

FOREWORD

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ABSTRACT

The strain rate and temperature dependencies of the low temperature deformation behavior of fine grained arc-melted columbium, 1 part per million hydrogen (1 ppm hydrogen) were evaluated for tensile strain rates of 0.005, 0.10 and 6.0 in/in/min. The effect of hydrogen content (1, 9, and 30 ppm H) on the mechanical behavior was also investigated in the temperature range 25 to -195°C, using a tensile strain rate of 0.005/min.

The existence of a hydrogen-dislocation interaction in columbium was confirmed by: (1) calculation of an apparent activation energy for the early stages of low temperature deformation, (2) observation of a hydrogen induced strain aging peak at -50°C, for columbium containing 30 ppm H, and (3) observation of a serrated stress-strain curve at 25°C in coarse grained columbium containing 89 ppm H.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. J. TRAPP
Chief, Strength and Dynamics Branch
Metals and Ceramics Laboratory
Materials Central

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INTRODUCTION

In the past decade the refractory metals of Group V A vanadium (V), columbium (Cb), and tantalum (Ta), and Group VI A chromium (Cr), molybdenum (Mo), and tungsten (W), have received increasing attention as potentially high temperature structural materials. Of considerable importance, from the standpoint of fabricating and handling these metals at ambient temperatures, is the phenomenon of low temperature brittleness. This ductile-brittle transition behavior has been found in all of the above metals except tantalum, and therefore considerable effort has been expended to evaluate the effect of different variables on the ductile-brittle transition temperature. A recent summary report (1) discusses the important factors affecting the transition temperature in these refractory metals.

Two of the most important variables have been found to be impurity content, particularly interstitial elements, and the strain rate used in mechanical deformation. This program was undertaken to provide information regarding the effects of interstitial content and tensile strain rate (0.005, 0.1, and 6.0/min) on the ductile-brittle behavior of one of the refractory metals, columbium. The interstitial element that varied was hydrogen, the three levels studied being 1, 9, and 30 ppm. The strain rate was varied for the 1 ppm H material only.

EFFECT OF HYDROGEN: To determine the influence of hydrogen on the mechanical behavior of metals has been the object of numerous investigations. Troiano (2) has summarized certain important aspects particularly the hydrogen embrittlement phenomenon. The work of Roberts and Rogers (3) and Loomis and Carlson (4) are also of significance, since they show that hydrogen can greatly embrittle vanadium. A similar behavior might therefore be expected in columbium, since both of these body centered cubic (BCC) metals have a relatively high solubility for hydrogen, and both exhibit similar deformation behavior. Also studies were made which aimed at evaluating the effect of hydrogen on dislocation locking in body centered cubic metals, and the influence of such a dislocation-interstitial atom interaction on the low temperature deformation behavior. Recent investigations (5,6) for example have shown that hydrogen can cause strain aging effects in columbium. A low temperature hydrogen yield point has been reported in electrolytically charged alpha iron (7,8,9), as well as quench aging effects in molybdenum due to hydrogen (10).

EFFECT OF STRAIN RATE: There are numerous discussions in the literature about the influence of strain rate on the ductile-brittle behavior of the refractory metals. The effect of strain rate on the ductile-brittle transition in V, and W was evaluated by Magnusson and Baldwin (11), who have also shown the effect of strain rate on the ductility of Ta (12). In addition, the strain rate sensitivity of the ductile-brittle behavior has been studied for Cr (13,14), Mo (15,16,17) and Cb (18). Reduction in area (RA) is the property generally examined, since percent RA values perhaps give the most meaningful measure of the ductile or brittle nature of these metals.

It has been generally observed that an increase in the strain rate causes an increase in transition temperature of the Group VI A metals, Cr, Mo, and W. This is apparently a normal behavior since such a relationship is also observed for the non-body centered cubic metals zinc (Zn), cadmium (Cd), tin (Sn), and magnesium (Mg) alloys (11). The

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strain rate used in tensile deformation (from 0.05 to 19,000 in/in/min) has little effect on the ductility of Ta, but it has been found that increased strain rates lower the ductile-brittle transition temperature of V, Cb, and steels containing hydrogen (32). This anomalous behavior has been attributed to slow strain rate hydrogen embrittlement, which will be discussed later in conjunction with the results of this investigation.

EXPERIMENTAL PROCEDURE

MATERIAL: The arc-melted columbium used was supplied by Fansteel in the form of 1/2-in. diameter rod having a fine grain size of about 600 grains/mm². The analysis in table 1 shows that the as-received material had a hydrogen content of 1 ppm. Material from the same heat was also hydrogen charged to 9 and 30 ppm H using the hydrogen annealing treatments given in table 1. The charging treatments slightly increased the carbon and oxygen content, but caused a marked decrease in the nitrogen content.

The hydrogen annealing treatments were performed on the 1/2-in. diameter rod prior to machining the tensile samples, (3 1/2 in. long, 1-in. gage length, 0.30-in. gage dia.). Following hydrogen annealing, and prior to machining, the samples were argon annealed as described in table 1, in order to achieve homogenization. Chemical analyses of the hydrogen-charged materials were made on specimen gage sections after they had been tensile tested.

EQUIPMENT: Tensile testing at strain rates of 0.005 and 0.10 in/in/min was accomplished on a "hard" Baldwin-Emery SR-4 Testing Machine, Model FGT; the load-strain curves were autographically recorded (see figure 1). The 6.0 in/in/min strain rate was achieved on a General Motors high speed testing machine. In order to record the load, a calibrated dynamometer was used in conjunction with a recording oscillograph as shown in figure 2. The specimen arrangement in the bath chamber is made clear in figure 3. Test temperatures were obtained between room temperature and -78°C by using a mixture of solid carbon dioxide and acetone. Mixtures of isopentane and liquid nitrogen provided the bath for the lower test temperatures, between -78°C and -195°C.

RESULTS

The effect of strain rate on the ductile-brittle transition of as-received columbium (1 ppm H) was investigated by measuring the temperature dependence of mechanical properties using strain rates of 0.005, 0.10, and 6.0 in/in/min. The effect of hydrogen (in solid solution) on the ductile-brittle behavior was studied in materials containing 1, 9, and 30 ppm H. A tensile strain rate of 0.005/min was used in all these tests.

The mechanical properties, as a function of temperature, are listed in table 2 for materials having various hydrogen levels and tested at different strain rates. The ultimate tensile strength, and 0.2 percent yield strength of as-received Cb (1 ppm H) are plotted as a function of temperature in figure 4. It is the general trend for increasing strain rates to cause an increase in strength at a given temperature. This is in accordance with the previous findings of Wessel et al. (20) on electron beam melted columbium. No curve of yield strength versus temperature is shown for the 6.0/min. strain rate since it was impossible to calculate the 0.2 percent yield strength from the oscillograph traces.

In figure 5 the ductility (percent RA and percent total Elongation) of the as-received Cb are plotted as a function of temperature for the three strain rates studied. Examination of the total elongation versus temperature curve reveals that, except at -195°C , the ductility decreases with increasing strain rate. On the other hand, the percent RA versus temperature plots indicate just the reverse of this. There is apparently no difference in the reduction in area as a function of temperature for material tested at strain rates of 0.005/min or 0.10/min. However the material tested at 6.0/min is considerably more ductile below -50°C , than material tested at slower strain rates. For example, samples tested at -195°C and strain rates of 0.005 and 0.10/min showed essentially zero percent RA, whereas samples tested at 6.0/min exhibited a reduction in area of 50 percent. Since percent reduction in area is considered to be a more valid measurement of ductility than percent total elongation, it is possible to conclude that increasing strain rates tend to lower the ductile-to-brittle transition temperature of columbium. This conclusion agrees with the results of Begley (18) on columbium, and Magnusson and Baldwin (11) on vanadium.

The ultimate tensile strength and 0.2 percent yield strength of columbium tested at a strain rate of 0.005/min are shown as a function of temperature and hydrogen content in figure 6. It is noted that there is a tendency for increasing hydrogen in solid solution to raise the tensile and yield strengths, at a given temperature, above those of the as-received material. Perhaps the most interesting feature of figure 6, however, is the strain aging peak at -50°C noted for the 30 ppm H curve only. A strain aging peak due to hydrogen is not too unexpected, however, in light of recent studies (5,6) showing that hydrogen can cause strain aging effects in columbium at low temperatures.

The ductility, both total elongation and reduction in area, are shown in figure 7 for columbium as a function of hydrogen content, the tests being run at a strain rate of 0.005/min. The data of Eustice and Carlson (19) on columbium containing 1 ppm H and 20 ppm H are also shown, for a comparison. It is seen that increasing the hydrogen content raises significantly the ductile-brittle transition temperature. For example 30 ppm H in Cb results in a transition temperature of approximately -150°C to -125°C as opposed to about -195°C to -175°C for uncharged material. Eustice and Carlson found a much larger increase in transition temperature due to hydrogen, the temperature being $<-195^{\circ}\text{C}$ for material containing 1 ppm H and approximately -75°C for Cb with 20 ppm H in solid solution. The difference in degree of embrittlement as a function of hydrogen level, revealed in this work and that found by Eustice and Carlson is not understood. It is conceivable, however, that a difference in metallurgical variables of the test materials such as grain size or the oxygen, nitrogen, and carbon content, could influence the ductile-brittle behavior. The possible effect of strain rate is ruled out since the 0.008/min. strain rate used by Eustice and Carlson is not significantly different from the 0.005/min. rate used in this work. Wood and Daniels (40) have recently reported some results which indicate that hydrogen can also have an embrittling effect in cold worked columbium. A ductile-to-brittle transition was observed at about room temperature for Cb containing more than about 120 ppm H.

The fracture stress (load at fracture divided by cross sectional area at fracture) is shown as a function of temperature and strain rate in figure 8 for as-received Cb. There appears to be no significant or consistent effect of strain rate on either the cleavage or shear fracture strengths. It should be remembered, however, that in the case of shear fractures where large reductions in area occur, the term strain rate is meaningless after necking occurs, since material in the necked down region is being deformed at a variable strain rate. The cleavage fracture strength is differentiated from shear fracture strength because in the former, essentially zero reduction in area occurs, while in the latter, considerable plastic deformation occurs prior to fracture.

The transition from shear to cleavage fracture with decreasing temperature is not an abrupt one; there is a definite transition range where fracture occurs partially by the shear mode, and partially by the cleavage mode. This transition range has been defined in electron beam melted Cb tested in compression by Wessel et al. (20) as existing from about -150 to -200°C.

The effect of hydrogen content on shear and cleavage fracture stresses is shown in figure 9. In the 30 ppm H material the temperature at which fracture becomes pre-dominantly cleavage is -150°C as opposed to -195°C for 1 ppm and 9 ppm H material. It appears (from two data points only) that there is a temperature dependence of the cleavage fracture stress for the 30 ppm H material, and that lower temperatures raise the stress to fracture. Wessel et al. (20) found, on the other hand, that in electron beam melted Cb, tested in compression, the cleavage fracture stress decreased with decreasing temperature. Another interesting feature revealed in figure 9 is that there is little or no temperature dependence of the shear fracture stress for 9 ppm and 30 ppm H material from 25 to -78°C, but there is a strong temperature dependence of the shear fracture stress for the columbium containing only 1 ppm H.

The microstructures near the fracture surfaces of both shear and cleavage type fractures are illustrated in figure 10. The ductile shear fracture of Cb plus 1 ppm H, tested at 25°C and a strain rate of 0.005/min reveals a deformed structure with voids appearing near the fracture surface (see figure 10a). The structure shown in figure 10b is of Cb plus 30 ppm H tested under the same conditions of temperature and strain rate. The microstructure is similar to that of the 1 ppm H material, but considerably more voids are present. This behavior was noted to be the general case. That is, the higher the hydrogen level, for a given test temperature and strain rate, the greater the void density near the fracture surface. This increased void formation might possibly be attributed to atomic hydrogen combining at an increased rate on vacancies, microcracks, or other imperfections to form H₂ "bubbles" during deformation.

The cleavage fracture shown in figure 10c illustrates the brittle behavior of columbium tested at low temperatures. Although the magnification is too low to show twins, in all samples tested at -195°C (except the 1 ppm material tested at 6.0/min) definite twinning was observed. The early portions of the stress-strain curves showed serrations due to twinning, the more pronounced serrations being accompanied by audible clicks. Some scattered twinning was also observed at -150°C, but not at higher temperatures.

DISCUSSION

STRAIN RATE EFFECTS: The effect of strain rate on the yielding behavior of molybdenum (16) and iron (21) has been treated by Sinclair, Wert, and their co-workers at the University of Illinois in order to determine an apparent activation energy for low temperature deformation of these BCC metals. They used a torsional testing method, and found that an increase in strain rate increased the yield stress (upper yield point) at a given temperature. A similar effect of strain rate on the 0.2 percent yield strength of arc-melted columbium containing 1 ppm H is seen in figure 4, and Wessel et al. (20) found the same behavior in compression tests on electron beam melted columbium. The University of Illinois investigators observed a stress dependence of the activation energy, and upon extrapolation of Q to zero stress the values found were: Q = 18,000 cal/mole for iron, and Q = 36,000 cal/mole for molybdenum. They postulated that the strain rate dependence of initial yielding, i.e. upper yield point, was dependent upon the

diffusion of interstitial elements, so that the interstitial diffusion rate acted as the rate controlling process in the early stages of plastic deformation. The agreement of the above activation energies for plastic deformation with those for interstitial diffusion: Q (N in Fe) = 18,200 cal/mole, Q (C in Mo) = 33,000 cal/mole, lends considerable credence to their theory. The stress dependence of the activation energy was rationalized by considering that the total activation energy for deformation was comprised of contributions by thermal energy and mechanical energy, in terms of stress. The extrapolation to zero stress should therefore eliminate mechanical energy effects. The model pictured is that the activation energy represents the energy required to dislodge dislocations from their pinning atmospheres, and the means whereby interstitial diffusion controls this process is analogous to that proposed by Clark, Wood and Hendrickson (22, 23, 24) for delayed yielding of BCC metals. That is to say, the stress induced short range diffusion of interstitial atoms is considered to be the rate controlling mechanism for yielding.

The temperature dependence of the strain rate necessary to cause yielding can be expressed by the equation:

$$\frac{1}{t} \sim \dot{\epsilon} = S \phi(\sigma) e^{-Q/RT} \quad (1)$$

where T is absolute temperature, Q is the apparent activation energy for plastic deformation, R is the gas constant, and S and $\phi(\sigma)$ indicates the rate dependence on stress (σ) and structure (S). The time, t , is the time interval necessary to allow dislocations to be torn away from pinning atmospheres*. If the temperature dependence of the strain rate to cause yielding, is evaluated at a constant value of strain prior to the onset of work hardening (for example, $\epsilon = 0.05$ percent, or $\epsilon = 0.2$ percent) it may be assumed that the structure is approximately constant. No proof has been presented to show that the structure is approximately constant. No proof has been presented to show that the structure is nearly constant at a constant value of strain regardless of the strain rate used, but this simplifying assumption is not entirely unreasonable. If, further, the temperature dependence of the strain rate is evaluated at a constant stress level, Equation 1 may be written as follows:

$$\dot{\epsilon} = A e^{-Q/RT} \Big]_{\sigma, S} \quad (2)$$

where $A = \text{constant}$. The activation energy may be evaluated from the ratio

$$\frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{e^{-Q/RT_1}}{e^{-Q/RT_2}} \Big]_{\sigma, S} \quad (3)$$

which can be rewritten as:

$$Q = \frac{RT_2 T_1}{T_1 - T_2} \ln \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} \Big]_{\sigma, S} \quad (4)$$

* The current concepts (5,6,25,26,27) of dislocation-interstitial atom interactions suggest that the locking is due not only to atoms segregated to dislocations but is also due to a clustering or micro-precipitation along dislocation lines, as a result of more atoms being attracted to the dislocations than can be retained in local solid solution. Direct evidence of these microprecipitates has been observed in alpha iron (27) using electron transmission microscopy.

The data in figure 5 for the 0.2 percent yield strength (Y.S.) was treated using Equation 4, and the apparent activation energy for low temperature plastic deformation was calculated for various stress levels. The data are listed in table 3 and the activation energy is plotted as a function of stress level in figure 11. The results of Wessel et al. (20) on the effect of compressive strain rate on the yielding behavior of electron beam melted columbium were also treated using Equation 4, and the data are shown in table 3 and figure 11 for comparison purposes. The two strain levels at which Wessel et al. determined the strength as a function of temperature were 0.05 and 3.0 percent. Examination of figure 11 reveals that the activation energies for $\epsilon = 0.2$ percent (this work) and $\epsilon = 0.05$ and 3.0 percent (Wessel et al.) are a linear function of stress, decreasing with increasing stress. These findings are in agreement with the work of the University of Illinois investigators on Fe and Mo, although they find a deviation from linearity at higher stress levels in their experiments on iron. The activation energies, extrapolated to zero stress were found to be:

$\epsilon = 0.2$ percent, tension, $Q = 8,300$ cal/mole, arc melted Cb

$\epsilon = 0.05$ percent, compression, $Q = 10,900$ cal/mole, electron beam Cb

$\epsilon = 3.0$ percent, compression, $Q = 24,600$ cal/mole, electron beam Cb

If the stress induced short range diffusion of interstitial atoms is the rate controlling mechanism for the early stages of yielding, i.e. prior to the onset of work hardening, in BCC metals at low temperatures, it is tempting to relate the activation energy at zero stress to the Q value for the diffusion of some interstitial element in columbium. The values of 8,300 and 10,999 cal/mole in figure 7 compare reasonably well with the data of Albrecht et al. (28) who give the following equation for the diffusion of hydrogen in columbium:

$$D = 0.0215 e^{-9370/RT} \quad (5)$$

The activation energies for the diffusion of carbon, oxygen, and nitrogen in columbium are considerably higher than 9370 cal/mole, being respectively 33,000, 27,600 and 34,800 cal/mole (29, 30). The activation energy of 24,600 cal/mole for $\epsilon = 3.0$ percent (see figure 11) does not represent a process which is controlled by stress induced diffusion of interstitial elements, since at this point strain hardening affects the deformation behavior. For this reason, Equation 4 was not applied to the ultimate tensile strength results of this work (see figure 4).

The fact that hydrogen can cause strain aging effects in columbium at low temperatures has been recently demonstrated by Wilcox and Huggins (5,6). An activation energy of 10,500 cal/mole was found for strain aging of arc-melted Cb containing 10 ppm H using the yield point return technique. The kinetics of strain aging were also evaluated on the same material using dynamic modulus of elasticity measurements, and the activation energy was found to be 7830-8280 cal/mole. In addition to these findings, there are two other related observations which will be discussed in detail later in the report: (1) a serrated stress-strain curve at room temperature for coarse grained columbium, charged to 89 ppm H, and (2) a strain aging peak at -50°C (see figure 6) for Cb charged with 30 ppm H. This abundance of evidence indicates that there is an interaction between dislocations and hydrogen in columbium, and that this interaction can measurably affect mechanical properties.

In connection with interpreting the results in figure 11, the question arises whether or not 1 ppm H is a high enough concentration to cause dislocation locking.

The method of Hundy (26), used to calculate the percent solute necessary to pin dislocations, gives the following equation:

$$X = \frac{100ND}{dAa} \quad (6)$$

where X is the weight percent solute, N is the atomic weight of the solute, D is the dislocation density in lines/cm², d is the density of columbium in gm/cm³, A is Avagadro's number and a is the lattice constant of columbium. If it is assumed that one atom per atom plane could cause locking, as Cottrell and Bilby (31) originally did, and that the dislocation density for recrystallized columbium is 10⁹, then X, for hydrogen locking, is about 6 x 10⁻⁷ weight percent. The assumption of 1 atom per atom plane being sufficient to cause locking is not considered to be correct (see footnote on p. 5). Thomas and Leak (25) have shown, for example, that as many as 15 carbon or nitrogen atoms are attracted to dislocations in strain aged alpha iron. If X is recalculated using 15 atoms per atom plane as being necessary to give hydrogen locking of dislocations in columbium, the value is 9 x 10⁻⁶ weight percent. The 10⁻⁴ weight percent hydrogen available in the arc-melted material would certainly be sufficient to cause locking.

The observation that increasing the strain rate to high levels (6.0/min) lowers the ductile-brittle transition of columbium, as measured by reduction in area (see figure 5), supports the findings of Begley (18) on Cb and Magnusson and Baldwin (11) on vanadium. This opposite effect of strain rate, as compared to its effects on Mo, W, and Cr is particularly intriguing. The vanadium used by Magnusson and Baldwin (11) had 80 ppm H, and these workers concluded that the anomalous strain rate behavior was associated with slow strain rate hydrogen embrittlement, which was earlier observed in hydrogen-containing steels (32). In the case of vanadium and steel containing hydrogen a second unusual effect was found, that being a return of ductility at low temperatures, i.e. a minimum in the ductility versus temperature curve for a given strain rate. The absence of this behavior for Cb in this work and in the work of Eustice and Carlson (19) might be explained by too low a hydrogen concentration. If the work on vanadium (11) can be taken as an indication, possibly 80 ppm H would give the same effects in columbium.

Neglecting for a moment the return of ductility at low temperatures, the increase in ductility with increasing strain rate can be explained qualitatively using various theories of hydrogen embrittlement, such as those advanced by Zapffe and Sims (33) or Petch and Stables (34). The former authors envisioned embrittlement to result from the precipitation of hydrogen in defects such as microcracks or voids. The precipitated hydrogen, possibly combined in the form of molecular hydrogen, would be expected to exert an increased pressure, promoting premature rupture. Figures 10a and 10b support the conclusion that hydrogen does indeed enhance void formation in Cb during deformation. Presumably straining enlarges the imperfections, thus reducing the hydrogen pressure, so that further precipitation of hydrogen is required to develop or maintain a pressure sufficiently high to cause rupture. When the strain rate is increased at a given temperature, the embrittlement should be lessened, since an increased rate of pressure lowering results from imperfection enlargement.

Petch and Stables (34), on the other hand, postulate that hydrogen embrittlement occurs as a result of a lowering of the surface energy for crack propagation as a result of hydrogen adsorption on the internal surface of microcracks. They propose a hydrogen diffusion controlled mechanism, so that the crack extension under stress will occur in steps when the hydrogen solute atoms arrive at the crack tip in the course of diffusion. Higher strain rates at a given temperature should promote ductility since hydrogen would have a lower probability of reaching a crack tip before a ductile fracture occurred.

An interesting explanation for the increase in ductility of Cb with increasing strain rate (at low temperatures) has been given by Begley and Wessel (35). They have suggested that a considerable adiabatic temperature rise due to high deformation rates could explain the experimental observations. Essentially the temperature in the sample just prior to fracture, would increase to a level significantly higher than the bath temperature. The measured strength and ductility properties would then correspond to those obtained at a higher temperature in the slow strain rate tests. Such a large shift of the ductility versus temperature curve due to a high strain rate induced temperature rise would not be expected for Mo, Cr, and W. In these refractory metals, the ductile-brittle transition is normally above room temperature, where there is considerably smaller temperature dependence of the deformation behavior than at subzero temperatures. An investigation using careful instrumentation, aimed at experimentally detecting a high strain rate induced temperature rise would appear to be a worthwhile endeavor.

EFFECT OF HYDROGEN LEVEL: The increase in the ductile to brittle transition temperature with relatively small increases in hydrogen content (see figure 7) is of considerable practical significance, since it dictates the necessity for minimizing hydrogen pickup during material processing of columbium and columbium alloys. One instance, for example, where detrimental hydrogen pickup might occur would be in a prolonged acid pickling treatment, particularly if the bath temperature were above room temperature. Another possible source of hydrogen contamination during fabrication would arise if heat treatment were performed in an impure inert atmosphere. For example if a gas-fired furnace were used, and incomplete combustion took place such that a significant pressure of hydrocarbons was present, hydrogen contamination might possibly occur. A third possible means of contaminating Cb with hydrogen might occur in electroplating processes such as those used to coat refractory metals to protect them against oxidation at high temperature.

The effect of hydrogen content at low strain rates, on the strength properties, is shown in figure 6, and indicates that it does cause some solid solution strengthening. As will be recalled from table 1, only a slight increase in carbon and oxygen levels was caused by the hydrogen charging, and the nitrogen content was considerably decreased. It is felt that the slight strengthening effects shown in figure 6 were therefore largely due to hydrogen in solid solution.

The most interesting feature of figure 6, however, is the strain aging peak at -50°C for columbium containing 30 ppm H. This is particularly intriguing since no peaks were noted for the 1 and 9 ppm H materials. It is felt that the peak is further evidence of the existence of a hydrogen-dislocation interaction in columbium at low temperatures. The generally accepted explanation of a strain aging peak, i.e. a maximum in a plot of strength versus temperature, was given by Nabarro (36). He reasoned that in the temperature range where a strain aging hump exists, the pinning atmosphere has sufficient mobility to diffuse along with gliding dislocations, and that this results in a "viscous drag" effect on the dislocations. At higher temperatures the atmosphere becomes so mobile, that essentially no locking exists, and at lower temperatures the interstitial atom

mobility is so low that the atmosphere cannot move with the dislocation. When more than one interstitial atom can cause locking in a given BCC metal, there may be several strain aging peaks in a strength versus test temperature curve. The ability to resolve the separate peaks depends on the difference in mobility of the various diffusing species. Wessel et al. (20) have shown, for example, the existence of both an oxygen and a nitrogen peak in columbium in the vicinity of about 300 and 400°C, respectively. It is of interest to note that another strain aging effect, due to a given interstitial element, is usually found in about the same temperature region as the strain aging peak. This phenomenon is the serrated stress-strain curve, which is thought to be the result of strain aging occurring simultaneously while the metal is being deformed.

It is well established that there is a measurable strain rate dependence of the temperature at which a strain aging peak or a serrated stress strain behavior occurs; the higher the strain rate, the higher the temperature. Cottrell (37) derived a relationship for the strain rate effects on repeated yielding (serrated stress strain curve) in alpha iron, where nitrogen was presumed to be the element responsible for dislocation locking. The following equation was deduced by considering the minimum temperatures for repeated yielding at various rates of strain:

$$\dot{\epsilon} = 10^9 D \quad (7)$$

where D is the interstitial diffusivity at the temperature of interest. Equation 7 has been successfully applied by various investigators (20,38,39) to predict the temperature ranges at which strain aging peaks and serrated stress-strain curves should be found in columbium due to oxygen and nitrogen locking.

If Equation 7 is combined with Equation 5, the temperature at which a strain aging peak should be found in columbium due to hydrogen is -95°C, at a tensile strain rate of 0.005/min. The observed peak temperature of -50°C can be considered to be in fair agreement with the calculated value. The discrepancy is attributed to the constant, 10^9 , in Equation 7 which was determined by Cottrell for strain aging of iron due to nitrogen. The constant would have to be on the order of 10^7 to correspond to a hydrogen peak at -50°C in columbium.

Although a strain aging peak was found at -50°C for the 30 ppm H material, there was only a slight waviness of the stress-strain curve indicating a tendency toward a serrated effect. To produce a more defined serrated stress strain curve, one sample was heated at 1600°C for 1 hour in a vacuum of 10^{-5} mm Hg to promote grain growth. The sample, with a grain size of about 1 grain/mm², was then hydrogen annealed at 500°C for 6 hours followed by a homogenization argon anneal at 500°C for 1 hour. All the heat treating was performed prior to machining the tensile sample from the 1/2-inch diameter rod. The above hydrogen charging treatment gave material of the following composition: 89 ppm H, 92 ppm O, 25 ppm N. Metallographic examination at 1000X revealed no second phase indicative of exceeding the solubility limit. The sample was then tested to failure at 25°C and a strain rate of 0.005/min. The early portion of the load-strain curve is shown in figure 12a, and it is noted that a definite serrated effect occurs after the yield drop. The serrations continued all the way to failure, which occurred after 71 percent reduction in area. The serrations can be attributed to hydrogen locking since this interstitial is the only one which can diffuse fast enough at room temperature to cause strain aging during deformation. The surface of the fractured sample is shown in figure 12b and the structure along a longitudinal section is seen in figure 12c. The surface along the specimen gage

length is seen to be very rough, and Luders bands are noted on the surface of the individual grains.

CONCLUSIONS

1. An increase in strain rate was found to raise the 0.2 percent yield strength and the ultimate tensile strength of columbium at a given temperature. An apparent activation energy of 8300 cal/mole was calculated for the early stages of low temperature deformation of arc-melted columbium. Agreement of this value with the Q value for hydrogen diffusion in columbium (9370 cal/mole) indicates that the stress induced diffusion of hydrogen may be the rate controlling mechanism for the early stages of low temperature deformation of columbium.
2. Increasing the strain rate from 0.005/min to 6.0/min causes a decrease in the ductile-brittle transition temperature of fine grained arc-melted columbium containing 1 ppm H. This behavior is possibly associated with slow strain rate hydrogen embrittlement.
3. Raising the hydrogen content of columbium from 1 ppm to 9 and 30 ppm by weight causes a measurable increase in the ductile to brittle transition temperature. The increase in hydrogen also has slight solid solution strengthening effect.
4. A hydrogen induced strain aging peak in strength versus temperature plots was found at -50°C for columbium containing 30 ppm H, and tested at a strain rate of 0.005/min. No peaks were found, however, for 1 and 9 ppm H material.
5. A serrated stress-strain curve in coarse grained arc-melted columbium containing 89 ppm H was observed at 25°C and a strain rate of 0.005/min. This behavior is believed to be the result of hydrogen induced strain aging occurring during tensile deformation.
6. The above conclusions, together with earlier work on strain aging effects in columbium due to hydrogen (5,6) indicate rather definitely that a hydrogen-dislocation interaction can influence the mechanical behavior of columbium at low temperatures.

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Table 1. CHEMICAL ANALYSES, WEIGHT PER CENT				
Condition	C	O	N	H
As-Received	0.009	0.0317	0.065	0.0001
Hyd. Ann, 400°C, 3 Hrs. Argon Ann, 400°C, 4 Hrs.	0.013	0.042	0.021	0.0009
Hyd. Ann, 400°C, 6 Hrs. Argon Ann, 400°C, 6 Hrs.	0.014	0.039	0.0085	0.0030

Controls

Table 2. MECHANICAL PROPERTY DATA SHOWING EFFECTS OF STRAIN RATE AND HYDROGEN CONTENT ON THE DUCTILE-BRITTLE TRANSITION TEMPERATURE OF COLUMBIUM									
Hydrogen Content ppm	Test Temp. °C	Strain Rate Min ⁻¹	0.2% Y.S. psi	U.T.S. psi	True Fracture Strength psi	Total El. (1" g.l.) %	Red. in area %		
1	25	0.005	36,600	53,100	74,200	44	79.4		
1	-50	0.005	45,980	61,550	139,450	45	75.7		
1	-78	0.005	-	67,800	144,200	40	71.5		
1	-105	0.005	64,100	72,600	160,600	-	68.0		
1	-105	0.005	103,000	108,900	208,100	25	50.5		
1	-195	0.005	-	118,000	119,000	0.1	0.9		
1	25	0.10	45,660	53,000	88,500	43	83.4		
1	-78	0.10	64,720	70,400	149,000	36	71.5		
1	-150	0.10	106,800	109,700	179,900	25	50.2		
1	-195	0.10	134,500	144,500	144,700	1	1.9		
1	25	6.0	-*	75,000	93,200	40	78.2		
1	-78	6.0	-	89,200	151,500	30	76.6		
1	-150	6.0	-	120,000	190,000	15	69.7		
1	-195	6.0	-	132,900	133,900	9	51.0		
1	-195	6.0	-	-	-	11	51.9		
9	25	0.005	49,200	68,900	142,200	35	70.4		
9	-50	0.005	69,600	89,400	144,500	31	51.3		
9	-78	0.005	75,300	97,300	142,100	30	45.4		
9	-150	0.005	99,000	110,200	180,300	20	38.8		
9	-195	0.005	132,200	150,500	153,500	1	1.9		

Table 2. MECHANICAL PROPERTY DATA SHOWING EFFECTS OF STRAIN RATE AND HYDROGEN CONTENT ON THE DUCTILE-BRITTLE TRANSITION TEMPERATURE OF COLUMBIUM (Cont'd)

Hydrogen Content ppm	Test Temp. °C	Strain Rate Min ⁻¹	0.2% Y.S. psi	U.T.S. psi	True Fracture Strength psi	Total El. (1" g.i.) %	Red. in area %
30	25	0.005	50,200	68,100	134,500	38	68.6
30	-30	0.005	70,400	88,200	137,000	32	50.0
30	-50	0.005	79,100	95,900	141,000	30	45.1
30	-78	0.005	69,800	89,700	134,700	30	45.9
30	-150	0.005	107,600	111,000	101,900	2	5.5
30	-195	0.005	138,200	156,700	157,600	1	0.9

* Could not obtain 0.2% Y.S. from oscillograph trace.

Contrails

Table 3. THE STRESS DEPENDENCE OF THE APPARENT ACTIVATION ENERGY FOR THE LOW TEMPERATURE DEFORMATION OF COLUMBIUM

Strain Rate (min^{-1})	Temperature, °K		Stress Level, psi	Activation Energy cal/mole	Remarks	Ref.
	T ₁	T ₂				
0.10	248	203	50,000	6700	$\epsilon = 0.2\%$, tension	this work
0.10	209	175	60,000	6450	"	"
0.10	183	155	70,000	6070	"	"
0.10	165	141	80,000	5810	"	"
0.10	150	129	90,000	5520	"	"
0.60	343	253	30,000	8880	$\epsilon = 0.05\%$ compression	Wessel et al (20)
0.60	275	208	40,000	7860	"	"
0.60	235	180	50,000	7080	"	"
0.60	193	153	60,000	6800	"	"
0.60	163	128	70,000	5490	"	"
0.60	143	113	80,000	4960	"	"
0.60	123	98	90,000	4440	"	"
0.60	348	288	40,000	15,380	$\epsilon = 3.0\%$ compression	Wessel et al (20)
0.60	273	233	50,000	14,650	"	"
0.60	228	193	60,000	11,580	"	"
0.60	193	163	70,000	9,660	"	"
0.60	173	138	80,000	6,280	"	"
0.60	153	123	90,000	5,780	"	"

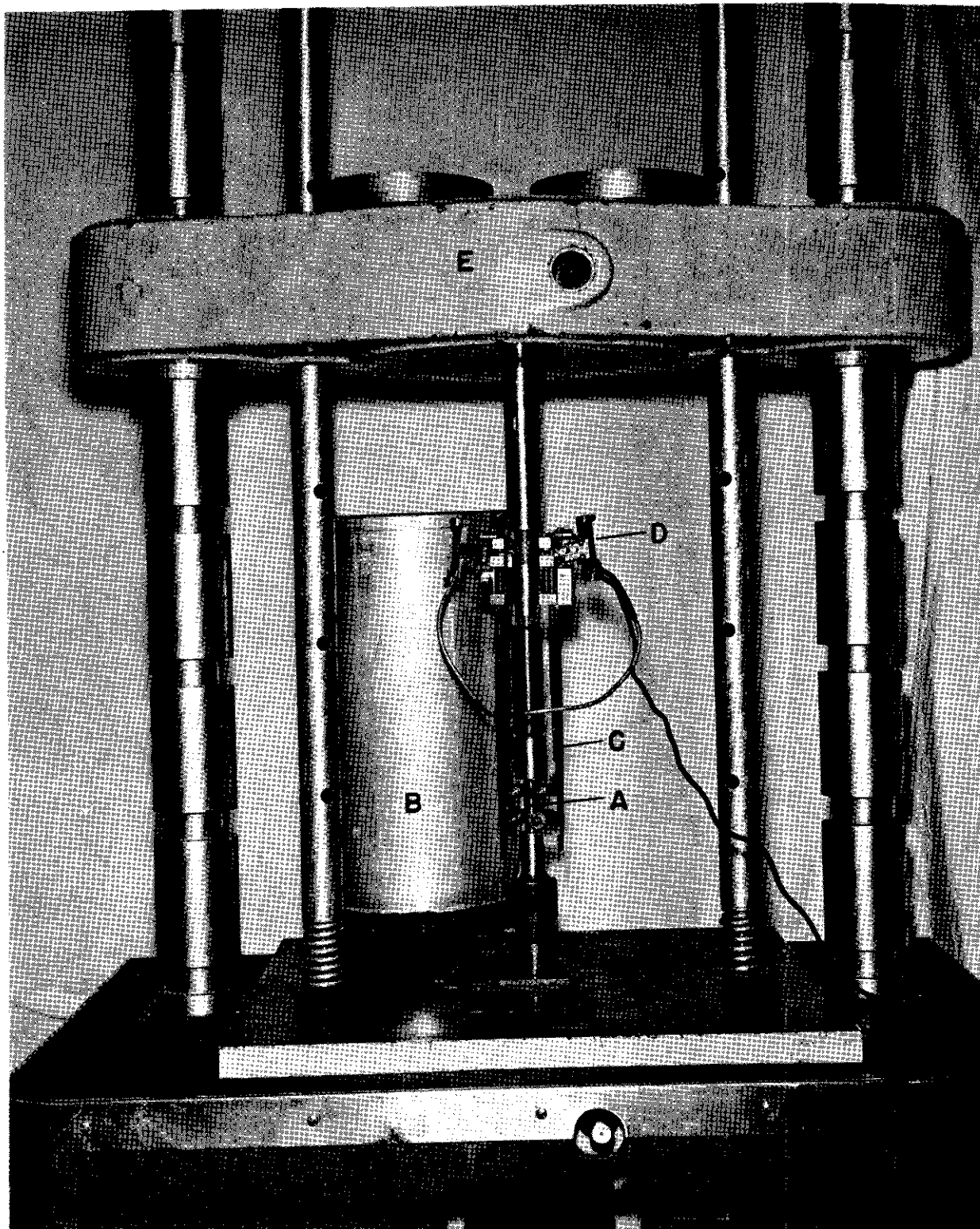


Figure 1. Tensile Test Arrangement Used for Testing at 0.005 and 0.10 in/in/min Strain Rates. (A) Test Specimen (B) Low Temperature Bath, (C) Extension Arms, (D) SR-4 Clip Gages, (E) Baldwin-Emery Test Machine, Model FGT.

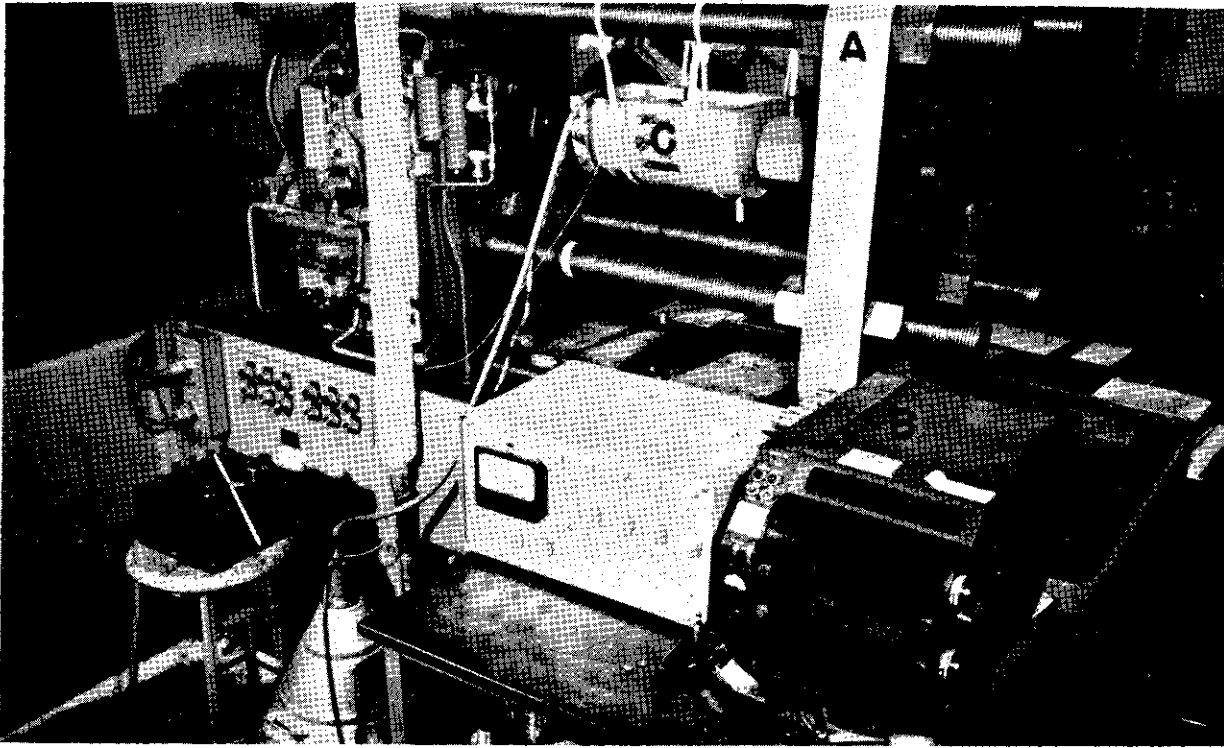


Figure 2. Test Arrangement for 6.0 in/in/min Tensile Tests. (A) General Motors Rapid Loading Machine, (B) Recording Oscillograph, (C) Low Temperature Bath.

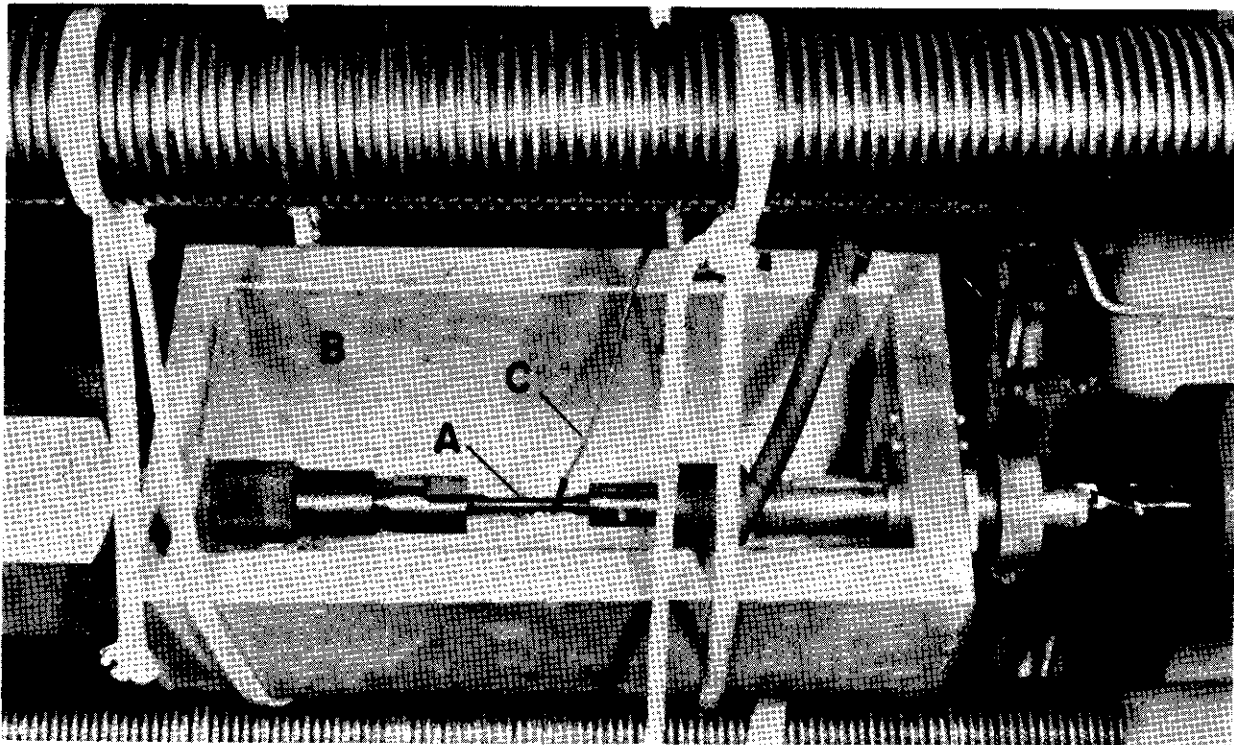


Figure 3. Close up View of (A) Test Specimen, (B) Low Temperature Bath, (C) Copper-Constantan Thermocouple.

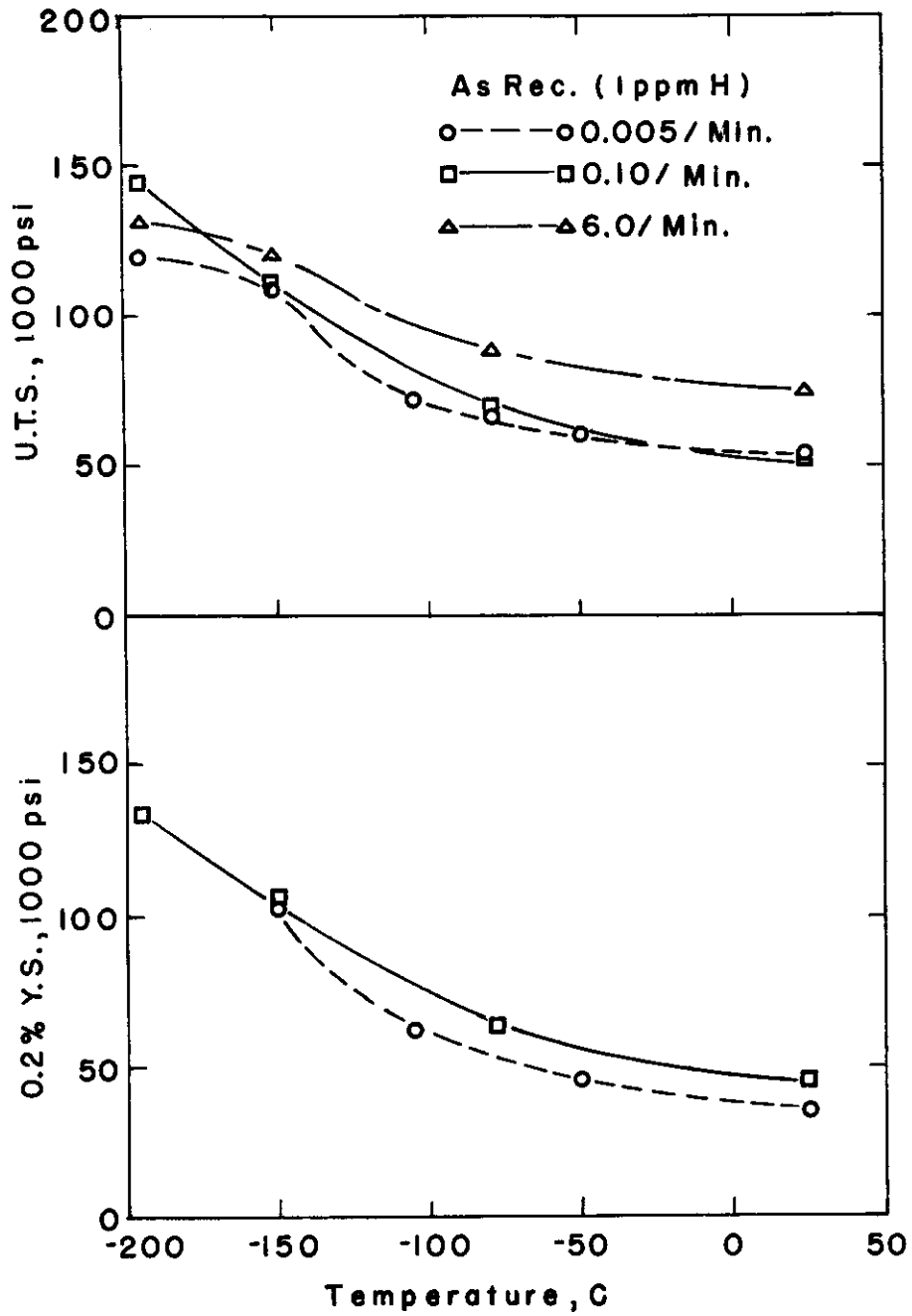


Figure 4. Effect of Strain Rate and Temperature on the Tensile and Yield Strengths of As-Received Columbium, Having 1 ppm H.

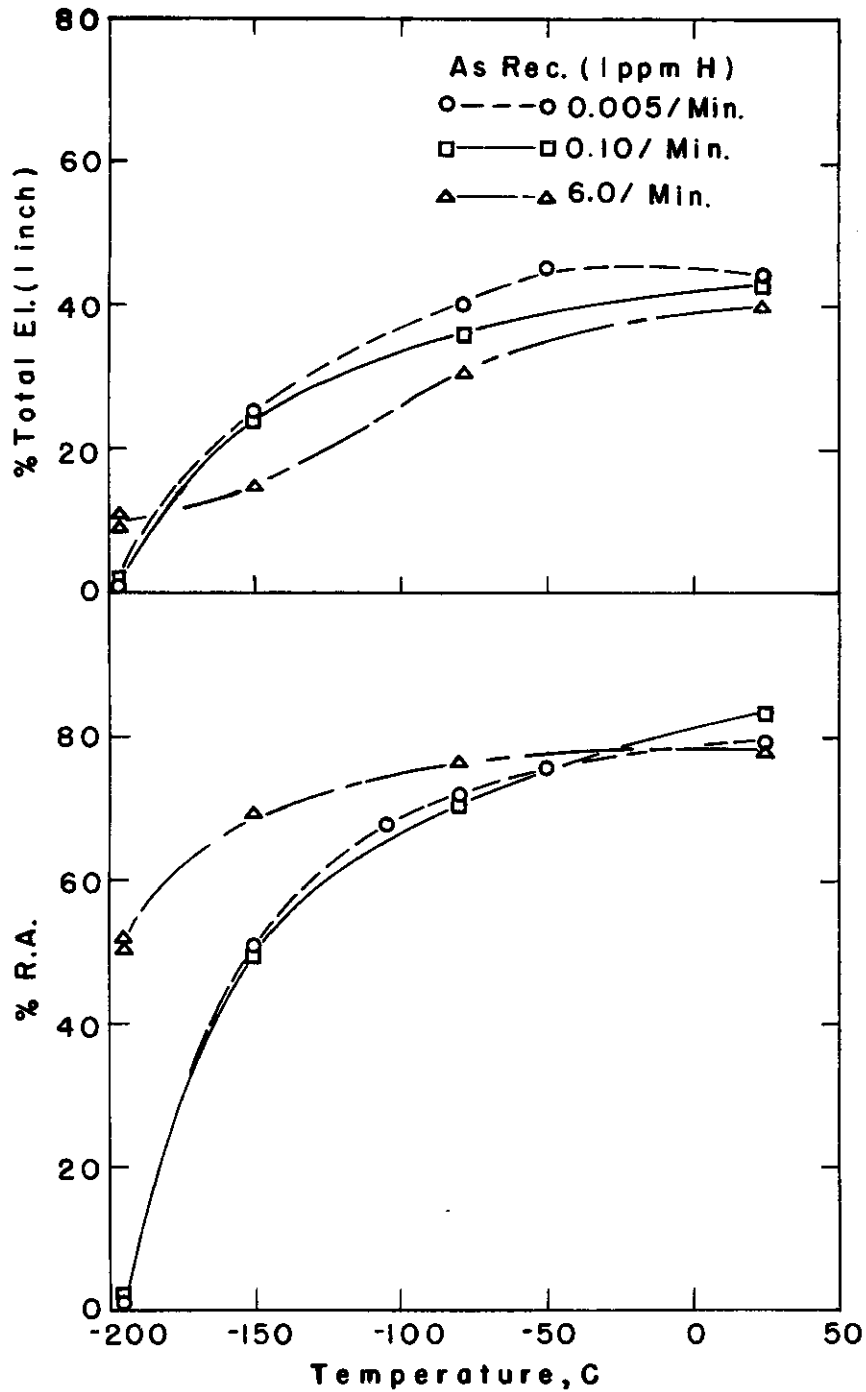


Figure 5. Effect of Strain Rate and Temperature on the Ductility of As-Received Columbium, Having 1 ppm H.

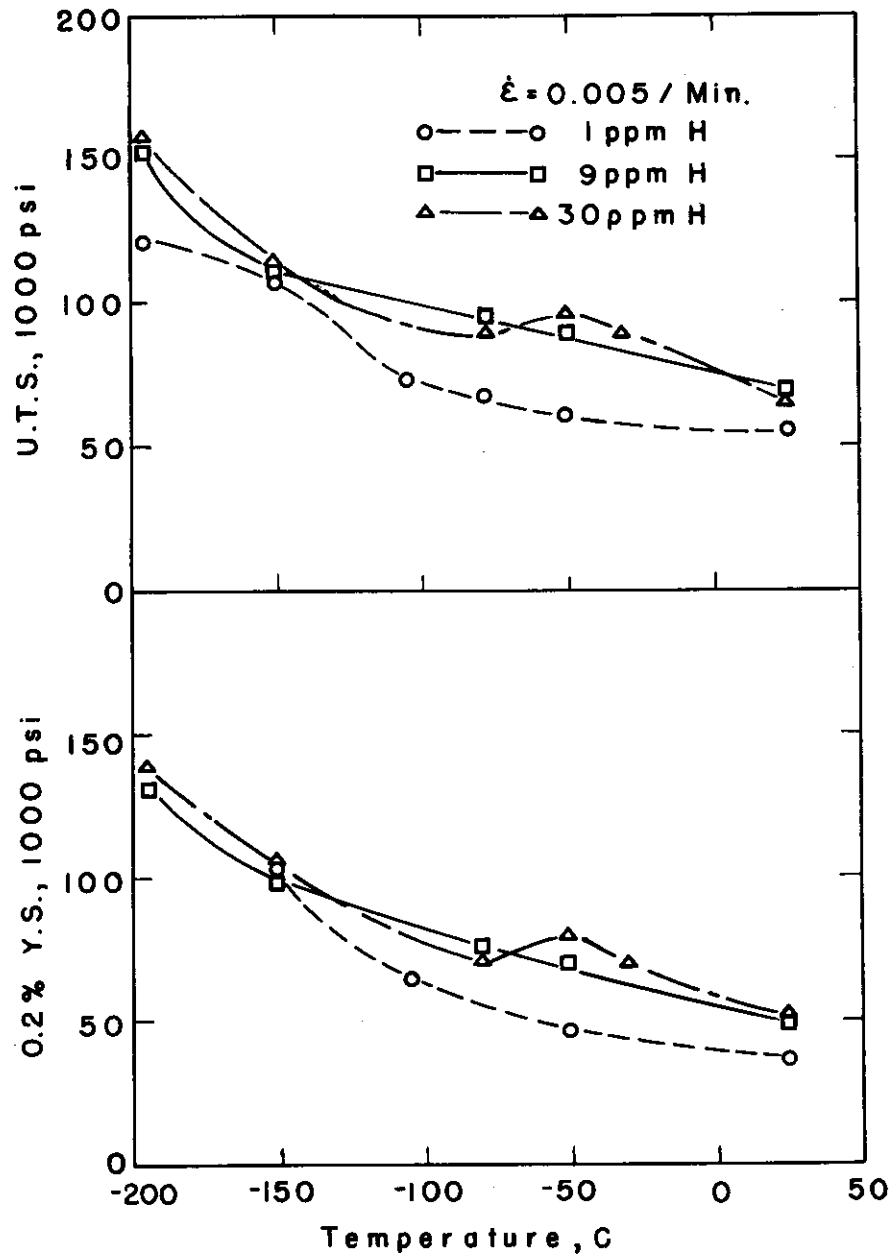


Figure 6. Effect of Hydrogen Content and Temperature on the Tensile and Yield Strengths of Columbium Tested at 0.005/min.

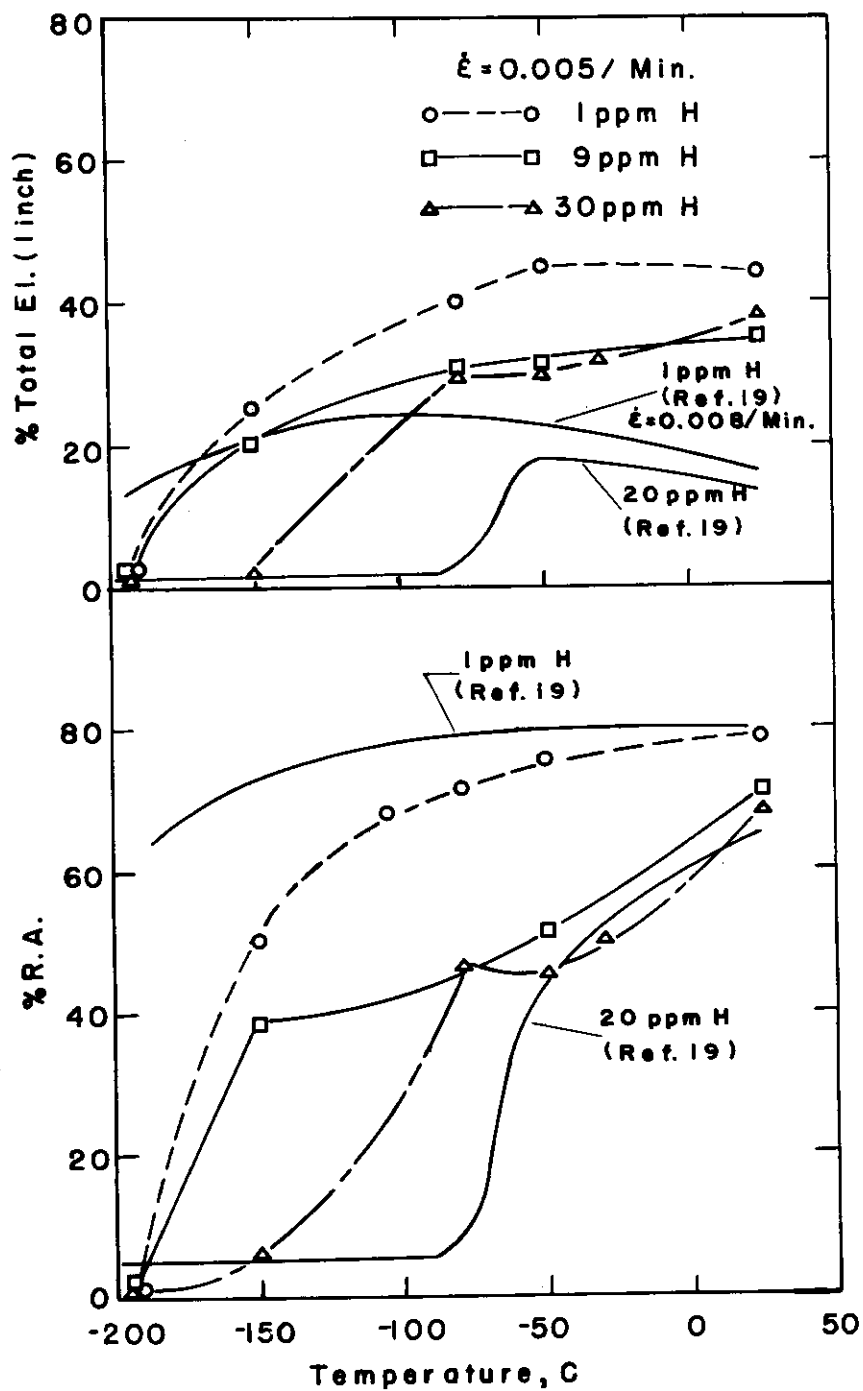


Figure 7. Effect of Hydrogen Content and Temperature on the Ductility of Columbium Tested at 0.005/min.

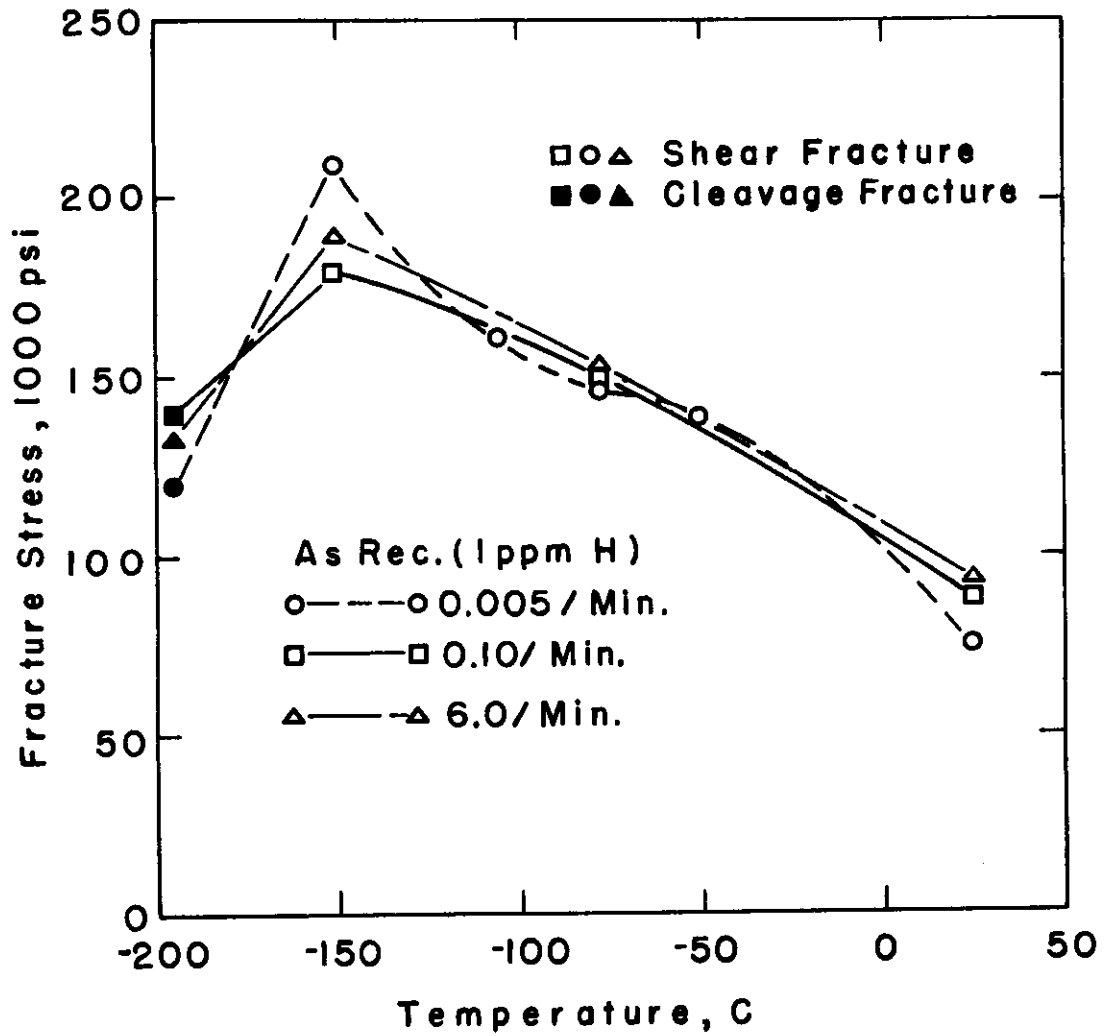


Figure 8. Effect of Strain Rate and Temperature on the Fracture Strength of As-Received Columbium, Having 1 ppm Hydrogen.

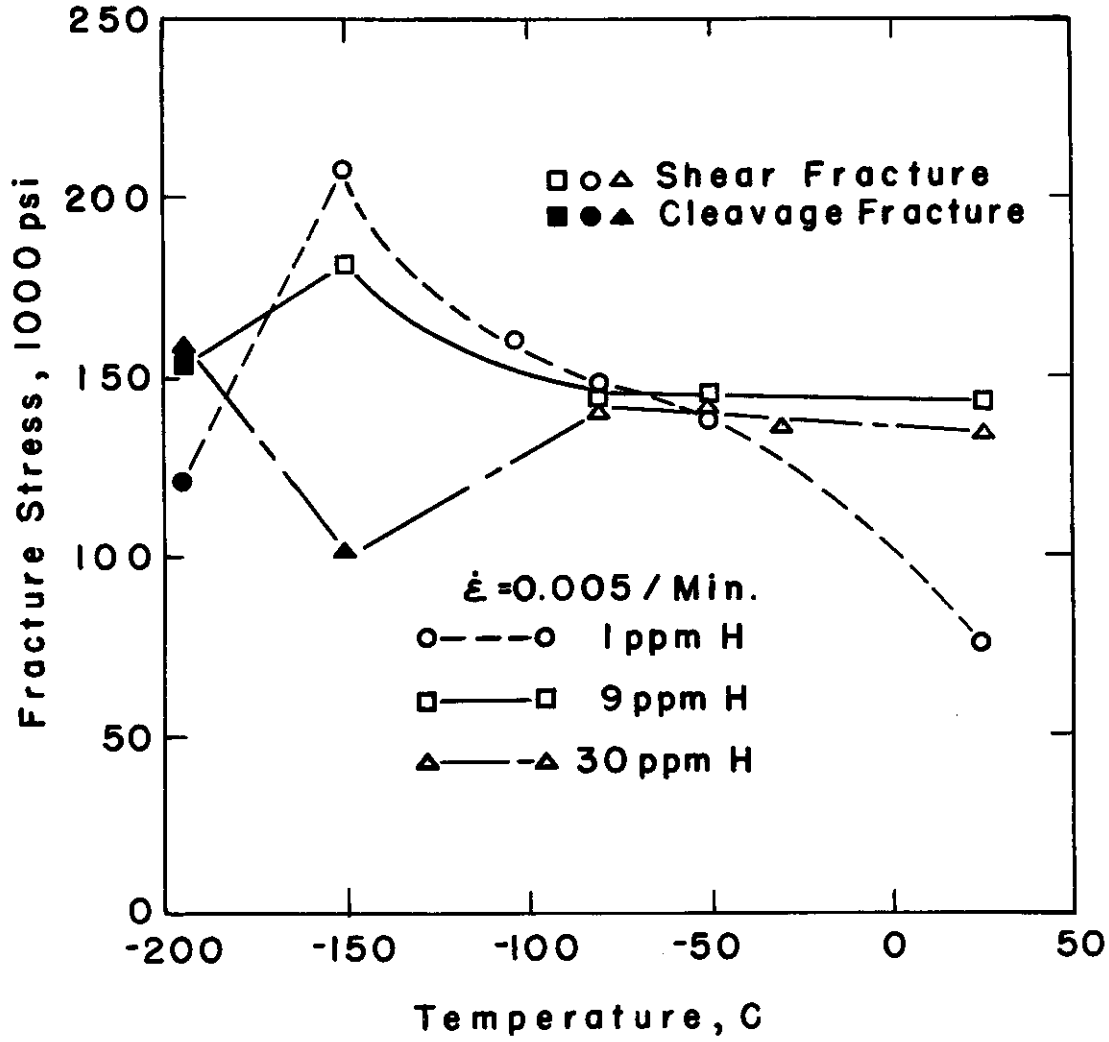
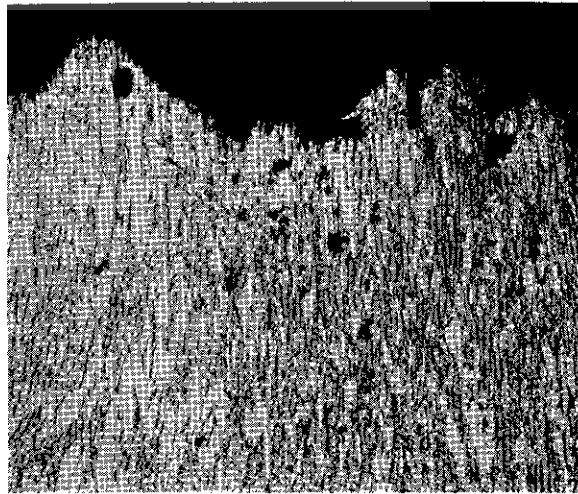
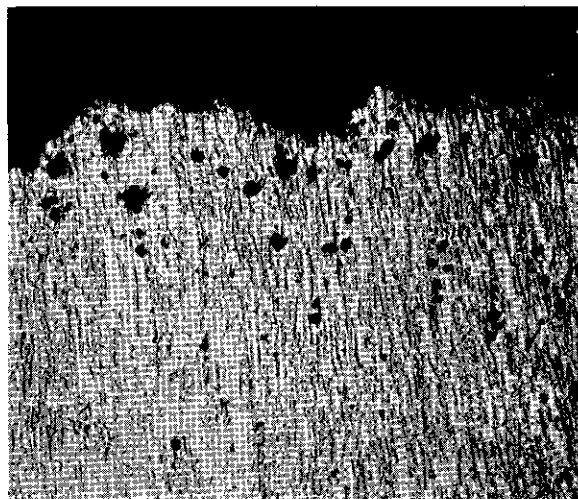


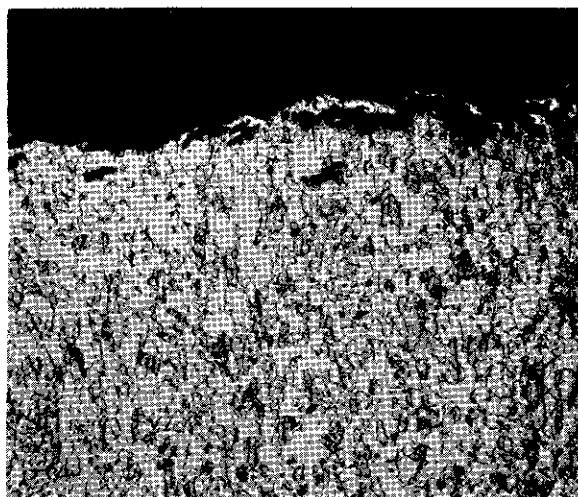
Figure 9. Effect of Hydrogen Content and Temperature on the Fracture Strength of Columbium Tested at 0.005/min.



(a)



(b)



(c)

Figure 10. Microstructures Near Fracture Surfaces of Samples Tested at a Strain Rate of 0.005/min, (a) As-Received, 1 ppm H, Tested at 25C, (b) 30 ppm H, Tested at 25C, (c) 30 ppm H, Tested at -195C, HF-HNO₃ Etch, 50X.

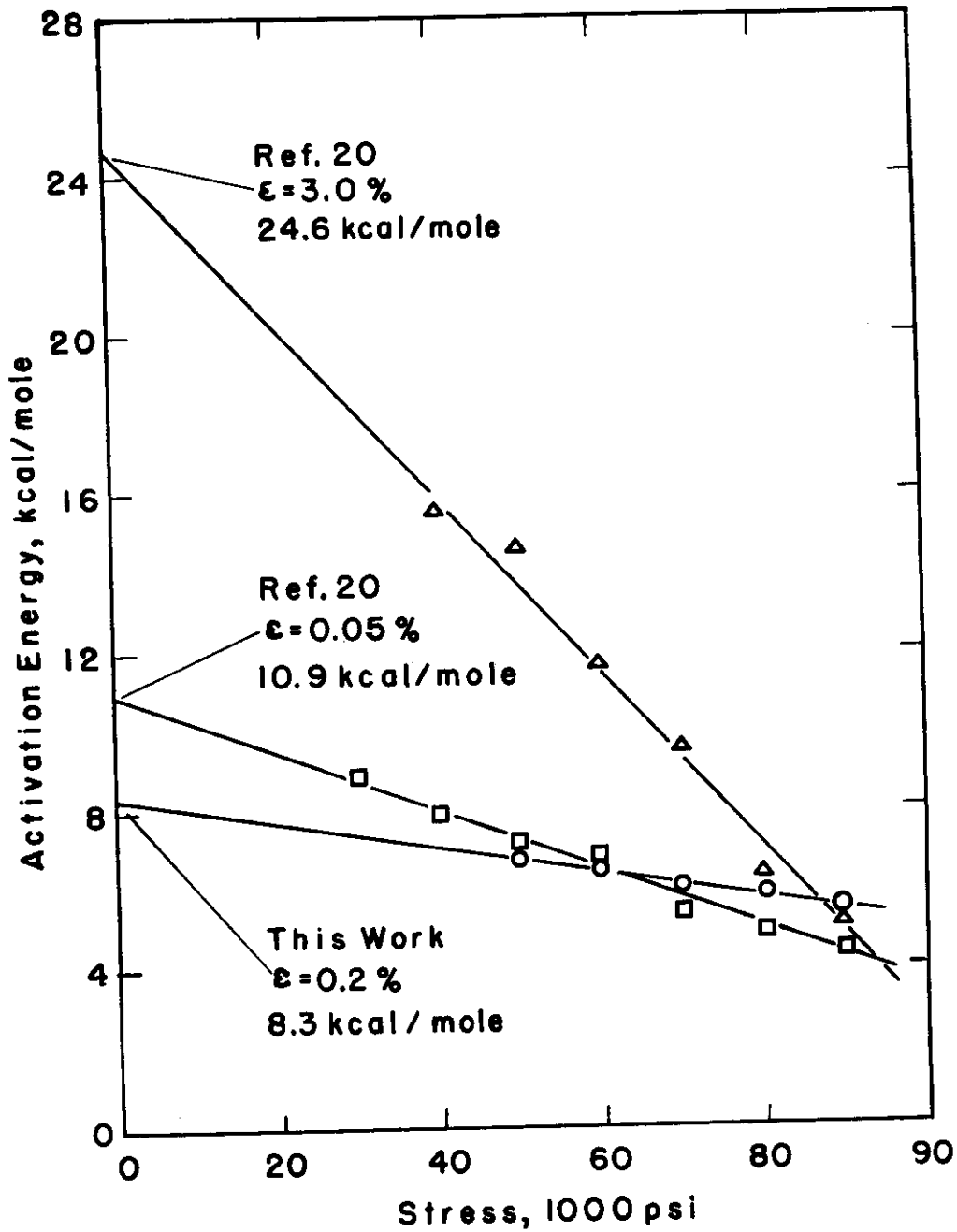


Figure 11. Apparent Activation Energy for Low Temperature Deformation of Columbium as a Function of Stress Level.

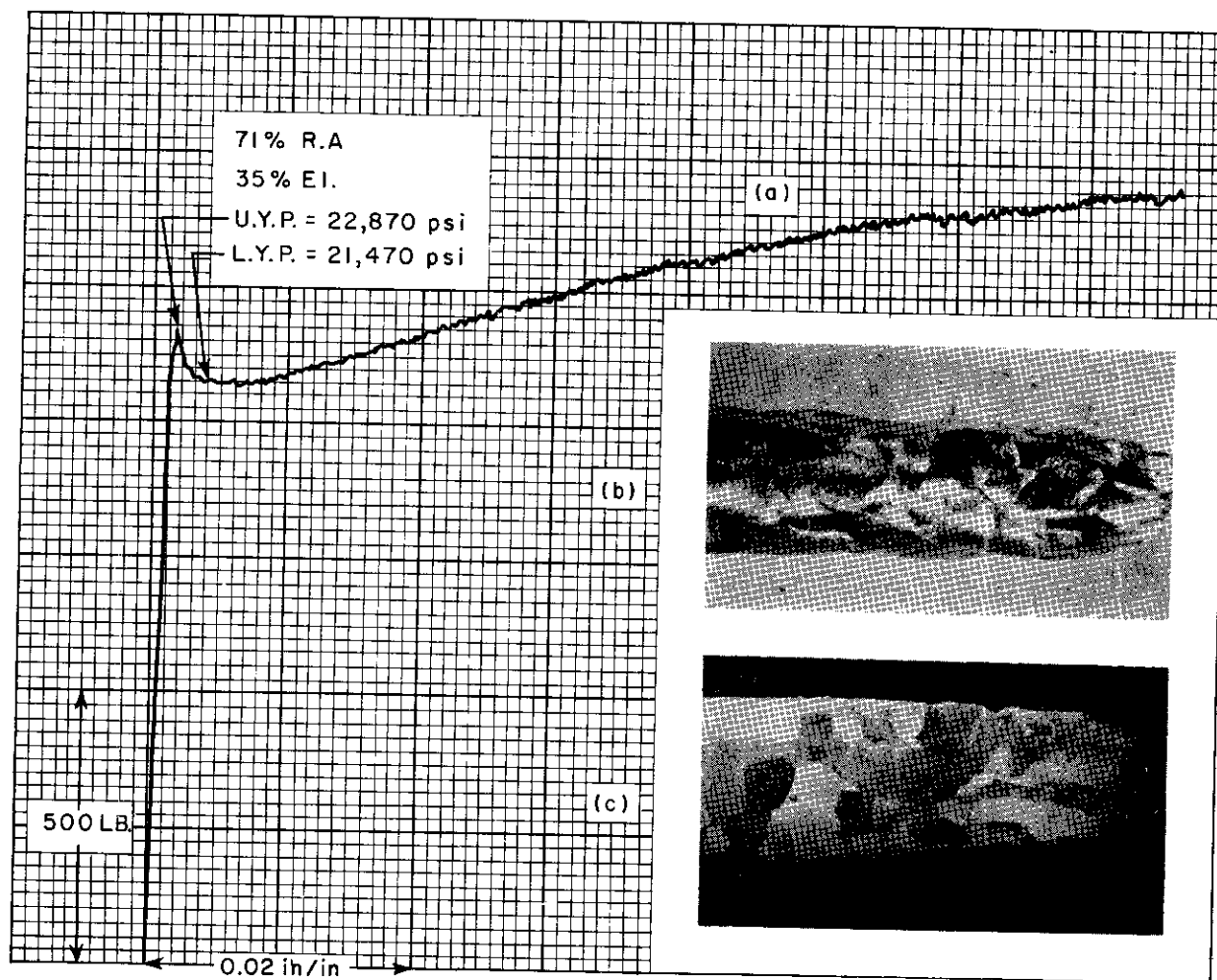


Figure 12. Sample of Columbium, Hydrogen Annealed 500C, 6 Hr, Argon Annealed 500C, 1 Hr (89 ppm H, 92 ppm O, 25 ppm N), Tested at 25C and a Strain Rate of 0.005/min. (a) Serrated Load-Strain Curve, (b) Surface of Sample After Tensile Testing, 4X, (c) Structure of Deformed Tensile Sample, 4X, HF-HNO₃ Macroetch.