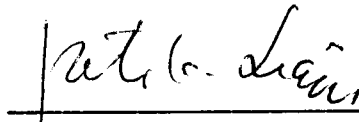


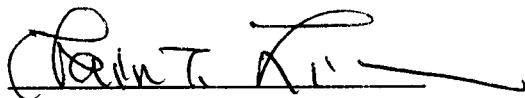
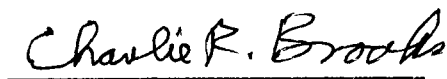
To the Graduate Council:

I am submitting herewith a thesis written by Jeffery Allan Cook entitled "The Effects of Microstructural Control on the Mechanical Behavior of Cr₂Nb-based Alloys." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.



Peter K. Liaw, Major Professor

We have read this thesis and
recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor and Dean
of the Graduate School

**THE EFFECTS OF MICROSTRUCTURAL CONTROL
ON THE MECHANICAL BEHAVIOR OF
Cr₂Nb BASED ALLOYS**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Jeffery Allan Cook
August 1995

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ABSTRACT

Microstructural evaluations and mechanical testing of Laves-phase alloys based on Cr_2Nb were examined in order to optimize microstructural and mechanical properties via secondary processing techniques and thermo-mechanical treatment at 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 coarse/brittle eutectic structure in the 94 at.% Cr - 6 at.% Nb (CN-7) alloy; (c) two different anneals, 1 hour (h) at 1600°C + 4 h at 1200°C and 4 h at 1550°C + 2 days (d) at 1200°C , lead to a substantial improvement in the room-temperature compressive ductility over previous annealing treatments (3d at 1100°C). In addition, Hot Isostatic Pressing (HIPping) + annealing led to a substantial refinement of the brittle eutectic structure in the CN-7 (Cr-6 at.% Nb) composition. HIPping led to only a marginal reduction in casting defects and a refinement of the eutectic structure in the CN-4 (Cr-12 at.% Nb) composition.

A combination of hot forging and annealing is promising in refining the brittle eutectic structure in the CN-7 composition. Tensile properties were found to be sensitive to the morphology of the Cr_2Nb Laves phase, even after HIPping to break up the interconnected Cr_2Nb phase. Solid state precipitation of Cr_2Nb particles was found to occur when annealing at temperatures well below the eutectic temperature (1100 - 1200°C) and these particles were found to be fairly resistant to coarsening, even after 30 days at 1200°C .

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I. INTRODUCTION

The necessity for very-high-temperature applications of structural materials with the desired properties of low density, good mechanical properties and resistance to environmental degradation has led to research on materials other than titanium, nickel, and iron aluminides. Chromides, such as Cr_2Nb -based alloys, are a strong candidate for use at very high temperatures in the range of 1000°C to 1300°C . However, after a careful review of the literature, little work appears to have been conducted in developing a good understanding of the effect of microstructural control on the mechanical behavior of Cr_2Nb -based alloys.

The development of this alloy is being carried out for use as critical hot components, such as in advanced fossil energy conversion systems. Cr_2Nb has a C15 (Laves phase) structure which is a relatively complicated crystal structure when compared with the more widely studied B2, L1₂, and D0₁₉ structures [1]. The crystal structure is so complex that dislocation motion is difficult at ambient temperatures. With regard to the Von Mises criteria, Cr_2Nb does not have a sufficient number of independent slip systems for uniform, extensive plastic deformation [2]. Since it has been shown [2] that the single-phase Cr_2Nb Laves alloys are extremely brittle at ambient temperatures, work has been concentrated on the Cr- Cr_2Nb two-phase compositions. The introduction of a soft Cr-rich phase has been shown [2] to have promising effects on improving the mechanical properties of Cr_2Nb intermetallics.

The objective of this research is to improve the ambient-temperature (near-room temperature) strength and compressive ductility of several two-phase Cr-Cr₂Nb Laves phase alloys through microstructural control via thermo-mechanical treatments. In addition, secondary processing techniques, such as hot forging and Hot Isostatic Pressing (HIPping), have been used to reduce casting defects and further refine (break up) the brittle, interconnected Cr₂Nb phase in the eutectic structure that is the cause of the poor toughness and fracture resistance of these alloys. An appreciation for the coarsening resistance of the Cr₂Nb precipitates in the Cr-rich solid solution phase was also investigated by performing extended anneals at 1200°C. Moreover, the results of this research can provide invaluable information for the development and selection of reliable intermetallics for ultrahigh-temperature (1000°C to 1300°C) structural applications.

II. LITERATURE REVIEW

A. Overview:

The Cr₂Nb Laves phase has a cubic crystal structure (C-15) with a stacking sequence of an XYZ type, where X, Y, and Z represent close-packed layers, similar to a face-centered cubic (f.c.c.) structure; however, each layer is composed of four interpenetrating atomic layers. The unit cell contains 24 atoms and has a lattice constant of 6.98 Å [3-6]. The advantages of this Cr-Cr₂Nb Laves-phase alloy include its relatively high melting point (1770°C) [7-8], relatively low density (7.7g/cm³) [9], and its potential resistance to oxidation and corrosion [7].

The most important concern with Cr₂Nb as well as other A₂B Laves phases is their poor ductility and fracture toughness at near-room temperatures [2,7,10]. Since the single-phase Cr₂Nb is very hard [800 Diamond Pyramid Hardness (DPH)] and brittle at near-room temperatures, the efforts of alloy development have been placed on the Cr-Cr₂Nb two-phase compositions containing the intermetallic phase Cr₂Nb and the chromium-rich solid solution phase [2,11-14]. Two-phase alloys that include an intermetallic and a metallic solid solution resulting from a eutectic reaction are of interest for high-temperature applications because the microstructures are (1) thermodynamically stable, (2) exhibit no interfacial reactions and (3) frequently resist coarsening upon exposure to elevated temperatures [15].

The binary Cr-Nb, Cr-Ta, Cr-Zr, and Cr-Hf phase diagrams include a eutectic reaction, thus providing for the ability of producing two-phase alloys of the type Cr-Cr₂X where X = Zr, Nb, Hf, or Ta. In addition, eutectic reactions of the type X-Cr₂X are typically seen in these systems; however, alloys in that portion of the phase diagram have higher densities, and are expected to be less resistant to oxidation. The eutectic decomposition in the two-phase Cr-Cr₂X region results in the formation of phases with a fibrous/rod morphology, and in the hypoeutectic alloys, the primary phase is the Cr solid solution. The Cr solid solution decomposes at temperatures below the eutectic temperature to provide secondary Cr₂X precipitates [15]. The intermetallic Cr₂X is a Laves phase with the hexagonal C14(MgZn₂), cubic C15(MgCu₂), or mixed C36(MgNi₂) structure [16-17]. These structures frequently exhibit a sluggish transformation from one to the other during heating and cooling.

In the existing binary phase diagrams, the transformation from a C14 to C15 structure has been preliminarily identified as a polymorphic transformation in the Cr-Hf system, while in the Cr-Ta and Cr-Ti systems, it has been identified as a first-order transformation occurring via a eutectoid transformation of the type C14 phase $\leftrightarrow$ C15 phase + Cr(ss) [18]. Work performed by Thoma and Perepesko [19] in the form of X-ray diffraction for the metastable room-temperature phase has provided more proof for the existence of a high-temperature hexagonal Laves structure (C14) at the Cr₂Nb composition. The faulted microstructures associated with the monolithic Cr₂Nb alloys, together with the analysis from X-ray diffraction (XRD) and thermal analysis studies,

show that the C14 $\leftrightarrow$ C15 transformation occurs via sequential peritectoid and eutectoid reactions with the C36 mixed structure as an intermediate step [19].

Various two-phase alloys on the Cr-Cr₂Nb side as well as the Nb-Cr₂Nb side of this binary system are under investigation [2,11-14,19]. Previous studies have indicated that the two-phase Cr₂Nb alloys show plastic deformation under compression at room temperature, with much greater strength than nickel-base superalloys at and above 1000°C [2,11-14]. The results obtained to date indicate that the Cr-Cr₂Nb alloys have excellent strength for structural use at ultrahigh temperatures (i.e., 1000°C to 1300°C) [2,11-14].

The work performed by Takeyama and Liu [2] on the Cr-Cr₂Nb system 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 given by Goldschmidt [7,8]; (b) the soft Cr-rich 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 [12]. It has been shown [2, 11-14] that the mechanical and metallurgical properties of the Cr-Cr₂Nb alloys can be improved through the dispersion of the ductile Cr-rich phase or the break-up of the coarse, brittle Laves-containing eutectic structure.

B. Microstructure and Phase Composition:

Work to improve the ductility and fracture resistance of two-phase Cr-Cr₂Nb alloys was performed by Liu *et al.* [11-13]. The alloys studied contained from 5.6 to 12 at.% Nb, which basically are comprised of a Cr-rich solid solution surrounded by the eutectic structure, a mixture of Cr₂Nb-type and Cr-rich phases. When annealed above 1000°C, the supersaturated Cr-rich solid solution precipitates Cr₂Nb Laves-type particles. In the eutectic structure, the brittle, coarse Cr₂Nb particles are usually interconnected into a skeleton which is thought to be one of the major reasons for the poor fracture resistance and ductility in the Cr-Cr₂Nb alloys [11-13].

Alloying additions, such as Re, Al, and Zr, were added in order to refine the coarse Cr₂Nb eutectic structure in the Cr-Cr₂Nb alloys [12,13]. Two beneficial elements were identified among all the alloying additions that were made to the alloys. One element is most effective in breaking up the brittle, interconnected eutectic structure. Another element was found to be most effective in improving the oxidation resistance of these alloys without sacrificing the ductility [13]. Unfortunately, the names of these two elements could not be identified due to a pending patent on these alloy compositions. Liu *et al.* found that the tensile properties of these alloys are sensitive to casting defects, such as microcracks and/or porosity. Hot Isostatic Pressing (HIPping) at 1450°C-1580°C and /or directionally solidifying via a floating zone remelting method did not effectively reduce these casting defects [13].

Previous work which has been performed on this project has shown [14] that annealing at temperatures close to the eutectic temperature is successful in improving the microstructure of these two-phase Cr-Cr₂Nb alloys by refining (breaking up) the brittle, interconnected Cr₂Nb phase in the eutectic structure which leads to the poor fracture resistance of these alloys. Annealing at high temperatures, such as 1500° to 1600°C, has proved to be successful in breaking up the coarse, brittle Laves-containing eutectic structure which is detrimental to the fracture resistance and ductility of this material. The hardness of these alloys can be controlled as well through thermo-mechanical treatments. Annealing at 1200°C after higher-temperature anneals (1500°C to 1600°C) has been shown to decrease the hardness. The decrease in hardness that results after lower-temperature anneals can be attributed to the coarsening of fine Cr₂Nb precipitates that form in the Cr-rich phase upon cooling [11,14]. Annealing once again at high temperatures has been shown [14] to dissolve these precipitates as the solubility limit of Nb in the Cr increases and, thus upon cooling, the particles re-precipitate once again with a fine particle size which causes the hardness to once again increase.

In the work performed by Kumar and Miracle [15], the cast, homogenized, and forged microstructures of a two-phase Cr-Cr₂Hf alloy (Cr-6.5 at.% Hf) were characterized via optical, scanning, and transmission electron microscopy. In their study, ingots were induction-melted in a Zr crucible and then tilt-poured into a graphite mold in an argon atmosphere. The ingots were then homogenized (annealed) for 24 hours at 1400°C in flowing argon. A section of the annealed ingots was isothermally forged in helium at 1400°C.

Several heat treatments were performed [15] for the following reasons: (1) to obtain an appreciation for the morphological stability of the eutectic Cr₂Hf phase, (2) to examine the coarsening response of the Cr₂Hf precipitates that formed by the solid state decomposition of the Cr solid solution, (3) to study the C14 ↔ C15 transformation of the Cr₂Hf phase. In the as-cast condition, a dendritic morphology exists with the final interdendritic liquid decomposing via the eutectic reaction to form Cr + Cr₂Hf. Even after annealing for 24 hours at 1400°C, the dendritic morphology is still seen with the eutectic Cr₂Hf phase retaining a ligament morphology in the interdendritic regions; however, there is some evidence of the ligaments starting to pinch off into shorter segments [15]. Transmission electron microscopy studies by Kumar and Miracle revealed the eutectic Cr₂Hf to consist of ligaments that exhibit periodic grooving and that these grooves are associated with grain and subgrain boundaries. When they are associated with subgrain boundaries, the dislocations that comprise the boundary are frequently the partials that are bounding the stacking faults. These grooves provide the curvature necessary for the spheroidization, and thus a morphological breakdown occurs when the eutectic microstructure is exposed to stress and temperature, either simultaneously or sequentially [15]. Furthermore, it is possible according to Butcher *et al.* [20] that the accelerated diffusion along these grain and subgrain boundaries can lead to enhanced spheroidization.

In the forged condition [15], the dendritic morphology is still present, but the eutectic Cr₂Hf network is no longer continuous, as it was in the as-cast and annealed conditions. In the forged condition, the eutectic Cr₂Hf is pinching off

and is in the process of breaking down coarse individual precipitates throughout the microstructure. As a result, the intermetallic eutectic phase Cr_2Hf is morphologically unstable after hot working and continues to degrade with an additional high-temperature exposure [24 hours (h) and 100 h at 1400°C]. The eutectic Cr_2Hf phase was found to remain in the C14 structure at room temperature despite that the stable phase at room temperature has been shown to be C15 [15,19]. A 1000 h anneal at 1000°C caused the C14 structure to become unstable and transform to the more stable C36 structure. Despite the extended heat treatments at 1000°C and 1100°C , the C15 Cr_2Hf phase was not seen in their study. In addition, solid state precipitation was observed in the Cr-rich phase, and these precipitates were found to be extremely resistant to coarsening; they were tentatively identified by Kumar and Miracle as C15 Cr_2Hf [15].

In the work performed by Anderson *et al.* [21], the thermal stability of a Cu-8Cr-4Nb alloy was studied for aging times up to 100 h at both 500°C and 700°C . Coarsening of the secondary Cr_2Nb particles was seen during aging at 773°C and 700°C , but the secondary-particle size remained around 150 nm even after 100 h of aging time. Despite particle coarsening, it was found that the particle distribution after long-time anneals was still favorable to maintain the good mechanical properties of this alloy.

The main strengthening mechanisms in the Cu-8Cr-4Nb alloy were attributed to the Hall-Petch and Orowan mechanisms. For large particles within the alloy, no significant strengthening contribution was found. It was discovered that the

small-particle volume fraction of the Cu-8Cr-4Nb alloy is sufficient to provide the stabilization of a fine grain size during heating to temperatures up to 700°C. In this manner, the grain-boundary-strengthening contribution is maintained following long-time anneals at elevated temperatures, and is the dominant room-temperature strengthening contribution in these alloys. In their investigation, experimental and calculated values of Orowan and grain boundary strengthening created by small particles indicate that the coarsening of the secondary precipitates in the Cu-8Cr-4Nb alloy leads to only a slight decrease in the mechanical strength due to aging for 100 h at a temperature of 700°C [21].

C. Deformation Behavior:

The Cr₂Nb ordered intermetallic system is a potentially attractive alternative to current high-temperature materials systems. The work by Vignoul *et al.* [22] has shown that Cr₂Nb and Cr₂(Nb, V) intermetallics are intrinsically strong and that this strength is maintained to very high temperatures. In their work, microindentation was used to study the static and time-dependent deformation behavior of these compounds. Microindentation hardness results in the temperature range of 25°C to 1400°C showed that these two alloys have greater strength than nickel-base superalloys and other ordered intermetallics that have been studied in greater detail, such as iron and nickel aluminides. Even though the Cr₂Nb and Cr₂(Nb, V) alloys remain brittle at high homologous temperatures, there is evidence of enhanced plasticity, or dislocation mobility, occurring at temperatures greater than 800°C for the ternary alloy and at temperatures above 1100°C for the binary compound [22].

Both of the alloys studied by Vignoul *et al.* were shown to have excellent intrinsic resistance to creep deformation. The high creep deformation resistance in these alloys was explained by the incorporation of a resisting stress against creep into the descriptive microindentation creep concept [22]. Even though specific deformation mechanisms for creep in these alloys have not been determined, it is suggested from dislocation studies in other C15 Laves phase materials that there exist strong pinning or resisting forces which limit dislocation motion in these materials. These pinning points are the result of the complicated crystal structure of the material and the synchro-shear glide mechanisms for deformation. The synchro-shear deformation mode is described in greater detail in the next paragraph. Furthermore, small vanadium additions to the Cr₂Nb alloy caused solid-solution softening and an increase in the effective fracture toughness of the Cr₂(Nb, V) alloy [22].

In general, Laves phases are extremely brittle at low temperatures, but work by Inoue *et al.* [23,24] has shown that a C15 Hf-V-Nb alloy can be deformed by large amounts at room temperature, and the subsequent work by Livingston and Hall [25] and Chu and Pope [26] has shown that twinning is the main deformation mode. A new deformation twinning mechanism is proposed by Chu and Pope for complex intermetallic compounds based on the synchro-shear mechanism. If twins actually do form in this way, then long shear vectors and/or atomic shuffles are not needed. In addition, they found that the mechanical behavior of this alloy is relatively strain-rate insensitive [27]. The work done by Pope and Chu has revealed that the mechanical properties of the C15 intermetallic HfV₂+Nb can be divided into three temperature regions. In the low

temperature region, the alloy is fairly ductile due to the formation of $\{111\}\langle 112\rangle$ type mechanical twinning. The twinning behavior takes place on $\{111\}$ planes by a shear in the $\langle 112\rangle$ direction. Twinning occurs via the synchro-shear mechanism which results in shear on selected $\{111\}$ planes, i.e. the shear is inhomogeneous. Only short displacements are needed for this synchro-shear, $1/6\langle 112\rangle$, and, according to Pope and Chu, no atomic shuffles are required. They suggest that deformation twinning appears to be facilitated by the substitution of Nb into HfV_2 , which increases the free volume in the planes undergoing synchro-shear. In the intermediate temperature region, the alloy shows a drop in ductility, and at high temperatures the alloy shows large plasticity via $1/2\langle 110\rangle$ dislocation slip. Pope and Chu report that the ductility drop is not the result of a phase transformation, but is most likely the result of atomic interference across (111) planes due to the low coefficient of thermal expansion and the relatively large atomic thermal vibrations which inhibit synchro-shear [27].

The high-temperature deformation behavior of a two-phase alloy consisting of Cr_2Nb , a C15 Laves phase, and a soft Nb-based solid solution, was studied by Takasugi *et al.* [1], along with measurements of oxidation. Compression tests were performed on these two-phase alloys in order to study the deformation behavior. It was found that these alloys are deformable at temperatures above 1000°C and that the extent to which the material can be deformed increases with a decrease in the Cr content between 61 and 51 at.% Cr. In addition, the 0.2% yield strength steadily decreased with increasing temperature and is only slightly sensitive to the composition of the alloy. The steady-state flow stress

was found to steadily decrease with increasing temperature and is dependent upon alloy composition. A constitutive equation was fitted to the experimental data with a composition-independent stress exponent of approximately 2.7 and an apparent activation energy ranging between 477 and 391 kJ/mol. The activation energy was found to also be dependent on the alloy composition. Microstructural examination reveals that the deformation in compression is caused by cracking (cavitation) and interfacial sliding between the two constituent phases, in addition to the bulk deformation of the constituent phases [1]. Studies on these same alloys also revealed that they have very good oxidation resistance. The oxidation rate was found to increase with decreasing amounts of Cr; thus revealing that Cr additions have the potential to reduce the oxidation rate in Cr₂Nb intermetallics at high temperatures [1]. The oxidation resistance of these alloys is superior to that of other previously studied alloys that are potential high-temperature structural materials, such as Nb₃Al [28].

As mentioned previously, most Laves phases consist of either the cubic C15 (MgCu₂ type) or the hexagonal C14 (MgZn₂ type) structure. The work performed by Livingston *et al.* [29] has shown that the dislocations present in MgCu₂ and MgZn₂ under compression at high temperatures have Burgers vectors similar to those found in f.c.c. (face-centered cubic) and h.c.p. (hexagonal closed-packed) structures, respectively. Networks are formed by the reaction of dislocations of different Burgers vectors and, at low strain rates and adequately high temperatures, well-defined sub-boundaries are formed from these reactions as well. Also seen in their work was evidence that dislocation

splitting, extended nodes, and stacking faults were occurring in these structures under compression [29].

In other experiments which have been performed as a part of this thesis work [30], a substantial improvement in room-temperature strength and compressive ductility was found for two alloy compositions which were annealed for 1h at 1600°C + 4h at 1200°C, as well as other annealing conditions. At 1000°C, it was observed that one of the compositions of the two-phase Cr-Cr₂Nb alloys studied, CN-7, could be deformed with compressive ductilities larger than roughly 30% due to the microstructural control via thermo-mechanical treatments and secondary processing techniques. These results show that the two-phase intermetallic alloys based on Cr₂Nb have high strength with decent ductility at all test temperatures. In addition, we see that the microstructural control via thermo-mechanical treatments and secondary processing is a viable method for improving the mechanical properties of this material.

Binary two-phase alloys in the Cr-Ti system have been examined [31], and it was found that substantial amounts of Ti were needed to provide any measurable resistance to cracking of the two-phase material at room temperature; however, this process resulted in a significant loss in the high-temperature strength when compared to the single phase Cr₂Ti. Ternary substitutions for Ti in the Cr-Ti alloys have been investigated, namely Al, Zr, and Nb; and Ti-Cr-Nb alloys have been tested in compression and bending [32]. A significant yield strength difference was found between these two types of tests at both room temperature and 1000°C. The room-temperature plastic strain was

not measurable, and the fracture toughness at room temperature using notched bend specimens was measured to be approximately $5\text{-}6 \text{ MPa}\sqrt{\text{m}}$ for all alloys studied [32].

The variation in the compressive yield strength with test temperatures in the range of 20°C - 1200°C for a Cr-6.5 at.% Hf alloy was investigated by Kumar and Miracle [15]. A characteristic body-centered cubic (b.c.c.) behavior was seen in that the strength begins to increase rapidly with decreasing temperature at near-room temperature. A gradual decrease in strength occurs with increasing temperatures in the intermediate regime (227°C - 827°C) and then rapidly falls off with increasing temperatures. From this behavior, it is evident that two distinct temperature regions exist - a low temperature region where the yield stress is essentially independent of test temperature and a high-temperature region where thermally activated deformation occurs. The bend ductile-to-brittle transition temperature for the Cr-6.5 at.% Hf alloy was found to be strain-rate sensitive, occurring at roughly 70°C - 150°C at a strain rate of $\dot{\epsilon} = 8.5 \times 10^{-4} \text{ mm/s}$. Notched-bend specimens in this study yielded fracture toughness values ranging from $\sim 7 \text{ MPa}\sqrt{\text{m}}$ at room temperature to $\sim 15 \text{ MPa}\sqrt{\text{m}}$ at 600°C . The fracture mode in all cases was transgranular cleavage in the Cr-rich phase and intergranular in the Cr_2Hf phase [15].

In the work performed by Davidson and Chan [33], the fracture behavior of several two phase alloys, or "*in situ* composites" based on the Nb-Cr system were evaluated and found to possess low fracture toughness values (less than $\sim 5 \text{ MPa}\sqrt{\text{m}}$) when compared with other engineering materials. They

determined that the low toughness characteristics of the Nb phase was to blame for the poor fracture toughness behavior of these alloys; and, as a result, alloying was chosen as a possible solution for this problem.

The fracture toughness of single-phase Cr_2Nb was measured in three-point bending tests to be $\sim 1.5 \text{ MPa}\sqrt{\text{m}}$. Davidson and Chan found that two-phase alloys of Cr and Nb (Cr_2Nb dispersed in a Nb solid solution) yielded a four-fold fracture toughness increase to $\sim 5 \text{ MPa}\sqrt{\text{m}}$. These results provide evidence of "ductile phase toughening", but this level of toughness is still too low for practical applications [33].

The fracture toughness levels (K_Q) of the Nb-Cr alloys were found to be too low for practical fatigue crack growth rate evaluation. Davidson and Chan discovered that Ti additions in the Nb-Cr composites provided the desired fracture toughness increase, but also had a very unexpected result of increasing the fracture toughness to $K_Q \sim 62 \text{ MPa}\sqrt{\text{m}}$ for an addition of ~ 37 at.% Ti in the Nb matrix alloy. This large toughness increase was attributed to the ductility and strength of the alloy, but has not been rationalized through an alloy theory. The increased toughness of the Nb matrix also increased the toughness of the composite from roughly 5 to $18 \text{ MPa}\sqrt{\text{m}}$. The use of notched, three-point bend tests to measure the effects of alloying on the fracture toughness levels proved to be very effective [33].

III. EXPERIMENTAL PROCEDURE

Table 1 lists the composition (at.%) of CN (Cr-Nb) [2] alloys investigated in this work. The alloys used in this study have base compositions of chromium with a variation of 6 to 18.5 at.% Nb. As shown in Table 1, the CN-45 composition contains 17 at.% Nb. It was once believed that the eutectic composition of this two-phase alloy was that of the CN-4 alloy (12 at.% Nb). However, the work by Takeyama and Liu [2] has since shown that the eutectic composition is more like that of the CN-45 composition (17 at.% Nb). The recent work done by Thoma and Perepesko [19] has indicated that the actual eutectic composition is closer to 18.5 at.% Nb, which is the composition of the CN-84 alloy investigated in this study. The modified binary Nb-Cr phase diagram based on their findings is represented in Figure 1* .

Chromium-niobium alloys weighing 350 grams 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. In addition, a titanium getter was melted immediately prior to and adjacent to the melting of the ingot in order to reduce interstitial levels. The ingots were then re-melted at least four times prior to drop casting to ensure chemical homogeneity. The preheating of the copper mold to 100°C before drop casting was done in order to control alloy solidification and reduce thermal shock and microporosity formation during drop casting [12-14].

* All figures are in the Appendix

Table 1. Alloy Compositions for the Cr₂Nb-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 %
CN-84	Cr - 81.5 % Nb - 18.5 %	Cr - 71.14 % Nb - 28.86 %

The alloys were placed in a covered alumina crucible and annealed under vacuum at various times and temperatures. The purpose of these anneals was to refine (break up) the brittle, interconnected Cr₂Nb phase in the eutectic structure of these alloys which leads to poor fracture toughness at ambient temperatures.

The effects of annealing and secondary processing on the microstructures and mechanical properties in compression and tension of these alloys were emphasized in this investigation. Microstructures of these alloys were examined via optical and scanning electron microscopy. The metallographic specimens were polished through 1 μ m using conventional techniques. Samples were then etched in a solution of 15 gm KOH, 15 gm K₃Fe(CN)₆, and 90 ml H₂O for approximately 5 seconds. Hot Isostatic Pressing (HIPping) to suppress and/or remove casting defects and refine the brittle, interconnected Cr₂Nb phase in the eutectic structure was carried out by Dr. Sarit Bhaduri of the Department of Mines, University of Idaho. HIPping was performed at 1610°C at a pressure of ~ 193 MPa. Hot forging was performed on the CN-7 alloy at 1200°C in vacuum to

roughly 20% deformation at a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$. The specimen size for hot forging was a cube-shaped piece of the as-cast material measuring ~ 1.5 cm on each side. Larger specimens could not be hot forged due to limitations of the equipment.

Microhardness readings were taken for each specimen using a LECO M-400 Hardness Tester with an indenter load of 1 kg. An average of three to five readings taken randomly across the sample gives the reported hardness values. Coarsening studies were performed on the CN-4 and CN-7 compositions at 1200°C for the following times: 3h, 6h, 1d, 3d, 7d, 14d, and 30d. The microstructures were then examined in the scanning electron microscope in order to qualitatively compare the coarsening behavior of the Cr₂Nb precipitates within the Cr-rich phase for different annealing times at 1200°C. Image analysis techniques were used to determine the average particle size and distribution of the Cr₂Nb precipitates in the Cr-rich phase of the CN-7 alloy due to different annealing times at 1200°C. High-magnification scanning electron microscope (SEM) images of 2 samples of the CN-7 alloy annealed for 3h at 1200°C and 30d at 1200°C were digitized by scanning them into a Macintosh Centris 610™ computer utilizing a Hewlett-Packard Scanjet IIcx™ scanner and the image software Adobe Photoshop®. Analysis of the Cr₂Nb precipitates within the Cr-rich phases was performed on the scanned images using the imaging software known as NIH Image 1.57®. The area fraction of the precipitates and the particle size distribution were determined for an average of several sample areas from each scanned image.

Nanoindentation tests were carried out on a selected number of specimens in order to determine the elastic modulus and hardness of the two phases within these alloys, Cr and Cr₂Nb. All tests were performed using a Nanoindenter® at the Oak Ridge National Laboratory. For the determination of the hardness and modulus, the indenter was first loaded and unloaded three successive times at a constant loading rate with each unloading stopping at 10% of the peak load in order to maintain contact between the sample and the indenter. A hold period of ~ 100 seconds was added at peak load prior to the final unloading. The multiple loading and unloading steps were performed in order that the unloading data used to determine the hardness and modulus would be mostly elastic. Shown in the schematic of Figure 2(a) are the experimental variables which are needed in order to determine the hardness and modulus of the material [34]. The three important variables to remember are the peak load (P_{max}), the penetration depth at the peak load (h_{max}), and the initial unloading contact stiffness (S) which is measured at the peak load. No restrictions are placed on the unloading data being linear at any time during the unloading [34]. The determination of the modulus is related to the following equation:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (1)$$

where E_r is the reduced modulus, A is the contact area, and S is the measured stiffness. The reduced modulus, E_r , takes the elastic deformation of the indenter into account by assuming that a similar elastic process occurs in the indenter as well as the sample [34]. Equation 1 holds for any indenter which can be described as a body generated by the revolution of a smooth function, and, as a

result, is not limited to a specific geometry [35]. The hardness is derived from the following equation:

$$H = \frac{P_{\max}}{A} \quad (2)$$

where $P_{\max}$ was previously defined as the peak load and A is the projected area at the peak load determined from the following equations:

$$A = F(h_c) \quad (3)$$

where the area is a function of the contact depth, h_c , given as:

$$h_c = h_{\max} - h_s \quad (4)$$

where $h_{\max}$ is the depth at the peak load and h_s is the surface displacement at the contact perimeter as given by the following equation and shown schematically in Figure 2(b):

$$h_s = \epsilon \frac{P_{\max}}{S} \quad (5)$$

where ϵ is a constant which is dependent on the indenter geometry and S is the contact stiffness [34]. Equations 1 through 5 were all adapted from work performed by Oliver *et al.* [34] at the Oak Ridge National Laboratory.

Compression specimens having a diameter of 6 mm and a length of 9 mm were cut by electro-discharged machining (EDM) from the annealed ingots. The specimens were tested under compression using an Instron testing machine at

room temperature and 1000°C with a nominal strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$. The elevated-temperature tests were carried out in vacuum (less than $7 \times 10^{-4} \text{ Pa}$). Load versus displacement curves were recorded on a pin plotter where the x-axis was placed at 1 V/in = .508 mm/in and the y-axis was set at 1V/in = 1000 kg/in. The yield and ultimate strengths were determined from these curves by dividing the load at yield and the maximum load by the cross-sectional area of the specimen in each test. Selected specimens were sectioned after testing and polished in order to characterize the deformation behavior of these alloys in compression.

Button-head tensile specimens were prepared from the annealed and HIPped ingots using EDM. Specimens used in performing these tension tests were 2.54 cm (1 inch) in length with a 0.9525 cm (3/8-inch) gage section. Tests were performed on an Instron testing machine at both room temperature and 1000°C in stagnant air. The strain rate in all tests was $3 \times 10^{-4} \text{ s}^{-1}$. Load versus displacement curves were recorded for the tension tests using a pin plotter set at a chart speed of 10"/min. with a load range of 2000 lbs. The fracture strength values were then determined from these curves by dividing the breakage load by the minimum cross-sectional area in the gage section of each sample tested. After testing, the fracture surfaces of selected specimens were examined in a scanning electron microscope in order to study the fracture surface and identify the mechanism(s) of fracture.

IV. RESULTS AND DISCUSSION

A. Microstructure and Phase Composition:

The CN alloys contain two phases, the Cr₂Nb 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, which agrees well with the results reported by Thoma and Perepesko [19].

The alloys studied in this work contain a primary Cr-rich solid solution which is surrounded by the eutectic structure, a mixture of the Cr₂Nb Intermetallic Laves phase and a Cr-rich phase. In each of these alloy compositions, the Cr-rich phase is the matrix, thus indicating from the phase diagram that these are hypoeutectic compositions. The supersaturated Cr-rich solid solution (bright-contrast phase in Figure 3) forms with a dendritic morphology with the remaining interdendritic liquid decomposing via the eutectic reaction to form the Cr₂Nb Laves-type phase and Cr-rich phases. The coarse, brittle Cr₂Nb phase in the eutectic structure (dark-contrast phase in Figures 3 and 4) is, in most cases, interconnected in a ligament-type morphology, as evidenced in the as-cast microstructures of the CN-7 and CN-4 compositions, respectively. Throughout this paper, the networked Cr₂Nb phase in the eutectic structure which causes the poor ductility and fracture toughness will be simply referred to as the networked eutectic structure for the sake of convenience.

Various annealing conditions were selected in order to refine this interconnected, brittle eutectic structure. The samples were annealed in a covered alumina crucible under vacuum for the chosen times and temperatures, and were then mounted in epoxy and metallographically prepared using conventional polishing techniques. Of the many heat treatments selected, several treatments were found to be beneficial in refining the brittle eutectic structure. Among these promising anneals were 1h at 1600°C + 4h at 1200°C, 4h at 1550°C + 2d at 1200°C, 1h at 1580°C, and 2d at 1580°C + 2d at 1200°C.

The microstructures of the CN-7, 4, and 45 compositions annealed for 1h at 1600°C + 4h at 1200°C are shown in Figures 5 through 7, respectively. In Figure 5, it is seen that the anneal has substantially refined the brittle eutectic structure (dark-contrast phase) when compared with the as-cast structure shown in Figure 3. To a lesser extent, this same anneal refined the eutectic structure in the CN-4 composition as shown in Figure 6, and virtually no change in the morphology is noted for the CN-45 composition as shown in Figure 7. In Figure 8, the microstructure of CN-7 annealed for 2d at 1580°C + 2d at 1200°C once again shows a substantial refinement of the brittle eutectic structure. The microstructure for CN-4 in this annealed condition is shown in Figure 9. Another anneal which was successful in refining the eutectic structure (4h at 1550°C + 2d at 1200°C) is shown in Figures 10 through 12 for the CN-7, 4, and 45 compositions. It is interesting to note in these microstructures (Figs. 10-11) that the Cr₂Nb precipitates which form in the Cr-rich solid solution have a different morphology than those seen in any of the other microstructures. The precipitates for this particular anneal tend to grow with a rod-like morphology as

seen in Figures 10 and 11 whereas the precipitates are found to be roughly spherical in all other anneals performed. It is not clear what caused the precipitates to grow with this unique geometry, but rod-like precipitates do not appear to coarsen any differently at lower temperatures (1100-1200°C) than any of the other spherical-type precipitates which were observed in other anneals. Despite a considerable break-up of the coarse, brittle eutectic structure in the CN-7 as a result of these high-temperature anneals, it should be noted that there still exists a very fine network of the Cr₂Nb Laves-phase particles along the grain boundaries of the Cr-rich regions which may continue to be a source of embrittlement in these alloys.

It should be noted that in many cases a two-step annealing process was used in this investigation. The purpose of the high-temperature anneal is to refine the brittle eutectic structure and the lower-temperature anneal, typically chosen to be around 1200°C, is used to precipitate and coarsen the fine Cr₂Nb particles which form due to solid-state decomposition of the Cr-rich solid solution when annealed at temperatures well below the eutectic temperature. It has been shown [15] that these precipitates are effective in pinning dislocations, and thus lend themselves to the possibility of improving the creep resistance of these alloys.

The compositions of the phases in the alloys CN-7, CN-4, and CN-45 annealed for 1h at 1600°C + 4h at 1200°C were determined by electron microprobe analyses for an average of three points in each respective phase, as reported in Table 2. From the phase diagram in Figure 1, we see that the

intermetallic phase in the eutectic structure has an average composition of ~ 68 at.% Cr - ~ 32 at.% Nb, which, according to the results in Table 2, reveals that the phase identified by microprobe analyses in the eutectic structure is in fact the Cr₂Nb Laves-type intermetallic phase. Microprobe analysis of the Cr-rich phase most likely contains some of the fine Cr₂Nb precipitates which precipitate in the Cr-rich matrix upon furnace cooling and/or annealing at lower temperatures (1100°C-1200°C) since, in most cases, they are beyond the limit of reliable detection and thus cannot be excluded from the Cr-rich analysis.

It has been shown [11-13] that the precipitation of the Cr₂Nb 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 3d at 1100°C [2,12]. Annealing at temperatures of 1500°C to 1600°C did not reveal the fine Cr₂Nb

Table 2. Electron Microprobe Analysis of the Cr₂Nb Alloys

Alloy	Anneal Condition	Cr ₂ Nb 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 %

* analysis of the Cr-rich phase also includes the fine Cr₂Nb precipitates

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 diffused into the Laves-containing eutectic structure,

thereby coarsening it. Thus, there are two competing mechanisms occurring during the annealing treatment; (1) the break-up of the eutectic structure and (2) the coarsening of the Laves-containing eutectic structure due to Cr₂Nb particles migrating from the Cr-rich phase at high temperatures. Upon furnace cooling from high annealing temperatures (1500°C to 1600°C), very fine particles once again precipitate out in the Cr-rich phase. Additional annealing at 1200°C causes a coarsening of these fine particles. This result can especially be seen in the micrographs shown in Figures 13 through 26 for the CN-7 and CN-4 compositions annealed at 1200°C for times ranging from 3 hours to 30 days.

B. Secondary Processing Techniques:

In the work performed by Liu *et al.* [13], the as-cast ingots were found to contain microporosity and casting cavities, which ranged from a few to several hundred microns in diameter. The as-cast ingots were HIPped at 1450°C and 1580°C at a maximum stress of 207 MPa in order to reduce and/or eliminate the casting defects. Metallographic examination showed only a marginal reduction in cast porosities by these HIPping treatments. Based on the results by Liu *et al.* [13] which show that the eutectic temperature of these alloys is actually closer to 1650°C than 1620°C, a HIPping temperature of 1610°C and a pressure of 193 MPa were chosen for new HIPping studies in the present investigation. HIPping was also utilized to see if the same or better level of eutectic refinement could be achieved as had already been accomplished via high-temperature annealing. Another reason for HIPping is that when annealing these alloys, such a high temperature is required to effectively refine the eutectic (1500°C to 1600°C) that Cr vaporization and partial melting become a problem when

scaling up these treatments from small metallographic specimens to ingot-size materials. As a result, it was hoped that HIPping of these ingots at 1610°C would enhance the spheroidization of the eutectic to a degree that lower temperatures and shorter time anneals could be subsequently used to further refine the eutectic and not detrimentally affect the material either through excessive vaporization and/or partial melting. Previous studies on Cr-Cr₂Hf by Kumar and Miracle [15] have shown that a combination of hot working and annealing can enhance the spheroidization of the brittle eutectic structure.

As-cast pieces of the CN-7 and CN-4 compositions were chosen based on their favorable response to earlier thermo-mechanical attempts to refine their microstructure. It was found that the HIPping treatment led to a considerable refinement of the brittle eutectic structure in the CN-7 composition, as shown in Figure 27, and a somewhat lesser level of refinement in the CN-4 composition, as evidenced in Figure 28. A 3 day anneal at 1200°C after HIPping did not reveal any further refinement of the eutectic structure in the CN-4 composition as shown in Figure 29. When the as-HIPped material was annealed for 12h at 1500°C, a substantial refinement of the eutectic was seen in the CN-7 alloy with the eutectic breaking down into coarse, individual particles in many areas as shown in Figure 30. Not only did the anneal at 1500°C for 12h further refine the interconnected Cr₂Nb phase in the eutectic structure, but it also coarsened the Cr₂Nb phase in the eutectic structure when compared with the as-HIPped material shown in Figure 27. An additional anneal at 1200°C for 2 days led to the coarsening of the fine Cr₂Nb precipitates in the Cr-rich regions as shown in Figure 31. Some continued refinement was also observed in the CN-4

composition for this same condition, as shown in Figure 32, but not to the same degree as that which was observed for the CN-7 composition. These results clearly illustrate that secondary processing in combination with thermo-mechanical treatment is a viable method for refining the interconnected, brittle Cr_2Nb phase in the eutectic structure in these alloys, and thus, improving their compressive ductility and fracture toughness at ambient (near-room) temperatures, as discussed in a later section.

Hot forging was another secondary processing method which was chosen for study in this investigation. An as-cast cube of the CN-7 alloy measuring ~ 1.5 cm on each side was isothermally forged in vacuum at 1200°C to 20%. Larger pieces could not be forged due to the operational limitations of the machine, and thus, this test was run as more of a feasibility experiment. The CN-7 composition was chosen for this preliminary test based on its superior response to hot working and annealing over the other compositions studied in this investigation. After forging, the sample was annealed for 6h at 1500°C in vacuum. Metallographic investigation revealed that the hot forging + annealing treatment was very effective in breaking down the interconnected eutectic structure into finer, individual particles (Figures 33 and 34), and thus, shows promise as another means of refining the microstructure in order to enhance the room-temperature fracture toughness of these alloys. Despite the advances made in refining the brittle eutectic structure through these secondary processing techniques, a continuous network of the Cr_2Nb phase in the eutectic structure is still present, as evidenced by the micrographs in Figure 30, 33, and 34. This continued presence of the networked Cr_2Nb phase in the eutectic

structure following HIPping and/or hot forging is attributed recrystallization of the Cr₂Nb phase along the Cr-rich grain boundaries during the slow cooling of the material from the HIPping and hot forging temperatures. In spite of the use of high-purity charge materials and good arc-melting technique, a fair number of oxide inclusions were still present in the as-cast material. These hard oxide particles can act as sites for crack nucleation and growth, thus further degrading the material properties.

C. Hardness/Coarsening Studies:

Microhardness results are presented in Table 3 for the CN-7, CN-4, and CN-45 alloys under different annealing conditions. The standard deviation in the hardness data presented is based on 1/2 of the difference between the maximum and minimum hardness values recorded for each annealed condition. The somewhat large deviation in the data is attributed to the significant difference in the hardness values of the Cr and Cr₂Nb phases and should only be interpreted in a qualitative manner when looking at the statistical significance of these measurements. The effects of the annealing temperature on hardness are shown in Figure 35(a) for the CN-4 alloy. No microcracking was observed at the tips of the microhardness indents as was previously reported for the single-phase Cr₂Nb alloys, thus indicating that the introduction of the soft, Cr-rich phase may be beneficial in improving the fracture toughness and ductility of these alloys at near-room temperatures [2]. The hardness decreases with decreasing niobium concentration and increasing the amount of the soft Cr-rich phase, as shown in Table 3 and again in Figure 35(b). Previous work by Liu [11] has indicated that the hardness tends to decrease

Table 3. Microhardness Values (DPH) for the Cr₂Nb-based Alloys

Annealing Treatment*	CN-4	CN-7	CN-45
6 h/1200°C**	476±33	373±12	
24h/1200°C**	453±18	339±13	
3d/1200°C**	454±21	327±18	
7d/1200°C**	423±11	324±7	
14d/1200°C**	416±22	319±23	
30d/1200°C**	405±17	308±18	
1h/1400°C	465±25	367±2	616±31
1h/1500°C	494±12	393±12	618±26
1h/1550°C	502±20	424±9	618±17
1h/1580°C	513±33	406±5	613±26
2d/1580°C	508±38	445±9	–
2d/1580°C + 2d/1200°C	418±28	341±10	–
1h/1600°C + 4h/1200°C	479±20	429±6	–

* all anneals shown are performed on as-cast material, unless otherwise noted

** hardness results from the precipitate coarsening study

as the coarsening of the fine Cr₂Nb particles within the Cr-rich phase occurs for temperatures ranging from 950°C to 1200°C, as shown in Figure 35(a). In the present investigation, it was found that annealing at high temperatures near the eutectic temperature (1400°C to 1600°C) leads to an increase in hardness, as shown in Table 3 and Figure 35(a). This increase in hardness is attributed to dissolution of the Cr₂Nb precipitates in the Cr-rich regions at temperatures near the eutectic temperature due to an increase in the solubility limit of Nb in Cr. Upon furnace cooling from these high temperatures (1500°C to 1600°C), the Cr₂Nb particles re-precipitate in the Cr-rich solid solution with a much finer size, thus leading to the increase in hardness that is observed. Continued annealing at temperatures below the eutectic temperature (i.e., 1200°C) once again

decrease the hardness due to coarsening of these Cr_2Nb precipitates. It should be noted that the microstructures of the CN-45 alloy are predominantly composed of the eutectic structure with widely scattered Cr-rich regions, and thus, the hardness values reported in Table 3 show no appreciable change with annealing time and/or temperature.

Annealing at these high temperatures (at or above 1400°C) has the following effects: (a) the 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) the coarsening of the Laves-containing eutectic structure due to the migration of the Cr_2Nb particles from the Cr-rich phase, (c) the breakup of the eutectic structure, and; (d) the re-precipitation of extremely fine Cr_2Nb particles in the Cr-rich phase upon furnace cooling from the high-temperature anneals (1500 to 1600°C), and (e) annealing at temperatures well below the eutectic temperature which tends to coarsen these precipitates. It is the fine re-precipitation that is believed to lead to the increase in hardness.

Upon additional annealing of the sample at 1200°C following high-temperature anneals, it is seen 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 [11] and observed in Table 3 and in Figure 35(a). In addition, we see that the hardness also decreases when the material is annealed for prolonged periods at a fixed temperature, such as the drop in hardness values from the coarsening studies reported in Table 3 and Figure 36 for the CN-4 and CN-7 compositions that were annealed at 1200°C over a period ranging from 3

hours to 30 days. Once again, this drop in hardness is attributed to the particle coarsening behavior of the Cr_2Nb precipitates within the Cr-rich regions. The microstructures for the CN-7 and CN-4 alloys annealed for these times are shown in Figures 13 through 26. From the optical micrographs in Figures 13 through 26, it seems that the Cr_2Nb precipitates remain fairly stable and only coarsen slightly after an anneal of 30 days at 1200°C , as shown in Figures 19 and 26 for the CN-7 and CN-4 compositions, respectively.

The precipitate coarsening studies at 1200°C were done in order to further understand the precipitation and growth kinetics of the Cr_2Nb particles in the supersaturated Cr-rich regions. A selected number of samples were examined at high magnification in a scanning electron microscope (SEM) using a backscatter electron detector to image the precipitates within the Cr-rich regions as shown in Figures 37 and 38 for the CN-7 composition annealed for 3h at 1200°C and 30d at 1200°C in vacuum and in Figures 39 and 40 for the CN-4 alloy, respectively. SEM micrographs for the CN-7 composition annealed for 3h at 1200°C and 30d at 1200°C were chosen for further study using image analysis techniques to qualitatively assess the amount of particle coarsening and the change in the particle size distribution between the 3 hour and 30 day anneals.

In Figure 41, the particle size distribution and average area fraction of particles for the CN-7 alloy that was annealed for 3h at 1200°C are reported. From the figure, it is seen that the average precipitate area fraction in the Cr-rich solid solution is $\sim 10.7\%$ with the largest distribution of particles averaging

around ~ 0.02 to $0.04 \mu\text{m}^2$. The results of the analysis for the CN-7 alloy annealed for 30d at 1200°C are reported in Figure 42. It is seen in Figure 42 that the average area fraction of the precipitates remained fairly constant with annealing time with a value for the 30 day anneal of $\sim 10.8\%$. This result suggests that the particle coarsening behavior is governed by an Ostwald ripening type of behavior whereby the volume fraction of precipitates in a solid solution remains constant with the smaller particles being sacrificed in favor of growth of the larger ones. For the 30 day anneal, the largest concentration of particles lies in the ~ 0.08 to $0.12 \mu\text{m}^2$ range, thus providing further evidence for particle coarsening for extended times at 1200°C . The results from the analysis of the precipitates reveals that the largest concentration of particles undergo a four-fold increase from the 3h anneal to the 30d anneal at 1200°C . As a result of this particle analysis, it is suggested that the precipitate coarsening kinetics of the Cr_2Nb Laves particles in the Cr-rich matrix are governed by the Ostwald ripening process. The results of this analysis are purely qualitative and provide evidence that these precipitates are fairly resistant to any significant coarsening with particles still less than $1\mu\text{m}$ in size, even after annealing for 30d (720h) at 1200°C . These results indicate that although the precipitates do coarsen, it is not believed that this coarsening will lead to any significant degradation of the mechanical properties of these alloys. The results of the image analysis work performed on these alloys are tabulated in Tables A-1 and A-2.

D. Nanoindentation:

Nanoindentation tests were carried out on a selected number of specimens in order to determine the elastic modulus and hardness of the two phases within

these alloys, Cr and Cr₂Nb. In this hardness testing method, the surface of the specimen is located for each indentation by lowering the indenter at a constant rate against the suspending springs of the system and detecting a change in the indenter tip velocity on contact with the surface. The force resolution of a typical nanoindentation system is 0.5 μ N. The procedure for determining the modulus involves a method of relating the elastic displacement of the material under the indenter to the Young's modulus of the material. The elastic displacement is determined from the data obtained during unloading of the indenter. In addition, a technique of subtracting the elastic displacement from the total displacement is used in order to obtain the hardness. All data are corrected for machine compliance when possible [34].

The nanoindentation results for the Cr₂Nb-based alloys were found to be fairly independent of the annealed condition for the CN-7 and CN-4 alloys. The modulus and hardness remained constant under different anneal conditions for the Cr₂Nb phase in the eutectic, while the Cr-rich phase showed only slight variations in the modulus and hardness for the anneal conditions studied, mainly attributed to slight Cr₂Nb precipitate coarsening within the Cr-rich phase. The CN-7 alloy was found to have an average Young's modulus (E) of 265 GPa and a hardness of $\sim$ 5.6 GPa for the Cr-rich phase and a modulus of 250 GPa and hardness of $\sim$ 12 GPa for the Cr₂Nb phase. For the CN-4 alloy, the average values for modulus and hardness of the Cr-rich phase were found to be E = 300 GPa with a hardness of $\sim$ 4.6 GPa and E = 256 GPa with a hardness of $\sim$ 13.6 GPa for the Cr₂Nb phase.

E. Compressive Properties:

The 0.2% yield strength and compressive ductility of the CN-7, CN-4, CN-45 and CN-84 alloys at room temperature are reported in Table 4 for various annealed and processed conditions. All the compressive results reported are for an average of two tests, except in a few limited instances where one result was used due to a limited number of samples being available or being damaged during machining. At room temperature, the yield strengths of CN-7 and CN-4 are higher than 1100 and 1500 MPa, respectively, for the as-cast condition. In Figure 43, the microstructure of the as-cast CN-7 alloy following compression testing at room temperature in air reveals microcracking solely within the interconnected Cr_2Nb phase in the eutectic structure, thus illustrating that the Cr-rich phase can be used as a ductile phase reinforcement to improve the fracture toughness and room-temperature ductility of these alloys.

A substantial improvement in the room-temperature compressive ductility was observed for the CN-7 and CN-4 alloys annealed for 1h at 1600°C + 4h at 1200°C over the results obtained in the as-cast condition. Two other anneals which led to a substantial improvement in the room-temperature compressive ductility in the CN-7 and CN-4 compositions include 4h at 1550°C + 2d at 1200°C and HIPped at 1610°C at 193 MPa + annealed 12h at 1500°C + 2d at 1200°C. Figures 43 and 44 for the CN-7 composition for two microstructural conditions illustrate how the refinement of the brittle eutectic structure can enhance the ductility and fracture resistance of these alloys at room temperature. In Figure 43, the as-cast CN-7 alloy tested in compression at room

temperature shows extensive microcracking and damage accumulation in the networked eutectic structure. The breakup of the eutectic, as shown in Figure 44, illustrates how the refinement of the interconnected Cr_2Nb phase in the eutectic can enhance the compressive ductility of these alloys. The microcracking that occurs in the Cr_2Nb -containing eutectic is not as detrimental to the ductility and toughness of the alloy, since the Cr_2Nb particles have been broken down into coarse, individual particles throughout the microstructure. Microcracking is seen to a lesser degree in the CN-7 alloy annealed for 4h at $1550^\circ\text{C} + 2\text{d}$ at 1200°C when tested in compression at 1000°C in vacuum, as shown in Figure 45. Although the refinement was seen to a lesser degree in the CN-4 composition than in the CN-7 composition, we find in Figure 46 that microcracking occurring in the brittle eutectic structure of the CN-4 alloy does not continue into the Cr-rich phase. This same result was seen with the CN-7 alloy in Figure 45. These results provide further evidence that the Cr-rich phase serves as a "ductile toughening phase" which blunts the cracks that originate in the brittle Cr_2Nb phase of the eutectic structure.

The CN-45 and CN-84 alloys tested showed fairly poor ductility with very high strength at room temperature for all annealed conditions, as reported in Table 4. Because of the poor ductility of these two compositions and predominately eutectic microstructures, as found in Figure 47 and 48 for the as-cast microstructures of CN-45 and CN-84, respectively, emphasis was placed on the CN-7 and CN-4 compositions which did show the refinement of the brittle eutectic and some ductility enhancement. The improvement in ductility in all

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

Alloy No.	Heat Treatment	Strength, MPa		Ductility (%)
		Yield	Ultimate	
CN-7	As-Cast	1106	1658	11.7
CN-7*	3d/1100°C	702	1261	9.5
CN-7	1h/1600°C + 4h/1200°C	1029	1733	20.7
CN-7	4h/1550°C + 2d/1200°C	668	1477	23
CN-7	HIP + 12h/1500°C + 2d/1200°C	668	1795	21.3
CN-4	As-Cast	1527	1843	9.2
CN-4*	3d/1100°C	960	1760	5.4
CN-4	3d/1200°C	1291	1560	7.8
CN-4	12h/1500°C	1424	1620	10.7
CN-4	1h/1600°C + 4h/1200°C	1327	1546	8.8
CN-4	4h/1550°C + 2d/1200°C	1247	1345	10.1
CN-4	HIP + 3d/1200°C	1077	1562	10
CN-4	HIP + 12h/1500°C + 2d/1200°C	1256	1504	13.9
CN-45	3d/1200°C	1887	1930	<1
CN-45	12h/1500°C	1872	1925	~ 1
CN-45	1h/1600°C + 4h/1200°C	1763	1824	<5
CN-45	4h/1550°C + 2d/1200°C	1698	1840	<5
CN-84	3d/1200°C	—	1868	<<1
CN-84	12h/1500°C	—	1830	<<1

* results obtained by Liu et al., 8th Annual Conference Proceedings of the Fossil Energy Materials Program, August 1994 [13].

cases can be attributed to the refinement of the networked coarse, brittle Cr₂Nb phase in the eutectic structure due to the HIPping conditions at 1610°C as well as the high-temperature anneals (at or above 1500°C).

Hot Isostatic Pressing (HIPping) at 1610°C + annealing 3d at 1200°C of the CN-4 composition showed only a marginal breakup of the brittle eutectic phase and negligible improvement in the room-temperature strength and compressive ductility over other anneals that have been performed, as reported in Table 4. Microcracking is easily seen in the CN-4 alloy for this condition, as shown in Figure 49. HIPping at 1610°C + annealing for 12h at 1500°C + 2d at 1200°C led to a substantial refinement of the brittle eutectic structure (Figure 31) and room-temperature ductility enhancement in the CN-7 composition when compared with the previous results obtained by Liu *et al.* [12,13] for specimens annealed for 3d at 1100°C (see Table 4). As a result, a room-temperature compressive ductility of greater than 20% was realized for the CN-7 composition, which was HIPped at 1610°C + annealed 12h at 1500°C + 2d at 1200°C, as reported in Table 4. In Figures 50 through 52, it is observed that the microcracking which occurs is no longer as detrimental to the compressive ductility as was seen in the as-cast condition due to the considerable refinement of the networked, brittle eutectic structure in the CN-7 composition. A HIPping + 12h at 1500°C + 2d at 1200°C annealing treatment on the CN-4 composition yielded a room temperature compressive ductility of ~ 14%, somewhat improved over other anneal conditions which yielded room-temperature compressive ductilities ranging between 8 and 10% for this alloy composition.

A comparison of the room-temperature strength values given in Table 5 shows that the Cr₂Nb-based alloys possess strength levels comparable to or better than most commonly used high-temperature structural alloys. In all of these room-temperature compression tests it is noted that the yield strength decreases slightly with an increase in the compressive ductility, thus indicating that the compressive yield strength and ductility are dependent upon the morphology of the Cr₂Nb phase in the eutectic structure. The ultimate strength in compression for these tests did not vary much for different anneal conditions or slight variations in composition, thus indicating that the ultimate strength is not as dependent upon the morphology of the Cr₂Nb phase in the microstructure, but may be controlled by the composition instead. In compression tests performed at 1000°C in vacuum, it is once again observed that the yield strength and ductility are dependent on the morphology of the Cr₂Nb phase in the eutectic structure and the ultimate strength is not as dependent on the microstructure as it is on variations in the alloy composition.

As reported in Table 6, samples annealed for 1h at 1600°C + 4h at 1200°C showed a slight improvement in strength at 1000°C over similar tests performed on samples annealed for 3d at 1100°C for both the CN-7 and CN-4 alloys. A considerable improvement in the compressive ductility at 1000°C was seen for all anneals when compared with the values obtained for the as-cast material, as given in Table 6. However, there was little change in the compressive ductility from the previous tests performed for samples annealed 3d at 1100°C by Liu *et al.* [12,13]. As the test temperature increased from room temperature to 1000°C, the strength decreased and the ductility increased for all tests. The CN-45 and

CN-84 alloys showed very limited ductility when compared with the CN-4 and CN-7 results at 1000°C. For the CN-4 alloy annealed 1h at 1600°C + 4h at 1200°C, the yield strength at 1000°C is approximately 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 [36]. A comparison plot of strength levels over a temperature range of 25°C to 1200°C given in Figure 53 shows that the Cr₂Nb-based alloys possess greater strength than many other high-temperature alloys, even at temperatures above 1000°C where other high-temperature alloys show a substantial loss in strength. In Figure 53, all strength values are for materials in the as-cast condition.

At 1000°C, both CN-7 and CN-4 can be deformed with compressive ductilities larger than roughly 20% and maintain strength levels greater than those found in nickel-base superalloys at this temperature. In particular, the CN-7 alloy in the HIPped + annealed condition yielded compressive ductilities greater than 30% with strength levels still greater than the nickel-base superalloys at 1000°C. These results reveal that the two-phase intermetallic alloys based on Cr₂Nb have high strength with decent ductility at all test temperatures. In addition, we can see that the breakup of the Laves-containing eutectic structure via annealing at higher temperatures (1500° to 1600°C) + Hot Isostatic Pressing (HIPping) results in a considerable increase in the compressive ductility at room temperature over both the as-cast and low temperature anneal (1100-1200°C) conditions, as shown in Table 4, and a substantial ductility increase at 1000°C in vacuum when compared with results for the as-cast materials for both the CN-7 and CN-4 compositions, as shown in

Table 5. Comparison of Room Temperature Mechanical Properties of Cr-Nb alloys, Nickel Aluminides, and other Structural Alloys

Material	Condition	Strength, MPa	
		Yield	Ultimate
CN-7*	As-cast	1106	1658
CN-7*	Annealed	1029	1733
CN-4*	Annealed	1424	1620
CN-4*	As-cast	1527	1843
CN-45*	Annealed	1763	1824
CN-84*	Annealed	—	1868
IC-218LZr†	Annealed	568	1337
	Cold rolled	1200	1580
IC-396M†	As-cast (C-R)	632	800
Inconel 718†	Annealed	450	870
	High Strength	1255	1410
	High Toughness	1027	1330
7075-T6 Aluminum†		510	570
250 Maraging Steel†		1585	1720
Ti-6Al-4V†		910	990

* strength values obtained in compression

† data adapted from research at the Oak Ridge National Laboratory (internal report)

Table 6. Compressive Properties of CN Alloys Tested at 1000°C in Vacuum

Alloy No.	Heat Treatment	Strength, MPa		Ductility (%)
		Yield	Ultimate	
CN-7	As-Cast	709	902	13.6
CN-7*	3d/1100°C	436	738	32.7
CN-7	1h/1600°C + 4h/1200°C	580	1069	27.9
CN-7	4h/1550°C + 2d/1200°C	405	790	31.4
CN-7	HIP + 12h/1500°C + 2d/1200°C	388	768	31.8
CN-4	As-Cast	991	1154	< 5
CN-4*	3d/1100°C	685	856	22.8
CN-4	3d/1200°C	672	740	n/a
CN-4	12h/1500°C	758	913	11.8
CN-4	1h/1600°C + 4h/1200°C	778	1079	19.8
CN-4	4h/1550°C + 2d/1200°C	711	845	17.1
CN-4	HIP + 3d/1200°C	658	711	16.6
CN-4	HIP + 12h/1500°C + 2d/1200°C	682	819	22
CN-45	3d/1200°C	1129	1224	< 5
CN-45	12h/1500°C	1168	1284	< 5
CN-45	1h/1600°C + 4h/1200°C	994	1076	8.1
CN-45	4h/1550°C + 2d/1200°C	738	1168	10.3
CN-84	3d/1200°C	604	675	2.9**
CN-84	12h/1500°C	679	715	2.7**

* results obtained by Liu et al., 8th Annual Conference Proceedings of the Fossil Energy Materials Program, August 1994 [13].

** tests performed at 1200°C in vacuum

Table 6. Moreover, hot forging performed on the CN-7 composition reveals that the networked Cr_2Nb phase in the eutectic can be broken up by hot forging + annealing at high temperatures, as was shown in Figures 33 and 34.

F. Tensile Properties:

Tensile properties of the as-cast + annealed specimens were determined at room temperature and 1000°C for the CN-7 composition. The specimens were tested in the as-cast + annealed condition for two different annealing treatments, 12h at 1500°C and 3d at 1200°C . These annealing conditions were chosen in order that the effects of eutectic structure refinement on the tensile behavior of this alloy could be examined. The 3 day anneal at 1200°C did not lead to any refinement of the networked eutectic whereas the 12 hour anneal at 1500°C led to some breakup of the interconnected brittle eutectic structure. Although these specimens contain casting defects, such as voids and cracks, their occurrence is extremely rare as is shown in Figures 54 and 55 for the CN-7 and CN-4 compositions, respectively. The poor fracture resistance is not as dependent on these isolated instances of defects as it is on the continued presence of the networked Cr_2Nb phase in the eutectic structure of these alloys, as will be shown in the results which follow. Tensile samples were only successfully EDM'ed from the CN-7 material, as the material for the CN-4, 45, and 84 compositions cracked during machining due to the continued presence of the networked Cr_2Nb phase in the eutectic structure which makes these alloys extremely brittle. Several of the samples failed in the fillet region of the sample, thus indicating the presence of some type of internal defects in the material.

In an attempt to remove the detrimental effects of the continued presence of the networked Cr₂Nb phase in the eutectic structure on the fracture resistance of these specimens, samples were prepared by electro-discharge machining from ingot material which had been HIPped + annealed 12h at 1500°C + 2d at 1200°C for the CN-7 composition. However, similar results were obtained in that some of the samples failed in the fillet region and tests performed at 1000°C still did not show any ductility on a macroscopic scale. Because of this result, as well as the lack of the HIPped material, no other compositions or annealing conditions were investigated for it had already been determined that this composition (CN-7) and processing condition yielded the best breakup of the brittle eutectic structure.

The samples tested show a fracture strength level ranging between 128-172 MPa at room temperature, which seems to be fairly independent of the annealed condition of the alloy. Due to the nature of these results, only the highest strength level was reported for each anneal condition tested, as shown in Table 7. The fracture strength levels at 1000°C in air for the CN-7 alloy range between 244-325 MPa. The lack of significant difference in the fracture strength at room temperature and 1000°C suggests that the failure mode is dominated by the continued presence of some networking of the Cr₂Nb phase in the eutectic structure. This continued presence of the networked Cr₂Nb phase can be clearly seen in Figures 56 and 57 for the CN-7 alloy, despite the secondary processing via HIPping and high-temperature anneals which have been shown

to refine the brittle, interconnected Cr₂Nb network in the eutectic. It should be noted that although these processing and high-temperature annealing conditions, such as HIPping + annealing at high temperatures, have been shown to substantially refine the networked eutectic structure, the breakup is not homogeneous and, in addition, slow cooling from the HIPping temperature

Table 7. Tensile Properties of CN-7 alloys under Different Annealed Conditions

Test Condition	Heat Treatment	Fracture Strength, MPa
Room Temperature in Air:		
	3d/1200°C	166*
	12h/1500°C	172*
	HIP + 12h/1500°C + 2d/1200°C	128*
1000°C in Air:		
	3d/1200°C	325
	12h/1500°C	279
	HIP + 12h/1500°C + 2d/1200°C	244

* samples failed in the fillet region outside the gage

leads to some recrystallization and growth of the Cr₂Nb phase along the Cr-rich grain boundaries, as seen in Figure 27 for the CN-7 alloy in the as-HIPped condition. As a result, the networked Cr₂Nb phase that is still present even after HIPping and annealing continues to play a detrimental role in the fracture resistance of these alloys. These results are in contrast with the values of compressive yield strength and ductility which were seen in Tables 4 and 6 where the refinement of the brittle, interconnected Cr₂Nb phase significantly improved the compressive ductility of the CN-7 alloy at room temperature without greatly sacrificing the strength. Thus, we see that the remaining interconnected Cr₂Nb phase in these alloys seems to degrade the tensile

properties more significantly when compared with the compressive properties. This result is illustrated in the schematic given in Figure 58. In this schematic illustration it is seen that the cracking which originates in the brittle, interconnected Cr_2Nb phase is not as detrimental to the strength and ductility in compression as it is in tension. In the tension tests, cracking that originates in the brittle Cr_2Nb phase acts as an effective notch, thus causing a stress concentration which leads to catastrophic failure of the material with poor strength and no ductility, as was seen in Table 7.

Fracture surfaces of the tensile specimens tested at room temperature and 1000°C were examined via a scanning electron microscope operated at 15 kV. The CN alloys show predominately cleavage fracture at both room temperature and 1000°C . The fracture surface of the CN-7 alloy annealed for 12h at 1500°C in vacuum and tested at room temperature in air is presented in Figure 59. The fracture surface is predominated by areas showing transgranular cleavage with some areas that show what appears as grain-boundary de-cohesion due to cracking and/or interfacial sliding between phases, as shown in Figures 60 and 61. Other fractographs for this annealed condition are shown in Figures 62 and 63. Fractographs for the CN-7 alloy HIPped + annealed 12h at 1500°C + 2d at 1200°C are given in Figures 64 and 65. In Figures 61, 63, and 65, back-scatter electron images revealed that the cleavage occurs predominately in the Cr-rich phase (dark-contrast phase) and that the appearance of grain-boundary de-cohesion or interfacial debonding occurs in the Cr_2Nb intermetallic phase (light-contrast phase), as was also verified by qualitative EDS analyses. The fracture surface of CN-7 annealed for 12h at 1500°C and tested at 1000°C in air

given in Figure 66 does not show any difference when compared with the room temperature fracture surface in Figure 59, other than the presence of some oxide debris on the fracture surface.

A cross-sectional view of a CN-7 alloy annealed for 3d at 1200°C and fractured in tension at room temperature in air is shown in Figure 67. In this figure, it is seen that the interconnected Cr₂Nb phase in the eutectic structure leads to a type of grain boundary de-cohesion and/or interfacial cracking, resulting in a poor fracture toughness of these materials. In Figures 68 and 69, the fracture surface of the CN-7 alloy that was HIPped + annealed 12h at 1500°C + 2d at 1200°C and tested in air at room temperature is shown in cross-section. From results shown previously, it is evident that the HIPping +12h at 1500°C + 2d at 1200°C anneal led to a considerable refinement of the networked structure; however, a very thin network of the brittle eutectic can still be clearly seen in Figures 68 and 69. This same type of grain-boundary embrittlement behavior attributed to the interconnected Cr₂Nb phase can also be clearly seen in Figures 70 and 71 for the CN-7 alloy that was HIPped + annealed 12h at 1500°C + 2d at 1200°C and was tested at 1000°C in air. The presence of what appears to be interfacial debonding and/or sliding between the Cr-rich matrix and the Cr₂Nb phase can be clearly observed in Figure 71.

As discussed previously, it is the continued presence of the networked eutectic that continues to predominate the poor room-temperature fracture resistance, and not the presence of casting defects, though certainly a factor, such as porosity and cracking, which were shown in Figures 54 and 55 to be

widely scattered and rare in appearance. However, many ingots were found to contain a fair number of oxide inclusions after HIPping, which can serve as areas for crack nucleation and growth, thus further degrading the material properties. As shown in Figure 72, subsurface cracks beneath the fracture surface can be clearly seen running along the networked eutectic and the interface between the eutectic and the Cr-rich solid solution. Taken together, all these results would seem to indicate that the continued presence of a networked eutectic structure is still detrimental to the fracture toughness and ductility of these materials, despite secondary processing techniques and high-temperature anneals which have led to a considerable breakup of the networked Cr_2Nb phase in the eutectic structure. Moreover in this investigation, it appears that the compressive properties are not affected as much by the continued presence of some networking of the Cr_2Nb phase in the eutectic structure as compared to the tensile properties. This trend in the data suggests that in tension the networked Cr_2Nb phase is much more effective in providing areas of stress concentration for crack initiation and growth which more readily degrade the material's strength and ductility relative to the tests carried out in compression.

V. CONCLUSIONS

From this investigation, the following conclusions are drawn:

- The alloys form with a Cr-rich solid solution that has a dendritic morphology with the remaining interdendritic liquid decomposing via the eutectic reaction to form Cr + Cr₂Nb. It is the brittle, interconnected intermetallic Cr₂Nb phase in the eutectic which causes poor fracture resistance of these alloys.
- High-temperature anneals (1500 to 1600°C) under vacuum have shown to be successful in refining the coarse, brittle eutectic structure in the CN-7 (94 at.% Cr-6 at.% Nb) and CN-4 (88 at.% Cr-12 at.% Nb) compositions. However, some networking of the eutectic is evident along the Cr-rich grain boundaries and is still believed to be a source of strength and ductility degradation, especially in tension loading.
- The Laves-containing eutectic structure is morphologically unstable after Hot Isostatic Pressing (HIPping) and hot forging, and continues to break up with subsequent high-temperature anneals.
- Solid state precipitation takes place in the Cr-rich phase when annealing at temperatures well below the eutectic temperature (1100°C to 1200°C). Although the Cr₂Nb precipitates in the Cr-rich phase were found to undergo a fair amount of coarsening, a four-fold increase in the average precipitate size from 3 hours at 1200°C to 30 days at 1200°C, their average size remains less than 1 µm after annealing for 30 days at 1200°C and is not believed to have a significant effect on mechanical properties of these alloys.

- The compressive yield strength and ductility were found to be sensitive to the morphology of the eutectic structure and not as dependent upon casting defects, such as microcracking and/or porosity, which were shown to be rare in occurrence. High-temperature anneals combined with secondary processing techniques led to a more than double increase in some instances of room-temperature compressive ductility with strength levels still much greater than Ni-base superalloys, even at test temperatures of up to 1000°C.
- Tensile tests performed on the CN-7 alloy revealed that the tensile properties of this material are still sensitive to the interconnected Cr₂Nb phase in the eutectic structure, even after secondary processing techniques and high-temperature anneals to refine this brittle network. Fracture strengths were found to be dependent on the interconnectivity of the Cr₂Nb phase for all tests performed and not on casting defects, which were shown to be rare in appearance. The fracture mode in all cases was transgranular cleavage in the Cr-rich phase with some evidence of what appeared as interfacial debonding and cracking in the Cr₂Nb intermetallic phase.
- The remaining interconnected Cr₂Nb phase in the eutectic structure seems to act as a site for crack initiation and propagation. This result is especially seen in the degradation of the tensile properties whereby the cracking which originates in the brittle Cr₂Nb phase acts as an effective notch, thus causing rapid crack growth, poor strength, and no ductility as the samples failed catastrophically in all cases in tension. These results are in contrast to the properties obtained in compression where the ductility could be enhanced by even a small level of refinement of the brittle, interconnected Cr₂Nb phase.

VI. FUTURE WORK

Despite the improvements seen as a result of annealing at high temperatures (1500-1600°C) and secondary processing techniques, there still exists a thin network of the brittle Cr₂Nb phase in the eutectic structure along the Cr-rich grain boundaries that is detrimental to the mechanical properties of this material, especially for the tensile properties. Continued work in this system should be undertaken to further explore other methods of microstructural refinement and ductility enhancement, such as hot forging and hot extrusion. In addition, the wide range of compositional homogeneity that these alloys possess would suggest that their properties could be enhanced through alloying additions. Work is already underway by Liu and co-workers to eliminate casting defects in the material and refine the networked eutectic by using elemental powders to produce an ingot via hot extrusion of the pressed powders. Preliminary results have shown that this method is successful in producing material which does not contain a detrimental concentration of defects, such as oxide inclusions, microcracks, and porosity.

It is hoped that a theoretical model, such as finite-element modeling of compression and/or tension tests, will one day be developed which will correlate the effects of changes in the microstructure via thermo-mechanical treatments with the mechanical behavior of these two-phase alloys based on Cr₂Nb. The fatigue behavior of these materials has been studied in only limited detail. Future work on this system should include a detailed study of the fatigue crack propagation behavior of these alloys under different environmental and

microstructural conditions, which is beyond the scope of the present investigation. In summary, it is hoped that these studies will continue to shed some light on the mechanistic understanding of the effects of microstructural control via thermo-mechanical treatment and secondary processing on the fracture and fatigue behavior of these alloys.

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REFERENCES

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APPENDIX

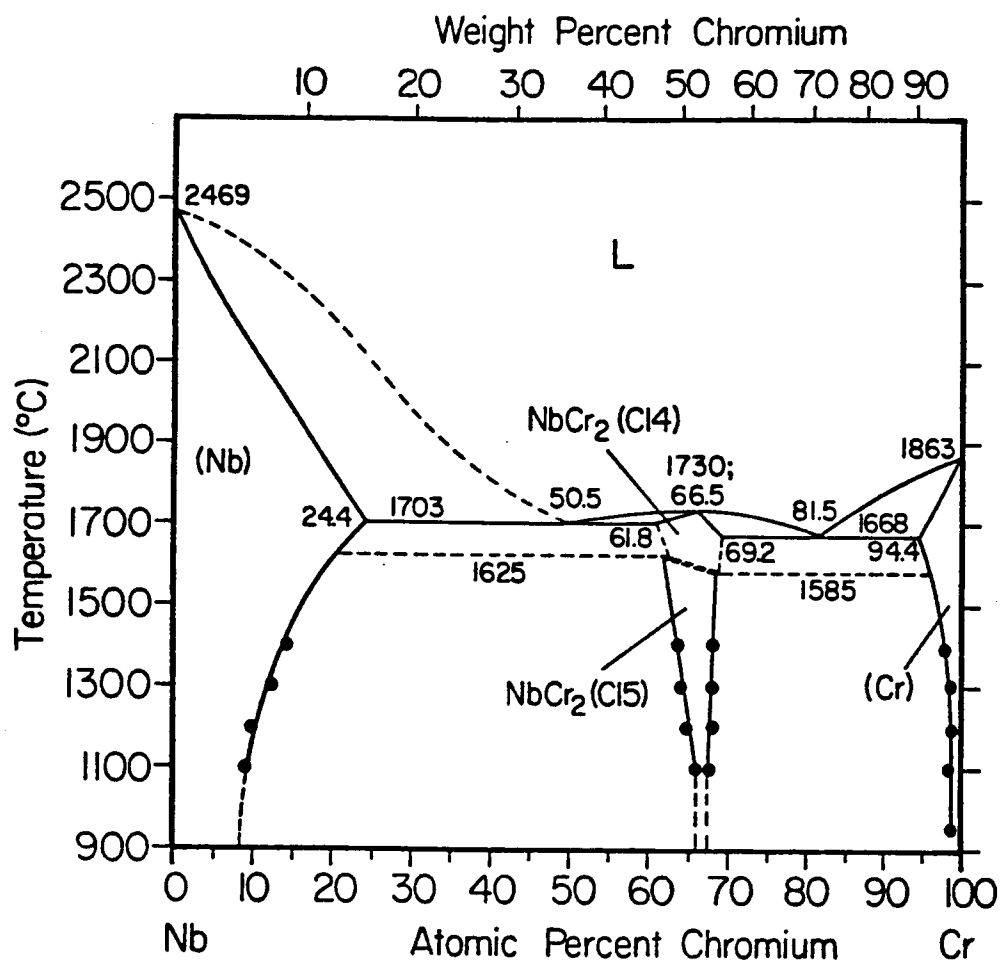
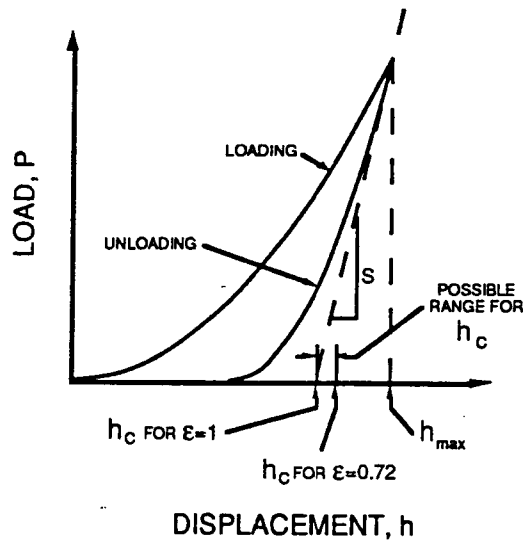
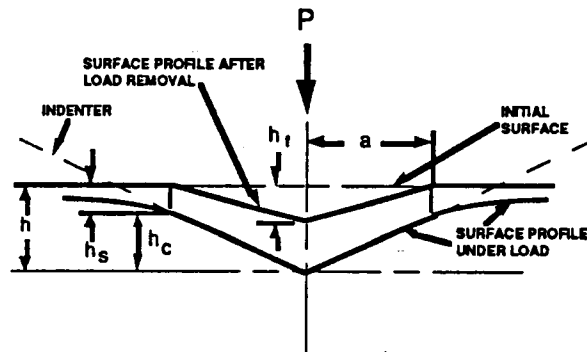


Figure 1. The Chromium-Niobium Binary Phase Diagram adapted from Thoma and Perepesko [19].



(a). Schematic representation of load vs. displacement data [34].



(b). Schematic cross-section of indentation under load [34].

Figure 2. Schematic illustrations showing important variables used in Nanoindentation

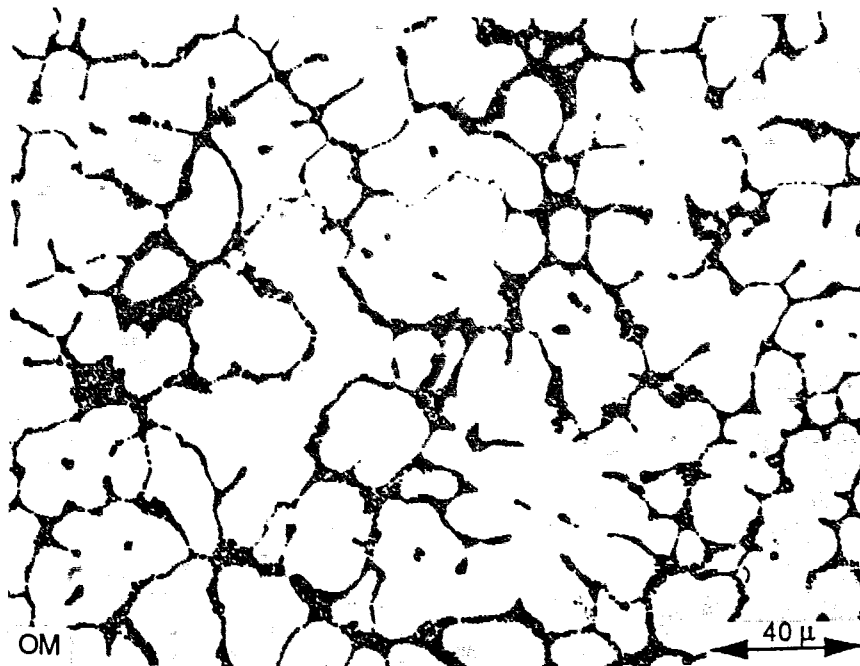


Figure 3. Optical micrograph of the as-cast microstructure of CN-7 (Cr-6 at.% Nb). The bright-contrast phase is the Cr-rich phase, and the dark-contrast phase is the Cr_2Nb Laves phase.

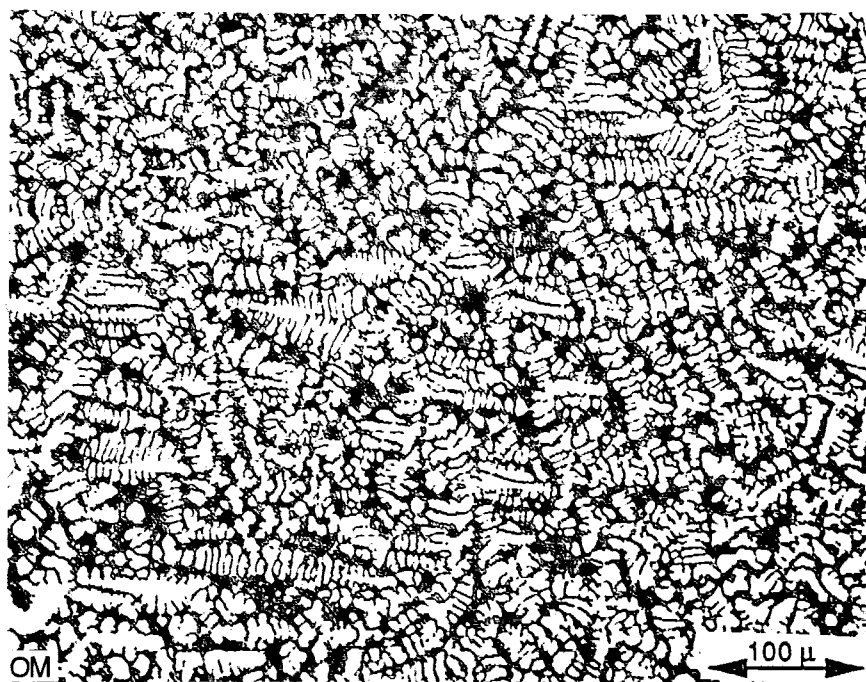


Figure 4. Optical micrograph of the as-cast microstructure of CN-4 (Cr-12 at.% Nb) showing the dendritic morphology of the Cr-rich phase. The remaining interdendritic liquid decomposes via the eutectic reaction to form $\text{Cr} + \text{Cr}_2\text{Nb}$.

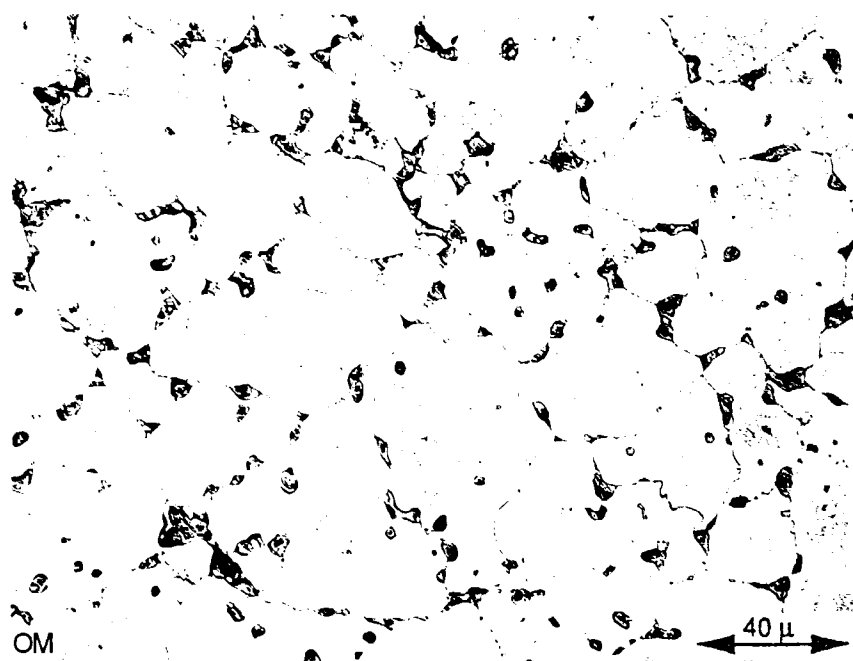


Figure 5. CN-7 : annealed 1h at 1600°C + 4h at 1200°C in vacuum showing a considerable refinement of the brittle eutectic structure.

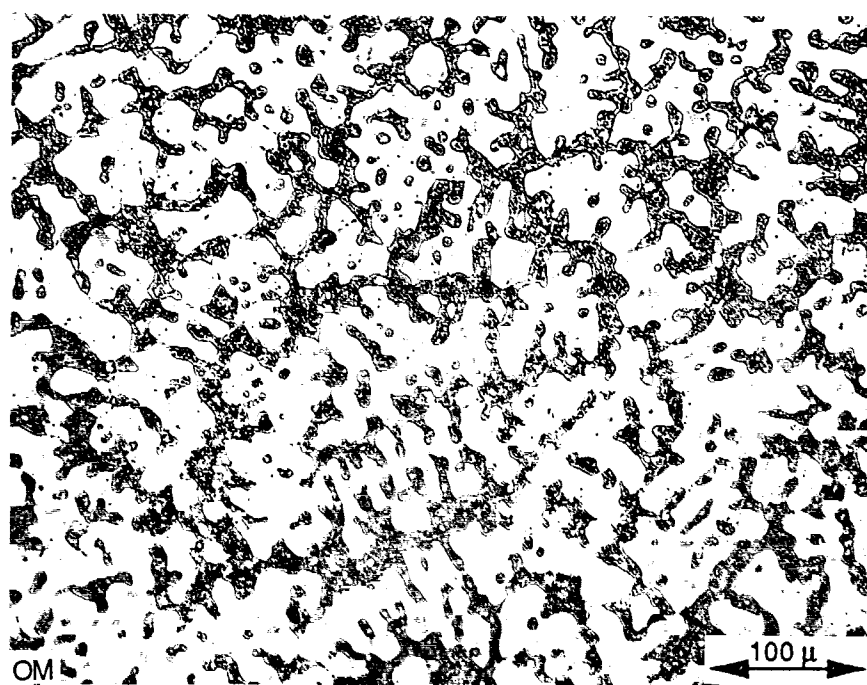


Figure 6. CN-4 : annealed 1h at 1600°C + 4h at 1200°C in vacuum.

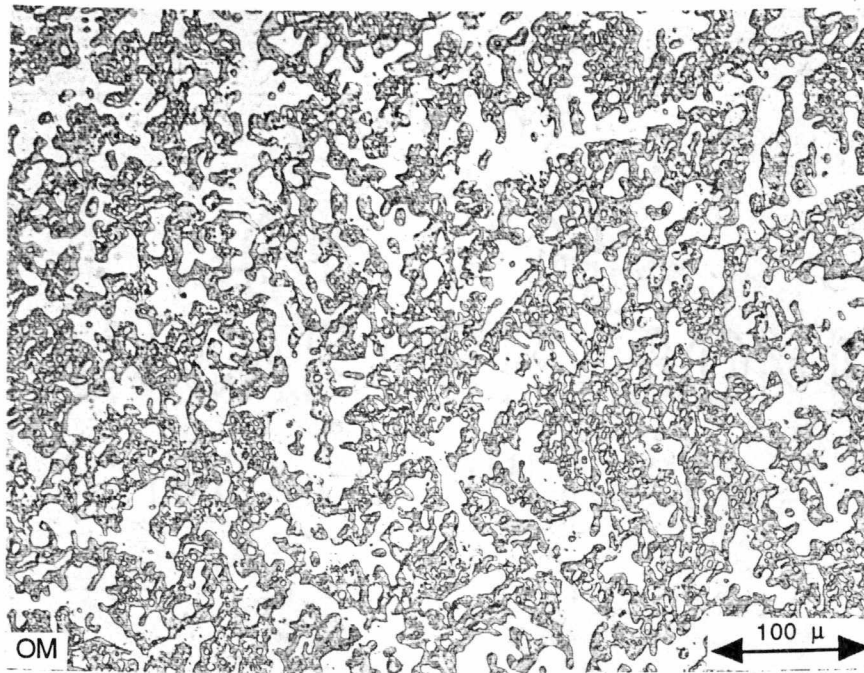


Figure 7. CN-45 : annealed 1h at 1600°C + 4h at 1200°C in vacuum.

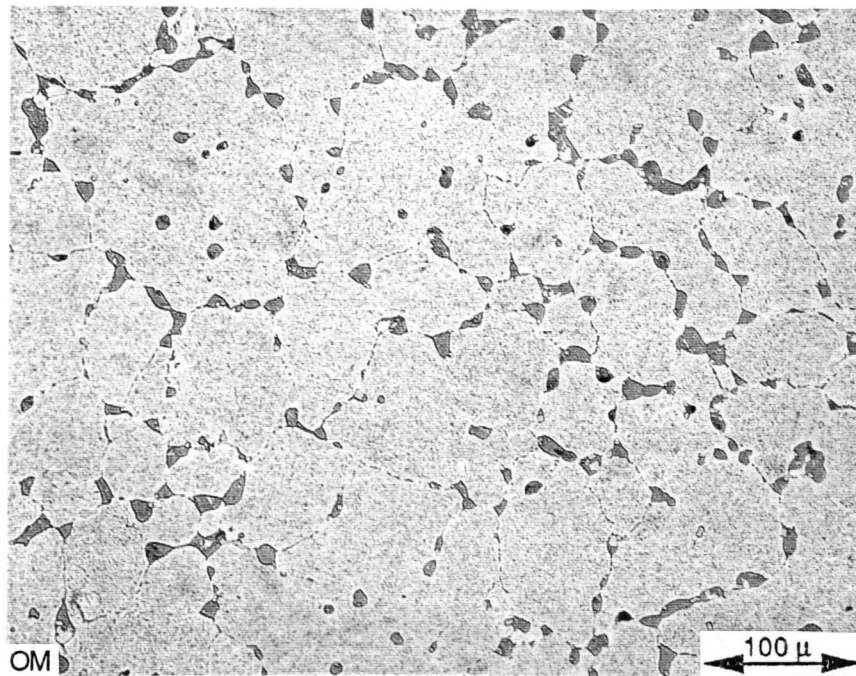


Figure 8. CN-7 : annealed 2d at 1580°C + 2d at 1200°C in vacuum showing a substantial refinement of the eutectic (dark-contrast phase).

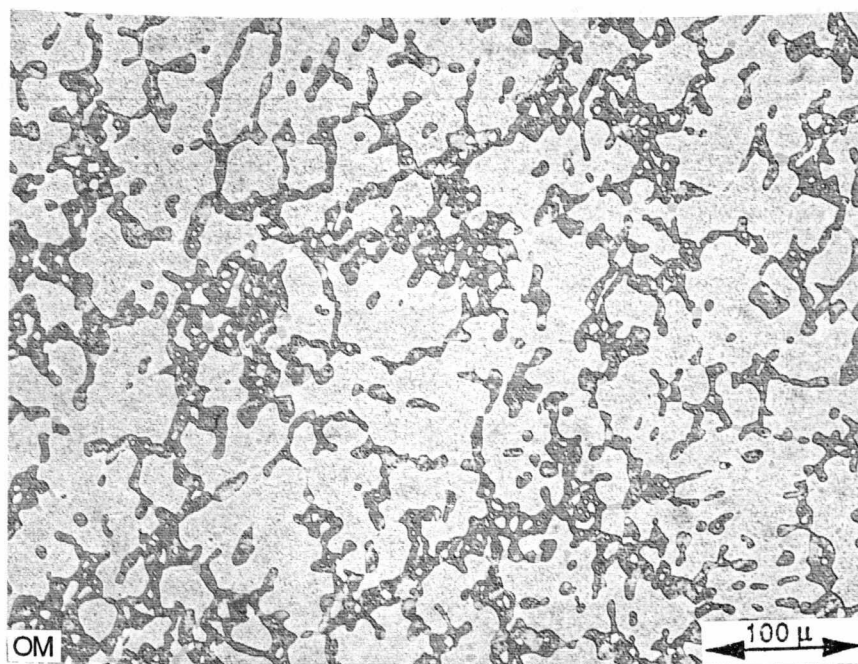


Figure 9. CN-4 : annealed 2d at 1580°C + 2d at 1200°C in vacuum.

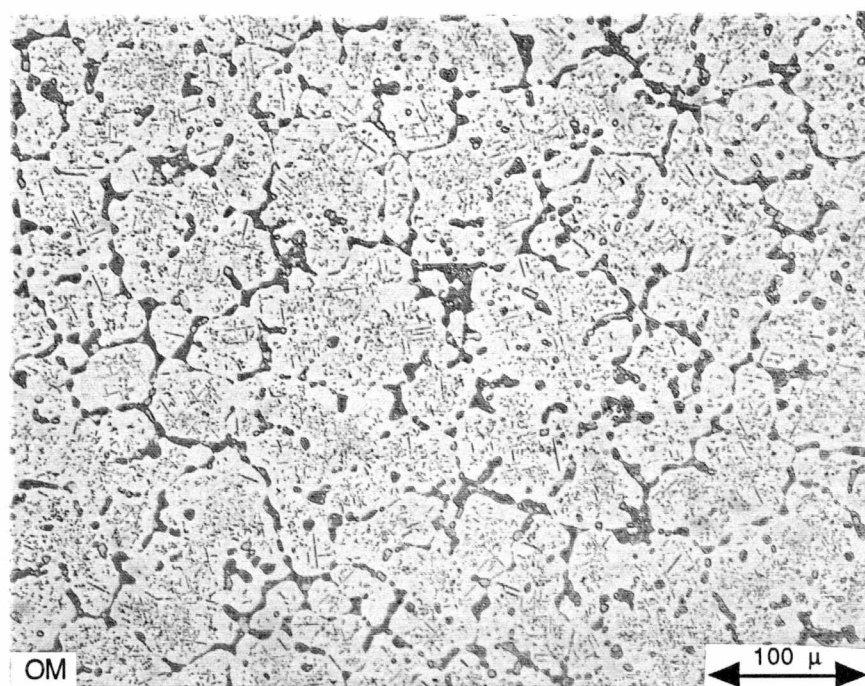


Figure 10. CN-7 : annealed 4h at 1550°C + 2d at 1200°C in vacuum.

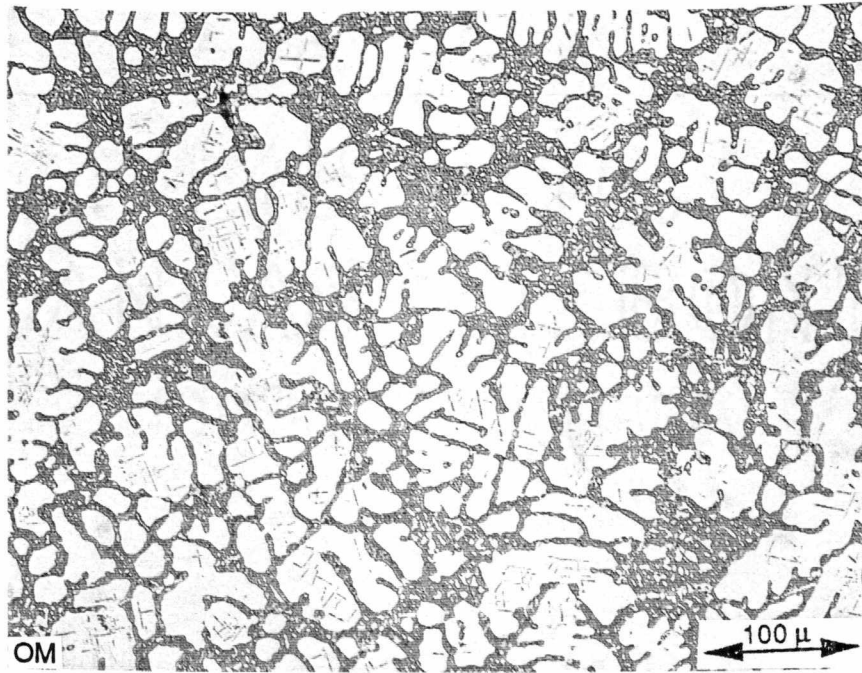


Figure 11. CN-4 : annealed 4h at 1550°C + 2d at 1200°C in vacuum.

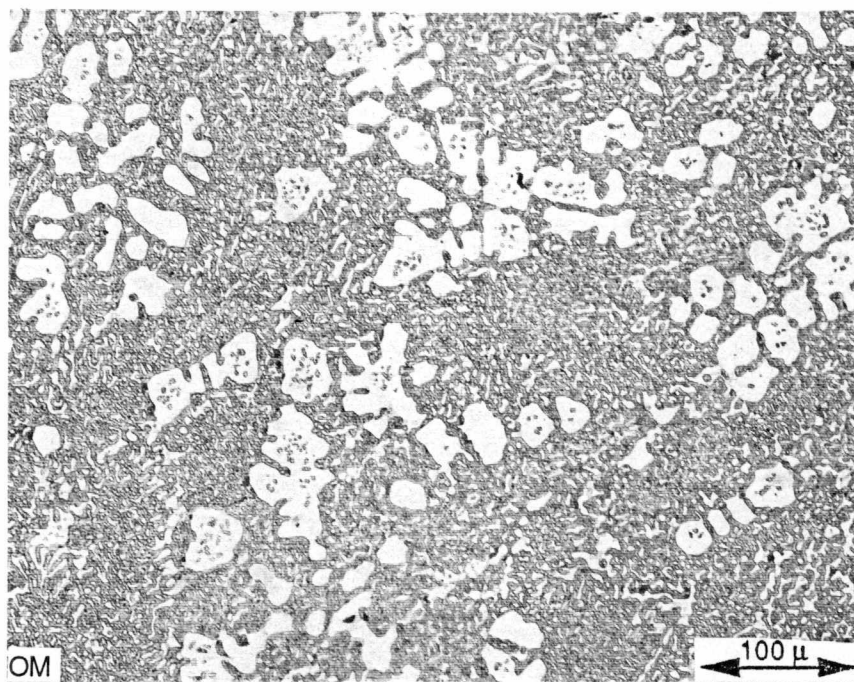


Figure 12. CN-45 : annealed 4h at 1550°C + 2d at 1200°C in vacuum.

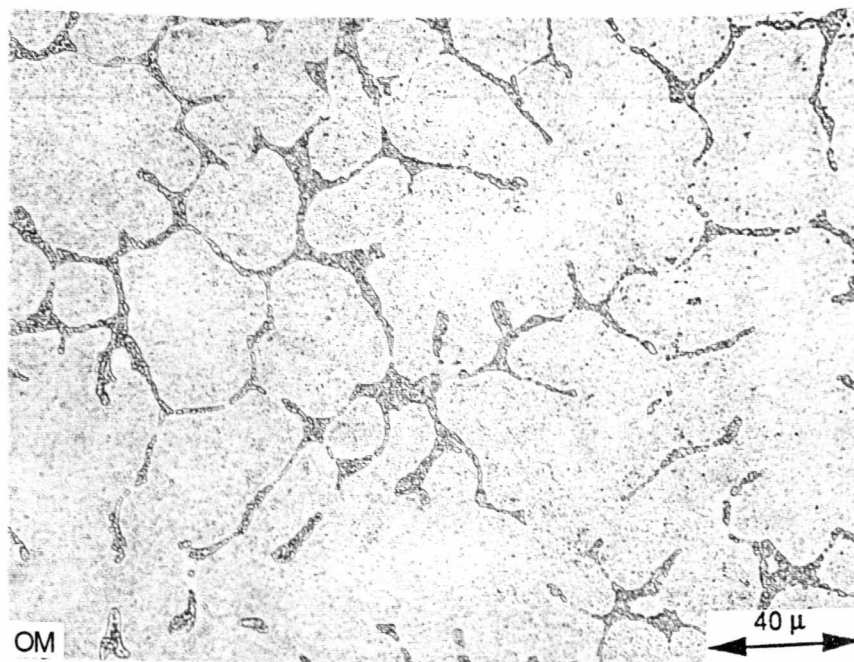


Figure 13. CN-7 : annealed 3h at 1200°C in vacuum.

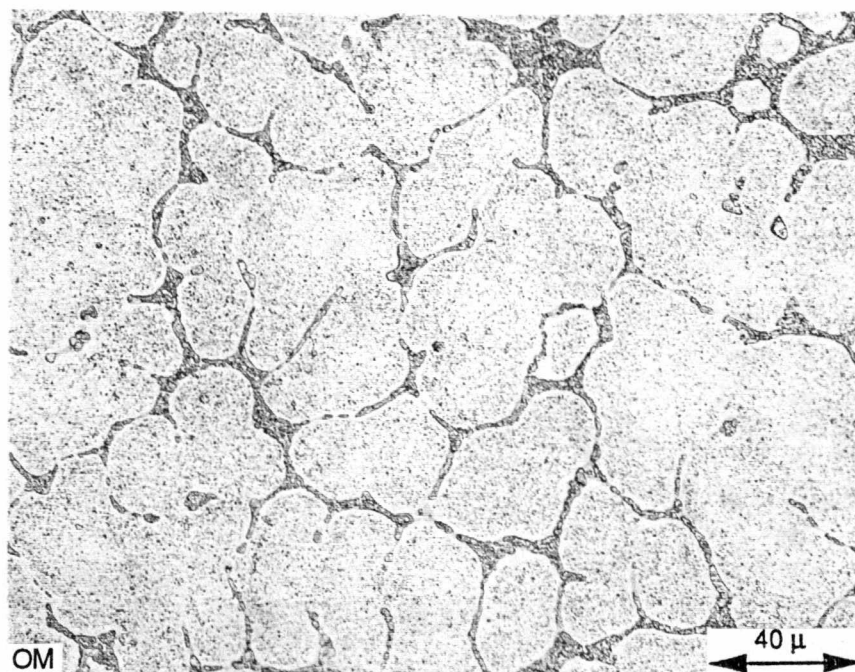


Figure 14. CN-7 : annealed 6h at 1200°C in vacuum.

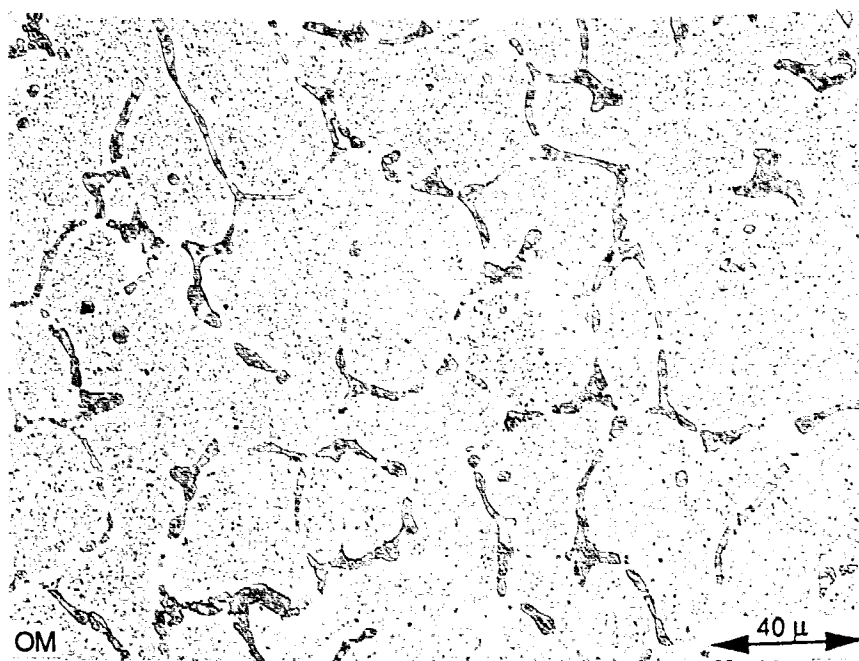


Figure 15. CN-7 : annealed 1d at 1200°C in vacuum.

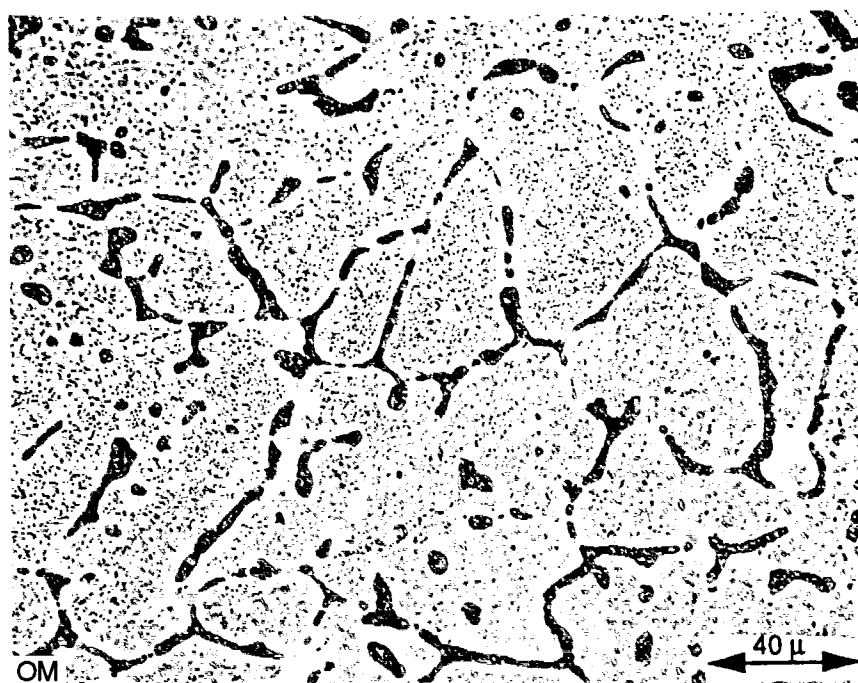


Figure 16. CN-7 : annealed 3d at 1200°C in vacuum.

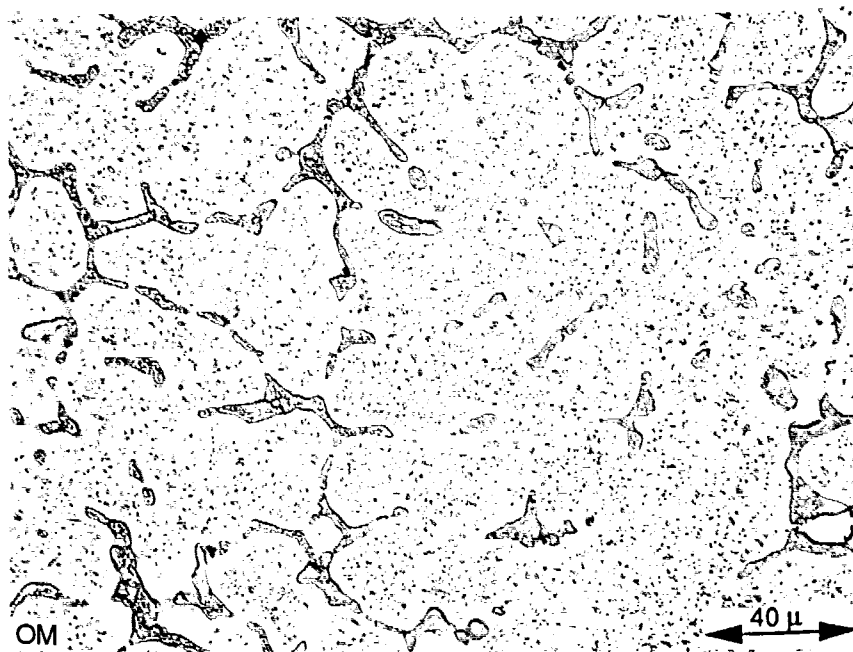


Figure 17. CN-7 : annealed 7d at 1200°C in vacuum.

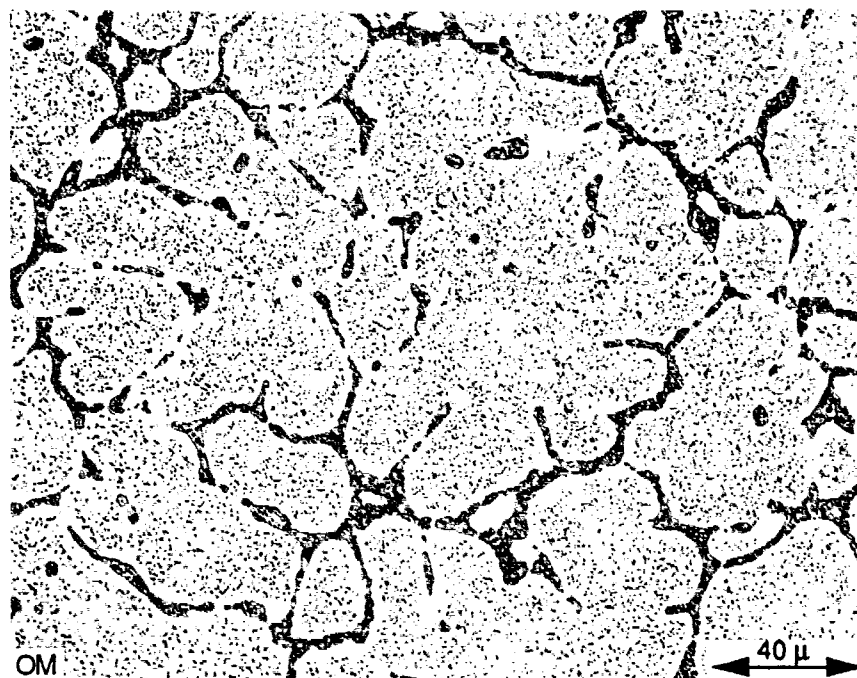


Figure 18. CN-7 : annealed 14d at 1200°C in vacuum.

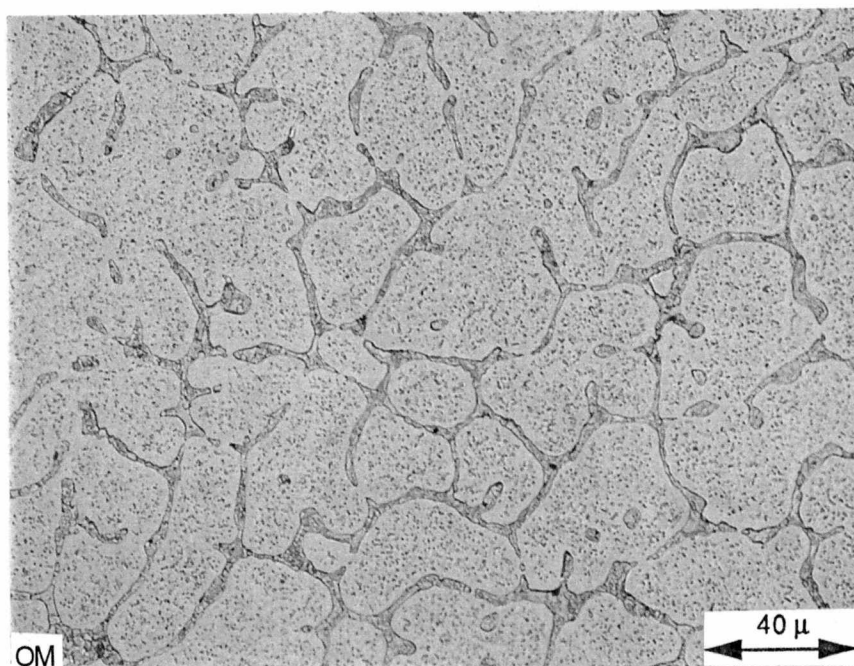


Figure 19. CN-7 : annealed 30d at 1200°C in vacuum.

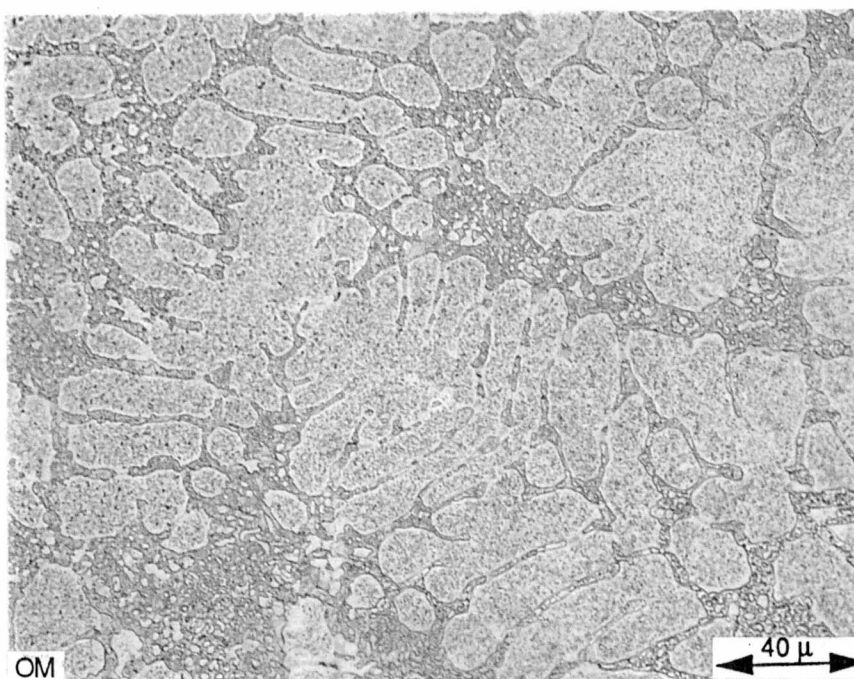


Figure 20. CN-4 : annealed 3h at 1200°C in vacuum.

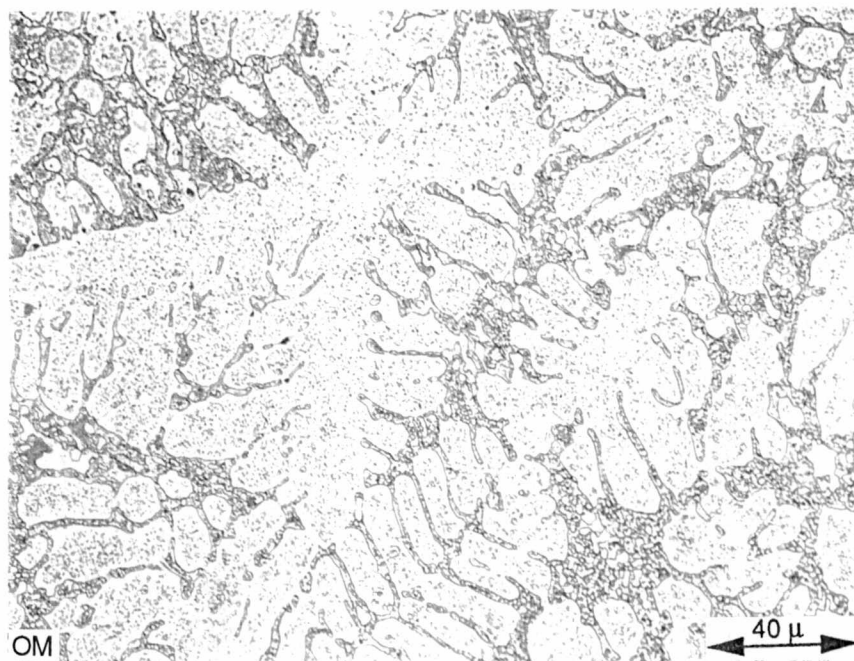


Figure 21. CN-4 : annealed 6h at 1200°C in vacuum.

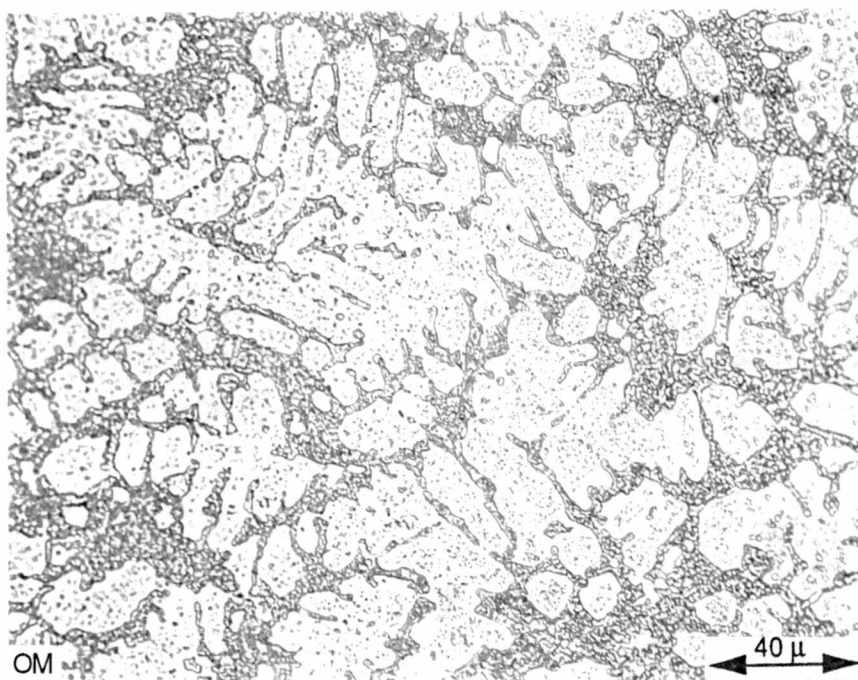


Figure 22. CN-4 : annealed 1d at 1200°C in vacuum.

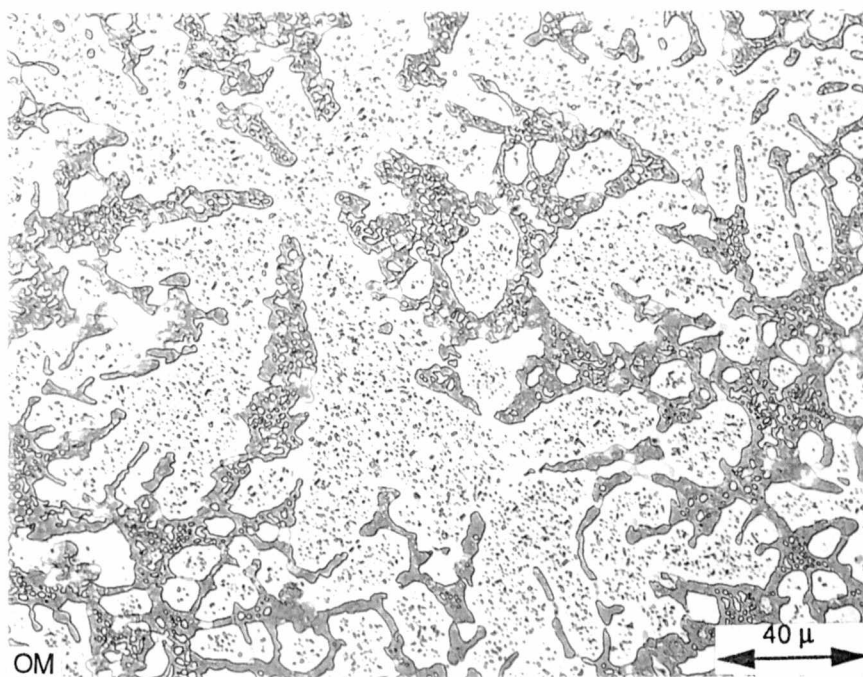


Figure 23. CN-4 : annealed 3d at 1200°C in vacuum.

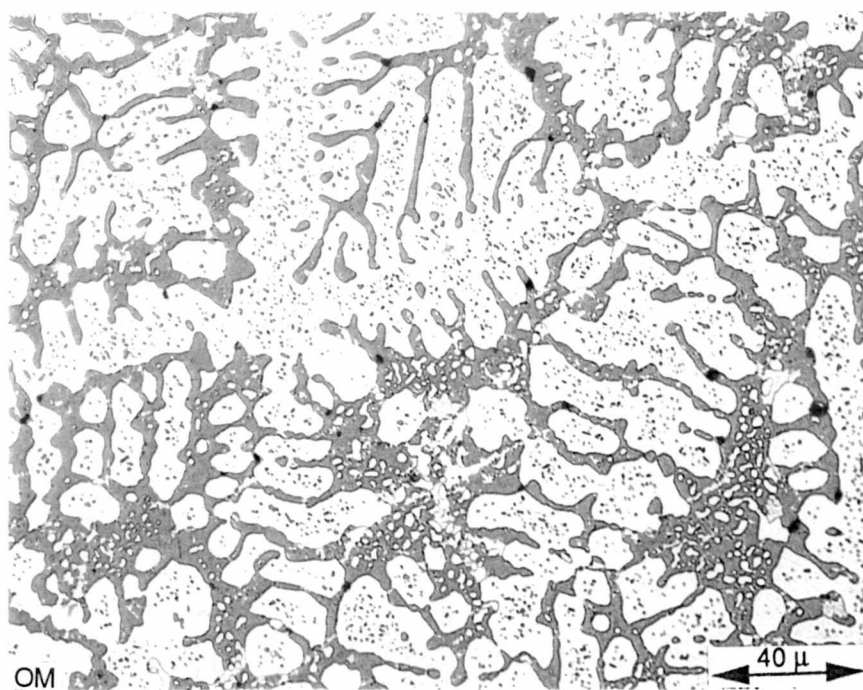


Figure 24. CN-4 : annealed 7d at 1200°C in vacuum.

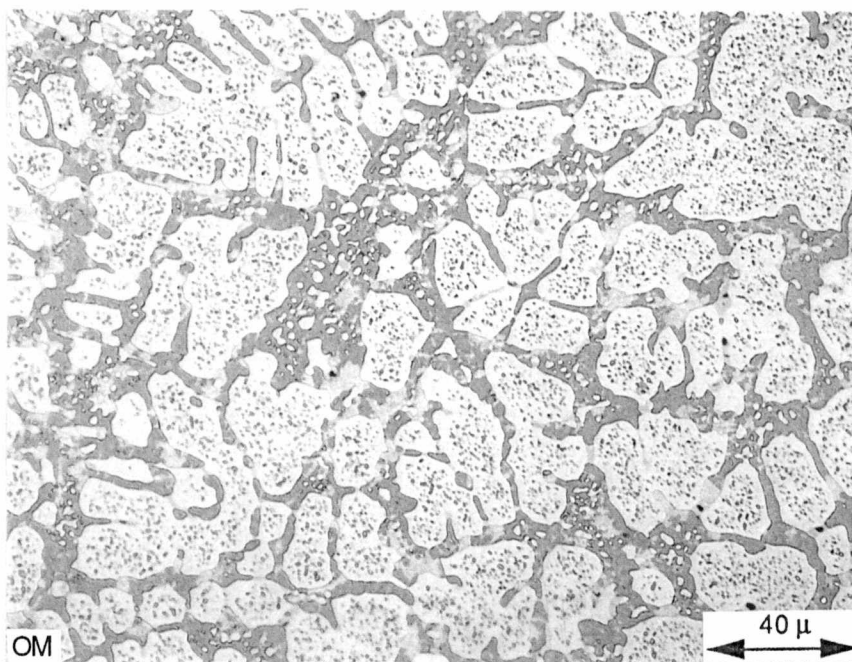


Figure 25. CN-4 : annealed 14d at 1200°C in vacuum.

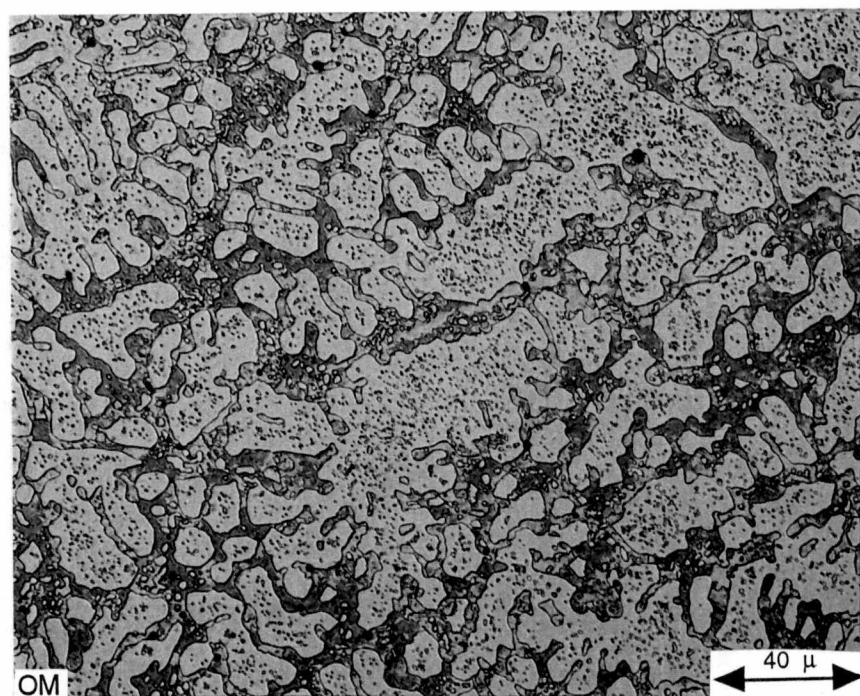


Figure 26. CN-4 : annealed 30d at 1200°C in vacuum.

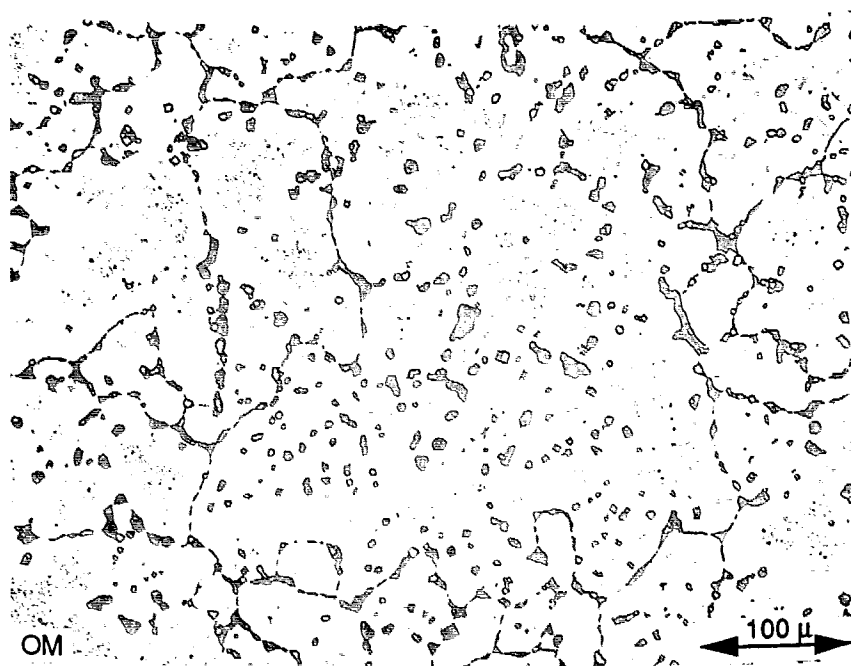


Figure 27. CN-7 : HIPped at 1610°C at 193 MPa.

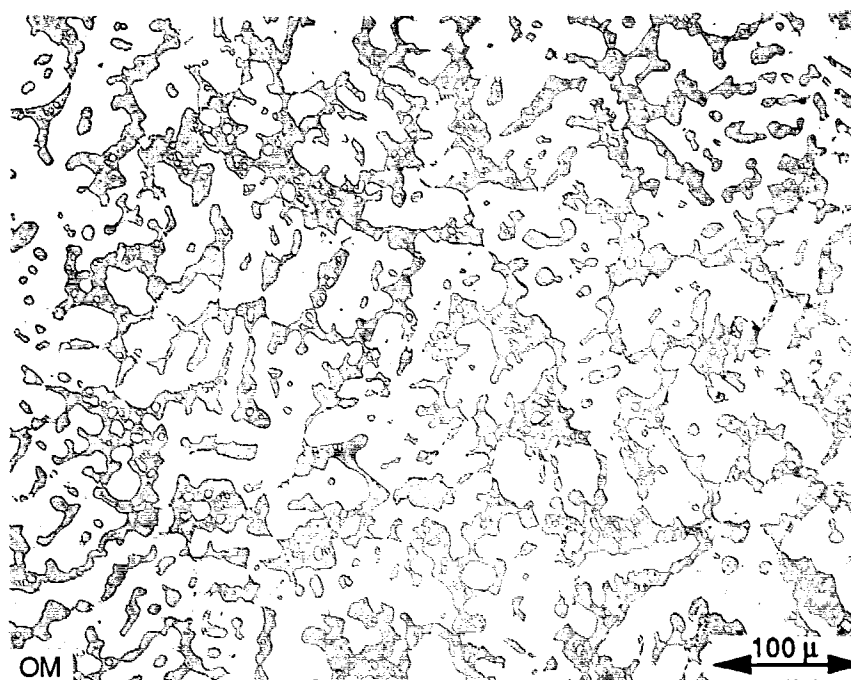


Figure 28. CN-4 : HIPped at 1610°C at 193 MPa.

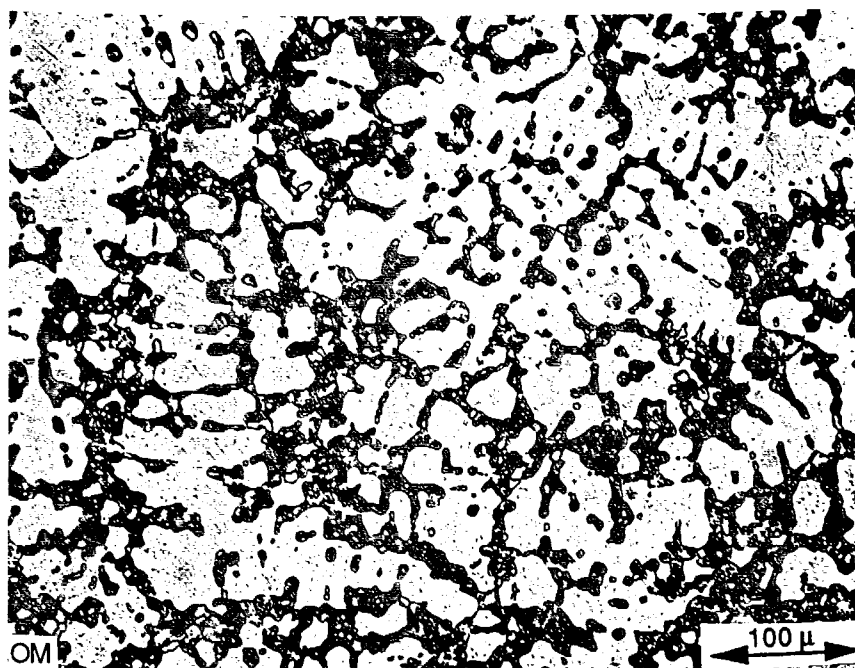


Figure 29. CN-4 : HIPped + annealed 3d at 1200°C in vacuum.

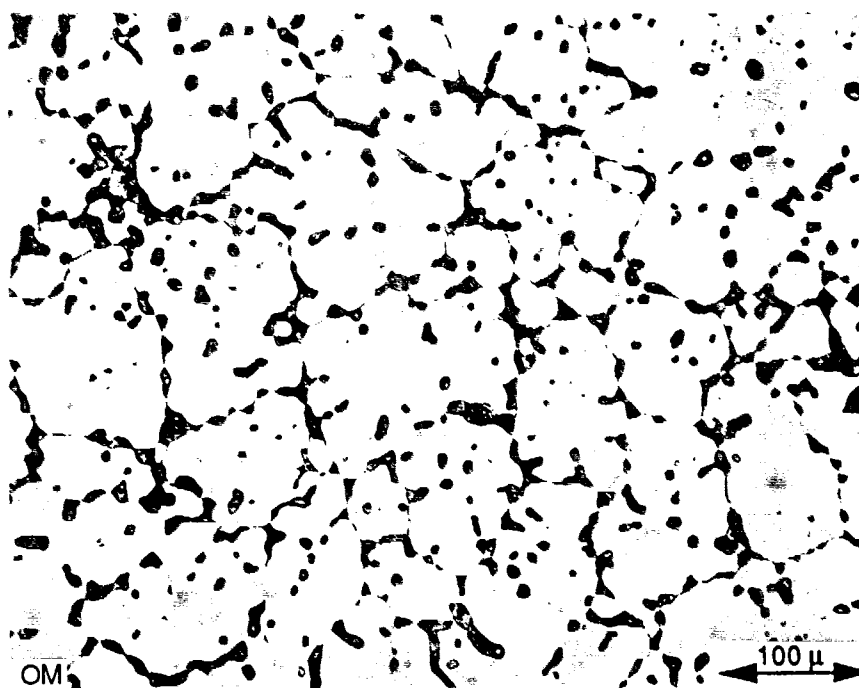


Figure 30. CN-7 : HIPped + annealed 12h at 1500°C in vacuum.

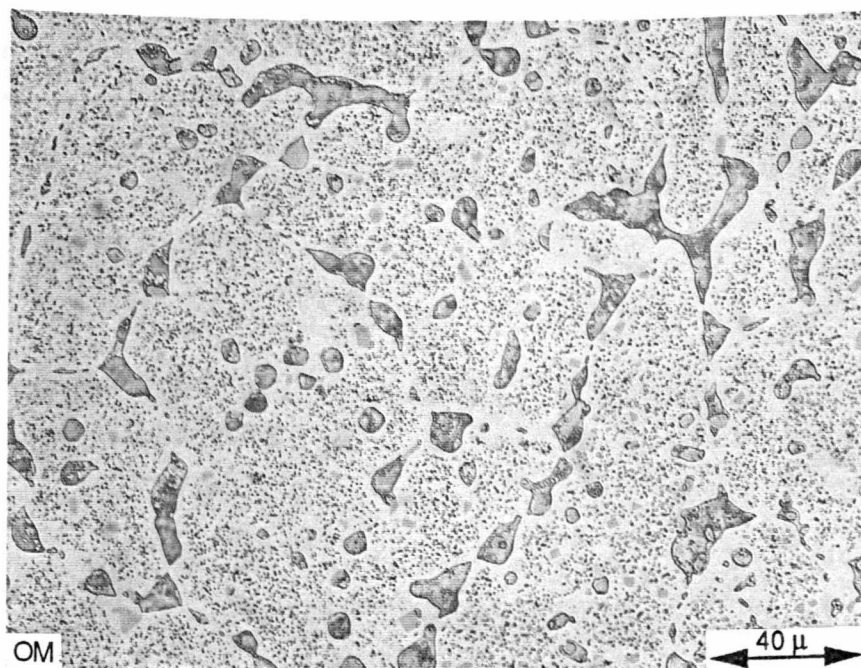


Figure 31. CN-7 : HIPped + annealed 12h at 1500°C + 2d at 1200°C in vacuum.

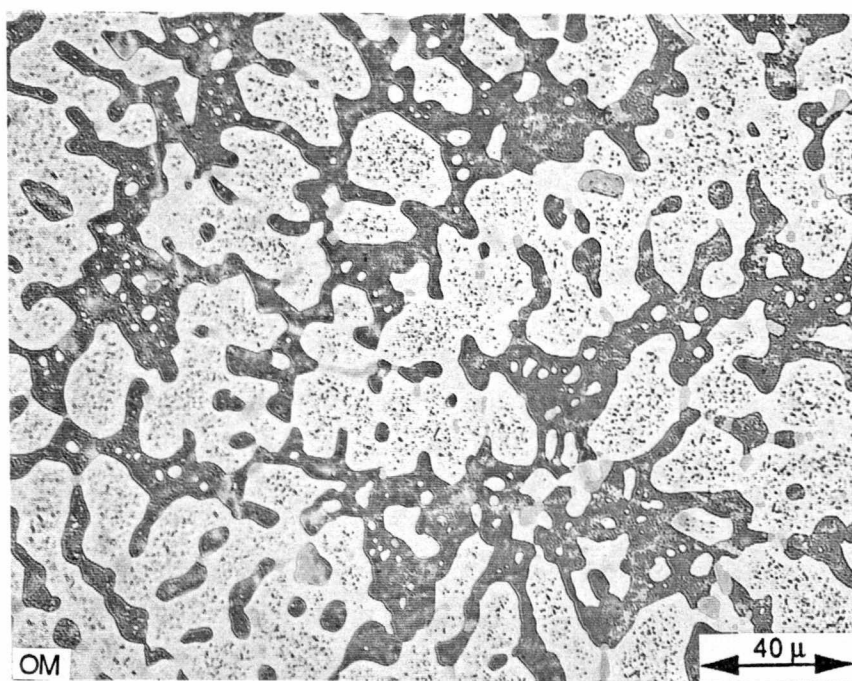


Figure 32. CN-4 : HIPped + annealed 12h at 1500°C + 2d at 1200°C in vacuum.

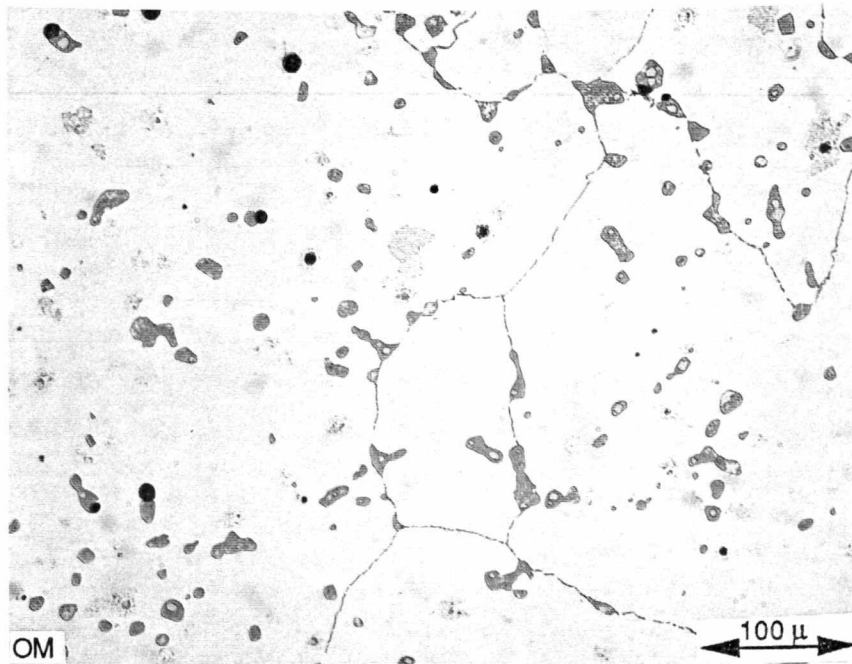


Figure 33. CN-7 : hot forged (HF) at 1200°C to 20% + annealed for 6h at 1500°C in vacuum.

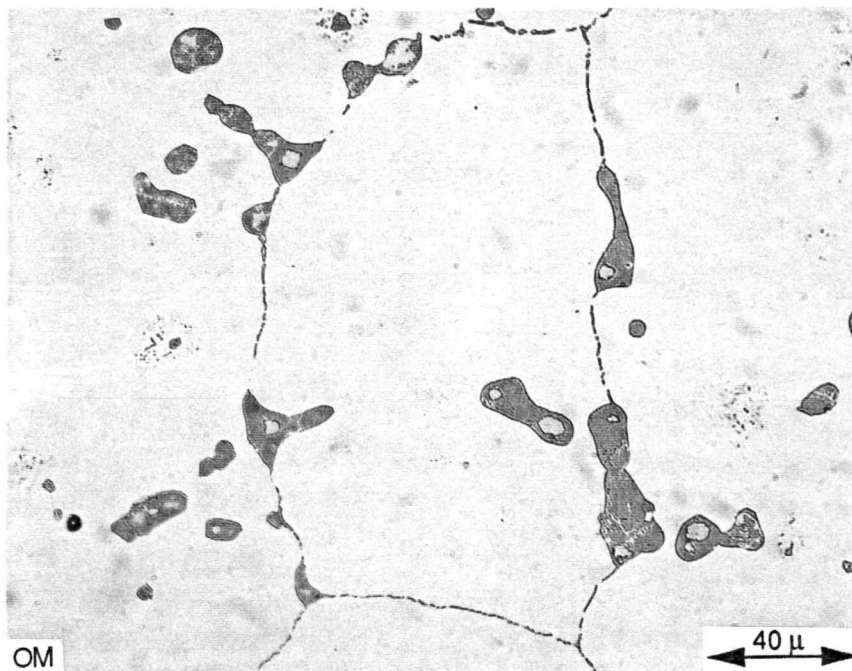
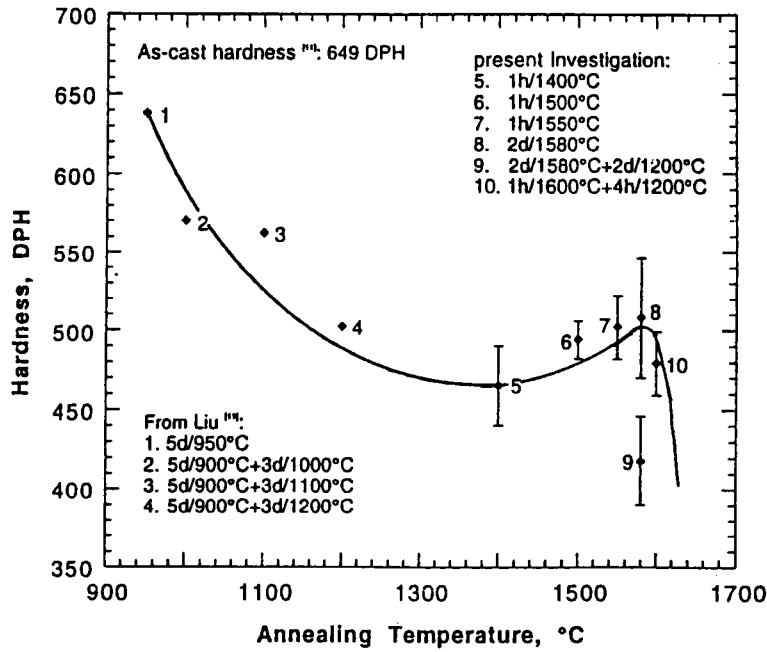
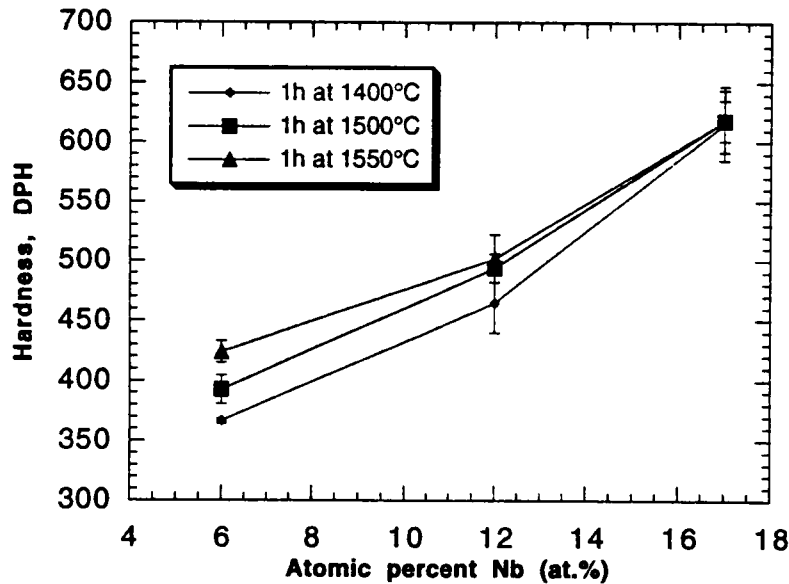


Figure 34. Higher magnification area of Figure 33.



(a). Hardness profile for CN-4 under various anneals.



(b). A plot of the change in hardness associated with the atomic percent of niobium present in the material.

Figure 35. Variations in material hardness associated with annealing conditions and alloy composition.

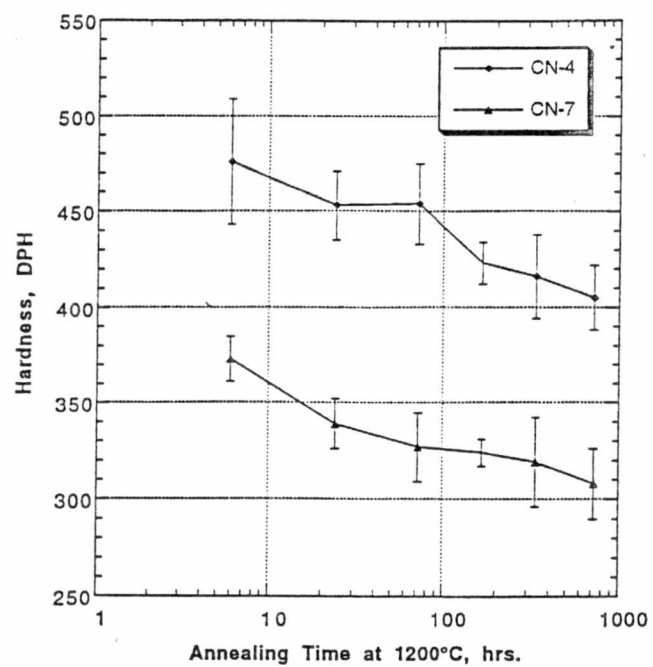


Figure 36. A plot of hardness vs. annealing time at 1200°C.

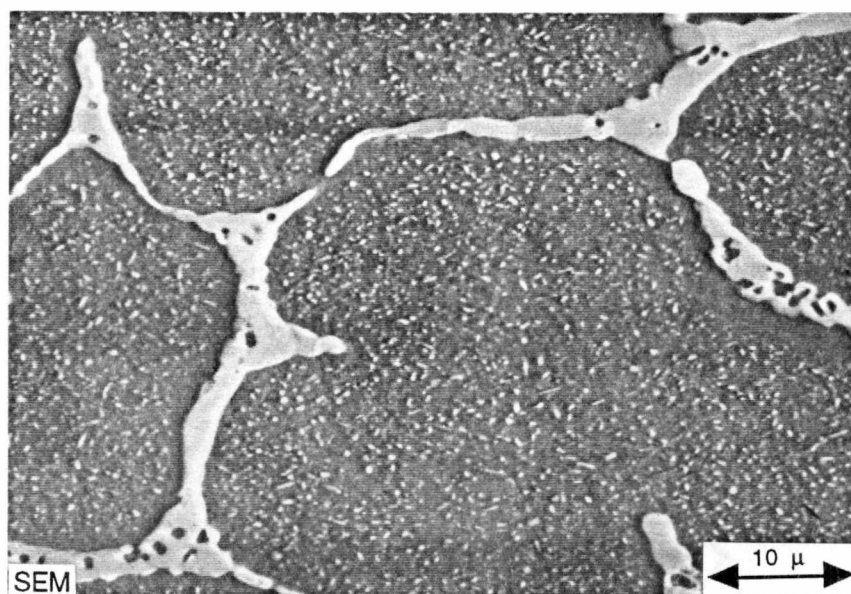


Figure 37. High-magnification back-scatter electron (BSE) image of CN-7 annealed 3h at 1200°C in vacuum.

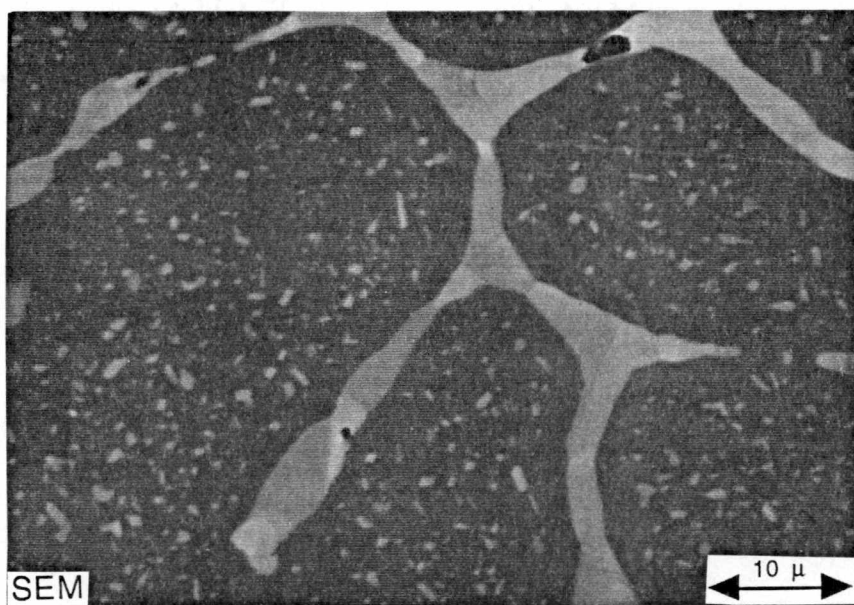


Figure 38. High-magnification BSE image of CN-7 annealed 30d at 1200°C in vacuum.

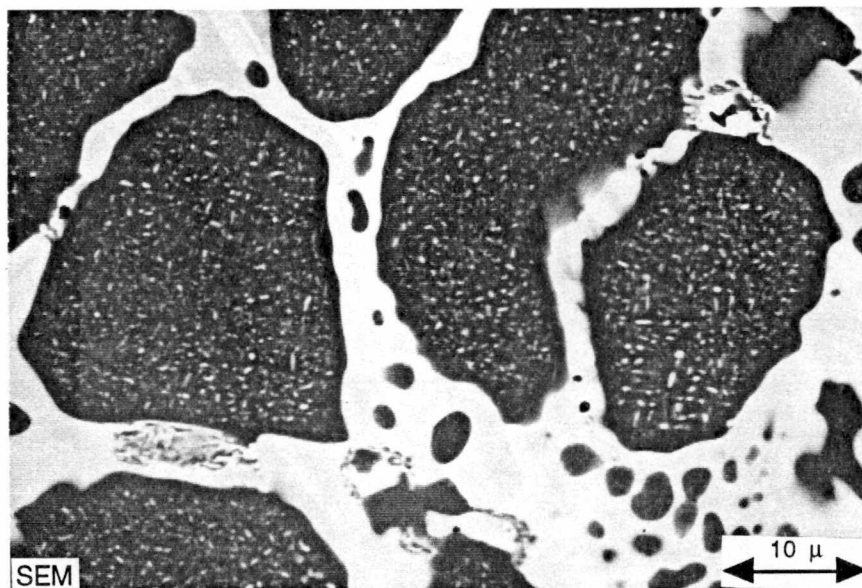


Figure 39. High-magnification BSE image of CN-4 annealed 3h at 1200°C in vacuum.

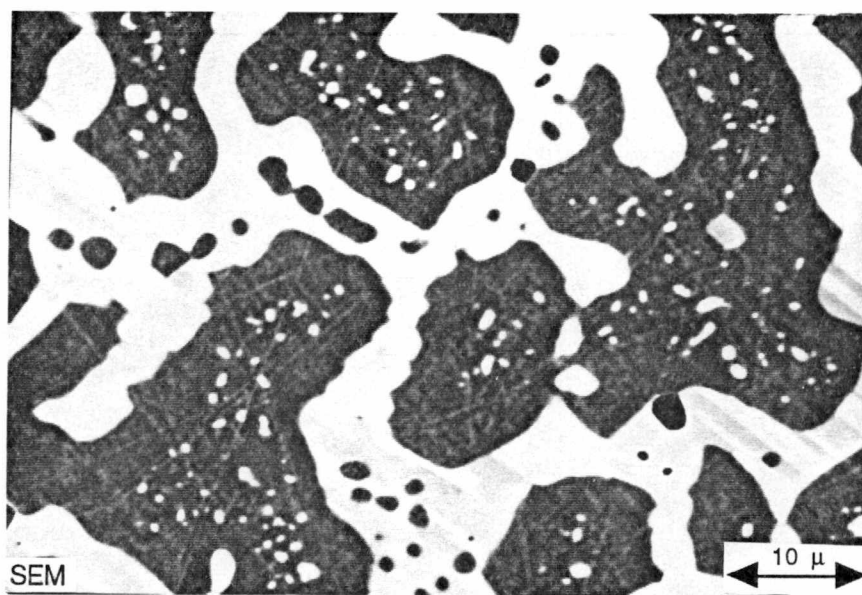


Figure 40. High-magnification BSE image of CN-4 annealed 30d at 1200°C in vacuum.

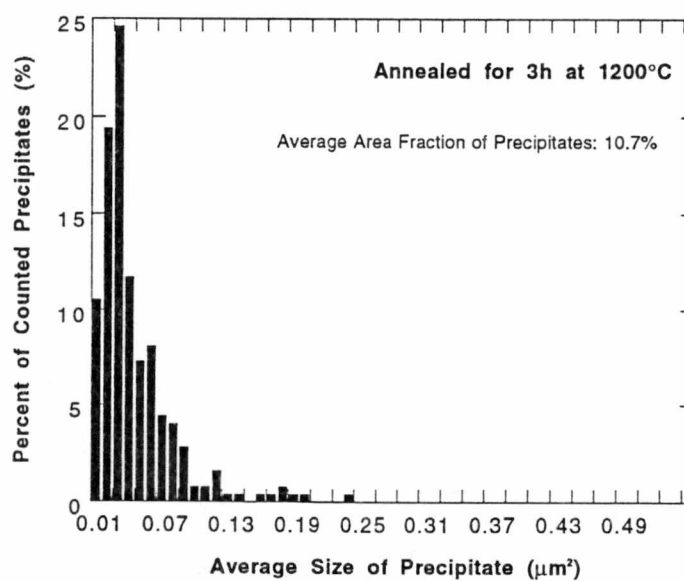


Figure 41. Plot of particle size distribution for CN-7 annealed 3h at 1200°C in vacuum.

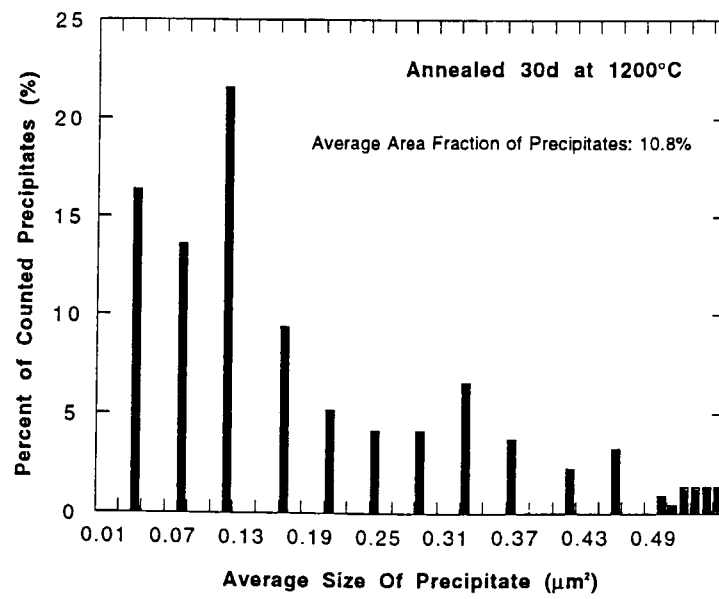


Figure 42. Plot of particle size distribution for CN-7 annealed 30d at 1200°C in vacuum.

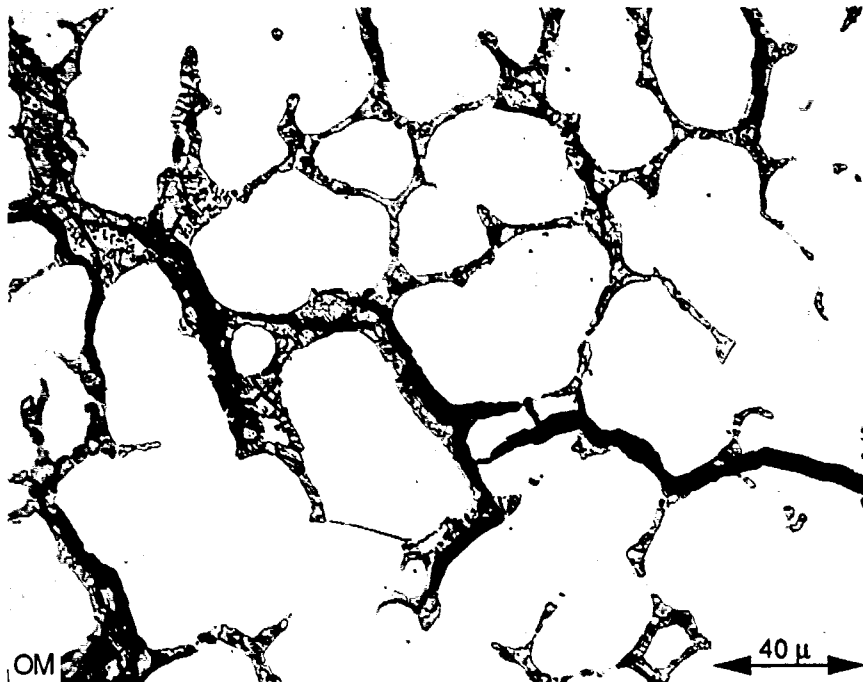


Figure 43. As-cast CN-7 tested in compression at room temperature in air.

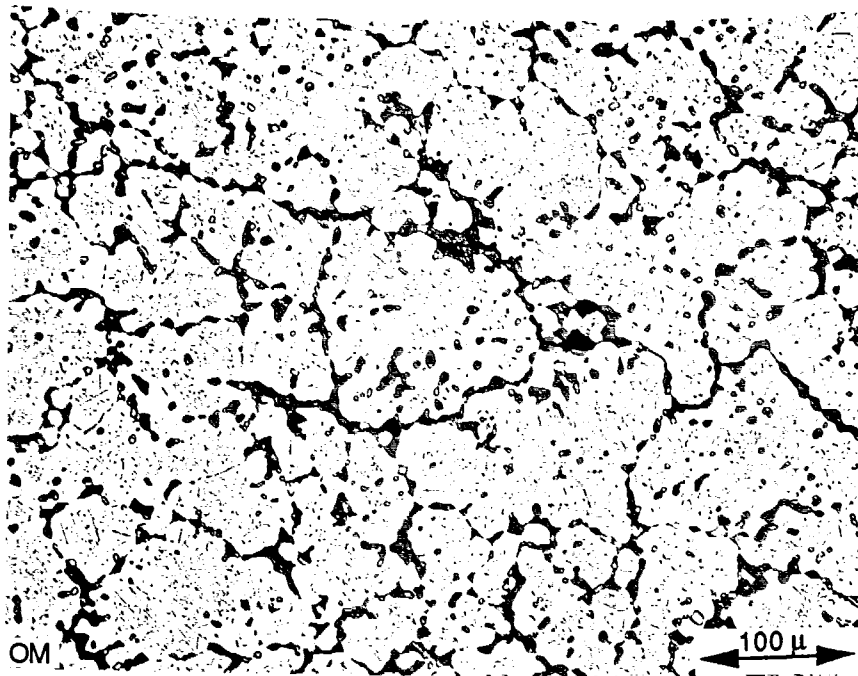


Figure 44. CN-7 annealed 4h at 1550°C + 2d at 1200°C in vacuum tested in compression at room temperature.

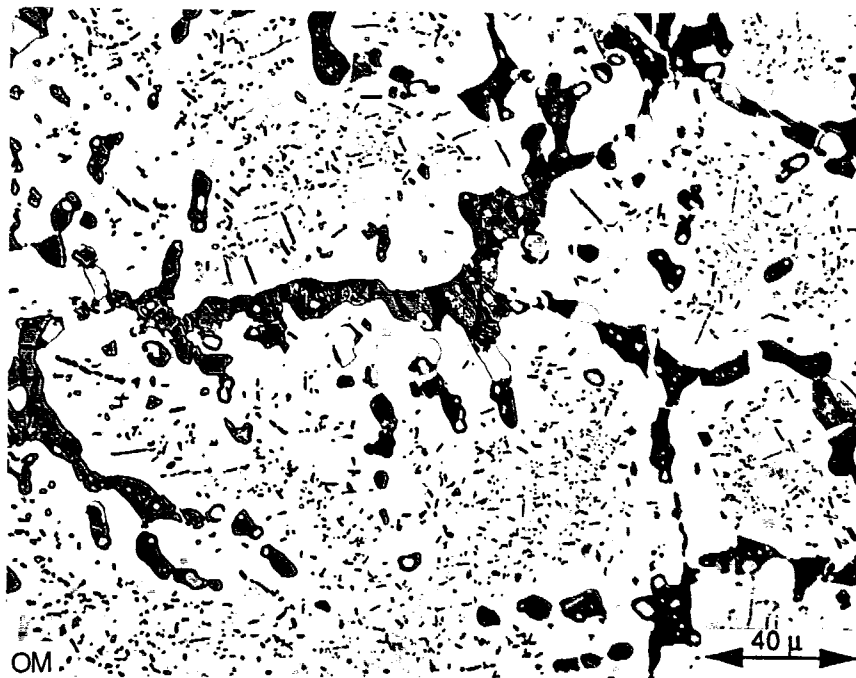


Figure 45. CN-7 annealed 4h at 1550°C + 2d at 1200°C in vacuum tested in compression at 1000°C in vacuum.

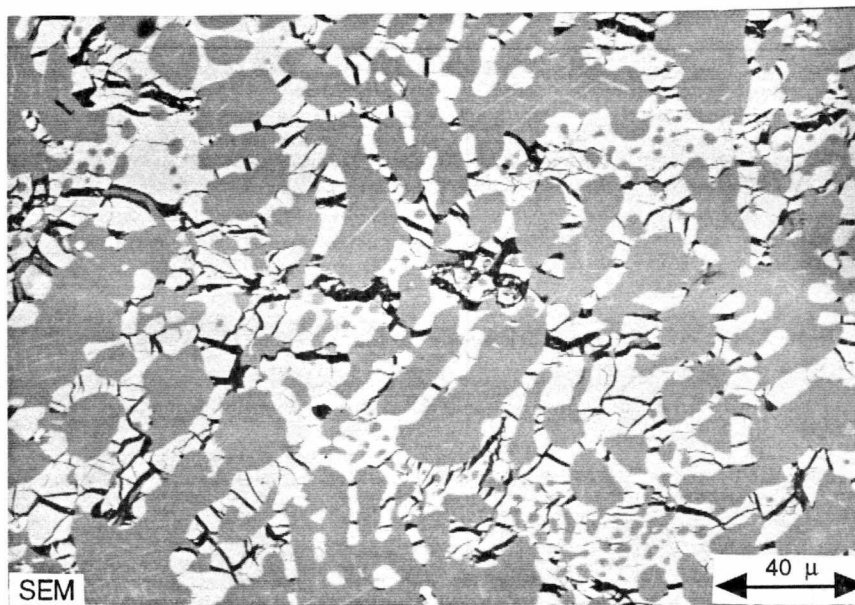


Figure 46. CN-4 annealed 4h at 1550°C + 2d at 1200°C in vacuum tested in compression at 1000°C in vacuum.

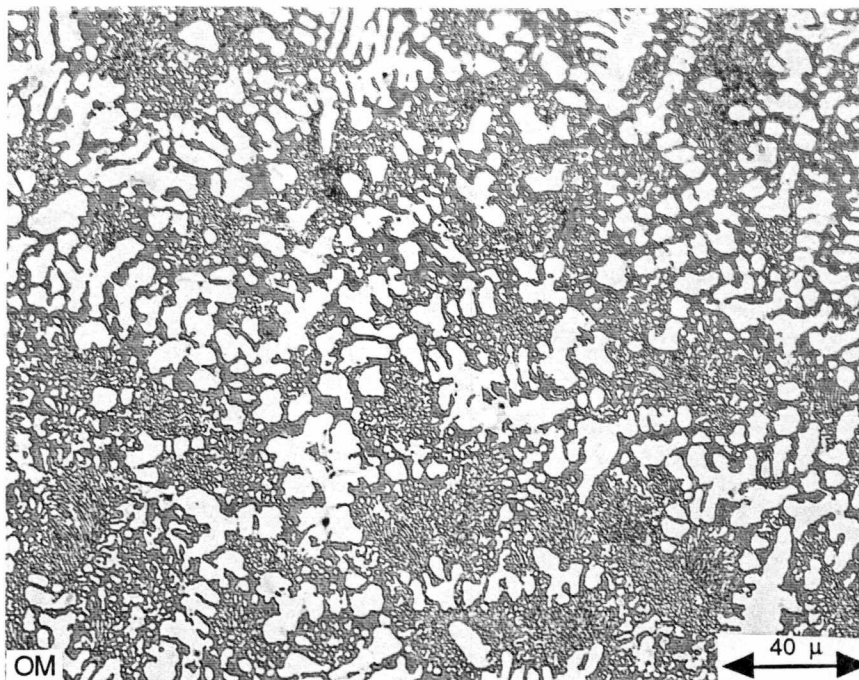


Figure 47. As-Cast microstructure of CN-45 (Cr-17 at.% Nb).

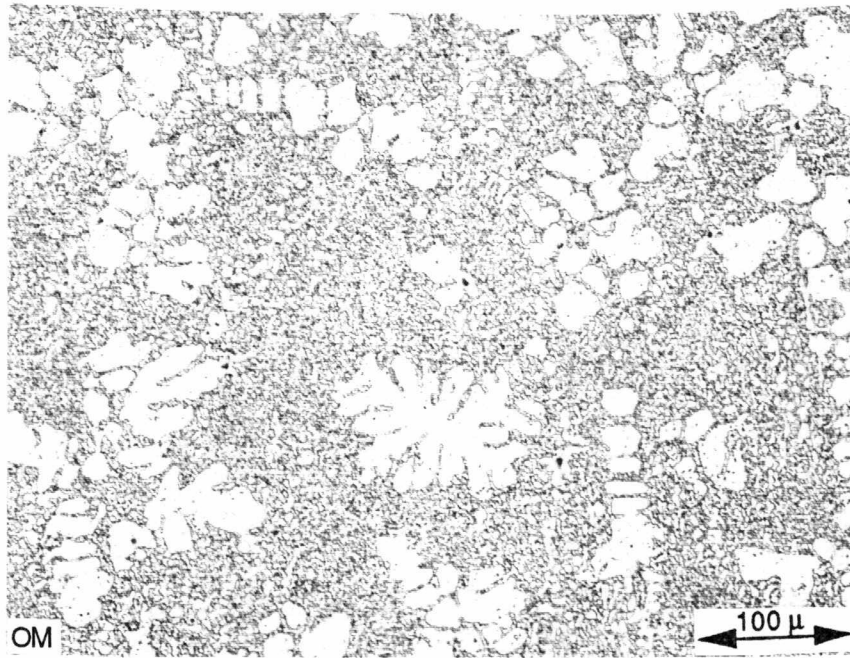


Figure 48. As-Cast microstructure of CN-84 (Cr-18.5 at.% Nb).

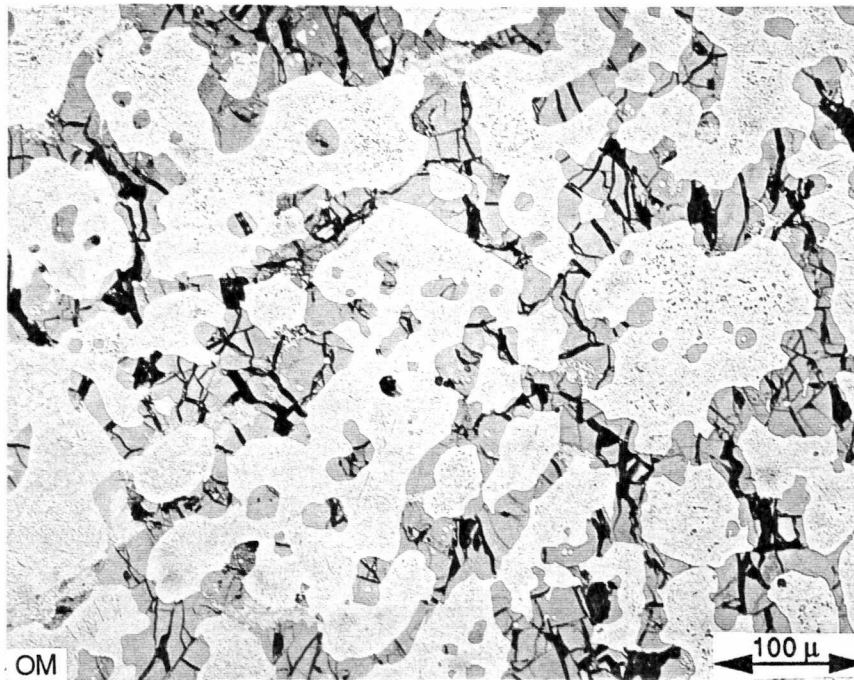


Figure 49. CN-4 : HIPped + annealed 3d at 1200°C in vacuum tested in compression at 1000°C in vacuum.

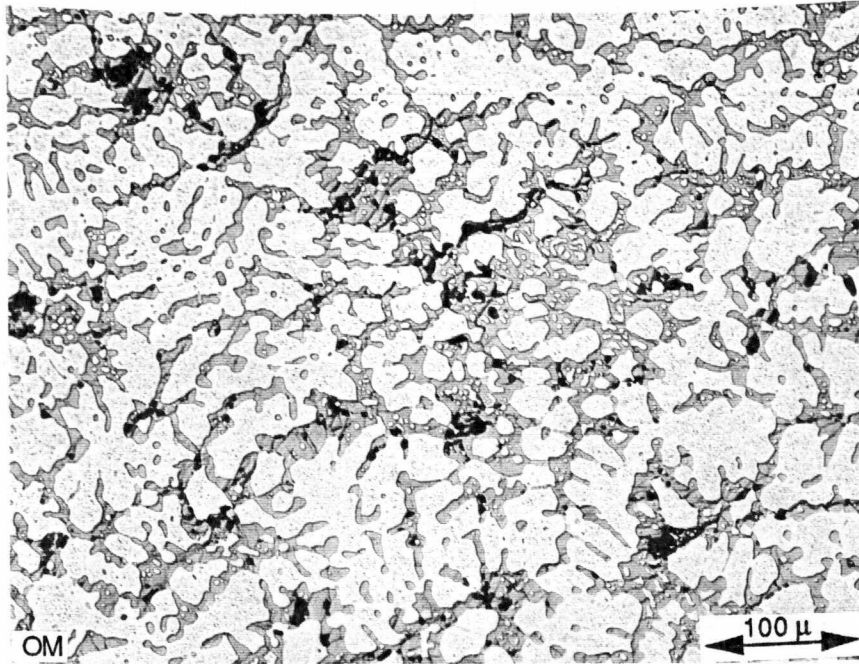


Figure 50. CN-4 : HIPped + annealed 12h at 1500°C + 2d at 1200°C in vacuum tested in compression at room temperature.

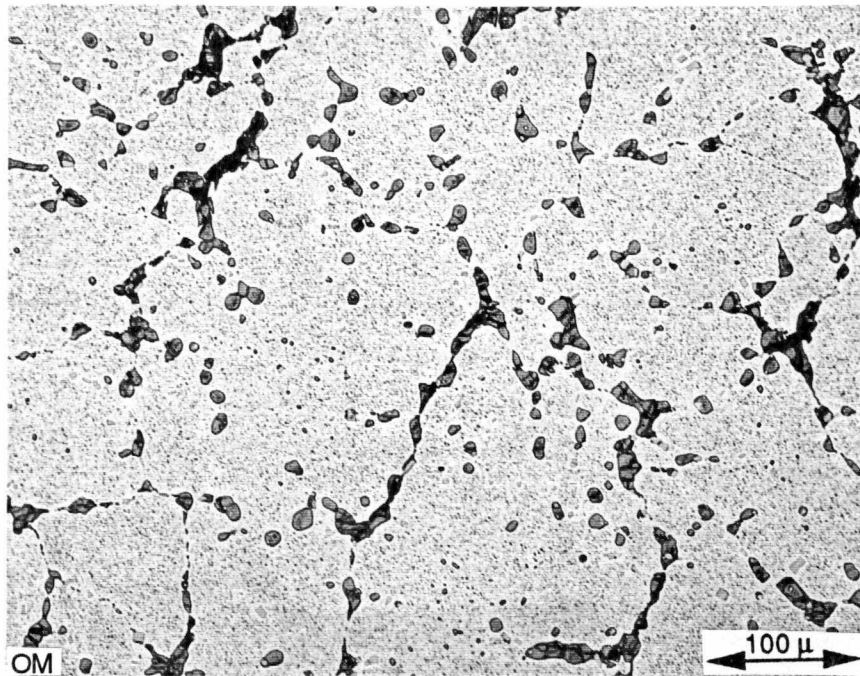


Figure 51. CN-7 : HIPped + annealed 12h at 1500°C + 2d at 1200°C in vacuum tested in compression at room temperature.

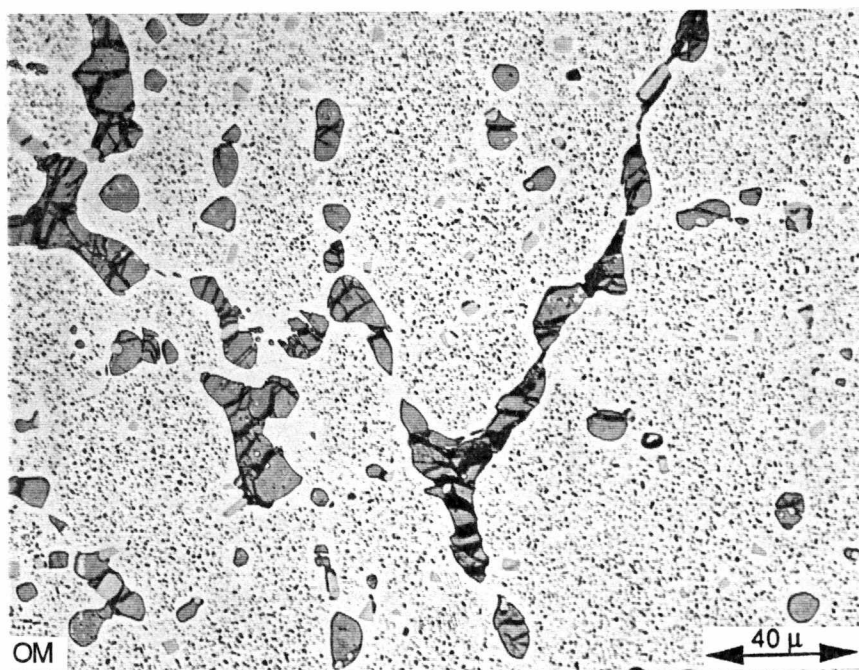


Figure 52. Higher magnification of Figure 51.

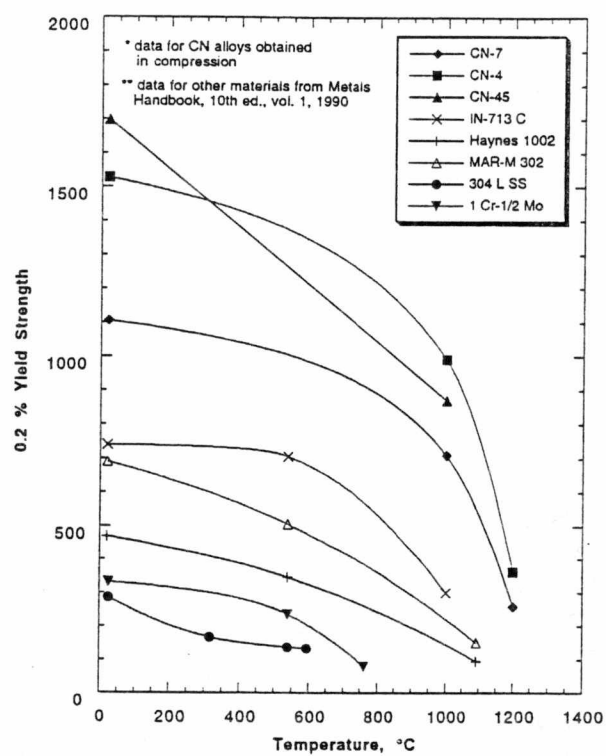


Figure 53. Strength comparison of Cr-Nb alloys with other high-strength, high-temperature alloys.

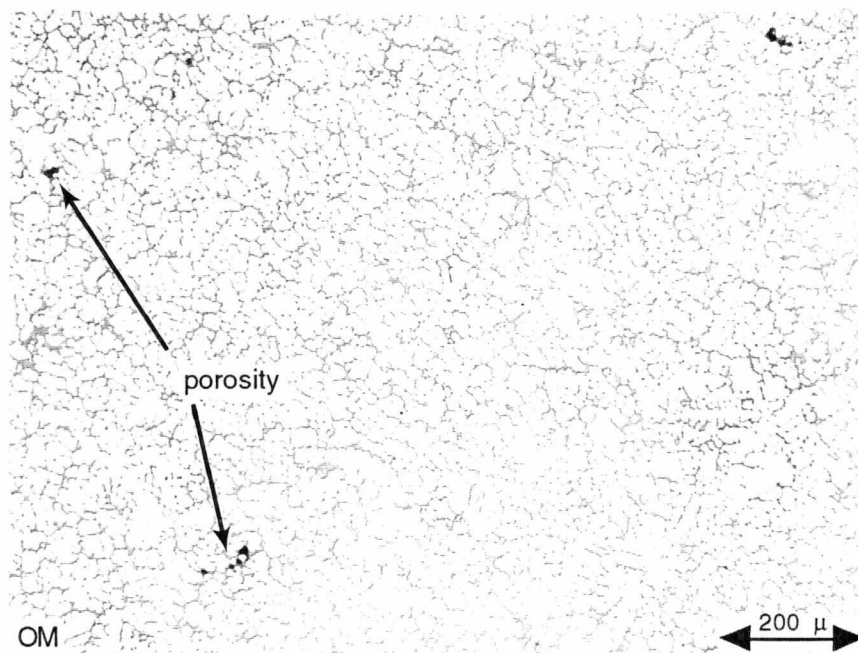


Figure 54. CN-7 : as-cast microstructure showing evidence of cast porosity.

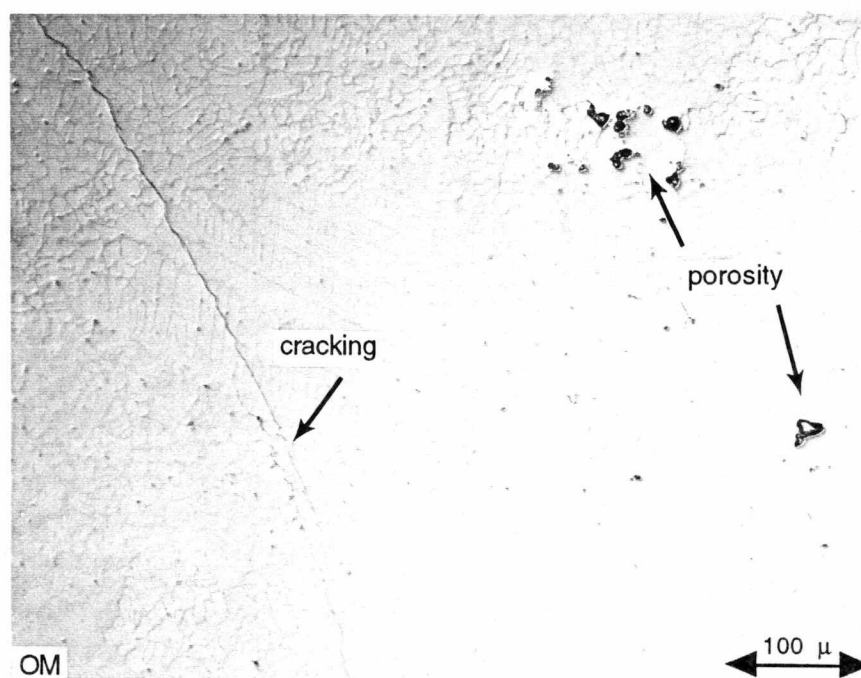


Figure 55. CN-4 : as-cast microstructure revealing porosity and cracking due to casting.

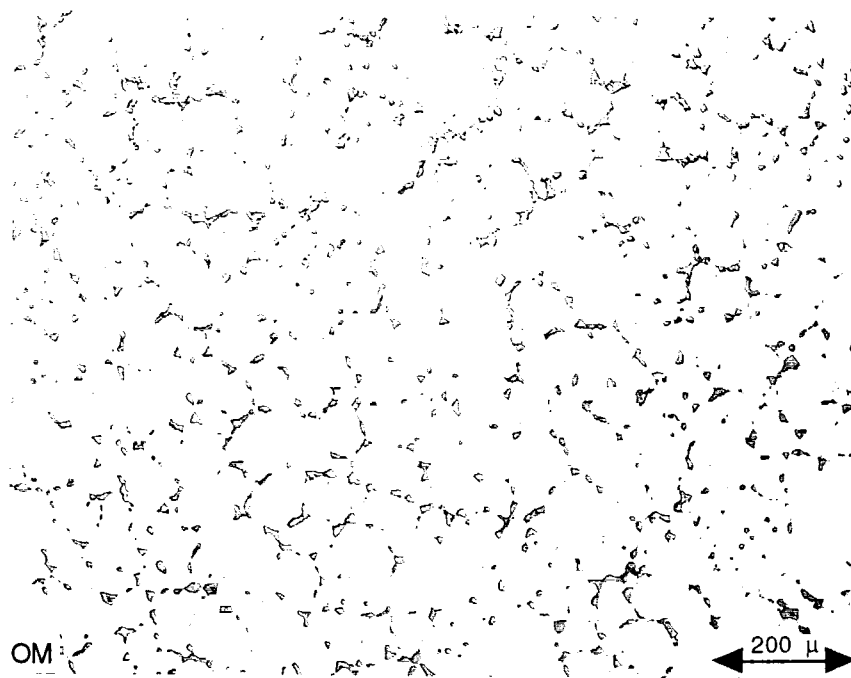


Figure 56. CN-7 : Microstructure of a specimen annealed for 12h at 1500°C in vacuum and tested in tension at room temperature in air.

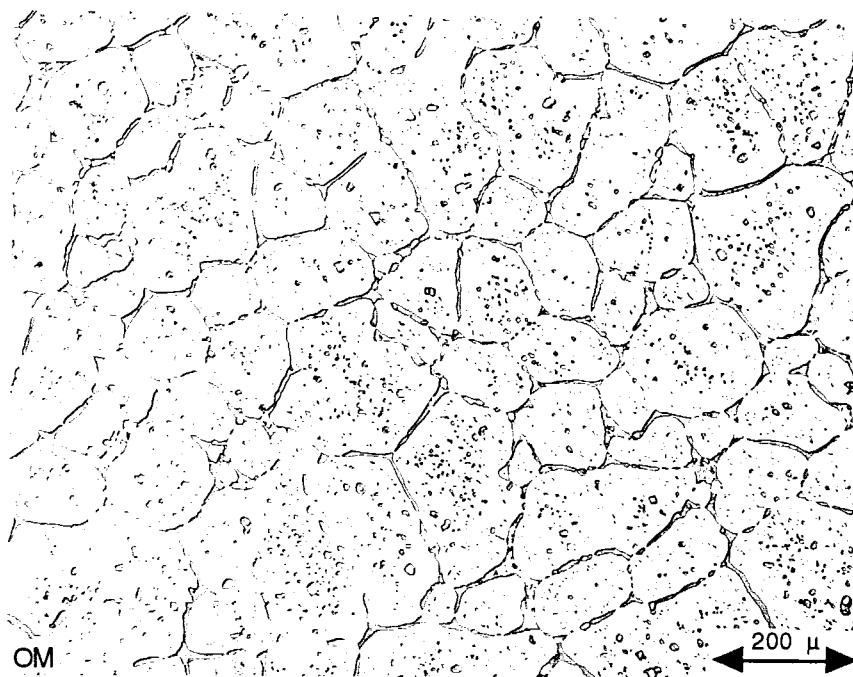


Figure 57. CN-7 : microstructure of a specimen HIPped at 1610°C at 193 MPa + annealed 12h at 1500°C + 2d at 1200°C and tested in tension at room temperature in air.

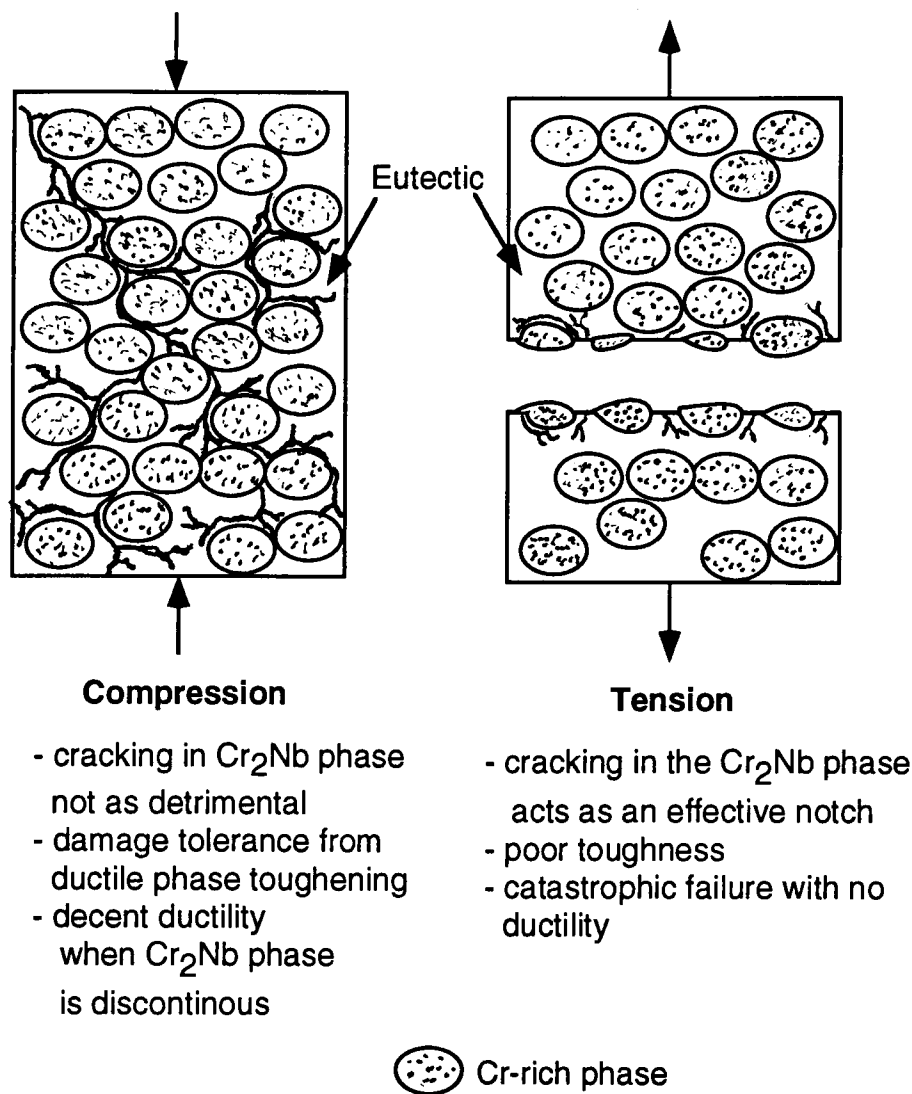


Figure 58. A schematic illustrating the mechanisms of failure in compression and tension.

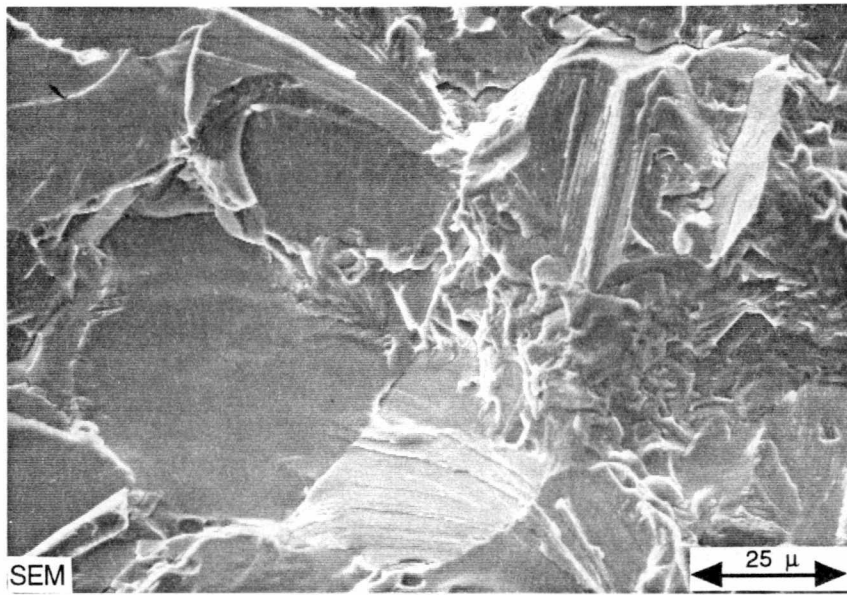


Figure 59. CN-7 : SEM fractograph of sample annealed for 12h at 1500°C in vacuum and tested in tension at room temperature in air.

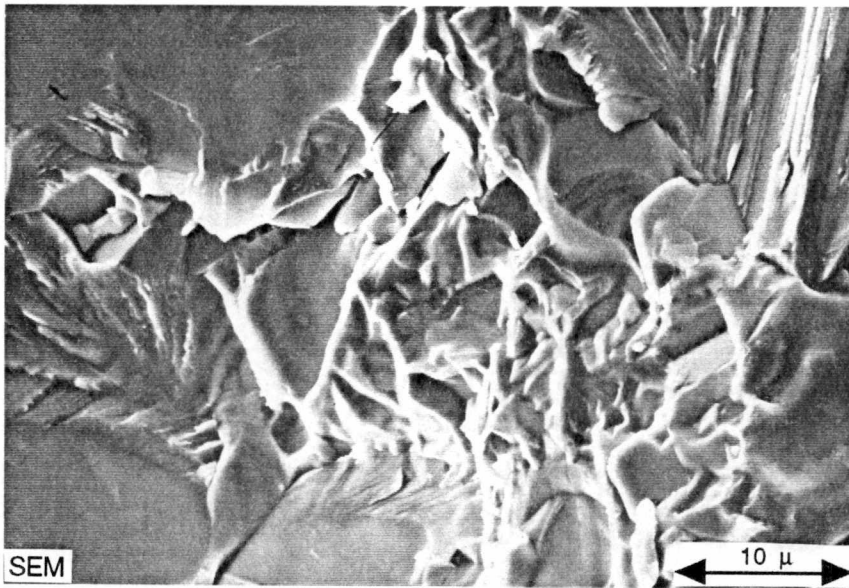


Figure 60. CN-7 : a higher magnification image of Figure 59 showing evidence of grain-boundary de-cohesion and/or interfacial debonding and cracking in the Cr₂Nb intermetallic phase.



Figure 61. CN-7 : back-scatter electron image (BSE) of a sample annealed 12h at 1500°C and tested in tension at room temperature in air. Light-contrast phase is the Cr_2Nb intermetallic and the dark-contrast phase is the Cr-rich matrix.

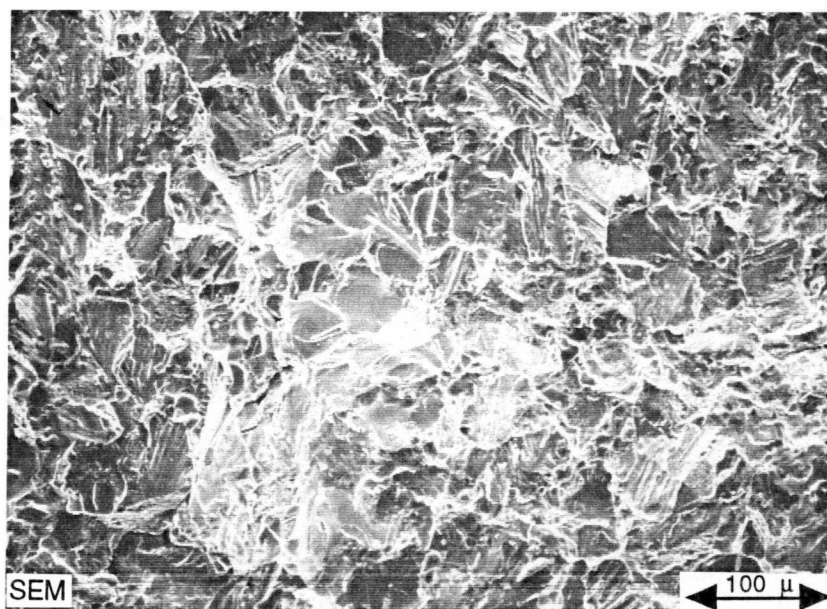


Figure 62. CN-7 : another SEM fractograph of a sample annealed for 12h at 1500°C in vacuum and tested in tension at room temperature in air.

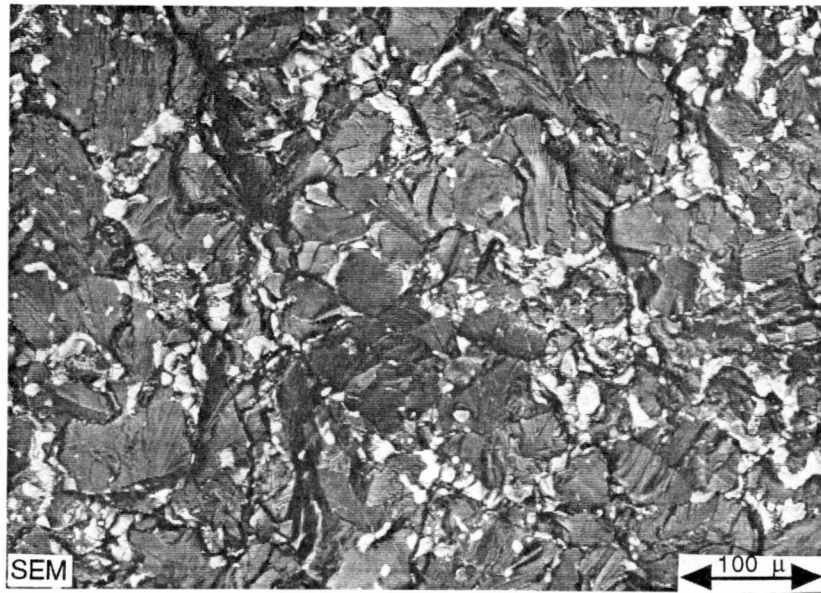


Figure 63. CN-7 : another back-scatter electron image (BSE) of a sample annealed 12h at 1500°C and tested in tension at room temperature in air. Light-contrast phase is the Cr_2Nb intermetallic and the dark-contrast phase is the Cr-rich matrix.

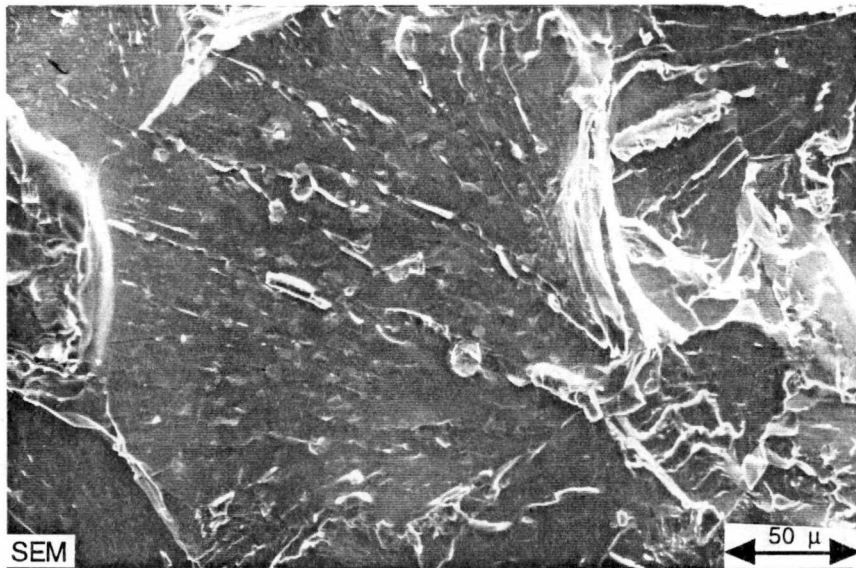


Figure 64. CN-7 : SEM fractograph of a sample HIPped at 1610°C at 193 MPa + annealed for 12h at 1500°C in vacuum and tested in tension at room temperature in air.

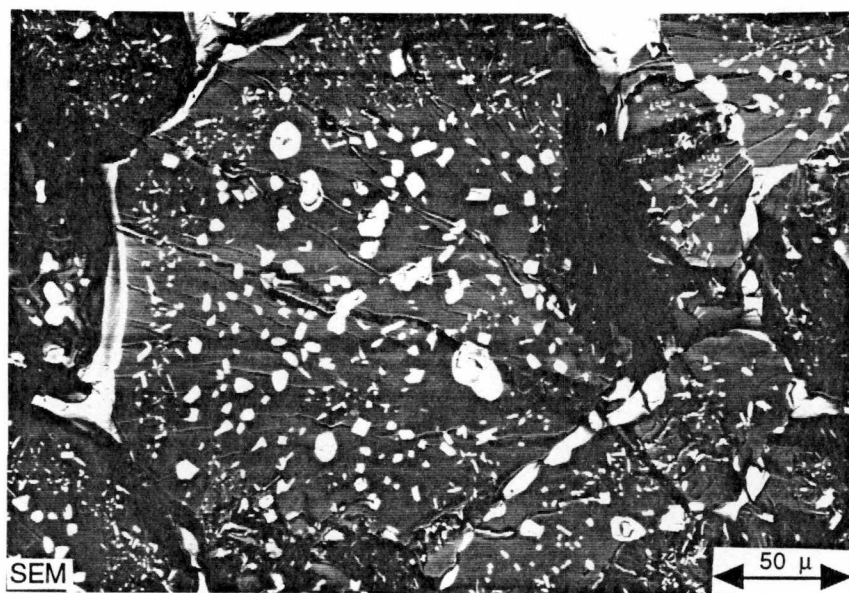


Figure 65. CN-7 : back-scatter electron image (BSE) of a sample HIPped at 1610°C at 193 MPa + annealed 12h at 1500°C and tested in tension at room temperature in air. Light-contrast phase is the Cr₂Nb phase and the dark-contrast phase is the Cr-rich matrix.

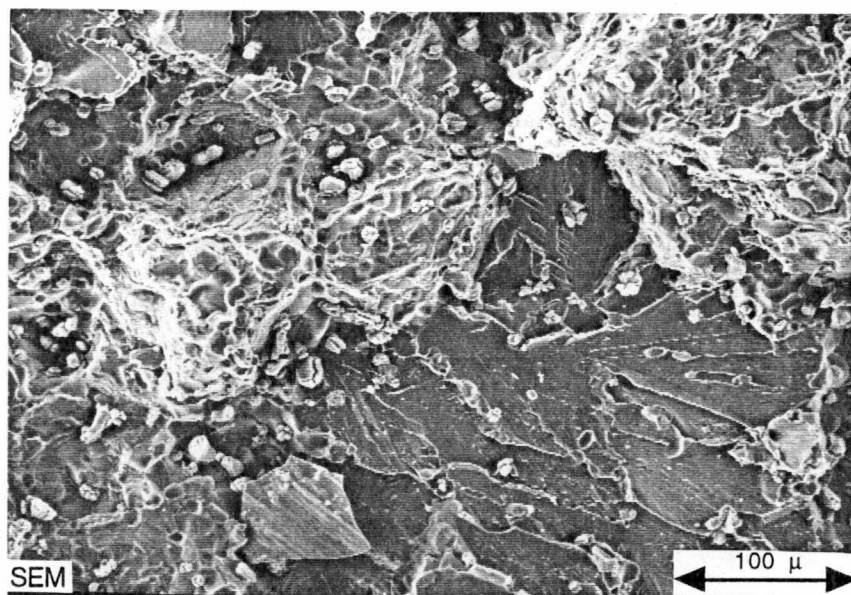


Figure 66. CN-7 : SEM fractograph of sample annealed for 12h at 1500°C in vacuum and tested in tension at 1000°C in air.

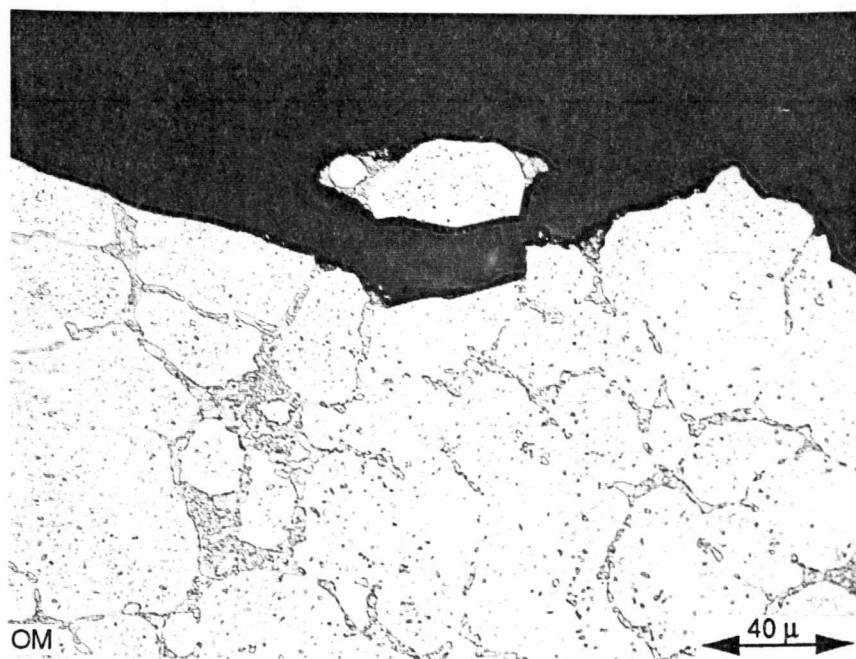


Figure 67. CN-7 : cross-sectional view of the fracture surface of a sample annealed for 3d at 1200°C in vacuum and tested in tension at room temperature in air.

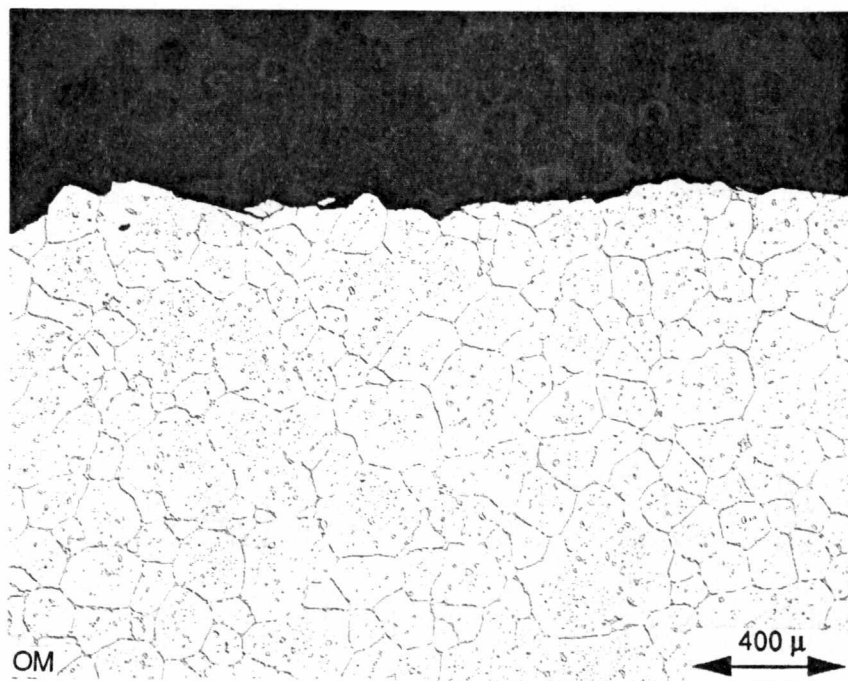


Figure 68. CN-7 : cross-sectional view of the fracture surface of a sample HIPped at 1610°C at 193 MPa + annealed for 12h at 1500°C + 2d at 1200°C in vacuum and tested in tension at room temperature in air.

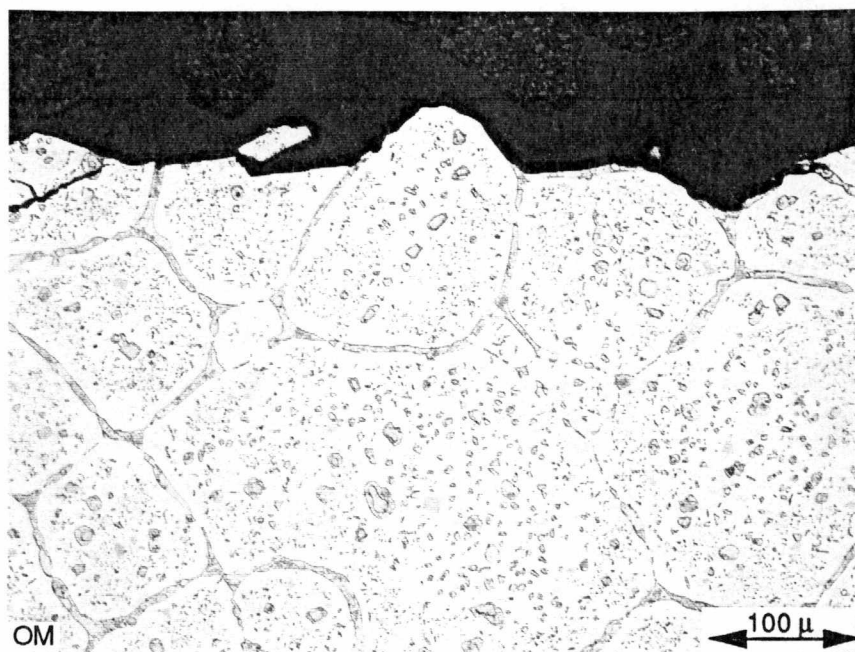


Figure 69. CN-7 : higher magnification of Figure 68.

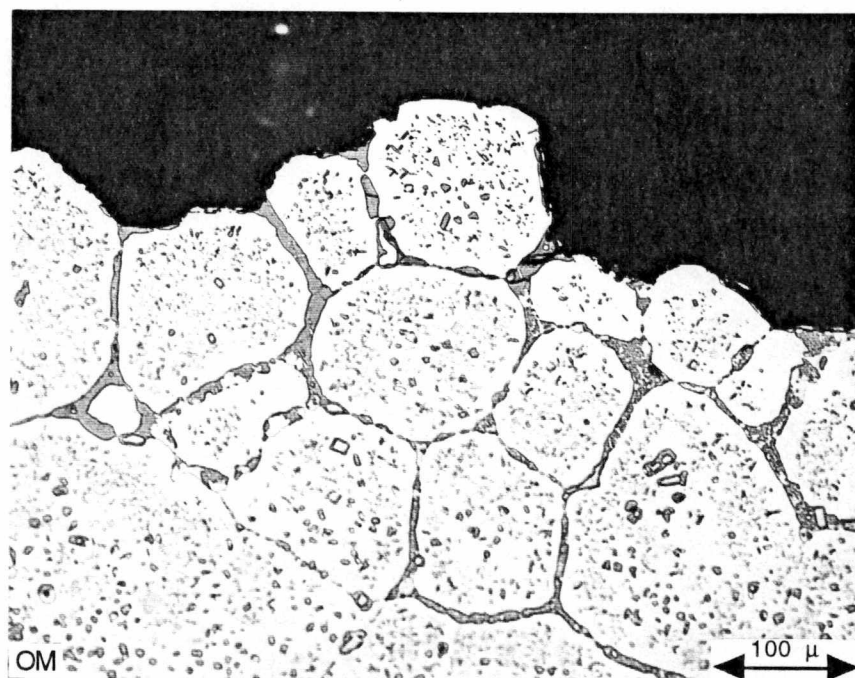


Figure 70. CN-7 : cross-sectional view of the fracture surface of a sample HIPped at 1610°C at 193 MPa + annealed for 12h at 1500°C + 2d at 1200°C in vacuum and tested in tension at 1000°C in air.

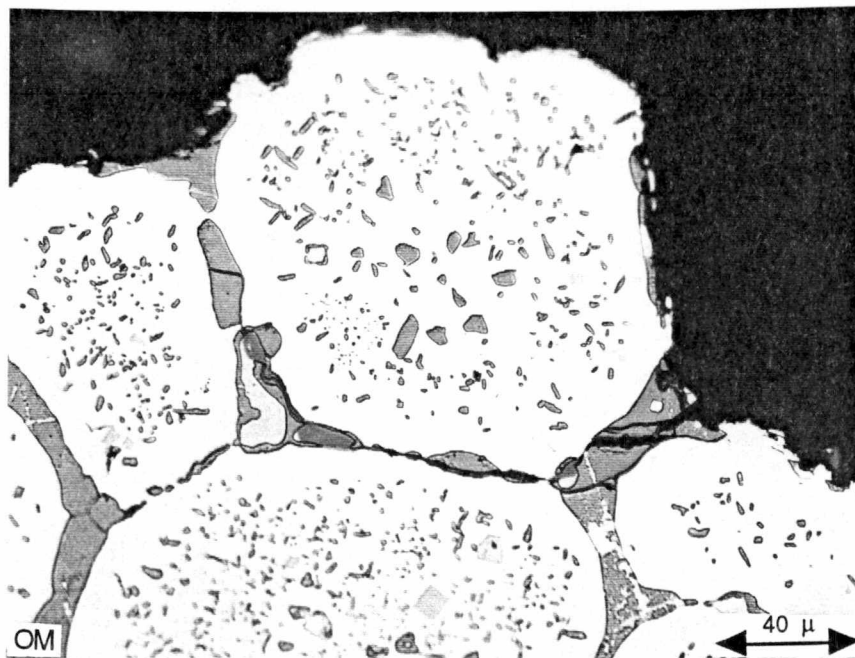


Figure 71. CN-7 : higher magnification of Figure 70.

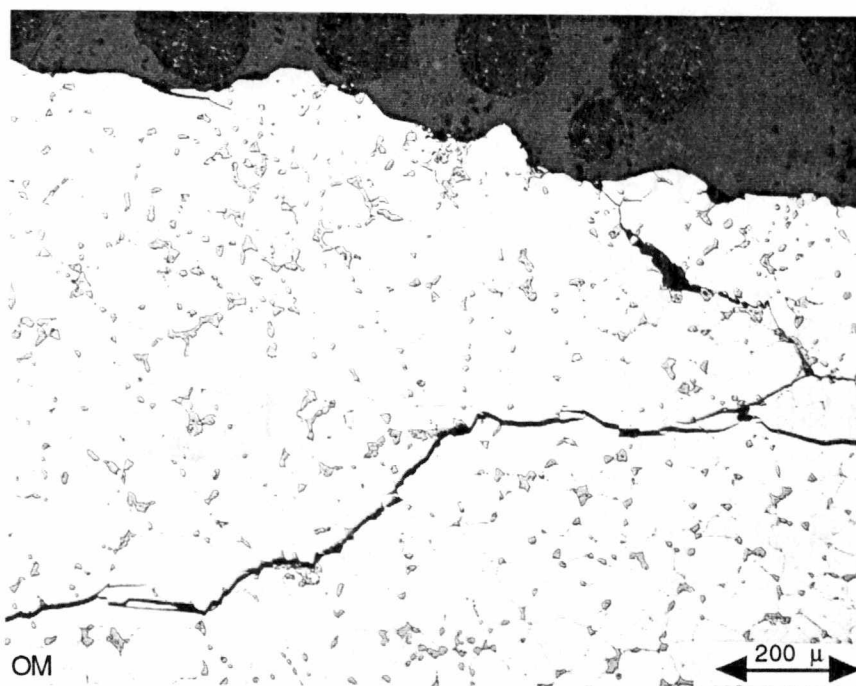


Figure 72. CN-7 : cross-sectional view of the fracture surface of a sample annealed for 12h at 1500°C in vacuum and tested in tension at room temperature in air.

Table A-1. Data Obtained from Image Analysis for the Coarsening of Cr₂Nb Precipitates in the CN-7 Alloy ann. 3h at 1200°C

Sample Area I		Sample Area II		Sample Area III	
Image Size (sq. cm)	True Size (sq. μ m)	Image Size (sq. cm)	True Size (sq. μ m)	Image Size (sq. cm)	True Size (sq. μ m)
0.07	0.07	0.03	0.03	0.02	0.02
0.12	0.12	0.02	0.02	0.09	0.09
0.04	0.04	0.07	0.07	0.03	0.03
0.06	0.06	0.03	0.03	0.05	0.05
0.08	0.08	0.11	0.11	0.02	0.02
0.03	0.03	0.04	0.04	0.02	0.02
0.03	0.03	0.03	0.03	0.12	0.12
0.08	0.08	0.17	0.17	0.06	0.06
0.02	0.02	0.07	0.07	0.02	0.02
0.08	0.08	0.02	0.02	0.05	0.05
0.04	0.04	0.01	0.01	0.08	0.08
0.1	0.1	0.03	0.03	0.01	0.01
0.19	0.19	0.02	0.02	0.02	0.02
0.01	0.01	0.04	0.04	0.02	0.02
0.06	0.06	0.06	0.06	0.04	0.04
0.03	0.03	0.02	0.02	0.02	0.02
0.01	0.01	0.06	0.06	0.01	0.01
0.24	0.24	0.03	0.03	0.01	0.01
0.03	0.03	0.09	0.09	0.04	0.04
0.04	0.04	0.02	0.02	0.06	0.06
0.04	0.04	0.18	0.18	0.03	0.03
0.03	0.03	0.03	0.03	0.03	0.03
0.05	0.05	0.03	0.03	0.02	0.02
0.06	0.06	0.02	0.02	0.02	0.02
0.08	0.08	0.04	0.04	0.05	0.05
0.03	0.03	0.02	0.02	0.04	0.04
0.03	0.03	0.03	0.03	0.04	0.04
0.04	0.04	0.12	0.12	0.06	0.06
0.02	0.02	0.03	0.03	0.02	0.02
0.14	0.14	0.02	0.02	0.01	0.01
0.03	0.03	0.03	0.03	0.16	0.16
0.03	0.03	0.02	0.02	0.06	0.06
0.06	0.06	0.04	0.04	0.08	0.08
0.06	0.06	0.03	0.03	0.01	0.01
0.02	0.02	0.05	0.05	0.03	0.03
0.03	0.03	0.02	0.02	0.02	0.02
0.03	0.03	0.09	0.09	0.03	0.03
0.05	0.05	0.03	0.03	0.02	0.02
0.06	0.06	0.03	0.03	0.03	0.03
0.03	0.03	0.02	0.02	0.06	0.06
0.05	0.05	0.01	0.01	0.02	0.02
0.01	0.01	0.02	0.02	0.07	0.07
0.01	0.01	0.02	0.02	0.02	0.02
0.03	0.03	0.13	0.13	0.04	0.04
0.01	0.01	0.02	0.02	0.08	0.08
0.04	0.04	0.06	0.06	0.06	0.06
0.01	0.01	0.09	0.09	0.03	0.03
0.01	0.01	0.02	0.02	0.03	0.03
0.05	0.05	0.03	0.03	0.03	0.03
0.05	0.05	0.04	0.04	0.02	0.02
0.04	0.04	0.03	0.03	0.03	0.03
0.01	0.01	0.02	0.02	0.03	0.03
0.03	0.03	0.04	0.04	0.03	0.03
0.2	0.2	0.01	0.01	0.07	0.07
0.09	0.09	0.06	0.06	0.02	0.02
0.04	0.04	0.04	0.04	0.04	0.04
0.03	0.03	0.03	0.03	0.01	0.01
0.03	0.03	0.03	0.03	0.02	0.02

Table A-1. (continued)

Sample Area I		Sample Area II		Sample Area III	
Image Size (sq. cm)	True Size (sq. μm)	Image Size (sq. cm)	True Size (sq. μm)	Image Size (sq. cm)	True Size (sq. μm)
0.03	0.03	0.03	0.03	0.06	0.06
0.07	0.07	0.04	0.04	0.03	0.03
0.01	0.01	0.05	0.05	0.03	0.03
0.07	0.07	0.06	0.06	0.04	0.04
0.08	0.08	0.02	0.02	0.03	0.03
0.11	0.11	0.02	0.02	0.02	0.02
0.04	0.04	0.18	0.18	0.01	0.01
0.05	0.05	0.07	0.07	0.02	0.02
0.02	0.02	0.02	0.02	0.03	0.03
0.03	0.03	0.08	0.08	0.05	0.05
0.03	0.03	0.02	0.02	0.02	0.02
0.03	0.03	0.02	0.02	0.12	0.12
0.01	0.01	0.04	0.04	0.03	0.03
0.05	0.05	0.02	0.02	0.05	0.05
0.03	0.03	0.03	0.03	0.05	0.05
0.01	0.01	0.07	0.07	0.03	0.03
0.02	0.02			0.07	0.07
0.03	0.03			0.01	0.01
0.07	0.07			0.04	0.04
0.09	0.09			0.01	0.01
0.09	0.09			0.17	0.17
0.04	0.04			0.1	0.1
0.01	0.01			0.04	0.04
0.03	0.03			0.05	0.05
0.03	0.03				
0.02	0.02				
0.04	0.04				
0.05	0.05				
0.05	0.05				
0.06	0.06				
0.01	0.01				
0.06	0.06				
0.08	0.08				
0.01	0.01				
Total area of precipitates = 4.48 sq. μm Sample size area = 30.46 square μm		Total area of precipitates = 3.32 sq. μm Sample size area = 34.95 square μm		Total area of precipitates = 3.37 sq. μm Sample size area = 43.15 square μm	
Area fraction of precipitates: 14.56%		Area fraction of precipitates: 9.5%		Area fraction of precipitates: 7.81%	

Table A-2. Data Obtained from Image Analysis for the Coarsening of Cr2Nb Precipitates in the CN-7 Alloy ann. 30d at 1200°C

Sample Area I		Sample Area II		Sample Area III	
Image Size* (sq. cm)	True Size* (sq. μ m)	Image Size (sq. cm)	True Size (sq. μ m)	Image Size (sq. cm)	True Size (sq. μ m)
0.01	0.04	0.03	0.12	0.03	0.12
0.1	0.42	0.08	0.33	0.07	0.29
0.09	0.37	0.04	0.17	0.11	0.46
0.03	0.12	0.04	0.17	0.03	0.12
0.03	0.12	0.03	0.12	0.02	0.08
0.01	0.04	0.04	0.17	0.03	0.12
0.02	0.08	0.01	0.04	0.02	0.08
0.17	0.71	0.09	0.37	0.09	0.37
0	0	0.02	0.08	0.02	0.08
0.04	0.17	0.06	0.25	0.03	0.12
0.02	0.08	0.03	0.12	0.03	0.12
0	0	0.09	0.37	0.01	0.04
0.08	0.33	0.05	0.21	0.07	0.29
0.04	0.17	0.07	0.29	0.01	0.04
0.03	0.12	0.15	0.62	0.02	0.08
0.04	0.17	0.02	0.08	0.04	0.17
0.01	0.04	0.11	0.46	0.18	0.75
0	0	0.02	0.08	0	0
0.02	0.08	0.03	0.12	0.05	0.21
0.06	0.25	0.03	0.12	0.05	0.21
0.09	0.37	0.03	0.12	0.02	0.08
0.05	0.21	0.02	0.08	0.09	0.37
0.07	0.29	0.03	0.12	0.16	0.67
0.15	0.62	0.04	0.17	0.01	0.04
0.02	0.08	0.03	0.12	0.04	0.17
0.03	0.12	0.11	0.46	0.03	0.12
0.03	0.12	0.02	0.08	0.04	0.17
0.02	0.08	0.02	0.08	0.05	0.21
0.03	0.12	0.05	0.21	0.01	0.04
0.04	0.17	0.01	0.04	0.1	0.42
0.11	0.46	0.01	0.04	0.01	0.04
0.02	0.08	0.03	0.12	0.01	0.04
0.01	0.04	0.08	0.33	0.02	0.08
0.03	0.12	0.03	0.12	0.03	0.12
0.08	0.33	0.04	0.17	0.09	0.37
0.03	0.12	0.03	0.12	0.06	0.25
0.03	0.12	0.06	0.25	0.05	0.21
0.06	0.25	0.05	0.21	0.08	0.33
0.05	0.21	0.08	0.33	0.15	0.62
0.08	0.33	0.08	0.33	0.01	0.04
0	0	0.03	0.12	0.02	0.08
0.08	0.33	0.02	0.08	0.11	0.46
0.02	0.08	0.07	0.29	0.02	0.08
0.07	0.29	0.04	0.17	0.04	0.17
0.04	0.17	0.01	0.04	0.03	0.12
0.01	0.04	0.01	0.04	0.06	0.25
0.09	0.37	0.09	0.37	0.03	0.12
0.08	0.33	0.08	0.33	0.03	0.12
0.17	0.71	0.17	0.71	0.03	0.12
0.01	0.04	0.01	0.04	0.04	0.17
0.01	0.04	0.01	0.04	0.03	0.12
0.03	0.12	0.04	0.17	0.11	0.46
0.01	0.04	0.03	0.12	0.02	0.08
0.01	0.04	0.01	0.04	0.02	0.08
0	0	0.08	0.25	0.01	0.04
0.08	0.33	0.03	0.12	0.03	0.12
0.01	0.04	0.01	0.04	0.05	0.21
0.01	0.04	0	0	0.08	0.33

Table A-2. (continued)

Sample Area I		Sample Area II		Sample Area III	
Image Size (sq. cm)	True Size (sq. μm)	Image Size (sq. cm)	True Size (sq. μm)	Image Size (sq. cm)	True Size (sq. μm)
0.04	0.17	0.08	0.33	0.03	0.12
0.1	0.42	0.01	0.04	0.03	0.12
0.18	0.75	0.01	0.04	0.06	0.25
0.02	0.08	0.03	0.12	0.05	0.21
0.03	0.12	0.04	0.17	0.08	0.33
0.12	0.5	0.1	0.42	0.03	0.12
0.07	0.29	0.18	0.75	0	0
0.01	0.04	0.02	0.08	0.08	0.33
0.16	0.67	0.03	0.12	0.03	0.12
0.08	0.33	0.03	0.12	0.02	0.08
0.02	0.08	0.02	0.08	0.07	0.29
0.11	0.46	0.12	0.5	0.04	0.17
0.06	0.25	0.07	0.29	0.01	0.04
0.13	0.54	0.01	0.04	0.01	0.04
0	0	0.01	0.04	0.1	0.42
		0.03	0.12		
		0.16	0.67		
		0.08	0.33		
		0.02	0.08		
Total area of precipitates = 3.69 sq. μm		Total area of precipitates = 3.66 sq. μm		Total area of precipitates = 3.37 sq. μm	
Sample size area = 31.43 square μm		Sample size area = 33.45 square μm		Sample size area = 33.78 square μm	
Area fraction of precipitates: 11.74%		Area fraction of precipitates: 10.94%		Area fraction of precipitates: 9.98%	

*Image size refers to the precipitate size as measured from the micrograph

**True size refers to the actual size of the precipitates as corrected for the magnification of the micrograph

VITA

Jeffery Allan Cook was born in Oak Ridge, Tennessee on November 29, 1970. He attended schools in the public system of Knoxville, Tennessee, the Knox County Public School System, where he graduated as valedictorian of his class from Karns High School in May, 1989. He entered the University of Tennessee, Knoxville during August of 1989 where in May, 1993 he received a Bachelor of Science degree in Materials Science and Engineering, graduating summa cum laude. After a summer internship at the Oak Ridge National Laboratory, he entered the master's program in Metallurgical Engineering at the University of Tennessee, Knoxville in August of 1993. The Master of Science degree in Metallurgical Engineering was received August, 1995.