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AGEING IN NIOBIUM-RICH NIOBIUM-HAFNIUM-CARBON ALLOYS

D. C. BRIGGS AND L. R. HARMATIUK

PHYSICAL METALLURGY DIVISION

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AGEING IN NIOBIUM-RICH NIOBIUM-HAFNIUM-CARBON ALLOYS

by

D. C. Briggs* and L. R. Harmatiuk**

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ABSTRACT

Dispersion hardening was investigated in niobium alloys with hafnium up to 12 wt% and carbon to 0.5 wt%. Experimental techniques included hardness measurement, metallography, and X-ray analysis. Age-hardening was found at 1100° - 1200°C and related to precipitation of the complex monocarbide (Nb, Hf) C. The constitution of the alloys was determined at 1200°C and conclusions drawn concerning the constitution diagram at higher temperatures to 2200°C. A phase resembling the zeta phase in Ta-C alloys was observed in low-carbon alloys.

RÉSUMÉ

Les auteurs ont étudié le durcissement de dispersion dans les alliages au niobium contenant, au poids, jusqu'à 12% de hafnium et 0.5% de carbone. Les techniques expérimentales comprenaient la mesure de la dureté, la métallographie et l'analyse aux rayons X. Le durcissement par vieillissement se situe de 1100° à 1200°C et se rattache à la précipitation du monocarbure complexe (Nb, Hf)C. La constitution des alliages a été déterminée à 1200°C et les conclusions relatives au diagramme de constitution portent sur des températures s'élevant jusqu'à 2200°C. Les auteurs ont observé dans les alliages à faible teneur en carbone une phase qui ressemble à la phase zêta dans les alliages Ta-C.

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INTRODUCTION

The carbides of zirconium and hafnium are known to be dispersion hardening agents in niobium alloys (1). The hafnium carbide HfC, in particular, possesses high hardness, a very high melting point, and favourable free energy of formation. This report describes an investigation of dispersion hardening in niobium-rich alloys of the Nb-Hf-C system. The work consisted of assessments of the effect of temperature on the stability of the carbides occurring in the system, and of the ageing reaction that was observed.

LITERATURE REVIEW

Niobium-Carbon System

The constitution diagram of the Nb-C system has been thoroughly investigated and much disputed (2-10). Reported values of the maximum solubility of carbon in niobium range from 0.03 to 0.80 wt% (0.25 to 6 at %) at the eutectic temperature 2335°C. Quenching rate is a critical factor in the use of metallographic methods to determine the constitution of this system. Consequently, the carburizing and chemical analysis technique by which Elliott found his value of 0.80 wt% (10) appears the most reliable method. With decreased temperature the solubility drops rapidly, being 0.1 wt% (0.8 at %) at 1800°C and 0.01 wt% (0.1 at %) at 1200°C.

The hexagonal hemicarbide (subcarbide) Nb_2C has a composition range from about 4.8 to 6.1 wt% (28 to 33.3 at %) at the eutectic temperature 2335°C (5); at lower temperatures this range appears to be very narrow and adjacent to the stoichiometric composition (5, 6).

The fcc monocarbide NbC has a homogeneity range extending from 8.3 wt% (41 at %) to about 10.3 - 11.4 wt%C (47-50 at %) at 2000°C (3, 5, 10). These limits of homogeneity vary only slightly between 1600 and 2400°C (5). Typical values of the lattice parameter measured across this composition range are those of Brauer and Lesser, 4.431 - 4.469Å (3). A value of 4.4704Å has been measured for fully carburized NbC (11).

Brauer and Lesser found one other carbide in the Nb-C system, - the zeta phase, so named because of its resemblance to the zeta phase found by them in the Ta-C system (3, 12). It occurred at compositions between the Nb_2C and NbC single phase fields. No other workers have reported finding this phase in Nb-C alloys.

Niobium-Hafnium System

Although literature dealing with the Nb-Hf system shows some disagreement, the form of the constitution diagram is established and it is certain that the solubility of hafnium in niobium is extensive, reaching 50-65 wt % Hf (34-50 at %) at 1000°C [13, 14]. The limit increases with temperature until there is complete mutual solubility above the transformation temperature of hafnium.

Hafnium-Carbon System

In the hafnium-carbon system there exists one intermediate compound, the fcc monocarbide HfC. In works cited by Rudy [15] the homogeneity range of HfC was given as 34 to 49.5 at % C at 2300°C, with the lower carbon boundary at 37.5 at % at 1500°C. The lattice parameter varies directly with carbon content from 4.608 to 4.640Å.

Niobium-Hafnium-Carbon System

At the inception of this research the constitution of the Nb-Hf-C ternary system had not been published, although some predictions had been made [16-18]. Isotherms have now appeared for 1800°C [19] and 2000°C [9, 20]. In addition, information is available on the related systems Ta-Hf-C [15, 16] and Nb-Zr-C [21].

The form of the diagram above the transformation temperature of hafnium appears to be established and is shown in Figure 1 for 2000°C. Complete miscibility exists between the two monocarbides NbC and Hf C [22].

The carbide Nb_2C dissolves up to 5 at % Hf at 1800-2000°C [19, 20]. By analogy with findings in the Ta-Hf-C system [15], this limit is likely greater at higher temperatures. No significant variation of lattice constants with hafnium content has been found for Nb_2C.

The composition range of the niobium-hafnium solid solution is limited to very low carbon contents and gives rise to a very broad two-phase region of metal plus monocarbide. The zeta phase has not been observed in ternary alloys of either the Nb-Hf-C or Ta-Hf-C system.

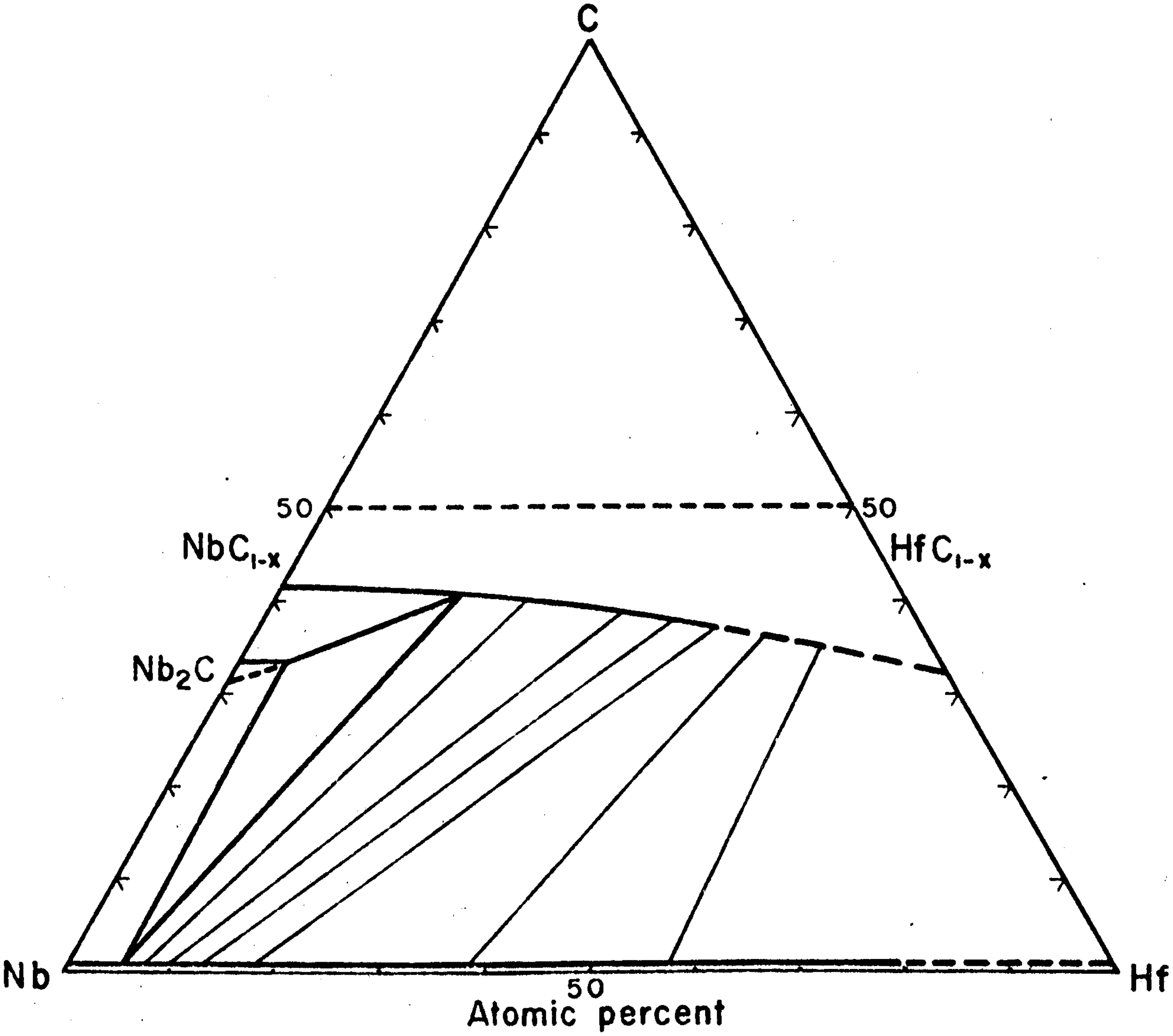


Figure 1. Nb-Hf-C system at 2000°C (after Stecher et al.(19)).

EXPERIMENTAL

The major portion of this study involved a survey of the variation of hardness with heat treatment temperature and time. A supporting program of phase identification was carried out by metallography and X-ray diffraction analysis.

Materials

Starting materials for all alloys were the following:

Niobium	- D-3 granules from E. I. duPont de Nemours and Co.
Hafnium	- sponge metal from The Carborundum Co.
Carbon	- foundry graphite

Analysis of these materials are given in Table 1.

Preparation of Alloys

A group of twenty alloys from the niobium-hafnium-carbon system was studied. Their compositions ranged up to 0.5 wt% C and 12 wt% Hf. These are shown in Table 2 and Figure 2.

The alloys were prepared as 40g buttons under argon in a cold-hearth arc furnace. At least three homogenizing melts were made on each alloy after the additions had been melted in. Hafnium was added directly as sponge metal. Carbon was added as graphite to 0.5% C alloys, and to 0.25 and 0.125% C alloys containing up to 4% Hf. For the remaining alloys, master alloys of about 1.5 wt% C were added, the additions being calculated on the basis of the analysed carbon content of the master alloy.

Carbon analyses were made on some alloys as a spot check on the attainment of target compositions. Spot analyses were also made for the impurities oxygen, nitrogen and tungsten. The last element, acquired from the electrode during melting, did not exceed 0.10% in the alloys checked. All analytical results are given in Table 2.

Ageing Treatments

Heat treatments were carried out in a Brew high-temperature vacuum furnace. Operating pressures ranged from 3 x 10^{-5} mm Hg at 2200°C to 10^{-6} mm Hg at 1000°C. Cooling of the specimens, which were cubes about 1/4 in. to a side, was effected by simultaneously shutting off the furnace power and admitting helium to a pressure of 500 mm Hg. In this fashion the specimens were cooled from 2200°C to 1500°C in 20 sec and to black heat in a total of 2 min.

TABLE 1

Analyses of Starting Materials[a]

	Nb	Hf	C[b]
O	44	980	
N	3	23	
C	22	< 80	99.2%[c]
Ta	480	< 100	
Fe	< 50	250	2100
Cr	< 30	60	200
Ni	< 30	< 20	100
Ti	< 50	< 20	200
W	< 50		
Nb	99.92%+[c]	50	100
Hf		97.2%	
Al		< 20	400
B		< 0.2	
Cd		< 2	
Co		< 5	
Mg		580	200
Mn		40	100
Pb		< 10	7
Si		< 20	1500
V		< 5	200
U		< 1	
Cl		150	
Sn		< 20	
Cu		20	30
Mo		< 5	50
Zr		2.8%	50
Ca			1000
Ag			10
Na			300
Zn			800
Sr			300
Brinell Hardness	48	255	

a - Ppm except where otherwise noted.

b - Semi-quantitative spectrographic analysis by the Spectrographic Laboratory, Mines Branch.

c - By difference.

TABLE 2

Composition of Experimental Alloys

Alloy Designation	Nominal Composition				Chemical Analysis			
	Weight, %		Atomic, %					
	Hf	C	Hf	C	C[a]	O[b]	N[c]	W[d]
N-C/8	0	0.125	0	0.96		0.025	0.006	
N-C/4	0	0.25	0	1.90				
N-C/2	0	0.50	0	3.74		0.060	0.015	
N-2H-C/16	2.00	0.06	1.05	0.47	0.082	0.031	0.004	
N-2H-C/8	2.00	0.125	1.04	0.97				
N-2H-C/4	2.00	0.25	1.03	1.92				
N-2H-C/2	2.00	0.50	1.02	3.78				
N-4H-C/16	4.00	0.06	2.11	0.47	0.07			0.10
N-4H-C/16	(2nd melt)				0.087	0.043	0.004	
N-4H-C/8	4.00	0.125	2.10	0.98				
N-4H-C/4	4.00	0.25	2.09	1.94		0.020	0.008	
N-4H-C/2	4.00	0.50	2.05	3.81				
N-8H-C/16	8.00	0.06	4.31	0.48	0.06			0.087
N-8H-C/8	8.00	0.125	4.29	1.00	0.14	0.023	0.003	0.084
N-8H-C/4	8.00	0.25	4.26	1.98	0.26			
N-8H-C/2	8.00	0.50	4.18	3.89				
N-12H	12.00	0	6.63	0	0.020	0.037	0.003	
N-12H-C/16	12.00	0.06	6.60	0.49	0.06			0.090
N-12H-C/8	12.00	0.125	6.57	1.02	0.13			0.078
N-12H-C/4	12.00	0.25	6.51	2.02	0.25			0.081
N-12H-C/2	12.00	0.50	6.40	3.96	0.51	0.041	0.007	

[a] Below 0.10%, by conductometric method; above 0.10%, by gravimetric method.

[b] Vacuum fusion analysis.

[c] Kjeldahl method.

[d] Semi-quantitative spectrographic analysis.

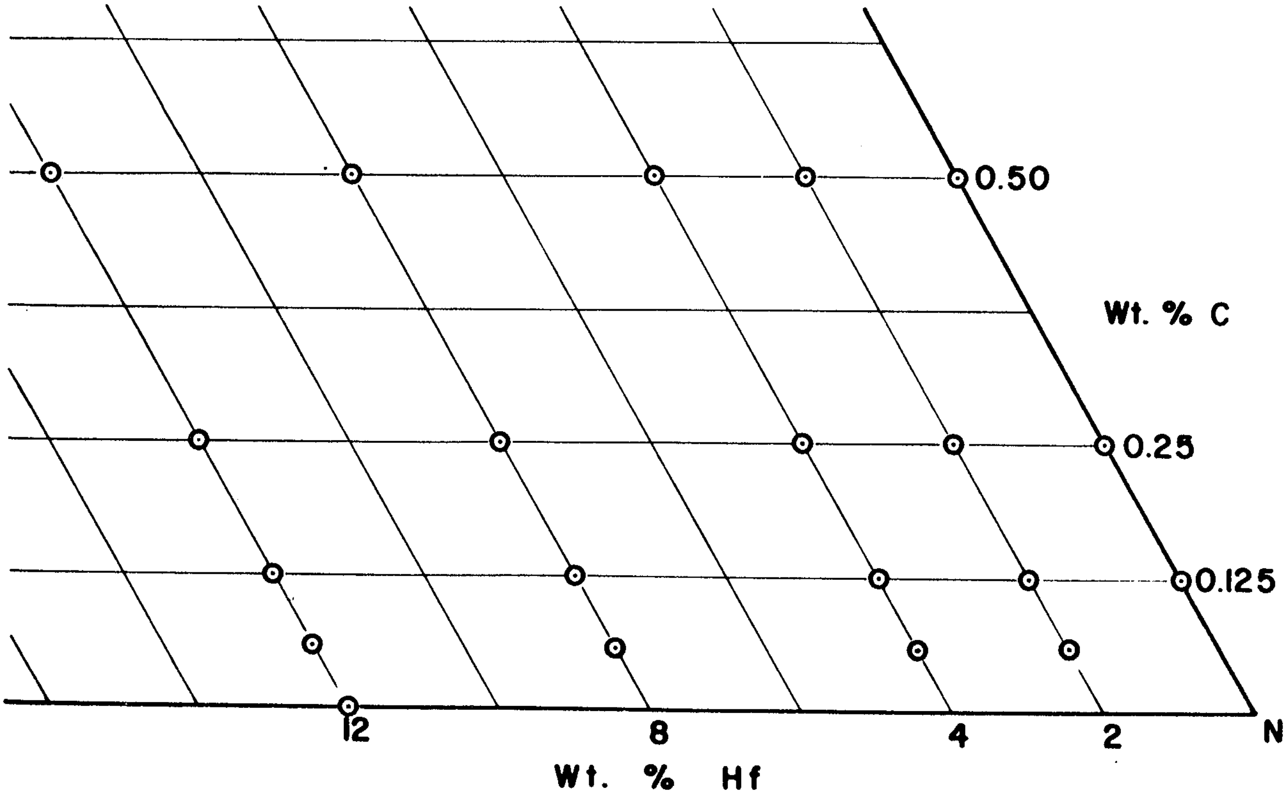


Figure 2. Composition of experimental alloys.

A one-hour anneal at 2200°C was used as a solution treatment prior to the ageing treatments. The ageing response of all alloys was studied for two-hour treatments at temperatures from 1000° to 1800°C. The effect of ageing time between 1 and 8 hr was studied at 1200°C. Hardness determinations were made on samples after preparation for metallographic examination.

Metallography

The specimens were abraded on silicon carbide papers through 600 grit. Polishing was performed mechanically on vibratory polishers. Alumina (0.3μ) in methyl alcohol on a PAN-W Pellon disc was used for rough polishing. Final polishing took place in two stages, the first with 0.05μ alumina in methyl alcohol and the second with 0.5μ chromic oxide in distilled water; microcloth was used for both stages. Periodically throughout the polishing, the specimens were given a chemical polish and etch with a solution of 25 parts lactic acid, 15 parts nitric acid and 1 part hydrofluoric acid. This solution also served as final etchant for most specimens. In some cases a stronger etchant was required, containing 30 parts lactic acid, 10 parts nitric acid, and 5-10 parts hydrofluoric acid.

X-Ray Analysis

X-ray diffraction powder photographs were taken of carbides extracted from selected alloys. The extractions were made in an electrolyte of 10% hydrochloric acid in methyl alcohol, with a stainless steel or nickel cathode and current density of the order of 0.5 to 1.0 amps/in^2.

RESULTS

Data from the hardness surveys are listed in Tables 3 and 4, and are presented graphically in Figures 3, 4 and 5.

Table 3 and Figure 3 show the variation of room temperature hardness with ageing temperature. Table 4 and Figure 4 give the variation of hardness with time of ageing at 1200°C. The effect of composition on hardness can be seen in Tables 3 and 4 for all heat treatments, and graphically in Figure 5 for the two conditions "solution treated" and "solution treated and aged at 1200°C for 2 hr". In particular, Figure 5 gives a measure of the age-hardening response of the alloys.

Results of the phase identification program, both through metallography and through X-ray analysis, are given in Table 5. Lattice constants for the monocarbide MC, and the hemicarbide M_2C calculated from the X-ray diffraction results, are listed in Table 6.

TABLE 3

Variation of Room Temperature Hardness with Ageing Temperature *

Alloy Designation	Heat Treatment (Temp. in °C)								
	As Cast (AC)	AC+ 1200 2 hr	2200 1 hr	2200°C for 1 hr and					
				1000 2 hr	1100 2 hr	1200 2 hr	1400 2 hr	1600 2 hr	1800 2 hr
N-C/8	106	94	76	72		75	78	72	84
N-C/4	124	118	83	83		85	80	79	78
C-C/2	156	141	101	97		96	101	101	
N-2H-C/16	131	104	108	99		102	107	110	111
N-2H-C/8	134	112	100	95		95	103	99	110
N-2H-C/4	136	116	109	109		114	114	111	109
N-2H-C/2	151	143	117	115		121	124	117	
N-4H-C/16	135	131	128	123		103	113	126	131
N-4H-C/8	136	141	128	122	129	129	109	121	138
N-4H-C/4	139	160	124	127	142	162	135	126	125
N-4H-C/2	146	181	148	148	150	164	145	140	
N-8H-C/16	152	138	155	143		123	123	136	158
N-8H-C/8	158	151	156	146		141	131	128	156
N-8H-C/4	167	173	159	147	164	160	146	136	141
N-8H-C/2	168	200	167	164	192	186	160	150	
N-12H	189	135	177	163		142	146	183	187
N-12H-C/16	170	142	180	174		142	138	154	177
N-12H-C/8	180	158	171	151		152	146	152	165
N-12H-C/4	182	172	163	164	176	170	160	150	154
N-12H-C/2	182	179	178	178	195	187	172	163	164

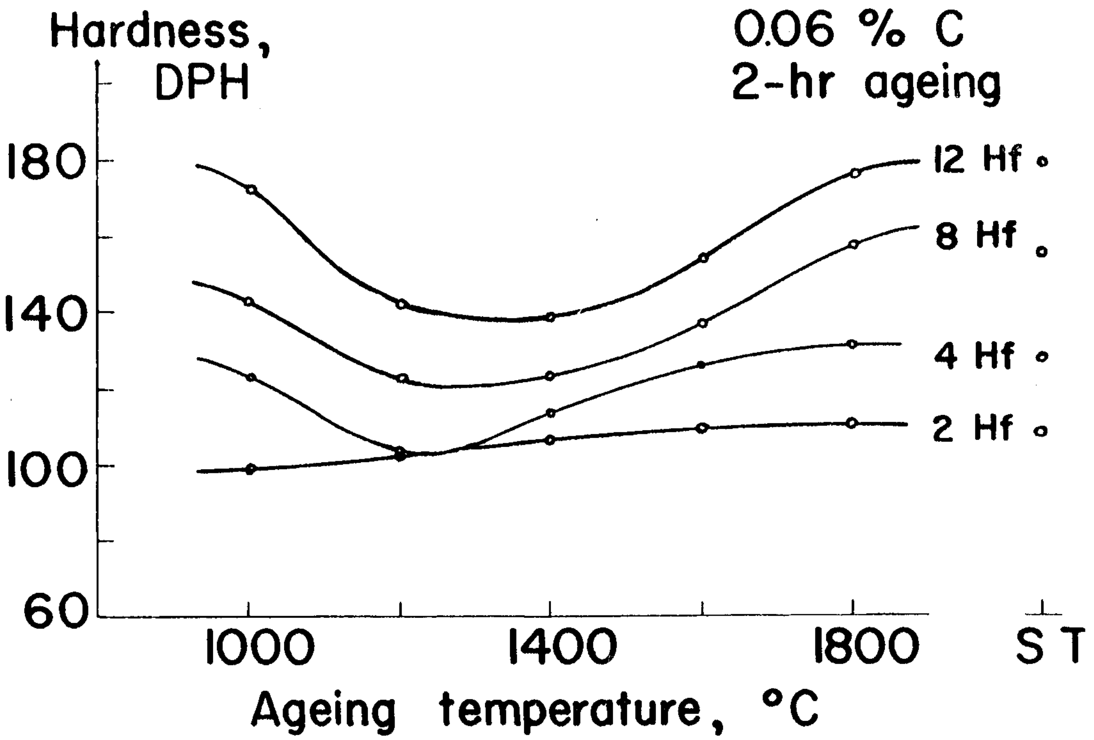
* Diamond pyramid hardness numbers, Vickers, 10-kg load.

TABLE 4

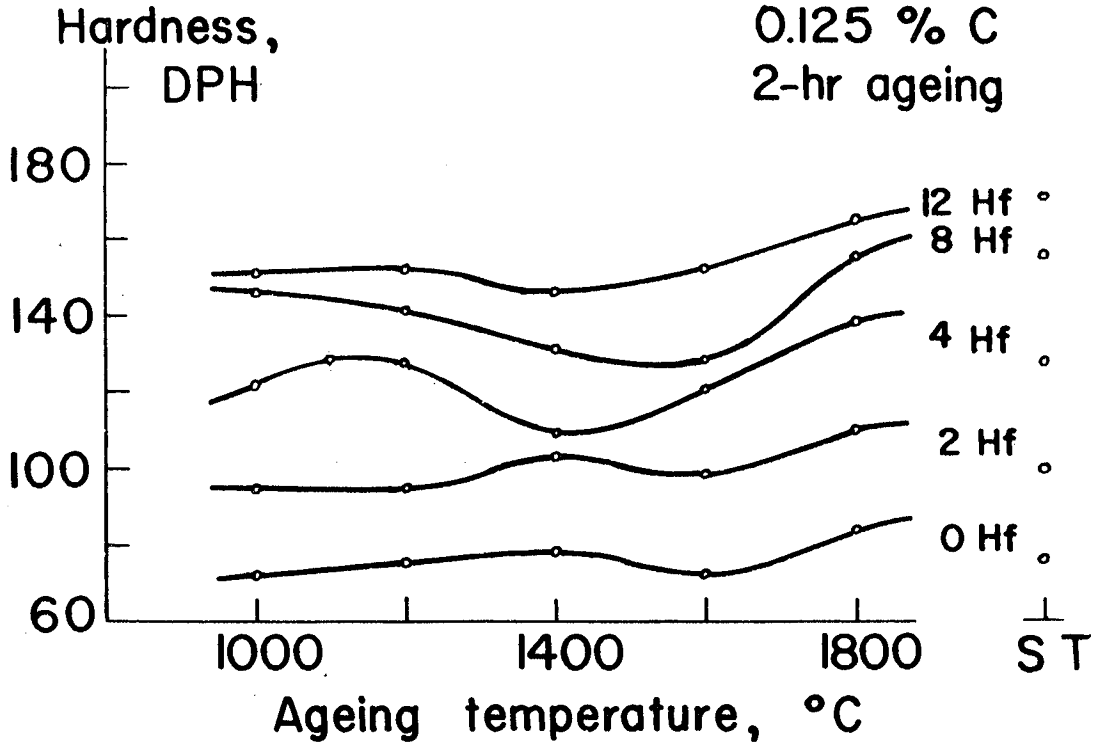
Variation of Room Temperature Hardness with Ageing Time at 1200°C *

Alloy	2200°C 1 hr	2200°C for 1 hr and 1200°C for			
		1 hr	2 hr	4 hr	8 hr
N-C/8	76	76	75	73	75
N-C/4	83	86	85	84	85
N-C/2	101	97	96	90	96
N-2H-C/16	108	104	102	102	100
N-2H-C/8	100	109	95	106	104
N-2H-C/4	109	109	114	110	115
N-2H-C/2	117	118	121	122	123
N-4H-C/16	128	119	103	108	99
N-4H-C/8	128	160	129	123	120
N-4H-C/4	124	144	162	143	153
N-4H-C/2	148	168	164	167	169
N-8H-C/16	155	129	123	122	120
N-8H-C/8	156	145	141	137	128
N-8H-C/4	159	159	160	153	146
N-8H-C/2	167	179	186	176	174
N-12H	177	143	142	142	142
N-12H-C/16	180	150	142	141	135
N-12H-C/8	171	157	152	149	138
N-12H-C/4	163	171	170	163	154
N-12H-C/2	178	192	187	193	191

* Diamond pyramid hardness numbers, Vickers, 10-kg load.

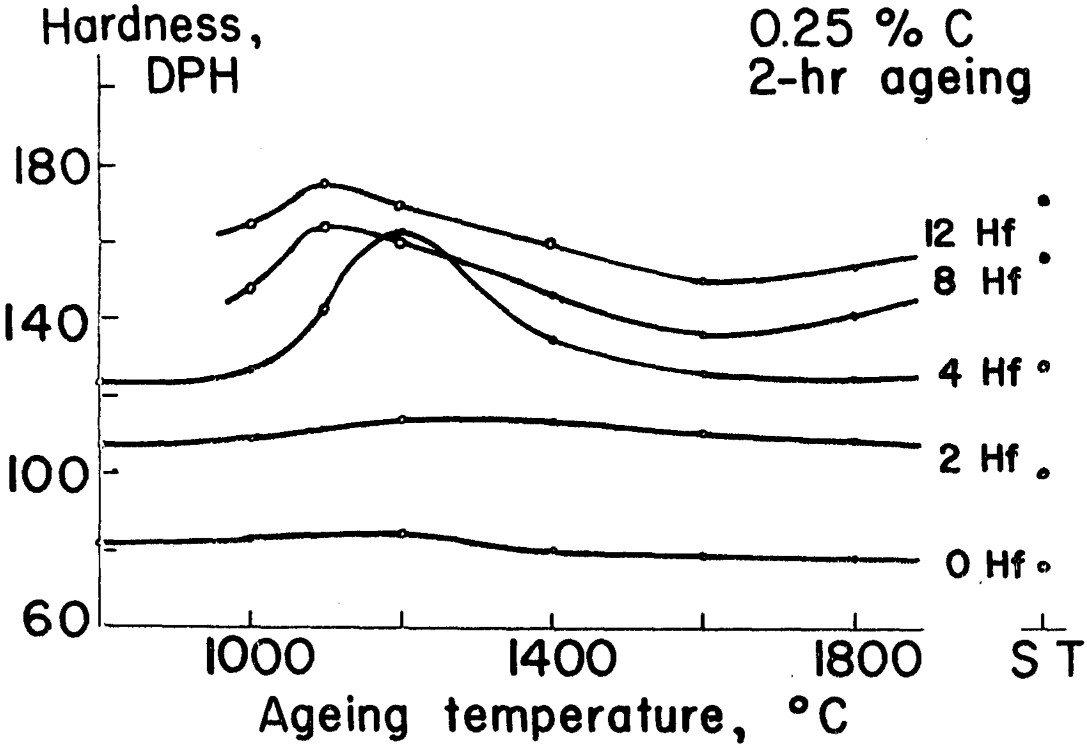


a. 0.06% C alloys

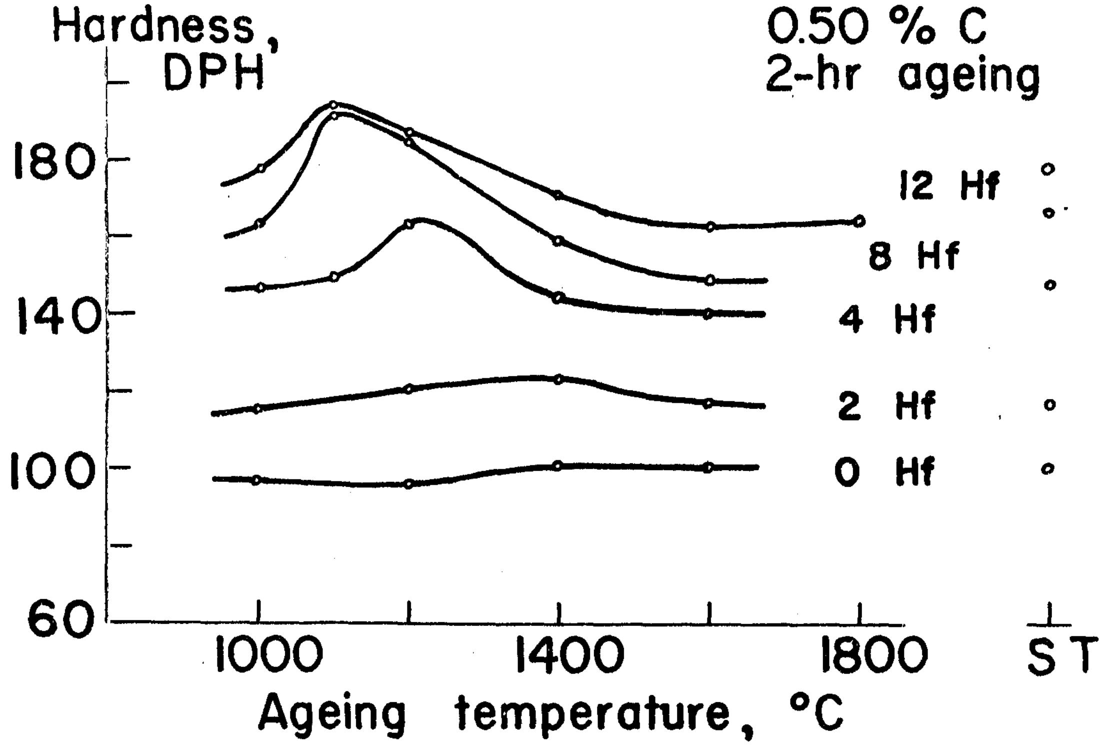


b. 0.125% C alloys

Figure 3. Variation of room temperature hardness with ageing temperature.

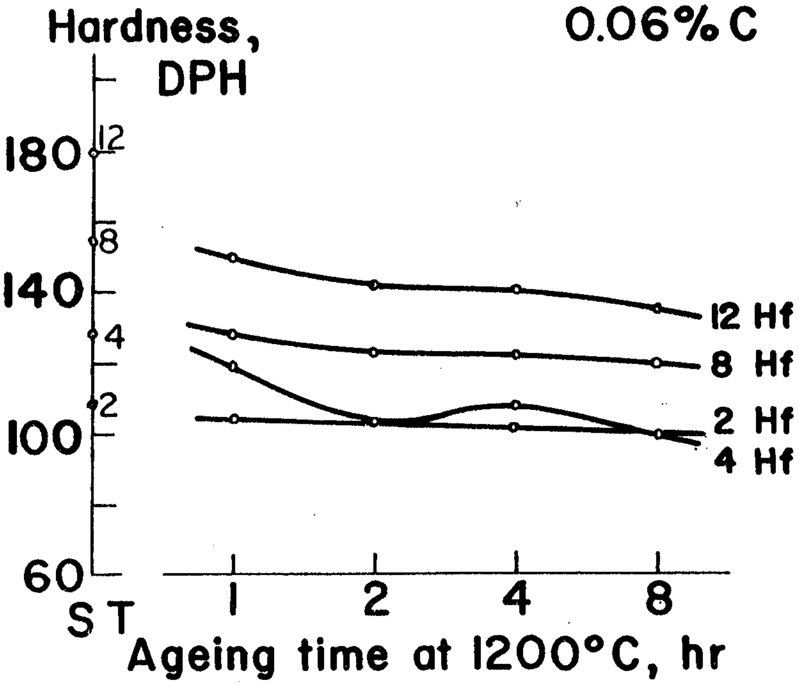


c. 0.25% C alloys

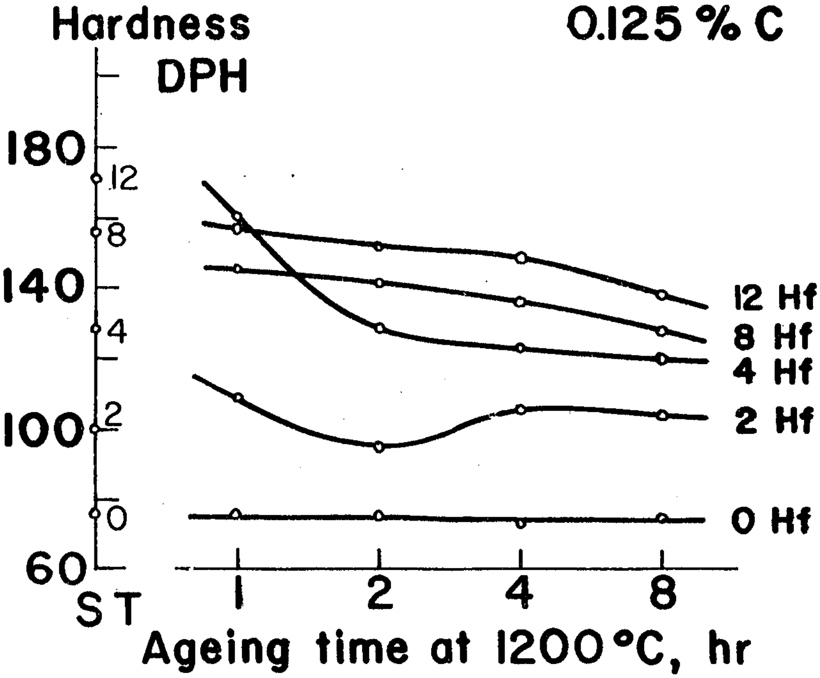


d. 0.50% C alloys

Figure 3 (continued). Variation of room temperature hardness with ageing temperature.

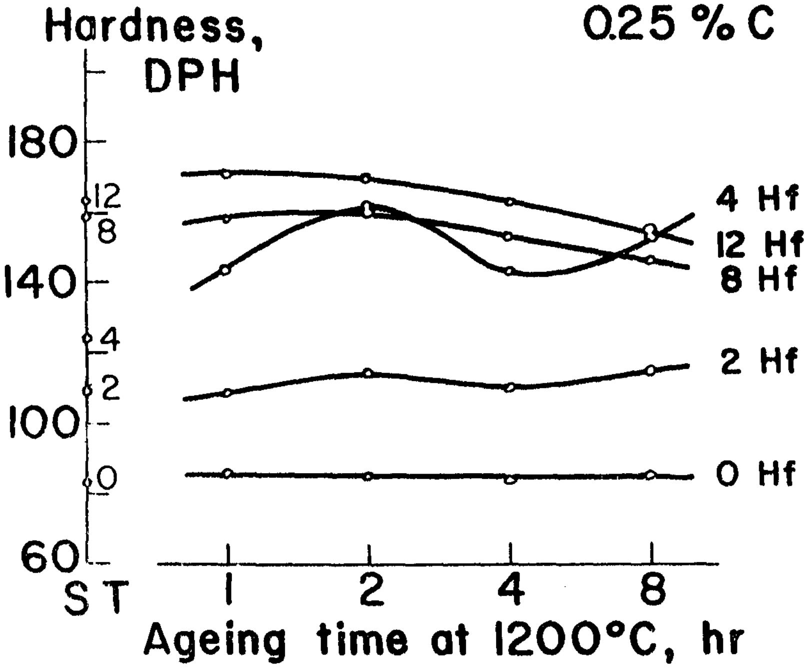


a. 0.06% C alloys

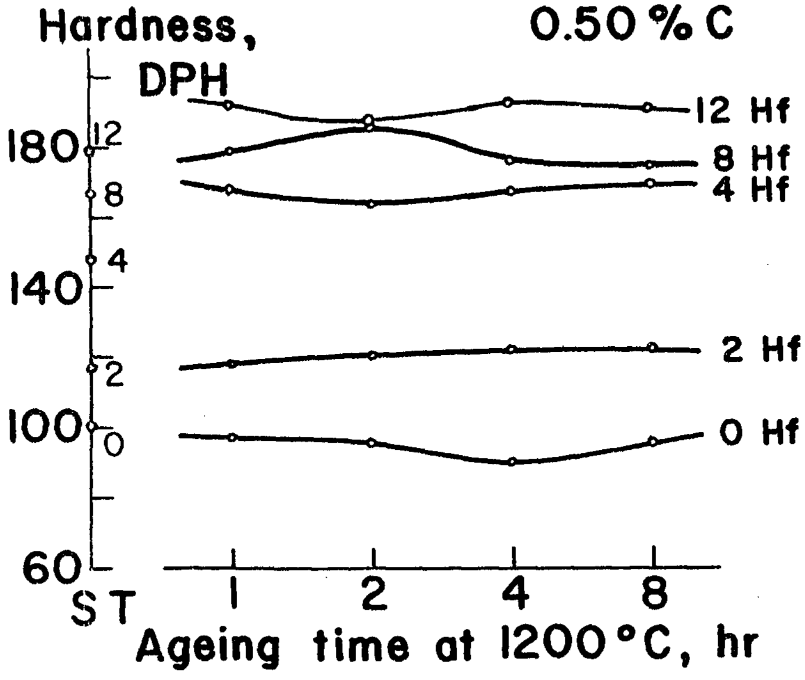


b. 0.125% C alloys

Figure 4. Variation of room temperature hardness with ageing time.



c. 0.25% C alloys



d. 0.50% C alloys

Figure 4 (continued). Variation of room temperature hardness with ageing time.

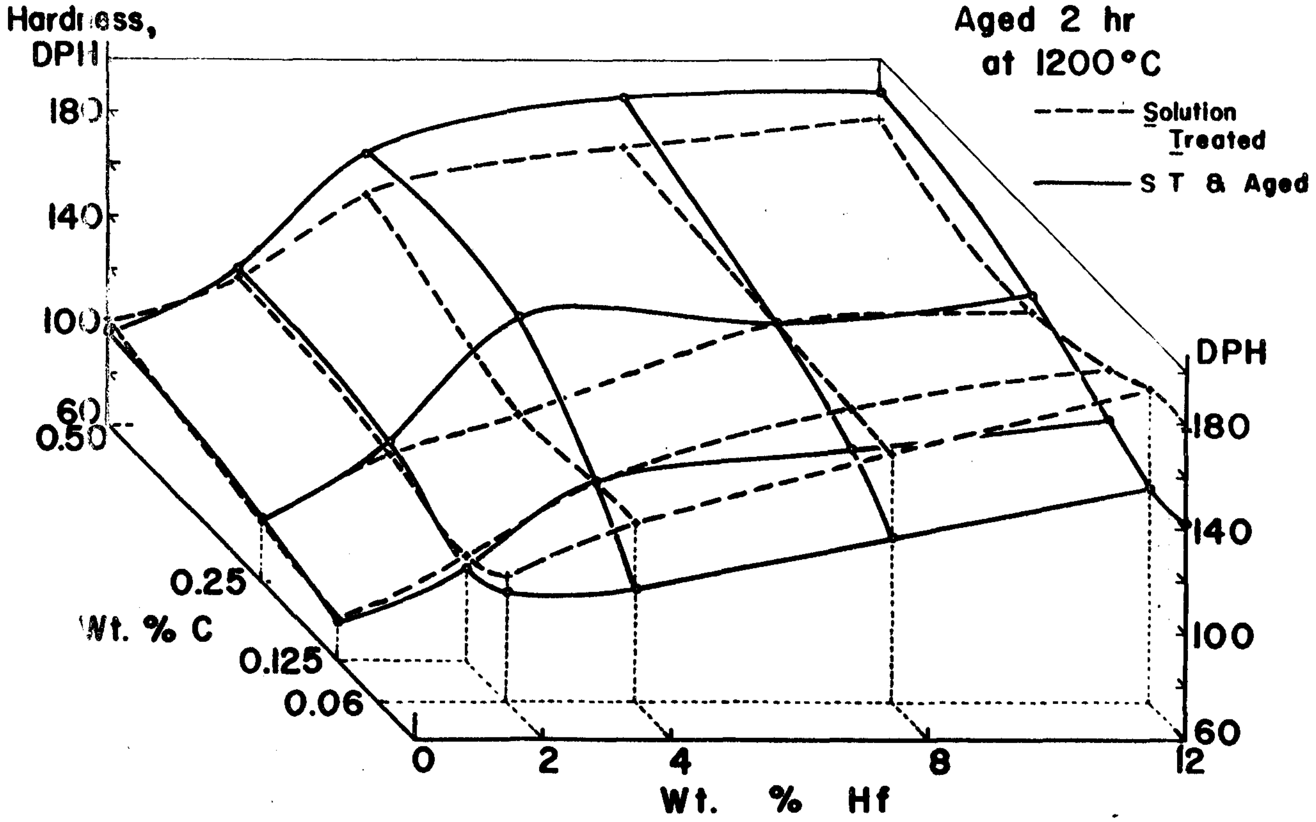


Figure 5. Variation of ageing response with composition.

TABLE 5

Constitution of Experimental Alloys

Alloy	Ageing Treatment				Soln. Treat.
	1200°C-8 hr	1400°C-2 hr	1600°C-2 hr	1800°C-2 hr	2200°C-1 hr
.125C	M, M_2C	M, M_2C	M, M_2C	M, M_2C	M, $\underline{M_2C}$
.25C	M, M_2C	M, M_2C	M, M_2C	M, M_2C	M, M_2C
.50C	M, M_2C	M, M_2C	M, M_2C		M, $\underline{M_2C}$
2 Hf-.06C	M, $\underline{M_2C}$, $\underline{MC}$[a]	M, (M_2C)[b]	M, ζ	M, ζ	M, $\underline{\zeta}$
2 Hf-.125C	M, M_2C, MC	M, M_2C	M, $\underline{M_2C}$	M, M_2C	M, M_2C
2 Hf-.25C	M, $\underline{M_2C}$, $\underline{MC}$	M, M_2C	M, M_2C	M, M_2C	M, M_2C
2 Hf-.50C	M, M_2C, MC	M, M_2C	M, M_2C		M, $\underline{M_2C}$
4 Hf-.06C	M, $\underline{MC}$	M, MC	M, $\underline{\zeta}$	M, ζ	M, $\underline{\zeta}$
4 Hf-.125C	M, $\underline{MC}$	M, $\underline{MC}$	M, $\underline{MC}$, $\underline{\zeta}$	M, M_2C	M, $\underline{M_2C}$
4 Hf-.25C	M, M_2C, MC	M, $\underline{MC}$	M, $\underline{MC}$	M, (MC)	M, M_2C
4 Hf-.50C	M, M_2C, MC	M, M_2C, MC	M, M_2C, MC		M, M_2C
8 Hf-.06C	M, MC	M, MC	M, ζ	M, ζ	M, ζ
8 Hf-.125C	M, MC	M, MC	M, MC, (ζ)	M, $\underline{MC}$, $\underline{\zeta}$	M, MC, ζ
8 Hf-.25C	M, $\underline{MC}$	M, MC	M, MC	M, $\underline{MC}$, $\underline{\zeta}$	M, $\underline{MC}$
8 Hf-.50C	M, $\underline{MC}$	M, MC	M, $\underline{MC}$		M, $\underline{M_2C}$, $\underline{MC}$
12 Hf-	M, MC	M, MC	M, (MC)	M	M
12 Hf-.06C	M, MC	M, MC	M, ζ	M, $\underline{\zeta}$	M, ζ
12 Hf-.125C	M, MC	M, MC	M, $\underline{MC}$	M, MC, ζ	M, MC
12 Hf-.25C	M, MC	M, MC	M, MC	M, $\underline{MC}$	M, MC
12 Hf-.50C	M, MC	M, $\underline{MC}$[c]	M, MC	M, MC	M, MC

a - Underlining of a phase indicates its detection by X-ray diffraction.
b - Parentheses indicate uncertainty as to the identity or presence of the phase.
c - Aged at 1100°C-1 hr before ageing at 1400°C.

TABLE 6

Lattice Constants of Extracted Phases

Alloy Designation and Heat Treatment	MC	M2C			"Zeta phase"
	a, Å	a, Å	c, Å	c/a	
2 Hf-.50C, ST+1100-2 hr	4.489				
Hf-.06C, ST+1200-8 hr	4.532	3.134	4.981	1.589	
Hf-.25C, "	4.50	3.117	4.965	1.593	
Hf-.06C, "	4.559				
Hf-.125C, "	4.560				
Hf-.25C, "	4.579				
Hf-.50C, "	(4.558 (4.497				
Hf-.125C, ST+1400-2 hr	4.543				
Hf-.25C, "	4.526				
2 Hf-.50C, ST+1100-2 hr +1400-2 hr	4.578				
Hf-.125C, ST+1600-2 hr		3.124	4.968	1.590	
Hf-.06C, "					Present
Hf-.125C, "	4.527				Present
Hf-.25C, "	4.506				
Hf-.50C, "	4.539				
2 Hf-.125C, "	4.579				
Hf-.125C, ST+1800-2 hr	(4.544 (4.492				Present
Hf-.25C, "	4.526				Present
2 Hf-.06C, "					Present
2 Hf-.25C, "	4.560				
125C, ST(2200°C-1 hr)		3.107	4.956	1.595	
50C, "		3.117	4.962	1.592	
2 Hf-.06C, "					Present
Hf-.50C, "		3.121	4.971	1.593	
Hf-.06C, "					Present
Hf-.125C, "		3.111	4.969	1.597	
Hf-.25C, "	(4.487 (4.525				
8 Hf-.50C, "	(4.459 (4.49	3.117	4.972	1.595	

DISCUSSION

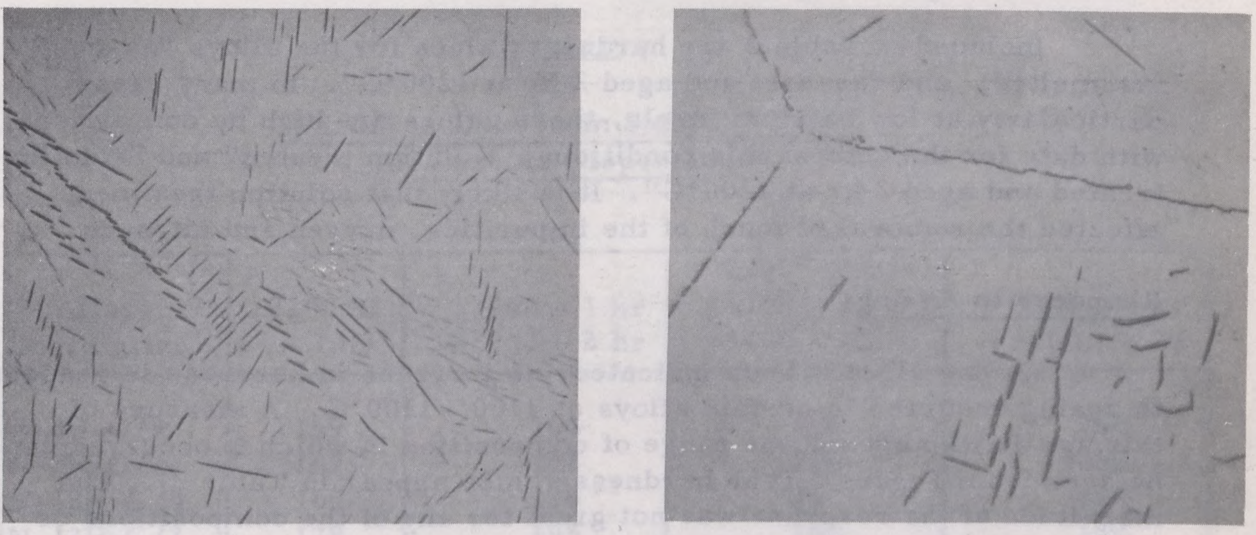
The effect of heat treatment temperature on the room temperature hardness of the experimental alloys, as shown in Figure 3, varies with carbon content. With 0.06% C the highest hardnesses are associated with the highest temperatures, 1800° and 2200°C, and can be attributed to solution hardening of the niobium matrix by hafnium. Ageing of the 0.06 C alloys at 1200°-1400°C precipitates the monocarbide (Nb,Hf) C which, because of its high hafnium content, extracts hafnium from the niobium-solid solution. The result is decreased solution hardening which is not fully compensated by precipitation hardening. The curves of Figure 4a show that time of ageing has a similar effect, - reduced hardness through concentration of hafnium in the monocarbide and agglomeration of the monocarbide.

The hardness values of many of the alloys after ageing at 1000°C differed by little from those for the solution-treated condition. This is particularly noticeable for the 0.06 C alloys and suggests that a two-hour treatment at 1000°C is insufficient to effect any structural change. This observation was in fact borne out by the metallography for all of the alloys. As illustration, microstructures for these two conditions of the 4 Hf-0.06 C alloy are shown in Figure 6, a and d. Ageing at 1200°C produced a very fine precipitate (Figure 6c), which coarsened with extended time at temperature. Ageing at 1400°C caused a coarser, more distinct precipitate.

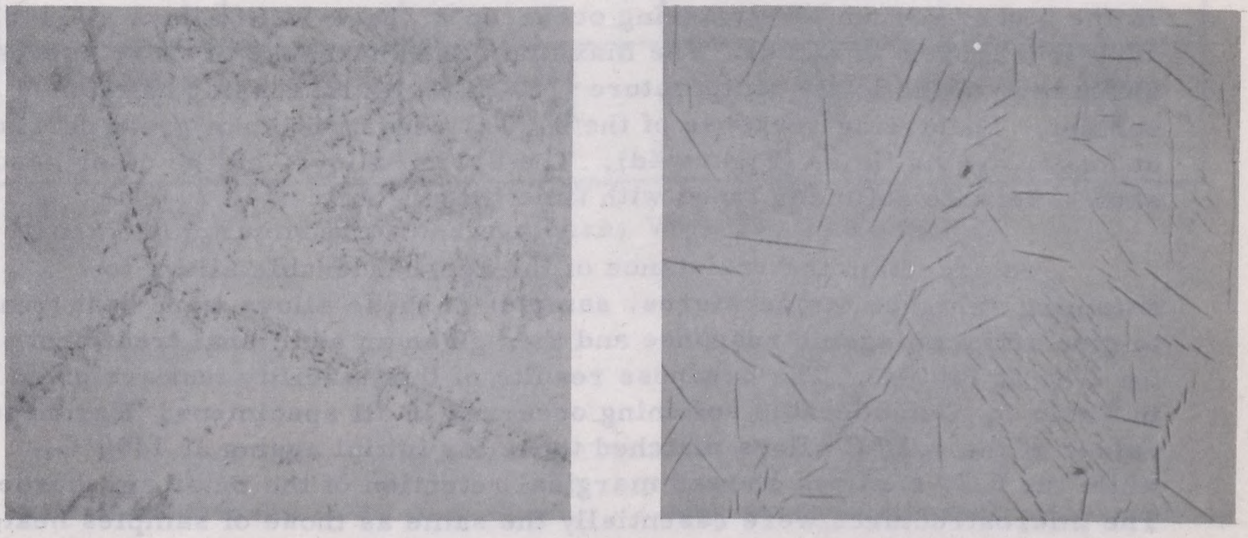
At higher carbon levels the trends with temperature shown by the 0.06 C alloys are modified. The precipitation of greater amounts of carbide causes softening through greater removal of hafnium from the matrix. However, precipitation hardening becomes apparent in some alloys at 1100° to 1200°C, with the result of a net increase in hardness with ageing.

The room temperature hardness of the 0 and 2% Hf alloys is relatively unaffected by ageing temperature or time at any carbon level. However, the carbide present in these alloys occurs in the form of large needles and platelets or massive particles, and contributes little to matrix hardening (see Figure 8a).

The individual effects of hafnium and carbon can be seen from the data of Table 3 and, for two specific heat treatments, in Figure 5. In general, hardness increases rapidly with the hafnium content at all carbon levels. Hardness values for the 0.06% C alloys and the 12% Hf-0% C alloy (0.02% C by analysis) are comparable with the published data of Begley (23) for the Nb-Hf system and are about 30 points DPH above those of Taylor and Doyle, also for the Nb-Hf system (13). On the other hand, the effect of carbon on hardness is only slight except for those alloys and heat treatments for which there is an ageing response. In fact, as pointed out above, in some cases



a. 2200°C-1 hr (ST) (X500) b. ST + 1600°C-2 hr (X1300)



c. ST + 1200°C-2 hr (X1300) d. ST + 1000°C-2 hr (X500)

Figure 6. Microstructures of Nb-4Hf-0.06C alloy.

such as alloys aged at 1800°C, increased carbon causes softening through its removal of hafnium from the niobium matrix.

Included in Table 3 are hardness values for the alloys "as-cast" (as-melted) and "as-cast and aged 2 hr at 1200°C". In many cases, particularly at low hafnium levels, these values are high by comparison with data for the comparable conditions, "solution treated" and "solution treated and aged 2 hr at 1200°C". It is likely that solution treatment effected the removal of much of the impurities, oxygen and nitrogen.

Response to Ageing

As has already been indicated, an increase in hardness in response to ageing occurred in certain alloys at 1100°-1200°C. A measure of this age-hardening and the range of composition in which it occurred can be seen from Figure 5 (the hardness values appear in Table 3). The magnitude of the response was not great for any of the compositions or conditions explored in this work.

Both hafnium and carbon are essential to the ageing reaction. At 0.125 C, only the 4 Hf alloy age-hardened; it showed a marked response for 1 hr at 1200°C but overaged rapidly with increased time (Figure 4b). At the higher carbon levels, ageing occurred in the 4-12 Hf alloys at 1100°-1200°C (Figures 3c and d). The maximum aged hardness of these curves shifts toward the lower temperature (1100°C) with increasing hafnium content. The ageing response of the 0.50 C alloys, while not great, persists at longer ageing times (Figure 4d). The 0.25 C alloys, on the other hand, show a definite softening trend with time (Figure 4c).

To ascertain the resistance of the age-hardenable alloys to softening at higher temperatures, samples of these alloys were heat treated to give optimum ageing response and then given an additional treatment for 2 hr at 1400°C. The hardness results of this stability test are given in Table 7. Considerable softening occurred in all specimens. Hardness values of the 0.25 C alloys matched those for initial ageing at 1400°C, while the 0.50 C alloys showed marginal retention of the prior age-hardening. The microstructures were essentially the same as those of samples heated at 1400°C without the intermediate treatment at 1100°C. Typical microstructures for each stage of the test are shown in Figure 7 for the 12 Hf-0.5 C alloy.

Relation of Ageing Response to Constitution

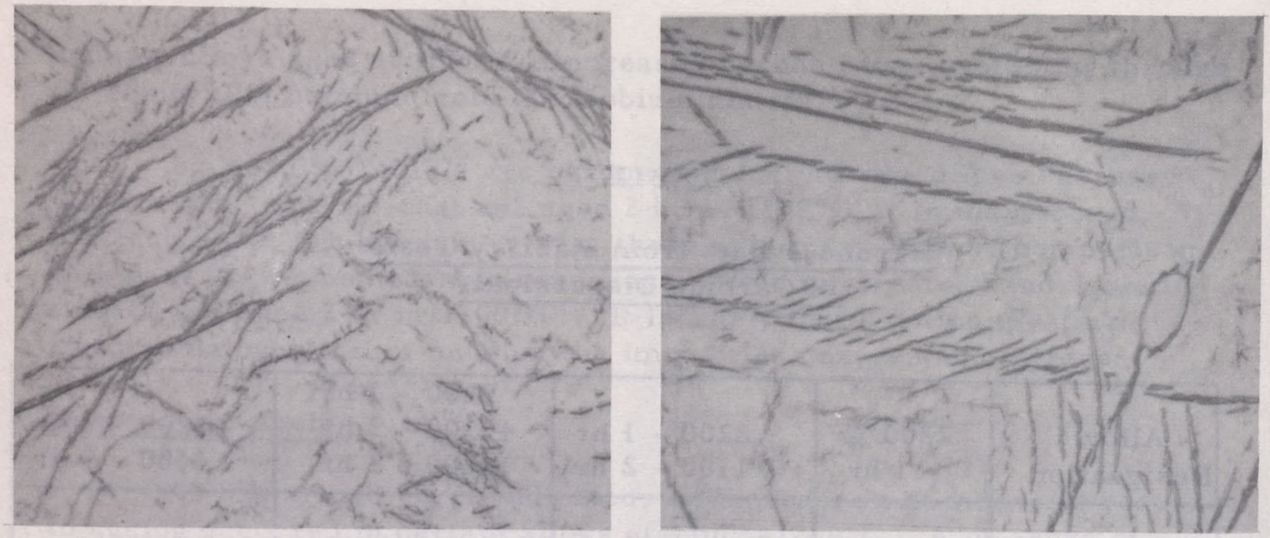
The hardening of the experimental alloys in response to ageing can be readily related to their constitution. The hemicarbide Nb_2C is the phase occurring as massive particles (see Figure 8a); it makes no significant

TABLE 7

Hardness Data from Stability Tests of Carbide Dispersions*

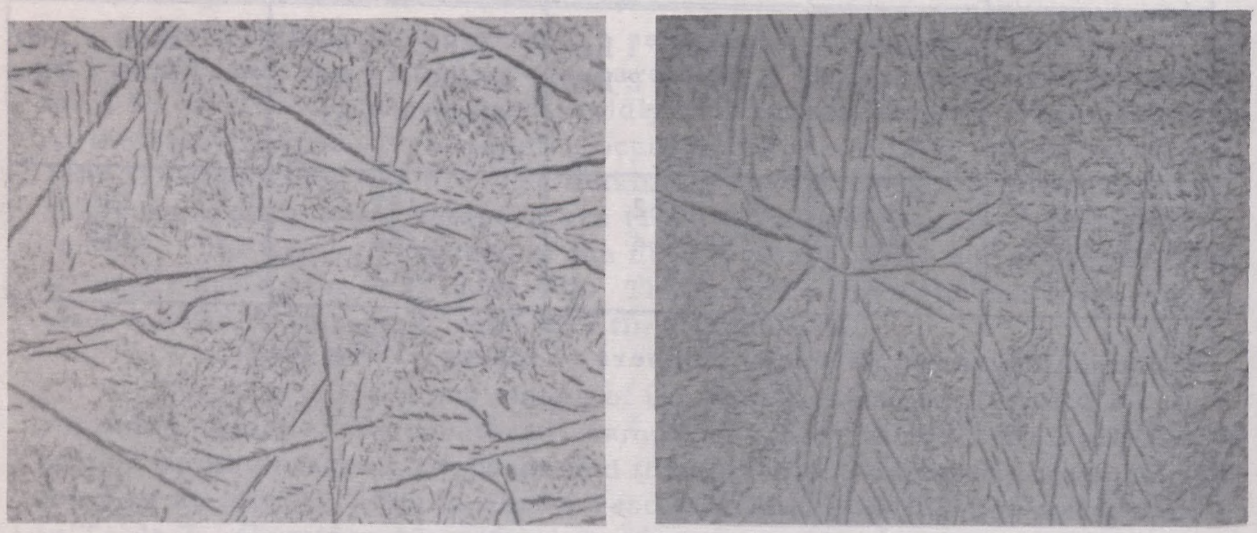
Alloy Designation	2200°C - 1 hr	2200 - 1 hr + 1100 - 2 hr	2200 - 1 hr +1100 - 2 hr +1400 - 2 hr	2200 - 1 hr + 1400 - 2 hr
N-8H-C/4	159	164	146	146
N-8H-C/2	167	192	176	160
N-12H-C/4	163	176	157	160
N-12H-C/2	178	195	180	172
	2200°C - 1 hr	2200 - 1 hr +1200 - 2 hr	2200 - 1 hr +1200 - 2 hr +1400 - 2 hr	2200 - 1 hr +1400 - 2 hr
N-4H-C/4	124	162	137	135
N-4H-C/2	148	164	152	145

* Diamond pyramid hardness numbers, Vickers, 10-kg load.



a. 2200°C - 1 hr (ST)

b. ST + 1100°C - 2 hr



c. ST + 1100°C - 2 hr + 1400°C - 2 hr

d. ST + 1400°C - 2 hr

(X1500)

Figure 7. Microstructures of Nb-12Hf-0.50C alloy.

contribution to hardening. However, the complex monocarbide (Nb, Hf) C does precipitate in a fine form, suitable for dispersion hardening (Figure 8b). Referring again to Figure 5, it will be seen that ageing response is first noticeable in alloys of 2% Hf, the hafnium content at which the monocarbide begins to precipitate. The response increases in the interval 2-4 Hf in which the proportion of (Nb, Hf) C increases at the expense of Nb_2C. Figure 8c shows such a three-phase structure. No further improvement in the ageing response takes place at hafnium contents beyond the three-phase field. Both solution-treated and aged hardnesses are higher, however.

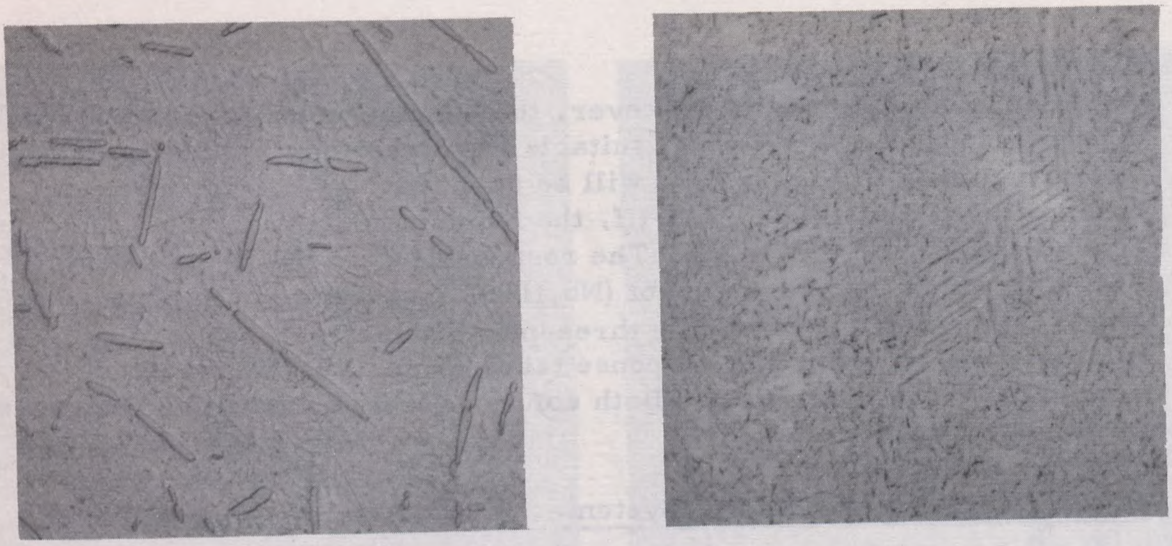
Observations on the Nb-Hf-C System

From the results of the X-ray data in Table 6 a trend can be seen toward a smaller lattice parameter of the monocarbide at the higher treatment temperatures. In particular, this pattern can be seen from data for the alloys 4 Hf-0.125C, 8 Hf-0.25C and 8 Hf-0.50C.

From the literature, three factors are known to affect the size of the monocarbide lattice, - the hafnium content, the nitrogen content, and the vacancy content; the vacancies exist at carbon levels below that of the stoichiometric composition. The lattice constant of stoichiometric (Nb, Hf) C has been reported to increase linearly with hafnium content from NbC to HfC (24). This dependence departs from linearity at lower carbon contents, but gives no indication of an intermediate maximum value.

The replacement of carbon in the monocarbide lattice by nitrogen, and perhaps oxygen, causes a reduction in the lattice parameter (5, 25). However, it has been shown that both nitrogen and oxygen can be removed effectively from NbC by heating in vacuum at 1900-2200°C (5), and similarly that vacuum annealing of niobium at high temperatures greatly reduces the level of oxygen, nitrogen and hydrogen (26). In the present investigation all ageing treatments except one set followed vacuum annealing at 2200°C for 1 hr.

The lattice constants of NbC and HfC vary directly with carbon content (3, 11, 15). In the present work the carbon content of the monocarbide is that of the low-carbon boundary of the single-phase region of the monocarbide in Figure 1. The variation of composition of this boundary with temperature has not yet appeared in the literature. The low-carbon limit of NbC decreases in carbon only slightly between 1600° and 2400°C (5); in HfC the temperature dependence is greater - from 37.5 at % at 1500°C to 34 at % at ~ 2300°C (15). Published constitution diagrams for the very similar system of Ta-Hf-C point to a temperature dependence of the corresponding MC/M+MC boundary somewhat greater than that of the low-carbon limit of HfC (15).



a. Nb_2C in Nb matrix. 0.25% C. Aged 1200°C-8 hr. (X500)

b. (Nb,Hf)C in Nb matrix. 8Hf - 0.25 C. Aged 1200°C-8 hr. (X1300)

c. Nb_2C + (Nb,Hf)C in Nb matrix. 4Hf - 0.50 C. Aged 1200°C-8 hr. (X1500)

Figure 8. Microstructures of aged alloys.

It is likely, therefore, that in the present work the vacancy content contributed in part to the reduction in lattice constant of the monocarbide at temperatures above 1600°C but not at lower temperatures. Oxygen and nitrogen are not likely to have significant effect, as annealing at 2200°C can be expected to reduce these well below the levels shown in Table 2. Thus, it is concluded that the hafnium content of the monocarbide decreases with increasing temperature.

The lattice parameter of the 12 Hf-0.50 C alloy aged at 1100°C appeared to contradict this trend. For this sample, a = 4.489Å. For NbC and HfC at the low carbon limit of the monocarbide, a = 4.43 and 4.608Å respectively. After subsequent ageing at 1400°C the monocarbide had a parameter a = 4.578Å, showing a substantial increase in hafnium content. It is apparent that a two-hour treatment at 1100°C can bring about structural changes causing hardening but that the alloy remains remote from equilibrium. At 1400°C the higher diffusion rate of hafnium allows equilibrium to be much more closely approached.

The data of Table 6 also show the expected increase in lattice constant of the monocarbide with increased hafnium content of the alloy. Although the data are sparse for any one temperature, they give some indication of the direction of the M + MC / M + M_2C + MC boundary. It can be seen that the lattice parameter of MC in the three-phase region decreases with increased temperature. Thus, it can be concluded that the MC vertex of the three-phase region shifts toward the Nb-C binary system with increase in temperature. Published work on the similar system of Ta-Hf-C shows the same shift (15).

Results of the phase identification by metallography and X-ray diffraction have been given in Table 5, and are plotted on the ternary diagram in Figure 9 for the conditions of 8 hr at 1200°C. The phase boundaries in Figure 9 do not represent equilibrium conditions, since many of the alloys after 8 hr at temperature were still undergoing microstructural changes and softening. Any influence of extended treatment time would shift the boundaries of the three-phase region slightly toward the Nb-C binary system.

The results in Table 5 merely list the phases observed in the alloys after cooling from the treatment temperature. The rate of the Nb_2C precipitation reaction is so great in niobium that single-phase alloys can be obtained at room temperature only at carbon levels much below the maximum solubility. From the present work, precipitation of the monocarbide (Nb, Hf) C appears to be similarly characterized. Consequently, the phases shown for treatment temperatures of 1600°C and above may include phases precipitated during cooling.

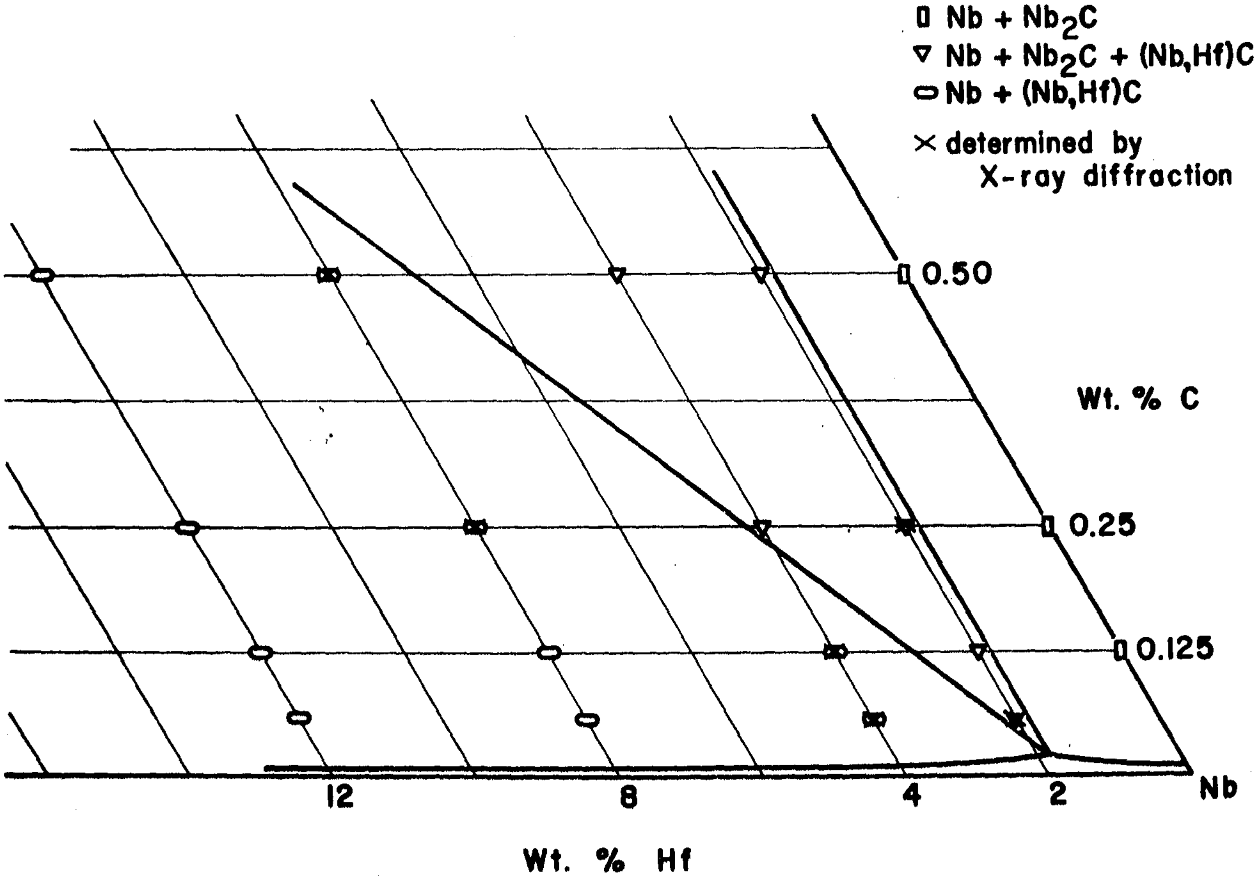


Figure 9. Constitution of experimental alloys after 8 hr at 1200°C.

The intended binary alloy Nb-12 Hf was found to contain 0.020% C by chemical analysis and to precipitate monocarbide during ageing at 1200°C. The solubility of carbon in this case is likely well below 0.02 wt% (0.15 at %) and is in agreement with the findings of Taylor (9).

The lattice constants for Nb_2C at the low carbon limit of its composition range have been variously reported in the literature in the range 3.113Å, 4.949Å (6) to 3.126Å, 4.965Å (5). The X-ray results of the present work do not reveal any alteration of the Nb_2C lattice with the addition of hafnium to the experimental alloys. This indicates a low solubility of hafnium in Nb_2C and is in agreement with reported findings and predictions (9, 16, 19, 20). Metallography did reveal, however, that Nb_2C occurs at the carbon content of the present alloys over an increasingly wide hafnium range with increasing temperature, i.e., that the $M + M_2C / M + M_2C + MC$ boundary moves to higher hafnium content. At 2200°C Nb_2C was the only carbide found up to 4% Hf (except for the 0.06% C alloys), whereas at 1200°C it was found along with the monocarbide at 2% Hf. Such behaviour parallels that of αTa_2C as described by Rudy for the Ta-Hf-C system (15). One must keep in mind, however, the difficulty in suppressing precipitation in these alloys during cooling from high temperature.

Changes in the $Nb + Nb_2C + (Nb,Hf)C$ region in Figure 9 with increasing temperature can be summed up as follows. The niobium solid solution vertex of the region will move to higher hafnium contents and somewhat higher carbon contents. The Nb-Nb_2C boundary of the region, which from the literature and this work appears to parallel the Nb-C binary (9, 19, 20), will shift to higher hafnium contents. The Nb-(Nb,Hf) C boundary will rotate toward the orientation of the Nb-C binary.

As shown in Table 5, another phase was found in many of the alloys heat treated at 1600°C or above. It occurred in all alloys of 0.06%C and in certain alloys of higher carbon content. This phase has been termed zeta (ζ) because of its similarity in X-ray diffraction pattern with the zeta-phase found by Lesser and Brauer in the Ta-C (12) and Nb-C (3) systems, although the latter phase occurred at compositions between M_2C and MC. There is also a similarity, both in diffraction pattern and conditions of occurrence, with the tetragonal δ-NbC reported by Pochon et al (4). "δ-NbC" was found in alloys of 0.066 wt % C or less, cooled rapidly from the molten state. Such a cooling rate is probably comparable to that which followed heat treatments in the present work. The carbon content of "δ-NbC" was 11.2 wt%, very close to the 11.44 wt%C of stoichiometric NbC. In Figures 6a and b the second phase is entirely "zeta". The X-ray diffraction powder pattern bore resemblance to both the fcc monocarbide and hcp hemicarbide patterns but has not yet been satisfactorily indexed.

In the Ta-C system the zeta phase has been found only when the monocarbide was also present (8); in some cases the hemicarbide was present as well. The " δ-NbC" found by Pochon occurred along with a trace of Nb_2C and was replaced by Nb_2C by heat treating at 1200°C. "Zeta phase" in the present work occurs as the only carbide or along with the monocarbide. In the 2 Hf-0.06 C alloy it is converted apparently to M_2C at 1400°C and to MC + M_2C at 1200°C. At higher hafnium contents the "zeta phase" is replaced only by MC (see Figure 6c).

The zeta phase in the systems Nb(Ta, V)-C is now commonly considered to be a metastable transition phase preceding precipitation of M_2C in certain conditions (4, 8). The present work has shown that it can also precede precipitation of MC. Its metastability is further indicated by the fact that it has never been produced as a single phase. Examination of analyses of starting materials and alloys provided in the literature suggests that purity has had little influence on its occurrence.

Included in the X-ray diffraction results in Table 6 are four cases in which two fcc phases were found. In all cases the lattice constants for both patterns were comparable with that of MC for the ternary Nb-Hf-C system and the constant for the phase having the denser pattern was most compatible with the other data of Table 6. No explanation can be offered other than to suggest the possible effect of impurities. A similar occurrence has been observed in the Nb-Zr-C system and discussed at length by Cornie and colleagues (21). They postulate that impurity oxygen and nitrogen cause the formation of an $(Nb, Zr)_2OC$ phase having a fcc structure and with nitrogen substituting for carbon.

CONCLUSIONS

A mild age-hardening response has been found in niobium-rich alloys of the niobium-hafnium-carbon system. The ageing is related to precipitation of the complex monocarbide (Nb,Hf)C and gives a maximum response at about 4 wt% Hf. Optimum ageing temperature for times up to 8 hr is 1100° to 1200°C. Age-hardened alloys showed little resistance to softening and agglomeration of the monocarbide at 1400°C.

The constitution of the system to 12 wt% Hf and 0.50 wt% C has been determined at 1200°C and indicated with less certainty at higher temperatures ranging to 2200°C.

A phase resembling the transition phase zeta in Ta-C alloys has been found in low-carbon alloys with up to 12 wt% Hf.

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DCB/LRH/gm