TT-66-31213, Joint Publications Research Service, Mar. 29, 1966.

13. Savitskii, E. M. (D. Sherby, trans.): The Influence of Temperature on the Mechanical Properties of Metals and Alloys. Stanford Univ. Press, 1961.

14. Westbrook, J. H., ed.: Mechanical Properties of Intermetallic Compounds. John Wiley & Sons, Inc., 1960.

15. Sinel'nikova, V. S.; Podergin, V. A.; and Rechkin, V. N.: Aluminides. Izdatel'stvo Naukova Dumka, Kiev, 1965.

16. Samsonov, G. V.: Refractory Compounds of Rare Earth Metals with Nonmetals. Metallurgizdat, Moscow, 1964.

17. Fomenko, V. S.: Handbook of Thermionic Properties. G. V. Samsonov, ed. Plenum Press, 1966.

18. Schmidt, Dietrich: Cermets as Material for Thermionic Emitters with Special Regard to Barium Calcium Tungstate Tungsten Electrodes. Rep. DLR-FB-69-96, Deutsche Forschungs-und Versuchsanstalt fuer Luft-und Raumfahrt, Stuttgart, Dec. 1969.

19. Ingold, J. H.; Blue, E.; and Ozeroff, W. J.: Thermionic Converter Experiments. Adv. Energy Conversion, vol. 2, July-Sept. 1962, pp. 363-373.

20. Ingold. J. H.: Thermionic Properties of Some Refractory Metal Carbides. J. Appl. Phys., vol. 34, no. 7, July 1963, pp. 2033-2039.

21. Lafferty, J. M.: Boride Cathodes. J. Appl. Phys., vol. 22, no. 3, Mar. 1951, pp. 299-309.

22. Ahmed, H.; and Broers, A. N.: Lanthanum Hexaboride Electron Emitter. J. Appl. Phys., vol. 43, no. 5, May 1972, pp. 2185-2192.

23. Dekker, Adrianus J.: Solid State Physics. Prentice-Hall, Inc., 1957.

24. Savitskii, E. M.; Tylkina, M. A.; and Povarova, K. B.: Rhemium Alloys. Rep. TT-69-55081, National Science Foundation, 1970.

25. Gonser, B. W., ed.: Rhenium. American Elsevier Publ. Co., Inc., 1962.

26. Povarova, K. B.; Tylkina, M. A.; and Savitskii, E. M.: Refractory Ternary Alloys of the Tungsten-Molybdenum-Rhenium System. Structure and Properties of Heat-Resistant Metals and Alloys. NASA TTF-557, 1970, pp. 82-88.

27. Quarrell, Arthur G., ed.: Niobium, Tantalum, Molybdenum and Tungsten. Elsevier Publ. Co., 1961.

TABLE I. - METALS WITH LOW VAPOR PRESSURES

At. no.	Element (symbol)		Approximate first-order transitions, °K								Vapor pressures, torr			
			Ref. 1		Ref. 2		Ref. 3		Ref. 4		Ref. 3		Ref. 4	
			M.Pt.	B.Pt.	M.Pt.	B.Pt.	M.Pt.	B.Pt.	M.Pt.	B.Pt.	1500 K	2000 K	1500 K	2000 K
40	Zirconium	(Zr)	2100	5270	2130	4650	2130	4760	2140	---	1×10^{-11}	2×10^{-6}	---	7×10^{-6}
41	Niobium	(Nb)	2690	----	2740	----	2760	4650	2740		$<1\times10^{-15}$	5×10^{-9}	---	----
42	Molybdenum	(Mo)	2890	5070	2880	----	2890	4910	2900	---	$<3\times10^{-13}$	2×10^{-7}	---	5×10^{-7}
43	Technetium	(Tc)	2410	----	----	----	2400	4900	----	----	$<6\times10^{-13}$	3×10^{-7}	---	----
44	Ruthenium	(Ru)	2670	5170	2700	4000	2700	4380	2760	----	$<4\times10^{-12}$	1×10^{-6}	---	8×10^{-10}
72	Hafnium	(Hf)	2400	5670	2500	----	2400	4740	2500	----	1×10^{-11}	2×10^{-6}	---	----
73	Tantalum	(Ta)	3270	5570	3270	5700	3270	5480	3270	----	$<4\times10^{-17}$	5×10^{-11}	---	3×10^{-10}
74	Tungsten	(W)	3650	6170	3650	5800	3640	5810	3650	----	$<1\times10^{-18}$	4×10^{-12}	---	1×10^{-10}
75	Rhenium	(Re)	3440	6170	3450	5900	3450	5940	3450	----	$<2\times10^{-16}$	1×10^{-10}	---	$\sim1\times10^{-8}$
76	Osmium	(Os)	2970	5770	3270	4500	3320	5250	2970	----	$<2\times10^{-16}$	$<3\times10^{-10}$	----	----
77	Iridium	(Ir)	2720	5570	2720	4400	2720	4800	2730	----	$<1\times10^{-12}$	2×10^{-7}	----	----
90	Thorium	(Th)	2070	4770	1970	4500	1960	5000	1980	----	5×10^{-11}	3×10^{-6}	----	2×10^{-5}

TABLE II. - EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

<u>Zr</u>:

Ref. 5:

Zr, Nb: minimum at ~22 atomic percent (a/o) Nb melting at 1740° C (between Zr at ~1860° C and Nb at 2435° C).

Zr, Mo: eutectic at ~30 a/o Mo melting at 1520±15° C (between Zr at ~1850° C and $ZrMo_2$ at 1880±20° C, Mo at ~2625° C).

Zr, Hf: melting point (solidus or liquidus) increases monotonically from 1860° C (Zr) to 2230° C (Hf).

Zr, Ta: eutectic at ~11 a/o Ta melting at ~1850° C (between Zr at 1920° C and possibly Zr_3Ta_2 or ZrTa, Ta at ~3000° C).

Zr, W : eutectic at 10 a/o W melting at ~1660° C (between Zr at 1852° C and ZrW_2 at 2150° C, W at 3410° C).

Zr, Th: minimum at ~54 a/o Th melting at ~1275° C or ~1350° C (between Zr at 1820° C and Th at 1675° C).

Ref. 6:

Zr, Nb: minimum at 21.7 a/o Nb melting at 1740° C (between Zr at 1850° C and Nb at 2460° C).

Zr, Hf: melting point (solidus or liquidus) increases monotonically from 1850° C (Zr) to 2220° C (Hf).

Zr, Ta: minimum (eutectic in ref. 5) at 14.4 a/o Ta melting at 1820±15° C (between Ta at 2940° C and Zr at 1830° C).

Zr, Re: eutectic at ~14 a/o Re melting at 1600° C (between Zr at 1860° C and Zr_2Re at 1900° C, $ZrRe_2$ at 2450° C, Zr_5Re_{24} at 2500° C, Re at 3160° C).

Zr, Th: minimum at 54 a/o Th melting at 1290±10° C (for alloys made of Zr containing 1 a/o Hf).

Ref. 7:

Zr, Ru: eutectic at ~26 a/o Zr melting at 1840±20° C (between Ru at 2280° C and $ZrRu_2$ at 1960±50° C), eutectic at ~79 a/o Zr melting at 1240±10° C (between ZrRu at ~2100° C and Zr at 1850° C

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Ref. 7 (Continued):

Zr, Ta: minimum at 15 a/o Ta melting at 1875^{o} C (results preferred over those of refs. 5 and 6)

Zr, W: eutectic melting at 1660 ± 25^{o} C (ZrW_2 at 2260^{o} C) (see ref. 5)

Zr, Re: use Zr,Re diagram of ref. 5 with caution

Nb:

Ref. 5:

Nb, Zr: see Zr, Nb

Nb, Th: eutectic at 18 a/o Nb melting at 1435^{o} C (between Th at 1700^{o} C and Nb at 2420^{o} C)

Ref. 6:

Nb, Zr: see Zr, Nb

Nb, Mo: minimum at 19.5 to 29.3 a/o Mo melting at 2345 to 2350^{o} C (between Nb at 2450^{o} C and Mo at 2630^{o} C)

Nb, Ta: melting point (solidus or liquidus) increases monotonically from 2420^{o} C (Nb) to 2940^{o} C (Ta)

Nb, W: melting point (solidus or liquidus) increases monotonically from 2450^{o} C (Nb) to 3400^{o} C (W)

Nb, Re: eutectic at 48 ± 1 a/o Re melting at 2435 ± 10^{o} C, eutectic at 88 ± 0.5 a/o Re melting at 2715 ± 15^{o} C (Nb at 2470^{o} C and Re at 3180^{o} C)

Ref. 7:

Nb, Mo: minimum at 34.3 a/o Mo melting at 2290^{o} C (see ref. 6)

Nb, Ru: local minimum at 39 a/o Ru melting at 1870^{o} C (between Nb at 2450^{o} C and a local maximum at 50 a/o Ru, but not designated as NbRu, melting at 1942^{o} C), eutectic at 65 a/o Ru melting at 1774^{o} C (between the previously mentioned local maximum at 1942^{o} C and Ru at 2270^{o} C, $NbRu_3$ below 1540^{o} C only)

Nb, Hf: minimum at ~75 a/o Hf melting at 2100^{o} C (between Nb at 2470^{o} C and Hf at 2190^{o} C)

Nb, W: in agreement with ref. 6

B

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Nb, Ref. 7 (Continued):

Nb, Ir: eutectic at 20 a/o Ir melting at 2110° C (between Nb at 2470° C and Nb_3Ir at 2130° C), eutectic at 45 a/o Ir melting at 1840° C (between Nb_3Ir and $NbIr_3$ at 2440° C), eutectic at ~83.5 a/o melting at 2400° C (between $NbIr_3$ and Ir at 2440° C)

Mo:

Ref. 5:

Mo, Zr: see Zr, Mo

Mo, Ta: melting point (solidus or liquidus) increases monotonically from 2620° C (Mo) to 3000° C (Ta)

Mo, W: melting point (solidus or liquidus) increases monotonically from 2500° C (Mo) to 3250±50° C (W)

Ref. 6:

Mo, Nb: see Nb, Mo

Mo, Ru: eutectic at 41.6 a/o Ru melting at 1945° C (between Ru at 2310° C and Mo at 2620° C, Mo_5Ru_3 below 1920° C only)

Mo, Hf: eutectic at 41.5 a/o Mo melting at 1930° C (between Hf at 2210° C and $HfMo_2$ at ~2180° C, Mo at 2620° C)

Mo, Ta: agrees with ref. 5

Mo, Re: eutectic at 50 a/o Re melting at 2440° C (between Mo at 2620° C and Re at 3200° C)

Mo, Os: eutectic at 18 a/o Os melting at ~2430° C (Mo at 2610° C, Mo_3Os below 2100° C only)

Mo, Th: simple eutectic at 15.4 a/o Mo melting at 1380° C

Ref. 7:

Mo, Zr: see Zr, Mo

Mo, Nb: see Nb, Mo

Mo, W: supports results given in ref. 5

Mo, Os: eutectic at ~21 a/o Os melting at 2380±10° C (between Mo at 2620° C and Os at 2970° C, Mo_3Os below 2210±10° C only)

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Mo, Ref. 7 (continued):

Mo, Ir: eutectic at 69 a/o Mo melting at 2080±5° C (between Ir at 2380° C and Mo at 2620° C, pure Mo_3Ir below 1975±5° C only)

Mo, Th: eutectic at 84.6±1 a/o Th melting at 1380±10° C (between Mo at 2620° C and Th at 1750° C)

Tc: no entries

Ru:

Ref. 5: no entries

Ref. 6:

Ru, Mo: see Mo, Ru

Ru, Ta: eutectic at ~29 a/o Ta melting at 1970° C (between Ru at 2280° C and Ta at 3010° C)

Ru, W: eutectic at ~55 a/o W melting at ~2205° C (Ru at 2282° C)

Ru, Th: eutectic at 16±1 a/o Ru melting at 1262±12° C (between Th and Th_7Ru_3)

Ref. 7:

Ru, Zr: see Zr, Ru

Ru, Nb: see Nb, Ru

Ru, Ta: confirms phases given in Ref. 6 but shifts compositions somewhat; eutectic details not given

Ru, Re: melting point (solidus or liquidus) increases monotonically from 2250° C (Ru) to 3170° C (Re)

Ru, Os: melting point (solidus or liquidus) increases monotonically from 2250° C (Ru) to 3050° C (Os)

Ru, Ir: melting point (solidus or liquidus) increases monotonically from 2280° C (Ru) to 2450° C (Ir)

Ru, Th: eutectic at 27 a/o Th melting at ~1535° C (between Ru and $ThRu_2$), eutectic at 43 a/o Th melting at 1438±12° C (between $ThRu_2$ and ThRu at 1462±12° C), eutectic at 59 a/o Th melting at 1388±12° C (between ThRu and Th_3Ru_2 at 1425±12° C), eutectic at 63 a/o Th melting at 1388±12° C (between Th_3Ru_2 and Th_7Ru_3 at 1412±12° C), eutectic at 84 a/o Th melting at 1262±12° C (between Th_7Ru_3 and Th)

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

<u>Hf</u>:

Ref. 5:

Hf, Zr: see Zr, Hf

Ref. 6:

Hf, Zr: see Zr, Hf

Hf, Mo: see Mo, Hf

Hf, Ta: minimum at ~20 a/o Ta melting at 2100° C (between Hf at 2220° C and Ta at 3000° C)

Hf, W: eutectic at 22±1 a/o W melting at 1930±10° C (between Hf at 2220° C and HfW_2 at ~2650° C, W at 3380° C)

Hf, Re: eutectic at 19 a/o Re melting at ~1880° C (between Hf at 2205° C and "$Hf_{11}Re_9$" at ~2780° C, $HfRe_2$ at 3280° C), eutectic at ~92.5 a/o Re melting at ~2880° C (between $HfRe_7$ at ~2980° C and Re at ~3200° C)

Hf, Th: eutectic at 68.4 a/o Th melting at 1450° C (between Hf at 2150° C and Th at 1760° C)

Ref. 7:

Hf, Nb: see Nb, Hf

Hf, Ta: minimum at 19.8 a/o Ta melting at 2110° C (between Hf at 2220° C and Ta at ~3000° C)

Hf, Re: eutectic at 23.5 a/o Re melting at 1840±15° C (between Hf at 2190° C and HfRe at 2445±15° C), eutectic at ~91.5 a/o Re melting at 2930±15° C (between $HfRe_2$ at ~3160° C and Re at 3170° C)

Hf, Ir: eutectic at ~16.9 a/o Ir melting at 1430° C (between Hf at 2215° C and Hf_2Ir at ~1720° C, Hf_3Ir_2 at 1920° C), eutectic at 62.3 a/o Ir melting at 2080° C (between HfIr at ~2400° C and $HfIr_3$ at ~2465° C), eutectic at ~85.1 a/o Ir melting at 2240° C (between $HfIr_3$ and Ir at 2350° C)

<u>Ta</u>:

Ref. 5:

Ta, Zr: see Zr, Ta

Ta, Mo: see Mo, Ta

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Ta, ref. 5 (continued):

Ta, W: "a continuous series of solid solutions."

Ref. 6:

Ta, Zr: see Zr, Ta

Ta, Nb: see Nb, Ta

Ta, Mo: see Mo, Ta

Ta, Ru: see Ru, Ta

Ta, Hf: see Hf, Ta

Ta, W: "miscible in all proportions"

Ta, Re: eutectic at 50.3 a/o Re melting at 2690° C (between Ta at 2940° C and a local maximum (78.5 a/o Re) at 2790° C), eutectic at 83.6 a/o Re melting at 2755° C (between the local maximum (78.5 a/o Re) and Re at 3180° C)

Ta, Os: eutectic at ~53 a/o Ta melting at ~2360° C (between Os at 3000° C and Ta at 3000° C)

Ta, Th: eutectic at 96.8 a/o Th melting at 1565±10° C (between Th at 1700° C and Ta at 2940° C)

Ref. 7:

Ta, Zr: see Zr, Ta

Ta, Ru: see Ru, Ta

Ta, Hf: see Hf, Ta

Ta, Ir: eutectic at 55.5±0.5 a/o Ta melting at 1950±15° C (between Ta at 3000° C and $TaIr_3$ at ~2450° C, Ta_3Ir mentioned but temperature of formation not given, Ir at 2357±25° C)

W:

Ref. 5:

W, Zr: see Zr, W

W, Mo: see Mo, W

W, Ta: see Ta, W

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

W (continued):

Ref. 6:

W, Zr: see Zr, W

W, Nb: see Nb, W

W, Ru: see Ru, W

W, Hf: see Hf, W

W, Ta: see Ta, W

W, Re: eutectic at 74 a/o Re melting at 2825° C (between W at 3380° C and Re at 3180° C)

W, Os: eutectic at ~58 a/o W melting at 2725° C (between Os at 2970° C and W at 3380° C)

W, Th: eutectic at ~8 a/o W melting at ~1380° C

Ref. 7:

W, Nb: see Nb, W

W, Mo: see Mo, W

W, Ir: eutectic at ~21 a/o W melting at 2305±25° C (between Ir at 2378° C and a local maximum (~58 a/o W) at 2490° C), eutectic at ~70 a/o W melting at 2460±25° C (between the local maximum (~58 a/o W) and W at 3380° C)

Re:

Ref. 5: no entries

Ref. 6:

Re, Zr: see Zr, Re

Re, Nb: see Nb, Re

Re, Mo: see Mo, Re

Re, Hf: see Hf, Re

Re, Ta: see Ta, Re

Re, W: see W, Re

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Re (continued):

Ref. 7:

Re, Zr: see Zr, Re

Re, Ru: see Ru, Re

Re, Hf: see Hf, Re

Re, Os: melting point (solidus or liquidus) increases monotonically from 3050° C (Os) to 3170° C (Re)

Re, Ir: liquidus temperatures increase monotonically from 2450° C (Ir) to 3170° C (Re); solidus temperatures increase monotonically from 2450° C to 2800±25° C at ~36 a/o Re, remain there up to ~56 a/o Re, then increase monotonically to 3170° C

Os:

Ref. 5: no entries

Ref. 6:

Os, Mo: see Mo, Os

Os, Ta: see Ta, Os

Os, W: see W, Os

Ref. 7:

Os, Mo: see Mo, Os

Os, Ru: see Ru, Os

Os, Re: see Re, Os

Os, Ir: liquidus temperatures increase monotonically from 2450° C (Ir) to 3030° C (Os); solidus temperatures increase monotonically from 2450° C to 2660±35° C at ~46 a/o Os, remain there up to ~62 a/o Os, then increase monotonically to 3030° C

Os, Th: eutectic at 13±1 a/o Os melting at 1287±12° C (between Th and Th_7Os_3), eutectic at 36±1 a/o Os melting at 1485±15° C (between Th_7Os_3 and $ThOs_x$), eutectic at 85±1 a/o Os melting at >1500° C (between $ThOs_2$ and Os)

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Ir:

Ref. 5: no entries

Ref. 6: no entries

Ref. 7:

Ir, Nb: see Nb, Ir

Ir, Mo: see Mo, Ir

Ir, Ru: see Ru, Ir

Ir, Hf: see Hf, Ir

Ir, Ta: see Ta, Ir

Ir, W: see W, Ir

Ir, Re: see Re, Ir

Ir, Os: see Os, Ir

Ir, Th: eutectic at ~10 a/o Th melting at >1500° C (between Ir and $ThIr_5$), eutectic at ~43 a/o Th melting at >1500° C (between $ThIr_2$ and ThIr), eutectic at 65±1 a/o Th melting at 1462±12° C (between $ThIr_x$ and Th_7Ir_3), eutectic at 85±1 a/o Th melting at 1337±12° C (between Th_7Ir_3 and Th)

Th:

Ref. 5:

Th, Zr: see Zr, Th

Th, Nb: see Nb, Th

Ref. 6:

Th, Zr: see Zr, Th

Th, Mo: see Mo, Th

Th, Ru: see Ru, Ta

Th, Hf: see Hf, Th

Th, Ta: see Ta, Th

Th, W: see W, Th

TABLE II. - Continued. EUTECTICS AND MELTING-POINT MINIMA FOR BINARY COMBINATIONS OF REFRACTORY METALS (FROM TABLE I)

Th (continued):

Ref. 7:

Th, Mo: see Mo, Th

Th, Ru: see Ru, Th

Th, Os: see Os, Th

Th, Ir: see Ir, Th

TABLE II. - Concluded. SUMMARY IN MELTING-POINT

ORDER (APPROXIMATE VALUES)

Composition atomic percent	Fusion point ^{o}C	Composition atomic percent	Fusion point ^{o}C
Th	1720	Zr, 14-Re	1600
Zr	1860	Zr, 10-W	1660
Hf	2210	Zr, 21.7-Nb	1745
Ru	2280	Nb, 65-Ru	1770
Nb	2450	Zr, 74-Ru	1840
Ir	2460	Nb, 45-Ir	1840
Mo	2610	Hf, 23.5-Re	1840
Ta	2980	Zr, 14.4-Ta	1850
Os	3010	Nb, 39-Ru	1870
Re	3180	Mo, 41.5-Hf	1930
W	3380	Hf, 22-W	1930
		Mo, 41.6-Ru	1945
Zr, 21-Ru	1240	Ta, 44.5-Ir	1950
Ru, 84-Th	1260	Ru, 29-Ta	1970
Os, 87-Th	1285	Mo, 31-Ir	2080
Zr, 54-Th	1300	Hf, 62.3-Ir	2080
Ir, 85-Th	1340	Nb, 75-Hf	2100
Mo, 84.6-Th	1380	Nb, 20-Ir	2110
W, 92-Th	1380	Ru, 55-W	2205
Ru, 59-Th	1390	Hf, 85.1-Ir	2240
Ru, 63-Th	1390	Nb, 34.3-Mo	2290
Hf, 16.9-Ir	1430	W, 79-Ir	2305
Nb, 82-Th	1435	Ta, 47-Os	2360
Ru, 43-Th	1440	Mo, 21-Os	2380
Hf, 68.4-Th	1450	Nb, 48-Re	2435
Ir, 65-Th	1460	Nb, 83.5-Ir	2440
Os, 64-Th	1485	Mo, 50-Re	2440
Os, 15-Th	>1500	W, 30-Ir	2460
Ir, 10-Th	>1500	Ta, 50.3-Re	2690
Ir, 43-Th	>1500	Nb, 88-Re	2715
Zr, 30-Mo	1520	W, 42-Os	2725
Ru, 27-Th	1535	Ta, 83.6-Re	2755
Ta, 96.8-Th	1565	W, 74-Re	2825
		Hf, 91.5-Re	2980

TABLE III. - Th-CONTAINING BIMETALLIC EUTECTICS MELTING

BELOW 1500° C FROM TABLE II (APPROXIMATE VALUES)

Amount of second metal, atomic percent		Fusion point, °C	Amount of second metal, atomic percent		Fusion point, °C
46	Zr	1300	31.6	Hf	1450
18	Nb	1435			
15.4	Mo	1380	8	W	1380
16	Ru	1260	13	Os	1285
37	Ru	1390	36	Os	1485
41	Ru	1390	15	Ir	1340
57	Ru	1440	35	Ir	1460

TABLE IV. - SOME NON-Th-CONTAINING BIMETALLIC EUTECTICS

FROM TABLE II (APPROXIMATE VALUES)

Composition, atomic percent	Fusion point, °C	Composition, atomic percent	Fusion point, °C
Zr, 30-Mo	1520	Ru, 29-Ta	1970
Zr, 21-Ru	1240	Hf, 22-W	1930
Zr, 10-W	1660	Hf, 23.5-Re	1840
Zr, 14-Re	1600	Hf, 16.9-Ir	1430
Nb, 39-Ru	1870	Ta, 50.3-Re	2690
Nb, 65-Ru	1770	Ta, 47-Os	2360
Nb, 45-Ir	1840	Ta, 44.5-Ir	1950
Mo, 41.6-Ru	1945	W, 74-Re	2825
Mo, 41.5-Hf	1930	W, 42-Os	2725
Mo, 31-Ir	2080		