# STRUCTURAL AND MECHANICAL EFFECTS

# OF INTERSTITIAL SINKS

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October 1966

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Solar, A Division of International Harvester Company

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National Aeronautics and Space Administration
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NOTICE

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# ABSTRACT

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The changes in mechanical properties and structure that occur in dispersion strengthened columbium-base alloys induced by loss of interstitials to more reactive metal coatings are discussed. The materials necessary for this investigation (Cb752 and D43) have been procured, analyzed chemically, and studied metallographically. A high-temperature vacuum creep facility is being constructed.

*Author*

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# I. INTRODUCTION

It has been shown that transport of interstitial elements can occur between refractory metals and many other metals placed in intimate contact. Such contacts occur when refractory metals are coated or joined and, in many cases, have resulted in very serious problems such as strength losses of up to 50 percent depression of recrystallization temperatures, and embrittlement on processing. Partition of interstitials with uphill (concentration-wise) diffusion occurs when the partial molal free energy of the interstitial element is lower in the second metal or alloy than in the refractory metal alloy, and the equilibrium partition can result in almost complete depletion of carbon or oxygen in the refractory alloy with conversion of the more active metal to a saturated solution that may contain free carbide or oxide. Thus, columbium alloys coated with Ti-Cr-Si protective coatings, molybdenum alloys such as TZM joined by brazing or diffusion bonded with group IV (titanium, zirconium, hafnium or group V (vanadium, niobium, tantalum) metals, and columbium or tantalum alloys in contact with group IV metals or alloys are susceptible to interstitial sink effects. In the case of dispersion strengthened columbium alloys, the magnitude of these effects is strongly dependent upon the thermal/mechanical processing history of the alloys.

The program is designed to study the mechanism of the strength loss which occurs in dispersion strengthened columbium alloys when coated, brazed, or diffusion bonded with particular reference to loss of creep strength. The mechanism whereby duplex heat-treated alloys are weakened more than stress relief annealed alloys, and whether this weakening is most severe during actual migration of interstitials or after completion of interstitial partition, will be studied by specially designed creep tests.

These studies will be performed on D43 and Cb752 alloys in the standard mill finished and duplex heat-treated conditions.

## II. INTERSTITIAL SINK EFFECTS

The term "Interstitial Sink" was coined by Metcalfe, et al[1] to describe the effects which occur when two different refractory metals are placed in intimate contact and partition of interstitials is allowed to occur. One of the earliest studies of this effect was by Darken [2] in connection with carbon diffusion between two iron-silicon alloys. It was shown that uphill diffusion could occur as a result of the difference in activity of carbon induced by the presence of silicon.

In the refractory metal field the problem of interstitial sinks has been recognized only recently, but recognition occurred almost simultaneously in several large hardware programs. A loss of over half the strength of solution-treated and aged D43 alloy resulted from brazing with B120VCA (Ti-13V-11G-3Al) and its being coated with the (Ti-Cr)-Si coating which, in turn, created the need for drastic changes in the ASCEP program. In another program on columbium honeycomb fabricated by diffusion bonding, the equilibrium partition of oxygen resulted in the conversion of the 0.0005-inch titanium foil to oxide. Similar effects were observed in diffusion bonded honeycomb core of TZM which was made by use of titanium foil. The TZM was stripped of carbon during annealing, thus lowering its recrystallization temperature by several hundred degrees, and carbides were formed in the titanium foil.

Not all interstitial sink effects are deleterious. It was shown recently in a chromium alloy coating program at Solar that a metallic vanadium/titanium alloy coating can prevent embrittlement due to nitrogen and oxygen contamination during elevated-temperature exposure to air, by acting as a sink or reservoir for these interstitial elements. However, this program is concerned with the strength losses and degradation of fabricated structures due to interstitial diffusion effects in refractory metal alloys.

## 2.1 EXAMPLES OF INTERSTITIAL SINK EFFECTS

An example of the interstitial sink effect causing an otherwise stable alloy to undergo recrystallization and grain growth on heating, with subsequent embrittlement, is shown in Figure 1A. Here TZM, diffusion bonded with a zirconium sink, was

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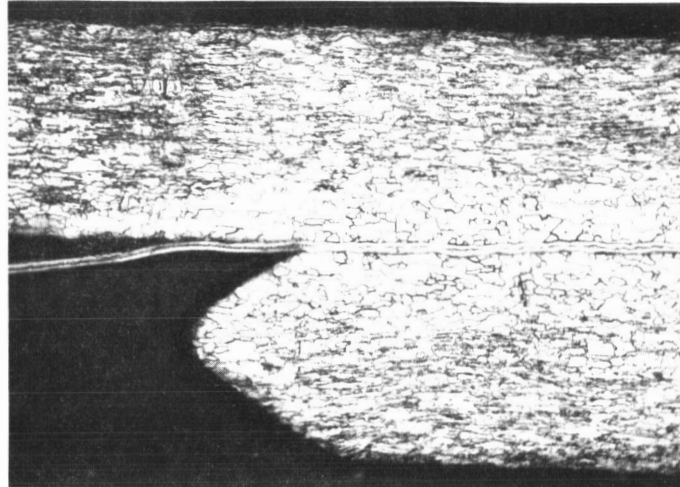
Etched                                    Magnification: 500X

A. TZM bonded with Ta-Zr-Ta foil; annealed at 2000 F for one hour
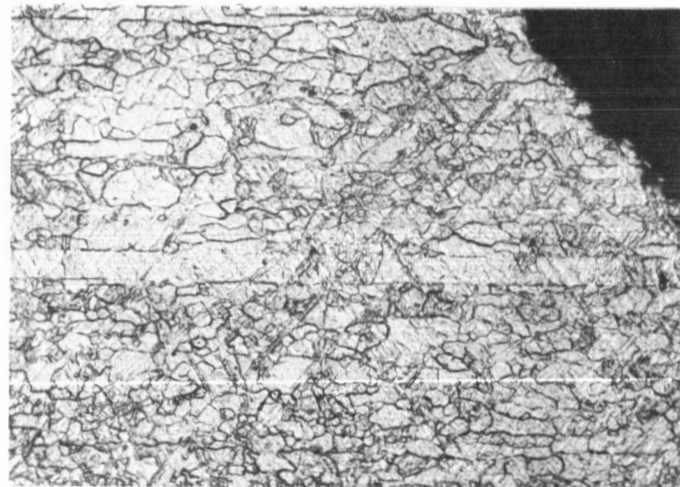


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B. TZM bonded with 0.0006-inch molybdenum; annealed at 2800 F for one hour

FIGURE 1.  COMPARISON OF MOLYBDINUM AND Zr-Ta AS SINK MATERIALS
          FOR TZM

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heated for one hour at 2000 F. Recrystallization resulting from carbon removal in the vicinity of the bond was as advanced as found for one hour at over 2800 F in the absence of a sink. Molybdenum does not act as a sink and recrystallization of the TZM proceeds slowly at 2800 F (Fig 1B).

The most dramatic effect of an interstitial sink is the strength reduction in the D43 and Cb752 columbium alloys in the duplex heat treatment condition (solution treat, cold work, and age). The D43 alloy after this treatment behaves in accordance with the data in Table I. The duplex processed Cb752 suffers a similar loss of properties as shown in Table II. The standard processed alloy (stress relieved), however, appears stable in a short term tensile test, although interstitial loss to the sink must occur. Other effects occur that may be equally deleterious, and it is possible that loss of the coarse dispersion may affect the creep behavior. Experiments with Cb132M alloy/titanium diffusion couples have shown that if the relative amounts of columbium and titanium are appropriate, the solubility boundary between interstitial and metal can be exceeded and massive carbides will precipitate in the sink layer.

TABLE I

EFFECT OF COATINGS ON MECHANICAL PROPERTIES OF D43 ALLOY AT 2200 F

| Specimen Condition (Transverse Oriented) | Tests | Yield Strength (psi) | Ultimate Tensile Strength (psi) | Elongation (%) |
|---|---|---|---|---|
| As received | 2 | 33,000 | 35,460 | 14 |
| Annealed 2400 F – 15 hours | 4 | -- | 30,800 | 20 |
| Tungsten foil + anneal | 2 | -- | 31,000 | 10 |
| Molybdenum foil + anneal | 2 | -- | 32,000 | 10 |
| Tantalum foil + anneal | 4 | 16,600 | 20,800 | 20 |
| Titanium foil + anneal | 2 | -- | 20,000 | 30 |

## TABLE II

### TENSILE PROPERTIES OF Cb752 ALLOY AT 2200 F

|  | Specimen Orientation | Tests | Yield Strength (psi) | Ultimate Tensile Strength (psi) | Elongation (%) |
|---|---|---|---|---|---|
| DHT, as-received | Longitudinal | 2 | 28,200 | 35,100 | 28 |
|  | Transverse | 4 | 30,100 | 33,800 | 22 |
| DHT, annealed 2400 F | Longitudinal | 4 | 26,200 | 30,000 | 30 |
|  | Transverse | 2 | 27,600 | 34,700 | 30 |
| DHT, tantalum foil + 2400 F | Transverse | 2 | 28,000 | 33.600 | 18 |
| DHT, Molybdenum foil + 2400 F | Longitudinal | 1 | 28,000 | 30,500 | 35 |
|  | Transverse | 3 | 24,700 | 30,900 | 33 |
| DHT, Titanium foil + 2400 F | Longitudinal | 3 | 21,300 | 22,700 | 26 |
|  | Transverse | 2 | 16,100 | 23,400 | 22 |
| ST, annealed 2400 F | - - | 2 | -- | 31,000 | 55 |
| ST, Titanium foil + 2400 F | - - | 2 | -- | 30,000 | 20 |

DHT = Duplex heat treatment

ST = Standard treatment (stress relief anneal)

## III. THEORETICAL DISCUSSION

The theory of partition of an interstitial between two phases has been developed primarily in connection with liquid metal technology. Circulation of alkali metals over titanium or zirconium for 500 hours at 1200 F is a typical hot trapping technique.

It has been shown that

$$\Delta F^{\circ}_{X \text{ in } M} = \Delta F^{\circ}_{MX} + RT\ln\left(\frac{X \text{ in } M}{\text{solubility of } X \text{ in } M}\right)_{T} \tag{1}$$

for a temperature T where X is the interstitial (oxygen, nitrogen, or carbon) and M is the solvent element (titanium, columbium, vanadium). It is assumed that the compound MX is in equilibrium with M(X) saturated, that the concentrations are low so that Henry's Law applies, and that the composition of the compound MX in equilibrium with M(X) saturated is stoichiometric (unless thermodynamic data are available for the exact composition).

Consider the partition of carbon between columbium and titanium. At equilibrium, the free energy functions in the two metals are given by

$$\Delta F_{C \text{ in } Ti} = \Delta F^{\circ}_{TiC} + RT\ln\left[\frac{C \text{ in } Ti}{\text{Sol } C \text{ in } Ti}\right] \tag{2}$$

$$\Delta F_{C \text{ in } Cb} = \Delta F^{\circ}_{Cb_2C} + RT\ln\left[\frac{C \text{ in } Cb}{\text{Sol } C \text{ in } Cb}\right] \tag{3}$$

When both are solid solutions, these become equal at equilibrium, i.e.,

$$\Delta F^{\circ}_{TiC} - \Delta F^{\circ}_{Cb_2C} = RT\ln\left[\frac{C_2 S_1}{S_2 C_1}\right] \tag{4}$$

where C is the final concentration, S is the concentration at saturation and suffixes indicate the appropriate metals.

Titanium and columbium are completely miscible so that at final equilibrium there will be a uniform (columbium, titanium, carbon) solid solution. However, carbon diffuses orders of magnitude more rapidly than the substitutional elements and the initial effect is for the sink to behave as a pure metal. The calculated partitions of carbon and oxygen between pure columbium and pure metal, M, are shown in Table III, and Figures 2 and 3 show thermodynamic data calculated for oxygen and carbon in various refractory metals at 1500 K. The most critical assumptions which were made to calculate these data were that ideal solid solutions and dilute solid solutions exist. The validity of the data for practical comparative purposes was demonstrated by the prediction that tantalum would be a sink for carbon strengthened alloys but not oxygen strengthened alloys. The prediction was experimentally verified as can be seen by reference to Tables I and II. Table III shows that although vanadium is not an interstitial sink in the same sense as titanium, partition of oxygen and carbon will occur between columbium and vanadium. The vanadium layer of the V-(Cr-Ti)-Si coating (currently under development at Solar) comprises approximately 5 percent of the weight of the columbium. Partition of an initial 1000 ppm carbon in the columbium with this amount of vanadium will reduce the carbon content in the columbium to 976 ppm while the concentration in the vanadium would reach 450 ppm. Alloying of vanadium with any free titanium which is present would increase the sink potential for carbon, but the net result would still be an enormous improvement over the (Ti-Cr)-Si coating.

TABLE III

CALCULATED PARTITION OF INTERSTITIALS BETWEEN
PURE COLUMBIUM AND METAL M AT 1500 K

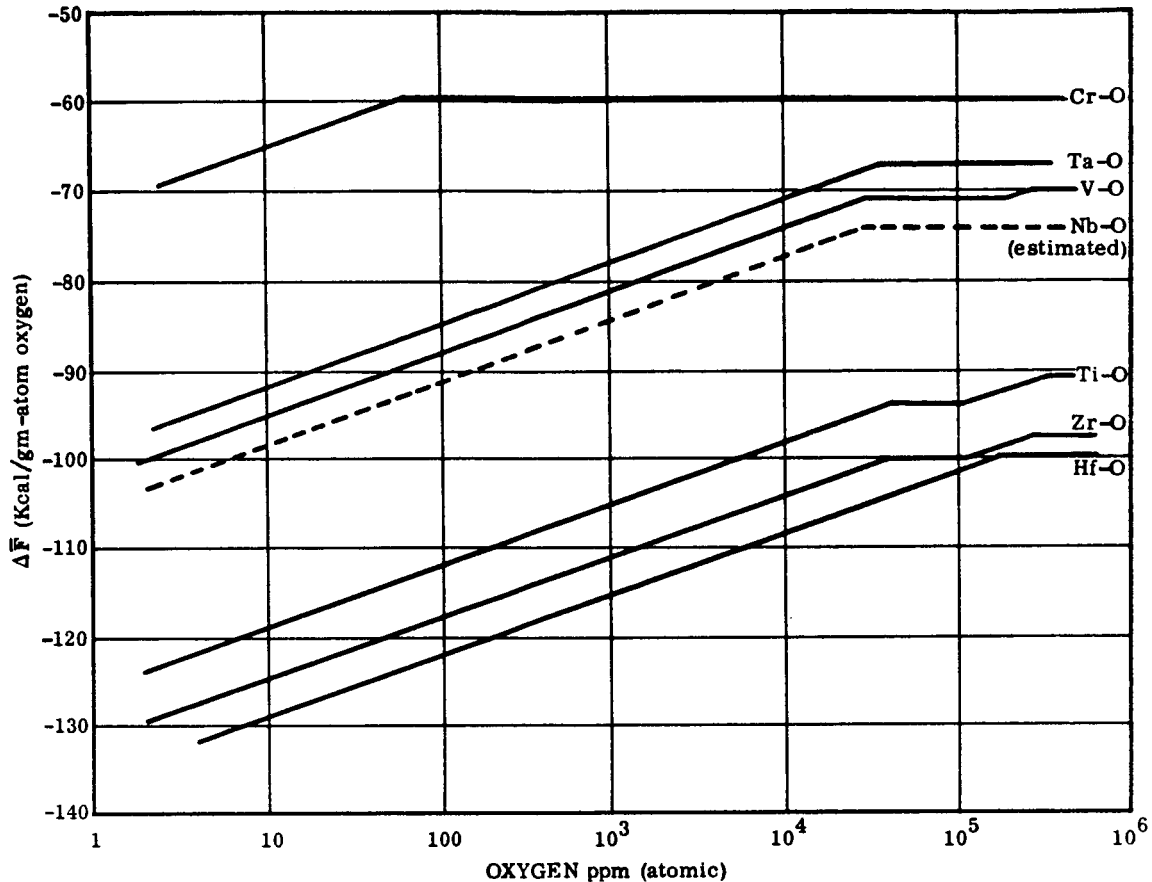| Sink Element M | Calculated Carbon (ppm) | | Calculated Oxygen (ppm) | |
|---|---|---|---|---|
| | Cb | M | Cb | M |
| Molybdenum | 100 | <1 | 100 | <1 |
| Tungsten | 100 | <1 | 100 | <1 |
| Vanadium | 100 | 45 | 100 | 33 |
| Tantalum | 100 | 370 | 100 | 10 |
| Titanium | 100 | 16,800 | 100 | 100,000 |

FIGURE 2. PARTIAL MOLAL FREE ENERGIES AT 1500 K;
Oxygen in Transition Metal

The composition of a potential sink can be critical when two phases may be
present and the (Ti-Cr)-Si coating again provides a very good example. Figure 4
shows the Ti-Cr phase diagram. A titanium-rich beta solid solution is stable at
1500 K up to 40 atomic percent chromium, with a two-phase region extending up to
$TiCr_2$. Between 40 and 60 atomic percent there is a Ti-40at%Cr solid solution in the
two-phase mixture so that the same sink potential persists up to 60 atomic percent.
Laves phase plus the chromium rich solid solution does not cause sink effects so that
an abrupt change occurs at 60 atomic percent chromium. In confirmation, it is ob-
served that D43 alloy coated from 80Cr-20Ti packs does not show the sink effect
whereas 60Cr-40Ti packs cause marked loss of carbon from the alloy.

A useful working definition of a sink might be where the concentration of
interstitial element becomes higher in the sink metal than in the columbium. The
partial molal free energies of a number of binary metallic solid solutions containing
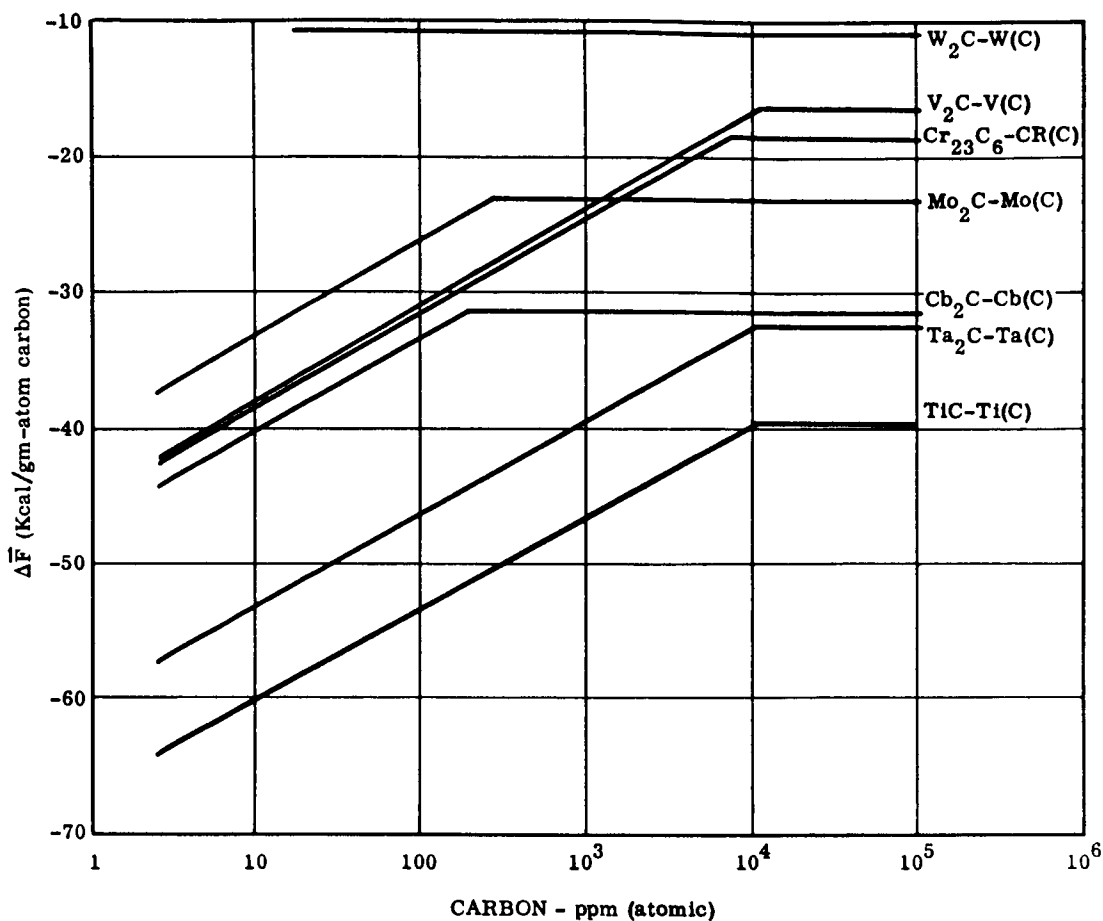
9

FIGURE 3. PARTIAL MOLAL FREE ENERGIES AT 1500 K;
Carbon in Transition Metal

1000 ppm oxygen are shown in Figure 5. The free energy data show that although Nb(O) is more stable than V(O), the relative oxygen concentrations are 1000 to 330 ppm when oxygen is equilibrated between the two metals (Table III). Figure 4 shows that the partial molal free energy of oxygen in a V-12at%Ti alloy equals that of oxygen in pure columbium. Therefore, assuming ideal solutions, V-12at%Ti and columbium will contain equal concentrations of oxygen at equilibrium. Thus, compositions richer in titanium will be sinks although V-12at%Ti will initially remove oxygen from columbium until the concentrations are equal. An infinite sink of V-12at%Ti, containing less oxygen than the columbium, would completely deplete the columbium of oxygen.
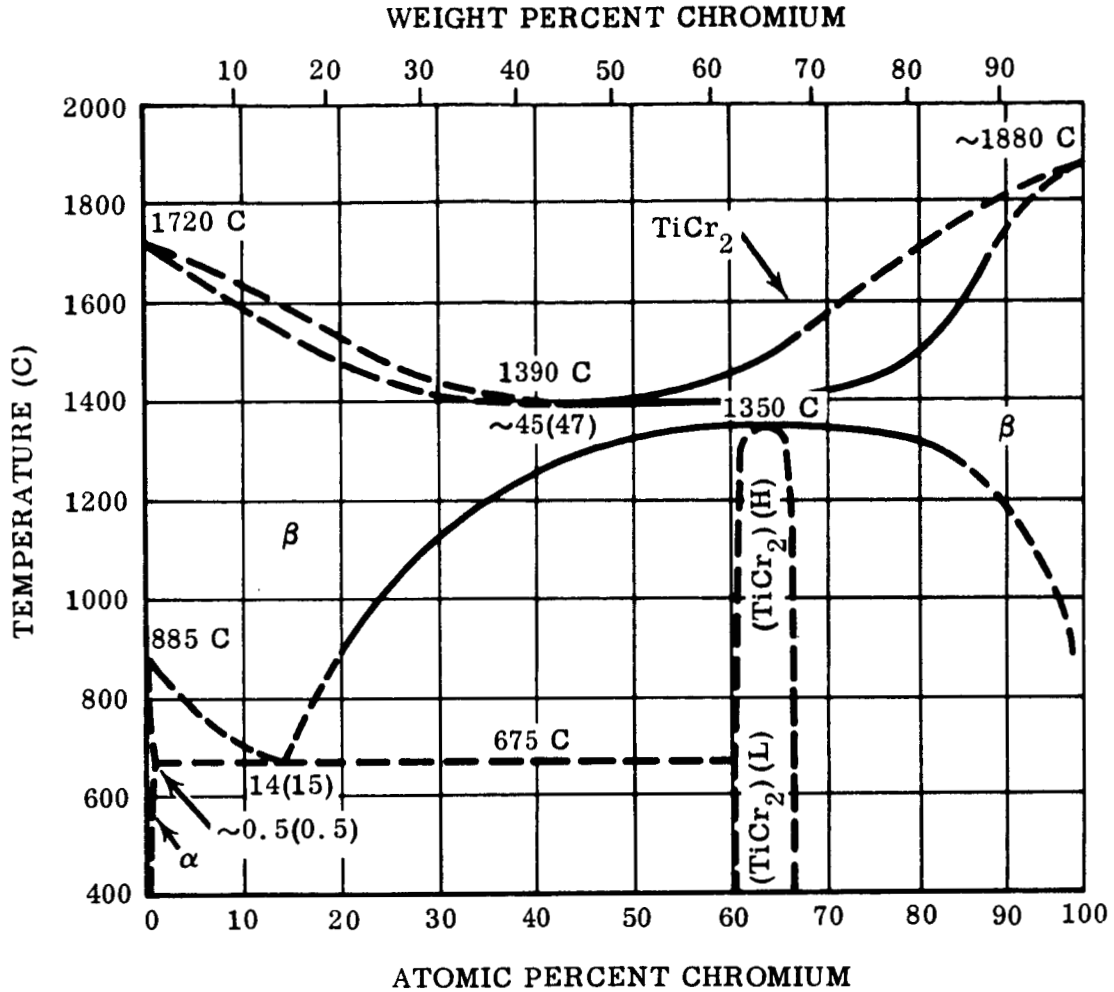
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**WEIGHT PERCENT CHROMIUM**

FIGURE 4. CHROMIUM-TITANIUM BINARY SYSTEM

For a typical dispersion strengthened columbium alloy, three separate equilibria need to be considered:

(a)   Between columbium and ZrX        $Cb + ZrX \rightleftharpoons Cb(Zr,X)$

(b)   Between columbium and sink        $Cb(X) \rightleftharpoons S(X)$

(c)   Between sink S and compound        $S(X) \rightleftharpoons SX$

Solution of ZrX in the columbium solid solution occurs after equilibrium (b) has reduced the dissolved interstitial content of the columbium below saturation. The rate of dissolution of ZrX compound will be dependent on many factors and will be influenced by:

• Zirconium banding as a result of melt segregation

• Zirconium concentrations as a result of solution of compound ZrX

• Chemical potential of the sink

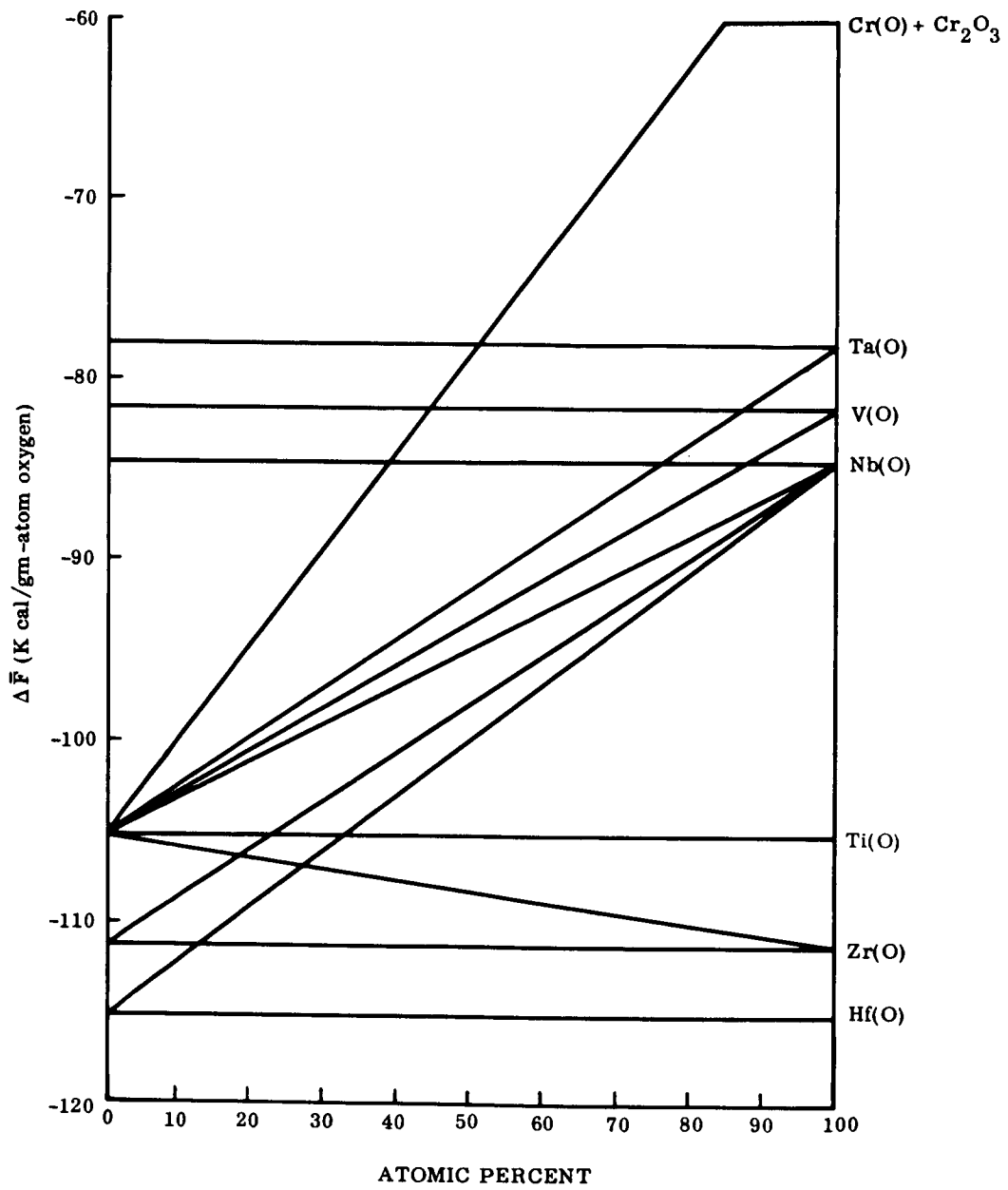• Morphology, size, and distribution of ZrX precipitate

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FIGURE 5. PARTIAL MOLAL FREE ENERGIES AT 1500 K OF BINARY METALLIC
SOLID SOLUTIONS CONTAINING 1000 PPM OXYGEN

The influence of localized zirconium concentrations can be seen in Figure 4, which shows that titanium will not act as a sink for oxygen until the columbium solid solution contains less than 78 atomic percent zirconium. Similarly, a V-20Ti alloy will only remove oxygen when the local zirconium concentration has fallen below 7.5 atomic percent. Thus, there will be an incubation period during which the local zirconium concentration falls to a critical level. Alloys containing hafnium as the reactive metal instead of zirconium might be expected to have longer incubation lives due to the slow diffusion rates of this element.

The preceding discussion, much of which has been presented in a recent paper[1], relates to the thermodynamic effects and some mechanical property effects of interstitial sinks.

Some important questions remain unanswered:

1.  What is the mechanism by which duplex heat-treated alloys are weakened more than stress relief annealed alloys?

2.  When is this weakening most severe? Is it during the metastability introduced by the outward diffusion of the interstitial element, or does it occur after completion of the interstitial partition?

3.  Is creep accelerated by superimposed dynamic effects of interstitial diffusion?

4.  What is the effect of transverse diffusion on mechanical properties such as creep and tensile strength?

Metastabilities such as recrystallization have been recognized to lead to accelerated creep, and metastabilities such as allotropic transportations have led to reduced strength and the phenomenon of superplasticity. McCoy and Douglas[3] have shown that certain gases, notably hydrogen and water vapor, have dramatic effects on the creep of columbium, but it was not determined if these effects resulted from chemical gradient diffusion or from structural interaction.

The interactions between dislocations and interstitial elements can be static, as in the case of precipitate stabilized cells or networks which form barriers to newly formed moving dislocations; or dynamic, as in the case of the Cottrell dynamic strengthening mechanism. In either case the introduction of an interstitial sink will cause an imbalance and affect the mechanical properties of the refractory metal. Also, the diffusion rate of interstitials and the stability of the substructure will be very much dependent upon test temperature. It has already been shown, with the

experiments on duplex processed and stress relief annealed Cb752 and D43 alloys, that thermal-mechanical processing can have a pronounced effect on the stability (in terms of retention of elevated temperature mechanical properties) of these alloys, but more work is necessary in order to understand the mechanism involved.

# IV. EXPERIMENTAL PROGRAM

The experimental program is designed so as to lead to a better understanding of the factors and mechanisms responsible for the observed degradation of mechanical properties in refractory metal alloys due to interstitial diffusion effects.

The majority of the work is to be conducted on D43 columbium alloy (Cb-10W-1Zr-0.1C) in the two standard commercial conditions - stress relieved and duplex heat treated. Pure titanium (0.002-inch foil) will be diffusion bonded to D43 specimens by the yield stress controlled diffusion bonding technique developed at Solar, using the production bonder shown in Figure 6. These samples will be annealed over the temperature range of 1800 to 2200 F for various times and evaluated by chemical analysis, metallography (light and electron microscopy) microprobe, microhardness, and solution temperature of final structure. A series of sink compositions, titanium, Ti-30Cb, Ti-60Cb, Ti-90Cb, Ti-99Cb, and columbium will be used for a particular set of test conditions to study the effect of substitutional diffusion between sink and the columbium alloy on interstitial partition.

These tests will form the basis for an evaluation of creep behavior at 1800 to 2500 F. The above methods of evaluation, and activation energy determinations will be used to study the creep process. If these tests indicate that actual migration of carbon or oxygen produces anomalous creep behavior, a series of tests will be conducted in which the sink is in the center of a creep specimen and the columbium side of the couple is continuously exposed to an atmosphere of carbon. By this means, the effect of steady state diffusion of interstitial element on the creep deformation process can be evaluated.

Additional tests are planned in which the Cb752, TZM, and T222 alloys will be used to study the behavior of other interstitial elements (oxygen) in columbium alloys and interstitial sink effects in other refractory metal alloys.

FIGURE 6.   PRODUCTION DIFFUSION BONDER

## V. EXPERIMENTAL PROGRESS

Progress during this report period has been restricted to material procurement and to modifications of creep test apparatus.

### 5.1 COLUMBIUM ALLOY PROCUREMENT AND PROCESSING

Obtaining sufficient quantities of D43 alloy sheet proved to be more difficult than anticipated. Eventually, however, material was obtained from du Pont's inventory stock. This material was supplied nominally in the stress-relieved condition and had the following specifications.

| Pieces | Thickness (in.) | Width (in.) | Length (in.) | Weight (lb) | Heat Number |
|--------|-----------------|-------------|--------------|-------------|-------------|
| 2 | 0.020 | 15 | 11 | 2.5 | 43-488 |
| 3 I | 0.040 | 13-1/8 | 15-3/8 | 4.1 | 43-487 |
| III | 0.060 | 12-13/16 | 25-1/8 | 6.5 | 43-487 |
| III | 0.060 | 12-3/8 | 29-5/8 | 7.5 | 43-487 |
| 1 | 0.120 | 7 | 17-7/8 | 5.0 | 43-487 |
| 1 | 0.150 | 6 | 36 | 11.6 | 43-498 |

Chemical Analysis (wt %)

| Heat Number | Oxygen | Hydrogen | Nitrogen | Carbon | Tungsten | Zirconium |
|-------------|--------|----------|----------|--------|----------|-----------|
| 43-488 | 0.0221 | 0.0001 | 0.0019 | 0.09 | 9.8 | 1.1 |
| 43-487 | 0.0042 | 0.0012 | 0.0034 | 0.08 | 9.2 | 0.99 |
| 43-498 | 0.0025 | 0.0003 | 0.0036 | 0.10 | 9.5 | 0.93 |

This material represents the D43 requirements for both this program and the related Air Force Program, Contract AF33(615)-5233. Metallography and microhardness studies showed the material to be in a fine-grained, recrystallized condition with coarse grain boundary carbide dispersions. As seen from the analysis specifications, the 0.020-inch sheet has a rather high oxygen content and it was decided not to use this material in the comprehensive test phase of the program.

A good price and delivery quotation for the Cb752 alloy (Fansteel designated FS86) was obtained from Fansteel Metallurgical Corporation, and it was further contracted for them to process both the D43 and Cb752 in the required condition.

A good quality sheet was obtained during final cold rolling and in some cases roller leveling was used prior to final vacuum annealing to improve sheet flatness. A stress relief temperature of 2300 F for both alloys and aging temperatures of 2400 F for Cb752 and 2600 F for D43 were used.

At this time, a major portion of the D43 and Cb752 alloy sheet has been received.

## 5.2 EQUIPMENT

Construction of an additional high-temperature vacuum creep facility is currently in progress. This apparatus will be capable of attaining temperatures up to 3700 F (2000 C), and will be capable of continuous operation at 3000 F (1600 C) under a dynamic vacuum of $10^{-6}$ Torr or better. It will incorporate a Solar designed high-temperature extensiometer which will allow a strain resolution of 50 micro-inches or better.

# VI. FUTURE WORK

During the next report period the rate of carbon removal to a titanium sink as a function of temperature and the concomitant changes in microstructure occurring in the D43 alloy will be evaluated. Baseline creep curves will be obtained for the as-received D43 alloy sheet over the temperature range of 1800 to 2500 F, and creep tests on material annealed in the presence of a sink will be initiated.

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2. Darken, L. S., Trans. AIME 180 (1949) p. 430.

3. McCoy, H. E., and Douglas, D. A., Effect of Various Gaseous Contaminants on the Strength and Formability of Columbium. Columbium Metallurgy, Vol. 10, AIME Meeting, June 1960, Published by Interscience (1961) pp 85-118.