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Quarterly Progress Report

STRUCTURAL AND MECHANICAL EFFECTS OF INTERSTITIAL SINKS

by

M. J. Klein, C. Antonick, A. G. Metcalfe

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
HEADQUARTERS, WASHINGTON, D. C.

June 1970

CONTRACT NAS 7-469



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FOREWORD

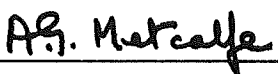
This is the Twelfth Quarterly Progress Report for Contract NAS 7-469, "Structural Effects of Interstitial Sinks", describing research activities for the period March 8 to June 8, 1970. The report was prepared at the Research Laboratories of Solar Division of International Harvester Company. The program is administered by the National Aeronautics and Space Administration, Headquarters, Washington, D. C. and is under the direction of Mr. J. Maltz.

Others contributing to the program, in addition to the authors, are M. Reid, activation energy analysis; R. Hutting, metallography; and P. Lind, manuscript preparation.

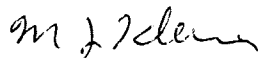
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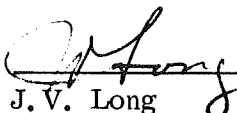
PUBLICATION REVIEW

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ABSTRACT

The contribution of solutes to the creep strength (σ) of columbium is being studied through their effect on the activation energy for creep (H) over the temperature range 1300–3400° F. During this period, H -temperature (H - T) and σ -temperature (σ - T) profiles were determined for Cb-2.5 at. % Hf, Cb-2.5 at. % Zr and Cb-5 at. % Zr. In addition, preliminary σ - T profiles were determined for Cb-2.5 at. % V and Cb-2.5 at. % Ta. The results show that reactive solutes hafnium and zirconium contribute most to the creep strength below about $0.63 T_M$, whereas tungsten is the most effective strengthener above this temperature.

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1

INTRODUCTION

In many practical applications, it is necessary to use refractory alloys strengthened with interstitial dispersions in contact with more reactive metals at elevated temperatures. Under these conditions, the interstitial elements in the refractory alloys tend to concentrate in the more reactive metals, and the alloys are weakened. The first phase of this program was concerned with this strength degradation problem. Under this phase of the program, the conditions required to avoid the loss of strength of refractory alloys in many practical applications (e. g., coatings and diffusion bonded joints) were defined.

In subsequent work, the scope of the program was broadened to include the effect of interstitial and substitutional solutes on the creep of columbium- and tantalum-base alloys with emphasis on the former. This phase of the investigation should provide information concerning the role that various solutes play in strengthening refractory metals; information of value in selecting solutes to optimize high-temperature strength of alloys. The approach used was to study the effect of various solutes on the activation energy and creep strength of these alloys. Since creep is thermally activated, the creep rate and, therefore, the creep strength should be a function of the magnitude of the activation energy for creep. There should, therefore, be a correlation between creep strength and activation energy.

In past work, anomalous increases in the activation energy were found for the commercial columbium-base alloys (C129, C103, Cb122) near 3000° F and large activation-energy peaks were detected below 2600° F for unalloyed columbium, Cb-2.5 atomic percent tungsten and Cb-2.5 atomic percent hafnium. The lower temperature peaks, which were attributed to strain aging, were accompanied by significant increases in creep strength.

During the present period, some additional binary columbium-base alloys were prepared for testing to determine the effect of substitutional solutes on creep strength and the results were correlated with the creep strength of commercial columbium-base alloys. For continuity, some of the results reported for the last period are included with the results for this period.

The experimental procedures used during the period covered by this report have been described previously (Interim Report, 8 March, 1969 - 8 March, 1970).

Therefore, the details of the experimental procedures will be described in this report only where new techniques are involved. For convenience in the discussion, the apparent or measured activation energy for creep is designated by H and the creep stress required to maintain a constant strain rate is designated by σ . The latter is used as a measure of creep strength in this study. In addition, the stress temperature and activation-energy temperature profiles are termed σ -T and H-T profiles respectively.

2

CREEP OF COLUMBIUM-BASE ALLOYS

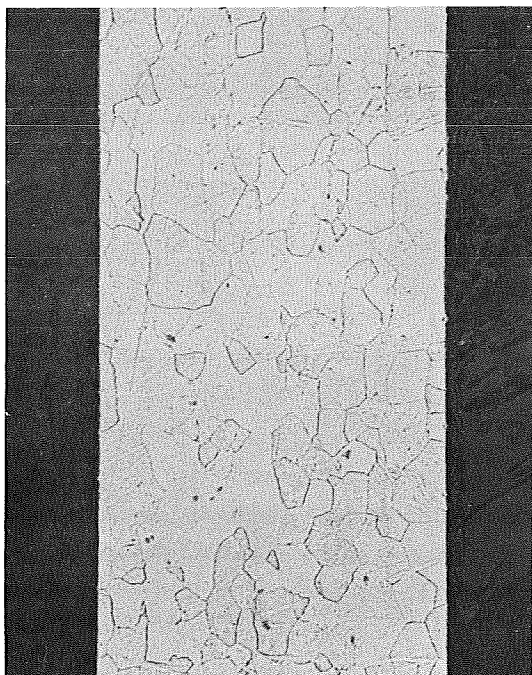
Specimens of columbium-base binary alloys containing hafnium, zirconium, tungsten, vanadium, tantalum, molybdenum or rhenium were prepared by arc-melting and rolling the arc-melted buttons into 0.013-0.016-inch sheet. Alloys containing 2.5 atomic percent of each of these solutes were prepared, together with an alloy containing 1.5 atomic percent rhenium and one containing 5 atomic percent zirconium. Creep specimens suitable for testing were machined from the alloy sheets, the structures of the specimens were examined, and their interstitial concentrations were determined.

Examination and testing of the Cb-2.5W alloy has been completed, and the results have been reported the previous quarter. During this period, H-T and σ -T profiles were determined for Cb-2.5Zr, Cb-5Zr and Cb-2.5Hf, and creep testing of some of the remaining alloys was initiated.

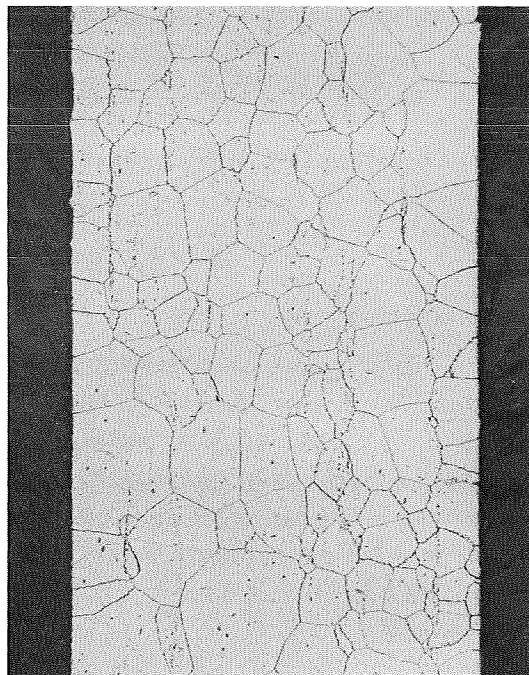
2.1 STRUCTURE AND INTERSTITIAL CONCENTRATION

All of the specimens were given pre-creep heat treatments at 3000° F for 30 minutes in a vacuum of 10^{-6} Torr. The intended purpose of this pre-creep heat treatment was to stabilize the grain structure and interstitial concentration during subsequent creep testing. The structures of the binary alloy specimens after this heat treatment are shown in Figure 1. Grain growth has been restrained most in the alloys containing zirconium and hafnium because these solutes combine with interstitial elements to form dispersed interstitial phases, whereas the other solutes probably remain uncombined. A dispersion in the Cb-5Zr alloy after the 3000° F heat treatment is shown in Figure 2.

The interstitial concentration in the alloy specimens after the pre-creep heat treatment (300° F for 30 minutes) is listed in Table I. The vanadium, rhenium, tantalum and molybdenum alloys have higher oxygen and nitrogen concentrations than the more reactive elements, zirconium and hafnium. Since this is rather unexpected, these analyses will be checked again.



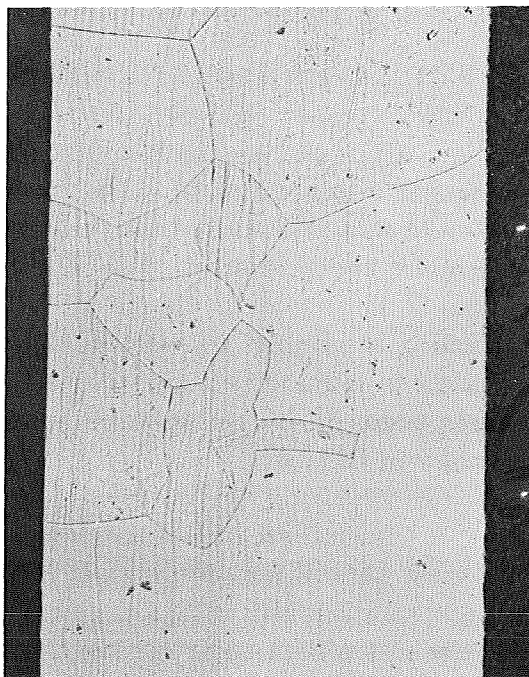
A. Cb-2.5Zr



B. Cb-5Zr



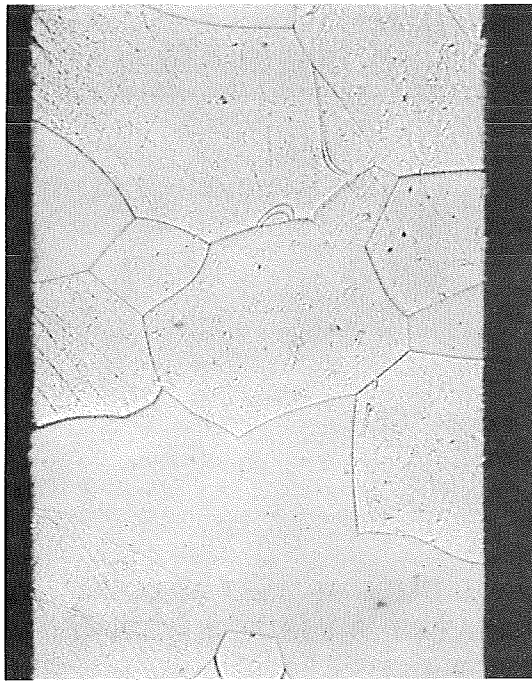
C. Cb-2.5Hf



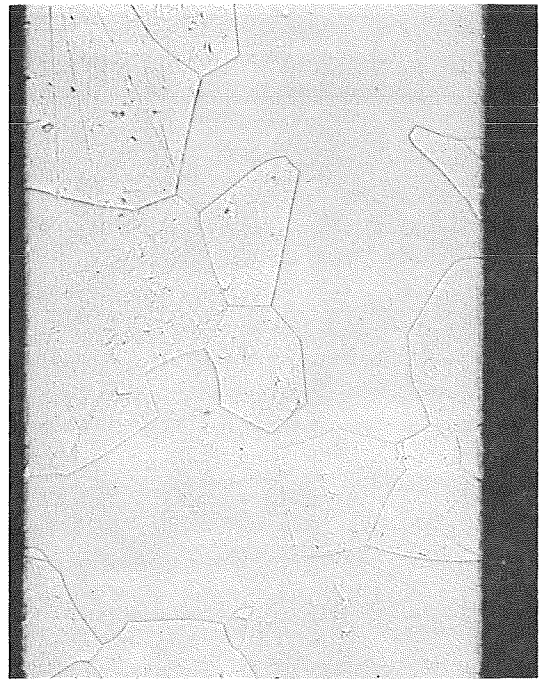
D. Cb-2.5W

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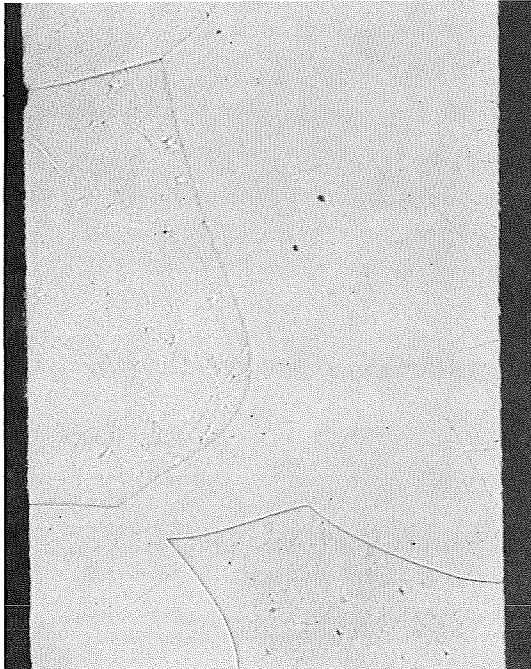
FIGURE 1. BINARY COLUMBIUM-BASE ALLOYS HEAT TREATED
30 MINUTES AT 3000°F (Sheet 1 of 3)



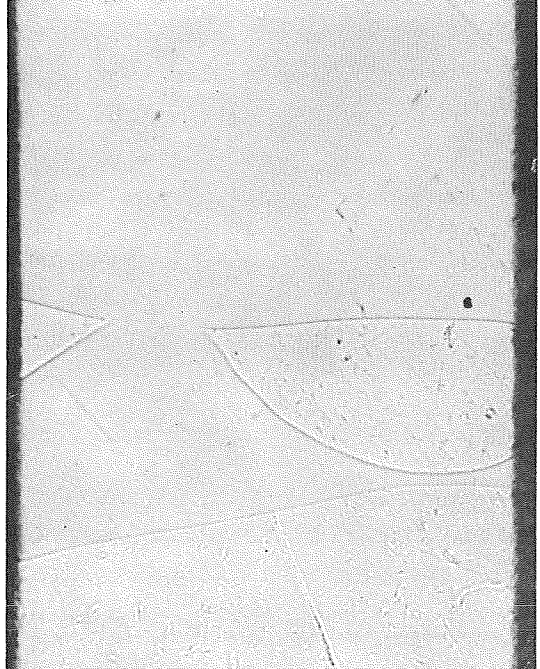
E. Cb-1.5Re



F. Cb-2.5Re



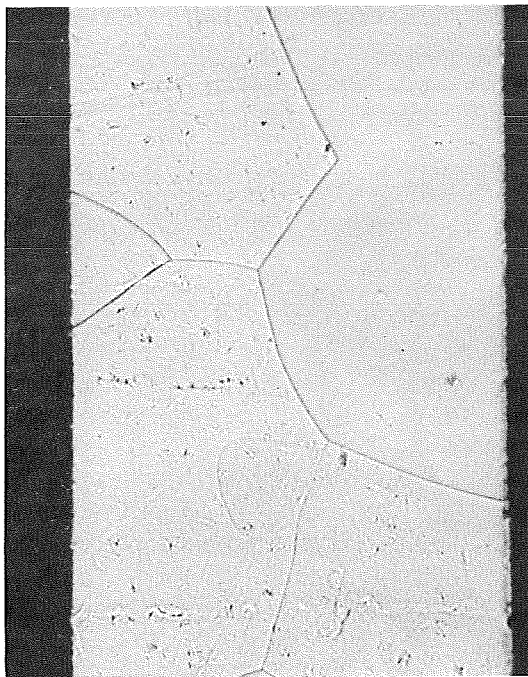
G. Cb-2.5V



H. Cb-2.5Ta

Magnification: 150X

FIGURE 1. BINARY COLUMBIUM-BASE ALLOYS HEAT TREATED
30 MINUTES AT 3000°F (Sheet 2 of 3)

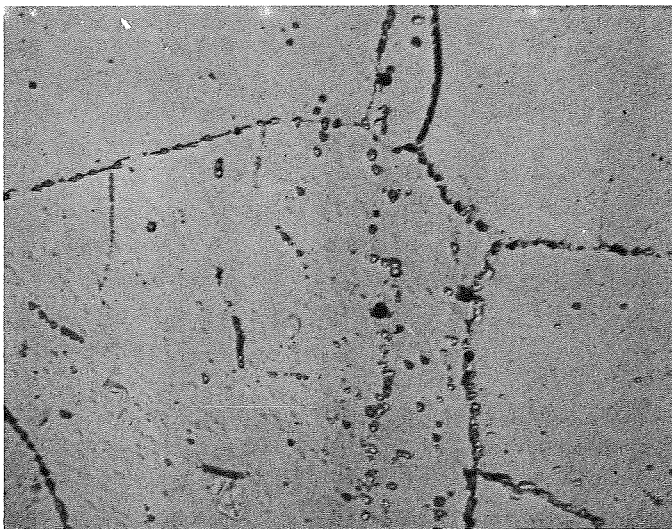


I. Cb-2.5Mo

Magnification: 150X

FIGURE 1.

BINARY COLUMBIUM-BASE ALLOYS
HEAT TREATED 30 MINUTES AT 3000°F
(Sheet 3 of 3)



Magnification: 1000X

FIGURE 2.

DISPERSED PHASE IN Cb-5Zr

TABLE I
INTERSTITIAL CONCENTRATIONS IN BINARY COLUMBIUM-BASE ALLOYS

Alloy		Interstitial Concentration (ppm wt)		
Atomic Percent	Weight Percent	C	O	N
Cb-2.5Zr	Cb-2.5Zr	98	427	40
Cb-2.5Hf	Cb-4.7Hf	165	476	90
Cb-2.5W	Cb-4.8W	250	380	26
Cb-2.5V	Cb-1.4V	44	700	255
Cb-2.5Ta	Cb-4.8Ta	52	470	170
Cb-2.5Re	Cb-4.9Re	58	720	270
Cb-1.5Re	Cb-2.9Re	90	800	280
Cb-2.5Mo	Cb-2.6Mo	95	990	250

2.2 CREEP OF Cb-Hf AND Cb-Zr ALLOYS

Activation energy and creep stress values were measured for Cb-2.5Hf, Cb-2.5Zr and Cb-5Zr and H-T and σ -T profiles were constructed for these alloys. Activation energies were calculated from changes in strain rate induced by abrupt shifts in temperature, and the creep stresses were those required to yield a mean strain rate of $\sim 10^{-5}$ /second at each test temperature. These experimental procedures have been described in detail in the Interim Report for 8 March 1969 to 8 March 1970.

The H-T and σ -T profiles for Cb-2.5Hf are shown in Figure 3. The results suggest that there is a peak in the H-T profile near 2100° F although the shape of the profile in this temperature region is not well defined. The data points connected by arrows indicate decreasing values of H with increasing creep strains. Based on the results for unalloyed columbium and Cb-2.5W, high values of H decreasing with strain, as well as activation energy peaks, seem to be characteristic of strain aging during creep. The creep strength rises rapidly in the temperature region where the values of H are high. Arrows by the data points in the σ -T profile indicate the maximum stress before specimen failure for specimens where steady-state creep was not readily attained.

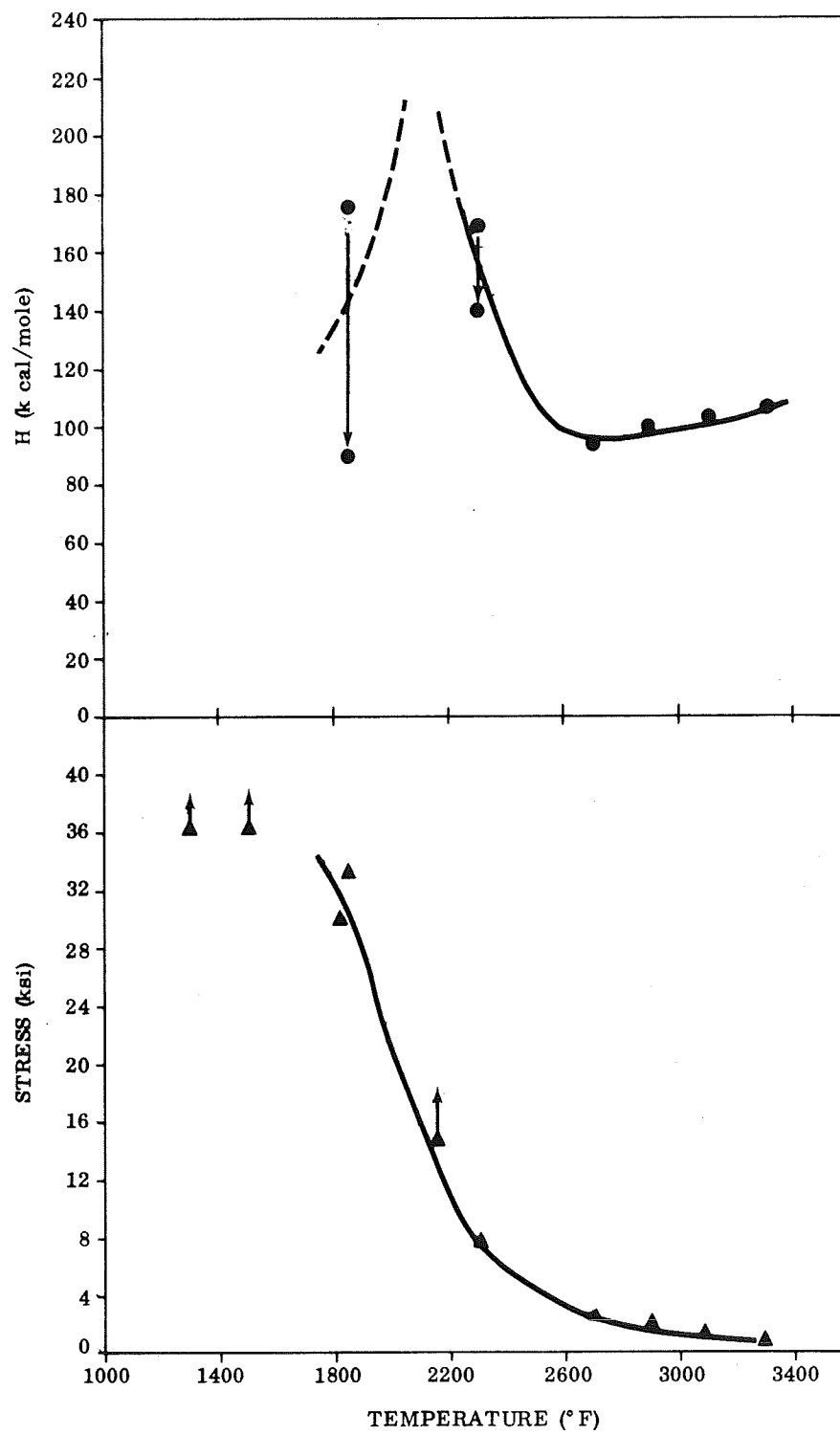


FIGURE 3. ACTIVATION ENERGY AND STRESS PROFILES FOR Cb-2.5Hf

Below about 2200° F, activation energy values and the creep stress required to maintain a constant strain rate were difficult to determine because of the unusual creep behavior at the lower temperatures. Some creep curves in the strain-aging region are shown in Figure 4. These curves are similar to those for unalloyed columbium in the strain-aging region. The elongation to failure is low (~5 percent) and the creep tends to be intermittent. When the creep stress is increased, very rapid creep is often followed by a period during which creep cannot be detected. This behavior can probably be explained as follows. When the stress is increased, new dislocations are generated and their movement along slip bands accounts for very rapid (primary) creep. However, the mobility of these dislocations is reduced to such an extent by subsequent interactions with solute atoms, precipitates, or other dislocations that creep almost ceases until additional stress is applied and new dislocations are generated. The cycle is repeated as these new dislocations become pinned. Recovery of the structure is so restricted that intermediate or steady-state creep rates are difficult to attain in this temperature range. When intermediate or steady-state creep rates were attained, they were often not reproducible for the same conditions of stress and temperature (e. g., see asterisks in Fig. 4A). At 1500° F (Fig. 4B) recovery is almost completely restricted since there is no evidence of time-dependent creep within the sensitivity of these measurements.

Room-temperature tensile data for the Cb-2.5Hf alloy after different pretest treatments are listed in Table II. The heat treatment at 3000° F for 30 minutes increased the tensile strength somewhat, but a subsequent aging at 1900° F after 0.5 percent strain at room temperature decreased both the yield and ultimate tensile strengths. There is no evidence to suggest that this alloy is strengthened by these solution annealing and aging treatments. In this regard, none of the specimens showed a yield drop, as would be expected for specimens in which aging or strain aging influenced tensile behavior. Thus, the creep behavior in the temperature region where H is very high is probably associated with an aging reaction occurring during creep (dynamic strain aging). Another point of interest is the strain to fracture. Specimens tested at room temperature have a greater strain-to-fracture than the specimens tested in creep at the temperature where H is high. Evidently, for the conditions of these tests, there is a ductility minimum near the temperature where H is high.

The H-T and σ -T profiles for Cb-2.5Zr and Cb-5Zr are shown in Figures 5 and 6. The activation energy and stress profiles are almost identical for the two alloys. In addition, there are no peaks or unusually high values of H in the H-T profiles, as were observed previously for unalloyed columbium, Cb-2.5W and Cb-2.5Hf. If strain aging is affecting the creep strength of these alloys, it is not revealed by a change in H. In this regard, there may be a critical concentration of interstitial and solute atoms required to induce peaks in H values. The sharp increase in creep strength with decreasing temperature below about 2400° F is probably caused by strengthening induced by a dispersed interstitial phase in these alloys.

TABLE II
ROOM-TEMPERATURE TENSILE DATA FOR Cb-2.5Hf

Pretest Condition	Ultimate Strength (ksi)		Strain to Fracture (%)
	Ultimate	Yield	
As fabricated (2500° F/30 min)	51	36	12.5
3000° F/30 min.	54	42	13.0
3000° F/30 min. plus 0.5% strain and 1900° F/2 hrs	51	37	>16.0

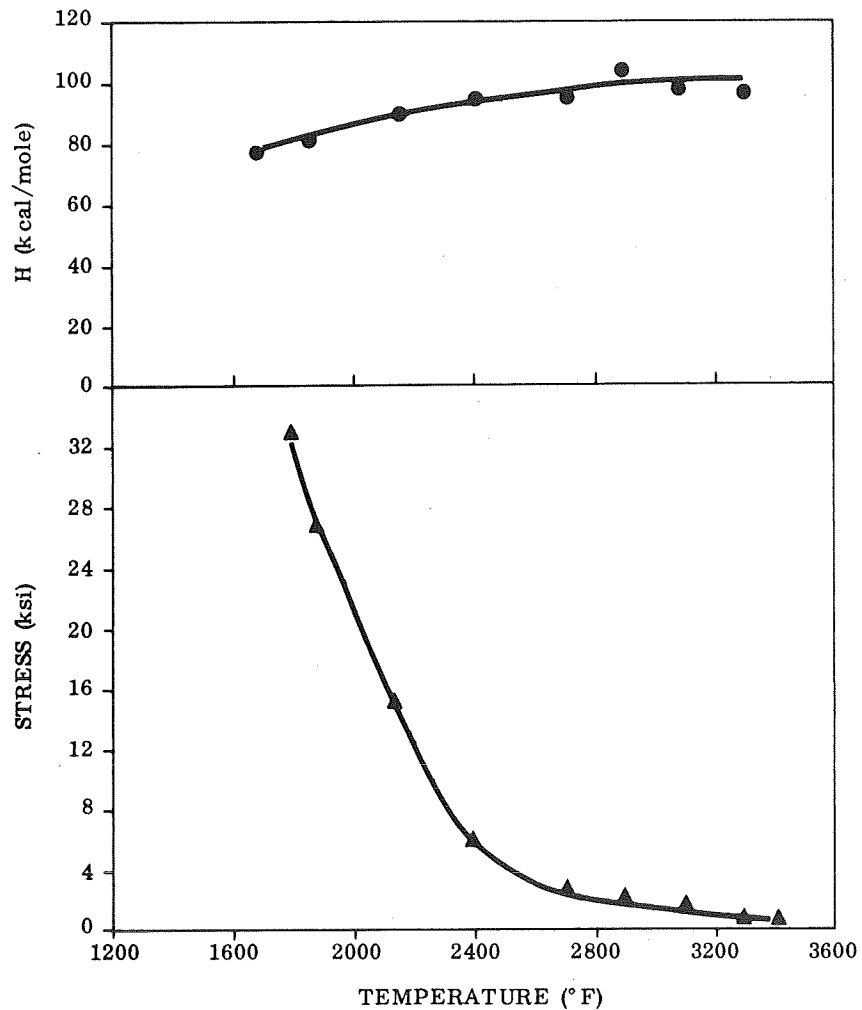


FIGURE 5. ACTIVATION ENERGY AND STRESS PROFILES FOR Cb-2.5Zr

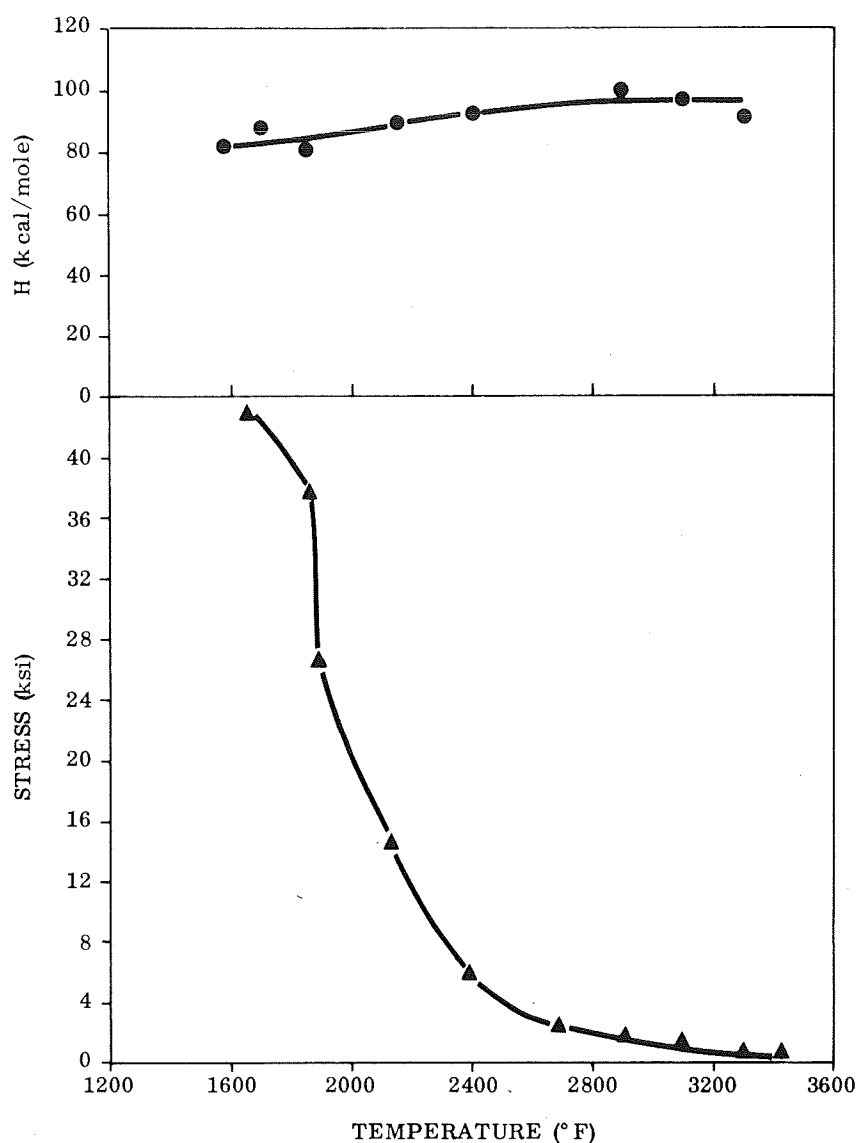


FIGURE 6. ACTIVATION ENERGY AND STRESS PROFILES FOR Cb-5Zr

The σ -T profiles for unalloyed columbium (for columbium showing strain aging) and the binary columbium-base alloys are compared in Figure 7. The reactive solutes, zirconium and hafnium, yield almost identical profiles above 1900° F. Below this temperature, Cb-5Zr is stronger than Cb-2.5Hf and Cb-2.5Zr. A comparison of these alloys containing the reactive solutes with the Cb-2.5W alloy defines the temperature region where dispersion strengthening of columbium is important. Below ~2650° F ($0.63 T_M$) the dispersion-forming solutes impart more strength to columbium than the solid solution strengthener, tungsten; above this temperature, tungsten contributes more to strength. However, all of the solutes impart some strength to columbium over the entire temperature span. This is in contrast with the results reported by McAdams*, who concludes that hafnium and zirconium make a negative

* McAdams, G. D., "Substitutional Niobium Alloys of High Creep Strength", J. Inst. Metals, 93, p. 559 (1964-65).

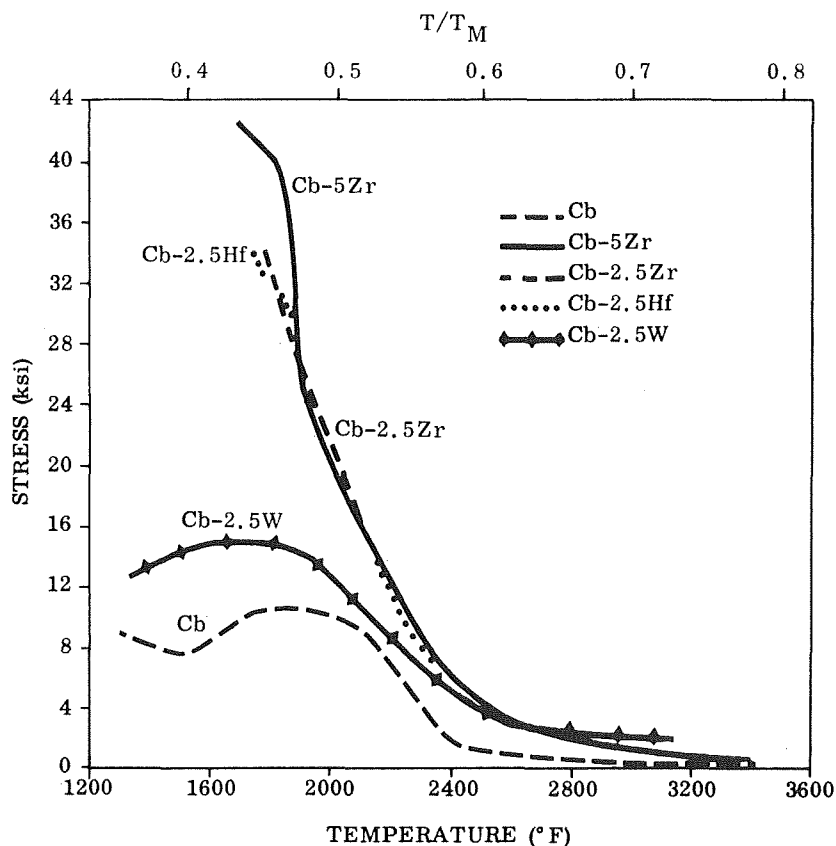


FIGURE 7. COMPARISON OF STRESS-TEMPERATURE PROFILES FOR COLUMBIUM AND SOME COLUMBIUM ALLOYS

contribution to the creep strength of columbium. However, McAdams' conclusions were based upon the rupture life for tests made for the most part at one temperature (1200°C) and load, and some hardness measurements. In addition, most of the specimens tested were ternary alloys so that the effect of individual substitutional solutes, even on creep life, is not clear.

The creep strength of the binary alloys is compared with the strength of two commercial columbium-base alloys in Figure 8. The binary alloys with the reactive solutes Hf and Zr (shown as a band in Fig. 8) are stronger than C103 (composition in weight percent is Cb-10Hf-1Ti-0.5Zr) below about 2200°F and are close to the strength of C103 above this temperature. C129Y (composition in weight percent is Cb-10W-10Hf-0.1Y) is stronger than all of the binary alloys except at 3000°F where its strength is about equal to that of Cb-2.5W. More detailed comparison will be made when data for additional binaries have been determined.

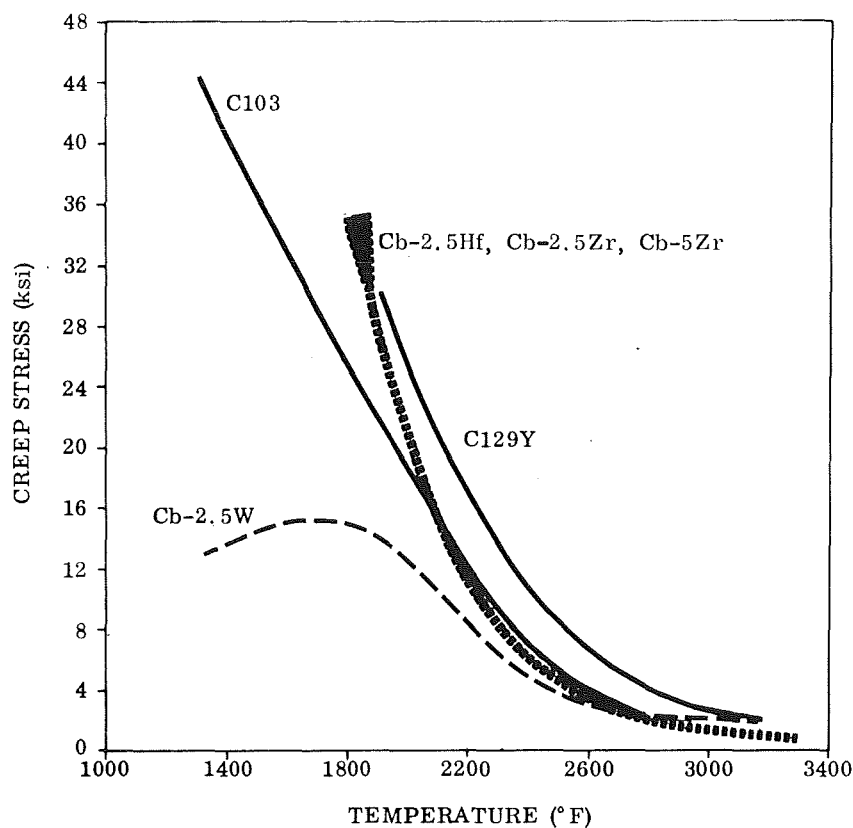


FIGURE 8. COMPARISON OF THE CREEP STRENGTH OF SOME BINARY ALLOYS WITH C103 AND C129Y

2.3 CREEP OF OTHER BINARY ALLOYS

2.3.1 Experimental Method

Thus far in the program a specimen was used for each temperature at which creep stress data were desired. This procedure, which is described in detail in the last Interim Report (8 March 1969 to 8 March 1970), is accurate but rather time-consuming. Therefore, a new testing method was devised to facilitate creep strength determinations of some of the new binary alloys. The new method involves using a single specimen to test the creep strength over a range of temperature rather than using a specimen at each temperature. The specimen is crept at high temperature, and the stress is adjusted until the creep rate is $\sim 10^{-5}$ /second. As the temperature is decreased the strain is increased until the creep rate is again about 10^{-5} /second. This procedure is continued until the entire temperature span selected has been covered.

A comparison of the stress-temperature data derived from a single specimen (new method) and the data derived using a specimen at each temperature (old method) is shown in Figure 9 for Cb-5Zr. The results for the new method compare reasonably

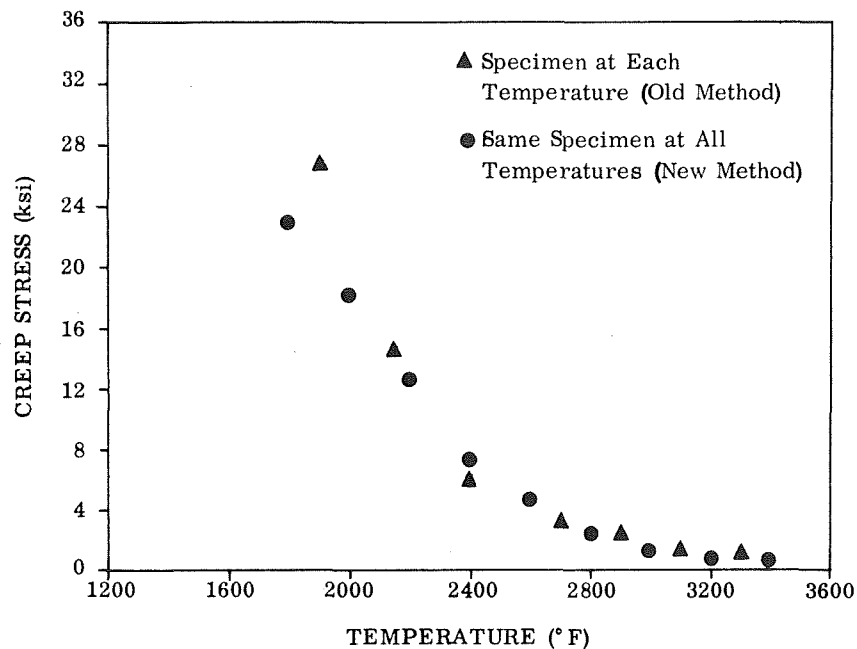


FIGURE 9. RESULTS DERIVED FROM A SINGLE SPECIMEN (NEW METHOD) COMPARED WITH RESULTS USING A SPECIMEN AT EACH TEMPERATURE (OLD METHOD) FOR Cb-5Zr

well for this alloy over most of the temperature span investigated. However, a similar comparison for Cb-2.5Zr showed good agreement between the new and old methods only at temperatures above 2400°F. At lower temperatures the new method showed lower creep stress value than the old method. Therefore, creep stress data below 2400°F generated using the new method will be verified in future work by testing a specimen at each temperature where stress values may be in question.

2.3.2 Experimental Results

Thus far, σ -T profiles have been determined for Cb-2.5V and Cb-2.5Ta using the new method. The results are shown in Figure 10, together with a σ -T profile for unalloyed columbium (showing no strain-age strengthening). The comparison with columbium should be qualified, however, because the strength of the columbium is affected by strain aging and other factors that alter its σ -T profile (Interim Report, 8 March 1969 - 8 March 1970). In addition, the results for the two alloys have not yet been verified using the old method. Nevertheless, the data are sufficient to show that 2.5 atomic percent tantalum is not as effective as the same percentage of vanadium. However, these results may be peculiar to low percentages of vanadium and tantalum, or to the grain structure in these specimens. Additional tests using higher percentages of these solutes will be required to fully evaluate their effect on creep strength.

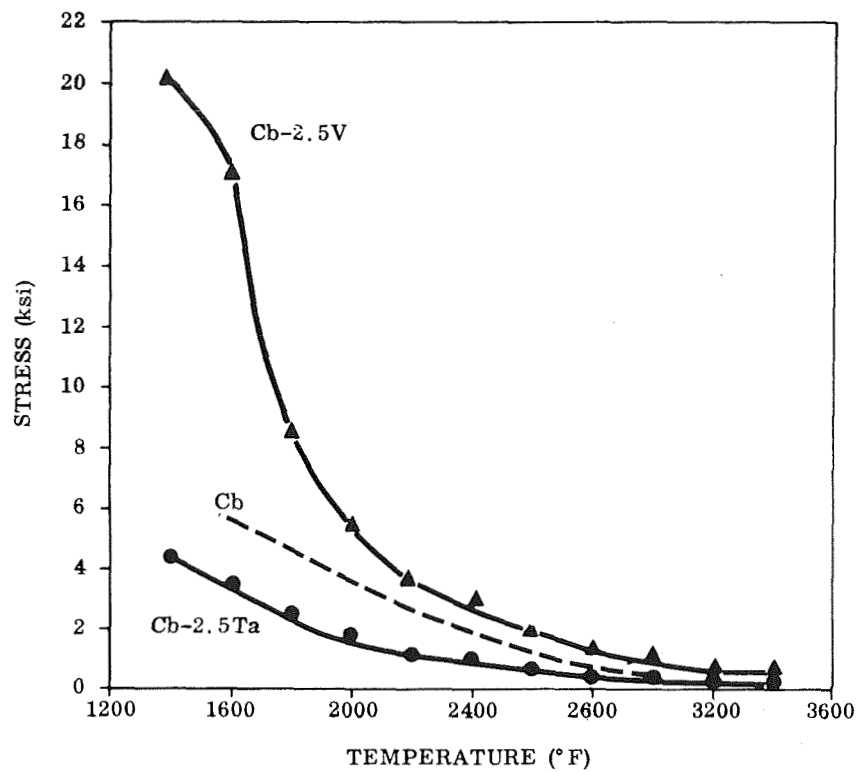


FIGURE 10. STRESS-TEMPERATURE PROFILES FOR SOME COLUMBIUM BINARY ALLOYS COMPARED WITH UNALLOYED COLUMBIUM

3

FUTURE WORK

Columbium-base binary alloys containing the same atomic percentages of selected solutes will continue to be creep tested to determine their individual effect on creep strength. When these tests have been completed, solutes will be combined to optimize creep strength. This study should show the contribution of solutes to creep strength and should provide information needed to develop more complex creep-resistant columbium-base alloys.