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FRACTURE BEHAVIOR OF Cr_2Nb-BASED INTERMETALLICS

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Abstract

Microstructural evaluations and mechanical testing of Laves-phase alloys based on Cr_2Nb were examined in order to determine phase relationships with heat treating temperatures up to 1600°C. At ambient temperatures, single-phase Cr_2Nb alloys are very hard and brittle due to the complicated crystal structure (C-15). The following results were revealed through examination of the Cr-Cr_2Nb two-phase region: (a) with increasing amounts of the soft chromium-rich phase, the compression strength and hardness decrease; (b) the annealing treatments studied provided the best break-up of the brittle Laves-containing eutectic phase in the 94 at.% Cr - 6 at.% Nb (CN-7) alloy; (c) annealing for 1 hour at 1600°C + 4 hours at 1200°C drastically improved the room temperature strength and compressive ductility over previous annealing treatments. Previous studies have shown [1] that the introduction of a soft chromium phase has promising effects in improving the mechanical properties of brittle Cr_2Nb Laves-phase alloys.

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Introduction

The Cr_2Nb Laves phase has a cubic crystal structure (C-15) with a stacking sequence of an XYZ type, where X, Y, and Z represent closed-packed layers, similar to a face-centered cubic (f.c.c.) structure; however, with each layer being composed of four interpenetrating atomic layers. The unit cell contains 24 atoms and has a lattice constant of 6.98 Å [2-5].

This Laves-phase alloy has been selected for this development because of its high melting point (1770°C) [6-7], relatively low density (7.7g/cm^2) [8], and potential resistance to oxidation and corrosion [6].

The most important concern with Cr_2Nb as well as other A_2B Laves phases is their poor ductility and fracture toughness at ambient temperatures [1,6,9]. Since the single-phase Cr_2Nb is very hard [800 Diamond Pyramid Hardness (DPH)] and brittle at ambient temperatures, the efforts of alloy development have been concentrated on the Cr-Cr_2Nb two-phase compositions containing the intermetallic phase Cr_2Nb and the chromium-rich solid solution phase [1]. Previous studies have indicated that the two-phase Cr_2Nb alloys showed plastic deformation under compression at room temperature, with much greater strength than nickel-base superalloys at and above 1000°C [1,10]. The results obtained to date indicate that the Cr-Cr_2Nb alloys have excellent strength for structural use at ultrahigh temperatures (i.e. 1000-1300°C) [1,10].

Work performed by Takeyama and Liu [1] has indicated the following: (a) the eutectic composition has a niobium concentration of 17 at.% rather than 12 at.% as reported in the phase diagram shown in Fig. 1 which was given by Goldschmidt [6,7]; (b) the soft regions are effective in preventing crack propagation originating in the brittle Laves-phase, which results in a high yield strength with moderate ductility up to 1000°C.

The potential applications of this Laves-phase alloy include hot components in advanced fossil energy conversion systems, advanced heat engines, and high-temperature cutting and grinding tools [11]. It has been shown [1] that the mechanical and metallurgical properties of the Cr-Cr_2Nb alloys can be improved through dispersion of the ductile Cr-rich phase or the break-up of the brittle Laves-containing eutectic phase. The goal of this work is to develop a new generation of high-strength, corrosion-resistant intermetallic alloys based on Cr_2Nb for use as critical hot components in advanced fossil energy conversion systems. In particular, we will be studying the effects of different annealing temperatures on the microstructure and mechanical properties of these alloys.

Experimental Procedure

Chromium-niobium alloys weighing 350 g were prepared by arc melting and drop casting into pre-heated copper molds. High-purity niobium and chromium metal chips were used as charge materials in order to reduce the interstitial impurity (i.e. oxygen), and the alloys were melted in a high vacuum (10^{-5} Pa) furnace. The preheating of the copper mold to 100°C was done in order to control alloy solidification and reduce thermal shock and microporosity formation during drop casting [11].

Table 1 lists the composition (at.%) of CN (Cr-Nb) alloys investigated in this work. The alloys have nominal compositions of chromium with a variation of 6 to 17 at.% Nb. The alloys were placed in a covered alumina crucible and annealed at 1600°C for 1 hour (h) + 4 h at 1200°C. Optical micrographs for CN-7 and CN-4 at this annealing treatment are shown in Figs. 2 and 3. An additional annealing treatment of 2 days (d) at 1580°C + 2 d at 1200°C was performed on the three alloy compositions listed in Table 1 and shown by the optical micrographs in Figs. 4 and 5. Other annealing treatments which have been performed previously [12] include 1 h at 1400°C, 1 h at 1500°C, 1h at 1550°C, 1h at 1580°C, and 2 d at 1580°C. All the specimens were furnace cooled. The effects of annealing on the microstructures and mechanical properties of these alloys were emphasized in this investigation.

Table 1. Alloy Compositions for the Cr_2Nb-based Alloys

Alloy	Atomic percent	Weight percent
CN-7	Cr - 94 % Nb - 6 %	Cr - 89.76 % Nb - 10.24 %
CN-4	Cr - 88 % Nb - 12 %	Cr - 80.41 % Nb - 19.59 %
CN-45	Cr - 83 % Nb - 17 %	Cr - 73.21 % Nb - 26.79 %

Microstructures of these alloys were examined by optical microscopy. The metallographic specimens were polished through 1 μm using conventional techniques. Samples were then etched in a solution of 15 gm KOH, 15 gm $K_3Fe(CN)_6$), and 90 ml H_2O for approximately 5 seconds. Microhardness readings were taken for each specimen using a LECO M-400 Hardness Tester. An average of three to five readings taken randomly across the sample gives the reported hardness values. Compression specimens having a diameter of 6 mm and a length of 9 mm were cut from the annealed ingots by electro-discharged machining (EDM). The specimens were tested under compression on an Instron testing machine at room temperature and 1000°C at a nominal strain rate of 3.3 x 10^{-3} s^{-1}. The elevated-temperature tests were performed in vacuum (7 x 10^{-4} Pa).

Results and Discussion

Microstructure and Phase Composition

The CN alloys contain two phases, the Cr_2Nb intermetallic phase and the chromium-rich solid solution which can contain as much as 5 at.% Nb at the eutectic temperature of 1620°C. Recent work by Liu, et.al. [13] however, has revealed that the eutectic temperature may actually be closer to 1670°C.

The composition of the phases in the alloys CN-7, CN-4, and CN-45 was determined by electron microprobe analysis for an average of three points in each respective phase as reported in Table 2. From the phase diagram in Fig. 1, we see that the intermetallic phase in the eutectic structure has an average composition of 65 at.% Cr - 35 at.% Nb which, according to the results in Table 2, reveals that the eutectic structure consists predominantly of the Cr_2Nb Laves-type intermetallic phase. Figure 2 shows the optical micrograph of CN-7 annealed for 1 h at 1600°C + 4 h at 1200°C. In this alloy, the Cr-rich patches cover most areas, and a small amount of the Laves-containing eutectic phase can be seen along the Cr-rich boundaries. At lower annealing temperatures which have been previously studied [12], this brittle eutectic phase exists as an interconnected skeleton along the Cr-rich regions as seen in Fig. 6, but in the case of the microstructure seen in Fig. 2, the anneal has broken up the eutectic phase that was once interconnected along the Cr-rich regions. The 88 at.% Cr - 12 at.% Nb (CN-4) alloy is shown in Fig. 3 with the same annealing history as CN-7 in Fig. 2. In this condition, the lighter patches in CN-4 are the chromium-rich phase which is surrounded by the Laves-containing brittle eutectic phase, indicating that this is a hypoeutectic structure. Some very fine dark spots that can be seen within the Cr-rich patches in both of these Figures are Cr_2Nb precipitates formed upon cooling from the melt.

Table 2. Electron Microprobe Analysis of the Cr_2Nb Intermetallics

Alloy	Anneal Condition	Cr_2Nb phase in Eutectic structure (at.%)	Cr-rich phase (at.%)
CN-7	1h/1600°C + 4h/1200°C	Cr = 68.8 % Nb = 31.2 %	Cr = 96.2 % Nb = 3.8 %
CN-4	1h/1600°C + 4h/1200°C	Cr = 69.3 % Nb = 30.7 %	Cr = 96.6 % Nb = 3.4 %
CN-45	1h/1600°C + 4h/1200°C	Cr = 68.6 % Nb = 31.4 %	Cr = 97.2 % Nb = 2.8 %

It has been shown [11] that the precipitation of the Cr_2Nb Laves-phase particles from the Cr-rich phase is sluggish. These precipitates are extremely fine, with a size of less than 1 μm for an alloy annealed for 3 days at 1100°C [1]. Annealing at temperatures of 1580°C and 1600°C did not reveal the fine Cr_2Nb particles within the Cr-rich phase. These precipitates were partially dissolved due to an increase in the solubility of Nb in Cr at these temperatures and the remainder of the particles migrated to the Laves-containing eutectic phase, thereby coarsening it. Thus, we see that there are two competing mechanisms occurring during the annealing treatment; (1) break-up of the eutectic phase and (2) coarsening of the Laves-containing eutectic phase due to Cr_2Nb particles migrating from the Cr-rich phase at high temperatures. Additional annealing at 1200°C causes a coarsening of the fine particles which precipitate out in the Cr-rich phase upon cooling from the higher annealing temperatures of 1580°C and 1600°C. This result can especially be seen in the micrographs shown in Figs. 4 and 5 for CN-7 and CN-4 annealed 2 d at 1580°C + 2 d at 1200°C.

Hardness

Microhardness results are presented in Table 3 for the CN-7, CN-4, and CN-45 alloys under different annealing conditions. The effects of annealing temperature on hardness is shown in Fig. 7 for the CN-4 alloy. No microcracking was observed at the tips of the microhardness indents as was previously reported for alloys in the as-cast condition [1]. The hardness decreases with decreasing niobium concentration and increasing amount of the soft Cr-rich phase. Previous work by Liu [10] has indicated that the hardness tends to decrease as the coarsening of the fine Cr_2Nb particles within the Cr-rich phase occurs for temperatures ranging from 950°C to 1200°C as shown in Fig. 7. In the present investigation, it was found that annealing at high temperatures near the eutectic temperature (1580°C and 1600°C) caused an increase in hardness as reported in Table 3. Annealing at these high temperatures has the following effects: (a) dissolution of the fine Cr_2Nb precipitates in the Cr-rich phase due to an increase in the solubility limit of Nb in Cr; (b) coarsening of the Laves-containing eutectic phase due to migration of the Cr_2Nb particles from the Cr-rich phase, (c) break-up of the eutectic phase, and; (d) re-precipitation of extremely fine Cr_2Nb particles in the Cr-rich phase upon cooling from the high temperature anneals. It is this fine re-precipitation which leads to the increase in hardness. Upon additional annealing of the sample at 1200°C after annealing for 1 h at 1600°C or 2 d at 1580°C, we see that the hardness once again decreases due to the coarsening of the Cr_2Nb precipitates within the Cr-rich region as discussed in the work by Liu [10] and seen by the results presented in Table 3 and Fig. 7.

Table 3. Microhardness Values (DPH) for the Cr_2Nb-based Alloys

Annealing Treatment	CN-4	CN-7	CN-45
1h/1400°C	465	367	616
1h/1500°C	494	393	618
1h/1550°C	502	424	618
1h/1580°C	513	406	613
2d/1580°C	508	445	--
2d/1580°C + 2d/1200°C	418	341	--
1h/1600°C + 4h/1200°C	479	429	--

Compression Testing

The 0.2 % yield strength and compressive ductility of 94 at.% Cr-6 at.% Nb (CN-7) and 88 at.% Cr-12 at.% Nb (CN-4) alloys at room temperature are reported in Table 4. At room temperature, the yield strengths of CN-7 and CN-4 are approximately 700 and 900 MPa, respectively for an annealing condition of 3 days at 1100°C. A substantial improvement in room temperature strength and compressive ductility was seen for the alloys annealed for 1 h at 1600°C + 4 h at

1200°C. The CN-45 alloy tested for this annealed condition showed negligible ductility at room temperature as reported in Table 4.

Table 4. Compressive Properties of CN Alloys Tested at Room Temperature in Air

Alloy No.	Heat Treatment	Composition (at.%)	Strength, MPa (ksi)		Ductility (%)
			Yield	Ultimate	
CN-7	3d/1100°C	94 Cr-6 Nb	702(102)	1261(183)	9.5
CN-7	1h/1600°C + 4h/1200°C	94 Cr-6 Nb	1029(149)	1733(251)	20.4
CN-4	3d/1100°C	88 Cr-12 Nb	960(139)	1760(255)	5.4
CN-4	1h/1600°C + 4h/1200°C	88 Cr-12 Nb	1327(192)	1546(224)	8.8
CN-45	1h/1600°C + 4h/1200°C	83 Cr-17 Nb	1763(256)	1824(265)	nil

As reported in Table 5, some improvement in strength over previous tests performed for the alloys annealed for 3 d at 1100°C was seen for the compression tests which were conducted at 1000°C in vacuum for the alloys annealed for 1 h at 1600°C + 4 h at 1200°C. However, there was little change in compressive ductility from the previous tests performed for samples annealed 3 d at 1100°C. As the test temperature increased, the strength gently decreased and the ductility increased for all tests. The CN-45 alloy showed very limited ductility at 1000°C. For the CN-4 alloy annealed 1 h at 1600°C + 4 h at 1200°C, the yield strength at 1000°C is about 780 MPa, which is substantially stronger than conventional nickel-base superalloys; for example, the yield strength of IN713C at 1000°C is about 300 MPa [14]. At 1000°C, both CN-7 and CN-4 can be deformed with compressive ductilities larger than roughly 20 %. These results reveal that the two-phase intermetallic alloys based on Cr_2Nb have high strength with decent ductility at all test temperatures. In addition, we can see that the break-up of the Laves-containing eutectic phase via annealing at higher temperatures results in a considerable increase in strength and compressive ductility at room temperature and a slight increase in strength with good ductility at 1000°C in vacuum. Further studies are required to characterize their tensile and fatigue properties at ambient and elevated temperatures.

Table 5. Compressive Properties of CN Alloys Tested at 1000°C in Vacuum

Alloy No.	Heat Treatment	Composition (at.%)	Strength, MPa (ksi)		Ductility (%)
			Yield	Ultimate	
CN-7	3d/1100°C	94 Cr-6 Nb	436(63)	738(107)	32.7
CN-7	1h/1600°C + 4h/1200°C	94 Cr-6 Nb	580(84)	1069(155)	27.9
CN-4	3d/1100°C	88 Cr-12 Nb	685(99)	856(124)	22.8
CN-4	1h/1600°C + 4h/1200°C	88 Cr-12 Nb	778(113)	1079(157)	19.8
CN-45	1h/1600°C + 4h/1200°C	83 Cr-17 Nb	994(144)	1076(156)	7.3

Future Work

Further work on this project will include continued compression testing for the alloys annealed for 4 h at 1550°C + 2 d at 1200°C as well as other annealing treatments which successfully break up the eutectic phase. Continued electron microprobe analysis of subsequent annealing treatments will be performed in order to determine phase compositions. Nanoindentation techniques will be used to characterize the hardness and elastic modulus of the individual phases in the material. In addition, secondary processing involving Hot Isostatic Pressing (HIPing) will be carried out on the cast ingots in order to suppress casting defects and thus improve the material's mechanical properties. Other planned work will include fracture and fatigue testing of these alloys and, correlation of the mechanisms of fracture and fatigue with microstructural observations. From these correlations, a theoretical model for predicting the microstructural effects on fracture and fatigue behavior may be developed.

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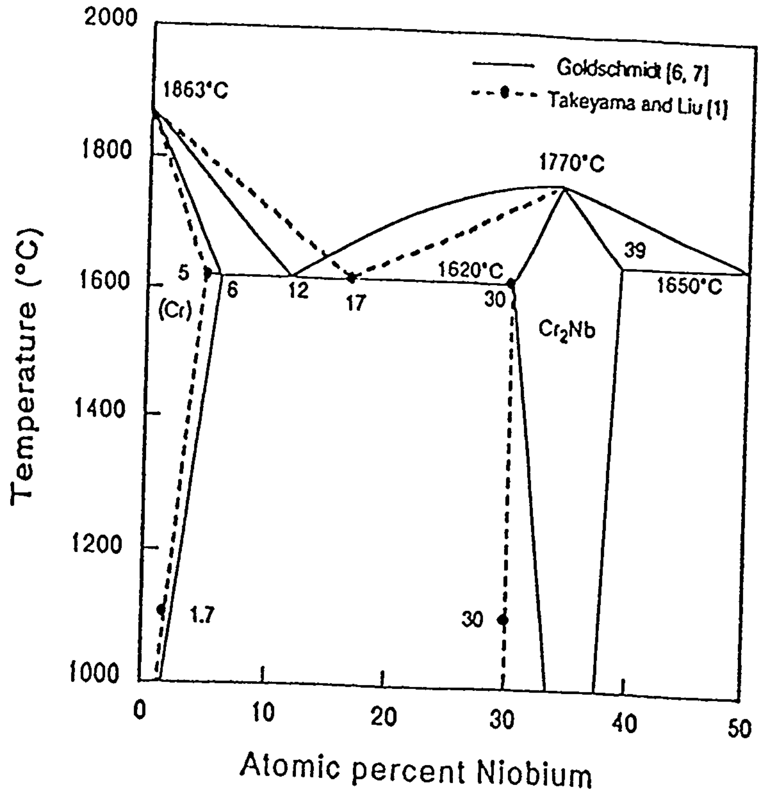

Figure 1. The Chromium-Niobium Binary Phase Diagram.

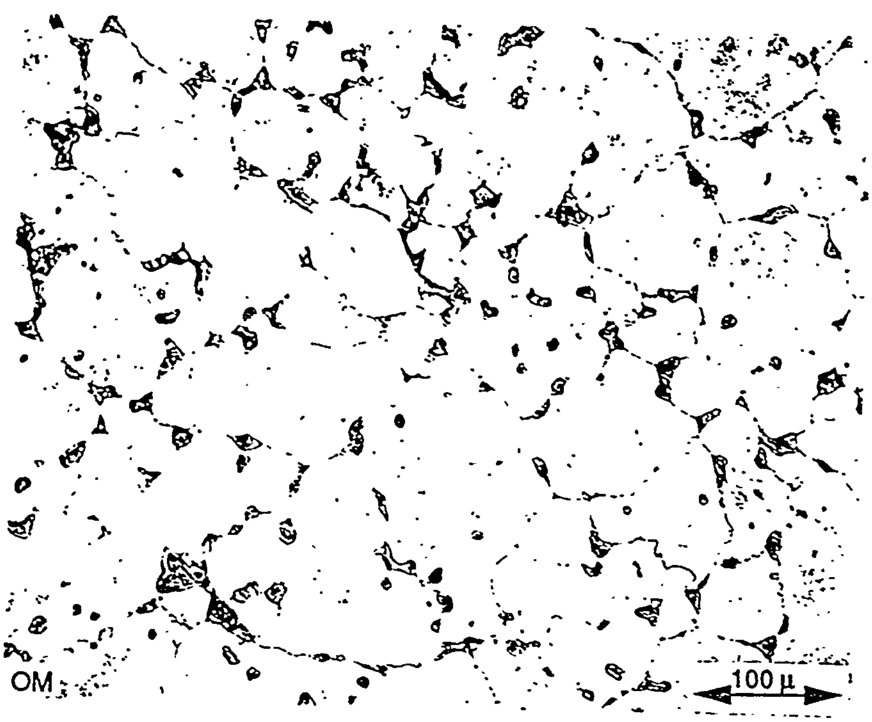

Figure 2. Sample CN-7 (94 at.% Cr-6 at.% Nb) annealed 1 hour at 1600°C plus 4 hours at 1200°C in vacuum. Cr-rich regions (light) surrounded by Laves-containing eutectic phase (dark).

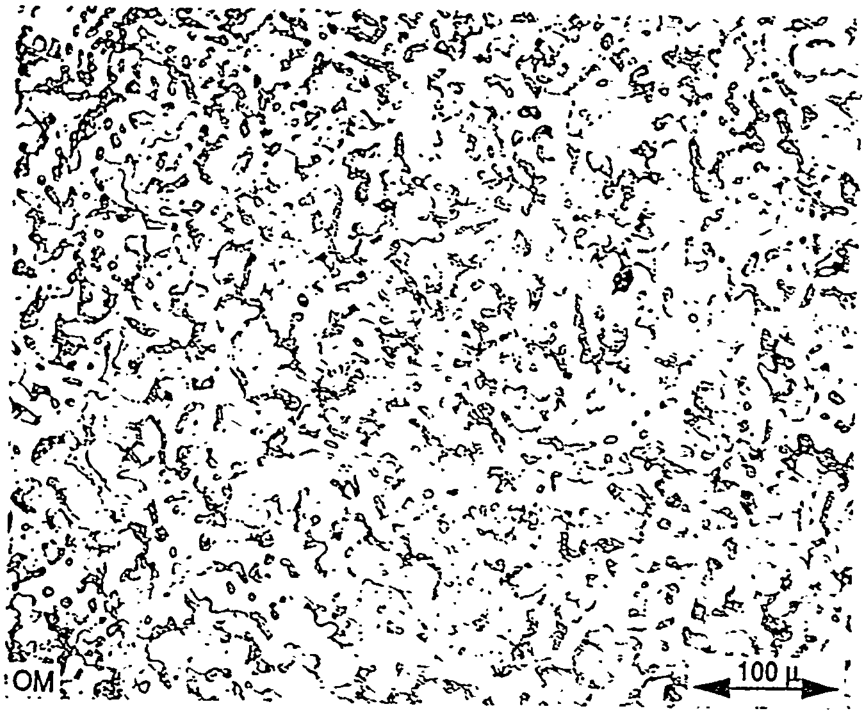

Figure 3. Sample CN-4 (88 at.% Cr-12 at.% Nb) annealed for 1 hour at 1600°C plus 4 hours at 1200°C in vacuum. Cr-rich regions (light) surrounded by Laves-containing eutectic phase (dark).

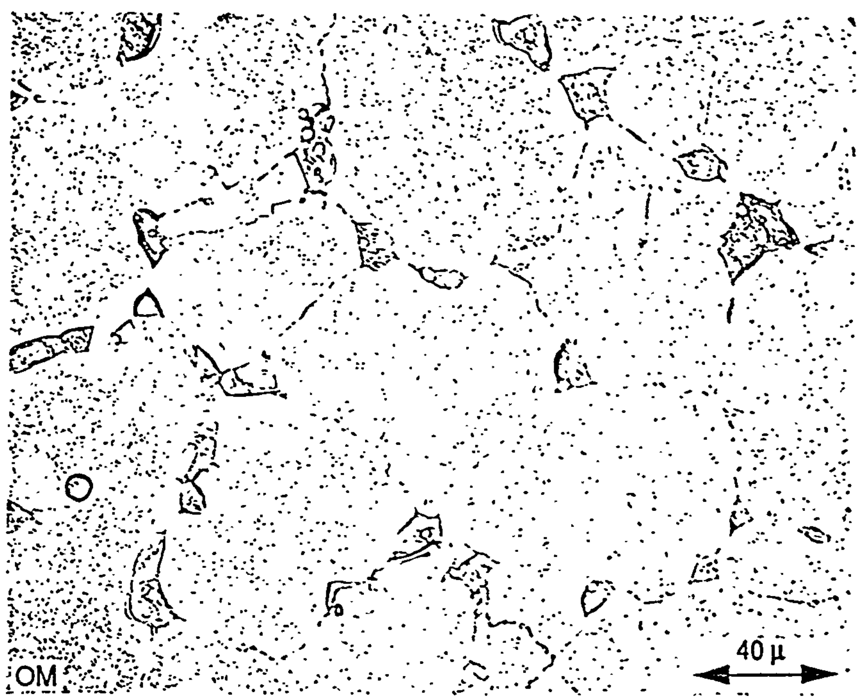

Figure 4. CN-7 - annealed for 2 days at 1580°C plus 2 days at 1200°C in vacuum.

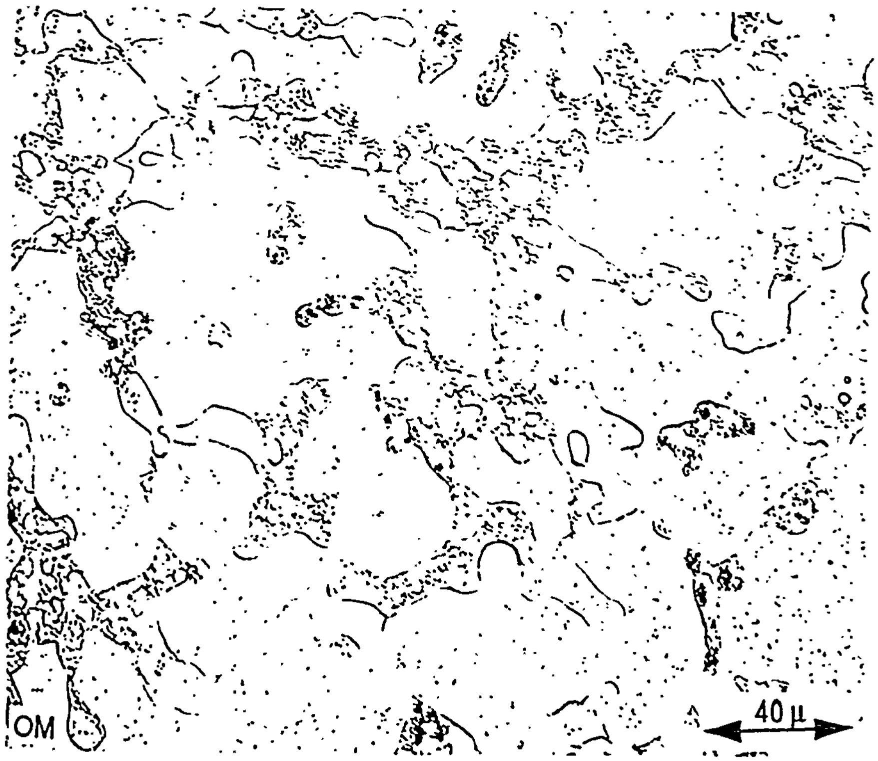

Figure 5. CN-4 - annealed for 2 days at 1580°C plus 2 days at 1200°C in vacuum.

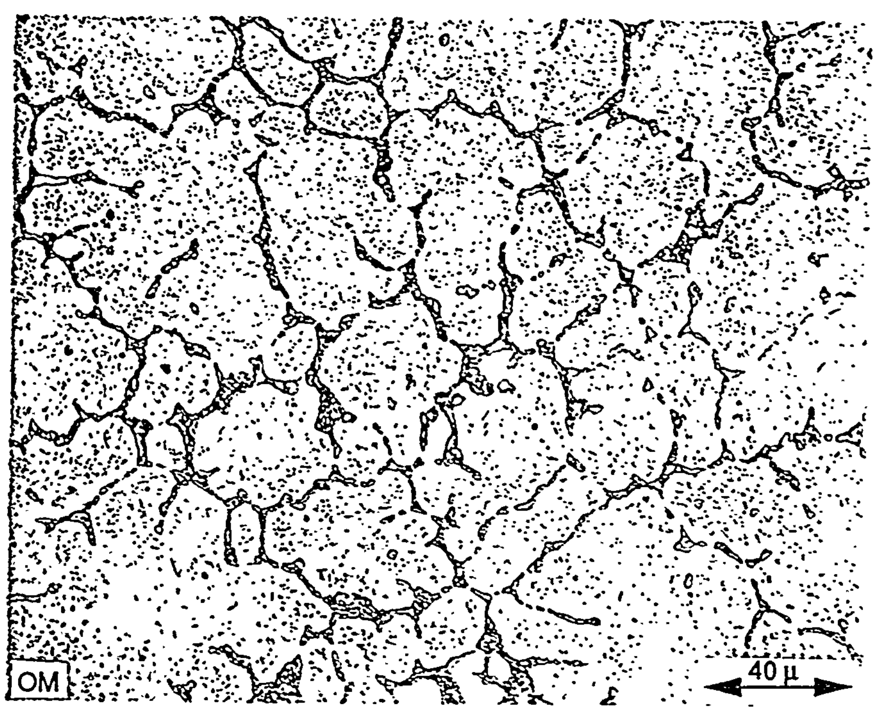

Figure 6. Sample CN-7 (94 at.% Cr-6 at.% Nb) annealed 1 day at 1300°C in vacuum. Cr-rich regions (light) surrounded by Laves-containing eutectic phase (dark).

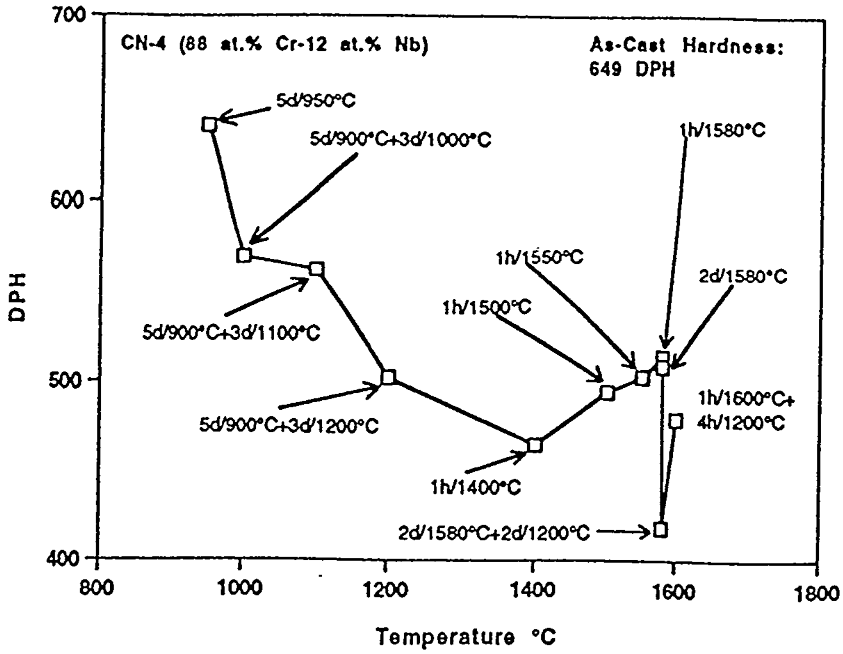

Figure 7. Hardness profile for CN-4 for a variety of annealing treatments.