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**STRUCTURAL AND MECHANICAL EFFECTS
OF INTERSTITIAL SINKS**

by
Mark J. Klein

October 1968

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ABSTRACT

The contribution of solutes to the creep strength of columbium and tantalum base alloys is being studied through their effect on the activation energy for creep. During this period the activation energy for creep of columbium was determined from $0.4T_M$ to $0.65T_M$, and the effects of changes in interstitial concentration on the activation energy for creep of columbium and D43 (Cb-10W-1Zr-0.1C) were studied. The results suggest that the activation energy for creep of these metals below about $0.5T_M$ increases with increasing interstitial concentration.

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INTRODUCTION

This is the seventh quarterly progress report for the Contract NAS-7-469, "Structural Effects of Interstitial Sinks" covering the period June 8 through September 8, 1968. In many practical applications it is necessary to use a refractory metal in contact with a more reactive metal. Under these conditions, the interstitial elements in the refractory metal tend to concentrate in the more reactive metal (the interstitial sink). This partition of interstitials can cause a serious decrease in the elevated temperature strength of the refractory metal. The first part of this program was primarily concerned with the change in structure, strength, and interstitial concentration in a refractory alloy induced by an interstitial sink. The loss of carbon from D43 (a columbium base alloy strengthened with a carbide dispersion) to a titanium sink was correlated with the creep behavior of the D43. The creep rate near $0.5 T_M$ was found to be proportional to the carbon lost to the interstitial sink.

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. Since creep is thermally activated, the creep rate is a sensitive function of the magnitude of the activation energy for creep. Therefore, the influence of solutes on creep is being studied through their effect on this parameter.

In past work on D43 the apparent activation energy for creep, H , was found to exceed that for self-diffusion just below $\sim 0.5 T_M$. During this period, the effects of interstitial elements in D43 and in columbium on H in this temperature region were investigated. In future work activation energy studies will be extended to higher temperatures where substitution elements are more likely to affect H . Other alloys will be selected to sort out the effect of the various substitutional solutes on the creep rate of columbium and tantalum base alloys. This phase of the investigation should provide information concerning the role that various solute additions play in strengthening refractory alloys.

The experimental procedures used in this investigation have been reported in the interim report covering the period 8 June, 1966 through 8 June, 1967. Therefore, experimental procedures will be considered in this report only when new techniques are involved.

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RESULTS AND DISCUSSION

Data are presented in this section showing how the activation energy for creep of columbium varies with temperature. This information will provide a basis to compare the effect of substitutional and interstitial solutes on H in more complex columbium base alloys to be studied in subsequent work.

In past work an anomalous increase in H for D43 was detected between 1650° F and 2400° F. During this period the effect of the interstitial concentration in D43 on H in this temperature region was also studied.

2.1 ACTIVATION ENERGY FOR CREEP OF COLUMBIUM

Activation energies were determined using the differential temperature method (100° F temperature shifts) previously described (Interim Tech. Rept. June 1966 - June 1967). To derive meaningful activation energies from experimental data, it is necessary to consider several factors that may affect the values of H . First, the differential temperature method is based upon measuring the change in creep rate induced by a sudden shift in temperature during constant stress creep tests. The results are valid only where the structure is constant just before and after the temperature shift. For columbium, the structure could only be maintained sufficiently constant to yield consistent values of H for downward shifts in temperature. For upward temperature shifts transient regions in the creep curve yielded widely scattered values of H . Second, the possibility of variations in H with strain must also be taken into account. In these tests it was found that H was independent of strain above about 1400° F but below this temperature H varied widely with strain. An example of this behavior is shown in Figure 1. Finally, in columbium and columbium alloys it is necessary to consider the effect of interstitial contamination during testing on the activation energy for creep. As shown in Figure 2, a specimen whose gage length was wrapped with W foil to minimize impingement by gaseous interstitials during testing yielded lower values of H than a specimen exposed to the vacuum (10^{-6} Torr).

Taking these factors into account, the variation in H with temperature for columbium was determined and is shown in Figure 3. The number of determinations at each temperature is indicated by the data points. The specimens tested below 2300° F were first annealed for five minutes at 2300° F in the creep furnace to stabilize their structure. Specimens tested above this temperature were given no prior annealing treatment but were held at the test temperature for five minutes before beginning the test.

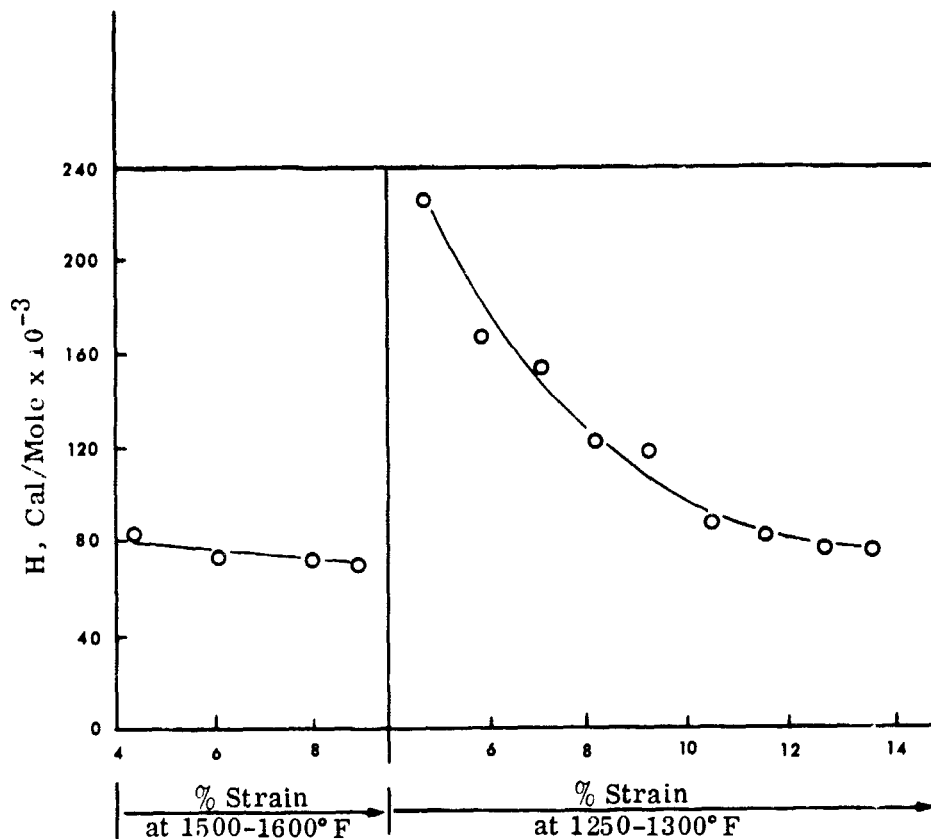


FIGURE 1. ACTIVATION ENERGY FOR CREEP VERSUS STRAIN FOR A SPECIMEN TESTED FIRST AT 1500-1600°F AND AGAIN AT 1250-1300°F

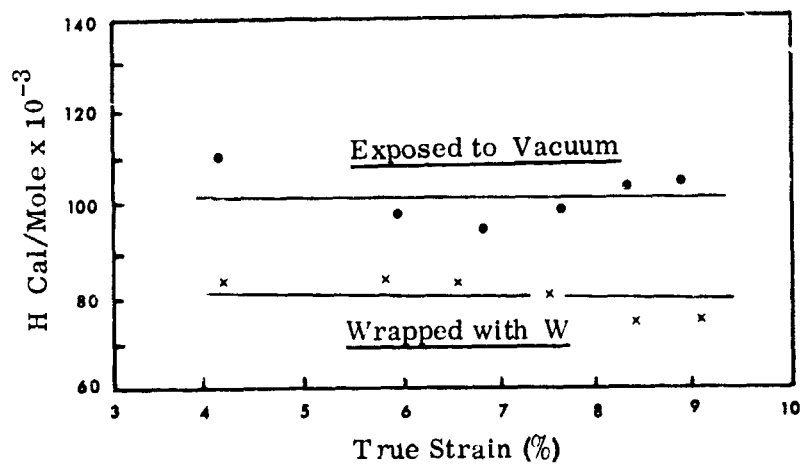


FIGURE 2. ACTIVATION ENERGY FOR CREEP OF COLUMBIUM VERSUS STRAIN AT 1850°F

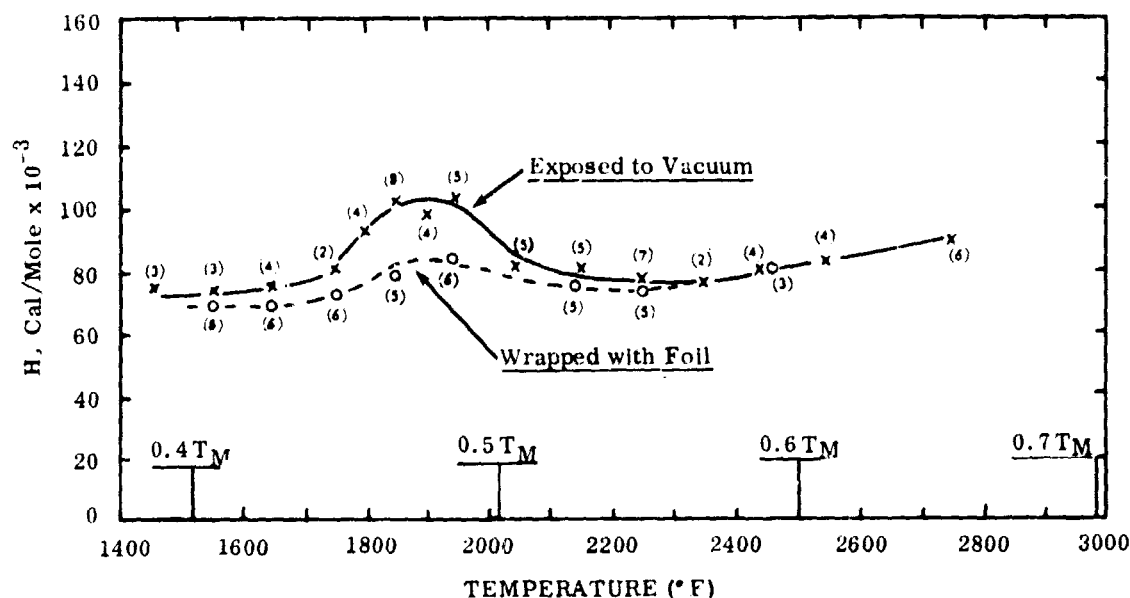


FIGURE 3. THE ACTIVATION ENERGY FOR CREEP OF COLUMBIUM FROM 1450° F TO 2750° F

There are several important points concerning the apparent activation energy for creep that these tests show. First, there is an anomalous maximum in H near 1900° F ($0.48 T_M$). Second, between about 1500° F and 2200° F H is noticeably less for the wrapped specimens than for the unwrapped specimens. This difference is greatest near 1800 to 2000° F, the temperature region of the peak in H values for the specimens exposed to the vacuum. This behavior suggests that interstitial contamination of the specimens during the precreep annealing treatment at 2300° F or during subsequent testing, increases the activation energy for creep. Although the way that interstitials change the value of H in columbium is not known, the effect is most pronounced near 1900° F. Finally, the values of H for the higher temperatures shown in Figure 3 are approaching the value of the activation energy for self-diffusion in columbium. At 2750° F ($0.65 T_M$) H is 90 K cal/mole, whereas the activation energy for self-diffusion in columbium is reported to be 96 K cal/mole. For the rate of increase in H with temperature shown in Figure 3 near 2700° F, H would equal the activation energy for self-diffusion at about $0.7 T_M$.

In a number of metals it has been found that H becomes stress dependent below the temperature range where it is equal to the activation energy for self-diffusion. Therefore, it is found that H decreases with decreasing temperature when activation energy measurements are made using higher stresses at lower temperatures. For these tests, the stress was increased from 1 ksi to 7 ksi between 2750° F ($0.65 T_M$) and 1500° F ($0.4 T_M$) so that the tests could be completed in a reasonable length of time. With the exception of the anomalous peak near 1900° F, H gradually decreases with decreasing temperature from 90 K cal/mole at 1750° F to about 70 K cal/mole at 1500° F. This decrease can be accounted for if H is stress dependent in the temperature region investigated.

The results of several tests performed to give additional information concerning the peak in H values near 1900°F are listed below:

Variation in H at 1850°F with Precreeep Treatment and Test Conditions

Specimen Number	Precreeep Treatment	Test Conditions	H
1	As Received	Not Wrapped	68
2	As Received	Wrapped	65
3	$2300^{\circ}\text{F}/5\text{ min}$ (not wrapped)	Not Wrapped	102
4	$2300^{\circ}\text{F}/5\text{ min}$ (wrapped)	Wrapped	79

Specimens that were not given the usual precreeep heat treatment at 2300°F (1 and 2) yielded lower values of H at 1850°F than those given this precreeep treatment (3 and 4). In addition, the specimens tested directly yield about the same value of H for the wrapped and unwrapped conditions (1 and 2). This behavior suggests that the interstitial contamination affecting H takes place primarily during the 2300°F anneal rather than during creep testing at 1800 - 1900°F . However, there are some reservations concerning this interpretation since the structure of the specimens annealed at 2300°F before testing would be different than those tested directly.

2.2 EFFECT OF THE INTERSTITIAL CONCENTRATIONS ON THE ACTIVATION ENERGY FOR CREEP OF D43

The variation in H with temperature for D43 from 1650 to 3200°F is shown in Figure 4 (Prog. Report March 8 - June 8, 1968). The data points below 2400°F show less scatter than those above this temperature because they indicate the average of multiple determinations. As indicated by the solid line in this figure, H is about 110 K cal/mole above about 2400°F , while below this temperature H exceeds this value. During this period, some of the factors affecting H below 2400°F were investigated further.

As previously discussed, the structure of D43 is sufficiently stable so that H can be determined for this alloy using both increasing and decreasing temperature shifts. Steady state creep is rapidly attained with each temperature shift without evidence of a transition region.

In addition, H is approximately independent of strain within the temperature range investigated, 1650 - 3200°F . This is illustrated in Figure 5 which shows H as a function of strain for one of these tests.

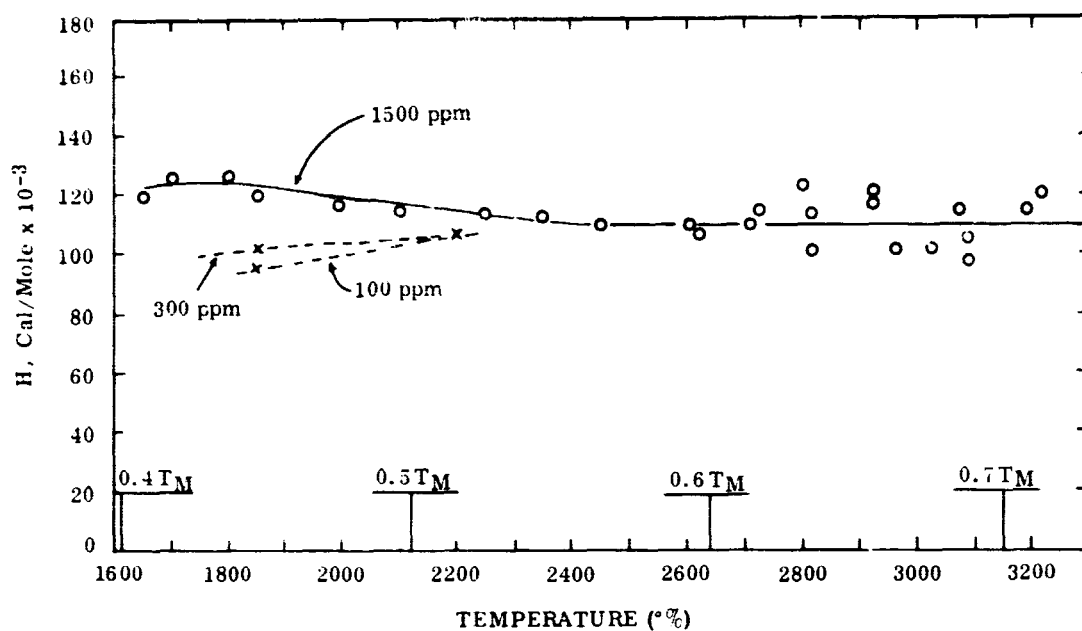


FIGURE 4. ACTIVATION ENERGY FOR CREEP OF D43 FROM 1650°F TO 3200°F

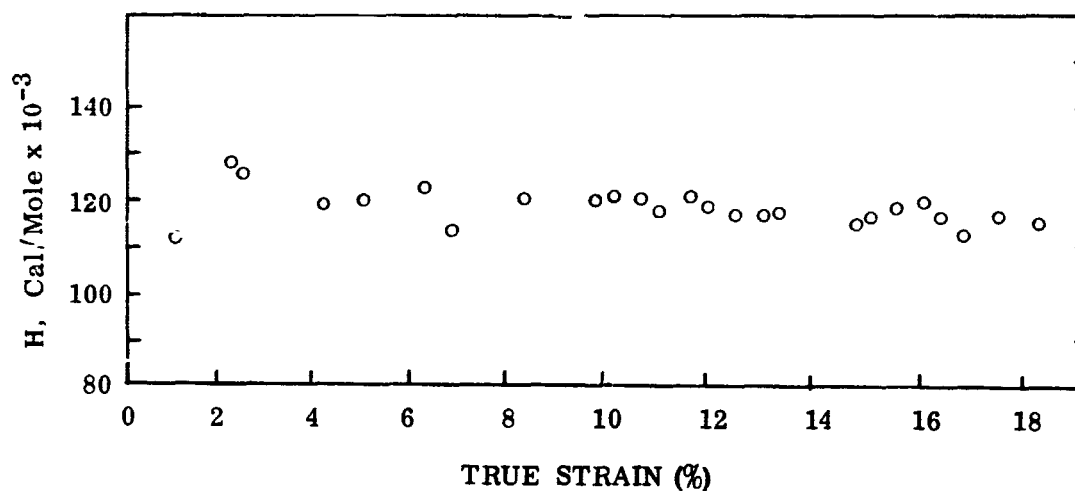


FIGURE 5. ACTIVATION ENERGY FOR CREEP OF D43 VERSUS STRAIN AT 2000°F

The effect on creep measurements of wrapping the specimens to reduce possible interstitial contamination during test was carefully investigated. Specimens were tested with their gage lengths wrapped with foil and the same specimens were tested again at the same temperature and stress with their gage lengths exposed to the vacuum. In addition, different wrapped and unwrapped specimens were tested for comparison under the same condition of stress and temperature. The activation energies derived from some of these tests are shown in Figure 6. In contrast with the results cited earlier for columbium, these results show that the activation energy is not significantly affected by protecting the gage length of the specimen with foil during testing.

However, evidence was obtained concerning the effect of interstitials on H by testing D43 specimens with reduced interstitial concentrations in the temperature region where H is greater than 110 K cal/mole. In Figure 7, H is shown as a function of strain at 1850° F for specimens whose combined carbon and oxygen concentrations were less than 100 ppm before testing (carbon and oxygen account for more than 90 percent of the interstitials in this alloy). The interstitial concentrations were reduced by heat treating the specimens (2200° F/60 hr) in contact with titanium, (Interim Tech. Rept. June, 1966-June, 1967). The interstitials concentrated in the titanium which was removed from the specimen before creep testing. After this heat treatment, the concentration of the elements in the specimens was carefully checked using the electron microprobe to ensure that the zone of Ti/D43 interdiffusion had also been removed.

There are several significant points revealed by these tests. First, the wrapped specimen yields lower values of H than the specimens exposed to the vacuum. Evidently restoration of interstitials during testing at 1850° F increases the activation energy for creep for specimens initially low in interstitials. Second, these tests show a dependence of H on strain (or structure) at 1850° F, whereas H is independent of strain for specimens with a higher interstitial concentration (Fig. 5). In addition, the specimens low in interstitials attain a lower value of H at 1850° F than those high in interstitials (compare Fig. 5 and Fig. 7). Finally, additional tests showed that the effect on H of wrapping the specimen and the dependence of H on strain shown in Figure 7 are no longer present when the tests are conducted at 2200° F. In summation, these results show that the concentration of interstitials in D43 has an influence on the activation energy for creep in the temperature range where H exceeds 110 K cal/mole.

The activation energy values for the D43 with the reduced interstitial concentration are shown in Figure 4 along the dashed line. These values of H are those taken from Figure 7 for large strains where H has apparently attained an equilibrium value. Approximate values of the combined oxygen and carbon concentrations for the as-received D43 and for the D43 with reduced interstitial concentrations are also shown in this figure. These results show that H is greater for D43 with a higher interstitial concentration in the temperature region below 2400° F.

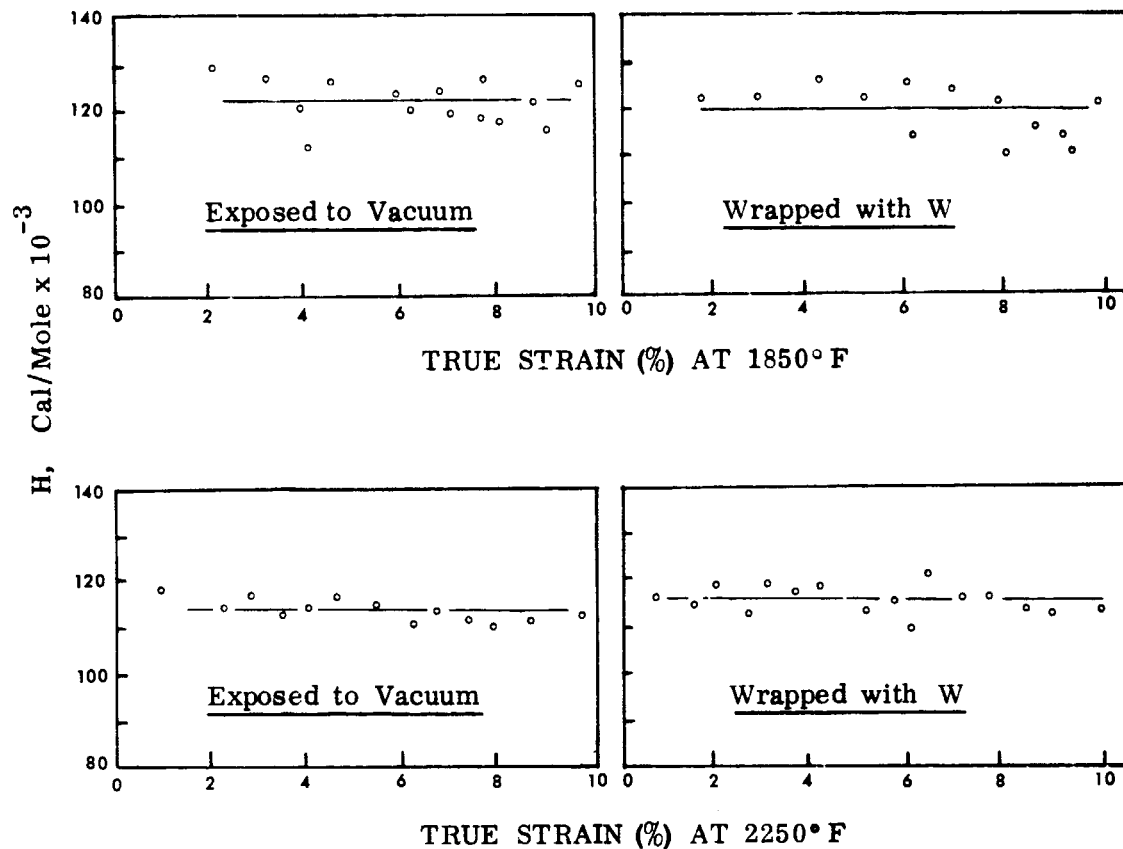


FIGURE 6. ACTIVATION ENERGY FOR CREEP OF D43 AT 1850°F AND 2250°F FOR SPECIMENS EXPOSED TO A VACUUM OF 10^{-6} TORR AND FOR SPECIMENS WRAPPED WITH TUNGSTEN FOIL

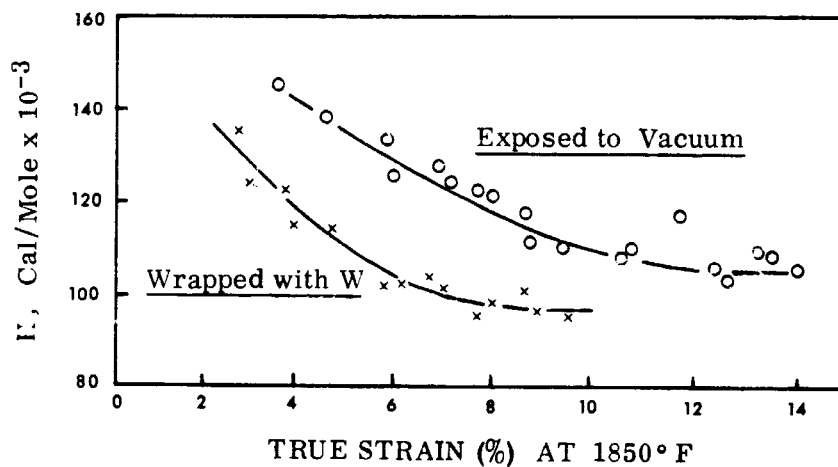


FIGURE 7. ACTIVATION ENERGY FOR CREEP AT 1850°F FOR D43 WITH A REDUCED INTERSTITIAL CONCENTRATION

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SUMMARY AND CONCLUSIONS

The activation energies for creep, H , of both columbium and D43 appear to be affected by their interstitial concentrations. The results indicate that H increases with increasing interstitial concentration in the temperature region investigated below $\sim 0.5 T_M$. Because of the apparent sensitivity of H to the interstitials and because of the difficulty in controlling interstitial concentrations, it will be difficult to sort out the effect of specific solutes in columbium alloys on H in this temperature region.

High values of H below $0.5 T_M$ in some alloys have been attributed to strain aging effects. When this involves an interaction between solute atoms and dislocations, H may include the temperature sensitivity of the concentration of solutes near dislocations as well as the regular temperature sensitivity of creep. Although the identity of the species likely to cause such an interaction is not known, a consideration of atomic mobilities in columbium and columbium alloys suggests that interstitial or solute atoms acting individually are not likely to give rise to interactions with dislocations during creep at temperatures just below $0.5 T_M$ (Interim Tech. Rept. June 1967 - March 1968). The mobility of interstitial elements is too high and the mobility of substitutional elements is too low. However, where solutes interact with each other, the temperature range of the dislocation-solute interactions during creep may be shifted or broadened and, therefore, could give rise to the observed increase in H through a postulated dislocation solute-atom interaction. In D43 the interacting species may be interstitials combined with the solutes tungsten or zirconium, while in columbium the species may be interstitials combined with substitutional impurity elements.

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FUTURE WORK

The factors affecting the activation energy for creep of columbium will be studied in greater detail since this information will provide a basis for comparing the effect of solutes on the activation energy for creep of columbium-base alloys.

Activation energy studies will be extended to higher temperatures where substitutional elements are more likely to affect the activation energy for creep. The creep behavior of a number of columbium and tantalum base alloys will be studied to determine the contribution of solutes to the elevated temperature strength of these alloys. The alloys will be selected to sort out the influence of various solutes on the creep strength through their effect on the activation energy for creep. This study should provide information that will be of value in selecting solutes to optimize the high temperature strength of alloys.