

To: Mr. L. M. Raring

From: W. R. Clough, E. C. Hiraikis
and R. C. Krutenat

Subject: Survey: Oxidation Characteristics
of Columbium and Columbium Base Alloys

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INTRODUCTION

The primary objective of this memorandum is to present unclassified experimental data concerned with the oxidation characteristics of columbium and columbium base alloys. An attempt has been made to present the data in the most concise form possible; however, there is a great deal of information to be covered. The survey for the case of pure columbium is not considered as being particularly complete, since there is such specialized information that is of no great consequence to CANEL interests. On the other hand, data concerned with columbium base alloys is as complete as practicable. The authors have made little if any attempt at data interpretation; this will be included in another memorandum which will approach the subject of columbium base alloys from an overall viewpoint. In the meantime, other memorandums will be issued dealing with surveys of mechanical metallurgy and physical metallurgy. Another objective of

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the memorandum is to bring together in only a very few publications much available information on the subject, and thus make this information readily available to CANEL personnel and consultants directly or indirectly concerned with alloy design and evaluation.

The bulk of oxidation information is contained in a comparatively large number of tables attached as an appendix; other information is contained in the text. Because of the great variance in testing procedures used by different workers, results have been cataloged under laboratory name sub-headings. Since identical alloy systems have been treated by several different laboratories, the first two tables of the appendix should facilitate the locating of data for a particular alloy system. Binary alloys are listed in Table A-1. All more complicated alloy systems have been treated as ternaries or their modifications, and a cross reference of basic ternary systems is included in Table A-2. Also included in the memorandum are short sections dealing with the theory of alloy design for oxidation resistance and methods of evaluating oxidation behavior.

It must be borne in mind that many of the compositions listed in the appendix are quite impractical from an engineering viewpoint: strength may be nil, brittleness may be excessive, or fabrication may be impossible. However, these same alloys should not be ignored since they may indicate to metallurgical research workers fundamental information of some importance, or may become very practical alloys when sufficiently modified.

For several reasons, studies of oxidation resistance have far outstripped other related fields of interest. Early in their programs, workers in several laboratories came to the conclusion that lack of oxidation resistance was the greatest single detriment to the commercial exploitation of columbium, hence the bulk of early work was concerned with alloying to improve oxidation characteristics. Comparatively brittle material could be used, while the pure, more ductile product could be conserved for mechanical and physical metallurgy considerations. Also, oxidation screening tests are comparatively rapid and inexpensive, involve only modest equipment and small test specimens, and can be carried out on as-cast material with a minimum of personnel, thus bypassing many economic difficulties. Several of the more advanced alloy programs are now desperately trying to supplement their extensive oxidation data with melting and mechanical metallurgy information. From a statistical mathematics viewpoint, however, it may be argued that the surface has hardly been scratched as yet, even for the case of oxidation determinations, since roughly a third of the periodic table is available for alloying studies. The number of possible alloy permutations and combinations is large, even without considering the fact that a large number of compositions in any specific ternary, quaternary, or more complicated system may have to be considered before truly optimum alloys are developed. Of course, one of the chief concerns of metallurgical research workers is to insure that alloy design programs do not degenerate into complicated statistical exercises.

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Several points concerning the appendix tables should be discussed. Unless specified, listed compositions are "nominal" - that is, the weight percentage of the charge before melting. There may be great differences between nominal and actual compositions, particularly for the case of those alloys containing constituents with relatively low boiling points or relatively high vapor pressures as compared to the columbium base (aluminum, chromium, beryllium, manganese, etc). Actual analyses are generally not determined unless something reasonably promising is developed, thus imposing only a minimal load on analytical chemistry laboratories (an exception to this statement, for the case of columbium, would possibly be determinations of interstitial content). Much data has been accumulated on specimens machined from as-cast buttons or bars which were not given a vacuum or inert atmosphere homogenization heat treatment prior to testing: gross inhomogeneity would be expected to greatly effect oxidation behavior. It should also be kept in mind that certain variations in oxidation test results should be expected, since data will be somewhat influenced by small differences in surface roughness and cleanliness, the oxygen partial pressure of the medium used in testing, the velocity and humidity of the oxidizing medium, the time length of exposure, the degree of contamination as regards SO_2 , CO_2 , etc.

THEORIES OF ALLOY DESIGN

The problem of building a considerable measure of oxidation resistance into columbium by alloying has been attacked by numerous investigators as the latter portions of this memorandum will show. Both fundamental and empirical methods have been used and promising results have been obtained. Progress in the engineering sense is considerably hampered by the fact that approaches to alloy design for obtaining oxidation resistance are not identical to those for seeking improved elevated temperature mechanical strength, decreased ductile-brittle transition temperature, improved workability, etc. In summary, the problem of alloying columbium to produce a desired combination of properties will be one of compromise: the contribution of the individual ingredients towards the various properties must be determined by theoretical considerations, by evaluation methods, and by inference from published data. Columbium base alloys combining a number of desirable properties will, undoubtedly be rather complex. Logical alloy development requires that consideration be given not only to strengthening and stabilizing additives, but also to metal additions designed to improve fabricability and to promote the solubility of other ingredients.

Space restrictions severely limit detailed discussions of the theoretical approaches to alloy design for increased oxidation resistance: excellent reviews on the subject have recently been prepared by Kubaschewski and Hopkins⁽¹⁾, and by Hauffe⁽²⁾. To proceed logically, it is necessary to have considerable information concerning the oxidation characteristics of the pure base metal (columbium). Fortunately, most, if not all of this type of information is contained in previously published literature, and some of it is included in this report. Kubaschewski and Hopkins⁽¹⁾ have classified the high temperature oxide (columbium pentoxide - Cb_2O_5) as a metal excess, n-type semiconductor, while Klepp, Maykuth, Sims and Jaffee⁽³⁾ state that the pentoxide may be a metal excess semiconductor, or an anion deficit semiconductor.

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For the case of the oxidation of an alloy, it is usual to initially determine which of the metal components is likely to be preferentially attacked. To a good first order of approximation, this can be accomplished by comparing the free energies of the compounds that could possibly be formed at the temperatures under consideration, although it may be sufficient to compare the heats of formation at room temperature for equivalent amounts of oxygen or other negative radical. Values of the free energies of formation (kcal/gram-atom of oxygen) at room temperature and at 1000°C are listed in Table A-3.

Having used free energy of formation data to establish the relative nobility of the components, the next usual procedure is to divide the oxide systems into several composition ranges which depend on the system and the temperature of interest. In practice, the limits of these oxide concentration ranges are not easy to determine, since they are not related to the phase boundaries of the metal alloy system.

- a. First, consider the case of the formation of an oxide layer composed of Cb_2O_5 with additive element ions in solid solution. Films of this type are possible when the additive metal, though highly reactive toward oxygen, is present in the alloy in only very low concentration levels, and also when the additive metal, though present in an appreciable concentration, is much less reactive toward oxygen than is columbium.
- b. The converse situation involving the formation of an additive-metal oxide film with columbium ions in solid solution may also be considered: oxide films of this type are theoretically possible when the additive metal, even at relatively low concentrations, is much more reactive toward oxygen than is columbium, and also when the additive metal, though somewhat less reactive toward oxygen than is columbium, is the preponderant component of the alloy.
- c. The third possibility encompasses several types of oxide film: this includes heterogeneous mixtures of simple or complex oxides of the various alloy components; homogeneous complex oxide scales; and multilayer films in which the homogeneous-complex and/or the heterogeneous types might participate.

In the first instance, the applicable theory is that postulated by Carl Wagner^(5,6). The theory was initially developed in an effort to explain the oxidation of pure metals and by definition concerns surface reactions which obey the parabolic weight gain-time law for which, consequently, a true diffusion process of ions in the oxide lattice is rate determining. In order to preserve electrical neutrality, cationic diffusion must be accompanied by the flow of electrons in the direction of material transfer; anionic diffusion requires that the electron flux travel in the opposite direction to that for material transfer. Applicable to the case of columbium, the following conclusion has been reached by Hauffe⁽⁷⁾: "The oxidation rates of metals forming oxidation layers consisting of metal-excess semiconductors can be decreased by adding metals of higher valency than that of the base metal." The object is the diminution of the defect concentration in anion-deficient, semiconducting columbium pentoxide with a resulting decrease in the rate of oxygen diffusion. The postulated mechanism for this effect is not the direct substitution of metal ions into the anion vacancies; rather, it is an alteration in valency electron distribution within the

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cation lattice with a consequent effect on anion defect density, and, for this reason, the oxygen diffusion rate. Also important, in addition to valence, is the ionic size effect: solution of smaller ions would be expected to decrease the lattice parameters of columbium pentoxide which, in turn, might be expected to decrease the metal to oxide volume ratio and allow a thicker film to form before cracking occurs, resulting in increased protection. The Wagner theory has been proven applicable for metals other than columbium. Unfortunately, based on this experience, there is little encouragement that improvements in oxidation resistance of more than one or two orders of magnitude can be expected even if the approach is successfully pursued for columbium.

Another approach, the second of the three listed, is the selection of an alloying element designed to participate in the formation of an additive-metal oxide film in which the columbium ion concentration would be consistent with the requirement for a single phase structure. For columbium, the practicability of this approach is doubtful since there are few metallic elements sufficiently reactive to function in the prescribed manner at concentration levels that are realistic in terms of mechanical and fabrication properties of the resultant alloys. It is desirable that the diffusion rate within the protective oxide film be low. A qualitative measure of the diffusion rate is available through determination of electrical conductivity; to a rough approximation, bulk diffusion rate and electrical conductivity vary directly with one another. The defect vacancies in the compound could, of course, be filled by further metal alloy additions at the ternary or more complex level.

In the range beyond the solubility limit of the alloying elements in columbium pentoxide, new compounds must be formed. These may consist of mixed simple oxides, spinels and other oxide complexes, or discrete oxide layers of the base and alloying metals. For the case of two simultaneous simple oxides, the more stable of the two should grow adjacent to the metal surface, and preferably should be one in which bulk diffusion rates are particularly low. Perhaps a most promising attack on the problem is the experimental addition of several alloying elements to columbium capable in combination with each other or in conjunction with columbium of forming complex oxide compounds, preferably spinels, when exposed at elevated temperatures. Characteristically, oxygen diffusion occurs at significantly lower rates in spinels than in their constituent oxides. Oxidation rate reductions measured in several orders of magnitude have been achieved by this method. Further improvements are then possible by the incorporation of additional alloying ingredients designed to affect the defect structure of the complex oxide such as has been accomplished for the case of nichrome by adding a fractional percentage of calcium or aluminum: the oxidation rate at 1200°C was decreased by a factor of two.

It must be admitted that there are other possibilities that are not covered by the previously mentioned three cases. Oxidation protection by means of coatings of one type or another affords a most practical solution to many problems; coatings research is active at several laboratories. The situation is considerably improved if coatings can be successfully applied to alloys which in themselves possess superior oxidation resistance as compared to columbium, since catastrophic failure

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would not then be expected to result from coatings defects or local failures. Though remote, it must be presumed that alloying offers the possibility of stabilizing CbO or CbO_2 at high temperatures as a subscale under the pentoxide. A retained monoxide layer in particular would be expected to considerably improve oxidation characteristics.

If an oxide melts or volatilizes at a temperature lower than that of interest, the degree of protection afforded will generally be poor. The molecular volume of the compound or compounds in the oxidation layer deserves special attention because, where it differs considerably from that of the alloy, the layer formed is likely to be either porous or highly compressed to the detriment of its protective nature. Compositions which when oxidized yield scales differing greatly in thermal expansion coefficient from the base metal may offer a high level of performance during static exposure but have little utility under cyclic heating conditions due to a tendency for spalling of the protective oxide film. Adjustment in the expansivity of oxide films is possible by further alloying of the base metal but the effect may be adverse in other areas of concern such as oxygen diffusion rate.

Included in Table A-4 are lists of oxide properties of general interest, such as valence, Goldschmidt atomic radius, melting point or temperature of transformation, electrical conductivity at 20°C , and oxide molecular volume. Table A-5, prepared by R. C. Krutenat, gives a listing of many known spinels of possible interest for the case of columbium alloying. Although the purpose of this report is not to interpret data, it would not be an overly difficult task to explain the choice of many constituents used by various investigators in their experimental alloy design programs by means of the information contained in Tables A-3, A-4, and A-5.

DETERMINATION OF OXIDATION RESISTANCE

The objective of this section of the memorandum is to briefly review the methods different investigators have used to evaluate the oxidation characteristics of columbium base alloys. Comprehensive general reviews on the subject have recently been prepared by Kubaschewski and Hopkins⁽¹⁾, Carl Wagner⁽¹²⁾, and H. Inouye⁽¹³⁾. In order to follow the rate of a chemical reaction, one may determine either the amount of the reaction product, or the decrease of mass or volume of one of the reactants. Each of the possibilities has been used practically with some advantage since the requirements vary considerably. To obtain a clear cut relation between oxidation rate and time, one would prefer methods which permit following a reaction continuously so that the progress of a reaction during a certain period is obtained with only one metal sample and incidental differences of samples are eliminated. Since reaction products are formed during the oxidation process, one of the most common approaches to the problem of measurement involves the weight change of an exposed sample. There are at least three methods, as follows:

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1. The metal specimen can be carefully weighed, placed in the hot zone of a furnace for a certain length of time, removed from the furnace, and reweighed after cooling. The process can be repeated a number of times for suitable times at temperature. When only one exposure is made, data may be reported as an average value of weight gain; unfortunately, for short exposures of a few hours, this type of test does not tell the investigator if linear (non-protective) or parabolic (protective) weight gain-time relations prevailed. The extra handling involved in multiple exposures presents the possibility of contamination and loss of reaction products, especially if the oxide scale is stressed and spalls on thermal cycling. In the event of spalling, a new, fresh surface is exposed to the oxidizing medium upon subsequent treatments in the furnace and the rate law will be complicated, the data actually representing a series of different rates.
2. The metal specimen is weighed, exposed to a hot oxidizing atmosphere for a predetermined period of time, cooled, and descaled by mechanical or chemical means. Sometimes the removed scale will be chemically analyzed. The loss of weight after descaling may be determined, and the result reported as an average value of weight loss. Objections to the process include the fact that it is cumbersome and does not allow a continuous monitoring of the reaction for rate studies. Complete removal of the scale without affecting the underlying metal is practically impossible in most cases.
3. The test specimen may be suspended in a hot vertical tube furnace from an inert wire connected to a suitable balance beam and continuous readings of the weight change can be taken or recorded without removing the specimen from the hot zone. The method is ideal for rate law determinations and alloy screening programs, and it is generally agreed that this is probably the most meaningful single type of test. Unfortunately, although maximum benefit to the individual research team may result from use of this type of test, the reporting of data presents a problem. When possible, mathematical formulations representing the weight gain-time relations may be presented. Often, average weight gain is reported, or total weight gain in a specified time period may be substituted - one being a multiple of the other. Finally, the weight gain rate during a specified portion of the exposure period may be indicated; unfortunately, in the case of work done in other laboratories this is often not sufficiently informative.

Measurements of internal oxidation due to oxygen diffusion through the oxide scale and into the base metal are also of importance, particularly since a severe embrittling effect may result. Microhardness techniques involving a traverse are generally used, although metallographic techniques may be applicable in certain cases.

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If the rate of recession of the metal surface approaches or equals the rate of oxygen diffusion in the base metal, measurements of the depth of contamination as the basis for oxidation resistance will lead to the erroneous conclusion that the alloy resists oxygen contamination. On the other hand, if the rate of recession of the metal surface is low, a somewhat similar erroneous conclusion can be reached if the diffusion of oxygen into the metal is ignored or not known. A most realistic evaluation of the oxidation resistance of alloys, therefore, should be based on the sum of internal contamination and the recession of the metal surface, and should include continuous weight gain measurements. Because most of the investigations conducted to date have not included composite data on the weight gain, oxygen penetration and metal surface recession for each alloy, it is difficult to accurately assess their resistance to oxidation in relation to other alloys due to the fact that materials exhibit both internal oxidation and scaling. The absence of detailed studies is a natural consequence of the screening nature of the bulk of present research.

THE OXIDATION OF PURE COLUMBIUM

In order to evaluate the present status of the oxidation resistance of columbium alloys, it is necessary to consider their merits in light of the oxidation characteristics of the "pure" metal. From cursory x-ray work, G. Brauer⁽¹⁴⁾ estimated the extent of the columbium primary solid solution with oxygen to be less than 4.76 a/o (0.86 w/o). A more detailed roentgenographic and microscopic analysis carried out by Seybolt⁽¹⁵⁾ in the temperature range from 775 to 1100°C (1427 to 2012°F) indicated that the oxygen solid solubility at the lower temperature was 1.4 a/o (0.25 w/o) and 5.5 a/o (1.0 w/o) at the higher temperature. Seybolt's data may be expressed by the relationship

$$N_o = 5.3 \exp(-12,000/RT)$$

where N_o is the atomic fraction of oxygen in solution.

Lattice parameter data for columbium-oxygen solid solution, as given by Seybolt⁽¹⁶⁾, yields the equation:

$$a_o (A^\circ) = 3.300 + 0.01625 (w/o O_2)$$

Seybolt⁽¹⁶⁾ also determined that oxygen has a considerable hardening effect on columbium, Vickers Hardness Numbers increasing from about 160 at 0.1 w/o oxygen to 350 at 0.74 w/o oxygen.

The oxides of columbium have been studied by Brauer⁽¹⁴⁾ and Zachariassen⁽¹⁷⁾. Three stable columbium oxides have been reported - CbO , CbO_2 and Cb_2O_5 . The monoxide has no extensive homogeneity range and possesses a cubic structure with $a = 4.211 A^\circ$ and six atoms per unit cell (NaCl lattice with ordered vacancies). CbO_2 has no homogeneity range of measurable extent. Powder diagrams^(14,18) showed lines in addition to the expected rutile diagram, and it is assumed that the lattice is not quite the

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same as that of rutile: the parameters of the rutile type of structure as reported by Goldschmidt, Zachariassen, et. al.⁽¹⁹⁾ are: $a = 4.84$ AU, $c = 2.99$ AU, and $c/a = 0.618$.

For the pentoxide, Brauer⁽¹⁴⁾ has reported three modifications: the "T" form stable to 900°C (1652°F), the "M" form stable from 1000 to 1100°C (1832 to 2012°F), and the "H" form stable above 1100°C (2012°F). The existence of these forms has been confirmed⁽²⁰⁾, although the temperature range of stability was questioned. The oxides were not found to be appreciably volatile at temperatures from 1000 to 1375°C (1832 to 2507°F). The pentoxide has a negative coefficient of thermal expansion between room temperature and 600°C (1112°F), above which it becomes positive⁽²¹⁾. The observation that conductivity increases with decreasing oxygen pressure has been interpreted⁽³⁾ as indicating the presence of interstitial metal ions or oxygen ion holes in the Cb_2O_5 lattice. X-ray patterns of the pentoxide ("L" form) were isomorphous with Ta_2O_5 ⁽¹⁴⁾. Brauer also reported that the pentoxide melts at $1460 \pm 5^{\circ}\text{C}$ ($2660 \pm 9^{\circ}\text{F}$) and that the homogeneity range extends down to $\text{Cb}_2\text{O}_{4.8}$. Zachariassen⁽¹⁷⁾ has also found Cb_2O_5 (unknown form) to be isomorphous with Ta_2O_5 . The crystal structure was pseudohexagonal orthorhombic, and cell dimensions were reported as $a_1 = 6.16 \pm 0.03$ AU, $a_2 = 3.65 \pm 0.02$ AU, and $a_3 = 3.94 \pm 0.02$ AU with the metal ions at $(0,0,0)$ and $(1/2, 1/2, 0)$. The calculated density was 4.95 g/cc.

Gulbransen and Andrew⁽²²⁾ initially studied the reaction of columbium with a pure oxygen atmosphere at a pressure of 76 mm Hg (0.1 atmospheres) in the temperature range from 250 to 375°C (482 to 707°F). A semi-constant weighing method, utilizing a microbalance, was employed. Under the stated conditions of testing, columbium formed a protective film and oxidized by a parabolic rate law for periods up to six hours - the maximum length of test. No evidence was found for a transition in the rate of oxidation. In order to calculate thickness, the film was assumed to consist of CbO , but the assumption has been questioned⁽¹⁾. The activation energy for the parabolic reaction was calculated to be $22,800$ calories per gram mole. In more recent publications^(23,24) the authors reported results obtained in the temperature range from 375 to 700°C (707 to 1292°F). In all cases at or above 400°C (752°F) a transition from an initial parabolic rate to a final linear weight gain-time relation was observed: in general, the time to the transition decreased with increasing temperature. The transition took place at a scale thickness corresponding to a weight gain of about 50 mg/cm². In the range from 500 to 625°C (932 to 1157°F) the linear rate of oxidation was practically independent of temperature, while from 625 to 700°C (1157 to 1292°F) the linear rate increased with increasing temperature. At the higher temperatures, the initial pseudoparabolic behavior lasted for only a few minutes. Cathcart, Campbell, and Smith⁽²⁵⁾ also showed that the reaction of columbium with oxygen at 500°C (932°F) consisted of an initially parabolic reaction which, after a certain temperature dependent period, changed to a linear rate. It is postulated that at this point the reaction reverted to linearity because the rate controlling step became one of diffusive exchange through a constant thickness, imperforate remnant of the initial oxide film. The theories of Cathcart, Campbell and Smith differ from those of Webb, Norton, and Wagner⁽²⁶⁾ as to whether

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breakdown of the protective film occurs simultaneously with its growth or step-wise after a certain critical thickness has been reached.

The reaction of columbium in a pure oxygen atmosphere at pressures from 14.7 to 605 psia in the temperature range from 400 to 800°C (752 to 1472°F) has been studied by Bridges and Fassell⁽²⁷⁾. Nearly six hours were required before the oxidation rate became linear at 400°C (752°F) and a pressure of one atmosphere. The temperature dependence of the rate of oxidation showed a reversal in sign between 550 and 650°C (1022 and 1202°F). In this temperature region, the rate of oxidation was very sensitive to pressure.

The rates of reaction for columbium in wet and dry air in the range of 400 to 1200°C (752 to 2192°F) has been measured by Inouye^(20,28) who used continuous weighing methods. A transition from parabolic to linear behavior after 21 hours at 400°C (752°F) was reported; linear reaction curves were obtained in the temperature range from 600 to 1200°C (1112 to 2192°F). The effect of moisture varied at different temperatures, increasing the rate of reaction at 400°C (752°F), decreasing the rate at 600°C (1112°F), and having little effect at 800°C (1472°F) or above. At higher temperatures, rod specimens exhibited faster oxidation rates than did sheet specimens. Activation energies were 13,400 calories per mole in the temperature range from 600 to 900°C (1112 to 1652°F) and 4,350 calories per mole from 900 to 1200°C (1652 to 2192°F). The transition in activation energy was thought to be associated with the change in form of columbium pentoxide at 900°C (1652°F). X-ray techniques identified all oxide scales as one or more of the Cb_2O_5 modifications.

Battelle Memorial Institute data on unalloyed columbium have been presented in two bound reports^(3,29) and one Geneva Conference Paper⁽³⁰⁾. Columbium was found to oxidize in a linear manner when exposed to oxygen at one atmosphere pressure in the temperature range from 600 to 1200°C (1112 to 2192°F). From 600 to 1100°C (1112 to 2012°F) the activation energy was determined as being 5,410 calories per mole while the reaction proceeded more rapidly above 1100°C (2012°F). The reaction was exothermic at 1400°C (2552°F). The scales consisted of a very thin adherent layer of oriented Cb_2O_5 containing traces of CbO , and a porous outer layer of Cb_2O_5 . The rate determining reaction was suggested to be diffusion of oxygen ions through the adherent, oxygen-deficient Cb_2O_5 . The reaction between columbium and undried air proceeded at a linear rate, although more slowly than the reaction of columbium with pure oxygen. The heat of activation for air oxidation was 10,100 calories per mole in the range 600 to 1200°C (1112 to 2192°F).

At temperatures in excess of 900°F, the embrittlement of the base metal by contamination with oxygen becomes a problem as serious as the scaling of the metal, since its effect in terms of the thickness of the metal affected can exceed the thickness of metal lost due to scale formation. For example, after 5 hours at 1000°C (1832°F) the metal is hardened to a depth of at least 50 mils compared with about 30-40 mils of metal lost by conversion to oxide.

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THE OXIDATION OF COLUMBIUM BASE ALLOYS

Union Carbide Metals Company

Research and development on the oxidation characteristics of columbium and columbium base alloys was initiated almost three years ago in the Metals Research Laboratories of the Union Carbide Metals Company (formerly Electro Metallurgical Company) and was preceded by a considerable amount of process metallurgy research. For the last ten months, half of the program has been under CANEL sponsorship, and results have been given in monthly progress reports⁽³¹⁾ and periodic bound reports^(32,33). Personnel at Niagara Falls have also made available considerable data obtained prior to the initiation of CANEL sponsorship.

A comparatively large number of columbium base alloy samples have been evaluated by oxidation tests. In general, continuous weight gain data has been obtained by the use of recording analytical balances. The vast majority of tests have been made in a pure oxygen atmosphere. In order to allow the rapid preparation of test specimens, most oxidation test pieces have been machined from as-cast material melted several times with a tungsten electrode under a stagnant argon atmosphere in a button type furnace. Proprietary columbium has been used for all experimentation. Oxidation tests were usually of about 22 hours duration, except for pure columbium and those alloys which oxidized in a very rapid manner. Since linear, logarithmic, parabolic, cubic, quartic and complex weight gain-time behavior has been noted, a direct comparison of rate constants was considered as misleading. In all applicable tables, alloys have been rated by comparing the total weight gain per unit area (mg/cm^2) in 100 hours, thus involving the use of projected values. In order to extrapolate, a straight line was fitted to the last five to ten hours of the recorded weight gain-time curves, and the intercept and slope of the line was noted. The value of 100-hour weight gain ($\text{mg}/\text{cm}^2/100$ hours) was then calculated from the straight line formula.

Before proceeding to a discussion of results obtained with alloy specimens, a most interesting type of behavior noted for coated pure columbium will be treated. A one-quarter inch diameter columbium rod which had been coated with 0.08 inches of IM-5 (proprietary Linde Mo-Si-Cr-B-Al) was exposed in air for about 1000 hours at 1150°C (2102°F). Sometime during the test a thin fissure opened up in the coating, and oxidation of the underlying columbium took place. Since all of the oxidation products were constrained by the surrounding unoxidized columbium, thermodynamically stable reaction products of pure columbium in air developed to a much thicker extent than would normally occur. The small inclusion which thus formed revealed, under petrographic examination, at least five distinct phases. Precision x-ray examination confirmed the presence of $\text{H-Cb}_2\text{O}_5$, Cb_2N , CbO_2 , CbN , and two other phases which cannot be identified. The results are most interesting since the usual products of the oxidation reaction include only various forms of columbium pentoxide.

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Work was initiated at the binary level, but was soon expanded to more complex alloy systems as considerable binary data began to appear in the published literature. As Table B-1 indicates, the majority of tests involving two component alloys were performed at one temperature only - 800°C (1472°F). Several alloys, including those with Be (1.1 w/o), Ce (0.5, 1.0, 5.0 w/o), Si (3.0 w/o), Th (1.0, 21.0 w/o) and Y (5.0 w/o) exhibited linear oxidation rates greater than that for pure columbium. A binary alloy containing 2.0 w/o copper exhibited linear behavior similar to that of unalloyed columbium. Five aluminum binaries also gave linear oxidation rates, but the rate decreased considerably with increasing aluminum content. Cobalt alloys at the 1.0, 5.0, and 10.0 w/o levels exhibited behavior characteristics somewhat similar to the case of aluminum, although the improvement with increasing alloy content was not so great. Chromium alloys at the 5.8 and 15.0 w/o Cr levels initially exhibited parabolic behavior, but reversion to a linear rate law took place after only two hours of exposure. The $CbCr_2$ intermetallic compound (52.8 w/o Cr) also demonstrated linear weight-gain behavior with respect to time, but the rate was about three orders of magnitude less than for the case of pure columbium. A binary containing 25.6 w/o Mo also exhibited pseudo-parabolic behavior, but there was a weight loss after only two hours of exposure indicating the volatilization of MoO_3 . Personnel of the Metals Research Laboratories generally regard alloys containing molybdenum as undesirable because of high oxidation rates accompanied by medium to severe volatilization (this opinion is not shared by many workers, as it appears that the behavior depends to a great extent on the concentration of molybdenum considered). Since weight-loss due to volatilization is substantially greater at higher temperatures, the weight gain for a given time, such as 100 hours at 1200°C (2192°F) will often be less than that measured at lower temperatures. All Cb-Ni binaries through 20 w/o Ni exhibited linear oxidation rates, but the rate decreased with increasing nickel content. Tin, at the 2.0 w/o level, resulted in a linear oxidation rate, and excessive spalling occurred.

Although not indicated in Table B-1, several binary alloys containing tantalum have been tested at each of the three usual temperatures. For alloys containing 5, 10, and 30 w/o Ta, linear oxidation rates were recorded. The 5 and 10 w/o Ta additions were almost equally effective in decreasing the oxidation rate at 1000 and 1200°C (1832 and 2192°F) to a level of about 6000 to 8000 mg/cm² for 100 hour exposure, but increased the rate at 800°C (1472°F) as compared to pure columbium. The 30 w/o Ta alloy was more oxidation resistant at 2192°F (1200°C) than the preceding two examples, but was prone to spalling at 1832°F and inferior to pure columbium at 1472°F. A binary with 7.0 w/o vanadium exhibited a parabolic rate constant of 3.82×10^{-7} mg²/cm⁴/min, and a 15.4 w/o V alloy also exhibited parabolic behavior, although there was evidence of the formation of a molten oxide in the latter case. Cb-W binaries in the 20 to 40 w/o W range spalled to such an extent that weight gain determinations were impossible. Alloys containing up to about 10 w/o Zr exhibited characteristics somewhat similar to those shown by pure columbium; near the 50 w/o Zr level a considerable improvement in oxidation resistance is gained, the rate remaining linear.

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In addition to the data contained in Table B-1, Cb-Ti, Cb-Fe, and Cb-Ti-Fe alloys have also been the subject of a special investigation⁽³²⁾. Chemical analysis was used to determine the composition of the oxides, and it was found that there was no preferential oxidation of the different elements in the alloys. Titanium alloys in the 10.0 to 25.6 w/o Ti range gave parabolic rate law behavior. The complex oxide $TiO_2 \cdot Cb_2O_5$, which is comparatively stable, was found to predominate in the outer oxidation layer, and when the composition of the base alloy was in the ratio of two atoms of columbium to one of titanium (20.5 w/o Ti) a minimum rate of oxidation was found to occur for the alloy system. Behavior essentially equivalent to that for the titanium-containing alloys was found in Cb-Fe binaries, the complex oxide $FeO \cdot Cb_2O_5$ being here applicable (minimum oxidation rate at 23.1 w/o Fe). A very hard zone in the metal adjacent to the oxide was double refracting, and was believed to be an oxygen contaminated region. Information concerning the chemical composition of oxide films formed on selected Cb-Ti, Cb-Fe, and Cb-Ti-Fe alloys is contained in Table B-2.

In the introductory section of this memorandum it was pointed out that most listed compositions are "nominal" compositions: the analysis of the charge material before melting. Charges containing as much as 15 w/o Mn have resulted in a recovery of as little as 0.01 w/o Mn at the button stage, the remainder of the manganese having been volatilized during arc melting. A considerable softening of the columbium results. Apparently one effect of the manganese addition is to promote the expected carbon monoxide boil and thereby to reduce both carbon and oxygen; another is to alter the distribution pattern of precipitates. The maximum effect would be expected when a careful stoichiometric balance exists between the carbon and oxygen contents of the manganese and the columbium being treated. A similar metal loss and softening effect should be expected for the case of cerium or thorium additions, and perhaps for beryllium additions as well. The effect of cerium additions on the reduction of retained oxygen has been treated in the published literature⁽³⁴⁾.

As is the case throughout this memorandum, all alloys more complicated than binaries have been considered as ternaries and their metallurgical modifications. Complications exist even for this type of classification, however, since a quaternary alloy may be thought of as a modification of several different basic ternary systems. The oxidation test results listed in Tables B-3 through B-7 indicate that at least one specific ternary composition in each of 18 different ternary systems have been considered.

Ten different systems and a few advanced modifications are listed in Table B-3, which is entitled "Miscellaneous Ternary Systems and Modifications." In addition, screening tests were accomplished on samples in the Cb-Cr-Si system. Alloys with a nominal composition of Cb-6Cr-3Si and Cb-12Cr-3Si when exposed to pure oxygen at 1472° (800°C) suffered such extreme spalling that the determination of actual rate constants was impossible. With one exception, alloys in the Cb-Al-Si system were characterized by linear oxidation rates of a most unpromising nature: the alloy containing the largest amount of silicon of any tested, Cb-10Al-5Si, exhibited a parabolic rate constant of $1.47 \times 10^{-8} \text{ g}^2/\text{cm}^4/\text{min.}$ for the first four hours of exposure after which a linear rate of $1.95 \times 10^{-5} \text{ g/cm}^2/\text{min.}$ became operative. With the exception of those alloys listed near the end of Table B-3, work on the other basic ternary systems has been terminated in favor of more promising systems.

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Work on columbium-high zirconium alloys is a comparatively new development apparently initiated as a result of exploratory research done at Ohio State University. In the last two month period work on the system has been curtailed in favor of more promising formulations from an overall viewpoint, but the system is still regarded as very promising with oxidation behavior as a prime consideration. Many of the high zirconium alloys suffer from an unusual spalling reaction at 800°C (1472°F) which appears to be associated with the ignition and sparking of the exfoliating material. To determine if behavior would be different in an air atmosphere, as compared to the flowing oxygen atmosphere ordinarily used, an oxidation test of an 38Cb-40Zr-15Ti-5Al-2V alloy was carried out in static air and the weight gain rate was found to be negligible. When the oxidizing medium was changed to flowing air, however, the rate of weight gain changed to 0.442 as compared to 0.596 mg/cm²/hr for 1832°F (1000°C) exposure in pure oxygen. After several hours in the flowing air atmosphere, spalling began to occur, but no severe exothermic reaction or sparking was observed. The tendency to sparking and exfoliation during the 800°C (1472°F) oxidation of Cb-Zr-Ti base alloys can be partially reduced by lowering the zirconium and titanium levels to 30 and 10 w/o, respectively. It was concluded that in the basic ternary system, maximum oxidation resistance in pure oxygen atmospheres could be obtained at the 60Cb-30Zr-10Ti level. Complete elimination of the spalling reaction is achieved with the addition of aluminum plus tin, or aluminum plus vanadium; Al-Sn-V combinations, or additions of Al only, were found to be ineffective. An alloy with a nominal composition of 48Cb-35Zr-10Ti-5Al-2V exhibited the formation of a liquid phase when attempts were made to hammer forge a button at 1280°C (2336°F), although it has been established by other tests that melting of the alloy begins at about 1830°C (3326°F) and is completed at about 1990°C (3614°F). It would appear that during fabrication that some type of reaction must have occurred while heating the forging, which produced a low melting point phase, possibly in the grain boundaries.

The high strength 85Cb-5Zr-10W and 92Cb-5Zr-3Cr alloys whose ultimate tensile strengths at 1200°C (2192°F) approach the 45,000 psi range have been found to be prone to spalling at 1472°F (800°C) and more reactive at 1000°C (1832°F) than pure columbium. Additions of titanium and vanadium to the basic ternary compositions have been effective both in preventing spalling and in greatly increasing oxidation resistance, but it is postulated that strength properties have been considerably reduced. Work on the two systems is currently quite active at Niagara Falls.

Table B-4 entitled "Alloys Containing Cb, Ti, Al and/or V" is primarily concerned with Cb-Al-V, Cb-Ti-Al, and Cb-Ti-V ternaries and the composite quaternary. At the present time a considerable amount of work is being accomplished with these basic systems, and it is expected that the data will be supplemented in the near future. It will be noted that oxidation resistance deteriorates when vanadium levels in excess of five weight percent are considered, undoubtedly due to the formation and loss of liquid complex vanadium oxides. Many if not all of the compositions listed in Table B-4 are characterized by parabolic oxidation rates. Analysis of data for the Cb-Al-V system indicated that maximum oxidation resistance was found in the range of 3 to 5 w/o Al and 3 to 5 w/o V. The preferred compositions contain equal

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weight percentages of aluminum and vanadium, or a slight excess of vanadium not exceeding 1 w/o.

Table B-5 is entitled "Cb-Ti-Cr and Cb-Cr-Al Systems and Modifications"; it will be noted that many of the quaternary and more complex alloys may also be thought of as modifications of the Cb-Ti-Al, Cb-Ti-V, and Cb-Al-V systems previously listed in Table B-4. While work on the basic Cb-Ti-Cr and Cb-Cr-Al systems has not been entirely dropped, it has been considerably curtailed. A Cb-12Cr-5Al sample exhibited a parabolic rate constant of $1.51 \times 10^{-8} \text{ g}^2/\text{cm}^2/\text{min}$, but the sample suffered from spalling which began after 750 minutes in pure flowing oxygen at 1472°F (800°C) and became critical after 1275 minutes at temperature.

The complex Cb-Ti-Cr-Al-V system listed along with a number of modifications in Table B-5 is one that was initially investigated almost two years ago. It has been modified a large number of times in an effort to increase mechanical strength and fabricability while retaining a high order of oxidation resistance. Modifications have not been particularly successful in obtaining mechanical metallurgy goals. A specific alloy in this quinary system is one of two components in a rather promising proprietary coating for columbium base alloys. The most recent modifications have consisted of dropping the titanium content to 10 w/o and the chromium content to between 4 and 8 w/o. It was found that these alloys were only slightly more oxidation resistant than Cb-Al-V ternaries and inferior to Cb-Ti-Al-V quaternaries.

The Cb-23Ti-15Cr-5Si alloy listed in Table B-5 is actually one developed by a competitors laboratory, as is the Cb-40Ti-5Cr-10Fe-5Si composition. Weight gain results for each of these alloys was excellent, but the materials exhibited considerable spalling on cooling from 1832°F . Fabrication was impossible primarily because of the high Cr, Si, and/or Fe contents which resulted in the formation of exceptionally brittle intermetallic compounds.

The Cb-Ti-W and Cb-Ta-W systems and their modifications are considered in Table B-6. Tantalum as an alloying addition has been essentially eliminated from consideration since there was thought to be little benefit to be derived from either an oxidation or mechanical metallurgy viewpoint. A tendency to an appreciable resistance to oxidation at higher temperatures, such as 2192°F , but also to pronounced spalling or high oxidation rates at lower temperatures is characteristic of Cb-Ta-W ternaries. Additions of titanium to this base promoted the spalling at 800 and 1000°C , but at 1200°C the addition served to improve the resistance to oxidation. Small additions of vanadium to the Cb-Ta-W base were ineffective in preventing the spalling reaction, but when combined with titanium no spalling occurred above 1472°F . Al, Ni, and Fe additions to the Cb-Ta-W base also resulted in alloys that spalled at 1472°F . It appears that the spalling reaction can be entirely prevented, however, by the simultaneous presence of 10 w/o Ti and 3 w/o V, with the possibility that molybdenum can be substituted for vanadium.

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Within the last two months, work has been concentrated on the basic Cb-10Ti-20W-3V composition. Attempts to improve the oxidation resistance by small additions of Al, Be, Cr, Fe, and Ni in various combinations limited to single phase systems have been interpreted as indicating the superiority of the Fe-Ni combination, but the Be effect should not be neglected.

Comparatively good oxidation resistance, as determined by continuous weight gain tests, may be achieved in the Cb-Ti-Fe ternary system, as the data contained in Table B-7 indicates. However, work on this system has not been emphasized because of other important considerations (extreme brittleness, lack of fabricability). Essentially all compositions are characterized by oxidation rates that decrease with increasing time (parabolic, logarithmic, etc.). An unusually rapid oxide formation, followed by a marked reduction in rate, characterizes alloys of the quaternary system Cb-Ti-Fe-Al, which in general exhibits logarithmic behavior in the composition ranges considered. Unfortunately, the oxide scales formed in the quaternary alloy appear to have little resistance to thermal shock. In addition to the data contained in Table B-7, results have also been obtained on the effect of misch metal additions on the oxidation characteristics of Cb-Ti-Fe alloys. These additions, in the range of 2 to 20 w/o misch metal, to the Cb-20Ti-20Fe alloy had a small beneficial effect at 2192°F, but were deleterious at lower temperatures.

E. I. duPont deNemours and Company

Information concerning the columbium base alloy program being carried out under the general direction of Dr. Mahla in the Pigments Department of the duPont Experimental Station is quite limited. The program is entirely proprietary, with the exception of a limited joint effort with Thompson Products apparently concerned with fabrication and sales. The overall research and development effort must be quite extensive and is probably wider in scope than that undertaken by the Union Carbide Metals Company if comments concerning yearly budgets are accurate. In addition to physical and mechanical metallurgy research, considerable work has been accomplished in the process metallurgy field, with concentration being given to the production of an ultra pure raw material which would require little if any upgrading by vacuum melting techniques. Unfortunately, the company has refused to sell raw unmelted columbium, claiming that examination of the product could reveal the nature of the proprietary reduction procedure; it is possible that the production of the pure raw product is now only sufficient to meet research and development requirements, since the Temescal electron beam melting process has been used by duPont to upgrade a comparatively large amount of material.

The majority of information concerning the oxidation testing program carried out by duPont personnel is contained in three recently granted United States Patents^(35,36,37). The first of these⁽³⁵⁾ is primarily concerned with an exploitation of the basic Cb-Ti-Al ternary system. Button compacts were melted into small ingots under an inert atmosphere using a thoriated tungsten electrode. A weighed sample of an alloy, in a porcelain crucible slotted to insure adequate access of air to the ingot, was placed in a "Globar" furnace and exposed for 16 hours at 1832°F (1000°C) to an air

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purge of two cubic feet per minute. After exposure, samples were cooled and re-weighed, and the amount of oxidation was reported as a percent weight gain of the original sample. Data for the Cb-Ti-Al system and its complex modifications, as reported by duPont investigators, is included in Table B-8.

The two more recent duPont patents^(36,37) deal primarily with the Cb-Fe-Al and Cb-Cr-Al ternary systems and their advanced modifications. As in the case of the earlier patent, test samples were initially prepared by non-consumable electrode melting processes. However, oxidation test data was obtained from carefully machined specimens by the use of recording thermobalances. Samples were maintained at 1832°F (1000°C) and 2192°F (1200°C) for 24 hours, and reported data consisted of the weight gain rate (mg/cm²/hr) during the last hour of the exposure cycle. Upon termination of the oxidation test, the samples were cooled and the protective nature and adherence of the oxide layers were evaluated by metallographic examination. Test results for the Cb-Fe-Al system and its modifications are included in Table B-9, while Table B-10 deals with the Cb-Cr-Al system and more complex modifications.

One of the two most publicized columbium-base alloys developed to date is a Cb-10Ti-10Mo composition announced by the duPont-Thompson Products team. The technical paper⁽³⁸⁾ and sales brochure⁽³⁹⁾ contain data related to two distinctly different effects resulting from air exposure at elevated temperatures. The first of these is the formation of the usual oxide scale, which results in a loss of effective metal thickness (surface recession, external oxidation). Data obtained at 2000°F is included in Table B-11. The second type of effect is due to the diffusion of oxygen into the base metal (internal oxidation) resulting in the formation of an oxygen affected zone of increased hardness. The latter type of oxidation does not result in a loss of metal thickness, and would be expected to result in increased load carrying capacity for tensile or creep-rupture specimens. The depth of the affected zone can be measured metallographically or can be determined by microhardness techniques. The results of tests in air at 2000°F for this type of internal oxidation are listed in Table B-12.

Fansteel Metallurgical Corporation

Dr. A. B. Michael⁽⁴⁰⁾ reported on the Fansteel Metallurgical Corporation columbium-base alloy program at the A.I.M.E. Third Annual Reactive Metals Conference in Buffalo during late May, 1958. Initial oxidation tests consisted of screening of a number of tungsten-electrode-melted binary compositions. Specimens originally 3/8" x 3/8" x 1/2" were hand ground through a 00 finish, and then were exposed in a furnace maintained so as to give a complete volume change of air for each minute of test. In the usual procedure, the initial thickness of a test coupon was accurately determined with the aid of micrometers. The specimen was then exposed to flowing air at 2000°F for 16 hours and upon removal from the furnace the oxide scale was mechanically removed. Final coupon thickness was measured and the difference between initial and final thicknesses, divided by two (since two surfaces are involved), was reported as the "displacement of the metal interface." This value constitutes the amount of metal consumed in oxide scale formation (external oxidation). Applicable test results obtained with binary alloys for this type of oxidation test procedure are listed in Table B-13.

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Of the binaries tested, those of the Cb-W system were the most resistant to scaling and the resistance increased with increasing W content in the range of 5.7 through 45.9 w/o W. The tendency to spalling on cooling also decreased with increasing tungsten content and all exposed samples were characterized by a black, dense, adherent subscale. Molybdenum concentrations of 3.1 to 10.3 w/o increased the resistance to scaling, but high concentrations (30.7 w/o) were detrimental to oxidation resistance due to the formation of volatile MoO_3 . Every binary alloy tested spalled upon cooling from the exposure temperature. Cb-Mo specimens also exhibited the formation of a black, dense, adherent subscale. Enhanced scaling resistance was also demonstrated Cb-Al, -Cr, and -Si binaries, but it became necessary to exceed the limit of solid solubility in order to achieve results competitive with Cb-Ta, Cb-Mo, and Cb-W solid solutions.

A maximum resistance to scaling in the columbium-tantalum system at temperatures between 1000 and 2000°F was found to occur at a composition of approximately 20 a/o Ta (32.7 w/o Ta). At temperatures in the range of 1500 through 2000°F the alloy was more resistant to scaling than either columbium or tantalum and the scale which formed on the alloy was more adherent, less porous, and had a tan color rather than the characteristic white of Cb_2O_5 and Ta_2O_5 . For the binary alloy, pure columbium and pure tantalum, the effective depth of oxygen and/or nitrogen diffusion into the base metal has been determined after a 16-hour air exposure at temperatures in the range of 1000 through 2000°F. The values given in Table B-14 are the depths below the metal-oxide interface at which there were abrupt changes in hardness as determined by microhardness traverses on cylindrical specimens having an original diameter of 0.375". The data included in Table B-14 may be regarded as a measure of "internal oxidation."

A total of sixteen ternary systems have been investigated in a manner identical to that used for the binary alloys; data is included in Table B-15 for the Cb-Cr-Co system and several of its more complex modifications, and in Table B-16 for other ternary systems and their derivatives. Many of the alloys are modifications of the Cb-32.7 Ta binary in which the ratio of four atoms of columbium to one of tantalum is maintained. Ternary alloys containing components capable of forming spinels, such as Cr or Fe with Co or Ni, had the highest resistance to scaling. For given percentages of alloying elements, the alloys containing Cr-Co had a higher resistance to scaling than those containing Cr-Ni, Fe-Co, or Fe-Ni. The scales formed on the Cb-Cr-Co alloys were more adherent than those for the other columbium-base alloys tested.

For several of those compositions which showed promising resistance to scaling, pseudo continuous weight gain tests were made. At 2000°F in slowly flowing air, the Cb-12.9Cr-8.8Co alloy was the only one to show a parabolic rate of oxidation for long periods of time. The rates for alloys containing Mo, W, and Ta were parabolic during the initial stages of oxidation and linear for the later stages. In Table B-17, the total weight gain after 10 hours at 2000°F and the rate of oxidation at that time and temperature are tabulated.

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Nuclear Metals Incorporated

The usual oxidation test performed in the Laboratories of Nuclear Metals Incorporated⁽⁴¹⁾ on arc cast and machined columbium alloy specimens consisted of a two hour exposure to air at 1800°F. Test pieces were accurately weighed before and after exposure; the data presented in Table B-18 is average weight gain in the units of mg/cm²/hr. Only a very few compositions in the Cb-Al, Cb-Ce, and Cb-Cr binary systems were investigated. All ternaries and quaternaries were composed entirely of Cb, Cr, Al, and/or Si.

Spectroscopic, x-ray fluorescent, and x-ray diffraction analyses were made on the oxide scales of several exposed samples in order to determine the elemental and chemical compound constituents. In the case of Cb-Cr binaries, it was found that the increase in oxidation resistance with increasing chromium content (0 to 20.9 w/o Cr) was accompanied by an increase in the amount of CrCbO₄ present in the scale. Although Cb₂O₅ (M form) was simultaneously present, Cr₂O₃ and CrO₃ were not detected. It may be hypothesized that the CrCbO₄ complex oxide affords some protection, but that the kinetics of the oxidation reaction together with the rate of diffusion of chromium in columbium is such as to prevent CrCbO₄ from completely covering the surface.

A quaternary 52 Cb-23Cr-10Al-15Si alloy of superior oxidation resistance was found to form a thin oxide scale consisting of alpha Al₂O₃ plus as yet unidentified compounds containing Cb, Cr, Si and perhaps Al. Neither Cb₂O₅ or Cr₂O₃ were detected in the film.

Kennecott-Battelle

At the Battelle Memorial Institute⁽⁴²⁾ oxidation tests have been performed on proprietary Kennecott columbium-base alloys prepared by button melting with a tungsten-tip electrode under a stagnant inert atmosphere. In general, tests consisted of 16 hours exposure to air at 1800°F. Specimens were carefully measured and weighed before test, and were reweighed after exposure so as to determine a total weight gain in 16 hours. Data for alloys of interest are included in Table B-19.

Seven compositions in the Cb-Ta binary system were exposed, and of the samples tested from five ternary systems and two quaternary systems, all but two had appreciable tantalum contents. It should be borne in mind that the Kennecott-Battelle program was one of the few research projects primarily interested in a study of the strengthening of columbium base alloys and that oxidation studies were of secondary interest only.

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Sylvania-Corning Nuclear Laboratory

H. P. Kling⁽⁴³⁾ has briefly reported on the columbium alloy research program being carried out in the Sylcor Laboratories. In the study of pure columbium oxidized at 1832°F (1000°C), a search was made for the lower oxides (CbO and CbO₂) without success. In some cases a gray or black phase appeared next to the metal in contrast to the bulk of the scale that was white or buff in color. It was established that some oxygen can be readily removed from the oxide scale, and that while the oxygen-deficient crystal is black, the stoichiometric compound is white.

For Cb-Mo and Cb-V binary systems, weight gain was measured after a one-hour exposure at 1832°F (1000°C). Plots of weight gain versus percent composition showed minimums at about 5.8 w/o V and 5.2 w/o Mo. In each case the weight gain value at the minimum was about one-eighth that of pure columbium. The basic mode of oxidation appeared to be similar to that for pure columbium. X-ray diffraction patterns indicated only the presence of "H" Cb₂O₅, although there were slight line shifts. In both instances the color and appearance of the oxide differed from that of "H" Cb₂O₅. An alloy containing 5.8 w/o V was found to have 4.09 w/o V in the oxide scale; 3.56 would be expected if the alloy oxidized quantitatively to Cb₂O₅ plus V₂O₅. An alloy containing 5.2 w/o Mo was found to have 3.05 w/o Mo in the oxide scale; 3.6 w/o would be expected in this instance.

Weight gain was also measured after a one-hour exposure in dried air at 1832°F for Cb-Ti binary alloys. A plot of weight gain versus percent titanium showed that the weight gain decreased, in a rather parabolic manner, the greater the titanium content; improvement was only marginal for titanium contents in excess of 11 w/o. The mechanism of oxidation was considered to be similar to that prevailing for the case of pure columbium. The oxide scale showed only the crystal structure of "H" Cb₂O₅ with slight line shifts (x-ray diffraction) despite the changed appearance and color of the oxide. An alloy containing 11.4 w/o Ti was found to have only 3.6 w/o Ti in the oxide scale, although 6.05 w/o would have been expected if the metal had oxidized to TiO₂ plus Cb₂O₅ without partitioning of the titanium content.

Lewis Flight Propulsion Laboratory

Messrs. F. J. Clauss and C. A. Barrett have presented two papers^(44,45) which review the columbium alloy program carried out at the Lewis Flight Propulsion Laboratory of the then National Advisory Committee for Aeronautics. The first of these⁽⁴⁴⁾ is concerned with the screening of a large number of binary systems. Samples were prepared by mixing columbium powder obtained from the Fansteel Metallurgical Corporation with appropriate alloying ingredients: buttons measuring 1/2 inch in diameter and 1/8 inch in thickness (about 2 gm. weight) were cold pressed in a closed die. The as-pressed buttons were vacuum sintered at a pressure of less than 5 microns, then repressed and resintered. The final sinter was conducted at 3500°F, or as close to that temper-

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ature as was deemed advisable in view of certain characteristics of the alloying elements (vapor pressure, melting point, etc).

Prior to testing, all specimens were polished through 000 emery paper, cleaned in acetone, and accurately weighed. After preparation was complete, test coupons were placed in ceramic boats and inserted into a tube furnace at the desired temperature. Air that had been dried by passing through a column of "Drierite" was slowly circulated over the specimen. Tests were run for four hours at 1832°F (1000°C) and for two hours at 2192°F (1200°C). Samples were accurately reweighed after test and weight gain was reported as the average over the duration of exposure. These weight gain values are not thought to be particularly meaningful, since specimens were somewhat porous, the percent of theoretical density varying from specimen to specimen. Oxidation weight-gain values undoubtedly reflect to a certain extent the porosity of the specimens being tested. The oxide scales were arbitrarily assigned a code number between 1 and 5 to catalog their appearance. Scales in Class 1 appeared dense, tight, and disc like: these were adherent at the test temperature but generally popped loose from the base metal during cooling. Scales from Class 1 were associated with the lower oxidation rates. At the other extreme were scales in Class 5: these were very porous, powdery, and had mushroomed out from the base metal. Intermediate numbers were assigned to scales between these extremes. Values of average weight gain together with the code number for scale appearance are listed in Table B-20. It was intended that each alloy system be investigated at the 1.0, 2.0, 5.0, 10.0, and 25.0 a/o levels.

The second Clausen and Barrett paper⁽⁴⁵⁾ was devoted entirely to a study of the oxidation behavior of Cb-Cr alloys. Alloys containing up to 10.3 w/o Cr were prepared by a powder metallurgy process identical to that previously described. During oxidation testing individual specimens were suspended from one arm of a "Chainomatic" balance into a vertical tube furnace that was closed at the bottom and open at the top. Exposures of 2.5 hours duration were made at 800°C (1472°F), 1000°C (1832°F) and 1200°C (2192°F). After test, the oxide was examined visually, the d-values determined by x-ray diffraction, and the chemical analysis of the scale determined.

At 1472°F, the dissolved chromium had two effects on the scale structure. First, at all chromium compositions, it resulted in a contraction of the Cb_2O_5 lattice: secondly, above about 2.5 w/o Cr it promoted the formation of the "H" form of Cb_2O_5 along with the usual "L" form. In the composition range of 2.5 to 5.2 w/o Cr, there appeared to be a critical ratio of the "H" to "L" oxide structures at which a hard, mechanically sound and adherent scale was formed. Below this range of compositions only the "L" form existed which was porous and not protective. Above 5.2 w/o Cr there was apparently an excessive amount of "H" form Cb_2O_5 and the scale became powdery. The best appearing scale in the entire study occurred in the composition range of 2.5 to 5.2 w/o Cr.

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At 1832°F only the "H" form of Cb_2O_5 was formed. As was the case with several of the scales formed at the lower test temperature, dissolved chromium apparently altered the lattice enough to make the scale more stable and mechanically sound. Increasing amounts of chromium within the range 2.5 to 10.3 w/o improved the character of the scale and reduced oxidation rates. However, the best scale obtained at 1832°F was not as tough as the scale formed at 1472°F on the 2.9 w/o Cr alloy.

Although the chromium solubility in the oxide lattice formed at 2192°F was substantially the same as that found in the lower temperature oxides, the protection afforded was poor, the scales having become porous and cracked as a result of exposure at the higher temperature.

Horizons Incorporated

Although the columbium program carried out under W.A.D.C. sponsorship at Horizons Incorporated was primarily concerned with coatings, E. C. Hrakis has reported on the oxidation behavior of a limited number of columbium base alloys. (46,47) Specimens were consolidated by double melting homogeneous compacts in a tungsten electrode furnace. A standard finish was produced on machined or hand ground pellets by hand rubbing the pieces through 000 emery paper lubricated with a light oil. Continuous weight gain data was obtained for air exposure, and was reported as such. Exposure was generally only for two or three hours, and reported data, in addition to sufficient information to allow construction of the weight change-time curve, usually included a value for the average weight gain and a description of the formed oxide film. A resume of Horizons Incorporated oxidation test data is included in Table B-21.

Ohio State University

The Department of the Navy supports a program at Ohio State University, under the direction of J. W. Spretnak and R. Speiser, aimed at the protection of columbium against oxidation at elevated temperatures. Samples of alloys were arc melted at least three times under an argon atmosphere in a tungsten electrode furnace containing a water cooled copper hearth. Prior to alloy melting, the atmosphere was gettered by melting a titanium button for two minutes. Alloy samples weighed approximately five grams each. Those compositions which were sufficiently ductile were cold rolled into 0.030 inch sheet. Otherwise, the buttons were machined into rectangular parallelepipeds approximately 0.3 x 0.15 inches or were left in the as-cast, hemispherical button shape. Samples for oxidation testing were polished through 0000 emery paper and were degreased in acetone. During exposure, specimens were suspended by a platinum wire into a vertical tube furnace operated at the desired temperature. The wire was attached to one pan of an analytical balance mounted above the furnace. Continuous weight gain versus time data were taken for each sample oxidized in still, undried air.

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Data concerning Cb-Ti and Cb-Cr binaries and the Cb-Ti-Cr ternary system are included in Table B-22.⁽⁴⁸⁾ All Cb-Ti alloys tested spalled upon cooling to room temperature, many so violently that pieces of oxide were thrown as far as one foot in the air. A preliminary investigation of the Cb-Cr binary system indicated that the oxides formed on these alloys did not spall upon cooling to so great an extent. The possibility thus existed that the addition of Cr to Cb-Ti bases might suppress spalling. The ternary system was investigated, first to determine if a composition could be found which exhibited a parabolic oxidation rate, and second to determine if the spalling on cooling could be suppressed. A Cb-27.8Ti-6.6Cr alloy exhibited true parabolic behavior at the testing temperature of 1652°F; upon cooling, the oxide scale spalled as readily as did that for the best Cb-Ti binary.

Previous work at Ohio State University had shown that small zirconium additions were actually detrimental to the oxidation of columbium. However, above 10 Zr, oxidation resistance increased significantly with increasing zirconium contents, and the oxide film became more adherent. As Table B-23 shows, continuous weight gain tests were performed on binary alloys containing 35 to 65 w/o Zr; an alloy containing 45 w/o Zr appeared to exhibit parabolic behavior for the first five hours of test, but the oxidation rate increased and became approximately linear as the exposure progressed. The change from a parabolic to a linear rate appears to be due to the shearing of the oxide film at the sample edges after the film has become sufficiently thick. Once the film has cracked, oxygen has direct access to the metal surface or to a very thin, sub-film adjacent to that surface; under these conditions a non-parabolic rate would be expected.

In a more recent report⁽⁴⁹⁾ it is stated that a number of alloys in the Cb-Zr-Ti system have been tested, and that an alloy containing Cb-50.8Zr-2.7Ti was found to possess the best combination of low oxidation rate and non-porous adherent oxide film. Continuous weight gain data obtained at 900, 1000, and 1100°C is included in Table B-24. The oxidation behavior can be described by the quartic relationship $W^4 = k t$. The unusual weight gain-time relationship results from two different oxidation processes occurring simultaneously on and in the alloy. One process is the usual formation of an external oxide layer; the other is the diffusion of additional oxygen into the base metal (internal oxidation). At room temperature, this internal oxidation is manifested as a peritectic-like dispersion of oxide phases in a solid solution matrix. X-ray diffraction has indicated that the outer oxide is primarily $6 \text{ ZrO}_2 \cdot \text{Cb}_2\text{O}_5$; the internal precipitate is primarily monoclinic ZrO_2 , although CbO has been detected. The room temperature hardness of the oxidized alloy reaches a maximum of 1212 VHN in the outermost region of internal oxidation. The hardness drops off rapidly toward the center of the specimen; in a specimen oxidized for 42 hours at 1832°F (1000°C), the as-cast hardness of 278 VHN was reached at a depth of 25 mils below the outer metal-oxide interface.

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Battelle Memorial Institute

In several respects one of the most comprehensive research programs concerned with the oxidation of columbium base alloys has been that carried out at the Battelle Memorial Institute under Government sponsorship. While the number of individual compositions considered has not been as large as in several other programs, a more complete evaluation procedure has been attempted. For several specific compositions, intermittent and continuous weight gain tests have been used, the amount of metal consumed in the formation of oxide scales has been evaluated, and the depth of internal oxidation has been determined. Results have been included in several reports and papers^(30,50,51) and have recently been summarized in one larger report.⁽³⁾

Initial data⁽⁵⁰⁾ were the result of a very preliminary type of program. Nine binaries at the nominally five weight percent level were considered, as were ternary modifications with 9.5 and 19.0 w/o Ti, making a total of 27 compositions in addition to pure columbium. To determine the effect of alloying on the oxidation characteristics of columbium, small specimens machined from arc cast buttons were checked for short time oxidation resistance by a weight gain method. The alloy specimens, machined to about 0.5 x 0.5 x 0.07 inches, were hand ground on 0000 grit emery paper, measured, washed in acetone, rinsed in absolute alcohol, and weighed. For testing, each specimen was exposed in a pre-fired porcelain crucible, each crucible having been weighed, exposed for one hour at 1800°F, and reweighed just prior to the oxidation test. The crucibles containing the specimens were then exposed for one hour at 1800°F in still air. After exposure, the crucibles, specimens, and collected oxide were reweighed and the weight gain during exposure was calculated as grams per square inch of original surface area; in Table B-25 the data have been converted to the more usual units of mg/cm²/hr so as to be more comparable with results reported by other laboratories.

A second series of tests was concerned with the evaluation of binary columbium-base alloys containing up to 35 a/o of additive element. The alloys were melted as small buttons in a helium atmosphere furnace on a water cooled copper hearth. Prior to testing, buttons were machined into rectangular specimens about 0.1 x 0.2 x 0.45 inches. For oxidation testing, the specimens were placed on inverted porcelain crucible covers and supported by one half inch diameter porcelain rings so that minimum contact area was maintained between the specimen and the support. Specimens were exposed to air at 600, 800, and 1000°C in a muffle furnace for periods up to 20 hours, depending on the oxidation rate. No attempt was made to control humidity. Weight data were recorded initially and after 1, 5, 10, 15, and 20 hours of exposure; the type of procedure used, involving intermittent cooling and heating, makes it difficult to determine the rate law governing the oxidation reaction. In Table B-26, average weight gain rate is reported in the units of mg/cm²/hr. After exposure, the oxide scale was carefully removed by mechanical means and the specimen reweighed. From known values of initial and descaled weight, it was

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possible to calculate an average rate of weight loss - an approximation of the amount of metal converted to oxide scale: average values of this parameter are included in Table B-26.

The mechanically removed scale was analyzed for columbium, additive element, and oxygen by standard analytical chemistry techniques. Quite often only two of the constituents were determined, and the third calculated. Data concerning the composition of the oxide scale for the binary alloys are included in Table B-27.

Following completion of the oxidation measurements, Knoop hardness traverses were made on cross-sections of the unreacted portions of the specimens in order to measure the depth to which contamination (or diffusion) by oxygen (or nitrogen) penetrated during air oxidation testing. Data for hardness versus depth of contamination were plotted for each alloy and test temperature. In the measurements, zero baseline depth was taken as the surface of the oxidized alloy following scale removal. Since the hardness-penetration curve for most of the alloys did not meet the uncontaminated base-level hardness value sharply, a finite point for maximum hardness-penetration was hard to obtain. Therefore, maximum depth of penetration was arbitrarily taken as the point where the hardness-penetration curve reached the base metal hardness value plus 50 KHN. Data on the depth of contamination, obtained in this manner and expressed in centimeters, are included in Table B-28.

The hardness-penetration data may also be utilized to calculate the diffusion of oxygen in columbium and the alloys studied. Diffusion and contamination are considered to be quite closely related, since contamination hardening is dependent on the extent to which oxygen diffuses into the metal. Activation energies for oxygen diffusion from air (cal/mol) are included in Table B-29.

Selected binary alloy systems were further evaluated by continuous weight gain oxidation tests in dry air at 1000 and 1200°C for periods up to six hours. Results of the continuous weighing tests generally confirmed the information obtained in the more extensive screening survey regarding the composition areas of maximum oxidation resistance and also showed that many of the attractive alloys oxidized parabolically and formed protective scales. Tables B-30 and B-31 give reaction data for all of the binary alloys investigated by the continuous weighing method at temperatures of 1832°F (1000°C) and 2192°F (1200°C), respectively.

Battelle Memorial Institute research workers have concluded that the effects of alloying on columbium oxidation can be related to certain properties conferred upon the oxide film by the additive. Three types of effect may be expected; these are valence effects, ionic size effects, and new scale effects. In the low-alloy range where the additive ions are soluble in Cb_2O_5 , the data lend strong support to the theory that the size effect predominates over other mechanisms, although valence effects were also observed in this range. Molybdenum, with a valence of +6 shows a greater specific effectiveness than does vanadium of valence +5. Similarly, zirconium with a valence of +4 is a detrimental addition at low concentration levels. Above the 10 to 15 a/o alloy addition level, the oxidation behavior of columbium alloys can be related to the properties of the addition-metal oxides. Thus, for higher alloys the oxidation behavior is determined by the properties of

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the new scales which form. For example, titanium and zirconium, which have a more negative free energy of oxidation than does columbium, would be expected to form either their own oxides or stable mixed oxides at moderate alloying levels.

The effect of ternary alloy additions were evaluated first by a screening survey on the oxidation behavior at 600 to 1000°C of a large number of cast alloys. The most attractive systems were subsequently studied by continuous weight gain tests on wrought ternary alloy strips at 1000 and 1200°C. The procedures followed in these tests were virtually identical to those used for binary alloys.

Ternary alloys were investigated by intermittent weight gain tests and the results obtained are listed in Table B-32. Data are presented as the average linear oxidation rate, since linear and parabolic behaviors are hard to distinguish in this type of test. Average values of weight loss data after removal of the oxide scale are also reported; hence this measure pertains to the amount of metal consumed in the formation of scales.

Eleven specific compositions were further evaluated by continuous weighing oxidation tests at 1832°F (1000°C) and 2192°F (1200°C). Pertinent information is included in Tables B-33 and B-34 for the two temperatures of interest. Nine of the alloys were columbium-titanium base with ternary additions of chromium, molybdenum, or vanadium, while two were Cb-Mo-Cr and Cb-Mo-V. The Cb-Ti base alloys were not fabricable but the other two compositions were not and hence were tested in the cast condition.

Stanford Research Institute

For a period of approximately one and one-half years the Sierra Metals Corporation has sponsored a program at the Stanford Research Institute on the oxidation resistance of refractory metal alloys. Results of the program have recently been summarized in a report by R. H. Thielemann. (53) To quote from the report, "The purpose of this study was to obtain a very rough idea of how the oxidation resistance of refractory metal alloys responded to wide changes in composition. The results are valid only for this survey where they serve as a basis for comparison of the alloys tested." In addition to columbium base alloys, other materials on a tungsten, tantalum, titanium, and chromium base have been considered.

Columbium base alloys were prepared by pressing well mixed metal powders of the desired composition under a force corresponding to a pressure of 50,000 psi in a one inch steel die, or by mixing various metals in place in the furnace without pressing, depending on whether starting metals were mainly powders or chunks. Alloys were melted in a non-consumable arc furnace equipped with a 2 percent thoriated tungsten electrode; the furnace had a six station rotating water cooled copper hearth. Each melting depression was two inches in diameter and 1/4 inch deep. Buttons were melted twice on each side in an argon atmosphere maintained at an absolute pressure of 20 inches of mercury; a getter button of Ti-Zr alloy was always first melted to insure

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an oxygen and nitrogen free atmosphere. Compositions were not analyzed after melting, hence reported analyses are nominal.

Specimens for oxidation testing were cut into slices about $1/2 \times 1/4 \times 1/4$ inches with two parallel sides. Hardness and thickness were measured prior to oxidation testing. The pieces were introduced into a Hevi Duty Globar furnace at 2000°F , and were held in still air at that temperature for 24 hours prior to air cooling. The resulting oxide scale was examined, then chipped off, and the specimen lightly sand blasted. Final thickness was measured across the initially parallel sides, and the rate of recession of the metal-oxide interface was then calculated.

As mentioned in the Stanford Research Institute report, there was a considerable problem with alloy inhomogeneity: this may possibly explain several discrepancies in test results. The rate of recession of the metal-oxide interface per hour at 2000°F for binary alloys of columbium with chromium, tin, titanium, tungsten and zirconium is listed in Table B-35. Ternary systems and their advanced modifications which have been considered include Cb-Ti-Cr (Table B-36), Cb-Ti-Ta (Table B-37), Cb-Ta-Cr (Table B-38) and Cb-Zr-Ti (Table B-39).

W. R. Clough
W. R. Clough

E. C. Hirakis
E. C. Hirakis

R. C. Krutenat
R. C. Krutenat

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Table A-1

BINARY ALLOYS

Cross Index Reference Table

<u>Code</u>	<u>Laboratory</u>
A	Union Carbide Metals Company
B	E. I. duPont de Nemours and Company
C	Fansteel Metallurgical Corporation
D	Nuclear Metals, Incorporated
E	Kennecott-Battelle
F	Sylvania-Corning Nuclear Laboratory
G	Lewis Flight Propulsion Laboratory
H	Horizons, Incorporated
I	Ohio State University
J	Battelle Memorial Institute
K	Stanford Research Institute

<u>Binary</u>	<u>References (Laboratory and Tables)</u>
Cb-Al	A(B1):C(B13):D(B18):G(B20):J(B25,B26,B27,B28,B29)
Cb-B	J(B26)
Cb-Be	A(B1):J(B26)
Cb-Ce	A(B1):D(B18)
Cb-Co	A(B1):C(B13):G(B20):J(B26,B28,B29)
Cb-Cr	A(B1):C(B13):D(B18):G(B20):I(B22):J(B25,B26,B27,B28,B29,B30,B31):
Cb-Cu	A(B1):G(B20)
Cb-Fe	A(B1,B2):C(B13):G(B20):J(B25,B26,B27,B28,B29,B30,B31)
Cb-Ge	G(B20)
Cb-Ir	G(B20)
Cb-Mn	A(B1):J(B26,B27,B28,B29)
Cb-Mo	A(B1):C(B13,B17):F:G(B20):J(B25,B26,B27,B28,B30,B31)
Cb-Ni	A(B1):C(B13):G(B20):J(B25,B26,B27,B28,B29)
Cb-Re	G(B20):J(B30,B31)
Cb-Se	G(B20)
Cb-Si	A(B1):C(B13):G(B20):J(B26,B27,B28)
Cb-Sn	A(B1):K(B35)
Cb-Ta	A(B1):C(B13,B14,B17):E(B19):G(B20):J(B25,B26,B27,B28,B29)
Cb-Th	A(B1)
Cb-Ti	A(B1,B2):C(B13,B17):F:G(B20):I(B22):J(B26,B27,B28,B29,B30,B31):
Cb-V	A(B1):C(B13):F:G(B20):J(B25,B26,B27,B28,B29,B30,B31)
Cb-W	A(B1):C(B13,B17):G(B20):J(B25,B26,B27,B28,B29,B30,B31):K(B35)
Cb-Y	A(B1)
Cb-Zr	A(B1):C(B13):G(B20):I(B23):J(B25,B26,B27,B28,B30,B31):K(B35)

Table A-2

TERNARY SYSTEMS AND MODIFICATIONS
Cross Index Reference Table

<u>Ternary</u>	<u>References (Laboratory & Tables)</u>
Cb-Al-Si	A(B3):D(B18)
Cb-Al-V	A(B4)
Cb-Co-Al	A(B3)
Cb-Cr-Al	A(B5):B(B10):D(B18):E(B19):H(B21):J(B32)
Cb-Cr-Co	C(B15,B17)
Cb-Cr-Mo	A(B3):H(B21):J(B32,B33,B34)
Cb-Cr-Ni	C(B16):J(B32)
Cb-Cr-Si	A:D(B18):J(B32)
Cb-Cr-V	J(B32)
Cb-Cr-W	C(B16):J(B32)
Cb-Fe-Al	A(B3):B(B9)
Cb-Fe-Co	C(B16):H(B21)
Cb-Fe-Ni	C(B16)
Cb-Mo-Al	J(B32)
Cb-Mo-Ni	J(B32)
Cb-Mo-Si	J(B32)
Cb-Mo-W	C(B16):J(B32)
Cb-Ni-Al	A(B3)
Cb-Ta-Cr	C(B16):J(B32):K(B36)
Cb-Ta-Mo	C(B16):E(B19):J(B32)
Cb-Ta-V	E(B19):J(B32)
Cb-Ta-W	A(B6):C(B16):E(B19)
Cb-Ta-Zr	C(B16)
Cb-Ti-Al	A(B4):B(B8):E(B19):H(B21)
Cb-Ti-Co	A(B3):J(B32)
Cb-Ti-Cr	A(B5):E(B19):H(B21):I(B22):J(B32,B33,B34):K(B36)
Cb-Ti-Fe	A(B2,B7):J(B32)
Cb-Ti-Mo	B(B11,B12):H(B21):J(B32,B33,B34)
Cb-Ti-Ni	A(B3):J(B32)
Cb-Ti-Si	J(B32)
Cb-Ti-Ta	C(B16):E(B19):J(B32):K(B37)
Cb-Ti-V	A(B4):E(B19):J(B32,B33,B34)
Cb-Ti-W	A(B6):C(B16):H(B21):J(B32)
Cb-V-Co	C(B16)
Cb-V-Mo	J(B32,B33,B34)
Cb-V-Ni	C(B16):J(B32)
Cb-V-W	J(B32)
Cb-W-Al	C(B16)
Cb-W-Si	C(B16)
Cb-Zr-Al	A(B3)
Cb-Zr-Cr	J(B32)
Cb-Zr-Ti	A(B3):I(B23,B24):K(B39)
Cb-Zr-V	J(B32)
Cb-Zr-W	A(B3)

Table A-3
Free Energy of Formation of Oxides (1,4)
Kcal/gram Atom of Oxygen

Oxide	-ΔF		Oxide	*ΔF	
	25°C	1000°C		25°C	1000°C
CaO	144.3	121	Cb ₂ O ₅	84.7	65
ThO ₂	139.6	118	Cr ₂ O ₃	83.6	63
Nd ₂ O ₃	137.6	117	Ga ₂ O ₃	79	52
Sm ₂ O ₃	137.0	117	ZnO	76.1	50
La ₂ O ₃	136.5	117	V ₂ O ₅	68.3	*
MgO	136.2	113	SnO ₂	62.2	37
BeO	136	113	WO ₃	60.8	42
Li ₂ O	133.8	100	Fe ₂ O ₃	59.1	39
Y ₂ O ₃	133	113	FeO	58.3	42
Al ₂ O ₃	126	101	CdO	55.2	24
HfO ₂	125.9	104	MoO ₃	54.0	*
ZrO ₂	124	102	NiO	51.4	31
CeO ₂	123.4	101	CoO	51.1	31
UO ₂	123.3	103	Re ₂ O ₇	36.3	*
TiO ₂	106.2	84	CuO	30.6	10
SiO ₂	98.6	77	SeO ₂	20.8	*
B ₂ O ₃	94.4	*	RuO ₂	19.8	-2
Ta ₂ O ₅	91.3	71	Rh ₂ O ₃	16.2	*
MnO	86.7	69	PdO	14	*

* Phase change, as melting or sublimation, at a temperature lower than 1000°C.

Table A-4

Metal Oxide Characteristics (1,4,9,10,11)

Metal	Oxide	Goldschmidt Atomic Radius A°	Valence	Transformation Temperature °C	Conductivity 20°C ohm ⁻¹ cm ⁻¹	Molecular Volume cm ³
La	La ₂ O ₃	1.14	3	2320		49.7
Nd	Nd ₂ O ₃	1.04	3	2545		-
Th	ThO ₂	1.02	4	2950		26.7
Sm	Sm ₂ O ₃	1.00	3	2150		-
Ca	CaO	0.99	2	2570	10 ⁻⁹	16.7
Cd	CdO	0.97	2	1832	10 ⁻³	15.65
U	UO ₂	0.97	4	2500		24.7
Cu	CuO	0.96	2	1336	5 x 10 ⁻⁷	12.2
Ce	CeO ₂	0.94	4	3000	10 ⁻⁴	25.3
Y	Y ₂ O ₃	0.92	3	2400		44.9
Pd	PdO	0.80	2	790		14.7
Mn	MnO	0.80	2	1790	10 ⁻⁸	13.15
Zr	ZrO ₂	0.79	4	2715	<10 ⁻⁸	21.9
Hf	HfO ₂	0.78	4	3063		-
Zn	ZnO	0.74	2	2248	1 x 10 ⁻⁴	14.2
Fe	FeO	0.74	2	1368		11.9/12.5
Co	CoO	0.72	2	1810	10 ⁻²	11.6/12.3
Sn	SnO ₂	0.71	4	1898	≈ 10 ⁻³	21.5
Cb	Cb ₂ O ₅	0.69	5	1733	12	20.5
Ni	NiO	0.69	2	1960	8 x 10 ⁻⁴	10.9
Rh	Rh ₂ O ₃	0.68	3	990		31.3
Ta	Ta ₂ O ₅	0.68	5	2150	10 ⁻⁵	55.2
Ti	TiO ₂	0.68	4	1860	4	18.8
Li	Li ₂ O	0.68	1	1300		15.0
Ru	RuO ₂	0.67	4	1400		26.8
Mg	MgO	0.66	2	2800	10 ⁻⁹	11.25
Fe	Fe ₂ O ₃	0.64	3			30.4
Cr	Cr ₂ O ₃	0.63	3	2440	1.2 x 10 ⁻⁴	29.0
Ga	Ga ₂ O ₃	0.62	3	1725		31.8
Mo	MoO ₃	0.62	6	795	1.3 x 10 ⁻⁷	30.5
W	WO ₃	0.62	6	1743	5 x 10 ⁻²	31.5
V	V ₂ O ₅	0.59	5	670	3	54.0
Re	Re ₂ O ₇	0.56	7	296	<10 ⁻⁸	59.1
Al	Al ₂ O ₃	0.51	3	2020	<10 ⁻⁸	25.6
Se	SeO ₂	0.50	4	603		-
Si	SiO ₂	0.42	4	1610	<10 ⁻⁸	22.5
Be	BeO	0.35	2	2520	<10 ⁻⁸	8.25
B	B ₂ O ₃	0.23	3	723	<10 ⁻⁸	-

Table A-5

COMPLEX OXIDES EXHIBITING A SPINEL STRUCTURE (1, 52)

Melting Point, Molecular Volume, and Cubic Cell Data

Spinel	Melting Point of	Molecular Volume	ρ_0	Spinel	Melting Point of	Molecular Volume	ρ_0
Ag ₂ MoO ₄		59.7	9.26	Fe ₂ MgO ₄	3180	44.3	8.366
Al ₂ CoO ₄	3560	39.4	8.101	Fe ₂ MnO ₄		46.0	8.457
Al ₂ CuO ₄			8.06	Fe ₂ NiO ₄		44.8	8.340
Al ₂ FeO ₄	2630	39.6	8.12	Fe ₂ PbO ₄			7.81
Al ₂ MgO ₄	3870		8.06	Fe ₂ TiO ₄		46.2	8.50
Al ₂ MnO ₄	2840	42.5	8.27	Fe ₂ ZnO ₄	3130	45.2	8.423
Al ₂ NiO ₄	3670	39.1	8.05	Ga ₂ CdO ₄		47.3	8.57
Al ₂ SnO ₄			8.12	Ga ₂ MgO ₄		42.7	8.279
Al ₂ ZnO ₄	3540	39.7	8.06	Ga ₂ ZnO ₄		43.3	8.323
Co ₂ CuO ₄		39.1	8.04	In ₂ MgO ₄		51.5	8.61
Co ₂ MgO ₄		40.1	8.12	Mg ₂ SnO ₄		47.5	8.58
Co ₂ NiO ₄		40.2	8.32	Mg ₂ TiO ₄	3300	44.7	8.44
Co ₂ SnO ₄		47.9	8.60	Mg ₂ VO ₄		44.7	8.386
Co ₂ TiO ₄		44.9	8.42	Mn ₂ TiO ₄			8.67
Co ₂ ZnO ₄		39.4	8.12	Ni ₂ GeO ₄		41.5	8.20
Cr ₂ CdO ₄		47.7	8.56	Rh ₂ MgO ₄			8.51
Cr ₂ CoO ₄		43.3	8.32	Rh ₂ ZnO ₄			8.52
Cr ₂ FeO ₄	3950	44.0	8.344	Ti ₂ FeO ₄	2700	45.6	8.50
Cr ₂ MgO ₄	4000	43.3	8.31	Ti ₂ MnO ₄	2650	49.1	
Cr ₂ MnO ₄		46.0	8.436	V ₂ FeO ₄		45.6	8.468
Cr ₂ NiO ₄		43.0	8.299	V ₂ MgO ₄		44.85	8.394
Cr ₂ ZnO ₄		43.3	9.92	V ₂ ZnO ₄		45.0	8.393
Fe ₂ CdO ₄		50.1	8.68	Zn ₂ SnO ₄		48.0	8.61
Fe ₂ CoO ₄		44.6	8.35	Zn ₂ TiO ₄		45.9	8.445
Fe ₂ CuO ₄	1650	45.3	8.35	Zn ₂ VO ₄			

Table B-1

Union Carbide Metals Company Oxidation Test Data (31)

BINARY ALLOYS

100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

Alloy Addition Weight Percent	Total Weight Gain, mg/cm ² /100 Hours			As Cast Hardness R _A
	1472°F	1832°F	2192°F	
304 Stainless Steel	2	8	839	-
316 Stainless Steel	5	41	131	-
None (Pure Cb)	3,630	6,670	24,000	51
0.3 Al	4,410	-	-	42
1.5 Al	3,990	-	-	48
4.0 Al	588	-	-	62
6.0 Al	191	-	-	67
46.0 Al	195	-	-	52
1.1 Be	9,380	-	-	50
0.5 Ce	12,000	-	-	41
1.0 Ce	17,000	-	-	31
5.0 Ce	18,000	-	-	28
1.0 Co	5,340	-	-	45
5.0 Co	2,650	-	-	73
5.8 Cr	1,810	-	-	56
52.8 Cr	30	-	-	65
2.0 Cu	3,550	-	-	49
25.0 Fe	13	171	323	82
3.0 Mn	5,311	-	-	44
1.0 Ni	5,860	-	-	57
5.0 Ni	2,200	-	-	67
10.0 Ni	1,170	-	-	69
20.0 Ni	279	-	-	77
0.6 Si	15,600	-	-	64
3.2 Si	39,600	-	-	75
2.0 Sn	1,816	-	-	46
1.0 Th	10,390	-	-	32
5.4 Ti	480	-	-	51
10.0 Ti	67	291	2,260	50
15.0 Ti	31	223	2,390	54
20.0 Ti	42	303	2,260	-
25.6 Ti	21	-	-	50
7.0 V	108	-	-	68
5.6 Zr	4,400	-	-	49
10.0 Zr	4,600	-	-	46
49.0 Zr	20	155	1,550	64

Table B-2

Union Carbide Metals Company Oxidation Test Data (32)
Cb-Ti, Cb-Fe, and Cb-Ti-Fe Alloys
Compositions of Oxide Scales

<u>Alloy Addition Weight Percent</u>	<u>Oxidation Temp. °C</u>	<u>Oxide Chemical Analysis, w/o</u>	<u>Calculated % Of Metal Oxidized</u>	<u>Calculated Mol. % Of Oxide Phases</u>
10Fe	1000	62.73 Cb 8.58 Fe	88.0 Cb 12.0 Fe	45.5 FeO·Cb ₂ O ₅ 54.5 Cb ₂ O ₅
25Fe	1200	52.16 Cb 19.54 Fe	72.8 Cb 27.2 Fe	80.3 FeO·Cb ₂ O ₅ 19.7 FeO
15Ti	1000	57.29 Cb 10.28 Ti	84.8 Cb 15.2 Ti	69.6 TiO ₂ ·Cb ₂ O ₅ 30.4 Cb ₂ O ₅
35Ti	1000	41.00 Cb 22.36 Ti	64.8 Cb 35.2 Ti	47.4 TiO ₂ ·Cb ₂ O ₅ 52.5 TiO ₂
10Ti-20Fe	1200	50.11 Cb 6.20 Ti 12.69 Fe	72.6 Cb 9.0 Ti 18.4 Fe	5.5 FeO·Cb ₂ O ₅ ·5TiO ₂ 75.7 FeO·Cb ₂ O ₅ 18.8 Cb ₂ O ₅
30Ti-10Fe	1000	42.81 Cb 16.15 Ti 8.37 Fe	63.5 Cb 24.0 Ti 12.5 Fe	17.5 FeO·Cb ₂ O ₅ ·5TiO ₂ 47.4 FeO·Cb ₂ O ₅ 34.9 Cb ₂ O ₅

Table B-3

CNLM- 1724

Date: May 20, 1959

Union Carbide Metals Company Oxidation Test Data (31)

MISCELLANEOUS TERNARY SYSTEMS AND MODIFICATIONS

100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

Alloy Additions Weight Percent	Total Weight Gain, mg/cm ² /100 Hours			As Cast Hardness RA
	1472°F	1832°F	2192°F	
304 Stainless	2	8	839	
316 Stainless	5	41	131	
None (Pure Cb)	3,630	6,670	24,000	51
2.0Al- 3.0Si	687	-	-	74
5.0Al- 3.0Si	1,380	-	-	81
10.0Al- 3.0Si	724	-	-	78
10.0Al- 5.0Si	84	-	-	79
9.0Co- 5.0Al	1,732	2,052	1,249	79
15.0Cr- 5.0Mo	8	40	1,311	-
12.0Fe- 2.0Al	3,580	-	-	76
12.0Fe- 4.0Al	2,380	-	-	78
9.0Ni- 5.0Al	2,910	2,590	3,590	76
20.0Ti- 5.0Co	28	320	2,850	66
20.0Ti-10.0Co	37	86	1,580	67
20.0Ti-20.0Co	18	48	682	67
30.0Ti-10.0Co	11	75	1,272	67
20.0Ti-12.0Co- 4.0Al	10	82	383	76
10.0Ti-10.0Ni	1,060	1,660	4,510	66
10.0Ti-20.0Ni	194	2,510	4,320	73
20.0Ti- 5.0Ni	20	73	385	64
20.0Ti-10.0Ni	15	90	1,680	63
20.0Ti-12.0Ni- 4.0Al	12	76	400	-
20.0Ti-20.0Ni	21	89	2,530	64
30.0Ti-10.0Ni	5	131	1,400	65
50.0Zr- 5.0Al	-	341	-	-
40.0Zr-15.0Ti- 2.0V	-	92	1,160	-
40.0Zr-15.0Ti- 5.0Al	-	118	571	-
40.0Zr-15.0Ti- 5.0Al-2.0V	-	44	-	-
30.0Zr-10.0Ti- 5.0Al-3.0Sn	20	77	576	-
30.0Zr-10.0Ti- 5.0Al-2.0V	16	83	602	-
5.0Zr-10.0W	Spalled	9,290	5,160	-
5.0Zr-10.0W -10.0Ti	Spalled	273	558	-
5.0Zr-10.0W -10.0Ti-3.0V	269	-	512	-
5.0Zr- 3.0Cr	Spalled	10,200	9,540	-
5.0Zr- 3.0Cr-10.0Ti-3.0V	87.6	183	1,050	-

Table B-4

Union Carbide Metals Company Oxidation Test Data (31)
ALLOYS CONTAINING Cr, Ti, Al and/or V
100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

Alloy Addition Weight Percent	Total Weight Gain, mg/cm ² /100 hrs.			As Cast Hardness RA
	1172°F	1832°F	2192°F	
304 Stainless Steel	2	8	839	
316 Stainless Steel	5	41	131	
None (Pure Cr)	3,630	6,670	24,000	51
3.OAl- 3.OV	98	139	675	-
3.OAl- 5.OV	28	104	738	-
5.OAl- 5.OV	60	144	474	-
5.OAl-15.OV	404	-	-	73
15.OTi- 3.OAl	41	122	1,350	29
15.OTi- 5.OAl	40	110	1,340	28
25.OTi--5.OAl	25	112	1,080	25
15.OTi- 5.OV	50	140	819	-
20.OTi- 5.OV	24	269	821	59
20.OTi- 5.OV - 2.OAl	20	270	800	61
20.OTi-10.OV	76	4,240	4,850	62
30.OTi-10.OV	33	3,800	4,140	56
40.OTi- 3.OV -20.OAl	-	141	240	-
10.OTi- 3.OAl- 3.OV	30	154	675	-
20.OTi- 4.OAl- 4.OV	28	87	665	-
20.OTi- 3.OAl- 5.OV	14	105	542	-

Table E-5

Union Carbide Metals Company Oxidation Test Data (31)
Cb-Ti-Cr and Cb-Cr-Al SYSTEMS AND MODIFICATIONS
100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

Alloy Additions Weight Percent	Total Weight Gain, mg/cm ² /100 Hours			As Cast Hardness R _A
	1172°F	1832°F	2192°F	
304 Stainless Steel	2	8	839	-
316 Stainless Steel	5	41	131	-
None (Pure Cb)	3,630	6,670	24,000	51
6.0Cr- 5.0Al	40	125	-	72
9.0Cr- 3.0Al	277	225	1,350	72
9.0Cr- 4.0Al	251	238	1,310	73
9.0Cr- 5.0Al	19	154	1,550	74
12.0Cr- 2.0Al	123	249	1,510	74
12.0Cr- 3.0Al	24	113	1,820	73
12.0Cr- 4.0Al	73	108	1,370	74
12.0Cr- 4.0Al- 2.0Ta	40	129	816	71
12.0Cr- 4.0Al- 5.0Ta	103	95	833	72
12.0Cr- 5.0Al	12	127	-	75
15.0Ti-10.0Cr	18	182	2,030	73
20.0Ti- 5.0Cr	26	190	2,738	76
20.0Ti-10.0Cr	20	258	1,661	68
20.0Ti-20.0Cr	23	51	174	76
30.0Ti-10.0Cr	18	133	794	69
10.0Ti- 5.0Cr- 2.0Al	19	154	1,930	68
10.0Ti- 9.0Cr- 4.0Al	28	118	896	73
10.0Ti-12.0Cr- 4.0Al	34	80	876	74
20.0Ti- 5.0Cr- 2.0Al	15	188	1,500	70
20.0Ti- 9.0Cr- 4.0Al	31	150	581	71
23.0Ti-15.0Cr- 5.0Si	4	39	49	82
36.0Ti- 6.0Cr- 2.0Al- 6.0Mo	5.3	1,243	3,040	66
10.0Ti- 6.0Cr- 3.0Al- 2.0V	61	108	596	-
10.0Ti- 6.0Cr- 3.0Al- 4.0V	61	99	401	-
10.0Ti- 9.0Cr- 3.0Al- 4.0V	35	105	532	-
10.0Ti-12.0Cr- 3.0Al- 4.0V	15	73	573	-
20.0Ti- 9.0Cr- 3.0Al- 5.0V	13	62	184	-
20.0Ti-12.0Cr- 3.0Al- 5.0V	17	519	459	70
25.0Ti- 8.0Cr- 3.0Al- 4.0V	-	450	382	69
26.0Ti- 6.0Cr- 2.0Al- 6.0V	15	358	417	67
36.0Ti- 2.0Cr- 2.0Al-10.0V	272	1,840	205	-
36.0Ti- 6.0Cr- 2.0Al- 6.0V	78	689	201	-
36.0Ti- 8.0Cr- 2.0Al- 4.0V	19	275	222	-
36.0Ti- 8.0Cr- 3.0Al- 3.0V	15	212	337	-
20.0Ti- 3.0Cr- 3.0Fe- 3.0Ni	26	125	1,860	71

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Table B-5
(Continued)

Alloy Additions Weight Percent	Total Weight Gain, mg/cm ² /100 Hours			As Cast Hardness RA
	1172°F	1832°F	2192°F	
20.OT1- 5.0Cr-10.0Fe- 5.0Si	5	33	82	81
40.OT1- 5.0Cr-10.0Fe- 5.0Si	5	13	70	81
25.OT1-10.0Cr-20.0Fe- 5.0Ta	13	44	100	81
18.OT1-13.0Cr- 2.7Al- 4.5V--5.0Fe	25	265	899	79
18.6Ti- 8.4Cr- 4.8Al- 4.6V--5.0Fe	18	249	258	79
19.OT1- 8.5Cr- 2.9Al- 4.8V--5.0Fe	22	483	288	79
20.OT1-10.0Cr- 4.0Al- 4.0V- 5.0Fe	10	48	132	71
23.OT1- 8.1Cr- 2.7Al- 4.5V- 5.0Fe	48	550	215	79
25.OT1- 8.0Cr- 3.0Al- 4.0V- 5.0Fe	14	44	400	-
35.OT1- 8.0Cr- 3.0Al- 4.0V- 4.0Fe	11	469	126	71
20.OT1-10.0Cr- 4.0Al- 4.0V- 5.0Ni	6	32	189	70
20.OT1-10.0Cr- 4.0Al- 4.0V- 5.0Ta	9	252	332	-
20.OT1-10.0Cr- 4.0Al- 4.0V- 5.0Zr	28	337	-	-
10.OT1- 9.0Cr- 3.0Al- 4.0V- 2.0Fe-1.0Ni	18	87	456	-
18.OT1- 8.1Cr- 2.7Al- 4.5V- 5.0Fe-5.0Zr	50	650	-	-
18.8Ti- 8.5Cr- 2.8Al- 4.7V- 5.0Fe-1.0Si	25	275	-	-

Table B-6

Union Carbide Metals Company Oxidation Test Data (31)
Cb-Ti-W and Cb-Ta-W SYSTEMS AND MODIFICATIONS
100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

Alloy Additions weight Percent	Total weight Gain, mg/cm ² /100 Hours		
	1472°F	1832°F	2192°F
304 Stainless Steel	2	8	839
316 Stainless Steel	5	41	131
None (Pure Cb)	3,630	6,670	24,000
20.0Ta-20.0W- 5.0V	Spalled	-	260
20.0Ta-20.0W- 5.0V - 5.0Al	Spalled	48	154
5.0Ti-10.0W	67	291	2,260
5.0Ti-20.0W	Spalled	-	-
5.0Ti-20.0W-20.0Ta	Spalled	260	-
5.0Ti-25.0W-20.0Ta- 3.0Fe- 2.0Ni	Spalled	38	107
5.0Ti-25.0W-20.0Ta- 2.0V - 3.0Al	Spalled	32	143
7.0Ti-20.0W- 3.0V - 3.0Fe	24	372	796
7.0Ti-20.0W- 3.0V - 2.0Fe- 1.0Ni	19	77	344
7.0Ti-20.0W- 3.0V - 3.0Fe- 2.0Ni	18	46	160
7.0Ti-20.0W-20.0Ta- 3.0V - 3.0Fe	36	48	224
10.0Ti- 5.0W	Spalled	338	1,120
10.0Ti-20.0W- 3.0V	21	185	376
10.0Ti-20.0W- 3.0V - 0.5Be	16	44	304
10.0Ti-20.0W- 3.0V -20.0Ta	-	141	240
10.0Ti-20.0W- 3.0V - 5.0Cr	20	256	862
10.0Ti-20.0W- 3.0V - 5.0Cr-20.0Ta	39	121	460
10.0Ti-20.0W- 3.0V -10.0Cr	10	294	935
10.0Ti-20.0W- 5.0V - 5.0Al	39	108	Excessive
10.0Ti-20.0W- 5.0V - 5.0Al-20.0Ta	185	61	Excessive
10.0Ti-20.0W- 3.0V - 2.0Ni- 3.0Fe	16	48	221
10.0Ti-20.0W- 3.0V - 2.0Ni- 3.0Fe-20.0Ta	14	344	266
10.0Ti-30.0W- 3.0V	30	91	231
10.0Ti-30.0W- 3.0V -20.0Ta	22	87	1,260

TABLE B-7

(31)

Union Carbide Metals Company Oxidation Test Data

Cb-Ti-Fe System and Modifications

100 Hour Weight Gain, mg/cm², Pure Oxygen Atmosphere

<u>Alloy Additions Weight Percent</u>	<u>Total Weight Gain, mg/cm²/100 hours</u>			<u>As Cast Hardness R_A</u>
	<u>1472°F</u>	<u>1832°F</u>	<u>2192°F</u>	
304 Stainless Steel	2	8	839	-
316 Stainless Steel	5	41	131	-
None (Pure Cb)	3,630	6,670	24,000	-
10.0 Ti- 5.0Fe	-	274	-	73
20.0 Ti- 5.0Fe	97	-	-	73
15.0 Ti-10.0Fe	37	218	-	74
20.0 Ti-10.0Fe	23	-	3,560	72
25.0 Ti-10.0Fe	16	174	-	72
30.0 Ti-10.0Fe	18	212	-	73
10.0 Ti-20.0Fe	13	45	-	78
20.0 Ti-20.0Fe	6	41	-	79
10.0 Ti- 5.0Fe-2.0Al	-	259	-	72
20.0 Ti- 5.0Fe-2.0Al	242	-	-	72
10.0 Ti- 9.0Fe-4.0Al	-	177	-	76
20.0 Ti- 9.0Fe-4.0Al	16	-	-	75
20.0 Ti-12.0Fe-4.0Al	17	-	-	77
20.0 Ti-20.0Fe-2.0Ta	13	66	296	78
20.0 Ti-20.0Fe-5.0Ta	11	43	280	-

Table B-8
(35)

duPont Oxidation Test Data

Cb-Ti-Al System and Modifications

Percent Weight Gain in 16 Hours at 1832°F in Air

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Total % Weight Gain</u> <u>16 hours at 1832°F</u>
None	20.0
7.0Ti- 3.0Al	2.5
20.0Ti-10.0Al	1.7
20.0Ti- 3.0Al- 2.0Co	2.5
15.0Ti- 5.0Al-15.0Mo	2.2
23.0Ti- 3.0Al- 4.0Ni	1.5
15.0Ti- 4.0Al- 1.0Si	2.0
5.0Ti-10.0Al- 2.5Mo-2.5Fe	2.1
13.5Ti- 3.0Al- 3.0Mo-2.5Fe	2.2
15.0Ti- 4.5Al- 7.0Mo-3.5Fe	1.9
29.0Ti- 1.0Al-10.0Mo-5.0Ni	1.3
10.0Ti- 6.0Al- 6.0Mo-8.0V	1.5
16.0Ti- 4.0Al- 5.0Mo-2.0Fe-3.0Be	1.8
5.0Ti- 3.0Al-15.0Zr-1.0V -1.0Ta	2.3
17.0Ti- 1.0W - 1.5Ta-0.5Be	2.0

Table B-9
(36)

duPont Oxidation Test Data

Cb-Fe-Al System and Modifications

Oxidation Rate During 24th Hour of Air Exposure

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Oxidation Rate During 24th Hour</u> <u>mg/cm²/hr</u>		<u>Adherence of</u> <u>Oxide Scale</u>
	<u>1832°F</u>	<u>2192°F</u>	
Nichrome	0.3	2.1	-
None (Pure Cb)	22.0	68.0	Very poor
10.0Fe-19.0Al	0.03	0.09	Good
20.0Fe- 9.0Al	0.08	0.20	Excellent
24.0Fe-20.0Al	0.04	0.08	Excellent
10.6Fe- 6.0Al- 2.0B	0.09	0.34	Good
20.0Fe-15.0Al- 5.0Mo	0.08	-	Fair
5.0Fe-10.0Al-10.0Ni	0.09	0.15	Good
9.0Fe-17.0Al-25.0Ni	0.01	0.04	Excellent
10.0Fe-14.0Al-15.0Co-4.0Mo-1.0Ce	0.01	0.05	Excellent

Table B-10
duPont Oxidation Test Data (37)
Cb-Cr-Al System and Modifications
Oxidation Rate During 24th Hour of Air Exposure

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Oxidation Rate During 24th Hour</u> <u>mg/cm²/hr</u>		<u>Adherence of</u> <u>Oxide Scale</u>
	<u>1832°F</u>	<u>2192°F</u>	
Nichrome	0.3	2.1	-
None (Pure Cb)	22.0	68.0	Very Poor
10.0Cr-15.0Al	0.05	-	Excellent
15.0Cr-20.0Al	0.03	-	Excellent
30.0Cr- 5.0Al	0.15	0.26	Good
20.0Cr-15.0Al- 2.0Ce	0.05	0.14	Good
19.0Cr-10.0Al-15.0Co	0.01	0.06	Excellent
26.0Cr- 5.0Al- 2.0Ni	0.05	0.16	Excellent
10.0Cr-10.0Al- 4.0W	0.05	0.17	Excellent
10.0Cr-10.0Al-15.0Ni-4.0W-2.0Ce	0.02	-	Excellent

Table B-11
duPont-Thompson Products Oxidation Test Data (38,39)
80Cb-10Ti-10Ni Alloy
Displacement of Metal Interface

<u>Test Temp.</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>	<u>Surface Recession</u> <u>mils</u>
2000	1.0	0.5
2000	2.5	1.1
2000	5.0	1.8
2000	8.0	2.8
2000	15.0	4.6
2000	30.0	7.8

Table B-12 (38,39)
duPont-Thompson Products Oxidation Test Data

80Cb-10Ti-10Mo Alloy

Depth of Internal Oxidation

<u>Test Temp.</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>	<u>Internal Penetration</u> <u>mils</u>
2000	1.0	2.3
2000	3.0	3.6
2000	5.0	5.3
2000	8.0	6.7
2000	15.0	9.3

Table B-13

(40)

Fansteel Metallurgical Corporation Oxidation Test Data

Binary Alloys

Displacement of Metal Interface in 16 hours at 2000°F

<u>Alloy Addition Weight %</u>	<u>Displacement Cm</u>	<u>Alloy Addition Weight %</u>	<u>Displacement Cm</u>
None	0.11	29.9Ta	0.02
0.6Al	>0.11	32.7Ta	0.01
1.5Al	0.11	45.5Ta	0.02
6.8Al	0.015	56.5Ta	0.04
6.6Co	>0.11	66.1Ta	0.07
21.4Co	>0.11	1.6Ti	>0.11
4.0Cr	>0.11	7.7Ti	>0.11
5.9Cr	0.025	20.2Ti	0.10
12.3Cr	0.02	40.6Ti	0.05
20.5Fe	>0.11	1.7V	0.07
3.1Mo	0.06	5.7V	0.06
10.3Mo	0.015	19.0V	>0.11
30.7Mo	>0.11	5.8	0.02
6.6Ni	>0.11	18.0W	0.015
21.3Ni	>0.11	33.1W	0.01
0.6Si	0.11	45.9W	0.01
2.2Si	0.08	0.5Zr	0.11
7.0Si	0.01	3.0Zr	>0.11
9.3Ta	0.07	9.8Zr	>0.11
17.8Ta	0.04	29.6Zr	0.07

Table B-14

(40)

Pansteel Metallurgical Corporation Oxidation Test Data

Effective Depth of Oxygen Penetration After 16 Hour Air Exposure

<u>Temperature</u> <u>°F</u>	<u>Cb</u> <u>Penetration, Cm</u>	<u>Ta</u> <u>Penetration, Cm</u>	<u>Cb-32.7Ta</u> <u>Penetration, Cm</u>
1000	0.01	0.01	0.01
1200	0.03	0.01	0.02
1400	0.05	0.03	0.03
1600	0.08	0.08	0.10
1800	0.10	0.15	0.30
2000	0.25	0.25	0.30

Table B-15

Fansteel Metallurgical Corporation Oxidation Test Data (40)Cr-Cr-Co SYSTEM AND MODIFICATIONSDisplacement of Metal Interface in 16 Hours at 2000°F

<u>Alloy Addition</u> <u>Weight Percent</u>	<u>Displacement</u> <u>cm</u>
None	0.11
1.7Cr- 1.3Co	>0.11
1.2Cr- 3.9Co	>0.11
5.4Cr- 4.1Co	0.02
7.3Cr- 5.5Co	0.01
3.1Cr-11.8Co	0.035
9.3Cr- 6.3Co	0.01
3.4Cr-13.2Co	0.015
12.9Cr- 8.8Co	0.01
6.5Cr-18.3Co	0.01
7.9Cr-35.5Co	Too brittle to machine
9.5Cr- 6.4Co- 0.7Al	0.01
9.3Cr- 7.0Co-11.5Mo	0.095
9.5Cr- 6.4Co- 2.0Si	0.02
8.4Cr- 5.7Co-19.8W	0.015
9.7Cr- 6.4Co-20.1W	0.015
2.0Cr- 1.7Co-31.6Ta	0.008
3.0Cr- 2.3Co-31.0Ta	0.007
8.0Cr- 4.2Co-28.8Ta	0.007
11.1Cr- 6.3Co-27.0Ta	0.004
14.5Cr- 7.9Co-25.4Ta	0.003
8.1Cr-14.6Co- 9.6W -5.0Mo	0.04

Table B-16

Pansteel Metallurgical Corporation Oxidation Test Data (40)

MISCELLANEOUS TERNARY SYSTEMS AND MODIFICATIONS
Displacement of Metal Interface in 16 Hours at 2000°F

<u>Alloy Addition</u> <u>Weight Percent</u>	<u>Displacement</u> <u>cm</u>
Nons	0.11
1.7Cr- 1.3Ni	> 0.11
1.2Cr- 3.9Ni	> 0.11
9.3Cr- 6.3Ni	> 0.02
12.9Cr- 8.7Ni	0.01
11.1Cr-19.6W	> 0.11
5.3Fe-11.2Co	0.05
17.6Fe- 8.9Co	0.015
8.5Fe-20.1Co	0.015
17.6Fe- 8.9Ni	0.015
13.5Mo-25.8W	> 0.11
32.3Ta- 1.4Cr	0.008
32.0Ta- 2.4Cr	0.008
31.3Ta- 4.5Cr	0.008
29.9Ta- 8.8Mo	0.007
31.1Ta- 4.9W	0.007
27.6Ta-15.6W	0.007
26.7Ta- 8.1W -4.2Mo	0.007
31.9Ta- 2.5Zr	0.008
27.1Ta-17.1Zr	0.007
2.2Ti-32.0Ta	0.008
4.6Ti-31.2Ta	0.008
7.1Ti-30.4Ta	0.008
9.8Ti-29.6Ta	0.008
5.2Ti- 8.0W	0.01
15.2Ti-10.8W	0.06
12.0Ti-20.1W	0.025
7.7V -19.4Co	> 0.11
17.8V - 9.1Co	> 0.11
4.9V -12.7Ni	> 0.11
7.7V -19.3Ni	> 0.11
17.8V - 9.1Ni	> 0.11
33.5W - 0.5Al	0.095
33.5W - 0.5Si	0.105
34.5W - 1.8Si	0.015

Table B-17
Fansteel Metallurgical Corporation Oxidation Test Data (40)
2000°F Continuous Weight Gain Tests

<u>Alloy Additions, Weight Percent</u>	<u>Total Weight Gain mg/cm²/10 hours</u>	<u>Oxidation Rate During 10th Hour mg/cm²/hour</u>
1.6 Ti	510	40.5
None (Pure Cb)	280	22.5
7.7 Ti	220	18.0
5.8 W	140	9.0
10.3 Mo	115	5.25
18.0 W	70	3.4
32.7 Ta	60	4.0
45.9 W	15	1.2
12.9 Cr- 8.8 Co	15	0.18

Table B-18

Nuclear Metals, Inc. Oxidation Test Data (41)

Average Weight Gain After 2 Hour 1800°F Air Exposure

<u>Alloy Additions Weight Percent</u>	<u>Average Weight Gain mg/cm²/hr 1800°F</u>	<u>Nature of Scale</u>
None	43	Heavy, flaked off
0.02Al	36	-
0.02Ce	55	-
0.90Ce	43	-
1.80Ce	31	-
14.30Ce	?	Pyrophoric
20.9 Cr	1.5	-
0.9 Al- 0.3Si	55	Very heavy
3.3 Al- 1.7Si	49	Heavy, flaked off
5.2 Al- 2.7Si	19	Hard, easily removed
7.4 Al- 3.8Si	-	Alloy too brittle to machine
3.0 Cr- 1.5Al	11	Easily fell off
6.3 Cr- 3.3Al	5	Hard, difficult to remove
14.5 Cr- 7.5Al	-	Alloy too brittle to machine
3.0 Cr- 1.6Si	44	Hard, brittle, non-adherent
6.1 Cr- 1.6Si	48	Hard, brittle, non-adherent
6.3 Cr- 3.4Si	60	Very hard, non-adherent
3.7 Cr- 1.6Al- 2.4Si	42	-
8.4 Cr- 3.7Al- 4.1Si	0.13	-
23.0 Cr-10.0Al-15.0Si	0.6	-

Table B-19

Kennecott-Battelle Oxidation Test Data (42)
16 Hour Weight Gain, mg/cm², 1800°F Air

<u>Alloy Addition Weight Percent</u>	<u>Total Weight Gain mg/cm²/16 hours</u>
None (Pure Cb)	177-382
5.OTa	121
15.OTa	127
30.OTa	120
50.OTa	126
60.OTa	132
70.OTa	104
15.OTa- 5.OMo	37-125
15.OTa- 5.OV	102
20.OTa-10.OV	4 403
15.OTa- 5.Ow	256
5.OTi-15.OTa	244
10.OTi-20.OTa	20
10.OTi-40.OTa	45
10.OTi-40.OV	109
20.OTa- 4.OMo-3.OV	308
42.OTi- 4.OCr-4.OAl	2

Table B-20

Lewis Flight Propulsion Laboratory Oxidation Test Data (44)

BINARY ALLOYS

Average Weight Gain mg/cm²/hr, Air Testing

<u>Alloy Addition Weight Percent</u>	<u>Average Weight Gain mg/cm²/hr</u>		<u>Scale Rating</u>	
	<u>1832^oF</u>	<u>2192^oF</u>	<u>1832^oF</u>	<u>2192^oF</u>
None	40	105	5	5
0.3 Al	20	103	1	4
0.6 Al	20	100	1	5
1.5 Al	20	95	2	3
3.1 Al	23	90	2	3
8.8 Al	27	78	Powdery	5
0.6 Co	47	103	4	4
1.3 Co	28	75	3	4
3.2 Co	25	52	2	1
0.6 Cr	18	65	1	1
1.1 Cr	17	85	1	2
2.9 Cr	10	70	1	3
5.9 Cr	35	85	2	2
10.3 Cr	33	80	2	2
0.7 Cu	60	102	4	4
1.4 Cu	45	83	4	3
3.5 Cu	36	58	3	1
0.6 Fe	47	102	4	4
1.2 Fe	40	100	4	4
3.1 Fe	25	40	2	1
0.8 Ge	57	122	5	5
1.6 Ge	56	160	4	4
4.0 Ge	51	125	4	4
8.0 Ge	66	97	5	4
2.1 Ir	55	100	5	4
4.1 Ir	56	110	5	5
9.9 Ir	56	92	5	2
18.8 Ir	52	82	5	2
40.9 Ir	43	60	5	1
1.0 Mo	55	100	4	2
2.1 Mo	35	105	2	2
5.2 Mo	45	102	3	3
10.3 Mo	58	85*	4	3
25.6 Mo	25	45*	4	4

Table B-20
(Continued)

CNLM-1724
Date: May 20, 1959

Alloy Addition Weight Percent	Average Weight Gain mg/cm ² /hr		Scale Rating	
	1832°F	2192°F	1832°F	2192°F
0.6 Ni	52	85	5	3
1.3 Ni	40	105	4	4
2.0 Re	32*	50*	3	1
3.9 Re	36*	63*	3	2
9.5 Re	36*	55*	4	2
18.2 Re	24*	40*	5	2
40.1 Re	-*	-*	-*	-*
0.9 Se	35	70	3	3
1.7 Se	45	75	3	3
4.3 Se	40	92	3	3
8.6 Se	24	95	3	3
0.3 Si	52	110	5	3
0.6 Si	51	115	5	4
1.6 Si	52	83	5	3
3.3 Si	51	55	5	2
9.2 Si	32	-	Powdery	-
1.9 Ta	38	100	4	2
3.8 Ta	35	87	3	2
9.3 Ta	32	82	3	2
17.8 Ta	40	55	4	3
39.3 Ta	46	100	5	4
0.5 Ti	45	90	3	3
1.0 Ti	35	100	3	3
2.6 Ti	35	85	3	2
5.4 Ti	35	80	2	2
14.7 Ti	25	50	1	1
0.6 V	20	65	2	3
1.1 V	12	95	2	4
2.8 V	10	70	1	3
5.8 V	11	55	1	2
15.5 V	65**	85**	Very vitreous scale	
2.0 W	57	135	5	3
3.9 W	53	97	4	5
9.4 W	51	100	4	3
18.0 W	50	103	4	3
39.8 W	43	80	5	4
1.0 Zr	42	96	4	2
2.0 Zr	37	70	3	2
4.9 Zr	36	90	4	3
9.8 Zr	55	90	5	5
24.6 Zr	53	95	5	5

* Oxide Volatilization

** Molten Oxide

CNLM-1724
Date: May 20, 1959

Table B-21

Horizons, Incorporated Oxidation Test Data (46,47)
Air Exposure at 2000°F

<u>Alloy Additions Weight Percent</u>	<u>Average Weight Gain mg/cm²/hour</u>	<u>Comments</u>
None	28-36	Ivory, gray underside, spalled on cooling
20.0Cr- 5.0Mo	14	Greenish yellow, brown underside
5.0Fe- 5.0Co	30	Olive drab scale spalled in cooling
25.0Ti- 2.0Mo	17	Yellow scale easily removed
25.0Ti- 2.0Mo-1.0Th	9.1	Pink scale spalled on cooling
10.0Ti-10.0W	10.6	Yellow scale splintered on cooling
25.0Ti-10.0W	19.7	Yellow scale spalled on cooling
5.0Cr- 5.0Al-1.0Th	11.7	Olive drab scale spalled on cooling
5.0Ti- 5.0Cr-5.0Al-5.0Ce	6.5	Light brown scale easily removed

Table E-22

Ohio State University Oxidation Test Data (48)
Cb-Ti, Cb-Cr, and Cb-Ti-Cr Systems
Weight Gain Rate During 20th Hour of Exposure

<u>Alloy Addition Weight Percent</u>	<u>Test Temp. °F</u>	<u>As Cast Hardness VHN</u>	<u>Weight Gain Rate mg/cm²/hr</u>	<u>Oxide Phases</u>
None	1652	160	15.8	Cb ₂ O ₅
10.8Ti	1580	-	2.7	Cb ₂ O ₅
19.5Ti	1580	-	2.4	TiO ₂ +TiO ₂ ·3Cb ₂ O ₅
27.2Ti	1580	294	2.0	TiO ₂ +TiO ₂ ·Cb ₂ O ₅
35.8Ti	1580	-	1.6	TiO ₂ +TiO ₂ ·Cb ₂ O ₅
50.0Ti	1580	-	1.9	TiO ₂ +TiO ₂ ·Cb ₂ O ₅
1.7Cr	1652	295	10.3	Cb ₂ O ₅
6.5Cr	1652	276	29.2	Cb ₂ O ₅
12.9Cr	1652	425	7.5	-
5.9Ti-10.8Cr	1652	383	2.4	-
6.3Ti-19.8Cr	1652	550	4.2	-
9.3Ti- 4.4Cr	1652	240	1.0	-
12.0Ti- 4.9Cr	1652	235	1.0	TiO ₂ ·3Cb ₂ O ₅
19.6Ti- 5.5Cr	1652	-	1.2	-
21.2Ti-10.7Cr	1652	240	3.5	TiO ₂ +TiO ₂ ·3Cb ₂ O ₅
27.8Ti- 6.6Cr	1652	215	0.8	TiO ₂ +TiO ₂ ·3Cb ₂ O ₅

Table B-23

(48)

Ohio State University Oxidation Test Data

Cb-Zr and Cb-Zr-Ti Systems

Weight Gain Rate After Exposure

<u>Alloy Additions Weight Percent</u>	<u>Test Temp. °F</u>	<u>As Cast Hardness VHN</u>	<u>Weight Gain Rate mg/cm²/hr</u>	
			<u>During 5th Hour</u>	<u>During 20th Hour</u>
35.0Zr	1472	339	4.8	2.4
40.0Zr	1472	370	3.3	1.7
45.0Zr	1472	354	3.1	1.6
47.0Zr	1832	-	10.7	4.9
65.0Zr	1832	264	9.5	-
45.0Zr-5.7Ti	1832	257	5.6	2.0

Table B-24

(49)

Ohio State University Oxidation Test Data

Cb-50.8Zr-2.7Ti Alloy

Continuous Weight Gain Data

<u>Time, Hours</u>	<u>Cumulative Weight Gain, mg/cm²</u>		
	<u>1652°F</u>	<u>1832°F</u>	<u>2012°F</u>
2	17	23	32
4	20	28	40
6	22	31	43
8	24	33	47
12	26	37	52
16	27	39	56
20	28	42	59
24	-	43	62
28	-	45	-
100(Extrapolated)	46	81	116

Table B-25

Battelle Memorial Institute Oxidation Test Data (50)

Miscellaneous Binary and Ternary Alloys

One Hour Weight Gain in 1800°F Air

Alloy Additions Weight Percent	Total Weight Gain mg/cm ² /hr	Color	Nature of Oxide	
			Tenacity	Texture
None	44.6-52.9	White	Fair	Smooth
5.0Al	51.0	White	Fair	Smooth
9.5Ti-5.0Al	12.5	White	Good	Glazed
19.0Ti-5.0Al	15.3	White-yellow	Good	Glazed
5.0Cr	35.4	Light Green	Good	Smooth
9.5Ti-5.0Cr	5.0	Light Green	Very Good	Smooth, flaked
19.0Ti-5.0Cr	4.9	Tan	Good	Powdery
5.0Fe	44.7	White	Fair	Smooth
9.5Ti-5.0Fe	36.2	Light Green	Fair	Smooth
19.0Ti-5.0Fe	7.8	Brown-gray	Poor	Smooth, flaked
5.0Mo	8.2	Gray	Poor	Coarse, powdery
9.5Ti-5.0Mo	8.5	Gray	Fair	Coarse, powdery
19.0Ti-5.0Mo	8.2	Gray	Good	Coarse
5.0Ni	52.4	Tan-brown	Fair	Smooth
9.5Ti-5.0Ni	16.0	Light Green	Poor	Smooth
19.0Ti-5.0Ni	12.4	Violet	Very good	Smooth, flaked
5.0Ta	57.1	White	Fair	Smooth
9.5Ti-5.0Ta	8.2	White	Fair	Smooth, flaked
19.0Ti-5.0Ta	7.3	White-green	Poor	Smooth, flaked
5.0V	8.2	Light Green	Fair	Smooth, flaked
9.5Ti-5.0V	6.7	Violet	Very good	Smooth, powdery
19.0Ti-5.0V	14.2	Violet	Very good	Powdery
5.0W	67.6	White	Fair	Smooth
9.5Ti-5.0W	8.4	White	Very good	Smooth, flaked
19.0Ti-5.0W	12.0	Yellow-white	Poor	Glazed
5.0Zr	108	White	Fair	Smooth
9.5Ti-5.0Zr	25.5	White	Good	Glazed
19.0Ti-5.0Zr	11.0	White-yellow	Good	Glazed

Table B-26

Battelle Memorial Institute Oxidation Test Data (3,30,51)

BINARY ALLOYS

Average Rate of Weight Gain and Weight Loss

Alloy Additions Weight Percent		As Cast Hardness VHN	Average Weight Gain Rate			Average Weight Loss Rate		
Nominal	Corrected		1112°F	mg/cm ² /hr 1472°F	1832°F	1112°F	mg/cm ² /hr 1472°F	1832°F
None	None	115	5.65	33.7	24.3	18.4	72.7	32.0
0.05 Al	-	132	7.5	39.2	19.8	16.2	89.9	49.7
0.29 Al	-	131	8.0	37.2	22.5	17.3	85.2	55.0
1.5 Al	<.2 Al	114	7.1	44.2	19.4	15.8	99.8	47.5
0.02 B	0.02 B	103	5.8	39.3	19.9	12.8	90.7	45.0
0.12 B	0.12 B	111	5.7	27.8	20.2	7.8	63.7	45.0
0.61 B	0.61 B	160	3.0	10.3	15.1	5.8	19.0	66.0
0.02 Be	-	122	5.7	27.6	24.0	12.5	63.3	59.4
0.10 Be	-	113	6.9	31.1	21.5	15.0	72.2	48.8
0.51 Be	<.01 Be	110	3.0	10.3	15.1	14.4	90.6	39.8
0.13 Co	-	136	5.2	40.8	43.8	10.8	94.0	54.5
0.64 Co	-	165	3.7	41.9	37.6	8.5	104.9	129.6
3.34 Co	-	249	4.1	39.2	38.5	9.0	102.5	70.1
0.56 Cr	0.34 Cr	120	3.4	29.8	33.2	7.0	56.7	64.1
2.9 Cr	1.7 Cr	124	3.5	24.2	28.2	4.7	32.0	58.7
6.2 Cr	3.6 Cr	147	1.3	24.4	26.2	0.7	44.5	55.6
14.0 Cr	7.3 Cr	233	0.06	6.8	8.8	-	-	-
18.6 Cr	9.5 Cr	345	0.50	5.1	6.1	3.7	4.6	32.4
23.9 Cr	11.8 Cr	327	0.75	4.6	15.1	-	-	-
30.1 Cr	14.4 Cr	429	0.08	0.42	22.3	0	0.9	48.0
0.12 Fe	<0.06 Fe	114	6.6	32.0	35.6	15.1	73.0	54.5
0.60 Fe	0.24 Fe	146	7.0	44.5	25.0	16.3	94.0	130.0
3.1 Fe	1.15 Fe	178	5.5	22.6	25.0	12.0	48.5	70.3
.12 Mn	-	140	7.8	40.0	21.8	15.6	90.1	51.0
.59 Mn	-	139	4.3	38.0	22.1	8.9	88.7	52.3
3.0 Mn	0.42 Mn	140	4.5	39.3	23.9	9.6	90.6	57.8
1.03 Mo	0.09 Mo	126	1.7	12.0	13.2	5.9	5.3	19.4
2.6 Mo	2.1 Mo	132	0.14	1.8	5.3	-	-	-
5.2 Mo	4.6 Mo	166	0.25	2.1	4.6	-	-	-
7.7 Mo	6.7 Mo	231	0.14	5.7	10.3	-	-	-
10.3 Mo	9.3 Mo	201	0.4	1.9	10.1	0.4	17.8	167.0
25.6 Mo	22.5 Mo	299	2.0	3.8	42.5	0.7	26.4	144.0

Table B-26
(Continued)

Alloy Additions Weight Percent		As Cast Hardness VHM	Average Weight Gain Rate			Average Weight Loss Rate		
Nominal	Corrected		1112°F	mg/cm ² /hr 1472°F	1832°F	1112°F	mg/cm ² /hr 1472°F	1832°F
0.13 Ni	0.06 Ni	114	7.2	27.3	30.3	16.9	65.3	67.3
0.63 Ni	0.31 Ni	147	5.2	26.5	58.5	12.9	68.9	141.1
3.2 Ni	1.5 Ni	230	5.1	31.5	46.3	14.8	82.2	112.5
0.06 Si	0.03 Si	156	6.9	52.0	21.4	15.5	93.8	53.9
0.30 Si	0.21 Si	186	6.1	53.3	46.5	12.9	96.4	96.9
1.56 Si	1.14 Si	330	10.3	67.0	103.8	23.3	148.2	231.1
1.93 Ta	-	125	6.2	29.0	68.2	15.3	70.0	161.5
9.3 Ta	-	122	8.4	34.7	25.5	19.0	79.6	54.6
17.8 Ta	-	120	10.3	39.7	20.3	17.6	96.0	38.7
39.3 Ta	-	130	2.0	26.3	61.3	5.0	70.4	51.8
0.52 Ti	0.47 Ti	108	5.8	21.6	26.0	11.7	52.0	61.7
2.5 Ti	2.4 Ti	115	4.7	21.0	15.7	7.6	45.7	35.4
5.4 Ti	4.9 Ti	135	0.2	7.5	7.7	0	17.8	17.9
8.3 Ti	7.7 Ti	151	0.072	2.4	5.7	-	-	-
11.4 Ti	10.4 Ti	150	0.11	2.1	5.3	-	-	-
14.7 Ti	13.4 Ti	156	0.036	0.61	1.9	0	0.9	5.0
18.1 Ti	16.7 Ti	189	0.90	0.51	3.8	-	-	-
21.7 Ti	19.9 Ti	181	0.14	0.70	4.3	0	0.3	7.9
0.56 V	0.50 V	114	3.60	6.3	13.8	9.4	8.3	32.3
2.80 V	2.51 V	160	0.90	1.4	4.6	1.3	0.6	11.0
4.26 V	3.67 V	164	0.18	2.0	6.9	-	-	-
5.73 V	4.85 V	172	0.051	0.71	3.5	(a)	(a)	7.0
7.25 V	6.35 V	218	0.094	1.2	4.5	-	-	-
15.43 V	13.05 V	194	0.20	6.1	192.0	(a)	13.9	399.0
1.96 W	-	127	6.1	41.0	59.0	14.2	95.3	132.2
9.4 W	-	165	3.1	12.3	54.0	7.2	33.2	139.7
18.0 W	-	196	2.9	17.0	26.0	7.0	43.8	72.5
39.8 W	-	299	8.3	31.0	94.0	27.1	86.9	253.4
0.98 Zr	-	176	7.1	64.8	71.0	11.0	104.2	106.9
4.9 Zr	-	167	3.8	42.2	135.0	9.8	77.8	142.5
9.8 Zr	-	209	0.3	25.2	101.0	0	55.0	137.8
24.6 Zr	-	272	4.7	10.7	49.5	19.3	26.5	86.4
34.6 Zr	-	289	0.2	2.2	30.0	1.2	2.1	60.5

(a) Specimen gained weight.

Table B-27

Battelle Memorial Institute Oxidation Test Data

BINARY ALLOYS (3, 50, 51)

Analysis of Oxide Scales Formed at 1472°F in Air

Alloy Addition Weight Percent		Exposure Time Hours	Chemical Analysis of Scale Weight Percent		
Nominal	Corrected		Alloy	Oxygen	Columbium
None	None	5	0	27.3	72.7
1.5 Al	<0.2 Al	5	0.05	30.65	69.3
2.9 Cr	1.7 Cr	5	0.22	28.4	67.8
15.7 Cr	9.1 Cr	5	2.56	-	-
0.6 Fe	0.24Fe	5	0.31	31.49	68.2
0.59Mn	0.04Mn	5	0.09	31.81	68.1
5.2 Mo	4.6 Mo	20	1.50	-	-
25.6 Mo	22.5 Mo	5	4.03	24.2	71.77
0.63Ni	0.31Ni	5	0.04	30.96	69.0
0.3 Si	0.21Si	5	0.60	31.5	67.9
9.3 Ta	9.3 Ta	5	9.40	30.0	60.6
39.3 Ta	39.3 Ta	5	40.0	23.4	36.6
2.6 Ti	2.4 Ti	5	1.40	28.0	70.6
5.4 Ti	4.7 Ti	10	4.02	23.7	72.28
14.7 Ti	13.6 Ti	20	10.0	-	-
2.8 V	2.5 V	10	1.34	-	-
5.8 V	4.85V	10	-	-	-
15.5 V	13.05V	5	8.1	18.1	52.7
9.4 W	9.4 W	5	6.0	27.6	66.4
39.8 W	39.8 W	1	21.2	23.3	55.5
4.9 Zr	4.9 Zr	5	4.5	25.5	70.0
24.6 Zr	24.6 Zr	5	24.0	21.8	54.2

Table B-28

Battelle Memorial Institute Oxidation Test Data (3,30,51)

BINARY ALLOYS

Depth of Contaminated Metal, Centimeters

<u>Alloy Addition</u> <u>Weight Percent</u>	<u>Initial</u> <u>Hardness</u> <u>KHN</u>	<u>1112°F Exposure</u>		<u>1147°F Exposure</u>		<u>1832°F Exposure</u>	
		<u>Hours</u>	<u>Depth, cm</u>	<u>Hours</u>	<u>Depth, cm</u>	<u>Hours</u>	<u>Depth, cm</u>
None	155	1	0.006	1	0.032	1	0.067
None	155	5	0.013	5	0.049	5	>0.12
None	165	10	0.013	10	(a)	10	>0.10
0.05 Al	128	10	0.016	5	0.075	5	>0.10
0.29 Al	138	10	0.013	5	0.067	5	>0.10
1.50 Al	132	10	0.013	5	0.041	5	>0.10
0.13 Co	142	10	0.016	5	0.053	5	>0.10
0.64 Co	175	10	0.024	5	>0.1	1	>0.10
3.34 Co	280	10	0.022	5	>0.1	5	>0.10
0.56 Cr	132	5	0.016	5	0.054	5	~0.12
2.90 Cr	132	5	0.018	5	0.052	5	>0.14
6.2 Cr	165	5	0.015	5	0.043	5	~0.10
18.6 Cr	405	5	0.0	5	0.015	5	0.05
30.1 Cr	315	20	>0.1	20	>0.1	5	<0.005
0.12 Fe	115	10	0.020	5	0.045	5	>0.10
0.60 Fe	163	10	0.019	5	0.068	5	>0.12
3.10 Fe	212	10	0.013	5	0.055	5	>0.10
0.2 Mn	137	10	0.018	5	0.040	5	>0.10
1.0 Mn	147	10	0.015	5	0.049	5	>0.10
5.0 Mn	164	10	0.015	5	0.048	5	>0.10
1.03 Mo	130	5	0.012	5	0.053	5	>0.10
5.2 Mo	155	20	0.038	20	~0.14	20	>0.14
10.3 Mo	215	5	0.022	5	0.070	5	(a)
25.6 Mo	345	5	0.007	5	0.024	5	(a)
0.13 Ni	134	10	0.008	5	0.037	5	>0.10
0.63 Ni	176	10	0.009	5	0.028	5	>0.10
3.2 Ni	250	10	0.033	5	0.044	5	>0.10
0.06 Si	172	10	0.013	5	0.031	5	>0.10
0.30 Si	266	10	0.004	5	>0.1	1	>0.10
1.56 Si	391	10	0.028	1	>0.1	1	>0.10

Table B-28
(Continued)

CNIM-1724
Date: May 20, 1959

Alloy Addition Weight Percent	Initial Hardness KHN	1112°F Exposure		1472°F Exposure		1832°F Exposure	
		Hours	Depth, cm	Hours	Depth, cm	Hours	Depth, cm
1.93 Ta	127	10	0.007	5	0.045	1	0.063
9.30 Ta	119	10	0.008	5	0.042	5	>0.1
17.80 Ta	104	10	0.013	5	0.032	5	>0.1
39.30 Ta	150	10	0.020	5	0.052	1	0.050
0.52 Ti	115	10	0.014	5	0.056	5	0.154
2.5 Ti	125	10	0.006	5	0.037	5	0.065
5.4 Ti	145	20	0.007	10	0.036	10	0.063
14.7 Ti	157	20	0.008	20	0.018	20	0.058
21.7 Ti	195	20	0.007	20	0.021	20	0.040
0.56 V	125	10	0.009	5	0.042	5	~0.12
2.80 V	165	10	0.008	10	0.044	10	>0.14
5.73 V	200	10	0.004	10	0.037	10	~0.10
15.43 V	283	10	0.012	5	0.018	1	0.01
1.96 W	145	10	0.030	5	0.076	1	0.068
9.40 W	190	10	0.028	5	0.084	1	>0.1
18.0 W	177	10	0.030	5	>0.1	5	>0.1
39.8 W	385	10	<0.002	1	0.029	1	0.054
0.98 Zr	185	5	0.008	5	0.050	5	0.100
4.9 Zr	180	5	0.006	5	0.012	5	(a)
9.8 Zr	210	5	0.008	5	0.013	5	0.006
24.6 Zr	295	5	0.016	5	0	5	0.006
34.6 Zr	334	20	<0.005	20	<0.005	5	<0.005

Table B-29
Battelle Memorial Institute Oxidation Test Data (3, 50, 51)

BINARY ALLOYS

Activation Energy For Oxygen Diffusion From Air

<u>Alloy System</u>	<u>Activation Energy, Q</u>
Pure Columbian	Cal/mole 24,900
Columbian-Aluminum	28,000
Columbian-Cobalt	21,700
Columbian-Chromium	21,300
Columbian-Iron	26,600
Columbian-Manganese	23,000
Columbian-Nickel	24,000
Columbian-Tantalum	35,100
Columbian-Titanium	30,800
Columbian-Tungsten	24,400
Columbian-Vanadium	31,600

Table B-30
Battelle Memorial Institute Oxidation Test Data (3,30)

Binary Alloys

Continuous Weight Gain Tests at 1832°F

<u>Alloy Addition</u> <u>Weight Percent</u>	<u>Parabolic Reaction Rate</u> <u>mg²/cm⁴/min</u>	<u>Time for Transition</u> <u>to Linear Rate,</u> <u>minutes</u>	<u>Linear Reaction</u> <u>Rate</u> <u>mg/cm²/hr</u>	<u>Total Five</u> <u>Hr. Wt. Gain</u> <u>mg/cm²</u>
2.68Cr*	0.99	15	6.8**	36
3.45Cr*	-	-	12.9**	37
7.4Cr*	-	-	4.7**	15
15.0Cr*	-	0	150.0..	750**
0.60Fe	-	0	25.2	130**
3.10Fe	-	0	26.3	130**
2.6Mo	3.72	240	3.6	33
5.2Mo	2.21	210	3.0	25
7.7Mo	0.58	>360	-	15
10.3Mo	1.28	100	3.3	23
9.6Re	-	0	77.0	390**
5.4Ti	3.67	30	11.3	61
11.4Ti	0.85	40	3.8	24
14.7Ti	0.85	250	2.6	17
18.1Ti	0.71	190	5.8	25
21.7Ti	0.92	20	5.2	30
2.8V	2.71	>360	-	27
4.26V	1.64	>360	-	22
5.73V	1.03	>360	-	17
7.25V	0.71	>360	-	15
8.82V	1.49	200	2.6	22
10.4 V	1.32	80	11.2	33
15.4 V	-	0	266.0	1330**
1.96W	-	0	34.9**	136
9.4 W	1.87	10	29.9**	150**
18.0 W	1.82	5	27.0**	106..
22.0 W	1.90	5	34.2..	170**
9.8Zr	-	0	62.0	310**
24.6Zr	25.0	35	25.5	135..
34.6Zr	17.7	120	9.8	78
44.6Zr	7.6	>360	-	48

*Corrected Composition

**Extrapolated values

Table B-31

Battelle Memorial Institute Oxidation Test Data (3,30)

BINARY ALLOYS

Continuous Weight Gain Tests at 2192°F

<u>Alloy Addition Weight Percent</u>	<u>Parabolic Reaction Rate mg²/cm⁴/min</u>	<u>Time for Transition to Linear Rate Minutes</u>	<u>Linear Reaction Rate mg/cm²/hr</u>	<u>Total 5 Hour Weight Gain mg/cm²</u>
2.68 Cr*	9.8	10	23.2	56
3.45 Cr**	-	-	29.9**	72
7.40 Cr*	-	15	33.1**	72
15.0 Cr*	-	0	71.0**	139
0.60 Fe	2.0**	10	36	79
3.10 Fe	3.2**	15	47	48
2.6 Mo	15.6	15	36	63
5.2 Mo	9.4	20	21	43
7.7 Mo	3.7	55	23	37
10.3 Mo	4.0	35	9	29
9.6 Re	-	0	68**	130**
5.4 Ti	-	0	41	91
11.4 Ti	10.0	20	23	53
14.7 Ti	3.2	30	10.5	27
18.1 Ti	3.6	25	10.0	27
21.7 Ti	5.0	10	17.6	39
2.8 V	9.5	35	17.9	44
4.26V	5.6	30	15.5	43
5.73V	3.0	50	15.2	36
7.25V	4.3	55	24.6	37
8.82V	4.5	20	28.5	57
10.4 V	3.4**	35	68.8	115
15.4 V	-	0	198	400**
1.96W	-	0	70**	140**
9.4 W	17.0	80	13.5	45
18.0 W	10.7	180	6.3	35
22.0 W	13.1	>360	-	39
9.8 Zr	19.3	20	48.7	97**
24.6 Zr	37.5	30	31.2	80
34.6 Zr	26.7	15	27.4	71
44.6 Zr	19.7	50	15.9	52

* Corrected Composition
** Extrapolated Values

Table B-32

Battelle Memorial Institute Oxidation Test Data (3,30)

TERNARY ALLOYS

Average Rate of Weight Gain and Weight Loss

Alloy Additions Weight Percent	As Cast Hardness VHN	Average Weight Gain Rate mg/cm ² /hr			Average Weight Loss Rate mg/cm ² /hr		
		1112°F	1472°F	1832°F	1112°F	1472°F	1832°F
None	115	5.7	33.7	24.2	18.4	72.6	32.0
12.1Cr- 0.16Al*	287	0.61	1.4	11.8	4.4	2.8	21.3
1.4Cr- 2.2 Mo*	155	0.18	2.4	4.1	0.28	7.7	7.1
0.8Cr- 4.4 Mo*	164	0.16	1.8	4.6	0.21	2.5	11.0
1.3Cr- 4.4 Mo*	196	0.13	1.7	6.5	0.21	12.5	21.0
6.2Cr- 5.1 Mo*	279	0.10	4.1	1.7	0.05	16.6	1.8
4.6Cr- 0.03Ni*	258	1.5	35.8	23.0	4.6	79.9	47.1
11.3Cr- 0.26Si*	325	0.72	9.3	23.6	3.4	34.4	41.6
0.2Cr- 1.1 V *	145	0.43	8.7	15.4	0.18	13.1	26.2
1.0Cr- 1.2 V *	166	0.17	7.7	9.5	+	8.7	16.4
0.4Cr- 2.1 V *	207	0.22	2.8	8.2	0.08	3.0	14.2
0.2Cr- 2.1 V *	201	0.12	3.6	8.7	+	4.0	15.5
8.5Cr- 2.9 V *	303	0.05	0.54	5.8	3.6	+	9.0
4.9Cr-10.3 W *	279	0.12	8.4	10.2	0.54	30.5	71.1
5.2Mo- 0.3 Al	172	0.19	1.9	3.6	0.12	4.2	9.3
5.2Mo- 3.2 Ni	256	0.45	3.2	7.2	2.9	6.4	13.6
5.2Mo- 0.3 Si	235	0.09	9.7	15.4	4.1	23.1	40.3
4.9Mo- 9.4 W	224	0.13	13.4	22.1	3.7	36.9	66.4
22.6Ta- 4.1 Cr*	192	0.86	6.6	34.0	2.6	17.5	71.1
21.8Ta- 4.6 Mo	186	0.10	7.6	4.4	0.2	18.1	11.3
9.5Ta- 2.7 V	188	0.09	7.3	16.2	+	4.4	30.0
14.1Ti- 0.3 Al	166	0.16	0.97	4.0	+	0.56	5.6
13.4Ti- 1.4 Co	213	0.08	0.72	3.7	+	+	5.1
5.1Ti- 0.6 Cr*	151	0.09	4.5	5.0	+	13.0	11.0
10.4Ti- 1.5 Cr*	165	0.29	1.0	2.5	0.40	1.0	34.2
6.9Ti- 2.2 Cr*	183	0.24	1.6	3.9	+	2.4	6.2
2.8Ti- 2.4 Cr*	180	0.08	5.4	5.3	+	17.1	8.6

CNIM-1724
Date: May 20, 1959

Table B-32
(Continued)

Alloy Additions Weight Percent	As Cast Hardness VHN	Average Weight Gain Rate ng/cm ² /hr			Average Weight Loss Rate ng/cm ² /hr		
		1112°F	1472°F	1832°F	1112°F	1472°F	1832°F
13.5Ti- 1.4 Fe	168	0.10	0.83	3.6	+	0.10	4.8
2.6Ti- 5.3 Mo	166	0.11	9.7	7.1	0.12	35.0	15.3
5.4Ti- 5.4 Mo	314	0.10	7.3	3.8	+	21.8	6.9
8.4Ti- 5.6 Mo	212	0.11	3.5	3.1	+	11.6	4.1
11.4Ti- 5.7 Mo	185	0.20	1.7	2.7	+	3.6	3.1
5.4Ti-10.8 Mo	225	0.16	7.1	3.3	+	23.1	5.8
13.4Ti- 1.4 Ni	215	0.22	1.1	7.9	1.7	2.4	12.1
15.0Ti- 3.7 Ni	253	0.10	0.68	7.5	+	+	4.4
14.1Ti- 0.3 Si	198	0.18	1.0	3.9	+	0.51	5.1
6.1Ti-23.1 Ta	143	0.10	5.8	7.9	+	16.4	13.8
10.0Ti- 1.5 V	168	0.11	1.4	3.4	+	2.8	4.2
2.7Ti- 2.9 V	170	0.10	2.1	5.5	+	4.1	9.4
5.6Ti- 3.0 V	179	0.16	3.5	4.0	+	11.2	5.9
8.6Ti- 3.0 V	193	0.12	1.5	3.3	+	3.6	4.2
11.7Ti- 3.1 V	194	0.10	0.94	2.8	+	0.12	3.2
1.3Ti- 4.3 V	185	0.11	1.6	4.3	+	0.19	10.7
10.8Ti-10.4 W	198	0.11	1.8	2.8	+	7.3	4.0
1.4V - 2.6 Mo	149	0.21	1.5	4.1	0.04	1.3	6.1
1.4V - 5.2 Mo	164	0.15	2.4	4.1	0.19	5.0	6.5
2.8V - 2.6 Mo	166	0.19	1.6	4.3	0.01	1.7	6.5
2.8V - 5.2 Mo	197	0.12	2.8	3.2	1.4	5.6	9.1
5.9V - 3.4 Ni	299	0.15	1.1	4.1	0.37	+	5.0
2.7V - 9.6 W	227	0.36	9.8	36.4	0.97	32.6	95.8
12.4Zr- 5.1 Cr*	299	3.2	5.9	37.0	13.8	23.3	73.9
13.1Zr- 6.9 Ti	197	0.04	3.0	10.5	1.7	11.9	14.9
20.2Zr- 2.8 V	287	0.68	7.8	20.1	2.1	18.8	34.7

* Composition corrected on basis of weight losses during melting.

+ Specimen gained weight

Table B-33

Battelle Memorial Institute Oxidation Test Data (3, 30)

TERNARY ALLOYS

Continuous Weight Gain Tests at 1832°F

<u>Alloy Additions Weight Percent</u>	<u>Parabolic Reaction Rate mg²/cm⁴/min.</u>	<u>Time for Transition to Linear Rate Minutes</u>	<u>Linear Reaction Rate mg/cm²/hr.</u>	<u>Total Five Hour Weight Gain mg/cm²</u>
6.2Cr-8.1Mo**	0.47	>360	-	11.9
6.6Ti-0.9Cr*	0.83	15	5.0	30.6
11.5Ti-1.3Cr*	0.13	60	3.0	13.6
17.3Ti-4.0Cr*	0.19	45	2.3	12.6
6.5Ti-4.4Mo*	1.1	>360	-	18.3
9.8Ti-6.7Mo*	0.83	>360	-	16.2
13.3Ti-9.3Mo*	0.77	>360	-	15.3
5.8Ti-2.9V *	0.91	70	2.9	20.3
9.1Ti-5.3V *	0.52	80	2.3	15.7
14.3Ti-7.1V *	0.82	25	10.1	46.5
4.5V -5.9Mo**	0.66	>360	-	11.9

* Composition corrected on basis of spectographic analysis.

** Composition corrected on basis of weight losses during melting.

Table E-34

Battelle Memorial Institute Oxidation Test Data (3, 30)

TERNARY ALLOYS

Continuous Weight Gain Tests at 2192°F

<u>Alloy Additions Weight Percent</u>	<u>Parabolic Reaction Rate mg²/cm⁴/min.</u>	<u>Time for Transition to Linear Rate Minutes</u>	<u>Linear Reaction Rate mg/cm²/hr.</u>	<u>Total Five Hour Weight Gain mg/cm²</u>
6.2Cr-8.1Mo**	0.8	10	8.3	19.1
6.6Ti-0.9Cr*	-	0	20.2	53.6
11.5Ti-1.3Cr*	1.6	5	16.2	39.7
17.3Ti-4.0Cr*	1.1	10	15.5	41.7
6.5Ti-4.4Mo*	2.8	10	15.5	40.0
9.8Ti-6.7Mo*	3.9	5	13.3	39.4
13.3Ti-9.3Mo*	4.0	10	15.5	30.5
5.8Ti-2.9V *	8.9	20	16.6	44.0
9.1Ti-5.3V *	4.4	40	13.3	27.2
14.3Ti-7.1V *	4.5	10	18.4	43.2
4.5V -5.9Mo**	6.1	240	5.5	26.6

* Composition corrected on basis of spectrographic analysis.

** Composition corrected on basis of weight loss during melting.

Table B-35

Stanford Research Institute Oxidation Test Data (53)

BINARY ALLOYS

Rate of Displacement of Metal Interface at 2000°F

<u>Alloy Addition Weight Percent</u>	<u>Rockwell Hardness As-Cast</u>	<u>Displacement Rate mils/hour</u>	<u>Alloy Addition Weight Percent</u>	<u>Rockwell Hardness As-Cast</u>	<u>Displacement Rate mils/hour</u>
None	-	Oxid.	5.0 Ti	C 27	0.42
2.0 Cr	-	2.00	10.0 Ti	C 40	0.17
4.0 Cr	-	Oxid.	15.0 Ti	C 40	0.33
6.0 Cr	-	0.48	20.0 Ti	C 36	0.13
8.0 Cr	-	1.70	25.0 Ti	C 36	0.58
10.0 Cr	-	0.54	30.0 Ti	C 34	1.00
12.0 Cr	-	0.42	35.0 Ti	C 33	0.46
14.0 Cr	-	0.87	40.0 Ti	C 31	1.10
16.0 Cr	-	2.30	45.0 Ti	C 27	0.53
18.0 Cr	-	0.58	50.0 Ti	C 24	1.20
20.0 Cr	-	1.40	50.0 W	C 41	Oxid.
25.0 Cr	-	0.58	60.0 W	C 45	"
30.0 Cr	-	0.12	65.0 W	Brittle	"
35.0 Cr	-	0.04	70.0 W	"	"
0.8 Sn	-	Oxid.	75.0 W	"	"
1.3 Sn	-	"	5.0 Zr	B 95	1.40
2.0 Sn	-	"	10.0 Zr	B 87	Oxid.
3.2 Sn	-	"	15.0 Zr	B 95	0.70
5.0 Sn	-	"	20.0 Zr	C 25	0.42
			25.0 Zr	C 26	0.50
			30.0 Zr	C 26	0.83
			50.0 Zr	C 29	-

Table B-36

Stanford Research Institute Oxidation Test Data (53)
Cb-Ti-Cr SYSTEM AND MODIFICATIONS
Rate of Displacement of Metal Interface at 2000°F

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Rockwell Hardness</u> <u>As-Cast</u>	<u>Displacement</u> <u>Rate</u> <u>mils/hour</u>
17.OT1- 7.0Cr	C 41	0.33
30.OT1- 7.0Cr	C 33	0.27
10.OT1- 5.0Cr- 5.0Al	C 40	0.12
10.OT1-10.0Cr- 5.0Al	C 45	0.33
10.OT1-15.0Cr- 5.0Al	C 45	0.12
38.OT1- 7.0Cr- 5.0Al	C 29	0.06
40.OT1-10.0Cr- 5.0Al	C 32	0.04
35.OT1-15.0Cr- 5.0Al	C 42	0.08
10.OT1- 5.0Cr- 5.0Co	-	0.75
10.OT1-10.0Cr- 5.0Co	-	1.60
10.OT1-15.0Cr- 5.0Co	-	0.21
17.OT1- 7.0Cr-10.0Co	C 51	0.50
17.OT1- 7.0Cr-10.0Fe	C 55	1.40
20.OT1- 5.0Cr- 5.0Ni	-	0.20
20.OT1-10.0Cr- 5.0Ni	-	0.27
20.OT1-15.0Cr- 5.0Ni	-	0.06
17.OT1- 7.0Cr-10.0Ni	C 46	0.33
10.OT1- 5.0Cr- 5.0Si	-	0.14
10.OT1-10.0Cr- 5.0Si	-	0.14
10.OT1-15.0Cr- 5.0Si	-	0.16
10.OT1- 5.0Cr-20.0Ta	-	0.16
10.OT1-10.0Cr-20.0Ta	-	0.16
10.OT1- 5.0Cr- 5.0V	-	0.67
10.OT1-10.0Cr- 5.0V	-	1.50
10.OT1-15.0Cr- 5.0V	-	Oxid.
20.OT1- 5.0Cr- 5.0V	-	0.70
20.OT1-10.0Cr- 5.0V	-	0.60
20.OT1-15.0Cr- 5.0V	-	0.40
10.OT1- 5.0Cr- 5.0W	-	0.16
10.OT1-10.0Cr- 5.0W	-	0.25
10.OT1-15.0Cr- 5.0W	-	1.40

Table B-36
 (Continued)

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Rockwell Hardness</u> <u>As-Cast</u>	<u>Displacement</u> <u>Rate</u> <u>mils/hour</u>
10.0Ti- 5.0Cr- 5.0Zr	-	0.46
10.0Ti-10.0Cr- 5.0Zr	-	0.75
10.0Ti-15.0Cr- 5.0Zr	-	2.10
20.0Ti- 5.0Cr- 5.0Zr	-	0.40
20.0Ti-10.0Cr- 5.0Zr	-	0.58
20.0Ti-15.0Cr- 5.0Zr	-	0.14
9.5Ti- 5.0Cr- 9.5Zr	C 45	0.25
9.0Ti-10.0Cr- 9.0Zr	C 40	0.41
19.0Ti- 5.0Cr- 4.8Zr	C 29	0.41
18.0Ti-10.0Cr- 4.5Zr	C 39	0.30
40.0Ti- 7.0Cr- 5.0Al- 3.0Ce	C 26	0.02
35.0Ti-10.0Cr- 5.0Al- 5.0Fe	C 43	0.04
35.0Ti- 7.0Cr- 5.0Al- 3.0Mn	C 31	0.10
40.0Ti- 7.0Cr- 5.0Al- 3.0Mn	C 30	0.02
35.0Ti- 7.0Cr- 5.0Al- 3.0Mo	C 33	0.38
25.0Ti- 7.0Cr- 5.0Al- 7.0Mo	C 34	2.00
20.0Ti- 7.5Cr- 5.0Al-10.0Mo	C 41	2.40
20.0Ti- 7.5Cr- 5.0Al-10.0Ta	C 37	0.16
37.0Ti- 7.0Cr- 5.0Al- 1.0Zr	C 31	0.02
22.5Ti- 7.5Cr- 6.0Al- 5.0Mo-4.0V	C 42	0.83
27.5Ti- 7.5Cr- 6.0Al- 5.0Mo-4.0V	C 41	0.06
32.5Ti- 7.5Cr- 6.0Al- 5.0Mo-4.0V	C 39	0.04
37.5Ti- 7.5Cr- 6.0Al- 5.0Mo-4.0V	C 39	0.02
25.0Ti- 7.0Cr- 5.0Al- 5.0W -5.0Co	-	0.08
20.0Ti- 5.0Cr- 4.0Al- 1.0Zr-5.0W	C 34	0.13
20.0Ti- 5.0Cr- 3.0Al- 1.0Zr-5.0W	C 35	0.21

Table B-37

Stanford Research Institute Oxidation Test Data (53)
Cb-Ti-Ta SYSTEM AND MODIFICATIONS
Rate of Displacement of Metal Interface at 2000°F

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Rockwell Hardness</u> <u>As-Cast</u>	<u>Displacement</u> <u>Rate</u> <u>mils/hour</u>
2.5Ti-19.5Ta	C 19	1.00
4.0Ti-19.2Ta	C 25	0.62
6.3Ti-18.8Ta	C 27	0.33
10.0Ti-18.0Ta	C 30	0.13
10.0Ti-20.0Ta	-	0.08
15.8Ti-16.8Ta	C 27	0.17
25.0Ti-15.0Ta	C 26	0.33

Table B-38

Stanford Research Institute Oxidation Test Data (53)
Cb-Ta-Cr SYSTEM AND MODIFICATIONS
Rate of Displacement of Metal Interface at 2000°F

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Rockwell Hardness</u> <u>As-Cast</u>	<u>Displacement</u> <u>Rate</u> <u>mils/hour</u>
20.0Ta- 5.0Cr	-	1.8
19.5Ta- 2.5Cr	C 43	1.0
19.2Ta- 4.0Cr	C 19	1.3
18.8Ta- 6.3Cr	C 31	1.0
18.0Ta-10.0Cr	C 21	1.3
16.8Ta-15.8Cr	C 52	1.1
15.0Ta-25.0Cr	C 57	0.5
18.7Ta- 1.6Cr-5.0Mn	-	1.2
18.5Ta- 2.5Cr-5.0Mn	-	1.3
18.2Ta- 4.0Cr-5.0Mn	-	1.3
17.7Ta- 6.3Cr-5.0Mn	-	1.1
17.0Ta-10.0Cr-5.0Mn	-	0.8

Table B-39

Stanford Research Institute Oxidation Test Data (53)
Cb-Zr-Ti SYSTEM AND MODIFICATIONS
Rate of Displacement of Metal Interface at 2000°F

<u>Alloy Additions</u> <u>Weight Percent</u>	<u>Rockwell Hardness</u> <u>As-Cast</u>	<u>Displacement</u> <u>Rate</u> <u>mils/hour</u>
5.0Zr-15.0Ti	B 95	0.45
5.0Zr-20.0Ti	B 93	0.17
7.0Zr- 8.0Ti	B 99	0.40
7.0Zr-23.0Ti	B 100	0.30
7.0Zr-38.0Ti	B 96	0.60
10.0Zr-10.0Ti	B 98	0.17
10.0Zr-15.0Ti	B 100	0.24
15.0Zr- 5.0Ti	B 100	0.17
15.0Zr-40.0Ti	B 99	0.71
15.0Zr-50.0Ti	B 97	1.10
20.0Zr- 5.0Ti	C 25	2.60
20.0Zr-10.0Ti	C 24	0.58
20.0Zr-15.0Ti	C 23	2.50
20.0Zr-20.0Ti	C 22	0.13
20.0Zr-25.0Ti	C 21	3.00
25.0Zr- 5.0Ti	C 22	3.30
25.0Zr-10.0Ti	C 25	0.88
25.0Zr-15.0Ti	C 24	0.42
25.0Zr-20.0Ti	C 23	0.46
25.0Zr-25.0Ti	C 21	4.10
35.0Zr-10.0Ti	C 30	-
35.0Zr-20.0Ti	C 25	-
40.0Zr-10.0Ti	C 25	-
50.0Zr-15.0Ti	C 26	-
4.5Zr-18.0Ti- 5.0Al	C 35	0.08
9.5Zr- 9.5Ti-10.9Al	C 35	0.08
9.8Zr- 9.8Ti- 4.4Al	C 34	0.21

END