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DEVELOPMENT OF PRECIPITATION STRENGTHENED COLUMBIUM BASE ALLOYS

J.A. Cornie

Astronuclear Laboratory
Westinghouse Electric Corporation

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FOREWORD

The work described in this report was carried out by personnel of the Westinghouse Astronuclear Laboratory under USAF Contract F33615-69-C-1464, entitled, "Development of Columbium Base Alloys." The contract was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Mr. J. K. Elbaum as Project Engineer.

This report describes the results of research conducted during the period 1 March 1969 to 30 September 1970.

The author wishes to acknowledge the assistance of J. Sundin (melting), C. Fitterer (forging and rolling), and E. Vandergrift (mechanical property testing) in conducting this program.

This technical report has been reviewed and is approved.

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Chief, Metals Branch
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Air Force Materials Laboratory

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I. INTRODUCTION

Recent advances in coating technology have resulted in columbium alloys being seriously considered for advanced gas turbine applications. This program was primarily concerned with developing columbium alloys for application as a turbine bucket material at service temperatures up to 2200°F. Previous studies carried out under Contracts AF 33(615)-67-C-1443 and AF 33(615)-1728[1,2] had resulted in the development of Cb-base alloys with excellent high temperature creep-rupture strength. The most attractive of these alloys, B-88 (Cb-28W-2Hf-0.067C), has a relatively high tungsten content which, while conferring excellent creep strength, results in a density penalty. Furthermore, the creep optimized treatment results in a structure having a relatively low yield strength at 1200-1600°F which presents problems in accommodating the high stresses developed in the root area of a gas turbine blade.

Studies conducted under contract AF 33(615)-67-C-1443[2] have shown that the intermediate temperature (1400°F) yield strength of Cb-base alloys can be effectively increased by strain hardening. Detailed recovery studies carried out on strain hardened B-99 (Cb-22W-2Hf-0.067C) had indicated that it is possible to retain a significant portion of the strengthening increment after short time exposure at elevated temperature. This approach would be compatible with some protective coating cycles providing accurate control of the thermal cycle is maintained.

Another approach also taken on that previous study was to add 300 to 400 ppm nitrogen to the B-99 alloy to promote the precipitation of hafnium carbonitrides (Hf(C,N). The response of the B-99N alloy (Cb-22W-2Hf-0.05C-0.04N) to thermal treatment appeared extremely promising since pronounced hardening was observed after heating solution annealed material at 1000-1200°C. Initial isothermal aging hardness data displayed double aging peaks at the 1000°C and 1100°C isotherms. Transmission electron microscopy studies had shown the aging reaction to be due to coherent precipitation. Subsequent attempts to reproduce the double aging peaks on the Cb-22W-2Hf-0.06C-0.04N alloy, however, were not successful. This indicated that the aging process is very complex and that other factors, such as local inhomogeneities or local phase relationships, may alter the aging response.

The aging response, though seemingly complex as of our present understanding, offers significant strengthening potential at the intermediate temperature range 1200°F to 1600°F. In addition, aging treatments can be relatively simple heat treatments and can potentially be incorporated into the coating thermal cycle. The purpose of this investigation, then, was to develop alloys with reproducible aging behavior suitable for the first stage gas turbine blade application and to develop fabrication and heat treating sequences that are compatible with a coating thermal cycle.

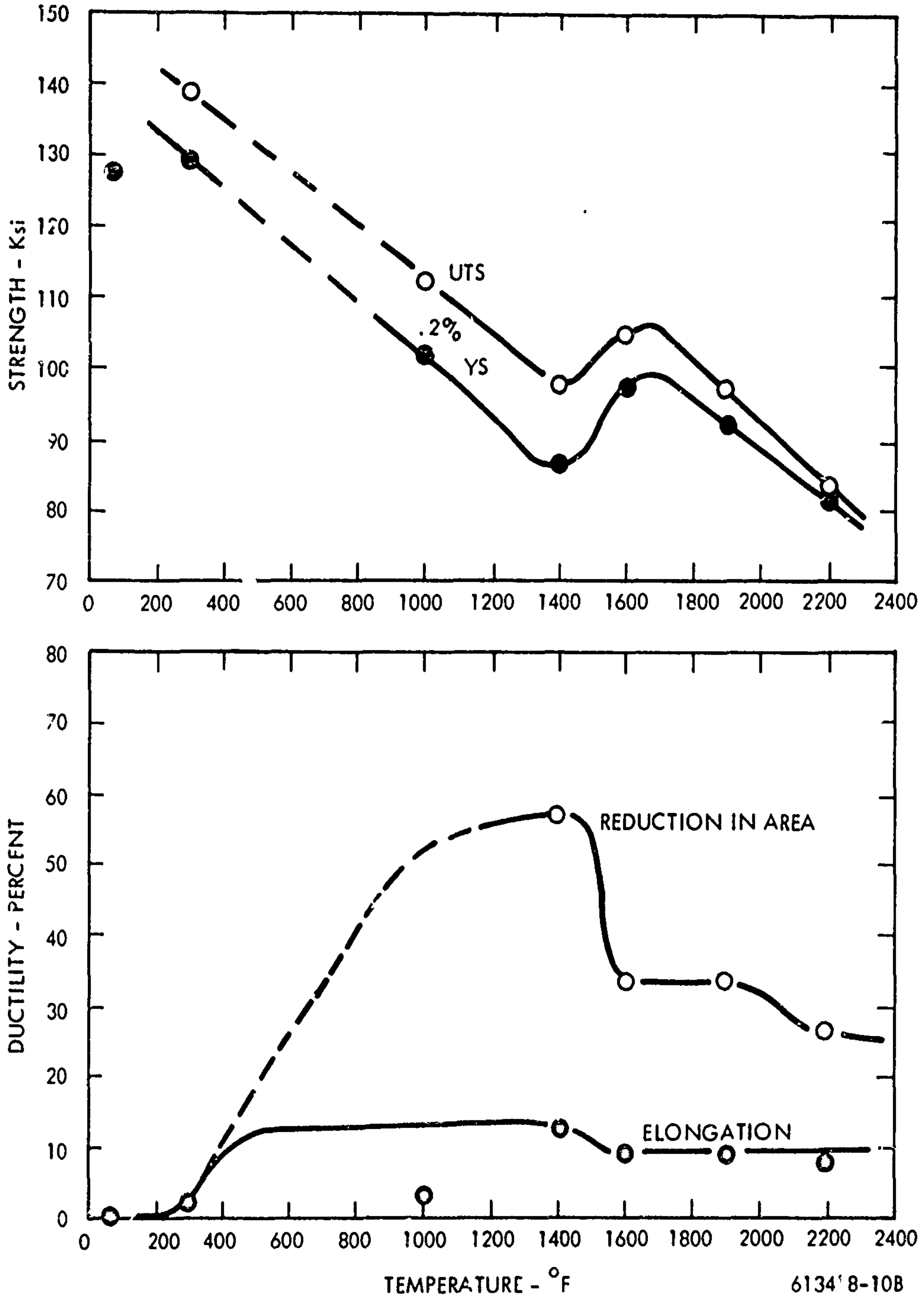


Figure 1. Variation of Tensile Properties of C-6 (Cb-22W-4Hf-0.05C-0.05N) with Temperature (Solution annealed 15 minutes at 1[illegible]00°C, rapidly cooled, then aged 2 hours at 1100°C.)

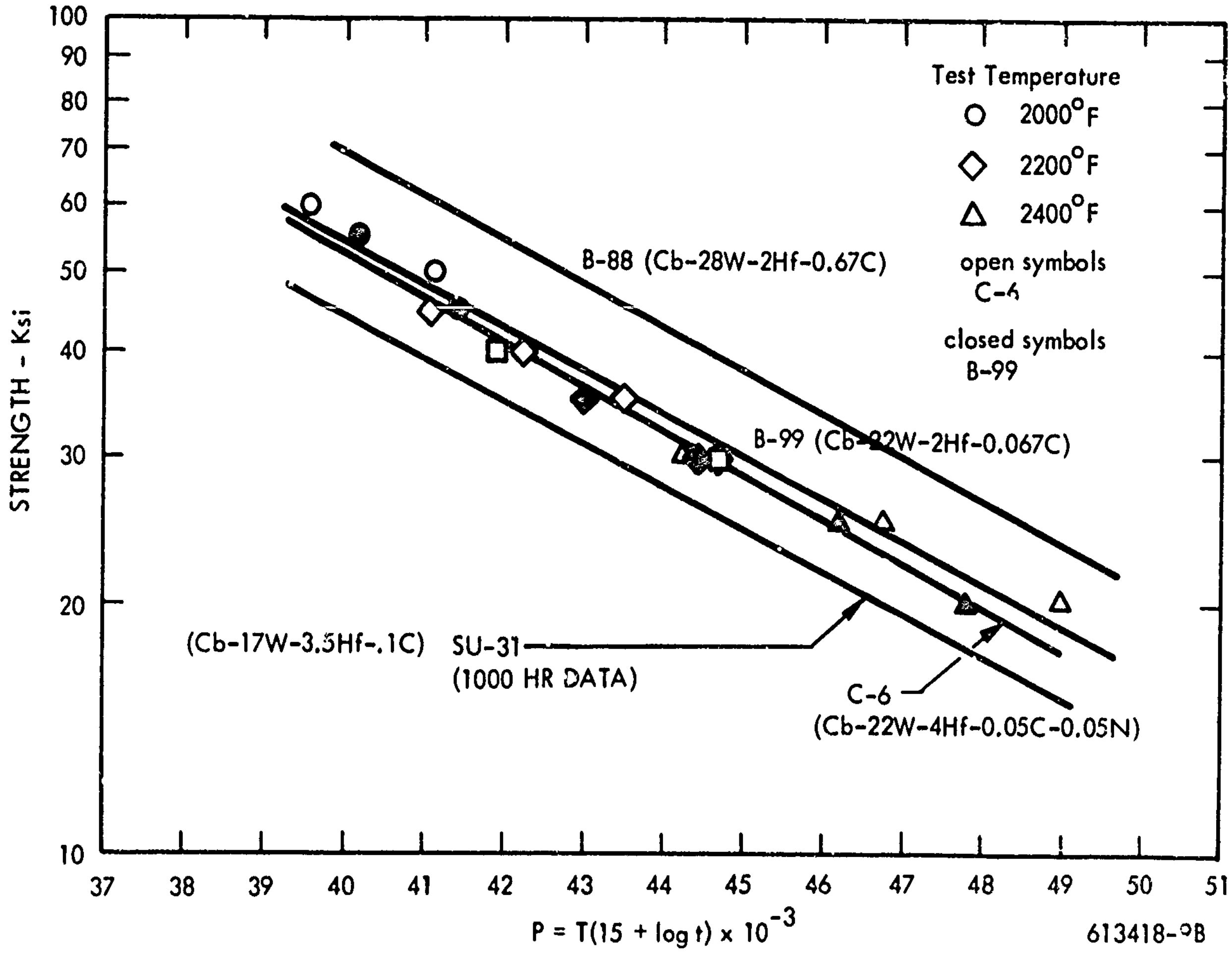


Figure 2. A Comparison of C-6 Creep Rupture Data to B-99, B-88, and SU-31

3. The aging effect is present in alloys containing as little as 250 ppm nitrogen.

4. Molybdenum is half as effective as tungsten in promoting creep resistance on an atom for atom basis.

5. Molybdenum on an atom for atom basis is equally as detrimental as tungsten in increasing the ductile to brittle transition temperature (DBTT).

III. MATERIAL PROCESSING

A. Melting

The columbium alloy compositions studied were prepared as nonconsumable electrode arc melted 250 gram button ingots and consumable electrode vacuum arc melted ingots two and three inches in diameter. Button ingots were evaluated in the as cast or as forged condition while the two and three inch diameter ingots were processed to 3/8 inch diameter rod by a combination of hot extrusion and swaging. Alloy compositions and the form of evaluation are listed below in Table 1.

Table 1. Experimental Columbium Alloys Evaluated

Alloy No.	Nominal Composition	Form
C-1	Cb-22W-2Hf-0.05C-0.04N	2" dia. ingot
C-2	Cb-22W-2Hf-0.05C-0.04N	250 gm button
C-3	Cb-22W-2Hf-0.08N	250 gm button
C-4	Cb-22W-1Zr-0.05C-0.04N	2" dia. ingot
C-5	Cb-12W-6Mo-2Hf-0.05C-0.04N	2" dia. ingot
C-6(Heat 1)	Cb-22W-4Hf-0.05C-0.04N	250 gm button
C-6(Scale up heat VAM-100)	Cb-22W-4Hf-0.05C-0.05N	3" dia. ingot
C-7	Cb-21W-3.6Mo-3.9Hf-0.05C-0.04N	2" dia. ingot
C-8	Cb-22W-2Zr-0.05C-0.05N	250 gm button

The description of the melting process for producing these forms follows:

<u>250 gm Button Ingots</u>

The constituents for the 250 gm button ingots were in the following forms:

•	Cb	sheared strips of .040" thick sheet
•	Hf	sheared strips of .040" thick sheet
•	Mo	sheared strips of .040" thick sheet
•	Zr	sheared strips of .040" thick sheet
•	C	graphite cloth
•	N	CbN powder wrapped in Cb foil

Past melting experience[2] has shown that all constituents may be added to the melt charge in stoichiometric amounts except nitrogen which must be added in an amount of 50% in excess of the nominal value.

The button ingots were consolidated by nonconsumable electrode d.c. arc melting in 3" diameter water cooled copper molds under a 1/3 atmosphere of purified argon. The melting furnace was evacuated to 1×10^{-5} torr leak checked and backfilled with high purity argon (99.995%) prior to the commencement of melting. Each button ingot was melted and turned over and remelted a minimum of three times before the final low power melting pass which minimized any surface irregularities.

Two Inch Diameter Ingots

Two inch diameter ingots were formed by first nonconsumable electrode arc melting the starting materials in a 22" x 1 1/4" x 1" deep water cooled copper trough. The melting practice was the same as previously described for button melting except that the constituents were loaded into the trough in ten 2" packets, each packet containing the nominal composition. Each trough melted ingot was remelted three times. Two trough melted ingots were welded together and then welded to a columbium adaptor to form a second melt electrode as shown in Figure 3. The second melt electrods were then consumable electrode vacuum arc melted into a two inch diameter mold.

Three Inch Diameter Ingots

The alloy C-6 was consolidated by double AC vacuum arc melting of consumable electrodes. Two first melt sandwich electrodes, weighing 40 lbs. each and 30 inches in length, were fabricated. Columbium, hafnium, and tungsten additions were assembled as 1 to 2 inch wide sheet of appropriate thickness to give the average nominal cross sectional composition. Carbon was added as graphite cloth and nitrogen was added in the form of CbN powder. The CbN was impregnated into the graphite cloth and enclosed in columbium foil envelopes. Ten 3 inch long foil envelopes containing the CbN and graphite were sandwiched between columbium strips in the electrode stack. The electrode assembly was then GTA tack welded together and GTA welded to a columbium adaptor.

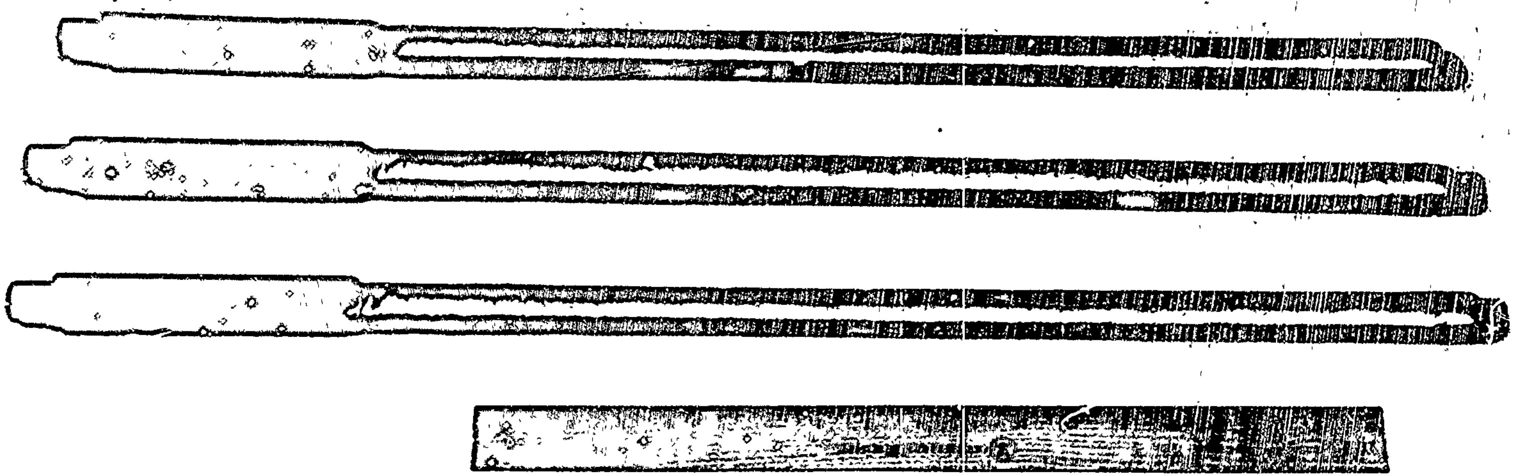


Figure 3. Second Melt Electrodes for 2 inch Diameter Ingots

The first melt electrodes were melted into a 3 1/2 inch diameter water-cooled copper mold. The two first melt ingots weighed 34 lbs. each. The ingots were quartered and reassembled into four second melt electrodes; a second melt electrode consisted of two quarters welded end to end and welded to a columbium arc furnace adaptor. The second melt electrode was melted into a 2 7/8 inch diameter mold. The four second melt ingots were surface conditioned and end cropped for extrusion. The machined billets were 2.75 inch diameter by approximately 5.5 inches long and weighed approximately 12 lbs. each. Samples for chemical analysis were taken from ingots VAM 100A, B, C, and D from the following locations:

• Metallics (W, Hf)	Machined chips from ingot end surface.
• O, N	Chunks from top skull.
• C	Machined chips from ingot end surface.

The analytical results of all the melts are given in Table 2. Alloy C-7 with a nominal composition of Cb-21W-3.6Mo-3.9Hf-.05C-.04N was analyzed at 280 ppm nitrogen or 120 ppm below the desired nominal.

Nitrogen losses will be a problem with any large-scale production of nitride containing Cb alloys. The data on the nitrogen retention during melting of nitrogen bearing columbium alloys are summarized in Table 3.

The conclusions drawn from the summary in Table 3 are:

1. The form of nitrogen addition, i.e., CbN powder or nitrided columbium strips, is not critical.

2. 20 to 40% loss of actual nitrogen added is to be expected.

3. For low levels of addition (300 to 800 ppm), a nitrogen addition of 50% in excess of nominal is required.

B. Extrusion

The initial program plan called for extrusion of the 2" diameter ingots C-1, C-4, and C-5 in the Dynapak press through 5.5:1 dies. Ingot C-1 (Cb-22W-2Hf-0.05C-0.04N) was plasma coated with molybdenum and Dynapak extruded at 1250°C producing a satisfactory extrusion.

Table 2. Chemical Analysis Results

Alloy No.	Nominal Composition	Spec.* Location	Element, %						
			W	Hf	Zr	Mo	C	N	O
C-1	Cb-22W-2Hf-0.05C-0.04N	A						0.033	
		B	21.7	1.96	---	---	0.051	0.055	0.0110
C-2	Cb-22W-2Hf-0.05C-0.08N	C	---	---	---	---	---	0.071	---
C-3	Cb-22W-2Hf-0.08N	C	---	---	---	---	---	0.084	---
C-4**	Cb-22W-1Zr-0.05C-0.04N	A	---	---	---	---	---	0.051	---
		B	21.8	---	0.92	---	0.053	0.043	0.0058
C-5	Cb-12W-6Mo-2Hf-0.05C-0.04N	A	---	---	---	---	---	0.054	---
		B	11.5	1.91	---	6.03	0.040	0.047	0.0088
C-6	Cb-22W-4Hf-0.05C-0.04N	C	---	---	---	---	---	0.046	---
C-6 (ingot heat)	VAM100A	B	21.4	4.2	---	---	0.050	0.044	0.0072
	VAM100B	B	---	---	---	---	0.054	0.044	---
	VAM100C	B	---	---	---	---	0.048	0.056	---
	VAM100D	B	21.7	4.2	---	---	0.052	0.051	0.0076
C-7	Cb-21W-3.6Mo-3.9Hf-.05C-.04N	B	---	---	---	---	---	0.028	---
		D	---	---	---	---	---	0.024	---
C-8	Cb-27W-2Zr-0.05C-0.06N	C	---	---	---	---	---	0.068	---

* A - Trough Melt
B - From Top of Ingot
C - Button Melt
D - From Swaged Rod

**Ingot subsequently remelted into button heats.

Table 3. Retention of Nitrogen in Columbium Alloys During Melting

Alloy No.	Nominal Composition	Melt Type and Sample Location	Form of Nitrogen Addition	Actual Nitrogen Added-%	Nitrogen Retained	% Loss
C-1	(Cb-22W-2Hf)-.05C-.04N	First Trough Melt 2" Ingot Top	CbN Powder CbN Powder	.06 .06	.033 .055	45 8.2
C-2	(Cb-22W-2Hf)-.05C-.08N	Button Melt	CbN Powder	.12	.071	41
C-3	(Cb-22W-2Hf)-.08N	Button Melt	CbN Powder	.12	.084	30
C-4	Cb-22W-1Zr-.05C-.04N	Trough Melt 2" Ingot Top	CbN Powder CbN Powder	.06 .06	.051 .043	15 28
C-5	Cb-12W-6Mo-2Hf-.05C-.04N	Trough Melt 2" Ingot Top	CbN Powder CbN Powder	.06 .06	.054 .047	10 22
C-6	Cb-22W-4Hf-.05C-.04N	Button Heat	CbN Powder	.06	.046	23
C-6	Cb-22W-4Hf-.05C-.05N	3" Ingot Heat	CbN Powder			
		VAM 100A		.075	.044	41.3
		VAM 100B		.075	.044	41.3
		VAM 100C		.075	.056	25.4
		VAM 100C		.075	.051	32
C-7	Cb-21W-3.6Mo-3.9Hf 0.05C-0.04N	2" Ingot Top Swaged Rod	CbN Powder	.06	.028 .024	53.3 60
VAM 98	Cb-22W-2Hf-.05C-.05N	3" Ingot Top 3" Ingot Bottom	Nitrided Cb Strip	.067	.049 .040	26.8 40.3
VAM 92	(Cb-1) Cb-30W 1Zr-.05C-.04N	3" Ingot Top 3" Ingot Bottom	Nitrided Cb Strip	.05	.035 .028	30 44

Ingot C-4 (Cb-22W-1Zr-0.05C-0.04N) was heated to 1250°C and placed in the billet container in precisely the same manner as the previous Dynapak extrusion of C-1. However, the stem sheared during the extrusion blow through no fault of the material. The billet was upset into the container and was severely cracked during its removal. Since the Dynapak extrusion press was out of commission for several weeks, the remaining 2" diameter ingots C-5 (Cb-12W-6Mo-0.05C-0.04N) and C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N) were jacketed with molybdenum and extruded at the AFML Extrusion Facilities at a reduction ratio of 5.5:1 at 3100°F. The resultant extrusions were 0.8" dia x 28" long and were of good quality.

The scale up heats of alloy C-3 were melted into 2 7/8 inch diameter molds. The ingots were surface conditioned to 2.75" and fitted into 0.125" wall thickness molybdenum extrusion jackets. The billets were extruded at the AFML metalworking facilities at 3000°F. This temperature is lower than previous extrusions of B-88 and B-99 in which occasional ruptures of the thin wall molybdenum cans caused poor quality extrusions. The resultant extrusion data are given in Table 4. All extrusions were of excellent quality except VAM-100B. In that case the die had been used on the previous extrusion VAM-100A. The ZrO_2 coating was eroded away and caused die wash during the extrusion of VAM-100B. Steel die material had melted during the extrusion and caused turbulance in the metal flow resulting in surface defects which had to be removed prior to swaging. These defects are similar in appearance to other defects encountered in the earlier B-88 alloy studies in which extrusion took place at 3200 to 3500°F. As a consequence of this experience, we recommend that dies not be used more than once and that temperatures not exceed 3000°F for extrusion of high-strength columbium alloys.

C. Swaging

No difficulties were encountered in swaging any of the materials evaluated in this program. Columbium alloys can be quite satisfactorily swaged in air to diameters above 0.4". However, below this diameter columbium alloys frequently exhibit radial cracks. This cracking is due to a combination of rapid loss of temperature due to the small rod diameter and the brittle oxide scale. Considerable loss of material can result from oxidation of the surface during swaging at temperatures of 2200 to 2500°F. For this reason and to prevent crack initiation, the molybdenum jacket residual from extrusion should be left on during swaging provided the cladding is sound.

Table 4. Summary of C-6 Extrusion Data

Extrusion Parameters	VAM-100 A	VAM-100 B	VAM-100 C	VAM-100 D
Ingot Length	5.5"	5.4"	5.25"	5.5"
Ingot Weight	12.125 lb	12.06 lb	10.1 lb	12.12 lb
Billet Length	6.625"	6.9"	6 5/8"	6 5/8"
Billet Weight	15.7 lb	15.9 lb	15.9 lb	15.9 lb
Temperature	3000°F	3000°F	3000°F	3000°F
Die	5.7:1	5.7:1	5.3:1	5.5:1
Load Maximum	380 Tons/103 ksi	420/113	410/111	390/105
Load Minimum	360 Tons/97 ksi	360/97	360/97	340/92
Ram Speed Maximum	6 ips	6 ips	6 ips	6 ips
Ram Speed Minimum	5.8 ips	6 ips	6 ips	6 ips
Reduction Ratio	5.7:1	5.5:1	5.3:1	4.5:1
Extrusion Constant (K)*	59.2 ksi	66.4 ksi	66.4 ksi	70 ksi
Extrusion Condition	Good	Fair	Good	Good

Billet Composition - Cb-22W-4Hf-.05C-.05N

Container Size - 3.072"
Container Temperature - 500°F

Die - 90° Conical, ZrO_2 Coated

Extrusion Constant (K)* = $\frac{F}{A \ln R}$

where F = extrusion force
A = cross-sectional area of container
R = reduction ration

All swaging operations during this program were conducted at 2200 to 2400°F. Heating took place in a SiC element box furance which was flooded with argon. All rod was reduced to 0.4 inches diameter, the starting stock for specimen machining.

IV. B-99N STUDIES

Early studies on the VAM-98 heat of B-99N (Cb-22W-2Hf-.05C-.04N) showed the existence of a double aging peak as shown in Figure 4. The structure associated with the second peak (12 hrs at 1100°C) shown in Figure 5 confirmed the existence of a coherent homogeneously nucleated second phase which was responsible for the aging effect. Phase extractions of samples from the 1100°C aging isotherm show a transformation from the metastable epsilon carbide in the as-solutioned condition to hexagonal $(Cb, Hf)_2C$ carbides plus a very weak cubic $(Cb-Hf)\,(C,N)_{1-x}$ carbide associated with the aging peaks. Since a coherent phase would not be retained, it was concluded that the coherent precipitate was probably a cubic (Cb,Hf)N or carbo-nitride with the very weak traces in Debye-Scherrer studies representing some overaged particles retained in the extraction.

Isothermal Aging Response of Conventionally Cooled B-99N

The double aging peak observed during the previous study could not be produced during a number of spot checks and thus the experiment was repeated. A bar of 0.4 inch diameter B-99N from the same VAM-98 heat was sectioned into 1/8" slices and wrapped individually in Ta foil. The specimens were loaded into the hot zone of a vacuum furnace with gaps between each specimen so as to allow free access of helium gas during quenching. After heating 1 hour at 1800°C in vacuo and introducing high purity helium into the chamber to increase the cooling rate to room temperature, one specimen was removed to represent the as solutioned condition. The remainder of the specimens were heated for various times at 1100°C with a specimen being removed after the desired cumulative time had been reached. Thus, each specimen experienced the same thermal cycle and environment of the preceding specimen plus an additional increment of annealing time. The resultant data are given in Table 5. An aging peak was not observed in this experiment. However, a relatively high hardness was maintained after heating for 12 hours at 1100°C.

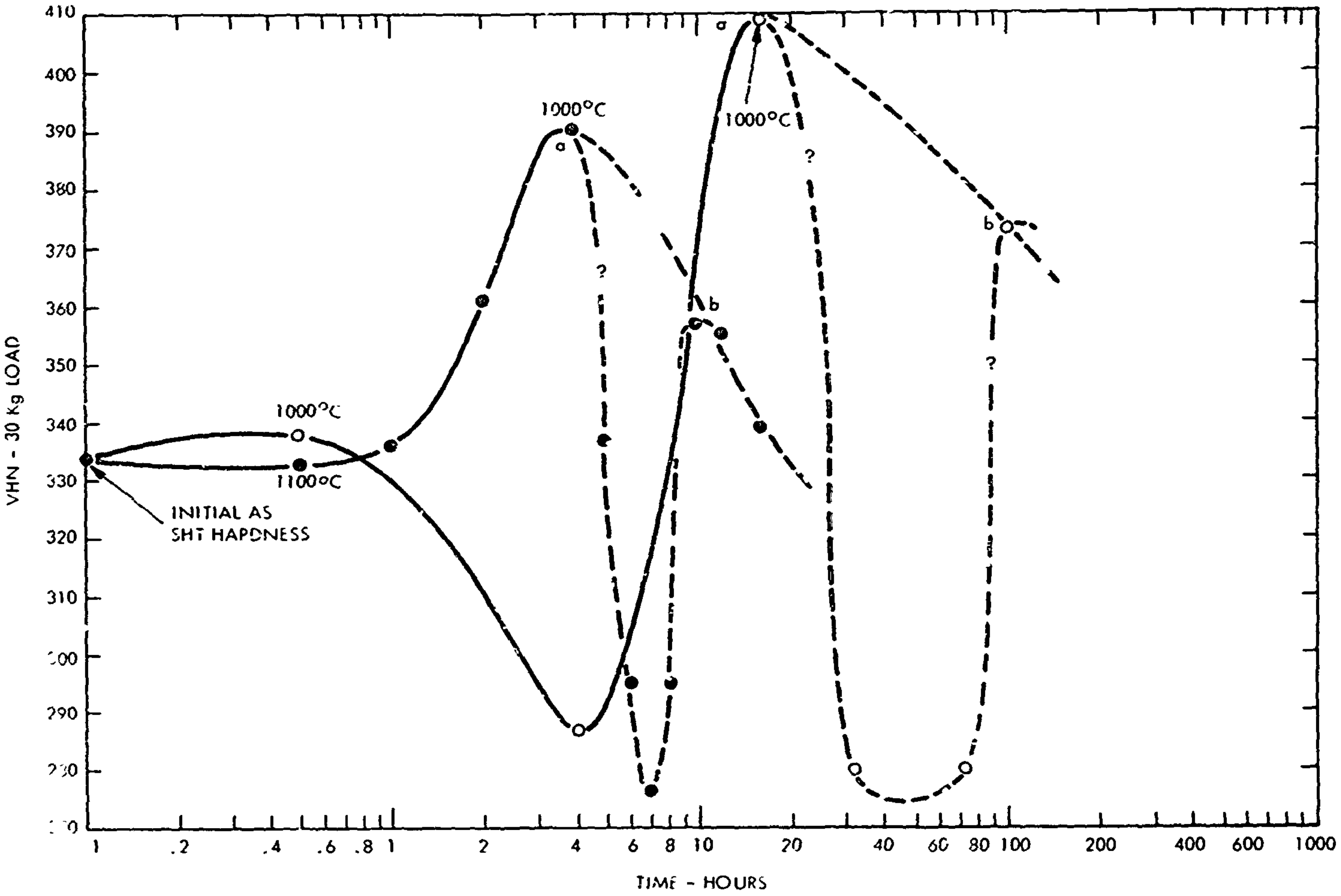


Figure 4. Isothermal Aging Behavior of B-99N (Cb-22W-2Hf-.05C-.04N) After Solution Heat Treatment

Figure 5. Transmission Electron Micrograph of Cb-22W-2Hf-0.05C-0.04N Alloy Solution Annealed 1 Hr. at 1800°C Plus Aged 12 Hrs at 1100°C 160,000X

Table 5. Aging Response of VAM-98 Solutioned 1 Hour at 1800°C, Helium Cooled Plus Aged at 1100°C

Cumulative Aging Time (Hours)	VHN	Previous Study* VHN
As-Solution Heat Treated	324	334
0.5	322	333
1	306	336
2	308	361
4	299	390
5		337
6	304	295
7		276
8	306	295
10		352
12	310	355
16	286	339
24	288	
48	298	

* Reference 2.

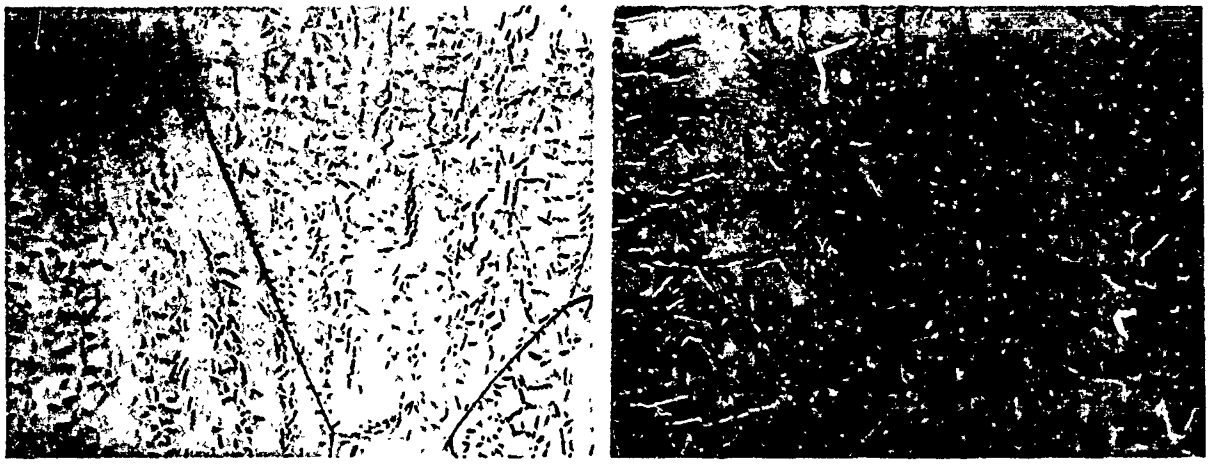
Optical photomicrographs of the heat treated specimens are presented in Figures 6 through 8. The microstructure of the as-solutioned 2 hours at 1800°C plus He cooled material (Figure 6a) is very similar in appearance to B-88 and B-99 in similar conditions. The visible precipitates are probably the metastable epsilon carbide (formerly called the zeta carbide[2]). Remnants of the epsilon carbide or carbo-nitride or its decomposition product are shown in Figure 6b after aging 1 hour at 1100°C. The most interesting and disturbing feature of the aged material in Figures 6, 7, and 8 is the occurrence of discontinuous precipitation on grain boundaries. This feature persisted through the 48 hour age. The large platelets appear to coarsen and branch during the aging exposure while fine particles within the matrix appear and then coarsen after 48 hours.

Isothermal and Isochronal Aging of Brine Quenched B-99N

The possible influence of cooling rate on the aging kinetics was briefly evaluated by brine quenching VAM-98 material (as described in Ref. 2) and performing isothermal and isochronal aging treatments on the solutioned material. The isochronal data in Figure 9 shows that the R.T. hardness response of the brine quenched material has a stable VHN 355 to 366 after aging 1 hr at temperatures up to 1200°C after which the hardness dropped rapidly to about 300 VHN after aging 1 hr at 1400°C. Another sample of VAM-98 was solutioned at 1800°C, brine quenched and subsequently aged at the 1100°C isotherm. The R.T. hardness results are given in Table 6. Here the peak of 390 VHN was re-established but the material had to be brine quenched from the solutioning temperature and the aging peak was 2 hours instead of 4 hours. Since brine quenching would be an unpractical method of producing reliable aging results in refractory metal hardware, other approaches such as alloy modification were considered.

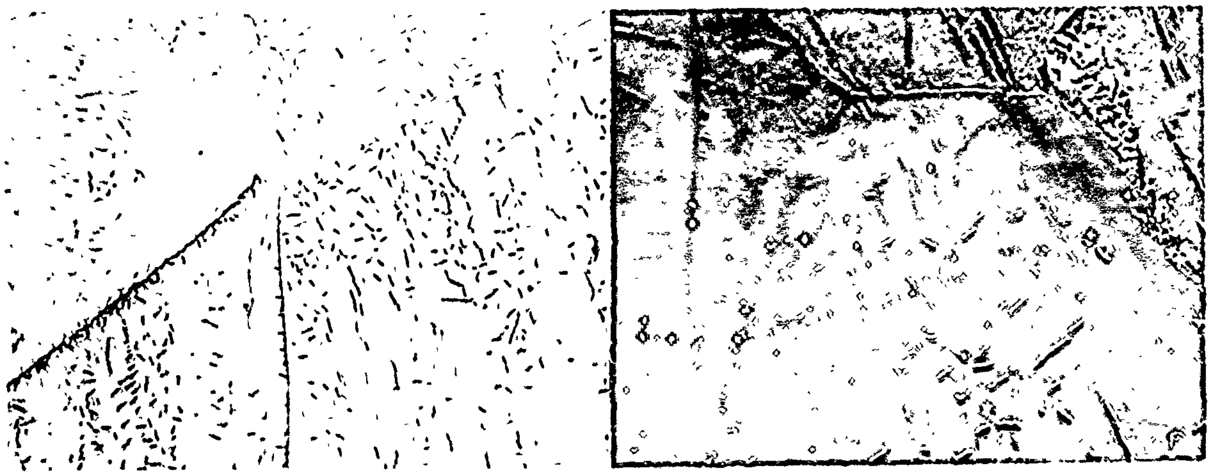
Effect of Prestraining B-99N (Cb-22W-2Hf-0.05C-0.04N) on Creep

A persisting problem in application of columbium alloys to gas turbine engines is the relatively large amount of primary strain which can be greater than 1% in the as solutioned condition. A creep specimen from the VAM -98 heat (22W-2Hf-0.05C-0.04N) was prestrained above the solvus temperature 1800°C (3270°F) to evaluate the effects of precipitation on dislocations



(a) As Solutioned 2 Hrs. at 1800°C (500X)
(No. 20,566)

(1500X)



(1500X)

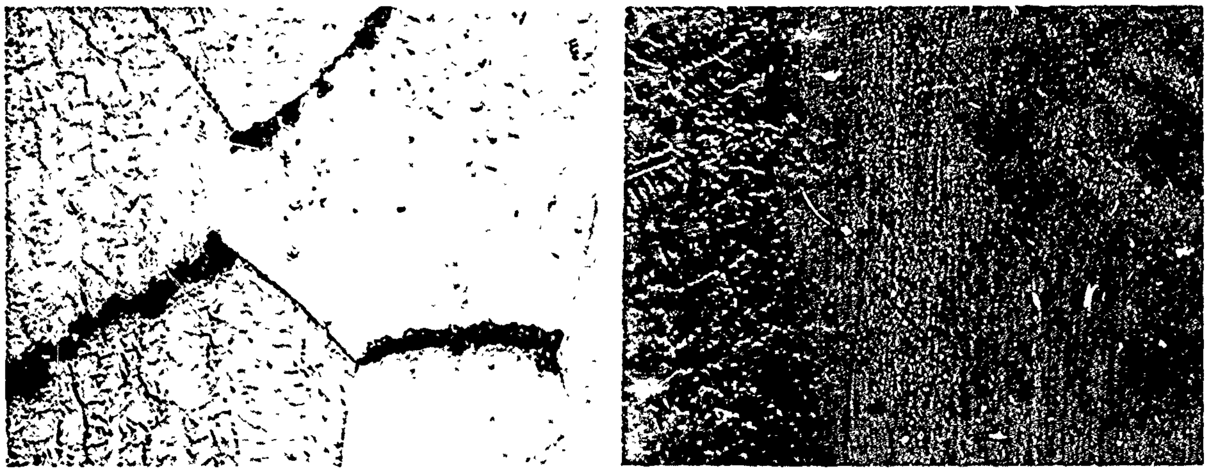
(b) Aged 1 Hr. at 1100°C (500X)
(No. 20,569)

Figure 6. Photomicrographs of B-99N
(a) As Solutioned at 1800°C + He Cool
(b) (a) Plus 1 Hr. at 1100°C

(a) Aged 4 Hrs. at 1100°C (500X) (1500X)
(No. 20,570)

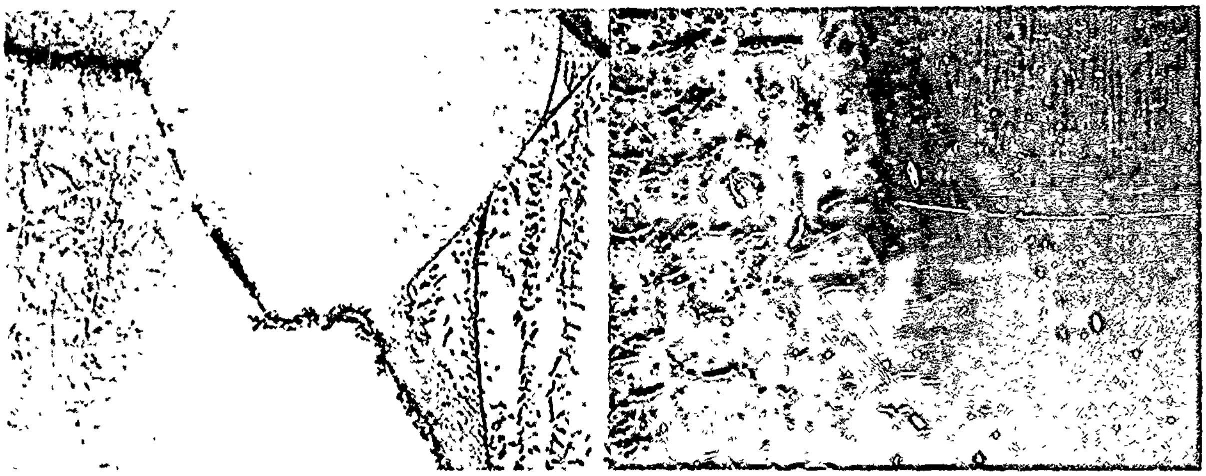
(b) Aged 16 Hrs. at 1100°C (500X) (1500X)
(No. 20,574)

Figure 7. Photomicrographs of B-99N Solutioned 2 Hrs. at 1800°C + Aged
(a) 4 Hrs. at 1100°C
(b) 16 Hrs. at 1100°C



(1500X)

(a) Aged 24 Hrs. at 1100°C (500X)
(No. 20,757)



(1500X)

(b) Aged 48 Hrs. at 1100°C (500X)
(No. 20,576)

Figure 8. Photomicrographs of B-99N Solutioned 2 Hrs. at 1800°C, He Cooled + Aged (a) 24 Hrs. at 1100°C (b) 48 Hrs. at 1100°C

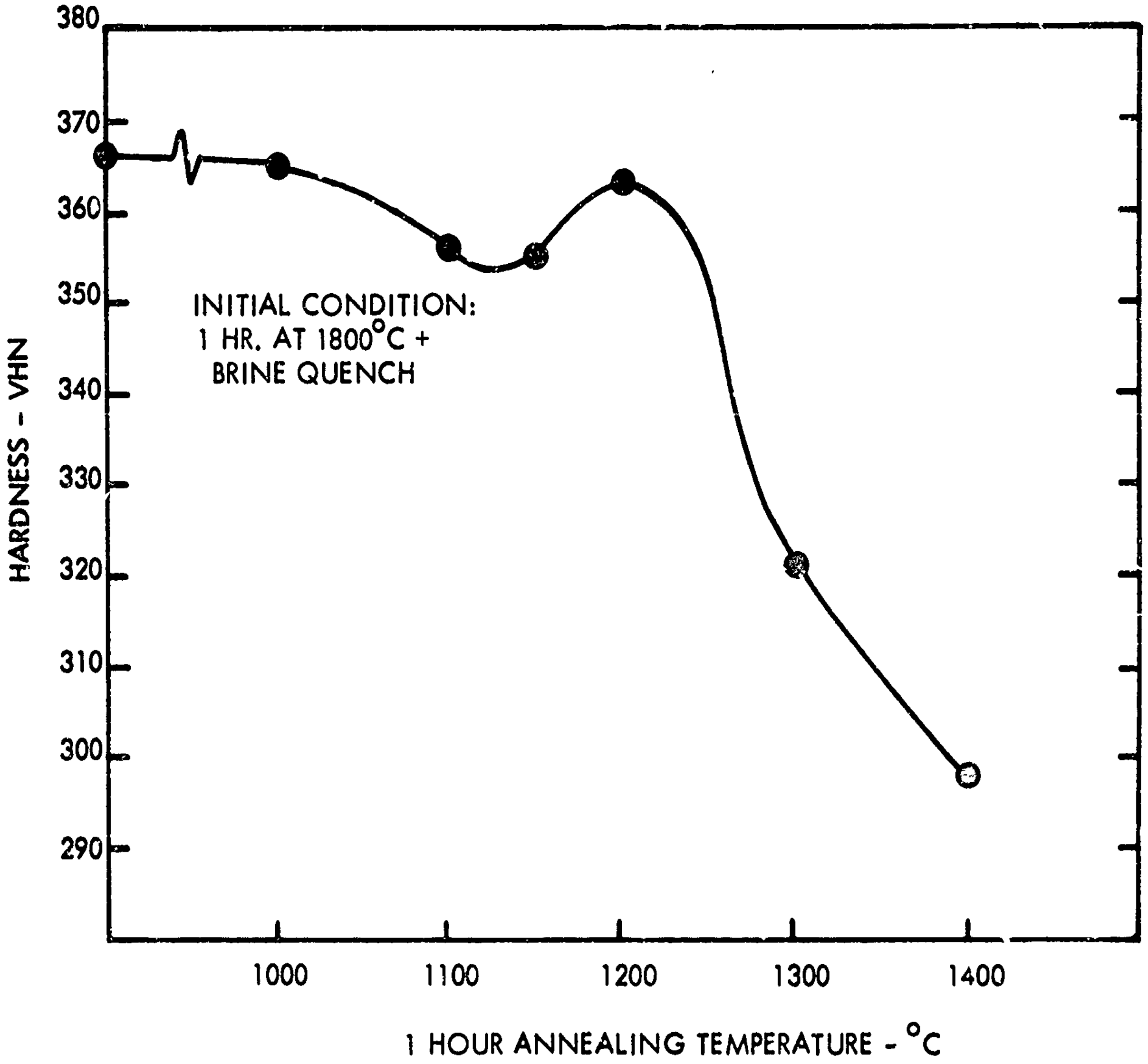


Figure 9. Isochronal Aging Behavior of Brine Quenched B-99N (Cb-22W-2Hf-0.05C-0.04N)

Table 6. Hardness of VAM-98 (Cb-22W-2Hf-0.05C-0.04N) as a Function of Heat Treatment

Condition	Hardness (VHN)
A. Solution Annealed 1 Hr. at 1800°C + Brine Quenched	351
B. A plus aged 2 Hrs. at 1100°C	390
C. A plus aged 4 Hrs. at 1100°C	357
D. A plus aged 7 Hrs. at 1100°C	317

generated during straining above the interstitial solvus. The effect of this high temperature prestrain on the 1205°C (2200°F) creep properties were evaluated. Although the target prestrain was 5-10%, the total strain was limited to 4% to prevent non-uniform straining. The resultant creep curve shown in Figure 10 shows some reduction in the amount of primary strain from the as annealed 1 hour at 1800°C specimens. A second specimen was solutioned 1 hour at 1800°C and prestrained 9% at 870°C (1600°F). The creep curve of this specimen is also given in Figure 10. The minimum creep rates for the three specimens are similar although primary strain is significantly reduced in the prestrained specimens. A direct comparison between the 1800°C (3270°F) and 870°C (1600°F) prestraining temperatures are confounded by the low (4%) prestrain obtained on the 1800°C specimen.

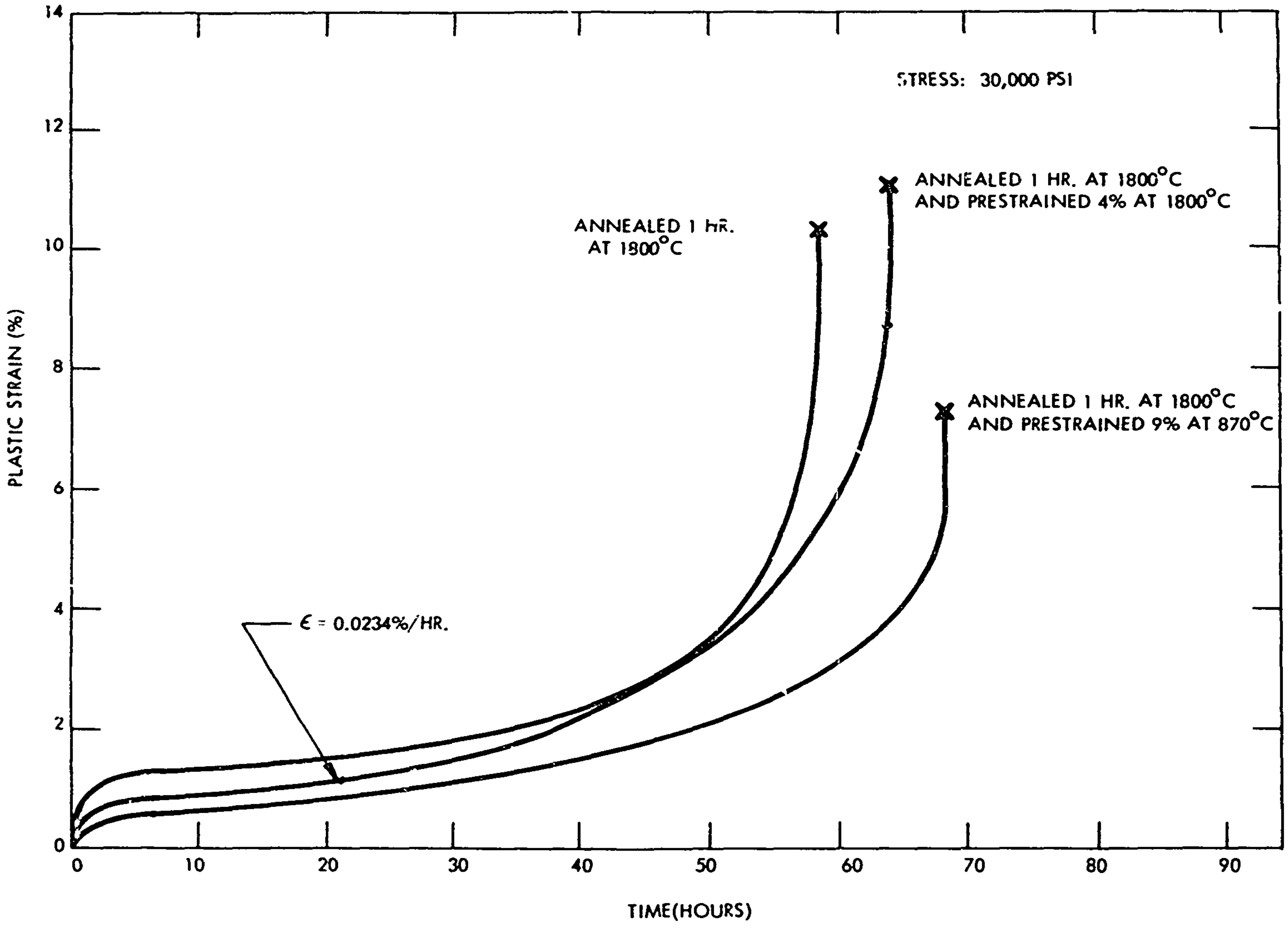


Figure 10. Creep Curves of Cb-22W-2Hf-0.05C-0.04N (VAM-98) at 2200°F (1205°C) and 30,000 psi

V. CRITERIA FOR ALLOY DESIGN

As the application of high strength columbium alloys to gas turbines comes closer to reality, the properties needed for such an application are becoming increasingly refined. The goals of this alloy development program have been established as follows:

1. 0.2% yield strength 1200°F-1400°F -- 120,000 psi
2. Rupture life at 2200°F and 30,000 psi -- 150 hrs.
3. Minimum creep rate at 2200°F and 30,000 psi -- 0.01%/hr.
4. Minimum elongation from ambient to 2200°F -- 5%

Not specified but implied in the program goals is an additional goal of maintaining the density near the level of B-99 (Cb-22W-2Hf-0.067C) at about 0.36 lb/in^3. The alloys developed during previous studies(1,2,3) miss these stated goals on one or more counts:

- B-88 (Cb-28W-2Hf-0.067C) has a 35,000 psi 150 hr. rupture life at 2200°F but is too dense at 0.373 lb/in^3 and has only a 55,000 psi yield strength at 1400°F in the reference condition.

- B-99 (Cb-22W-2Hf-0.067C) has only 26,000 psi 150 hr. rupture life at 2200°F and insufficient 1200 to 1600°F yield strength in the reference condition.

Solid Solution Solute Additions

In designing an alloy composition for the stated application, a balance must be struck between addition of sufficient solute for creep resistance but not so much as to increase (1) density beyond 0.36 lb/in^3 and (2) ductile-brittle transition temperature above room temperature.

A plot of stress for 150 hour rupture life versus atom percent tungsten in recrystallized Cb-W-Hf-C alloys is shown in Figure 11. The target property of 30,000 psi stress for 150 hour rupture would be met by an alloy containing an effective tungsten content of 14.3 a/o. The word "effective" is underscored because other solutes such as molybdenum may be substituted for a portion of the tungsten in order to reduce the alloy density. McAdams(4) has ranked the strengthening effects of potential solid solution strengtheners in columbium as compared to tungsten, the most effective strengthener. McAdam's data in Figure 12 shows that a molybdenum substitution

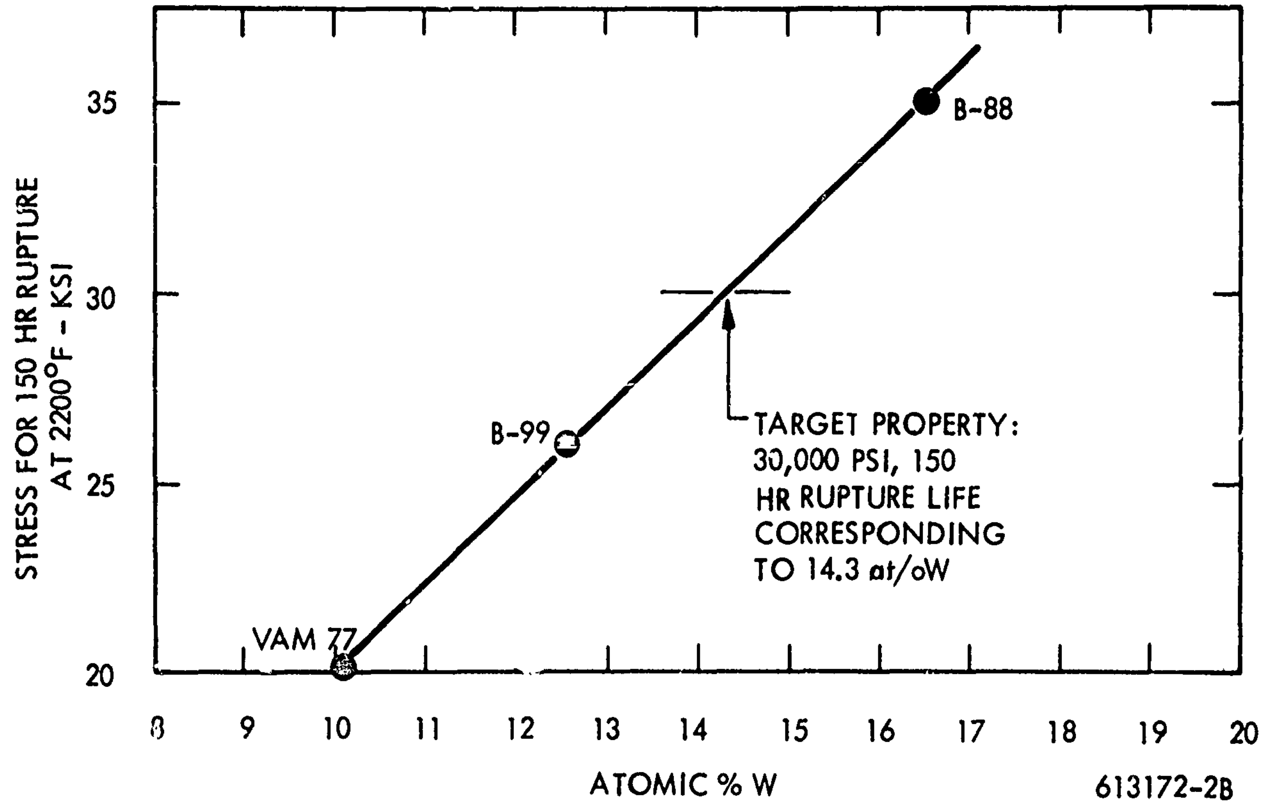


Figure 11. Effect of Atomic Percent Tungsten on the 150 Hr. Rupture Life of Cb-W-Hf-C Alloys

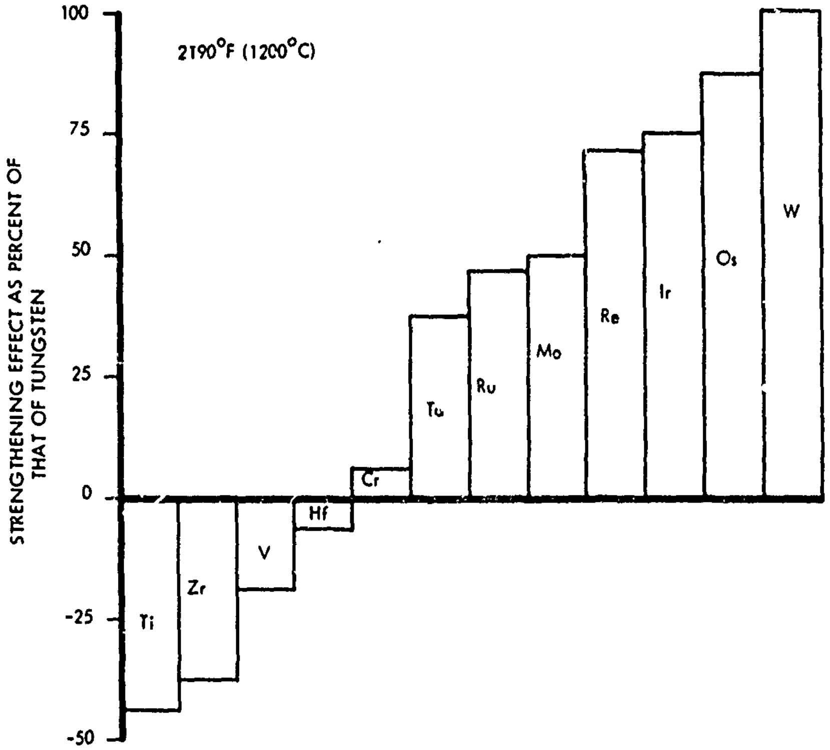


Figure 12. Strengthening Effect in Columbium of Selected Substitutional Solutes as Compared to Tungsten (Reference 4)

for tungsten in Cb must be done on a 2 a/o Mo for 1 a/o W basis if creep strength is to be maintained at a given level. Zirconium may likewise be substituted for hafnium but would require the addition of approximately 0.35 a/o W for each a/o Zr substituted.

The DBTT ductile-brittle transition temperature consideration is also related to solute content. Both tungsten and molybdenum increase the DBTT of columbium. Although there is very little substantiating data, most alloy developers assume that one atom percent molybdenum has the same effect as 1 atom percent tungsren in increasing the DBTT. (This assumption was validated and is documented in this study). B-88, in the reference condition (1 hr. at 1700°C) containing 16.5 a/o W, had an elongation of 11% at room temperature. The hardening due to the aging reaction of nitride containing alloys will no doubt increase the DBTT. For that reason a solute limit of 16 a/o W +Mo was set as a boundary condition for the alloy design.

Data discussed later in this report shows that 2.4 a/o (4 w/o) Hf in the C-6 alloy resulted in a strong age hardening effect and can potentially meet the yield 1400°F yield strength requirement. In the absence of more refined data on the amount of Hf (or other reactive metals required to produce the aging effect in nitride containing alloys) the 2.4 a/o reactive metal level was set as that Hf or Zr content required in the optimized alloy. A substitution of Zr for Hf is tempting in order to reduce alloy density. However McAdam's data shows that additional tungsten would have to be added to compensate for the loss of creep strength.

The optimized alloy based on Hf as the reactive element addition would contain 14.3 a/o W-2.4 a/o Hf-.44 a/o C-.38 a/o N. The density of this base would be about .37. To reduce the density to the target .36, some Mo would have to be added. The alloy C-7(Cb-21W-3.6Mo-3.9Hf-.05C-.04N) was designed in response to the creep and density restrictions given in Figures 11 and 13 above. McAdam's data indicates the relative effectiveness of Mo as a creep strengthener. However, data did not exist as to the effect of molybdenum on the DBTT relative to tungsten. Since ductility and workability are important a preliminary scale up heat of C-7 was consolidated and processed to rod stock.

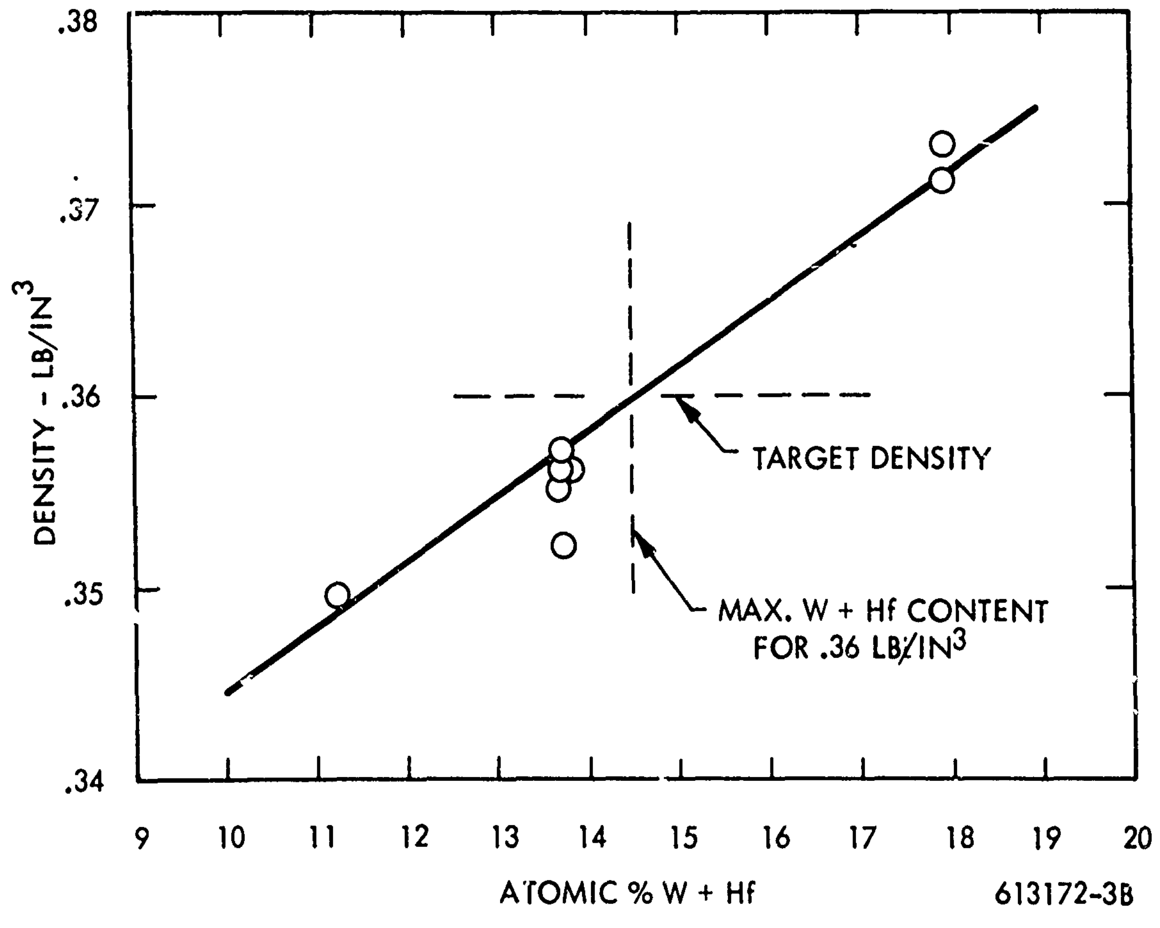


Figure 13. Effect of Atomic Percent Tungsten Plus Hafnium on the Density of Cb-W-Hf Alloys

Mechanical property data presented in the next sections verified the above approach for optimizing creep and density. However, a DBTT study on C-1, C-5, and C-7 shows molybdenum to be equally detrimental as tungsten in increasing the DBTT.

The alloy C-6 was selected, by virtue of its demonstrated fabricability and potential for lower DBTT, as the scale-up heat for alloy characterization.

VI. AGING STUDIES OF EXPERIMENTAL ALLOYS

Effect of Nitrogen and Hf Concentration on Aging

A double aging peak was observed at 1100°C at 4 and 12 hours in the B-99N alloy (Cb-22W-2Hf-0.05C-0.04N) in the solutioned plus quick cooled condition.[2] Subsequent attempts to repeat this experiment on material from the same heat were unsuccessful. Possible explanations of the inconsistent observations of this phenomena include:

1. The aging effect could be due to local Hf inhomogenities, i.e., the aging reaction will only occur when the proper phase relationships exist. The 3 inch segment of bar stock selected for sectioning into aging specimens was enriched in Hf as compared to adjacent sections of rod from the same heat.
2. Insufficient nitrogen may have been present to properly display the aging effect.

These two possibilities were tested by repeating the aging experiments on the alloys C-2 (Cb-22W-2Hf-0.05C-0.08N), C-3 (Cb-22W-2Hf-0.08N) and C-6 (Cb-22W-4Hf-0.05C-0.04N). Alloy C-2 is charged with twice the nitrogen content of B-99N and is a test of condition 2. Alloy C-3 contains no carbon and may indicate the interaction between carbon and nitrogen when compared to C-2. The Hf content was doubled in C-6 in order to test explanation 1.

Specimens of C-2, C-3, and C-6 were taken from forged buttons and were solutioned 1 hour at 2000°C to insure solutioning and homogenization. These specimens were aged for varying times at 1100°C. The resultant plot of hardness versus aging time at 1100°C in Figure 14 shows hardness peaks after aging 4 and 12 hours for the C-6 alloy but relatively little response in the C-2 and C-3 alloys. A lesser peak was observed in alloy C-2 after 2 and 12 hours.

A metallographic examination was conducted on the specimens used for the hardness measurements plotted in Figure 14. These photomicrographs are shown in Figures 15 through 23 for the alloys C-2, C-3 and C-6. The initial condition (as solutioned 1 hour at 2000°C) for the

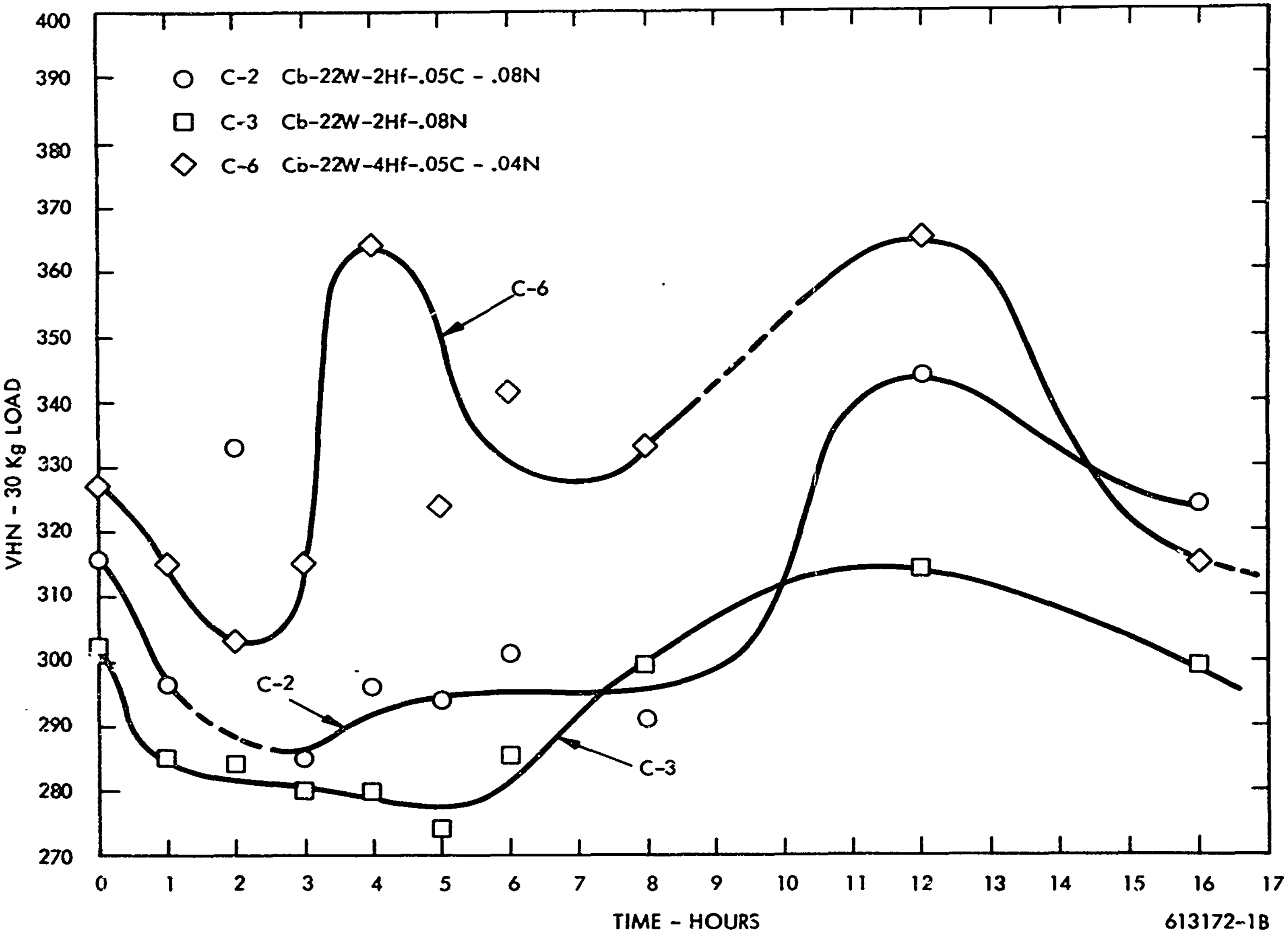


Figure 14. 1100°C Aging Behavior of Cb Alloys C-2, C-3 and C-6 Solutioned 1 Hour at 2000°C, He Cooled and Aged at 1100°C

Cb-22W-2Hf-
0.05C-0.08N

C-2 As SHT 1 Hr. at 2000°C 20,752

Cb-22W-2Hf-
0.08N

C-3 As SHT 1 Hr. at 2000°C 20,753

Cb-22W-4Hf-
0.05C-0.04N

C-6 As SHT 1 Hr. at 2000°C 20,754

Figure 15. Microstructure of Alloys C-2, C-3 and C-6 Button Forged at 1250°C, Solutioned 1 Hr. at 2000°C, plus He Cooled to Room Temperature (Mag = 1500X)

Cb-22W-2Hf-0.05C-0.08N

C-2 1 Hr. at 1100°C 20,755

Cb-22W-2Hf-0.08N

C-3 1 Hr. at 1100°C 20,756

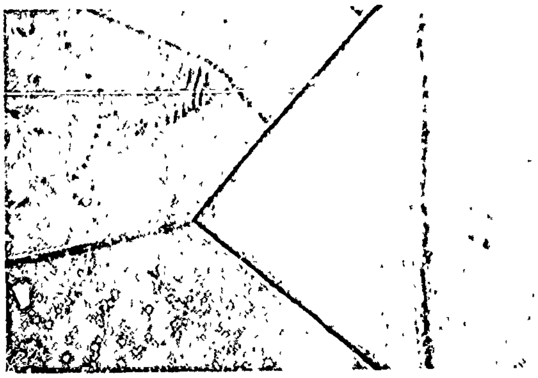
Cb-22W-4Hf-0.05C-0.04N

C-6 1 Hr. at 1100°C 20,757

Figure 16. Microstructure of Cb Alloys Solutioned as Shown in Figure 15 and Aged 1 Hr. at 1100°C (Mag = 1500X)

Cb-22W-2Hf-0.05C
-0.08N

C-2 2 Hrs. at 1100°C 20,758



Cb-22W-2Hf-0.08N

C-3 2 Hrs. at 1100°C 20,759

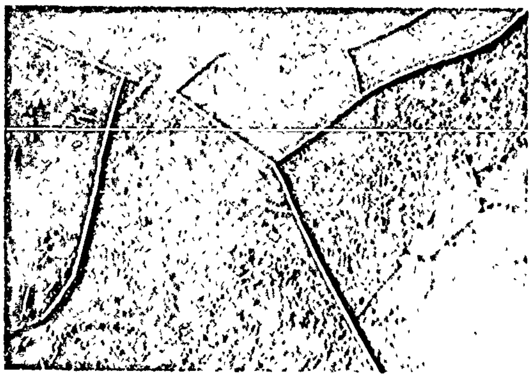
Cb-22W-4Hf-0.05C-
0.04N

C-6 2 Hrs. at 1100°C 20,760

Figure 17. Microstructure of Cb Alloys Heat Treated as Shown in Figure 16 Plus an Additional 1 Hr. for a Total Aging Time of 2 Hrs. at 1100°C (Mag = 1500X)

Cb-22W-2Hf-0.05C-0.08N

C-2 3 Hrs. at 1100°C 20,761



Cb-22W-2Hf-0.08N

C-3 3 Hrs. at 1100°C 20,762

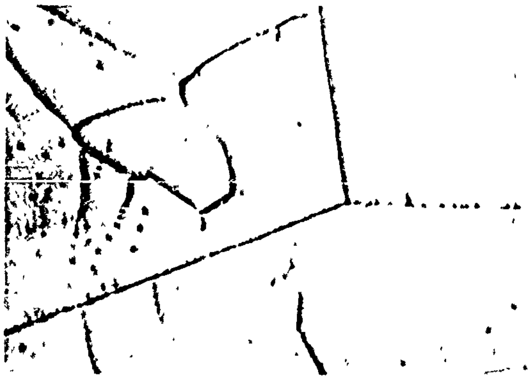
Cb-22W-4Hf-0.05C-0.04N

C-6 3 Hrs. at 1100°C 20,763

Figure 18. Microstructure of Cb Alloys Heat Treated as Shown in Figure 17 Plus an Additional 1 Hr. for a Total Aging Time of 3 Hrs. at 1100°C (Mag = 1500X)

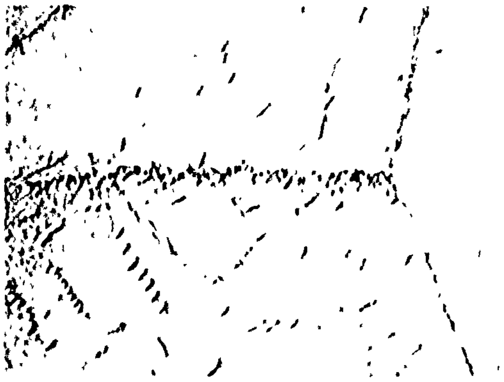
Cb-22W-2Hf-0.05C-0.08N

C-2 4 Hrs. at 1100°C 20,764



Cb-22W-2Hf-0.08N

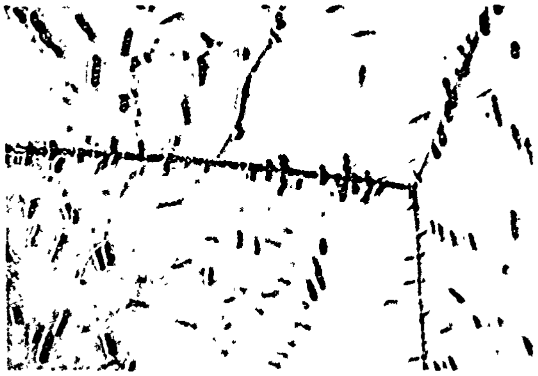
C-3 4 Hrs. at 1100°C 20,765



Cb-22W-4Hf-0.05C-0.04N

C-6 4 Hrs. at 1100°C 20,766

Figure 19. Microstructure of Cb Alloys Heat Treated as Shown in Figure 18 Plus an Additional 1 Hr. for a Total of 4 Hrs. at 1100°C - Time of First Aging Peak in the High Hf Alloy C-6 (Mag = 1500X)



Cb-22W-2Hf-0.05C-0.08N

C-2 5 Hrs. at 1100°C 20,774

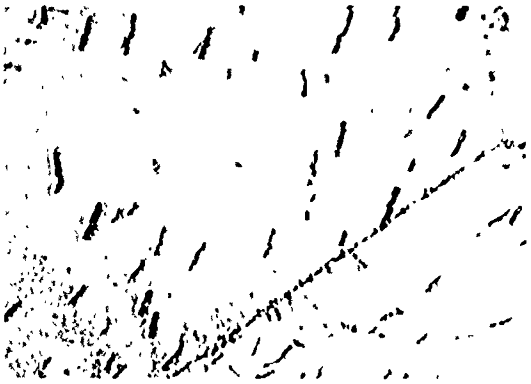
Cb-22W-2Hf-0.08N

C-3 5 Hrs. at 1100°C 20,775

Cb-22W-4Hf-0.05C-0.04N

C-5 5 Hrs. at 1100°C 20,776

Figure 20. Microstructure of Cb Alloys Heat Treated as Shown in Figure 19 Plus an Additional 1 Hr. for a Total of 5 Hrs. at 1100°C (Mag = 1500X)



Cb-22W-2Hf-0.05C-
0.08N

C-2 8 Hrs. at 1100°C 20,780

Cb-22W-2Hf-0.08N

C-3 8 Hrs. at 1100°C 20,781

Cb-22W-4Hf-0.05C-
0.04N

C-6 8 Hrs. at 1100°C 20,782

Figure 21. Microstructure of Cb Alloys Heat Treated as Shown in Figure 20 Plus Additional Increments of 1 and 2 Hrs. for a Total of 8 Hrs. at 1100°C (Mag = 1500X)

Cb-22W-2Hf-0.05C-0.08N

C-2 12 Hrs. at 1100°C 20,783

Cb-22W-2Hf-0.08N

C-3 12 Hrs. at 1100°C 20,784

Cb-22W-4Hf-0.05C-0.04N

C-6 12 Hrs. at 1100°C 20,785

Figure 22. Microstructure of Cb Alloys Heat Treated as Shown in Figure 21 Plus an Additional 4 Hrs. for a Total of 12 Hrs. at 1100°C Time of Second Aging Peak in the High Hf Alloy C-6 (Mag = 1500X)

Cb-22W-2Hf-0.05C-0.08N

C-2 16 Hrs. at 1100°C 20,786

Cb-22W-2Hf-0.08N

C-3 16 Hrs. at 1100°C 20,787

Cb-22W-4Hf-0.05C-0.04N

C-6 16 Hrs. at 1100°C 20,788

Figure 23. Microstructure of Cb Alloys Heat Treated as Shown in Figure 22 Plus an Additional 4 Hrs. for a Total of 16 Hrs. at 1100°C (Mag = 1500X)

three alloys is shown in Figure 15. Precipitation during cooling is evident in all three alloys although the carbon containing heats (C-2 and C-6) show more abundant precipitation. The precipitation appears more abundant in the C-6 alloy in spite of the lower total interstitial content. The initial precipitates are most likely carbides.

The changes in optical microstructure of the carbon free, high nitrogen C-3 alloy (Cb-22W-2Hf-0.08N) with aging time is not marked, though extensive decoration of substructure is developed (Figure 20) and a general background nonresolved precipitation becomes evident after 12 and 16 hours at 1100°C (Figures 22 and 23). The correlation between hardness and microstructure is not obvious in the carbon free C-3 alloy.

The C-2 (Cb-22W-2Hf-0.05C-0.08N) alloy is essentially a high nitrogen variation of the B-99N alloy. The age hardening behavior is very similar to the later B-99N data reported previously in section IV. The aged microstructure is very similar to that reported earlier for B-99N with the exception that massive grain boundary precipitates were not observed. Like B-99N, C-2 appears to transform from platelet dominated appearance (Figures 16 and 17) to a general, fine background type precipitate that is below the limits of optical resolution (Figure 17) and with the increasing aging time back to a platelet type precipitate with an increasing profusion of fine but coarsening background precipitates that are optically resolvable.

Alloy C-6, the high hafnium modification of the B-99N composition, shows the characteristic double aging peak observed earlier in B-99N at the same times (although the interpeak valley is not as low in hardness). The platelets and substructure decoration present in the as-solutioned plus helium cooled material degenerates after 1 hour at 1100°C to fine unresolved background precipitates that remain throughout aging apparently coarsening after 16 hours at 1100°C to fine but resolvable precipitates (Figure 23).

Comparison of Zr to Hf Additions for Nitride Age Hardening

Aging experiments were also conducted on alloys C-4 (Cb-22W-1Zr-0.05C-0.04N), C-8 (Cb-22W-2Zr-0.05C-0.05N), C-5 (Cb-12W-6Mo-2Hf-0.05C-0.04N), and the initial scale-up alloy C-7 (Cb-21W-3.64Mo-3.9Hf-0.05C-0.04N) at 1100°C. Aging studies of alloys C-7 and C-5 were made on sections of swaged rod, alloys C-4 and C-8 on segments cut from button melts and alloy C-6 (Cb-22W-4Hf-0.05C-0.04N) on segments cut from forged buttons. The hardnesses of these alloys are plotted as [illegible]tion of aging time at 1100°C in Figure 24. These data show an extremely high hardness for the C-8 alloy (2 a/o Zr) as compared to the absence of hardening response in alloy C-4 (1 a/o Zr and slightly less N). Double aging peaks were noted in alloy C-8 after 1 hr and 8 hrs at 1100°C at 432 VHN and 403 VHN respectively. Alloy C-4 containing only 1% Zr did not display the first peak (peak "a") but did show a modest second peak ("b") at 8 hrs. These data compare quite well to Chang's(3) aging data on Cb1 (Cb-30W-0Zr-0.06C-0.04N) which displayed strong aging peaks after 1 hr and 10 hrs at 1092°C after first solutioning at 1930°C. The alloy C-7 shows rather uniformly high hardness 310 VHN or greater for aging times up to 16 hours with a 330 VHN peak at 3 hours. This alloy displayed considerably less hardness response than the C-6 alloy from which it was derived. The second peak (peak "b") was absent in alloy C-7. The C-5 alloy shows softening upon aging at 1100°C. (The specimens of alloys C-8 and C-4 were 1/4" cubes cut from nonconsumable arc melted buttons, C-6 specimens were cut from a hot forged button and C-7 specimens were cut from .44 inch diameter rod stock.)

A comparison of the aging behavior of C-6 (Cb-22W-4Hf-0.05C-0.04N) and C-8 (Cb-22W-2Zr-0.05C-0.05N) can be made from Figure 24. Both alloys were nonconsumable arc melted although C-6 was open die forged into a pancake configuration. Both alloys displayed marked "a" and "b" peaks. The zirconium containing C-8 alloy displayed a 432 VHN "a" peak at 1 hr as compared to a 362 VHN peak at 4 hours in the Hf containing C-6. The "b" peak of C-8 occurred at ~ 8 hours as compared to 12 hours for alloy C-6.

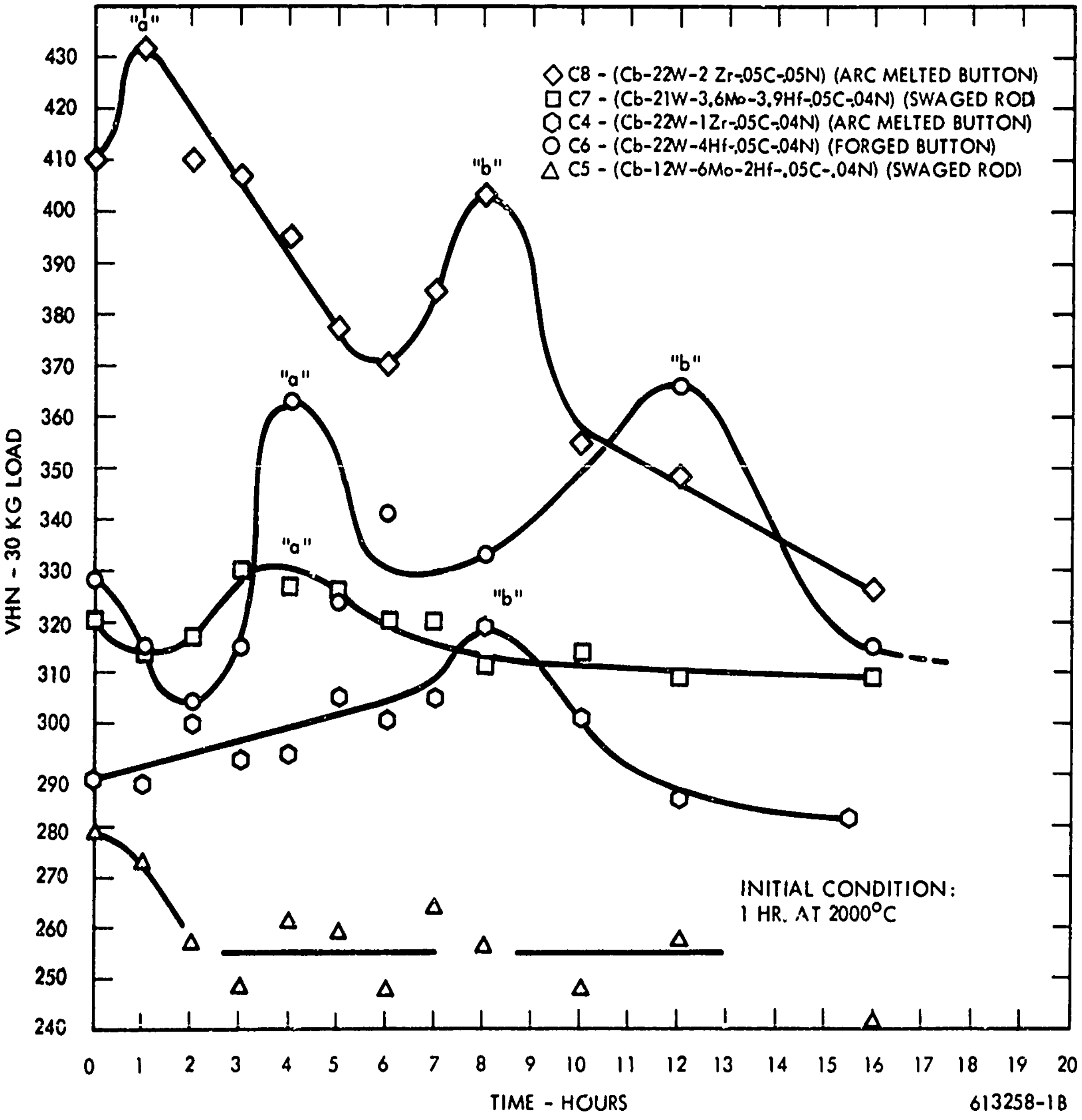


Figure 24. 1100°C Aging Isotherm of Nitrogen Containing Columbium Alloys

These data show that 1 a/o reactive metal additions are not sufficient to produce the aging reactions, but that 2 a/o Zr or Hf was sufficient to induce aging in alloys C-6, C-7, and C-8. The 1100°C aging kinetics are somewhat more rapid for the zirconium containing alloy. The "b" peak can appear in lower reactive metal containing alloys as shown by alloy C-4 in Figure 24 and alloys C-2 (Cb-22W-2Hf-0.05C-0.08N) and C-3 (Cb-22W-2Hf-0.08N) in Figure 14.

Aging data were also generated at the 1000°C isotherm for alloys C-5, C-7, and C-8. These data, shown in Table 7, also demonstrate the superiority of Zr over Hf in promoting the aging reaction as well as the necessity of having at least 2 a/o reactive metal present.

The 1000°C data is somewhat more erratic than that generated at the 1100°C isotherm. Closer inspection of the C-8 specimens from which the hardnesses were taken showed fewer precipitates near the surface than near the center. No difference between surface and centrally located material could be observed metallographically for the C-7 alloy. Nitrogen determinations were performed on alloys C-6, C-7, and C-8 in various stages of processing, annealing and aging. The results are given in Table 8. These data coupled with metallographic and hardness profiles across a specimen show that nitrogen is lost through prolonged exposure at the solutioning and aging temperatures. The data also show that aging response is possible with as little as 240 ppm nitrogen as was the case for alloy C-7. It is also suspected that the overaging from the second peak is associated with the loss of nitrogen.

The above data points to a potential stability problem in nitride containing columbium alloys. In evaluating these data, the following should be considered: first, the nitrogen determinations were performed on material solutioned at 2000°C, a temperature 250 to 350°C higher than the expected optimized solutioning treatment. Thus, less nitrogen will be lost during solutioning in the optimized heat treatment. Secondly, during use of the alloy, loss of nitrogen from the hot air foil section of the turbine blade will have no effect on the creep resistance of the alloy at 2200°F. Third, nitrogen is added to these alloys to improve the tensile strength at 1200 to

Table 7. 1000°C Aging Hardness of Alloys C-8 (Cb-22W-2Zr-.05C-.06N), C-7 (Cb-21W-4Hf-.05C-.04N), and C-5 (Cb-12W-6Mo-2Hf-.05C-.04N)

Heat Treatment	Alloy Hardness (VHN)		
	C-8	C-7	C-5
As solutioned 1 hr at 2000°C	404	325	323
Aged 1 hr at 1000°C	435	361	271
Aged 2 hrs at 1000°	418	338	270
Aged 4 hrs at 1000°C	433	355	278
Aged 6 hrs at 1000°C	432	346	262
Aged 8 hrs at 1000°C	415	351	257
Aged 10 hrs at 1000°C	419	351	273
Aged 16 hrs at 1000°C	390	336	261
Aged 20 hrs at 1000°C	327	358	236
Aged 50 hrs at 1000°C	304	321	254
Aged 80 hrs at 1000°C	356	300	238
Aged 110 hrs at 1000°C	362	330	230
Aged 130 hrs at 1000°C	360	320	246

Table 8. Nitrogen Analysis of Experimental Columbium Alloys

Alloy	Condition	% Nitrogen
C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N)	As melted ingot top	0.028
	As swaged	0.024
	As solutioned 1 hr at 2000°C	0.011
	As solutioned plus aged 16 hrs at 1100°C	0.0085
C-6 (Cb-22W-4Hf-0.05C-0.04N)	As forged (from arc melted button)	0.047
	As solutioned 1 hr at 2000°C and aged 12 hrs at 1100°C	0.032
C-8 (Cb-22W-2Zr-.05C-.05N)	As melted (button)	0.068
	As solutioned 1 hr at 2000°C plus aged 16 hrs at 1100°C	0.030

1600°F in the root section of the blade. Nitrogen losses should be a minimal problem at these temperatures. However, problems could arise if escaping nitrogen is allowed to accumulate at the coating-matrix interface. This aspect of the nitrogen depletion problem should receive serious consideration.

Aging studies were also conducted on alloys C-2 (Cb-22W-2Hf-0.05C-0.08N), C-3 (Cb-22W-2Hf-0.08N) and C-6 (Cb-22W-4Hf-0.05C-0.04N) at 1315°C (2400°F) to evaluate the possibility of combining aging and coating heat treatments. The data are given in Table 9. No obvious aging effect was observed in either of the alloys. It would appear that one way the coating and heat treating thermal cycles could be combined would be to first solution treat the alloy to the desired grain size and morphology, coat at lower temperatures, and finally re-solution the nitrides at or near the solvus temperature by a "flash" heat treatment of short duration.

Discussion of Aging Results

Precipitation hardening is best accomplished by a general distribution of homogeneously nucleated precipitates. Active sites such as grain boundaries, substructure and dislocations are favored nucleation sites and are not as effective in promoting strengthening. Active site nucleation is a more likely mechanism in the precipitation of the metastable epsilon phase[1,2,5,6] (formerly called the zeta phase[2]) and the hexagonal carbides (or Cb_2 (C,N) carbo-nitride in this study) because only interstitial diffusion is required. Since interstitial diffusion is so rapid, carbon and nitrogen can move relatively large distances to active sites where the mean-matrix composition is sufficient to supply the metallic constituents of the hexagonal or epsilon phases. The cubic carbide or nitride on the other hand, requires 20 to 35 atomic percent reactive element (Hf or Zr). Hafnium or zirconium diffuse slowly compared to carbon and nitrogen and would not be expected to move the relatively large distances to active sites to engage in discontinuous precipitation. The cubic carbides and nitrides would be expected to nucleate homogeneously at small clusters of reactive elements distributed uniformly throughout the matrix. Such a precipitate should enhance strength.

Table 9. Effect of 2400°F Aging Treatment on R.T. Hardness of Experimental Columbium Base Alloys

Heat Treatment	R.T. Hardness (VHN) After Aging at 1315°C (2400°F) C2 Cb-22W-2Hf-0.05C-0.08N	C3 Cb-22W-2Hf-0.08N	C6 Cb-22W-4Hf-0.05C-0.04N
Initial Condition*	315	302	327
Aging Time at 1315°C (Hrs.)			
0.1	310	281	316
.2	299	273	[illegible]37
.4	286	273	294
.5	283	265	286
.6	284	262	295
.7	281	272	290
.8	276	265	290
.9	268	264	275
1.0	280	287	274
1.2	269	259	278
1.5	290	278	278
2.0	257	249	300
3.0	256	242	264
4.0	259	258	275

*1 hr. at 2000°C + He Cool

A schematic quaternary isotherm of the Cb-Hf-C-N system is shown in Figure 25. It appears from the phase extraction data and inconsistent aging data of B-99N that this composition is either very close to or in the cubic phase field. If the quaternary section in Figure 25 is accurate in general morphology, higher Zr or Hf contents would be expected to place the alloy in the FCC (Cb, Hf) $(C,N)_{1-x}$ + BCC matrix phase field. Equilibrium phase relationships may not apply to the precipitation associated with the aging peaks since coherent precipitates are likely to be metastable. Nevertheless, if the equilibrium phase is hexagonal, coherent cubic precipitates will quickly overage.

Lattice Misfit

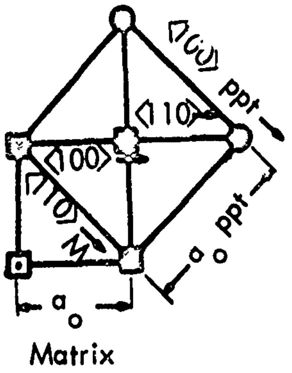
Age hardening is associated with continuous precipitation of coherent or semi-coherent precipitates. There are two interrelated factors important to coherent precipitation; lattice misfit and strain energy. The lattice misfit factor will be considered here.

A number of habit plane relationships between the matrix and precipitate are possible. The particular habit plane will depend on that orientation which will most effectively reduce the total energy of the system. Ryan et al(7) have analyzed the precipitation of Zr, Hf and Ti carbides and nitrides in molybdenum and have predicted, on the basis of lattice misfit and strain energy analysis, that Zr and Hf carbides and nitrides will precipitate on cube habit planes with the following relationships:

$$\{100\}_{Mo} // \{100\}_{ppt}$$

$$\langle 100\rangle_{Mo} // \langle 110\rangle_{ppt}$$

$$\langle 110\rangle_{Mo} // \langle 100\rangle_{ppt}$$



This relationship is illustrated in the margin sketch. The carbides and nitrides of titanium, on the other hand, were predicted to have the following habit plane and orientation relationships:

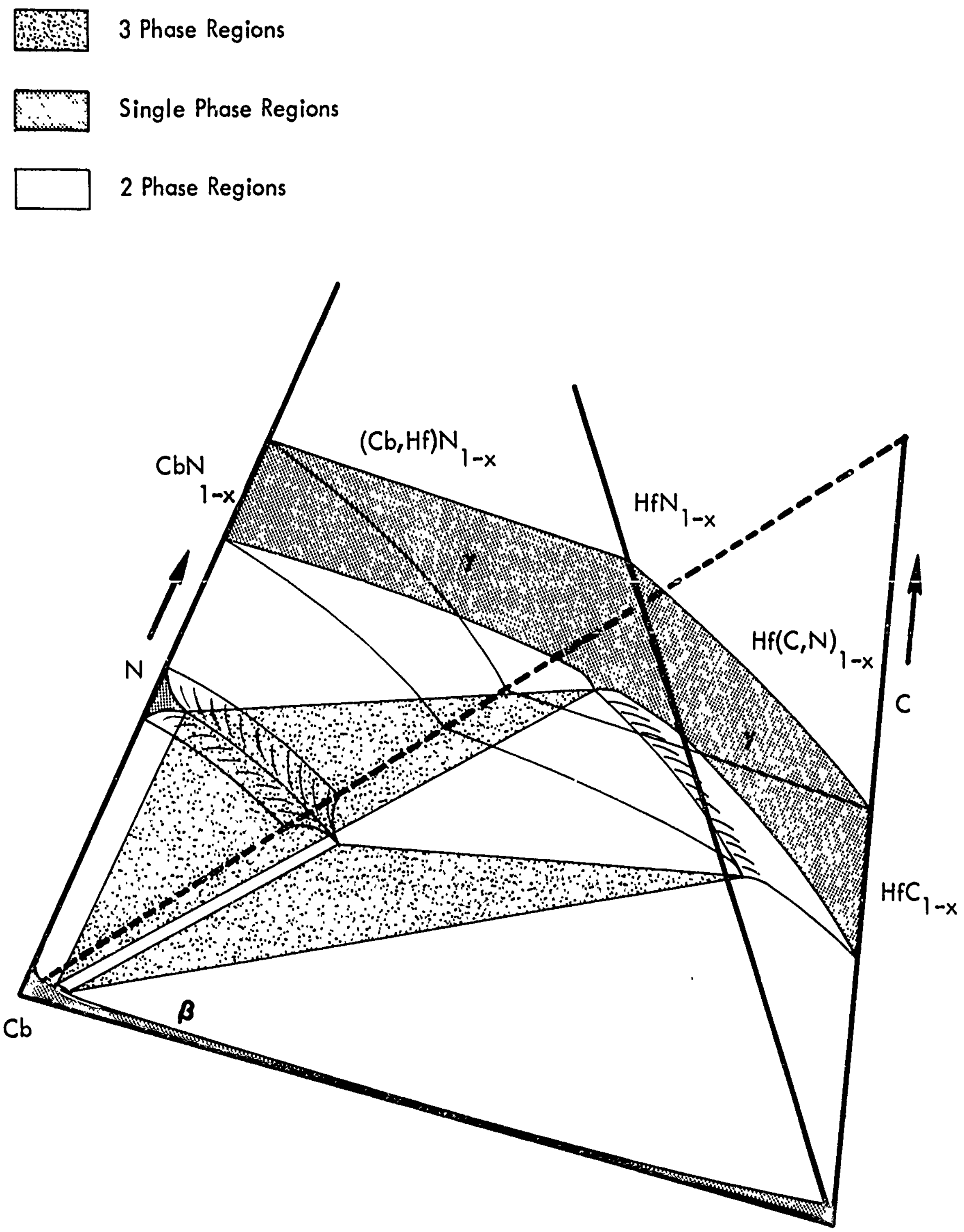


Figure 25. Schematic Quaternary Isotherm of Cb-Hf-C-N System

$\{310\}_{Mo} // \{113\}_{ppt}$

$\langle 113\rangle_{Mo} // \langle 112\rangle_{ppt}$

$\langle 100\rangle_{Mo} // \langle 110\rangle_{ppt}$

These results cannot be related directly to columbium base alloys studied in this program because of the differences in lattice parameter of the base alloy (Cb-22W) matrix (3.28 Å versus 3.15 Å for Mo). By selective alloying it is possible to alter either the habit plane relationships or the degree of coherency on a given habit plane. Calculations of atomic mismatch on nominated directions on a number of matrix-precipitate habit planes are given for the Cb-22W alloy matrix in Table 10. These mismatch data are actually related to the ideal lattice parameter of the precipitate which would produce a 0% mismatch along a specified direction in the habit plane. These data show that the ideal structure for coherent cube habit plane precipitation ($\{100\}_M // \{100\}_{ppt}$, $\langle 100\rangle_M // \langle 110\rangle_{ppt}$, $\langle 110\rangle_M // \langle 100\rangle_{ppt}$) would have a lattice parameter of 4.64 Å. The $(310)_M // (113)_p$ habit planes, which are the TiC and TiN habit plane relationships in the molybdenum, would require a precipitate lattice parameter of approximately 4.45 Å for minimum atomic mismatch.

A problem arises when attempting to rationalize precipitation of cubic carbides in the Cb-Zr-C or Cb-Hf-C system because the equilibrium cubic carbides reactive metal content and hence its lattice parameter changes greatly with equilibration temperature, as shown in Figure 26. The composition of the carbides also changes from essentially $CbC_{(1-x)}$ (low Zr or Hf content) to the equilibrium reactive metal content (from 20 to 45 atomic % Zr or Hf) with isothermal aging.(1) This may account for the apparent lack of coherency in the Cb-Zr or Hf-C systems. The data on Table 10 coupled with the above experimental observations lead to the prediction that the initial carbide with either Hf or Zr present would precipitate on the

$\{310\}_M // \{113\}_{ppt}$

$\langle 113\rangle_M // \langle 112\rangle_{ppt}$

$\langle 100\rangle_M // \langle 110\rangle_{ppt}$

Table 10. Ideal Lattice Parameter of Precipitates to Produce 0% Mismatch along Nominated Directions

Matrix (Cb-22W)		Precipitate			Possible Habit Planes Containing Related Direction
Direction	Atomic Spacing Å	Direction	Atomic* Spacing	la [illegible]	Matrix Ppt.
<110>	2.84	<110>	$1/2\sqrt{2}\ a_p$	4.01	(110) // (111)
<100>	3.28	<110>	"	4.64	(100) // (100)
<110>	4.64	<100>	a_p	4.64	(100) // (100)

<311>	5.43	<211>	$1/2\sqrt{6}\ a_p$	4.44	(112) // (110)
					(310) // (113)
					(114) // (210)

<331>	7.15	<310>	$1/2\sqrt{10}\ a_p$	4.52	
<210>	7.34	<310>	"	4.60	(100) // (100)
<210>	7.34	<111>	$\sqrt{3}\ a_p$	4.25	(113) // (320) (210) // (112)
<211>	8.05	<321>	$1/2\sqrt{14}\ a_p$	4.31	
<221>	9.83	<210>	$\sqrt{5}\ a_p$	4.41	(114) // (210)
<310>	10.38	<210>	"	4.64	(100) // (100)

<310>	10.38	<332>	$1/2\sqrt{22}\ a_p$	4.42	(210) // (112)
					(114) // (210)
					(310) // (113)
					(113) // (320)

<332>	15.38	<320>	$\sqrt{13}\ a_p$	4.26	

a_p = Lattice parameter of precipitate.

* Spacing of metallic species in precipitate.

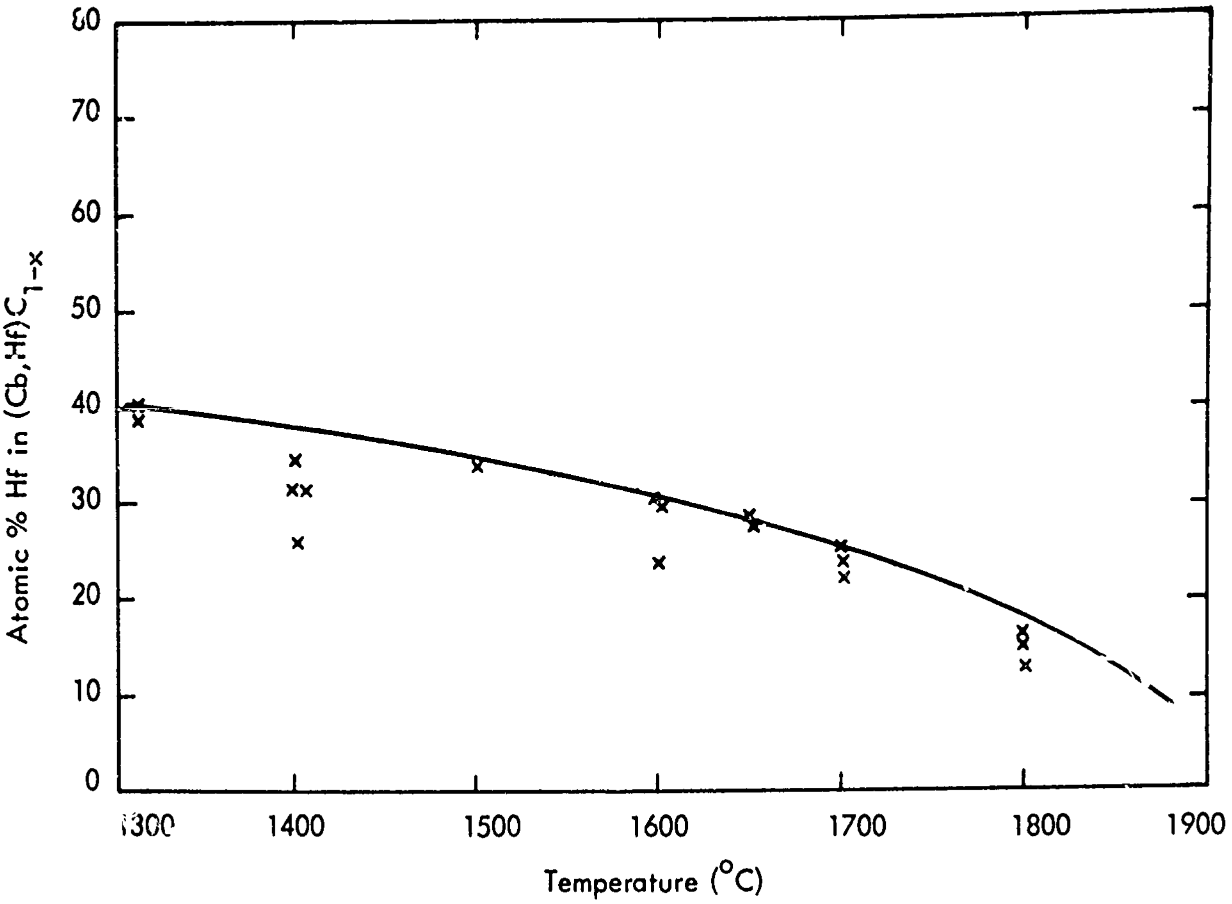


Figure 26. Variation of Composition of (Cb,Hf)C$_{1-x}$ with Temperature as Determined by Lattice Parameter Measurements

habit similar to TiC and TiN in Mo. Aging would increase the lattice parameter as Zr or Hf migrates to the carbide and coherency would soon be lost completely.

The above analysis suggests an intriguing possibility for developing cubic habit coherency in alloys such as B-88 (Cb-28W-2Hf-0.067C) and B-99 (Cb-22W-2Hf-0.067C). The equilibrium carbides $(Hf,Cb)C_{1-x}$ and $(Zr,Cb)C_{1-x}$ have a lattice parameter of 4.58 and 4.61 respectively after equilibrating at 1200°C. This carbide would not be on the preferred habit plane. However, if the alloy was heated above the carbon solvus for a short period of time so as to solution the carbon but leave a cluster of reactive metal in-situ and then quenched and re-aged at 1200°C, we would expect the equilibrium carbides to reprecipitate at the clusters of Hf or Zr coherently on the cube habit planes. This thermal treatment might produce very high short time properties at intermediate temperatures.

The Cb-(Zr or Hf)-N system offers interesting possibilities for developing coherency in as solutioned plus quenched material. Figure 27 is the phase diagram of the Ta-Hf-N system at 1500°C.(8) Note that the equilibrium cubic nitride in the three phase region has a composition of approximately 45%Hf. Unlike the Ta-Hf-C system, there is little temperature dependence on the location of the cubic nitride corner of the three phase region. Extending the analogy of the Ta-Hf-N system to the Cb-(Hf or Zr)-N system, it is predicted that the initial composition would be relatively temperature independent.

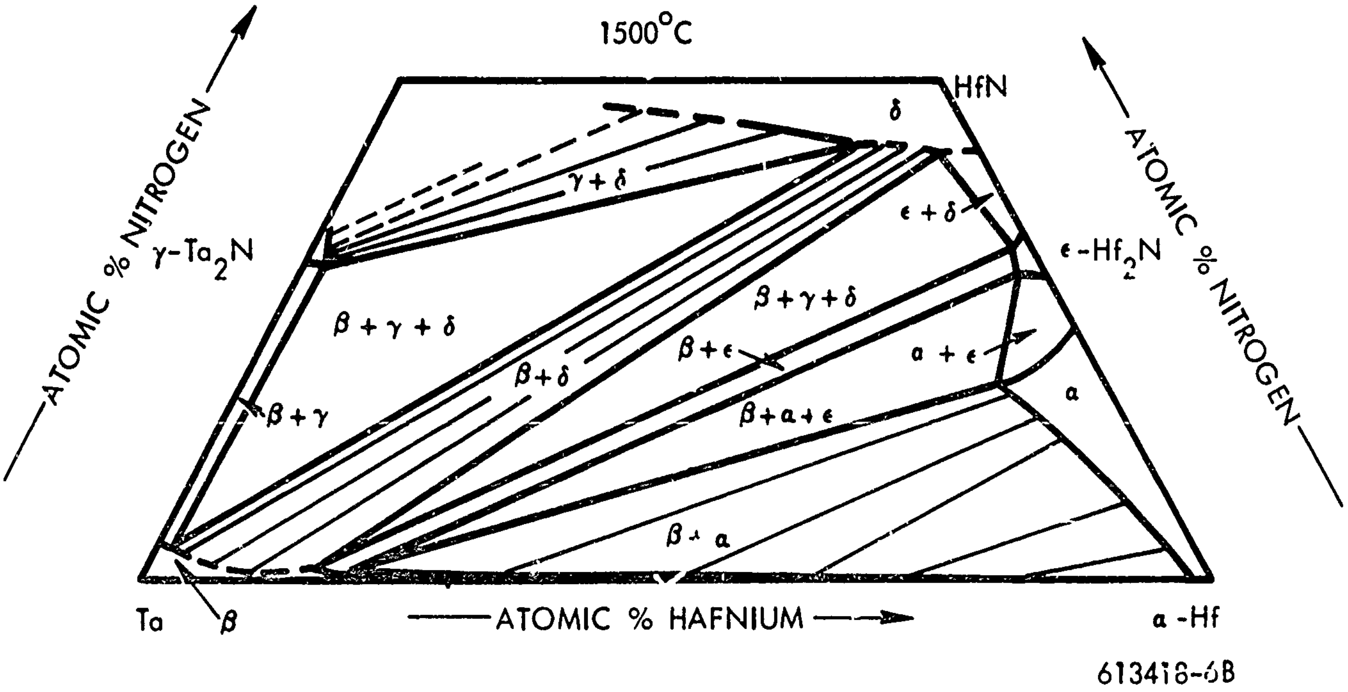


Figure 27. Isothermal Section of the Hf-Ta-N System at 1500°C from E. Rudy, Reference 8.

VII. MECHANICAL PROPERTY EVALUATION OF EXPERIMENTAL ALLOYS

The goals of the composition modifications of the basic B-99N alloy were:

1. Determine the reactive element (Zr or Hf) level required for reproducible age hardening.
2. Determine the effect of nitrogen level on the aging behavior.
3. Evaluate trade offs between density and creep strength by substituting Mo for W.
4. Determine the effect of Mo for W on the DBTT.

Effect of Mo for W Substitution on DBTT

The two alloys C-1 (Cb-22W-2Hf-.05C-.04N) and C-5 (Cb-12W-6Mo-2Hf-.05C-.04N) were prepared with the same total atomic percent tungsten plus molybdenum.

Ductile-to-brittle tensile tests were conducted on alloys C-1, C-5, and C-7. The alloys C-1 and C-5 were heat treated 1 hour at 1800°C to produce a recrystallized though not necessarily optimized structure. The DBTT results given in Figure 28 and Table 11 sh essentially no difference in the DBTT behavior of C-1 and C-5. The DBTT of C-1 and C-5 could have been lowered considerably below room temperature by heat treating at lower temperature as was done for alloy C-7 also shown in Figure 28. Specimens of C-7 were heated 1 hour at 1700°C and 1800°C prior to low temperature tensile testing. The 1 hour at 1700°C and 1 hour at 1650°C heat treatments produced more ductility than the 1 hour at 1800°C treatment but the DBTT is still above 300°F. Heating 1 hour at 1600°C or below would probably result in a 5% R.T. ductility.

1400°F Tensile Properties

Most of the aging hardness data presented previously was obtained on materials solutioned one hour at 2000°C. This temperature was used because in addition to solutioning the interstitials, homogenization of the Hf was necessary for obtaining reproducible hardness data. The large

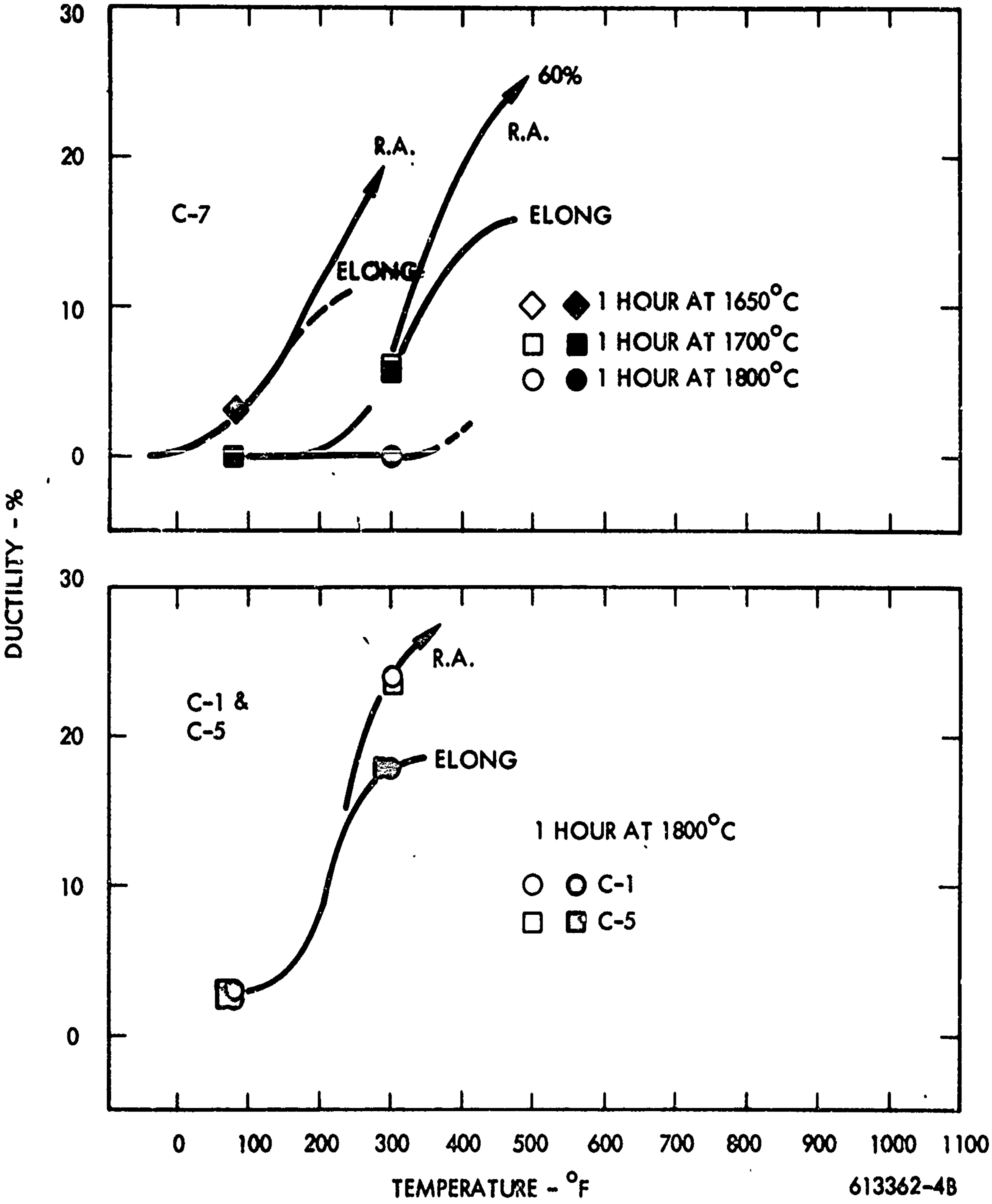


Figure 28. Ductile to Brittle Behavior of Alloys C-1 (Cb-22W-2Hf-0.05C-0.04N), C-5 (Cb-12W-6Mo-2Hf-0.05C-0.04N), and C-7 (Cb-21W-3.6Mo-3.9Hf-0.05C-0.04N)

Table 11. Low Temperature Tensile Properties of Alloys C1* and C5*

Alloy	Test Temp. °C	Test Temp. °F	0.2% Y.S.** ksi	UTS ksi	Elong. (%) Uniform	Elong. (%) Total	Red. in Area %
C1***	27	80	109.8	118.6	3.00	3.00	2.8
	149	300	86.8	103.8	13.27	18.00	24.0
C5	27	80	103.01	109.84	2.00	2.00	2.81
	149	300	79.20	94.0	14.06	18.00	23.60

*C1 - (Cb-22W-2Hf-.05C-.04N), B-9YN

C5 - (Cb-12W-6Mo-2Hf-.05C-.04N)

**Strain rate = .05 in/in/min

***Recrystallized during 1 hr. at 1800°C solution anneal.

grain size which result from the higher solutiong treatments lead to a high DBTT and shortened creep rupture life. The C-7 alloy (Cb-21W-3.6Mo-3.9Hf-.05C-.04N) was evaluated to determine the effects of solutioning temperature and aging treatment on 1400°F tensile properties. Specimens of alloy C-7 were solution annealed for one hour at 1600-2000°C followed by aging for up to 4 hours at 1100°C. The room temperature hardness and 1400°F tensile properties were determined to assess the effect of the prior heat treatments. The resulting data are listed in Table 12 and presented graphically in Figure 29. The hardness test samples were heat treated along with the tensile specimens to insure identical thermal treatments. From the room temperature hardness data, plotted in the lower half of Figure 29, it appears that the solvus temperature is at 1700-1750°C. At 1400°F, a yield strength of 83.6 ksi was measured on material that had been solution annealed for one hour at 1700°C followed by aging for 4 hours at 1100°C. Increasing the solution annealing temperature results in a decrease in the tensile strength as well as tensile elongation (See Figure 29 and Table 12) and is no doubt caused in part by excessive grain growth. The nitrogen analysis in Table 8 shows the C-7 alloy to contain less than the nominal nitrogen content. The aging hardness curves in Figure 24 show that alloy C-7 is softer than the chemically similar alloy C-6 at the aging peak. The potential strengthening of alloy C-7 was not realized due to the lower than nominal nitrogen content. Nevertheless, with that nitrogen present, the 1400°F strength of the alloy was nearly double that of the nitrogen free B-99 alloy.

Summary of Creep-Rupture Testing

One of the objectives of this program was to evaluate the effect of a partial substitution of Mo for W on creep of Cb alloys. This effect was studied on three alloys:

- C-1 (Cb-22W-2Hf-.05C-.04N)
- C-5 (Cb-12W-6Mo-2Hf-.05C-.04N)
- C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N)

Creep rupture was conducted at 2200°F at stress levels of 30,000 psi and 40,000 psi. The data obtained are given in Table 13. The rupture data for the three alloys are compared to B-99 in Figure 30. The stress dependence is greater for the alloys C-7, C-1, and C-5 because of either the lower carbon content or larger grain sizes. Annealing alloy C-7 at 1750°C and

Table 12. Tensile Properties of C-7 and B-99N

Specimen/Alloy No.	Heat Treatment	.2% YS ksi	UTS ksi	Ductility %			Test Temp.	
				RA	Elong.	Uniform	(°C)	(°F)
C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N)								
C7-T4	1 hr at 1650°C	65.5	109.8	51.3	20.0	11.62	760	1400
C7-T6	1 hr at 1700°C	64.0	109.0	47.6	19.0	12.0	760	1400
C7-T7	1 hr at 1750°C	60.1	105.6	48.1	21.0	13.7	760	1400
C7-N1	1 hr at 1700°C & age 4 hrs at 1100°C	83.6	95.4	62.6	16.0	6.83	760	1400
C7-N2	1 hr at 1800°C & age 4 hrs at 1100°C	79.2	90.1	58.1	13.0	5.34	760	1400
C7-N3	1 hr at 2000°C & age 4 hrs at 1100°C	66.2	74.4	1.8	2.0	1.80	760	1400
B-99N (Cb-22W-2Hf-.05C-.04N)								
VAM 99-24	As swaged at 1300°C (90% R.A.)	89.7	91.6	66.3	8.0	1.5	760	1400
C7-T5	1 hr at 1650°C	122.4	129.0	2.8	1.0	2.68	25	80
C7-M5	1 hr at 1700°C	---	116.5	-0-	-0-	-0-	25	80
C7-M6	1 hr at 1700°C	101.8*	110.8*	5.9	6.0	5.78	150	300
C7-N6	1 hr at 1800°C	---	107.0	-0-	-0-	-0-	25	80
C7-N7	1 hr at 1800°C	---	109.2	-0-	-0-	-0-	150	300

* Upper Yield = 101.8

Lower Yield = 100.8

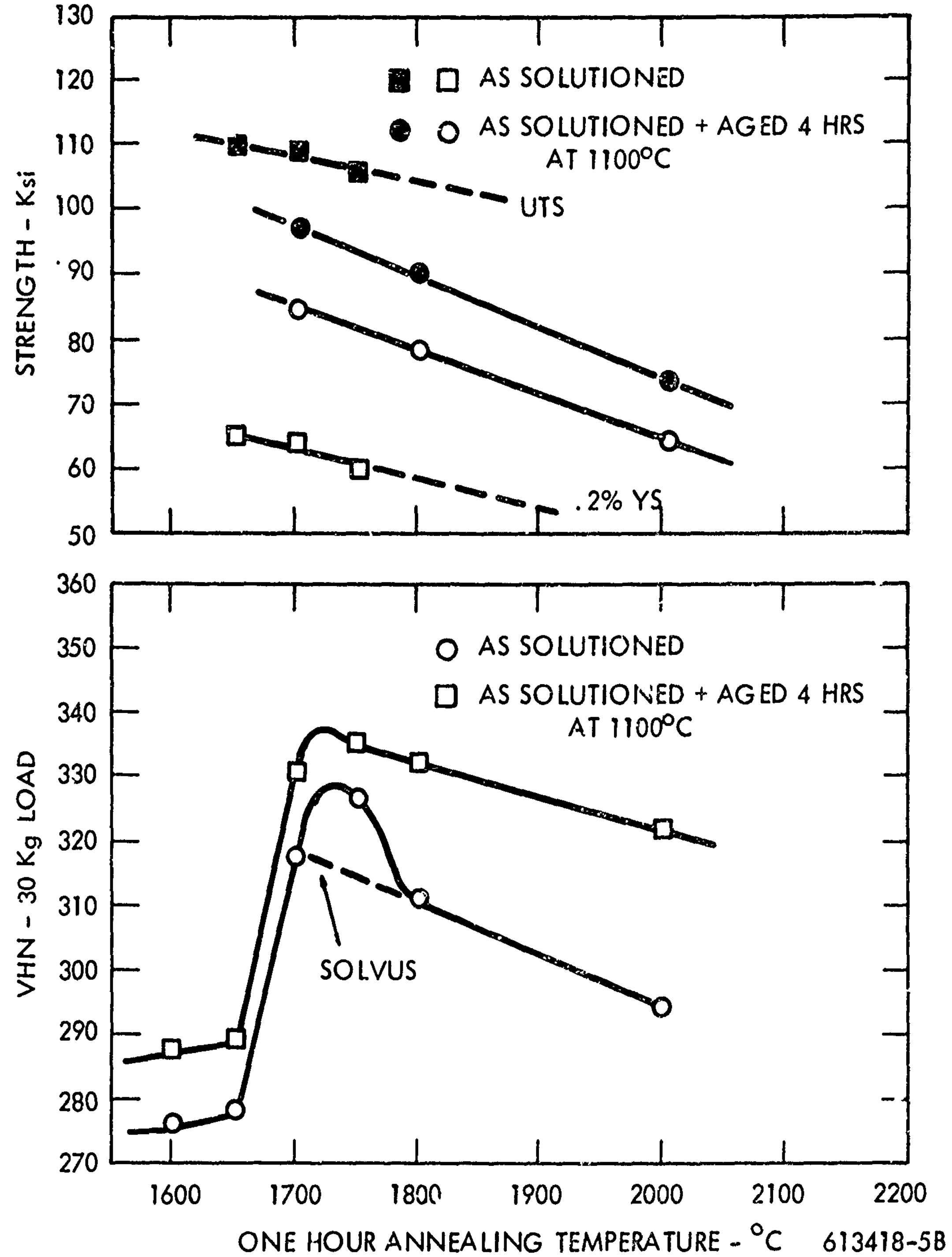


Figure 29. Effect of Solutioning Temperature on As-Solutioned and As-Solutioned and Aged Properties of Alloy C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N)

Table 13. Creep Rupture Behavior of Experimental Alloys C-1, C-5, and C-7

Alloy/Spec. No	Initial Heat Treatment	Test Temp (°C)	Test Temp (°F)	Rupture Properties Time (hrs)	Rupture Properties Deformation-% RA	Rupture Properties Deformation-% Elong.	Min. Creep Rate %/hr	Transition Time (hrs)	Transition Strain %	Stress ksi
C1 (Cb-22W-2Hf-.05C-.04N)										
C1-3	1 hr at 1800°C	1205	2200	7.2	25.6	4	.084	5.0	.91	40
C1-4	1 hr at 1800°C	1205	2200	29.2	22.6	4	0282	23.0	1.02	30
C5 (Cb-12W-6Mo-2Hf-.05C-.04N)										
C5-3	1 hr at 1800°C	1205	2200	2.4	31.1	4	.210	1.9	.65	40
C5-4	1 hr at 1800°C	1205	2200	11.3	24.5	5	.070	5.0	.67	30
C7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N)										
C7-N4	1 hr at 1800°C	1205	2200	74.3	33.8	9	0146	24.0	.85	30
C7-N5	1 hr at 1800°C	1205	2200	16.6	26.0	6	.0310	9.8	.64	40
C7-T1	1 hr at 1650°C	1205	2200	214.0	75.0	20	.01925	90.0	2.21	30
C7-T8	1 hr at 1750°C	1205	2200	93.2	69.2	20	.0435	19.2	1.23	30

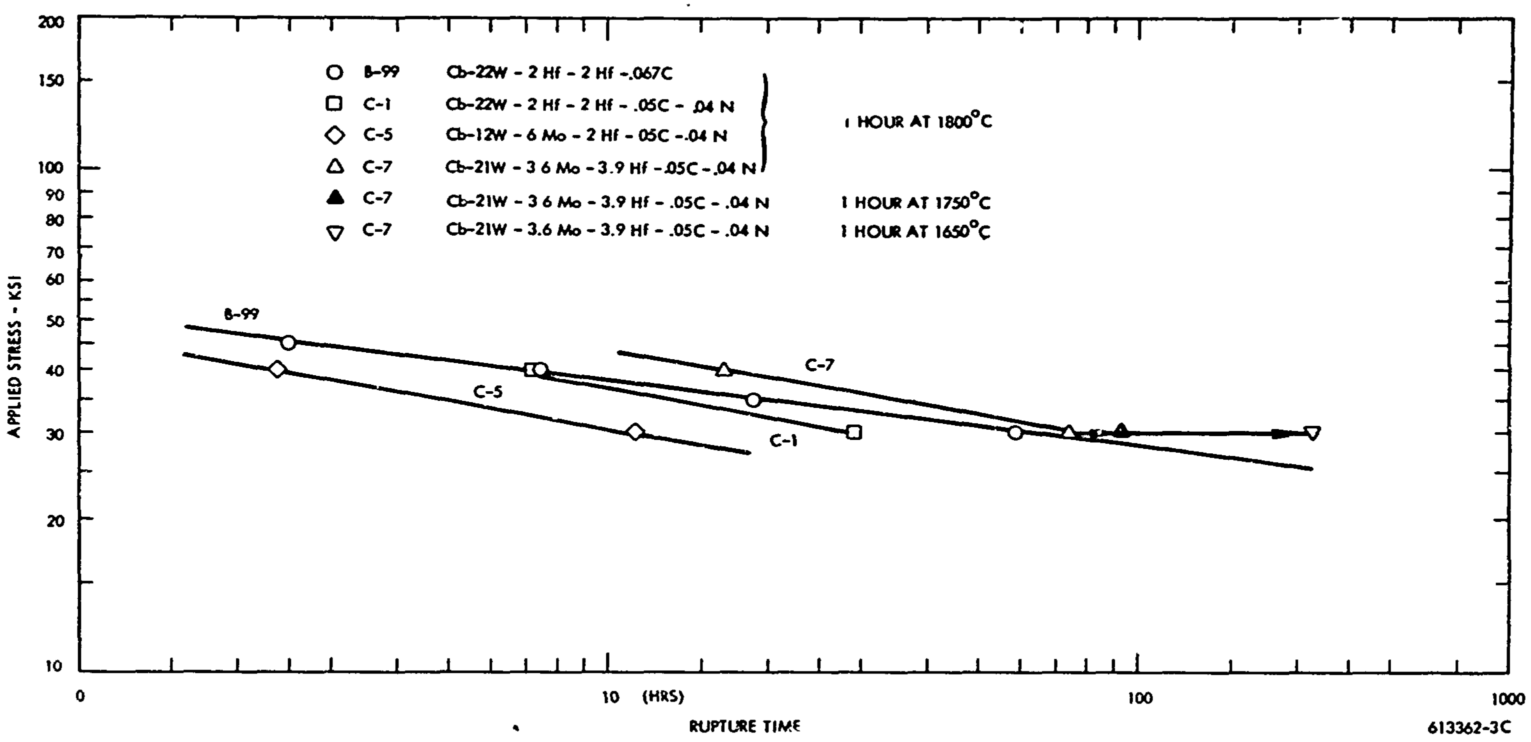


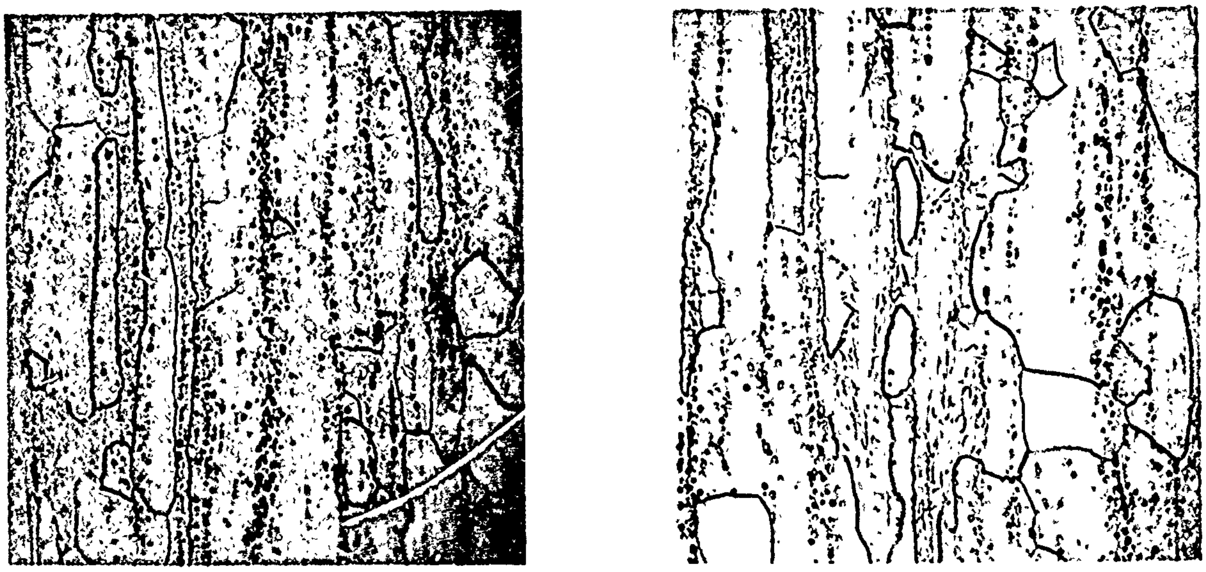
Figure 30. Summary of Rupture Data for Experimental Columbium Alloys

1650°C resulted in longer rupture times at 30,000 psi. An examination of the creep data in Table 13 shows that all three heat treated conditions of C-7 tested at 30,000 psi and 2200°F had similar secondary creep rates from .014 to .04%/hr. but the specimens heated at higher temperatures failed by early entry into third stage creep. Microstructures supporting this statement are shown in Figure 31. The specimen heated for 1 hour at 1650°C is characterized by a relatively fine grained elongated structure. Earlier work on B-88(1) demonstrated the desirability of grains elongated in the direction of the stress axis. Boundaries so oriented tend to transmit the load from one grain to another rather than slide. Grain boundary sliding in high strength materials leads to the formation of separations on grains normal to the stress axis. This separation results in early entry into third stage creep.

Molybdenum was utilized in alloy C-7 to increase the 150 hour rupture stress of the Cb-22W base to 30,000 psi. McAdams data(4) in Figure 12 shows molybdenum to be half as effective as tungsten in strengthening columbium. An extrapolation between the 150 hour rupture stresses of B-99 (12.6 a/oW) and B-88 (16.6 a/oW) would place the atomic percent tungsten necessary to give a 30,000 psi 150 hour rupture life at 14.2 a/oW. The alloy C-7 was designed to give this effective tungsten content (12.2 a/o W + (.5) (4 a/o Mo) = 14.2 a/o effective tungsten content).

The 150 hour rupture stress of alloys C-1, C-5, and C-7 along with results from earlier studies of B-88 and B-99 are plotted vs "effective" tungsten content (atomic percent tungsten plus half of the atomic percent molybdenum present) in Figure 32. These results seem to justify McAdam's conclusion that molybdenum is half as effective as tungsten as a solid solution creep strengthener.

In conclusion, Mo for W additions on an atom for atom basis are half as effective as tungsten as a creep strengthener and are equally as detrimental as tungsten in increasing the DBTT. Attempts to optimize alloys for creep, density, and low temperature ductility by substituting Mo for W soon degenerate into exercises in futility.



A. 1 hr at 1600°C (No. 21,335)

B. 1 hr at 1650°C (No. 21,337)

C. 1 hr at 1700°C (No. 21,339)

D. 1 hr at 1750°C (No. 21,341)

Mag. = 500X

Figure 31. Microstructure of Alloy C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N) after Indicated Heat Treatment

E. 1 hr at 1800°C (No. 21,343)

F. 1 hr at 2000°C (No. 21,347)

Figure 31. Microstructure of Alloy C-7 (Cb-21W-3.6Mo-3.9Hf-.05C-.04N) after Indicated Heat Treatment

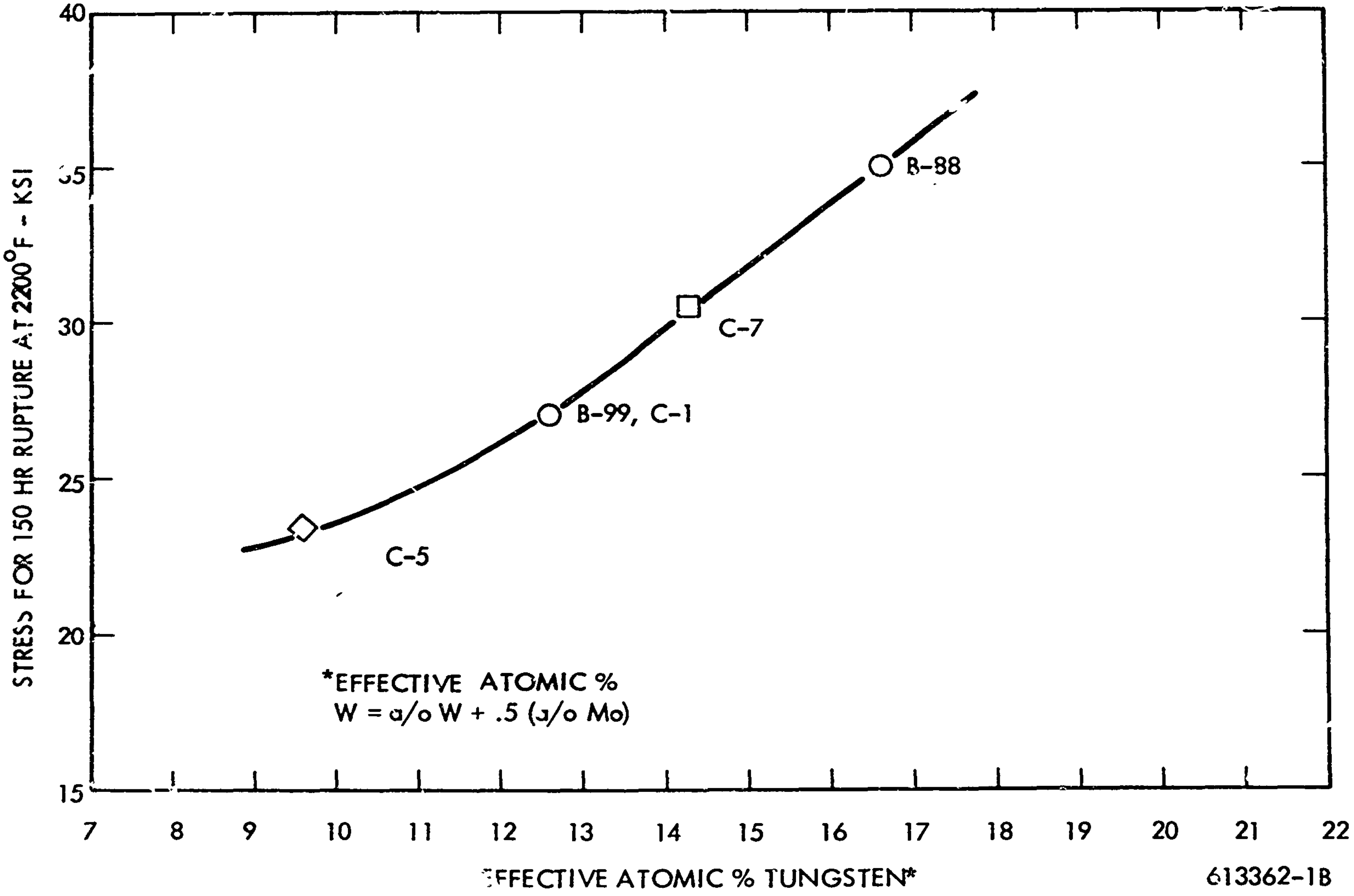


Figure 32. Dependence of 150 hr Rupture Stress on Effective Atomic Percent Tungsten

VIII. WORKABILITY STUDIES ON ALLOY C-6

In the course of fabricating the various alloys, alloy C-6 (Cb-22W-4Hf-.05C-.05N) stood out as a very forgeable composition. The original 250 gm button heats of this alloy and alloys C-2 (Cb-22W-2Hf-.05C-.08N) and C-3 (Cb-22W-2Hf-.08N) were placed in a heavy walled, evacuated molybdenum cans,heated to 1300°C and Dynapak forged a total reduction of 60%. The resultant forgings after decanning are shown in Figure 33. Alloys C-2 and C-3 were badly cracked but alloy C-6 was defect free. A trimmed section of this forging was subsequently rolled unprotected at 1000°C from 0.2 inch to 0.1 inch thickness without edge cracking, although the surface was heavily oxidized.

Two sections of extrusion VAM-100D (from the scale up heat of alloy C-6) approximately 1.25 in. diameter by 1" thick were heated to 1500°C, dropped into 3 in. OD, 1.25 in. ID mild steel retaining rings(that had previously been heated to 700°C) and upset forged for a 60% reduction in thickness. The resulting forgings are shown in Figure 34. The surface cracks visible are in the residual molybdenum extrusion jacket and do not extent into the columbium alloy forging. The two forgings were trimmed square and clad in 316 SS picture frame cans. The cans were initially rolled from .6 inch to .1 inch thickness at 1100°C to produce a unidirectional worked structure. The resulting sheets after decanning are shown in Figure 35. These pieces were of excellent quality, again with no edge cracking. The two pieces were then trimmed, stress relieved 1 hr at 1500°C and rolled at 600°F and 1000°F respectively from .1 in. to .040 in. thickness. Both pieces worked well but the piece rolled at 600°F was of higher quality with no edge cracking. The piece worked at 600°F rolled more easily than the sheet worked at 1000°F. The resultant sheet is shown in Figure 36.

The .04 in. sheet rolled at 600°F was stress relieved 1 hr at 1500°C and cut into 1" by 1/2" tabs. Half of the tabs were 2T bend ductility tested in the stress relieved condition. The remaining tabs were solutioned 15 min. at 1750°C and aged 1 hr at 1100°C prior to 2T bend testing. The resultant data are given in Figure 37. Photomicrographs of the sheet structure after the stress relieved and solutioned plus aged conditions are shown in Figure 38. The stress

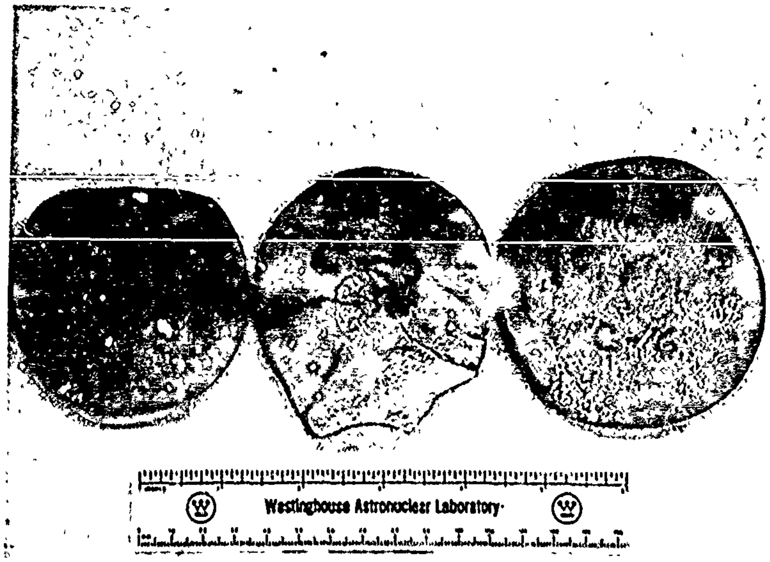


Figure 33. Forged Buttons, Alloys C-2 (Cb-22W-2Hf-0.05C-0.08N), C-3 (Cb-22W-2Hf-0.08N), C-6 (Cb-22W-4Hf-0.05C-0.04N)

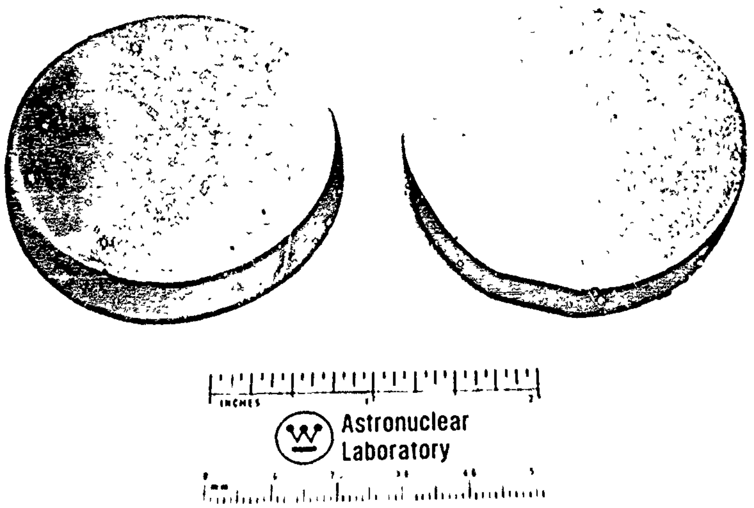


Figure 34. Alloy C-6 (Cb-22W-4Hf-.05C-.05N) upset Forged 60% at 1500°C

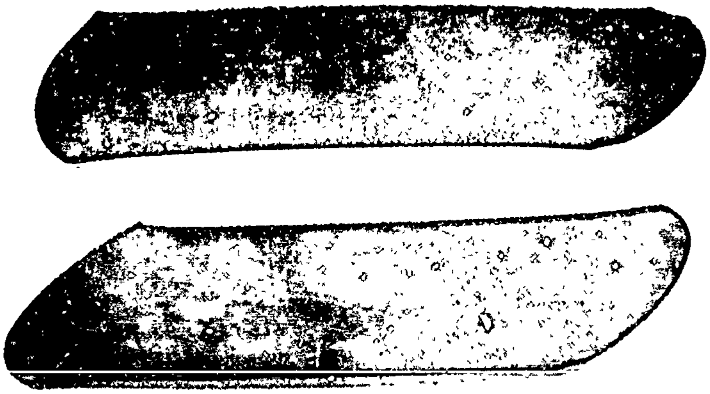


Figure 35. C-6 Sheet Rolled in Evacuated Stainless Steel Cans at 1100°C

Figure 36. Trimmed Sheet Shown in Figure 35 after Rolling at 1000°F and 600°F

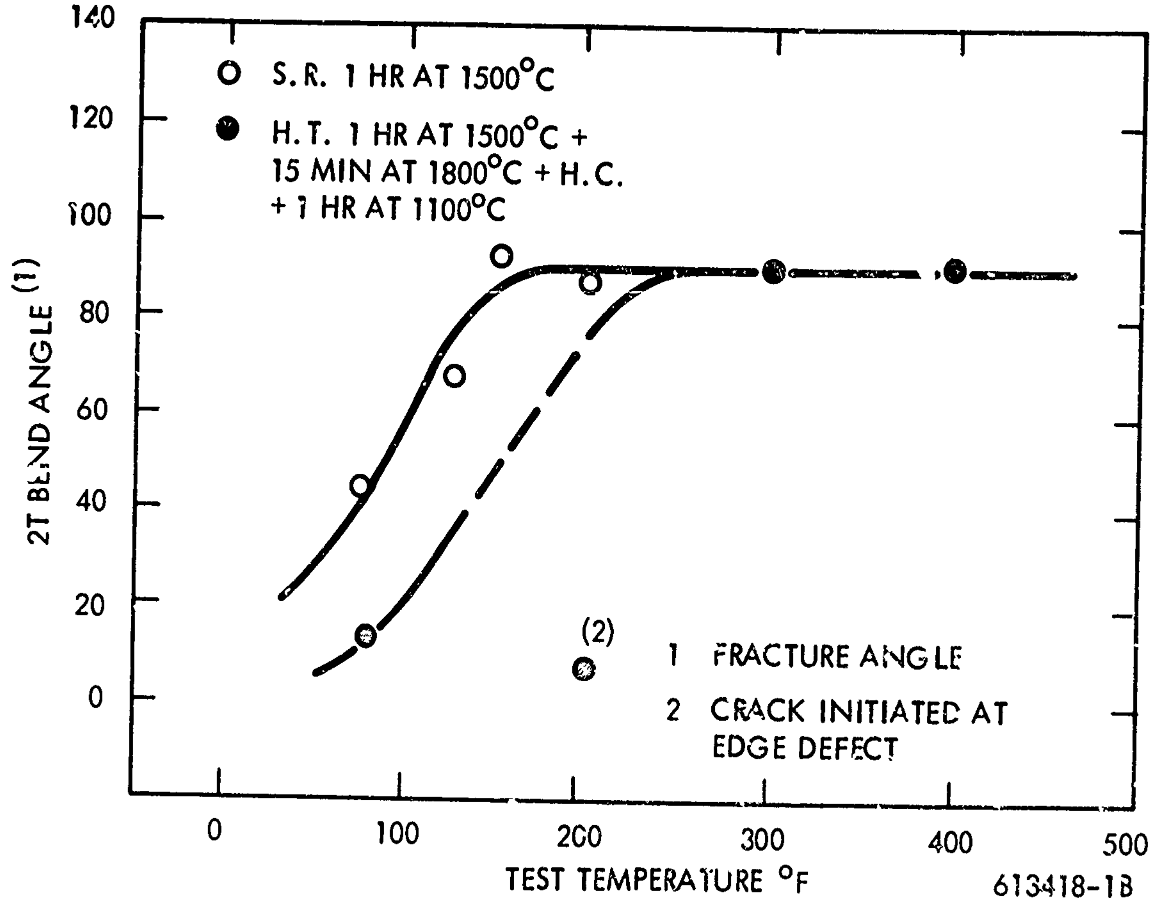


Figure 37. Bend Ductility Behavior of C-6 (Cb-22W-4Hf-.05C-.05N) Sheet

22,099 100X

C-6 Stress Relieved 1 hr at 1500°C

22,100 100X

C-6 Sheet H.T. 1 hr at 1500°C + Solutioned 15 min. at 1750°C + Aged 1 hr at 1100°C

Figure 38. C-6 Sheet Microstructures after Stress Relieving and Solutioning + Aging Heat Treatments

relieved structure displays many more grain boundaries than equivalent swaged structure. The solutioned and aged structure is completely recrystallized with grain size of .037 mm (ASTM No. 7) which is somewhat larger than equivalent swaged plus solutioned and aged materials (G.S = .024 mm, ASTM No. 8).

It is concluded that the excellent workability of this alloy is due to the high Hf content.

IX. EVALUATION OF ALLOY C-6

Selection of Reference Condition

After the scale up alloy was selected, consolidated and fabricated, the task then became one of optimizing creep-rupture, 1200-1600°F tensile, and low temperature ductility properties. Both creep-rupture and 1200-1600°F tensile properties are optimized by heat treating at or slightly above the interstitial solvus temperature. Unfortunately, low temperature ductility is optimized in materials that have been stress relieved but not recrystallized.

Preliminary solutioning and aging experiments were conducted on alloy C-6 swaged rod to determine the lowest solutioning temperature limit for producing the aging effect. Solutioning time was also a variable in this study since grain growth had to be controlled. Figure 39 shows the hardness response as a function of solutioning time at 1700, 1750, and 1800°C. Also shown in Figure 39 are the hardness responses of the same specimens after aging 4 hrs at 1100°C. The variation of microstructure with solutioning time at 1700°C, 1750°C, and 1800°C are shown in Figures 40, 41, and 42 respectively. Although there is some indication of a hardness peak from the 1/2 hr at 1700°C solutioning, the microstructures reveal that the precipitates were not solutioned even after 1 hr at 1700°C as is evident from the partial recrystallization, the elongated grain boundaries, and the stringers of undissolved precipitates in the high magnification photomicrograph (Figure 40C, 1500X). Solutioning at 1750°C produced a much more uniform hardness response, both in the as-solutioned and as-solutioned plus aged at 1100°C conditions as shown in Figure 41. The photomicrographs in Figure 41 show elongated grains but near 100% recrystallization even at short times. The high mangification photomicrographs show undissolved precipitates after 3/4 hr at 1750°C (Figure 41C) but few if any residual precipitates after 1 hr at 1750°C (Figure 41D). Most of the precipitates shown in these photomicrographs formed during cooling from the solutioning temperature.

Undissolved precipitates remain after 1/2 hr at 1800°C but disappear after 3/4 hr at 1800°C as shown in Figure 42A through 42D. Progressive solutioning of the carbides and nitrides is

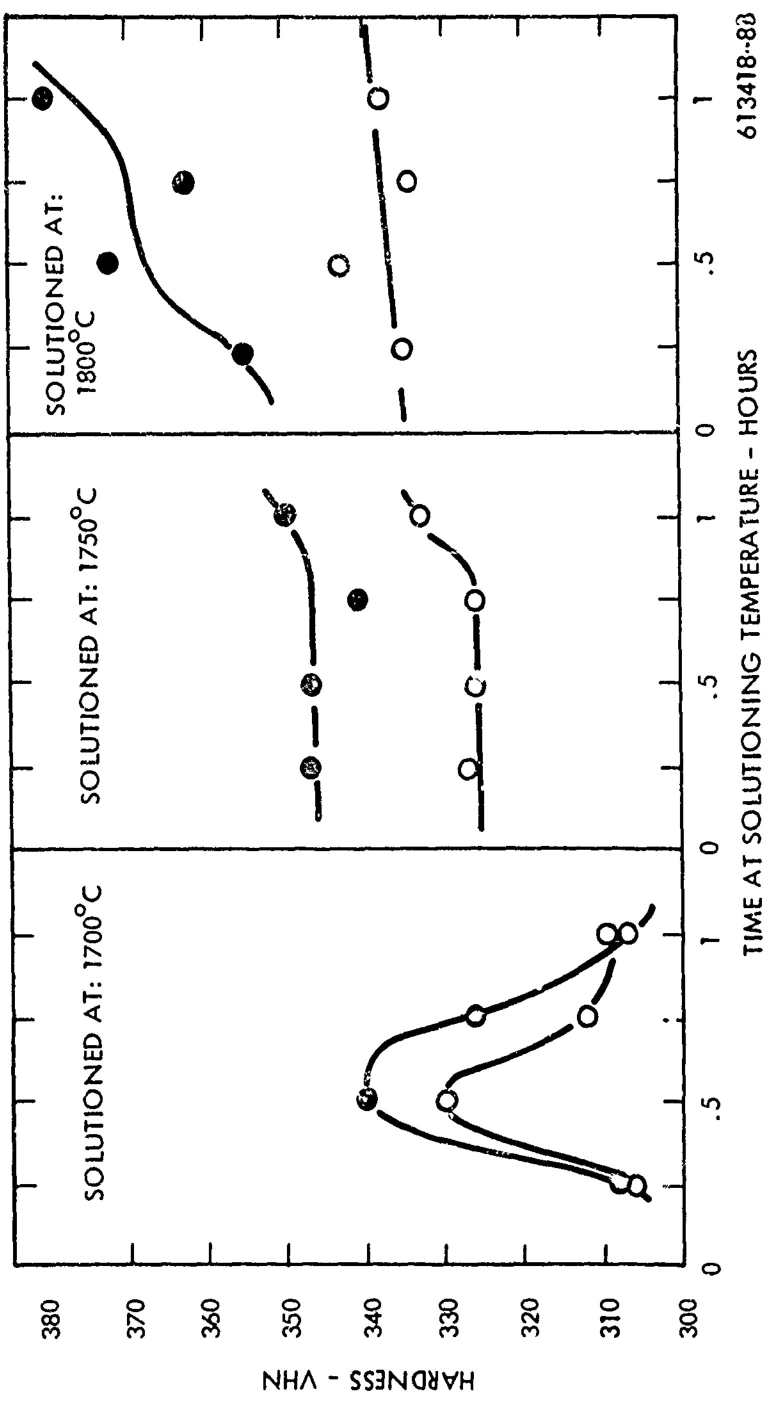
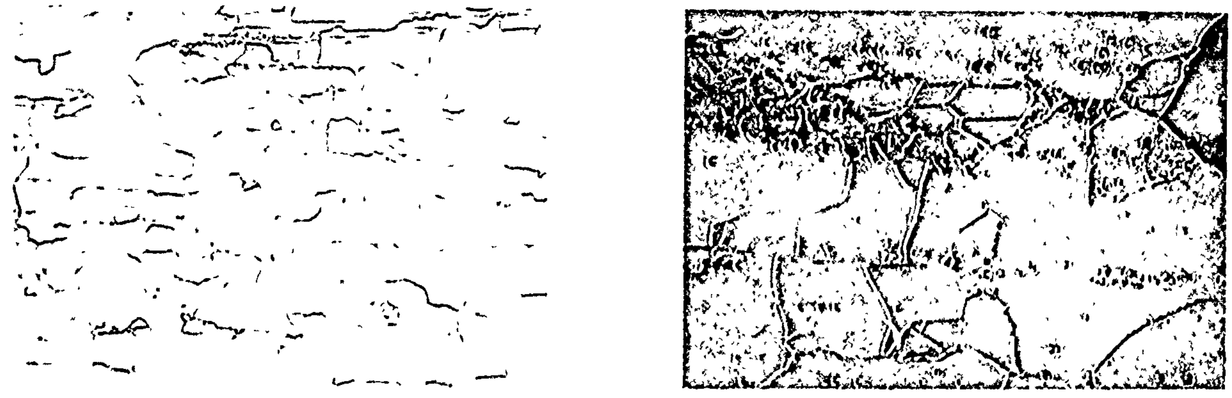


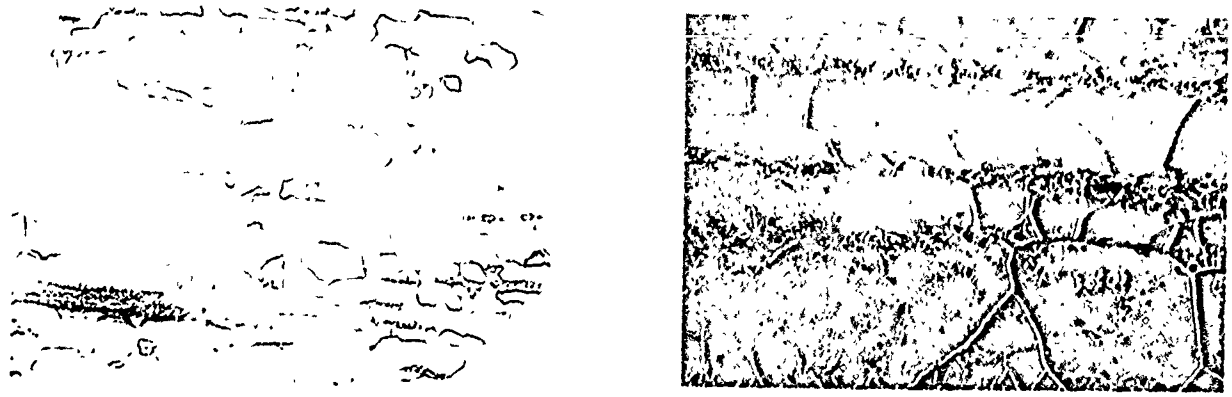
Figure 39. Effect of Solutioning Time and Temperature on As Solutioned and 4 hrs at 1100°C Age Hardness of C-6



A. 150X

21759 A. 1500X

1/4 hr at 1750°C + H.Q.

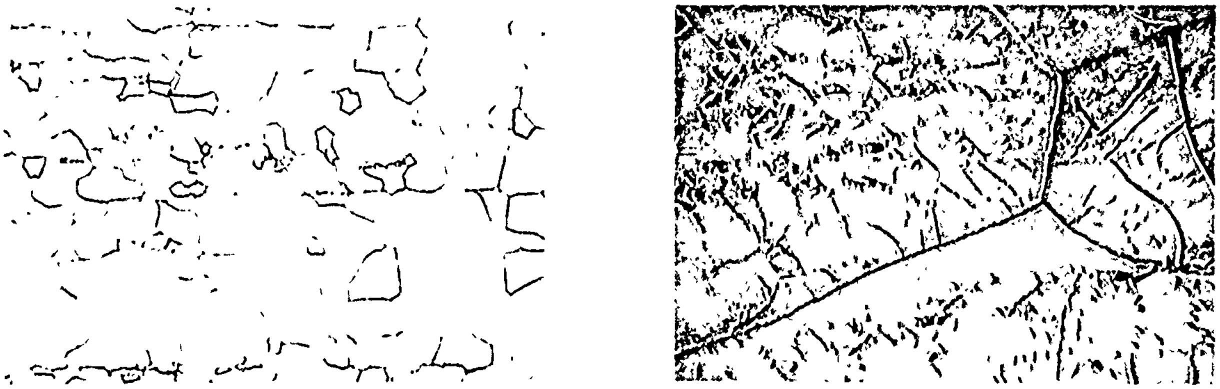


B. 150X

21760 B. 1500X

1/2 hr at 1750°C + H.Q.

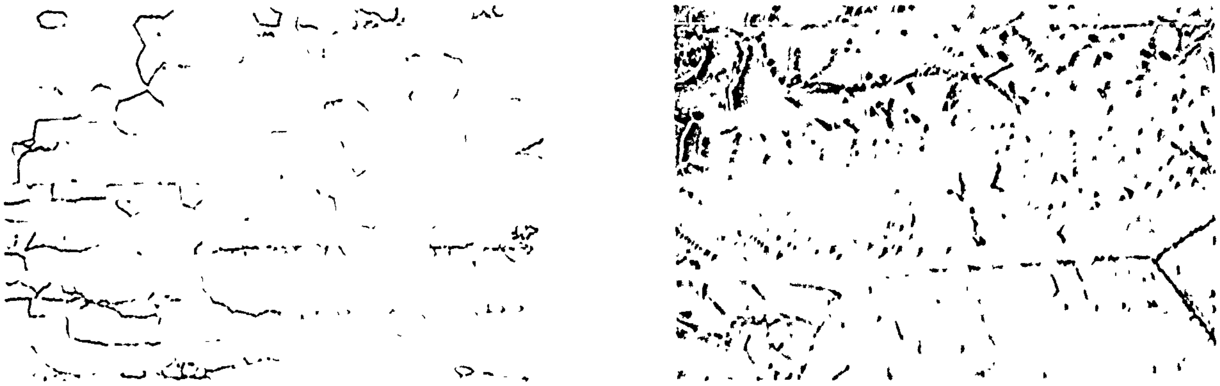
Figure 41. Microstructure of C-6 (Cb-22W-4Hf-.05C-.05N) as a Function of Time at 1750°C Solutioning Temperature



C. 150X

21761 C. 1500X

3/4 hr at 1750°C + H.Q.

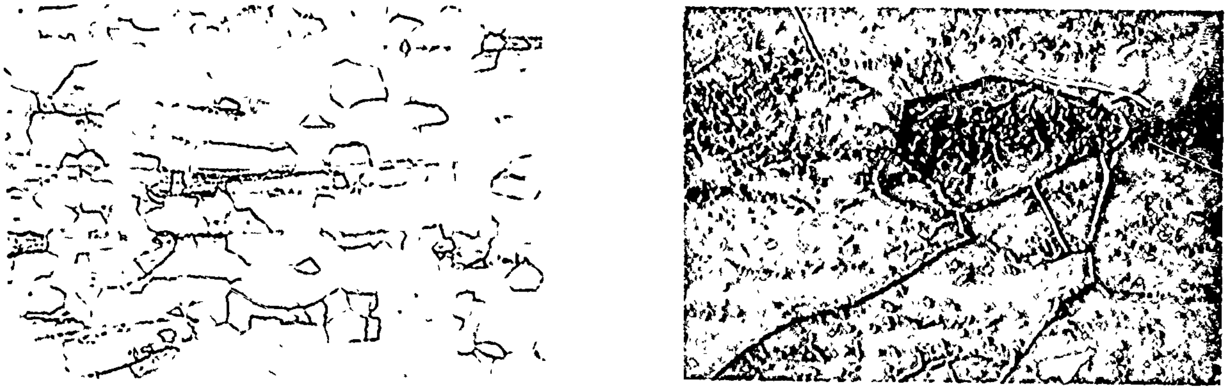


D. 150X

21762 D. 1500X

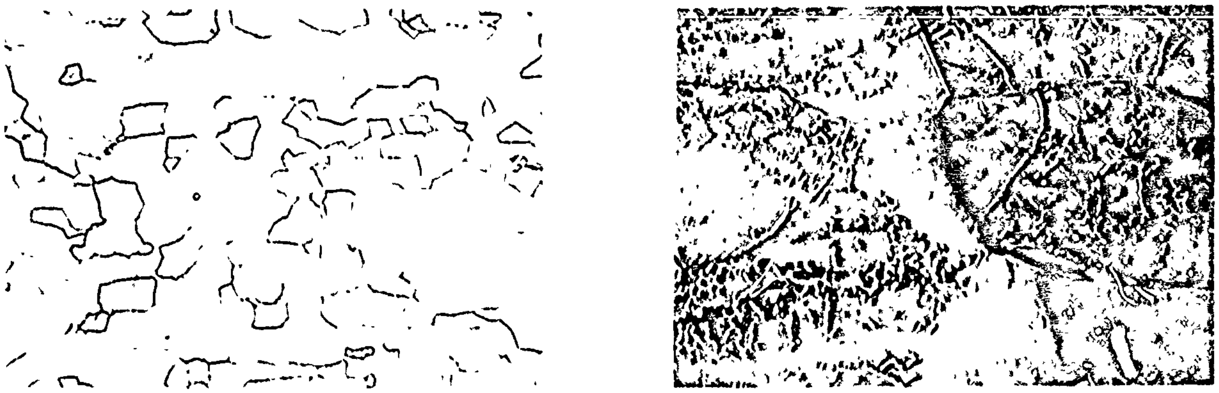
1 hr at 1750°C + H.Q.

Figure 41. Microstructure of C-6 (Cb-22W-4Hf-.05C-.05N) as a Function of Time at 1750°C Solutioning Temperature (Continued)



A. 150X 21763 A. 1500X

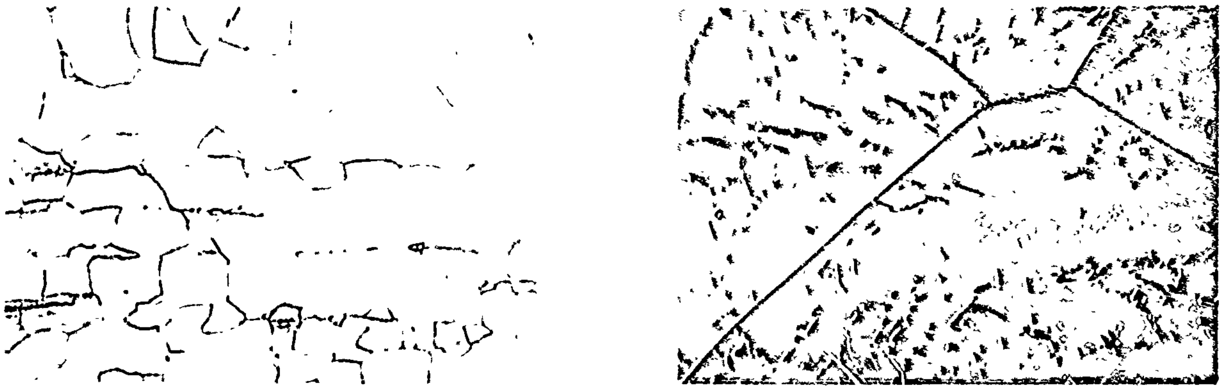
1/4 hr at 1800°C + H.Q.



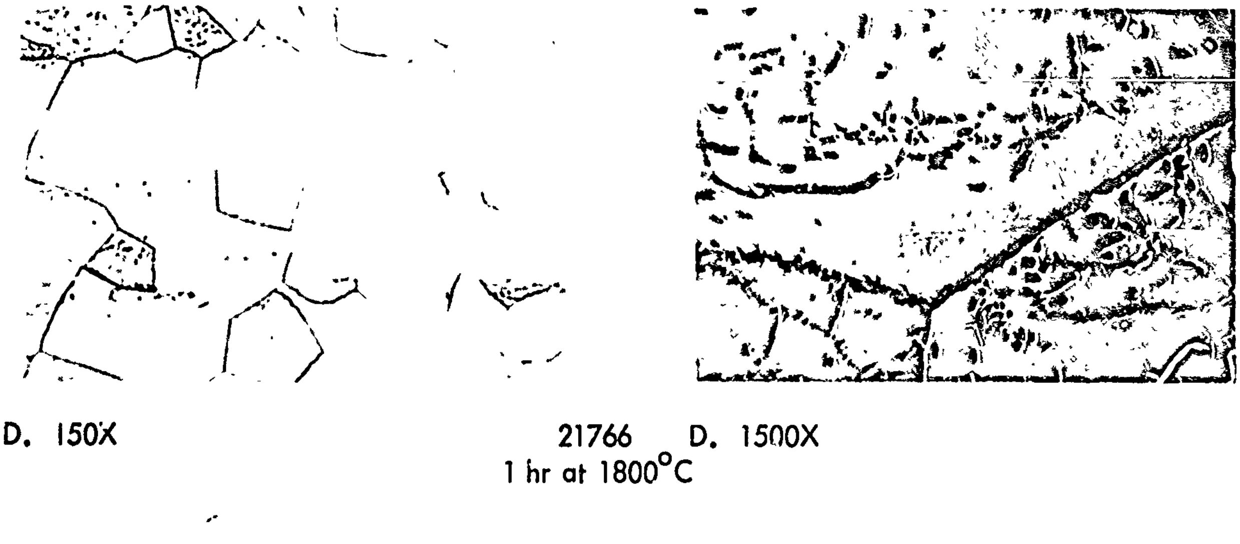
B. 150X 21765 1500°C

1/2 hr at 1800°C + H.Q.

Figure 42. Microstructure of C-6 (Cb-22W-4Hf-.05C-.04N) as a Function of Time at 1800°C Solutioning Temperature



C. 150X   21764   C. 1500X
3/4 hr at 1800°C



D. 150X   21766   D. 1500X
1 hr at 1800°C

Figure 42. Microstructure of C-6 (Cb-22W-4Hf-.05C-.04N) as a Function of Time at 1800°C Solutioning Temperature (Continued)

associated with a modest increase in as-solutioned plus helium gas cooled and a more marked increase in the aging hardness as shown in Figure 39.

Grain sizes were measured after the above described solutioning treatments. These results are given in Figure 43. The slightly higher grain size indicate at lower times at 1700°C and 1750°C are probably due to the poor definition of boundaries in partially recrystallized materials. The comparison of the metallographic structures shown in Figures 40 through 42 with the grain size variation in Figure 43 demonstrates that rapid grain growth occurs with the dissolution of residual precipitates.

Aging Response

The reproducibility of the aging effect has been the most serious problem in selecting optimized heat treatments. Figure 44 shows the hardness response from separate aging experiments. Curve A shows the double aging peaks at 4 and 12 hours respectively. The specimens were taken from the forged button melt. Curve B was run on 1/16" slices from swaged rod from ingot VAM-100D. The solutioning treatment was 1 hr at 1800°C. The specimen stock was a half inch segment of swaged rod and a broken tensile specimen button head that had been previously solutioned 1/4 hr at 1750°C plus aged 1 hr at 1100°C. Rockwell C (150 Kg) hardnesses on the specimen were used here and the hardnesses were converted to VHN. This experiment showed a strong 1 hr peak. Duplicate test on the button head of the broken tensile specimen duplicates the results on the swaged rod. Test D was run on two 1" sections of swaged rod after a 1 hr at 1800°C solutioning treatment. This test again revealed a 1 hr peak. All of the tests show a high general hardness even after aging 6 hrs at 1100°C.

Initial 1400°F and R.T. tensile tests were conducted on C-6 to verify the R.T. tensile results and to aid in the selection of a reference condition. The tensile specimens were solutioned .5 hr at 1700°C, .25 hr at 1750°C, or .25 hr at 1800°C prior to aging 1 hr at 1100°C. These results are given in Table 14.

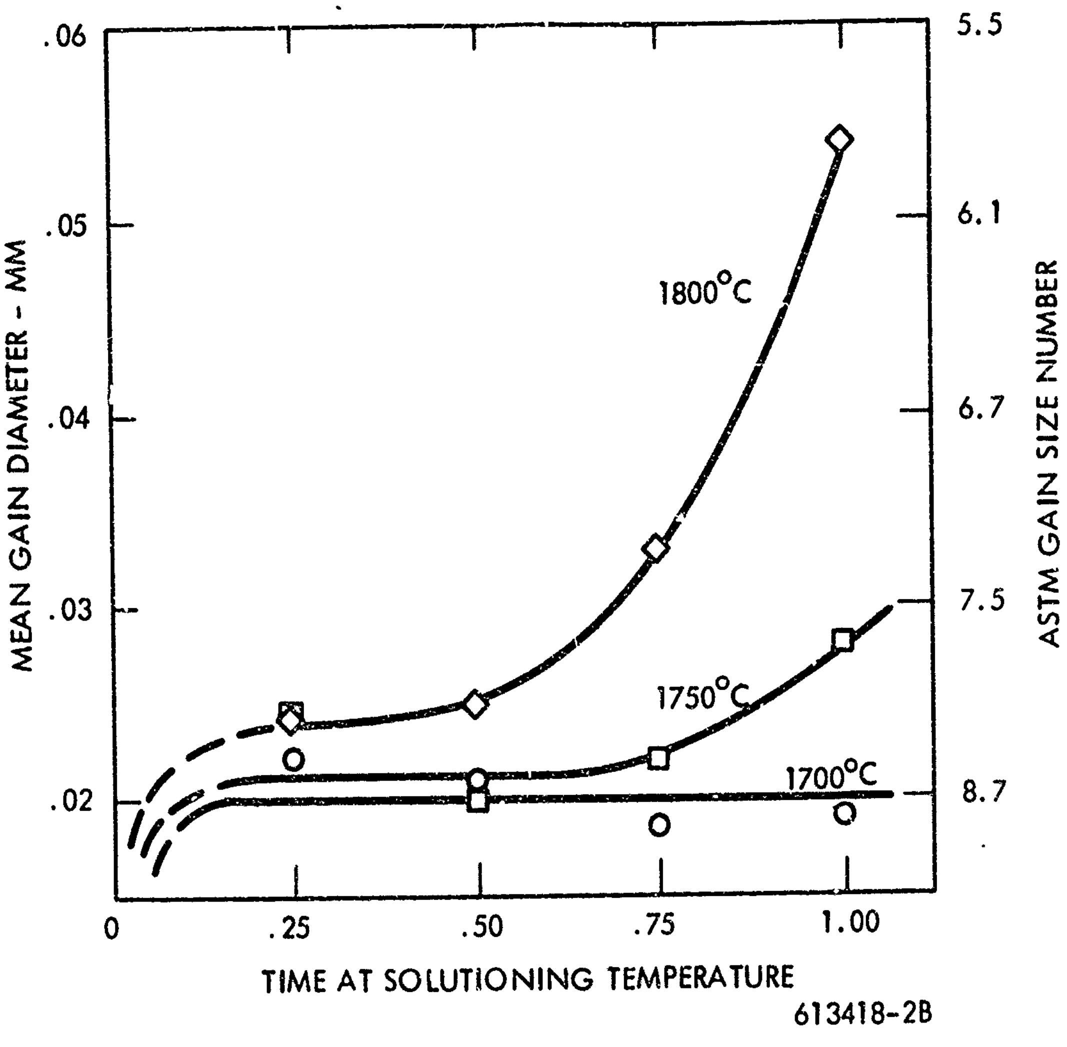


Figure 43. Variation of Mean Grain Diameter with Time at Solutioning Temperatures

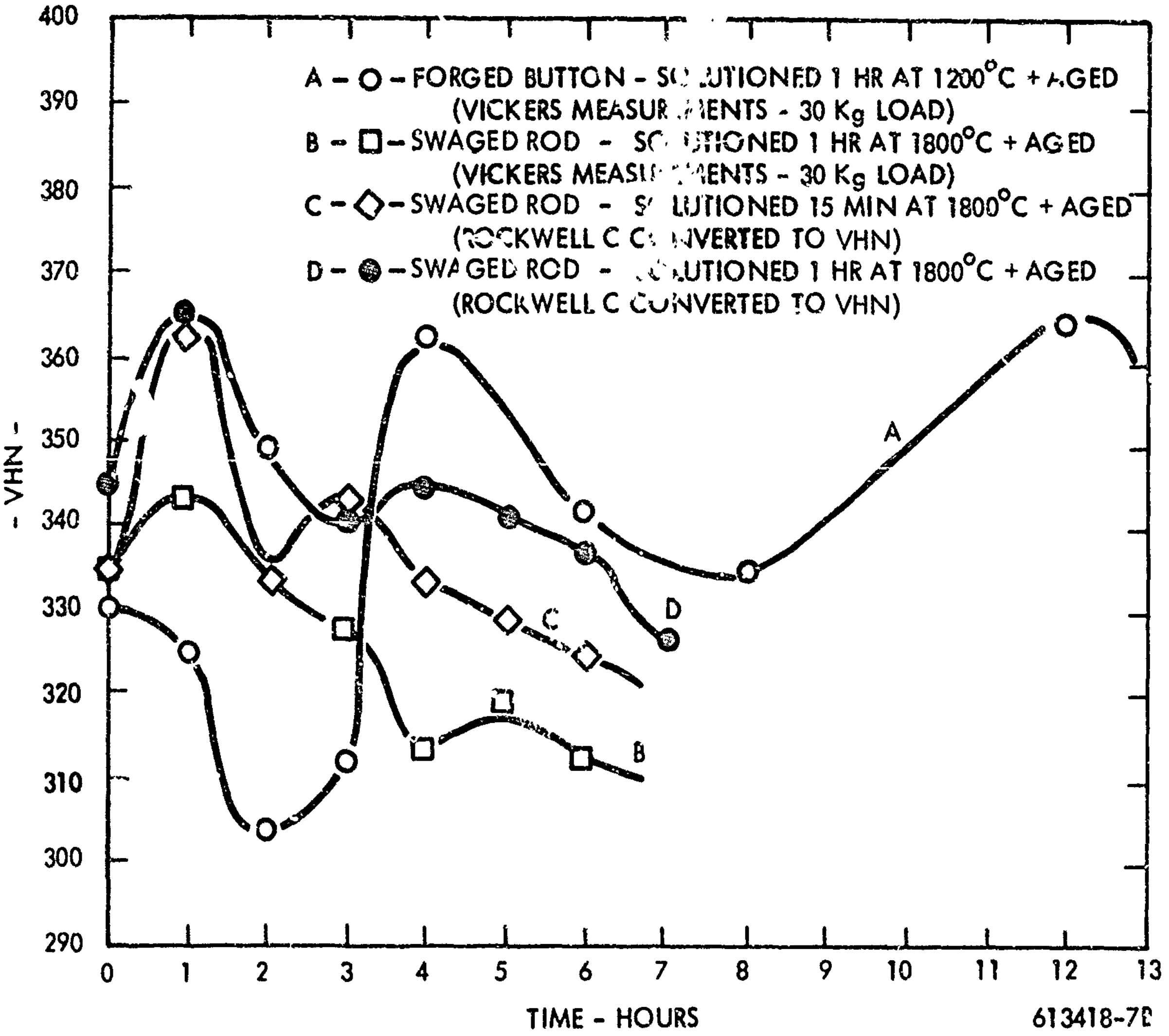


Figure 44. Variation of Aging Effect from Heat to Heat and from Experiment to Experiment for C-6 (Cb-22W-4Hf-0.05C-0.04N)

Table 14. Effect of Heat Treatment on Tensile Properties of C-6 Alloy

Specimen No.	Heat Treatment	Test Temp. °F	Strength - ksi		Ductility - %		
			.2% YS*	UTS	RA	Elong.	Uniform
C6-1	A**	R.T.	106.1	110.0	.08	---	.08
C6-2	A	1400	57.5	84.0	74.2	21.0	10.6
C6-4	B	R.T.	126.0	134.0	.14	1.0	1.0
C6-5	B	1400	87.3	99.3	54.6	13.0	4.7
C6-7	C	R.T.	---	134.2	0	0	0
C6-8	C	1400	104.0	116.0	41.0	7.0	3.3
C6-10	D	1400	60.5	79.7	71.9	19.0	7.8

*Strain Rate: .05 in/min

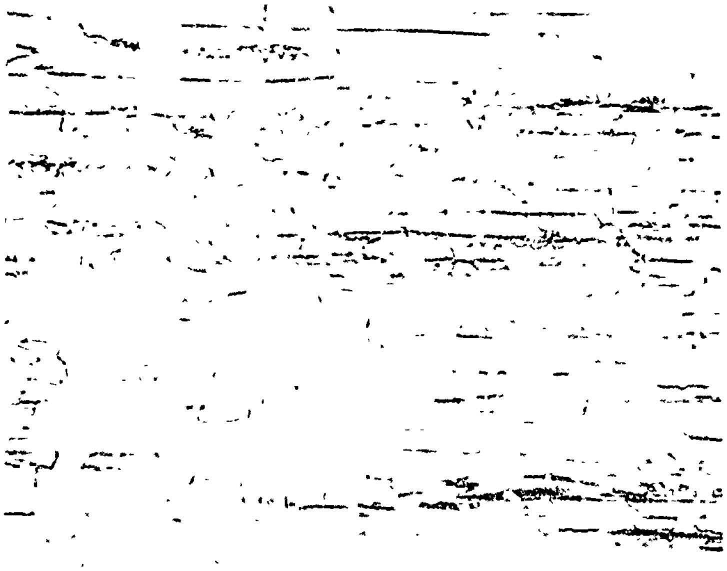
**Heat Treatments
A - .25 hr at 1700°C + 1 hr at 1100°C
B - .25 hr at 1750°C + 1 hr at 1100°C
C - .25 hr at 1800°C + 1 hr at 1100°C
D - .25 hr at 1750°C + 4 hrs at 1100°C

These initial results revealed low R.T. ductility below the goal of 5% over the temperature range R.T. to 2200°F. Program resources did not permit further optimization so the .25 hr at 1750°C + 1 hr at 1100°C treatment was initially selected as the reference condition and used for remaining tensile specimens. The tensile results obtained after this treatment are given in Table 15.

All six specimens were all heat treated in the same furnace run. The tensile strengths received were low, and testing was terminated on the remaining specimen. Metallographic studies on specimens C6-5 (VHN = 340) and C6-20 (VHN = 302) as shown in Figure 45 reveals a very similar structure in spite of the differences in hardness. Both of these specimens had ostensively received the same heat treatment although they were heated in different furnace runs.

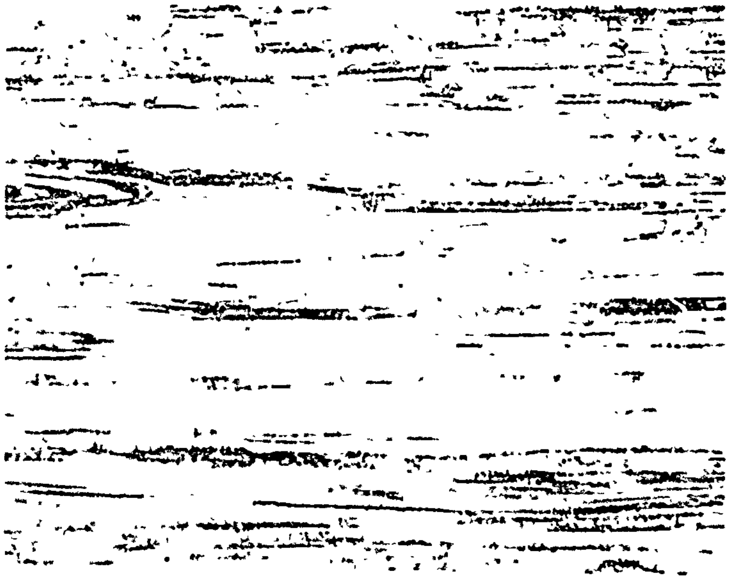
It was then obvious that the nitrogen solvus had not been exceeded during the heat treatment of specimen C6-20. Sections of specimen C6-18 (from the same furnace run as C6-20) from button head and shoulder area were given solutioning heat treatments at 1750°, 1775°, and 1800°C and aged up to 4 hours at 1100°C. Surface hardnesses were measured on the Rockwell C scale. These results with conversions to VHN are given in Table 16.

The data listed in Tables 15 and 16 show that 15 min at 1750°C is insufficient as a solutioning temperature· 1750°C is very close to the solvus temperature for this alloy. The aging effect is possible only when the interstitials have been taken into solution so that they may contribute to continuous precipitation processes during aging at lower temperatures. The 15 min. at 1800°C treatment was chosen as the reference solutioning treatment fc this alloy because very little difference in grain size was noted between specimen heated for that time at 1800°C and 1750°C. The aging data in Figure 44 indicated a peak at 1 hr at 1100°C. Since this treatment produced a very high yield strength at 1400°F but zero ductility at R.T., the 2 hr at 1100°C overaged condition was chosen.



22097 100X

Microstructure of Specimen C6-5
VHN = 340



22098 100X

Microstructure of Specimen C6-20
VHN = 302

Figure 45. Comparison of Microstructure of Specimen Given Same Heat Treatments (15 min at 1750°C + 1 hr at 1100°C but Different Furnace Heats (Note Hardness Difference)

Table 15. Tensile Properties of Solution Annealed and Aged C-6 Alloy*

Specimen No.	Test Temp.	Strength, ksi 2% YS	UTS	Ductility, % RA	Elong.	Uniform	VHN**
C6-17	200°F	104.6	126.[illegible]	45.8	25.0	15.3	293
C6-18	400°F	93.7	113.7	59.0	31.0	17.5	293
C6-19	600°F	73.0	93.6	65.9	29.0	14.3	293
C6-20	1000°F	59.9	86.0	67.9	21.0	10.9	293
C6-21	1200°F	60.7	95.0	67.5	20.0	10.8	301
C6-22	1600°F	55.3	81.9	66.7	20.0	9.8	293

* Heat Treatment - .25 Hr. at 1750°C + 1 Hr. at 1100°C.

** Post Test Hardness

Table 16. Effect of Heat Treatment on Room Temperature Hardness of C-6 Alloy

Heat Treatment	Hardness	
	R_c	VHN
A. Initial Condition (.25 hr at 1750°C + 1 hr at 1100°C)	29.5	299
A + Resolution .25 hr at 1750°C	33.5	332
A + Resolution .25 hr at 1750°C + 1 hr at 1100°C	29.5	297
A + Resolution .25 hr at 1750°C + 3 hrs at 1100°C	28.0	286
A + Resolution .25 hr at 1750°C + 4 hrs at 1100°C	25.5	269
A + Resolution .25 hr at 1775°C	33.5	332
A + Resolution .25 hr at 1775°C + 1 hr at 1100°C	32.5	323
A + Resolution .25 hr at 1775°C + 3 hrs at 1100°C	33.0	327
A + Resolution .25 hr at 1775°C + 4 hrs at 1100°C	32.0	318
A + Resolution .25 hr at 1800°C	34.5	340
A + Resolution .25 hr at 1800°C + 1 hr at 1100°C	34.5	340
A + Resolution .25 hr at 1800°C + 3 hrs at 1100°C	33.0	327
A + Resolution .25 hr at 1800°C + 4 hrs at 1100°C	32.5	323

All of the specimens had been previously solutioned 15 min at 1750°F and aged 1 hr at 1100°C. These specimens were resolutioned 15 min at 1800°C and aged 2 hours at 1100°C.

The resulting tensile data from this "reference" condition is shown in Figure 46.

The ductility data are lower than could be obtained with further overaging. These data should not be taken as typical of optimized C-6 since the specimens had to be resolutioned at 1800°C. There appears to be sufficient latitude for compromise of strength for ductility as shown in Figure 46. This alloy in the aged condition is surprisingly strong and stable to 2200°F. The 81,600 psi .2% yield is the highest value ever reported for a columbium alloy at 2200°F. B-88, by comparison, had a .2% yield at 1400°F and 2200°F of 53,500 and 48,400 psi respectively. The C-6 alloy is stronger than B-88 in the intermediate temperature range even in the under-solutioned" condition shown in Figure 46.

Creep Rupture

The creep rupture specimens were also initially "solutioned" .25 hr at 1750°C and aged 1 hr at 1100°C. The creep specimens were resolutioned .25 hr at 1800°C, He cooled, and aged 2 hrs at 1100°C. The resultant creep-rupture data are given in Table 17. The rupture life and minimum creep rate data are plotted vs. applied stress in Figures 47 and 48. Also plotted in these figures are the B-99 and B-99N data points. The stress dependence of both rupture life and minimum creep rate is greater for alloy C-6 than the B-99 or B-99N alloys. Dislocation climb is an important mechanism at the higher temperature. Since climb is diffusion controlled, the additional Hf in C-6 is thought to be the cause of the higher stress dependence.

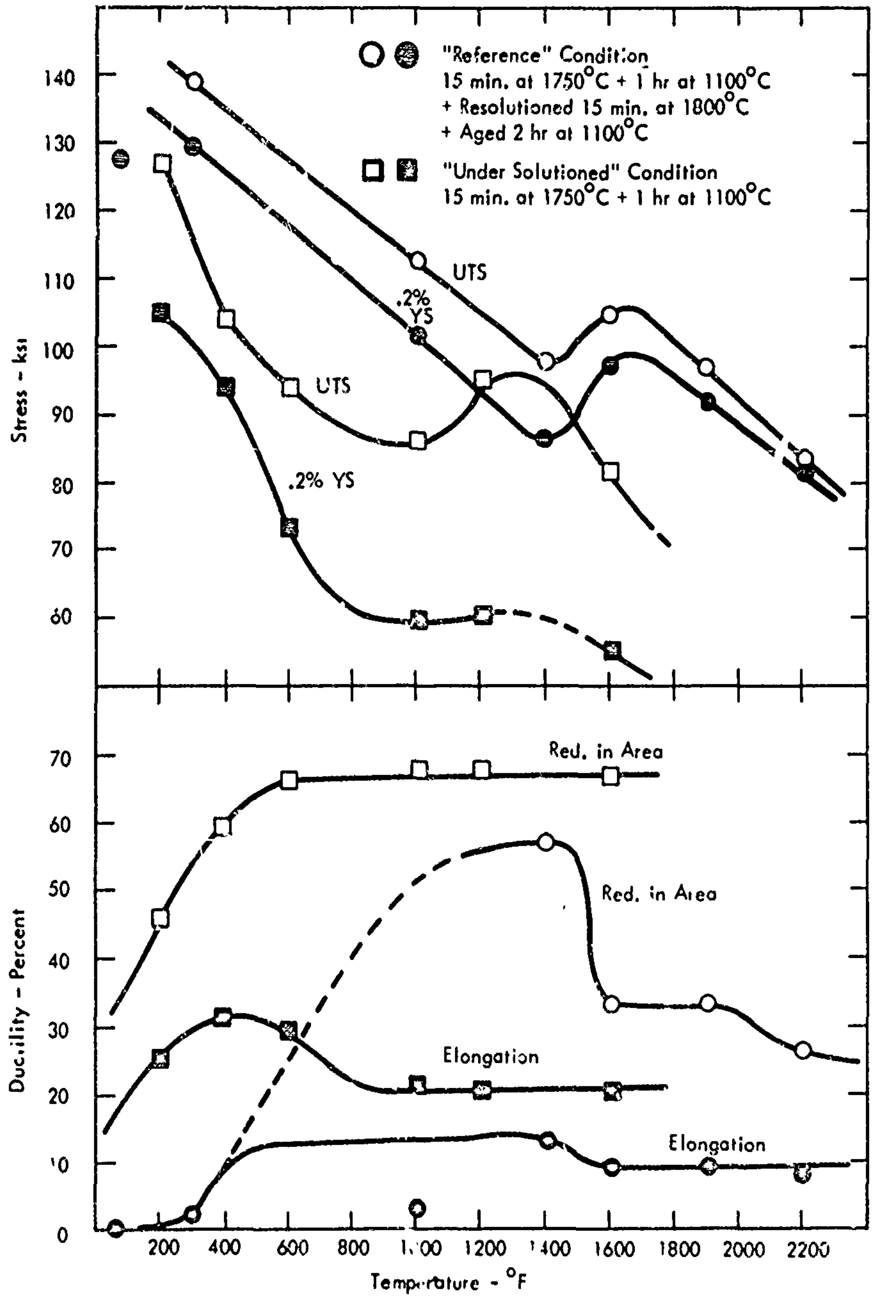


Figure 46. Variation of Tensile Properties of C-6 (Cb-22W-4Hf-.05C-.05N) with Temperature and Heat Treatment

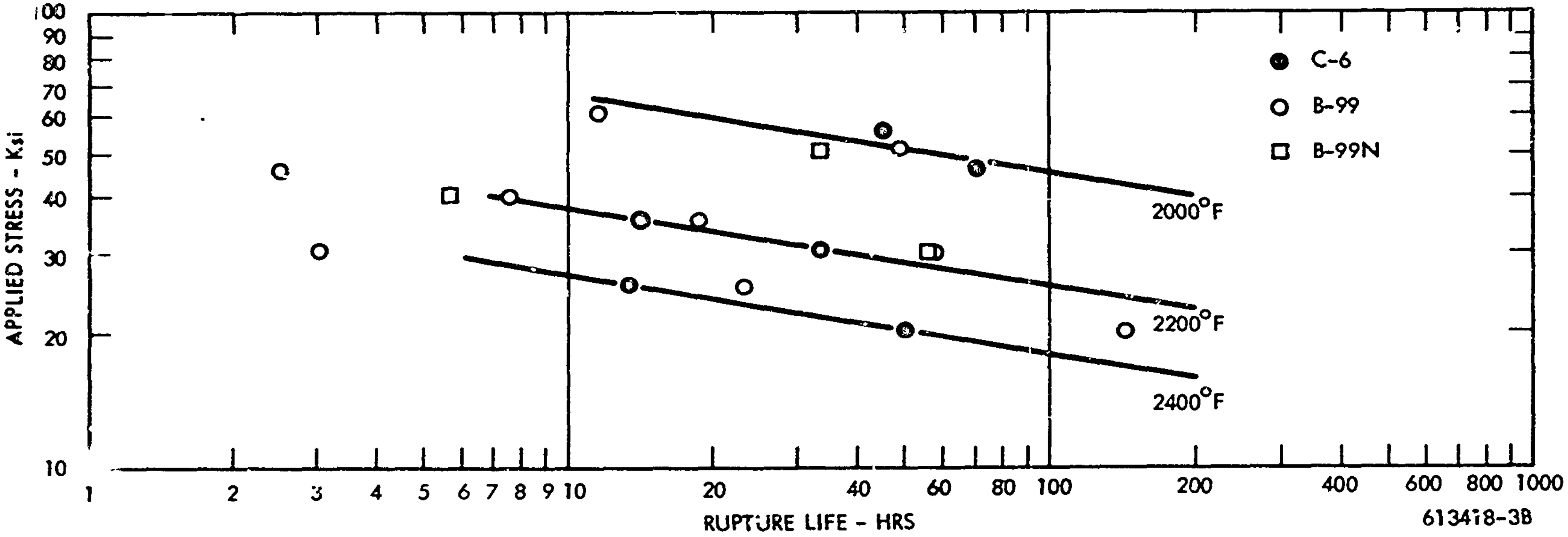


Figure 47. Effect of Applied Stress on the Rupture Life of C-6, B-99, and B-99N

Table 17. Creep-Rupture Data for C-6* (Cb-22W-4Hf-.05C-.05N)

Specimen No.	Test Temperature (°C)	Test Temperature (°F)	Stress (ksi)	Rupture Time (hrs)	$\dot{\epsilon}$ (%/hr)	Transition Time (hrs)	Reduction in Area %	Elong. %	Hardness Pretest	Hardness Post Test
C6-14	1315	2400	20	50.1	.1016	23.2	73.6	23	344	264
C6-15	1315	2400	25	13.6	.312	5.3	65.4	22	344	257
C6-9**	1205	2200	30	47.6	.040	20.7	60	13	344	
C6-11	1205	2200	35	14.4	.088	5.3	59.7	13	344	264
C6-16	1093	2000	55	23.4	.045	17.9	45.6	8.0	344	334
C6-26	1093	2000	45	69.2	.0116	44.5	54.3	11.0	344	293

*Reference H. T. .25 hr at 1750°C + H.C, age 1 hr at 1100°C
Reference H. T. .25 hr at 1800°C + H.C, age 2 hrs at 1100°C

**H.T. .25 hr at 1800°C + H.C, age 1 hr at 1100°C

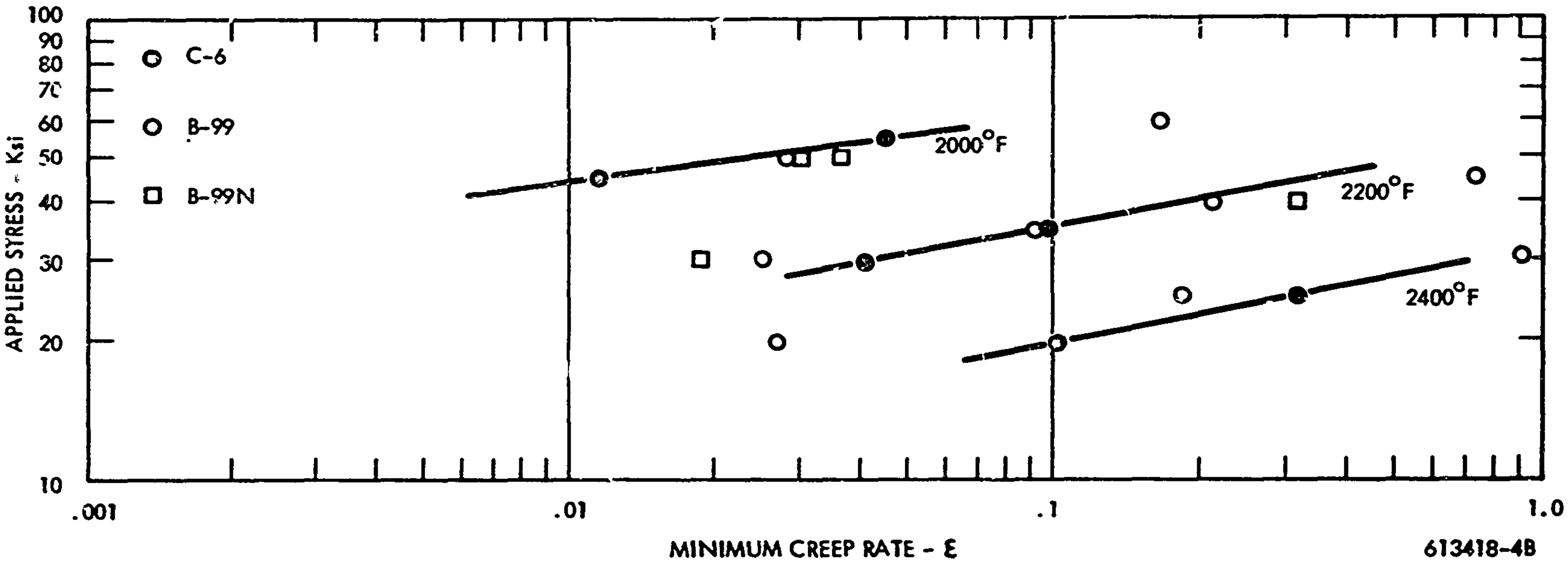


Figure 48. Effect of Applied Stress on Minimum Creep Rate of C-6, B-99, and B-99N

Properties of Silicide Coated C-6 Alloy

Two C-6 alloy test specimens were silicide coated by Sylvania and were processed as follows:

1) Solution annealed at 1800°C for 15 minutes followed by rapid cooling in Argon.
2) Coated with Si-20Fe-40Cr; heated at 1420°C for 5 minutes, quick cooled in Argon.
3) Heated at 982°C for 15 minutes followed by rapid cooling in Argon.

The last step simulated application of a coating to the root portion of a turbine blade. One of the specimens was tensile tested at 1400°F and the remaining specimen was creep rupture tested at 2000°F. Both tests were conducted in air and the specimens were tested in the as-coated condition. At 1400°F, the tensile properties were as follows:

0.2% offset yield strength	58,800 psi
ultimate tensile strength	66,500 psi
uniform elongation	1.6%
total elongation	4.5%

The relatively low value for the .2% offset yield strength was most probably caused by overaging during the coating treatment. As solution annealed (1/4 hour at 1800°C) C-6 has a room temperature hardness of about 320 DPH (See Table 9). The hardness of the as-coated material was 262-268 DPH, confirming that overaging had indeed occurred during the coating cycle. As solution annealed C-6 has a tensile yield strength of 104,000 psi (See Table 14). However, an attempt to solution anneal coated C-6 test specimens was unsuccessful as an inadvertent overtemperature excursion resulted in melting of the coating and rendered them unsuitable for testing.

Overaging does not explain the relatively low value of the ultimate tensile strength. Examination of the fracture revealed an inclusion (See Figure 49) which caused the anomalous low tensile strength. The inclusion was examined by x-ray diffraction and electron-microprobe and identified as pure tungsten. It is assumed that this was a piece of unmelted

Figure 49. Fracture Surface of C-6 Tensile Specimen Tested at 1400°F in Air

tungsten occluded during the melting operation. Lack of additional specimens prevented further tensile testing.

The remaining silicide coated specimen was creep-rupture tested in air at 2000°F and the resulting creep curve is shown in Figure 50. Initially, the applied stress was 30,000 psi. After a primary creep strain of approximately .3% which occurred in less than five hours, a secondary creep rate of 0.0025%/hour was established and persisted out to 94 hours at which time the stress was increased to 40,000 psi. After another brief period of transient creep, a new secondary creep rate of 0.045%/hour was established but persisted for only about 20 hours at which time third stage creep was entered followed by rupture at 130 hours. The rupture elongation was >6%. Oxidation of the fracture surfaces made a precise final elongation measurement difficult.

Comparing steady state creep rates for as coated material with C-6 alloy in the reference condition, i.e. 1/4 hour at 1800°C + 1 hr at 1100°C, would indicate a lower creep strength for the as-coated material (See Figure 51). The diameter of the test specimen had increased approximately 3% during coating and the final coated diameter was used to calculate the load for the stress rupture test. If the coating contributes nothing to the load carrying capacity, an error in the actual stress would be 9% and making this adjustment would result in essentially no difference in the creep strength of the coated compared to uncoated material. Although the coated C-6 specimen was creep-rupture tested in the overaged condition, it has been shown that the nitride precipitate has its most potent effect on short time properties with little contribution to the creep rupture strength at 2000°F and above. (See Table 14 and Figure 47).

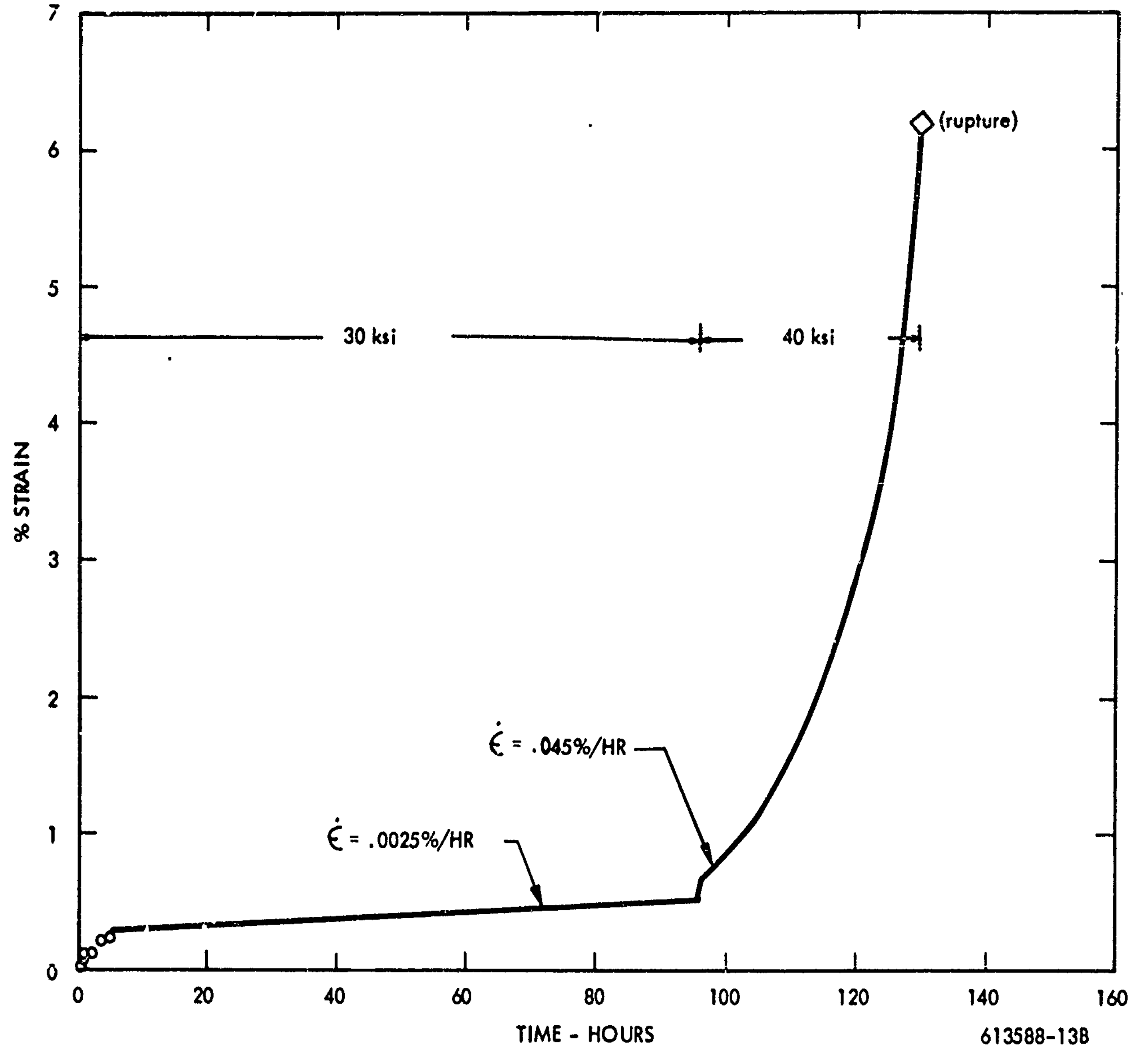


Figure 50. Creep Rupture Curve for Silicide Coated C-6 Alloy at 2000°F in Air

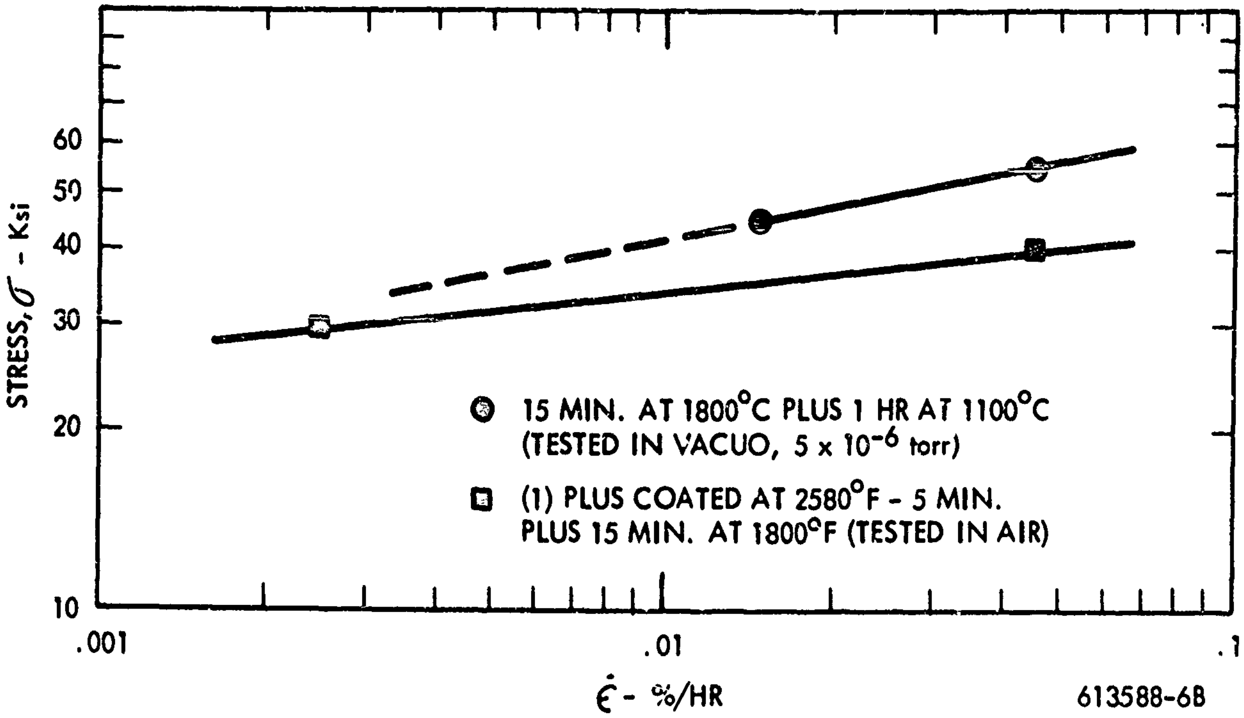


Figure 51. Comparison of Secondary Creep Rates of Bare and Coated C-6 Alloy

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