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C-44a Nuclear Technology—Materials

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CLASSIFICATION CHANGED TO:
BY AUTHORITY OF: AEC 9-6-66
BY: Gx Schermeister 7-18-67

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EFFECT OF ALLOYING ELEMENTS ON THE STRENGTH, STABILITY, AND CORROSION AND OXIDATION RESISTANCE OF COLUMBIUM

A LITERATURE SURVEY

D. O. Hobson

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ORNL-3212

C-44a Nuclear Technology—
Materials
M-3679 (25th ed.)

Contract No. W-7405-eng-26

METALLURGY DIVISION

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EFFECT OF ALLOYING ELEMENTS ON THE STRENGTH, STABILITY, AND CORROSION AND OXIDATION RESISTANCE OF COLUMBIUM

D. O. Hobson

ABSTRACT

This survey attempts to compile data relating the effect of additions of W, Re, Ta, Mo, Hf, V, Cr, Zr, Ti, and Al on the strength, oxidation resistance, corrosion resistance, aging characteristics, and compositional stability of columbium.

All the above elements improved the strength of columbium. Generally, this is accompanied by a decrease in ductility, especially with rhenium, molybdenum, tungsten, and zirconium. On the basis of strengthening and the retention of low-temperature ductility, the addition of vanadium gives the best results.

Oxidation resistance is obtained in columbium only when alloyed with large additions of elements which result in the formation of brittle intermetallics. It is believed that a fabricable, oxidation-resistant columbium-base alloy does not presently exist. Coatings are available which give good oxidation resistance, but these are subject to thermal damage and chemical incompatibility; therefore, more research is required.

Theories are presented as to the effect of alloying on the corrosion resistance of columbium in molten lithium. It is noted that the corrosion of unalloyed columbium can be correlated with its oxygen content.

Data on the aging of columbium are presented and a mechanism by which this aging might occur is described.

It is concluded that a columbium-vanadium alloy with an oxygen-scavenging third element can produce an alloy combining the best properties of strength, ductility, corrosion resistance, and high-temperature stability.

INTRODUCTION

It is well-known that extensive research has been carried out to develop alloys which combine the properties desirable for elevated temperature service, namely, good fabricability into a variety of shapes, good weldability, high strength, good ductility, adequate ductility which is not significantly impaired by a prolonged thermal exposure,

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good oxidation resistance, and good corrosion resistance in various environments. In this connection, emphasis is currently being placed on the refractory metals, columbium, tantalum, molybdenum, and tungsten, because of their potential in pushing forward the so-called "thermal barrier" which restricts the useful operating temperature for conventional iron-, nickel-, and cobalt-base alloys. Two of the most authoritative properties of the refractory metals are their high melting points and their strength. Unfortunately, these metals all have very poor oxidation resistance.

One of the principal interests in the refractory metals at the Oak Ridge National Laboratory (ORNL) is the use of columbium or a columbium-base alloy as the structural material for a high-temperature, liquid-metal-cooled reactor. Preliminary studies have been carried out which have demonstrated the usefulness of columbium and particularly the alloy Cb–1% Zr for this application. The continuation of these studies will have as an objective the optimization of the properties of columbium through alloying; thus, this survey summarizes the effects that have been found of various alloying elements on enhancing the strength, corrosion resistance, fabricability, and/or oxidation resistance of columbium and its alloys by numerous investigators since 1957. Data generated prior to this time were generally subject to substantial variation due to uncontrolled contamination of the metal and are therefore not included.

STRENGTH

Since columbium is easily contaminated with oxygen and other impurities and since data on the testing atmospheres used by various concerns are usually unavailable, no effort will be made to report the virtually nonexistent long-time creep data. Instead, relatively short-time tensile data will be used.

High-purity unalloyed columbium is one of the weaker refractory metals. Typical strength data are given in Table 1.

The strength of unalloyed columbium is very dependent upon the impurity level. Carbon, oxygen, nitrogen, and hydrogen all contribute to the strength of columbium. Carbon has perhaps the smallest strengthening effect on unalloyed columbium. A carbon increase of from 0.035 to 0.53 wt % causes an

Table 1. Typical Strengths of Unalloyed Columbium

Material	Analysis (ppm) O	C	N	Test Temperature (°C)	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Data Source
Arc-Melted, Recrystallized Condition	200	86	54	Room Temperature	26,000	15,500	a
Electron-Beam Melted, Recrystallized Condition	200	200	260	Room Temperature	40,000	21,000	b
Electron-Beam Melted, Recrystallized Condition	200	200	260	1095	~ 9,000	~ 7,500	c
Electron-Beam Melted, Recrystallized Condition	220	30	100	982	6,900	3,500	

[a]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part II, pp. 6–7 (1959).

[b]Unpublished data by author.

[c]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, pp. 56, 61 (1961).

increase in the ultimate tensile strength from approx 38,000 to approx 44,000 psi (ref 1). Tottle[2] has reported that the ultimate tensile strength of columbium is raised from 41,000 to 131,250 psi by an oxygen increase from 0.03 to 0.41 wt %.

According to Begley et al.,[3] nitrogen additions up to 0.06 wt % greatly increase the as-cast hardness of columbium. A nitrogen increase from

[1]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 34 (1961).

[2]C. R. Tottle, "The Physical and Mechanical Properties of Niobium," J. Inst. Metals 85, 375 (1956–57).

[3]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 12 (1961).

approx 0.01 to 0.06 wt % caused a hardness change of approx 100 VPN. A further nitrogen increase, from 0.06 to approx 0.72 wt %, caused a further hardness change of only 55 VPN.

Recent work by McCoy[4] has shown that the strength of columbium is increased with oxygen additions with no great loss in ductility. Environmental stress-rupture tests were made at elevated temperatures in argon, wet argon, nitrogen, wet hydrogen, and dry hydrogen. The creep rate was decelerated by the presence of nitrogen and accelerated by hydrogen or water vapor.

Strengths greater than those of unalloyed columbium can be achieved by two methods: interstitial or precipitation strengthening and solid-solution alloying.

Interstitial or Precipitation Strengthening

According to generally accepted theory, substantial amounts of hardening and strengthening can be obtained in an alloy in which interstitial or precipitate particles are present in the correct size, shape, and number. As shown above, the presence of oxygen, nitrogen, or carbon in the lattice of unalloyed columbium produces wide variations in the strength or hardness.

Recent work by the author[5] has demonstrated that a Cb–1% Zr alloy is capable of aging with a resultant increase in hardness and strength. The preliminary results found in this work indicated that carbides and/or nitrides might be responsible for the observed aging. However, later work showed that oxygen, precipitated as ZrO_2, was the main agent in the strengthening process. It is postulated that in columbium-base alloys the addition of a minor alloying element having a greater affinity than columbium for carbon, nitrogen, or oxygen would decrease the solid solubility of these impurities with a subsequent precipitation resulting. It would appear from this study that commercial, age-hardenable refractory alloys can be developed, although more work is required to demonstrate the elevated temperature stability of such alloys.

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[4]H. E. McCoy and D. A. Douglas, Jr., "Effect of Various Gaseous Contaminants on the Strength and Formability of Columbium," pp. 85–118 in Columbium Metallurgy, Vol. 10, ed. by D. L. Douglass and F. W. Kunz, Interscience, New York, 1961

[5]D. O. Hobson, "Aging Phenomena in Columbium-Base Alloys," paper presented at High Temperature Materials Conference, AIME, Cleveland, April 26–7, 1961.

Solid-Solution Strengthening

The most dependable method for achieving high strengths with accompanying high-temperature stability is through the use of solid-solution alloying additions. Table 2 lists elements considered as strengthening additions to columbium.

These elements are considered both as single additions to columbium and as alloying additions in more complex columbium-base alloys in the following sections.

Table 2. Solubilities of Strengthening Elements

Element	Solid Solubility	Data Source
W	Unlimited	a
Re	60 wt % Re @ 1200°C	a
Ta	Unlimited	a
Mo	Unlimited	a
Hf	72 wt % Hf @ 1000°C	a
V	Unlimited	a
Zr	Unlimited above ~ 1000°C	a
Cr	16 wt % Cr @ 1650°C	b
Al	2 wt % (est)	c
Ti	Unlimited above 850°C	a

[a] M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.

[b] V. P. Elintin and V. F. Funke, "Some Data on the Equilibrium Diagram of the Chromium-Niobium System," Acad. Sci. U. S. S. R. 3, 68–76 (1956).

[c] W. Hume-Rothery, The Structure of Metals and Alloys, The Inst. of Metals (London) (1954).

Tungsten

Tungsten forms a continuous series of solid solutions with columbium. Begley et al.,[6,7] investigated the strength of columbium-tungsten alloys at room temperature and 1095°C (2000°F) and compositions from 1 to 20 wt %. Results of this work, which are presented in Table 3, show that the ductilities

[6] R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part IV, pp. 56–7 (1960).

[7] R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, pp. 48–9 (1961).

Table 3. Effect of Tungsten Additions on the Strength of Columbium

Composition, wt % W	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)
0.87	Room Temperature	48,150	44,200	36
0.87	1095	11,590	10,800	25
2.47	1095	13,990	11,500	23
9.72	Room Temperature	64,650	43,250	34
9.72	1095	22,040	19,500	41
19.9	Room Temperature	82,600	81,600	0.2
19.9	1095	34,800	26,500	18

of the alloys generally decreased and the strength increased with increasing tungsten content with virtually no ductility in the 20 wt % W alloy at room temperature.

Arc-melted alloys containing 10, 20, 30, 40, and 50 wt % (nominal) tungsten were hot forged at 1200°C (2200°F). The 10, 20, and 30 wt % W alloys reduced approx 70%, with some edge cracking in the 20 and 30% specimens. Specimens containing 40 and 50 wt % W reduced approx 60%, with severe edge cracking. The as-cast hardness of the alloys ranged from 120 VPN for unalloyed columbium to 420 VPN for the 50 wt % W alloy.

Ternary and more complex alloys of columbium and tungsten have been investigated by various concerns. Perhaps the outstanding alloy from a strength standpoint is the F-48 alloy (Cb—15% W—5% Mo—1% Zr) developed by General Electric Flight Propulsion Laboratory.[8] Table 4 lists the tensile properties of the alloy.

While the F-48 alloy has great strength at elevated temperatures, it also has associated problems of fabrication. Due to its high-temperature strength, the alloy ingot must be forged at temperatures from 1550 to 1650°C and subsequently hot rolled at 1200°C.

[8] T. K. Redden, "Processing and Properties of F-48 Columbium Alloy Sheet," Columbium Metallurgy, Vol. 10, ed. by D. L. Douglass and F. W. Kunz, Interscience, New York, 1961.

Table 4. Tensile Properties of F-48 Sheet*

Material: Heat S90T, 0.040-in. Sheet
Condition: 1200°C, 1 hr, vacuum stress relief
Test Conditions: Vacuum, strain rate 0.1 in./in.-min, held 15 min at temperature before test

Test Temperature (°C)	Ultimate Strength (psi)	0.2% Yield Strength (psi)	Elongation (% in 1 in.)
- 54	136,500	125,000	17
- 54	139,900	127,200	12
25	121,000	100,400	16
25	118,200	99,900	17
538	79,100	75,800	8
538	83,800	74,500	7
871	78,500	72,500	8
871	79,200	72,200	7
1093	65,300	59,000	9
1093	63,700	57,200	11
1204	53,100	45,500	16
1204	53,800	48,100	15
1286	45,200	39,000	20
1286	43,100	38,000	15
1371	32,300	27,900	36
1371	34,000	30,000	22
1483	24,800	22,800	55
1483	24,300	23,700	54

*T. K. Redden, "Processing and Properties of F-48 Columbium Alloy Sheet," p. 286 in Columbium Metallurgy, Vol. 10, ed. by D. L. Douglass and F. W. Kunz, Interscience, New York, 1961.

Tensile test data on alloys of the Cb-Ti-W-V and Cb-Ti-W-V-Zr systems developed by Pratt & Whitney Aircraft are shown in Table 5.[9] These alloys, with tungsten as the major alloying element, are stronger than the binary columbium-tungsten alloys tested at Westinghouse but are not as strong as the General Electric F-48 alloy.

Another experimental alloy developed by Union Carbide Metals Company[10] is Cb-74, a nominal Cb–5 wt % Zr–10 wt % W alloy. Tensile data are given in Table 6.

[9]PWAC-594, p. 120 (Oct.–Dec., 1959) (classified).

[10]Data sheets from Union Carbide Metals Company, 1961.

Table 5. Tensile Test Data on Pratt & Whitney Alloys

Nominal Composition (wt %)	Test Temp (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	% Reduction in Area
Cb-10 Ti-20 W-3 V	1200	26,800	23,400	60	83
Cb-10 Ti-20 W-3 V	1093	> 32,700	22,400	> 16	--
Cb-10 Ti-20 W-3 V	1000	49,300	40,800	32	59
Cb-10 Ti-20 W-3 V-2 Zr	1000	68,400	65,200	6	36
Cb-10 Ti-20 W-3 V-2 Zr	1200	31,800	25,800	25	34

Table 6. Tensile Properties of Union Carbide Metals Company Alloy (Cb-74)

Condition	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Elongation (% in 1 in.)
Stress Relieved, 1095°C	Room Temperature	115,300	101,200	21
Recrystallized, 1500°C	Room Temperature	88,100	70,200	26
Recrystallized, 1500°C	300	74,700	52,200	24
Recrystallized, 1500°C	600	74,700	47,700	22
Recrystallized, 1500°C	800	78,200	45,500	20
Recrystallized, 1500°C	1000	61,200	40,600	18
Recrystallized, 1500°C	1200	38,600	33,100	25

This alloy shows good ductility at all test temperatures. Its strength, although not as high as F-48, is higher than the Cb—10 wt % Ti—20 wt % W—3 wt % V—3 wt % Zr alloy.

Rhenium

Rhenium has a solid solubility of 60 wt % in columbium at 1200°C. Tensile data generated by Begley et al. are shown in Table 7.[11]

Table 7. Tensile Strengths of Columbium-Rhenium Alloys

Composition (wt %)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)
1.46	Room Temperature	61,800	47,750	31.4
1.46	1095	14,000	12,600	26.9
7.88	1095	30,900	27,100	9.4
14.38	1095	45,100	41,800	6.7

Comparison of these data to those of the columbium-tungsten alloys shows that, while rhenium is a more potent strengthener than tungsten, it also causes a greater loss in ductility than tungsten.

Tantalum

Tantalum forms a continuous series of solid solutions at all temperatures. Perhaps the best known columbium-base tantalum alloy is FS-82 developed by Fansteel Metallurgical Corporation.[12—14] This is a Cb—33 wt % Ta—0.7 wt % Zr alloy. Tensile data on recrystallized material are given in Table 8.

No data on columbium-base binary tantalum alloys can be found in the literature. However, tantalum-base binary alloys containing up to 50 wt % Cb have been tested by Battelle Memorial Institute.[15] Tensile data are given in Table 9.

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[11]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, pp. 49—50 (1961).

[12]Fansteel Metallurgical Corporation Data Sheet, ca. 1959.

[13]R. T. Torgerson, "Evaluation of Forming Characteristics of Columbium Alloys," pp. 31—52 in Columbium Metallurgy, Vol. 10, ed. by D. L. Douglass and F. W. Kunz, Interscience, New York, 1961.

[14]Unpublished data by author.

[15]F. F. Schmidt, Tantalum and Tantalum Alloys, DMIC Rep. 133, pp. 270—72 (July 25, 1960).

Table 8. Tensile Properties of Fansteel 82

Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Elongation [% in ( ) in.]	Data Source
Room Temperature	70,000		11 (2 in.)	a
1093	44,700	40,300	8 (1 in.)	a
649	53,000	39,400	10 (1 in.)	b
Room Temperature	73,500	62,000	22 (2 in.)	c

[a]Fansteel Metallurgical Corporation Data Sheet, ca. 1959.

[b]R. T. Torgerson, "Evaluation of Forming Characteristics of Columbium Alloys," pp. 31–52 in Columbium Metallurgy, Vol. 10, ed. by D. L. Douglass and F. W. Kunz, Interscience, New York, 1961.

[c]Unpublished data by author.

Table 9. Tensile Properties of Tantalum-Columbium Alloys*

Composition (wt % Ta)**	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Elongation (% in 1 in.)
100	Room Temperature	31,000	28,000	35
100	1200	12,000	----	45
80	Room Temperature	41,000	30,000	29
80	1200	13,000	----	46
50	Room Temperature	42,000	33,000	27
50	1200	11,000	----	53

*Values approximate; taken from graph.
**All specimens tested in recrystallized condition.

It is seen that no great strengthening is gained by alloying tantalum and columbium in the range reported. This is to be expected since the elements are so similar.

Molybdenum

Molybdenum exhibits unlimited solid solubility in columbium. The results of tensile tests at various temperatures are shown in Table 10.

Molybdenum acts much like tungsten, giving some strengthening effect with an accompanying drop in ductility.

Table 10. Tensile Properties of Columbium-Molybdenum Alloys

Composition (wt % Mo)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	Data Source
0.72	Room Temperature	52,850	43,840	26	b
0.72	1095	11,100	7,500	37	b
5.03	Room Temperature	55,100	45,500	27	b
5.26	1095	17,400	15,700	26	b
7.2	Room Temperature	77,000	63,000	20	c
7.2	316	67,000	46,000	14	c
7.2	650	44,000	36,000	3	c
10[a]	Room Temperature	66,500	56,650	6.6	b
10[a]	1095	24,600	20,500	30	b
20[a]	1095	43,700	36,800	6	d

[a]Nominal composition.

[b]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part IV, pp. 56–7 (1960).

[c]D. J. Maykuth et al., Development of Corrosion-Resistant Niobium-Base Alloys, BMI-1437 pp. 66–7 (May 12, 1960).

[d]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, pp. 48–9 (1961).

Data obtained on a semicommercial Cb-Mo-Ti alloy (D-31) are summarized in Table 11.[16]

Table 11. Tensile Properties of D-31 (Cb–10 wt % Ti–10 wt % Mo)*

Test Temperature (°C)**	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Elongation (% in 1 in.)	% Reduction in Area
Room Temperature	100,000	92,000	22	47
427	67,000	54,000	22	75
427	63,000	49,000	5	12
1038	40,000	38,500	13	13
1095	34,500	33,000	12	9
1420	11,000	----	--	40

*As extruded.

**All specimens tested in air.

[16]Technical Memorandum, Niobium–10% Titanium–10% Molybdenum, published by E. I. du Pont de Nemours and Company and Thompson Products, Inc., June 5, 1958.

This alloy shows a higher strength than the Cb–10% Mo alloy at both room temperature and 1095°C, with greater ductility at room temperature and less at 1095°C.

Pratt & Whitney Aircraft, in their alloy development program, present data on a Cb–5 wt % Mo–2 wt % Ti–2 wt % Zr alloy.[17] Data are shown in Table 12.

Table 12. Tensile Properties of Cb–5 wt % Mo–2 wt % Ti–2 wt % Zr*

Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	% Reduction in Area
Room Temperature	75,600	59,000	27	68
982	57,000	42,500	8	25
1095	39,800	38,200	8	33

*Recrystallized condition.

This alloy shows poor ductility at elevated temperatures.

Hafnium

Hafnium has a solid solubility in columbium of 72 wt % at 1000°C. Tensile data for some columbium-hafnium alloys are shown in Table 13.[18]

Table 13. Tensile Properties of Columbium-Hafnium Alloys

Composition (wt % Hf)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)
5	Room Temperature	43,600	26,900	21
10	Room Temperature	58,300	41,800	28
10	1095	30,000	18,200	16
20	Room Temperature	66,300	50,700	22
20	1095	37,300	27,900	31

The above data indicate that hafnium, on a weight percent basis, is little, if any, better than molybdenum or tungsten as a strengthening element.

[17] PWAC-602, p. 121 (April–June, 1960) (classified).

[18] R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part IV, pp. 56–7 (1960).

Some fabrication work reported by Pratt & Whitney Aircraft indicate that columbium containing up to 9 wt % Hf could be forged up to 30% at 1315°C with slight edge cracking.[19] Subsequent cold rolling was successful only on a 1.8 wt % Hf alloy.

Chromium

Chromium has limited solubility at low temperatures and approx 25 wt % at approx 1650°C. Battelle Memorial Institute reports the maximum chromium content for good cold workability to be 1.7 wt % (ref 20).

Begley[21] reports the strength of columbium-chromium alloys as shown in Table 14.

Table 14. Tensile Properties of Columbium-Chromium Alloys

Composition (wt % Cr)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)
1.25*	Room Temperature	65,900	50,900	34.4
1.0	1095	21,330	21,200	36.0
1.57	Room Temperature	76,100	58,100	34.1
1.57	1095	25,940	24,500	37.9
1.57	1205	16,600	15,600	55.4

*Nominal composition.

Zirconium

The binary columbium-zirconium system has been widely studied by several laboratories. The Cb–1% Zr alloy, one of the first "commercial" columbium alloys, is under serious consideration as a structural material in liquid-metal-cooled reactors. This alloy, while not as strong as some ternary and quaternary alloys, has good strength and excellent fabrication characteristics. Unfortunately, the alloy is subject to an aging phenomenon which makes its mechanical properties difficult to describe. All data presented in this section will deal with the as-annealed material with a later section devoted to aging.

[19]PWAC-594, p. 121 (Oct.–Dec., 1959) (classified).

[20]D. J. Maykuth, Development of Corrosion-Resistant Niobium-Base Alloys, BMI-1437, p. 12 (May, 1960).

[21]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 48 (1961).

Typical tensile properties are given in Table 15.

Table 15. Tensile Properties of Columbium-Zirconium Alloys

Composition, (wt % Zr)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	Analysis			Data Source
					C	O	N	
1.08	927	35,500	----	10	200	360	70	*e*
1.00	927[a]	33,300	----	27	230	150	60	*e*
1.00	RT[b]	54,000	----	18	300	200	200	*f*
1.00	927	47,000	----	7	300	200	200	*f*
1.14	927	35,500	25,640	10	120	320	46	*g*
3[c]	982	41,090	40,050	5	---	---	---	*h*
5[c]	RT	59,310	53,930	4	---	---	---	*h*
5[c]	982	53,750	37,000	7	---	---	---	*h*
5[c]	1095	28,500[d]	27,166	4.6	---	---	---	*h*
0.64	1095	15,900	13,800	15.6	---	---	---	*i*
5[c]	RT	64,400	49,600	19.4	---	---	---	*i*
5[c]	1095	25,100	23,500	5.1	---	---	---	*i*
10[c]	RT	76,500	60,450	13	---	---	---	*i*
10[c]	1095	48,400	38,000	28	---	---	---	*i*
20.24	RT	116,000	103,500	1.7	---	---	---	*i*
20[c]	1095	53,000	48,000	19.9	---	---	---	*j*

[a]Annealed at 1200°C; all others at 1600°C.

[b]Room temperature.

[c]Nominal composition.

[d]Strain rate = 0.0005 in./in.-min to yield point.

[e]PWAC-601, p. 88 (Jan.–Mar., 1960) (classified).

[f]D. O. Hobson, A Preliminary Study of the Aging Behavior of Wrought Columbium–1% Zirconium Alloys, ORNL-2995, p 5 (January, 1961).

[g]Ibid, p. 19.

[h]PWAC-594, p. 120 (Oct.–Dec., 1959) (classified).

[i]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57–344, Part IV, pp. 56–7 (1960).

[j]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57–344, Part V, pp. 48–9 (1961).

Alloys containing more than 10 wt % Zr are difficult to fabricate either hot or cold.

Vanadium

According to Begley,[22] vanadium is one of the most potent strengtheners for columbium. In the range above 10 wt % alloy addition, only rhenium and zirconium approach it in strengthening power. However, in this range, both rhenium and zirconium reduce the low-temperature ductility of the alloy.

Higher concentrations of vanadium, up to approx 40 wt %, continue to increase the strength, according to Rajala and Van Thyne.[23] These data are shown in Table 16.

Table 16. Tensile Properties of Columbium-Vanadium Alloys

Composition (wt % V)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	Data Source
1[a]	Room Temperature	52,800	47,800	26	b
1.6	816	28,500	16,500	30	c
4.86	Room Temperature	86,200	74,400	27	b
4.86	1095	36,900	33,500	37	b
5[a]	816	40,000	20,000	37	c
7.6	816	53,000	34,000	34	c
10[a]	Room Temperature	117,400	96,500	20	d
10[a]	1095	46,000	42,500	48	d
19.03	Room Temperature	136,000	110,100	25	b
19.03	1095	54,000	----	0.4	b
25[a]	1095	61,700	53,400	32	d
40[a]	1095	63,000	57,200	31	d

[a]Nominal composition.

[b]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part IV, pp. 56–7 (1960).

[c]D. J. Maykuth et al., Development of Corrosion-Resistant Niobium-Base Alloys, BMI-1437, p. 75 (May, 1960).

[d]B. R. Rajala and R. J. Van Thyne, "Vanadium-Columbium Alloys for 1800 to 2200°F Service," paper presented at the AIME High Temperatures Materials Conference, Cleveland, April 27, 1961.

[22]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part IV, pp. 56–7 (1960).

[23]B. R. Rajala and R. J. Van Thyne, "Vanadium-Columbium Alloys for 1800 to 2200°F Service," paper presented at the AIME High Temperatures Materials Conference, Cleveland, April 27, 1961.

It should be noticed that ductility is high in all cases except the Cb–19.0 % V alloy tested at 1095 °C. The higher vanadium content alloys, when subjected to oxygen contamination, can form an oxide film in the grain boundaries, leading to hot-shortness. This particular specimen was probably thus contaminated.

Aluminum

Aluminum has been studied as an addition for binary or higher columbium-base alloys on the basis of its strengthening effect and its oxidation retarding properties.

Tensile data from several sources are presented in Table 17.

Table 17. Effects of Aluminum on Binary and Higher Columbium-Base Alloys

Composition (wt %)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	Data Source
Cb–0.44 Al	Room Temperature	52,700	37,800	24.0	c
Cb–0.44 Al	1095	15,300	13,000	44.0	c
Cb–1.88 Al	Room Temperature	75,700[a]	67,500	2.8	c
Cb–1.88 Al	1095	19,200	17,600	44.0	c
Cb–1.88 Al	1205	12,000	11,400	77.0	c
Cb–2.5 Al[b]	Room Temperature	60,700[a]	----	0.1	c
Cb–2.5 Al[b]	1095	19,300	17,600	26.0	c
Cb–3 Al–3 V[b]	850	62,800	61,000	17.0	d
Cb–3 Al–3 V–1 Zr[b]	850	86,800	76,600	19.0	d
Cb–3 Al–3 V–7 Ti[b]	850	44,800	44,000	52.0	d
Cb–3 Al–3 V[b]	982	38,900	29,800	11.0	d
Cb–3 Al–10 Ti[b]	982	34,500	31,700	2.0	d

[a]True stress at fracture.

[b]Nominal composition.

[c]R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 50 (1961).

[d]PWAC-594, p. 120 (Oct.–Dec., 1959) (classified).

Aluminum contents above 1 wt % lower the ductility of the alloy.

Titanium

Titanium has unlimited solid solubility in columbium above 850°C. Tensile results are shown in Table 18.

Table 18. Tensile Properties of Columbium-Titanium Alloys

Composition (wt % Ti)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	0.2% Yield Strength (psi)	Total Elongation (%)	Data Source
3	982	28,400	21,900	5	a
6	982	29,100	26,300	0.5	a
6.72	Room Temperature	51,600	40,300	31	b
6.72	427	33,400	24,200	30	b
6.72	650	31,200	20,400	26	b
6.72	871	18,800	12,500	55	b
6.72	1095	9,400	8,000	104	b
6.72	1200	6,300	5,600	86	b
20	Room Temperature	78,100	70,300	25	c
20	538	35,000	25,300	15	c
20	982	20,600	17,800	17	c
20	1095	8,100	7,500	134	c
20	1200	4,400	4,300	> 100	c

[a]PWAC-594, p. 120 (Oct.–Dec., 1959) (classified).

[b]PWAC-601, p. 88 (Jan.–Mar., 1960) (classified).

[c]PWAC-603, p. 155 (July–September, 1960) (classified).

Titanium is one of the least effective high-temperature strengthening agents studied. At high temperatures and low alloy contents, the alloys sometimes exhibit brittleness, as seen in the Cb–6% Ti alloy at 982°C.

Summary of Strength Data

Figures 1 and 2 summarize the effect of various alloying additions on the high-temperature strength of columbium. All elements added to columbium enhance the strength, usually with a decrease in ductility.

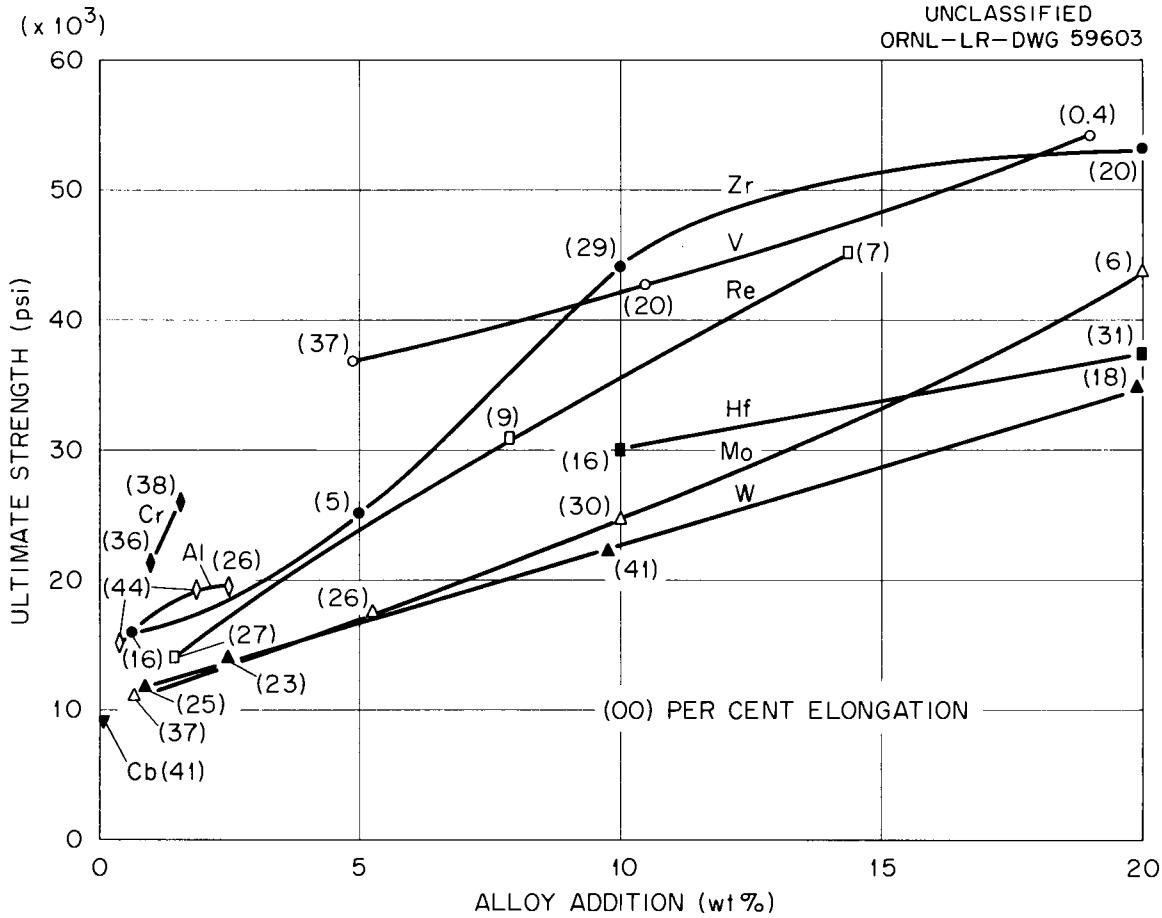

Fig. 1. Effect of Binary Alloy Additions on the Ultimate Tensile Strength of Columbium at 1095°C (2000°F). Ref: R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 60 (1961).

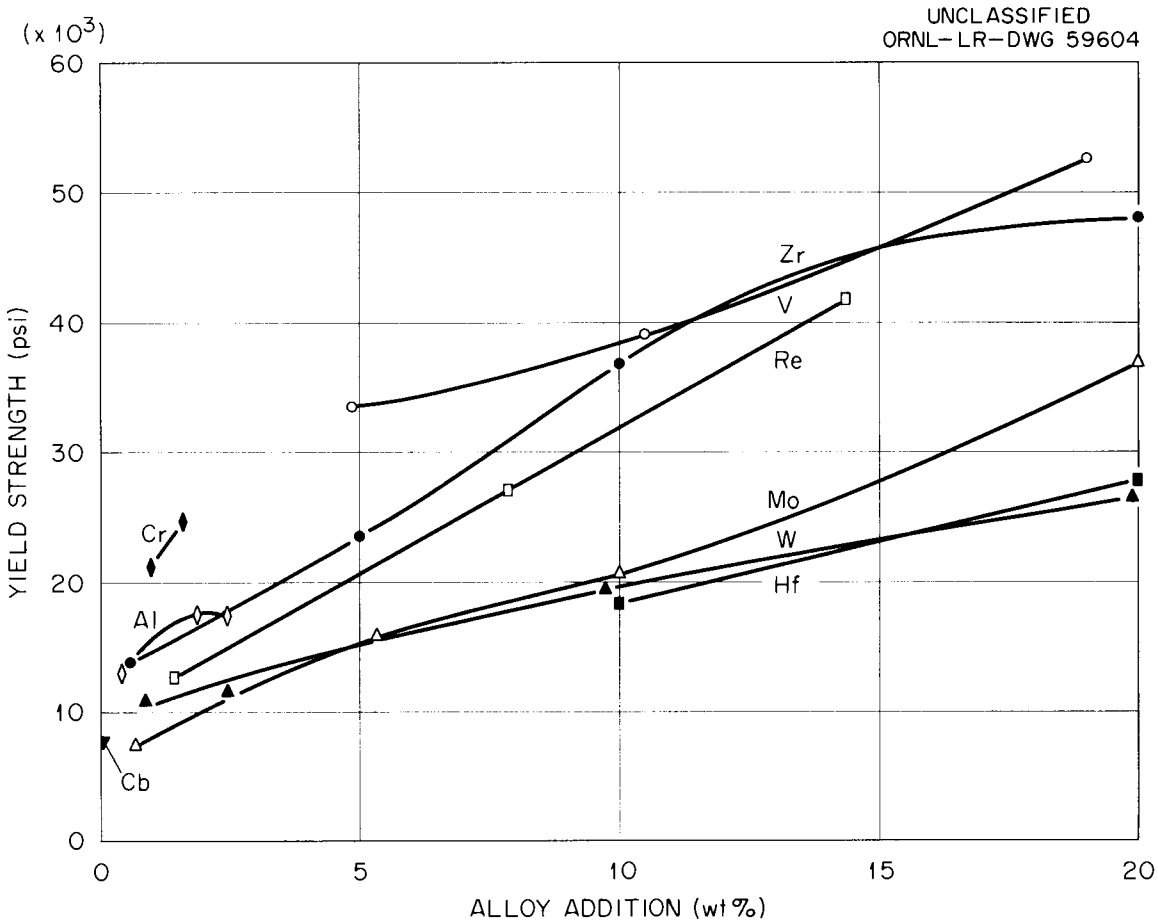

Fig. 2. Effect of Binary Alloy Additions on the Yield Strength of Columbium at 1095°C (2000°F). Ref: R. T. Begley et al., Development of Niobium-Base Alloys, WADC Tech. Rep. 57-344, Part V, p. 61 (1961).

Vanadium has the greatest effect on the ultimate and yield strengths, especially at the higher alloy contents. From 10 to 20 wt %, vanadium and zirconium are about equal. The Cb–40% V alloy has a very high strength with good ductility. Tungsten, molybdenum, titanium, and hafnium have the least effect on the strength with rhenium falling between vanadium and molybdenum. Chromium and aluminum were not tested above approx 1.5 and approx 2.5 wt %, respectively, due to fabrication difficulties, but they both increase the strength – chromium more than aluminum.

In the preceding section, little has been said about the impurity content of the alloys. In order to put the various alloys on a strictly comparable basis, they should contain equal amounts of oxygen, carbon, nitrogen, and hydrogen. This was not the case; but, within practical limits, the ranking is appropriate.

CORROSION RESISTANCE

The compatibility of columbium and columbium-base alloys with the molten-alkali metals, lithium, sodium, potassium, and rubidium, is a recurring problem in the design of high-performance aircraft and space reactors. The alkali metals, at temperatures of interest, generally exhibit very attractive physical properties with regard to use in reactors. Their low melting points combined with a wide liquid-temperature range, low density, high-thermal conductivity, and low thermal-neutron-absorption cross section make them good choices as reactor coolants. The liquid metals are, however, all active chemically and care must be exercised in the choice of their containment material. The energies of reaction of various metals and oxides relative to Li_2O are given in Table 19.

The mechanisms of liquid-metal corrosion are varied and not completely understood. One factor which greatly influences this corrosion is the relationship between the free energy of oxide formation and the oxygen contents of the materials in question.

Lithium has the greatest negative-free energy of oxide formation of the alkali metals and it forms a more stable oxide than all the refractory metals except zirconium and hafnium which equal it in stability. It would be expected that lithium, in contact with a refractory metal having a less

Table 19. Standard Free Energy Changes for Reactions Between Lithium and Various Metal Oxides*

$$2Li + \frac{1}{y} M_xO_y \rightarrow Li_2O + \frac{x}{y} M$$

M_xO_y	$\Delta F^\circ_{816°C}$	Relative Stability
ReO_2	- 78	
Cs_2O	- 69	
MoO_2	- 63	Oxide less stable than either CbO or Li_2O
WO_2	- 60	
K_2O	- 58	
Na_2O	- 44	
Ta_2O_5	- 32	Same as CbO
VO	- 30	
Al_2O_3	- 2	Oxide more stable than CbO; less stable than Li_2O
HfO_2	~ 0	Same as Li_2O
ZrO_2	~ 0	
Y_2O_3	+ 10	More stable than either CbO or Li_2O
BeO	+ 10	
La_2O_3	+ 13	
ThO_2	+ 15	

*A. Glasner, The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750.

stable oxide, would reduce that oxide. Hoffman[24] has found that the corrosion of columbium by lithium can be correlated with the oxygen content of the columbium. Unalloyed columbium containing over 500 ppm O_2 is attacked by lithium. This attack is thought to be due either to the direct reduction of columbium oxide in the grain boundaries and along certain crystallographic planes or else due to the diffusion of dissolved oxygen to those sites and subsequent reaction with the lithium.

[24]E. E. Hoffman, ORNL-2674 (March, 1959) (classified).

The addition of 1% Zr to the columbium prevents corrosion by lithium, provided the alloy is heat treated so that the zirconium reacts with the oxygen in the metal.

In the refractory-metal systems containing sodium, potassium, or rubidium, the role of oxygen may be somewhat different. These metals have free energies of oxide formation less negative than lithium. Therefore, the purity of the liquid metals may be an important corrosion variable because of the tendency of the refractory metals to extract oxygen from them.

As an example of this, data are available on the compatibility of columbium with liquid sodium or sodium-potassium.[25] The oxygen level in the sodium is found to be the controlling factor. The main reaction is the oxidation of the container and specimen material. The product is nonadherent to the columbium allowing fresh surface to be continuously exposed to the flowing liquid metal. The cold-trapped corrosion product has been shown to be $(Na_2O_4)\ Cb_2O_5$.

In addition to the intergranular and oxide-scaling types of corrosion due to oxygen, other forms of corrosion are associated with liquid metals.[24] These are simple-solution, temperature-gradient mass transfer, and dissimilar-metal mass transfer.

Simple-solution corrosion is analogous to the solution of sugar by water to form a saturated solution.

Temperature-gradient mass transfer is due to the temperature dependency of solubility of most container materials in the liquid environment: Solution in the hot section and subsequent deposition in a cooler section can occur.

Dissimilar-metal mass transfer can occur when two or more solid metals are in contact with the same liquid metal which may act as a carrier in transferring atoms of one solid metal to the surface of the other solid metal.

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[25] L. R. Williams and T. J. Heal, "The Consolidation, Fabrication, and Properties of Niobium," p 359 in Plansee Seminar "De Re Metallica" 3rd, Reutte/Tyrol, Plansee Proceedings 1958, Metallwerk Plansee A.G., Reutte/Tyrol, Austria, 1959.

One of the serious consequences of this effect is the marked change in the properties of each metal as the surface chemistry is altered. Brittle layers, aging, and loss of strength are some of the effects which may occur.

Several testing methods have been used by various investigators in studying liquid-metal corrosion. These include (1) static-capsule tests where the specimen is immersed in stagnant liquid in a sealed capsule, (2) tests in seesaw apparatus where the capsule is rocked to alternately submerge and uncover the specimen, (3) thermal-convection loops where the liquid is made to flow due to a change in density with temperature, and (4) forced-convection loops where the liquid is pumped through the system.

Experiments using some or all of the described procedures have been performed by Hoffman[24] on columbium and other refractory metals in lithium and by researchers at Pratt & Whitney Aircraft (CANEL)[26] who have tested a large number of refractory metals and alloys in forced-convection pump loops using lithium, sodium, and sodium-potassium.

Rather than going into the detailed results of the various experiments, it would be better to summarize the conclusions which have been drawn from these tests together with any pertinent remarks.

The refractory metals, columbium, molybdenum, vanadium, zirconium, tantalum, and tungsten, have excellent corrosion resistance to lithium in both static and dynamic test systems. However, the corrosion resistance of columbium, and presumably the other easily contaminated refractory metals, is dependent upon the amount of oxygen in those metals. An oxygen content greater than 500 ppm in columbium can cause detectable corrosion. Care must be taken in all fabrication or welding operations to prevent contamination and subsequent corrosion.

The refractory metals also show good corrosion resistance in the other alkali metals. This corrosion resistance is, however, dependent upon the oxygen content of the alkali metal for the reasons mentioned earlier.

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[26]PWAC-583, -584, -591–94, and -601–4 (July, 1958–December, 1960) (classified).

HIGH-TEMPERATURE STABILITY

As discussed in the strength section of this survey, certain columbium-base alloys are subject to an aging reaction. This reaction, at least in the more dilute alloys, seems to be due to the interaction of oxygen and possibly nitrogen and carbon with the solute element. If the alloying element has limited solid solubility in the columbium, there is also the possibility of forming an intermetallic phase which might cause aging.

It would be expected that an alloy consisting of two or more pure components with complete solubility in each other would be stable as far as any aging reactions were concerned. However, any alloy which goes through melting or sintering, fabrication, and heat treatment will contain impurities such as oxygen, carbon, nitrogen, etc. It is the interaction of these impurities with the alloying elements which often results in a deleterious aging reaction in the alloy. Work by the author[27] indicates that the zirconium in the columbium-zirconium alloy reacts with the oxygen in the alloy to precipitate ZrO_2. The solubility of oxygen in unalloyed columbium at the aging temperature (927°C) is approx 5000 ppm (ref 28). However, columbium-zirconium alloys have aged with as little as 120 ppm oxygen.[27] Work by the author has also shown that the addition of zirconium to the columbium greatly reduces the solubility of oxygen in the columbium.[29] Therefore, it would seem that the addition of a solute material with a higher affinity for oxygen, carbon, or nitrogen than the unalloyed columbium would reduce the solubility of those impurities. In addition to zirconium, those metals which could possibly cause such a reduction in solubility are aluminum, hafnium, yttrium, beryllium, lanthanum, thorium, and vanadium.

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[27]D. O. Hobson, "Aging Phenomena in Columbium-Base Alloys," paper presented at the High Temperature Materials Conference, AIME, Cleveland, Ohio, April 26–7, 1961.

[28]R. P. Elliott, "Columbium-Oxygen System," paper presented at the Annual Convention of ASM, Nov. 2–6, 1959, Preprint No. 143.

[29]Unpublished work by author.

OXIDATION-RESISTANT ALLOYS

Perhaps more study has been devoted to the oxidation characteristics than any other phase of columbium work. Reports on the oxidation behavior of unalloyed columbium are too numerous to attempt to completely evaluate here.[30-41]

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[30]E. A. Gulbransen and K. F. Andrew, "Kinetics of the Reactions of Columbium and Tantalum with O_2, N_2, and H_2," Trans. Met. Soc. AIME 188, 586 (1950).

[31]D. W. Bridges and W. M. Fassell, "High Pressure Oxidation of Niobium," J. Electrochem. Soc. 103, 326 (June, 1956).

[32]H. Inouye, Scaling of Columbium in Air, ORNL-1565 (Aug. 29, 1956).

[33]J. V. Cathcart, J. J. Campbell, and G. P. Smith, "The Microtopography of Oxide Films on Niobium," J. Electrochem. Soc. 105, 442 (1958).

[34]H. J. Goldschmidt, "A High-Temperature X-Ray Investigation on Niobium Pentoxide and Some Problems Concerning the Oxidation of Niobium," J. Inst. Metals 87, 235 (1958).

[35]E. A. Gulbransen and K. F. Andrew, "Oxidation of Niobium Between 375 and 700°C," J. Electrochem. Soc. 105, 4 (Jan., 1958).

[36]W. D. Klopp, C. T. Sims, and R. I. Jaffee, "High-Temperature Oxidation and Contamination of Columbium," Trans. Am. Soc. Metals 51, 282 (1959).

[37]W. D. Klopp, D. J. Maykuth, C. T. Sims, and R. I. Jaffee, Oxidation and Contamination Reactions of Niobium and Niobium Alloys, BMI-1317 (Feb. 3, 1959).

[38]T. Hurlen, H. Kjollesdal, J. Markali, and N. Nico, "Oxidation of Niobium," Central Institute for Industrial Research, Norway, Tech. Note No. 1, Contract No. AF 61(052)-90 (April, 1959).

[39]T. L. Kolski and W. T. Hicks, "Columbium-Oxygen Reactions from 450 to 1200°C," paper presented at AIME Symposium on Preparation, Purification, and Properties of Refractory Metals, Chicago, Nov., 1959.

[40]H. Inouye, "The Oxidation of Columbium at Low Oxygen Pressures," paper presented at the Columbium Metallurgy Symposium, Lake George, New York, June, 1960.

[41]W. D. Klopp, Oxidation Behavior and Protective Coatings for Columbium and Columbium-Base Alloys, DMIC Rep. 123 (Jan. 15, 1960).

The references given generally agree that, at atmospheric pressure and temperatures above approx 600°C, columbium oxidizes linearly with time with the formation of Cb_2O_5. At lower pressures, < 1 μ, oxidation proceeds through a series of stages, each stage following a different rate law.

Contamination of columbium metal during oxidation in both air and oxygen is appreciable due to the high solubility and diffusion rate of oxygen in columbium. The depth of contamination may easily exceed the amount of metal consumed by oxidation.

Many columbium-base alloy systems have been studied in the attempt to develop oxidation-resistant alloys. Unalloyed columbium oxidizes at a rate approx 400 times that of type 316 stainless steel at 1000°C in air. Most columbium-base alloys have an oxidation rate 1/10 to 1/100 that of unalloyed columbium. Two rather complicated alloys with oxidation rates approx 10 times better than unalloyed columbium are reported by du Pont.[42,43] One alloy (Cb—nominal 19 wt % Cr, 10 wt % Al, 15 wt % Co) contains 38 at. % Cb. The other alloy (Cb—nominal 10 wt % Fe, 14 wt % Al, 4 wt % Mo, 15 wt % Co, 1 wt % Ce) contains 37 at. % Cb. These alloys, although oxidation resistant, are probably unfabricable due to the formation of brittle intermetallics.

A complete survey on the theoretical aspects of alloying for oxidation resistance and also the effect of various alloying elements on the oxidation of columbium has been published by Pratt & Whitney, CANEL.[44] This reference is recommended and no further data will be tabulated on this subject.

Coatings and Claddings for Oxidation Resistance

At a recent conference on high-temperature materials, the statement was made that it was unlikely that a good oxidation-resistant columbium-base alloy

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[42]T. N. Rhodin, Jr., "Metal Production," U. S. Patent No. 2,838,396 assigned to E. I. du Pont de Nemours and Company, Inc. (June 10, 1958).

[43]T. N. Rhodin, Jr., "Niobium-Base High Temperature Alloys," U. S. Patent No. 2,838,395 assigned to E. I. du Pont de Nemours and Company, Inc. (June 10, 1958).

[44]PWAC-321 (Feb. 15, 1961) (classified).

could be produced.[45] If this statement is true, then many service applications of columbium-base alloys await the development of an effective, oxidation-resistant coating or cladding which is protective in high-temperature, oxidizing environments.

More time has been spent on coatings development than on claddings. Several different types of coatings and methods of application have been studied by various concerns. These experimental coatings may be either metallic or nonmetallic and may be applied by electroplating from aqueous or fused-salt baths, vapor or pack-deposition, spraying, or by liquid-phase diffusion. Examples of metallic coatings are Nichrome, aluminum-silicon-chromium, and modified aluminum dips. Nonmetallic coatings include glasses and refractory oxides. Table 20 and Fig. 3 summarize data on the comparison of coatings on columbium.

An ideal coating must meet the following criteria to be useful in high-temperature, oxidizing environments. It must (1) be oxidation resistant, (2) be self-healing, (3) be ductile at both high and low temperatures, (4) have minimum diffusion and/or reaction with base metal, (5) have thermal-expansion characteristics compatible with the base metal, (6) withstand high-velocity air streams, and (7) be amenable to the coating of complex structures. No coating listed above is 100% effective in each of the above criteria. Although all have good oxidation resistance, they are either brittle or they react with the base metal. Some coatings depend on a vapor phase for their self-healing properties, e.g., zinc. However, if such a coating is subjected to a high-velocity air stream, it is possible that self-healing would not be obtained.

Some work has been done on the cladding of columbium with oxidation-resistant metals and alloys. Early work was done by Inouye and Page[46] who studied the compatibility of columbium in contact with Inconel and also columbium in contact with various barriers. The Inconel-Fe-Cu-Cb composite appeared worthy of consideration.

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[45] J. J. Gangler, "Status and Future of High Temperature Coatings for Refractory Metals," paper presented at AIME High Temperature Materials Conference, Cleveland, April 26–7, 1961.

[46] H. Inouye and J. P. Page, Metallurgy Information Meeting, Ames, Iowa, May 2–4, 1956, TID-7526 (Pt. 2b) pp. 368–83 (classified).

Table 20. Comparison of Coatings on Columbium

Coating Composition, (wt %)	Method of Application	Static Oxidation Life at Temperature Indicated, hr (°F)							Data Source
		1800	2000	2100	2200	2300	2500	2730	
100 Cr (2 mils)	Aqueous electroplate	--	--	--	--	--	1	--	*d*
Ni + (Cr-B-Fe-Si)[a]	Fused-salt electroplate	--	19	--	--	--	--	--	*e*
Ni + (Si-Cr)[a]	Fused-salt electroplate[b]	--	--	--	--	--	1-3	--	*e*
Ni + (Al_2O_3-ThO_2-SiO_2)[a]	Fused-salt electroplate[b]	--	--	--	--	--	0.2-9	--	*e*
100 Si	Vapor deposited	10	--	--	--	--	--	--	*f*
c	Vapor deposited	--	--	--	--	25	2	--	*g*
W-2 (Si-Cr)	Modified pack deposition	320	--	--	--	--	--	--	*f*
Cr-34Si-20Al	Sprayed[b]	--	--	--	--	--	1-6	--	*e*
Fe-25Cr-5Al	Sprayed[b]	--	--	--	--	--	2	--	*e*
$CrSi_2$-20Al	Sprayed[b]	--	--	--	--	--	<2	--	*e*
$TiSi_2$-25Al	Sprayed[b]	--	--	--	--	--	1	--	*e*
Ni-32Al	Sprayed[b]	--	--	--	--	--	<1	--	*e*
Al-Si	Sprayed	--	--	--	--	--	1-2	--	*h*
Al + Al_2O_3	Sprayed	--	--	--	--	--	1-2	--	*h*
Duplex LM-5 (40Mo-40Si-10B-10Al)	Sprayed	--	--	1000	--	700	--	108	*i, j*
Al-10Cr-2Si	Dipped	--	--	--	--	--	>2	--	*d*
B_2O_3 + additive	Dipped	--	--	--	--	--	2	--	*h*
Al-Si	Slurry dipped and baked	--	--	--	--	--	>2	--	*d*
Ni-Cr	*c*	--	--	--	>1000	--	--	--	*f*
Zn	Dipped	>100	10-100	--	--	--	--	--	*k*
(Nb-Ti)Zn_3	Dipped	>100	--	--	--	--	--	--	*k*
Zn-Al-Si	Dipped	--	--	--	--	10-100	--	--	*k*

[a]Materials in parentheses were occluded in the nickel plate.

[b]Samples were aluminum dipped after indicated coating.

[c]Proprietary composition or process.

[d]Refractory Alloys for Use as Structural Materials in Re-Entry or Boost Glide Vehicles, General Electric Rep. No. 7148 (Quar. Rep. No. 2 for the McDonnell Aircraft Company, Dec. 1, 1959).

[e]E. C. Hirakis, Research for Coatings for Protection of Niobium Against Oxidation at Elevated Temperature, WADC Tech. Rep. 58-545 (Feb., 1959).

[f]"Fansteel Metallurgy," Fansteel Metallurgical Corporation (July, 1958).

[g]Refractory Alloys for Use as Structural Materials in Re-Entry or Boost Glide Vehicles, General Electric Rep. No. 6994 (Quar. Rep. No. 1 for the McDonnell Aircraft Company, Sept. 1, 1959).

[h]W. D. Klopp, Oxidation Behavior and Protective Coatings for Columbium and Columbium-Base Alloys, DMIC Rep. 123, pp. 85–7 (Jan. 15, 1960).

[i]"Materials Advisory Board Rep. on Columbium and Tantalum," Natl. Acad. Sci. – Natl. Research Council, Publ. (Jan. 13, 1959).

[j]"New Product Data Sheet on Duplex Columbium Coating," Union Carbide Metals Company (Nov. 1, 1959).

[k]B. F. Brown et al., "Protection of Refractory Metals for High Temperature Service," U. S. Naval Research Laboratory, Prog. Rep. 1 (Nov. 28, 1960).

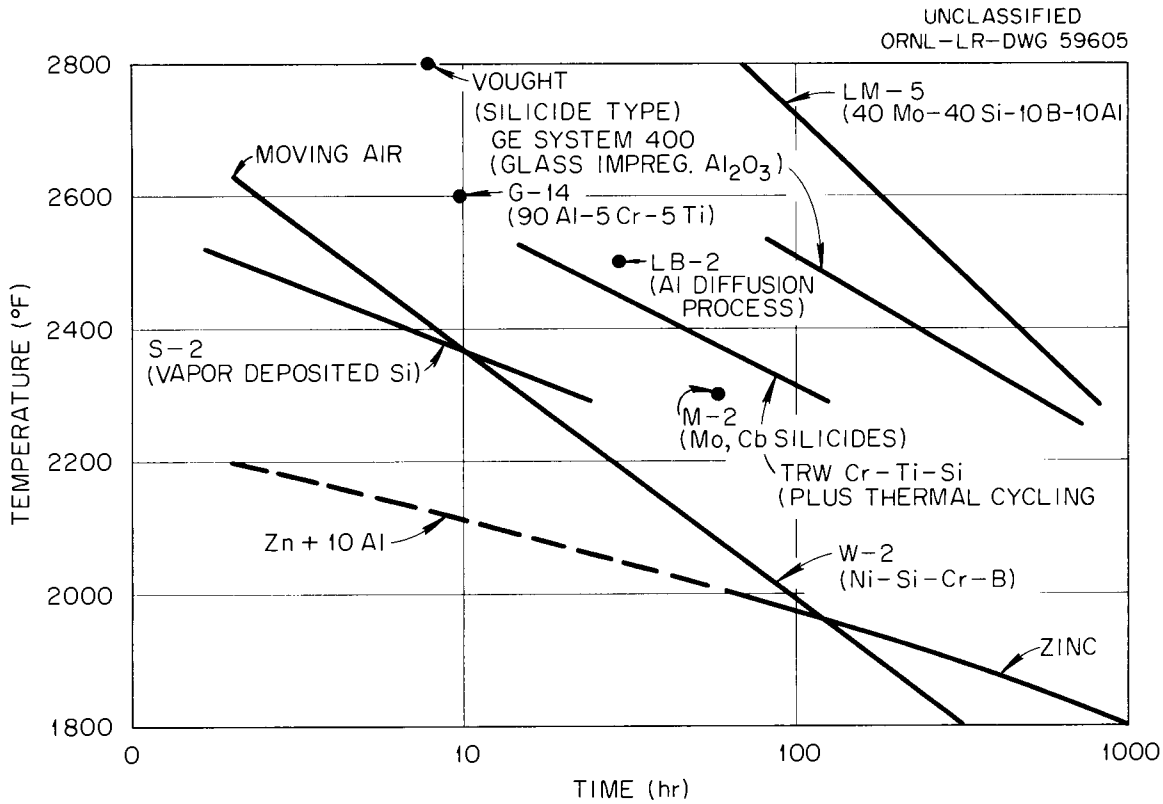

Fig. 3. Average Oxidation Life of Coated Columbium at Elevated Temperatures in Static Air. Ref: J. J. Gangler, "Status and Future of High Temperature Coatings for Refractory Metals," paper presented at AIME High Temperature Materials Conference, Cleveland, April 26-7, 1961.

Studies have been conducted at the Naval Research Laboratory[47,48] on the diffusion of columbium in various elements and with several stainless steels. These studies indicate that serious cracking occurs between columbium and stainless steel or iron, chromium, nickel, cobalt, etc., due to the formation of hard, brittle phases of simple stoichiometric compositions such as $CbCr_2$, $CbFe_2$, CbNi, and others. It is evident that a barrier should exist between columbium and its clad to prevent diffusion and subsequent formation of brittle phases.

CONCLUSIONS AND RECOMMENDATIONS

The construction of an engineering device for operation at temperatures in excess of 2000°F and in contact with liquid metals appears feasible.

Unalloyed columbium is unacceptable as a structural material for a reactor subject to a high-temperature, oxidizing environment that contains a liquid metal as a heat-transfer medium. In order for it to be acceptable in the above situation, substantial improvements must be made in its strength, oxidation resistance, and corrosion resistance.

It is possible to increase the strength of columbium by alloying. The most attractive binary strengthener is vanadium. Columbium-vanadium alloys retain good low-temperature ductility over a wide alloy range. One problem anticipated in this system is that of high-temperature brittleness. This has been found in some of the higher vanadium-content alloys and is due to the formation of a grain-boundary oxide phase. The use of a stable-oxide-forming element as a third alloying element might eliminate this problem as well as that of liquid-metal corrosion. It is probable that the addition of such an element would render the alloy susceptible to aging due to the precipitation of a stable oxide. This should be investigated as alloy development proceeds.

This investigation shows that no columbium-base alloy exists having usable oxidation resistance. It is also unlikely that one will be developed

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[47] L. S. Birks and R. E. Seebold, Diffusion of Nb with Cr, Fe, Ni, Mo, and Stainless Steel, NRL Rep. 5461 (March, 1960).

[48] R. E. Seebold and L. S. Birks, Elevated Temperature Diffusion in the Systems Nb-Pt, Nb-Se, Nb-Zr, Nb-Co, Ni-Ta, and Fe-Mo, NRL Rep. 5520 (September, 1960).

in the near future which will have commercial fabricability. Coatings having very good oxidation resistance are available but are not completely reliable from a thermal- or chemical-compatibility standpoint when undergoing temperature fluctuations.

It is recommended that the columbium-vanadium system be investigated, especially around the Cb–40 wt % V portion of the phase diagram. It is also recommended that zirconium or possibly hafnium be used as the third element addition.

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