CONF-9505204--7

Cr_2Nb-BASED ALLOY DEVELOPMENT

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ABSTRACT

Two-phase Cr-Cr_2Nb alloys (designated as CN alloys) were prepared by arc melting, followed by directional solidification, HIPping, or hot extrusion at 1450 to 1500°C. The microstructure of CN alloys containing 6 to 12 at.% Nb depended strongly on alloying additions, heat treatment, and material processing. Tensile properties were sensitive to defects. Hot extrusion at 1480°C was most effective in reducing as-cast defects and refining the cast Cr-Cr_2Nb eutectic structure and thus improving ductility. Beneficial alloying elements that modified the eutectic microstructure, improved oxidation resistance, or increased high-temperature strength were identified. One particular composition had a room-temperature fracture strength of 548 MPa and an ultimate tensile strength of 388 MPa, and 23% elongation at 1200°C. Another CN alloy showed a fracture toughness of 7.6 MPa$\sqrt{}$m at room temperature and 24.4 MPa$\sqrt{}$m at 1000°C. Silicide coatings applied by a pack cementation process substantially improved the oxidation resistance of the Cr-Cr_2Nb alloys at 950 and 1100°C.

INTRODUCTION

The objective of this task is to develop a new generation of structural materials based on intermetallic alloys for use as critical hot components in advanced fossil energy conversion systems. The intermetallic phase, Cr_2Nb, with a complex cubic structure (C-15)[1,2] has been selected for this development because of its high melting point (1770°C),[2-4] relatively low material density (7.7 g/cm^2),[5] excellent high-temperature strength (at 1000 to 1250°C),[6,7] and potential resistance to oxidation and corrosion.[3,8,9] This intermetallic phase, like many other Laves phases, has a wide range of compositional homogeneity[2,4] suggesting the possibility of improving its mechanical and metallurgical properties by alloying additions.

The major engineering concern with Cr_2Nb and other A_2B Laves phases is their poor fracture toughness and fracture resistance at ambient temperatures.[3,6,7,10] The single-phase Cr_2Nb is very hard (~800 DPH) and brittle at room temperature.[11] Because of this brittleness, the development effort has concentrated on two-phase structures containing the hard intermetallic phase Cr_2Nb and the softer Cr-rich solid solution phase. Previous studies indicate that the two-phase CN alloys exhibited significant plastic deformation prior to fracture under compressive tests at room temperature.[6,7,11] The alloys showed excellent compressive strength at room and elevated temperatures, with the yield strength much

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superior to nickel-base superalloys and Ni_3Al alloys at and above 1000°C. The CN alloys, however, showed poor fracture strength in tension at ambient temperatures.

Potential applications of Cr-Cr_2Nb alloys include hot components (for example, air heat exchangers and turbine blades) in advanced energy conversion systems and heat engines, wear-resistant parts in coal handling systems (e.g., nozzles), drill bits for oil/gas wells, and valve guides in diesel engines. Current studies are focused on enhancement of fracture resistance in tension at ambient temperatures and oxidation resistance above 1000°C. This report summarizes recent progress on controlling microstructure and improving the mechanical and metallurgical properties and the high-temperature corrosion behavior of Cr-Cr_2Nb alloys through alloying additions, material processing, and heat treatment.

ALLOY PREPARATION AND PROCESSING

Cr(Nb)-Cr_2Nb alloys weighing 400 g were prepared by arc melting and drop casting in a copper mold (2.5 cm diam x 7.6 cm long) preheated at 100 to 300°C. High-purity niobium and chromium metal chips were used as charge materials. The alloy ingots generally contain certain defects, including oxide inclusions and as-cast porosity ranging in size from a few to several hundred microns. The alloys also exhibit a coarse eutectic structure including interconnected Cr_2Nb plates, which adversely affect their mechanical (tensile) properties.

In order to minimize the casting defects and to refine the cast eutectic structure, selected alloy ingots were clad inside molybdenum billets and hot extruded at 1450 to 1500°C at an extrusion ratio of 4 to 1. Some alloys were successfully hot extruded into 1.3 cm bar stock, and others were cracked into pieces. The tendency for cracking was not simply correlated with alloy composition. It appeared that the cracking may be related to casting defects.

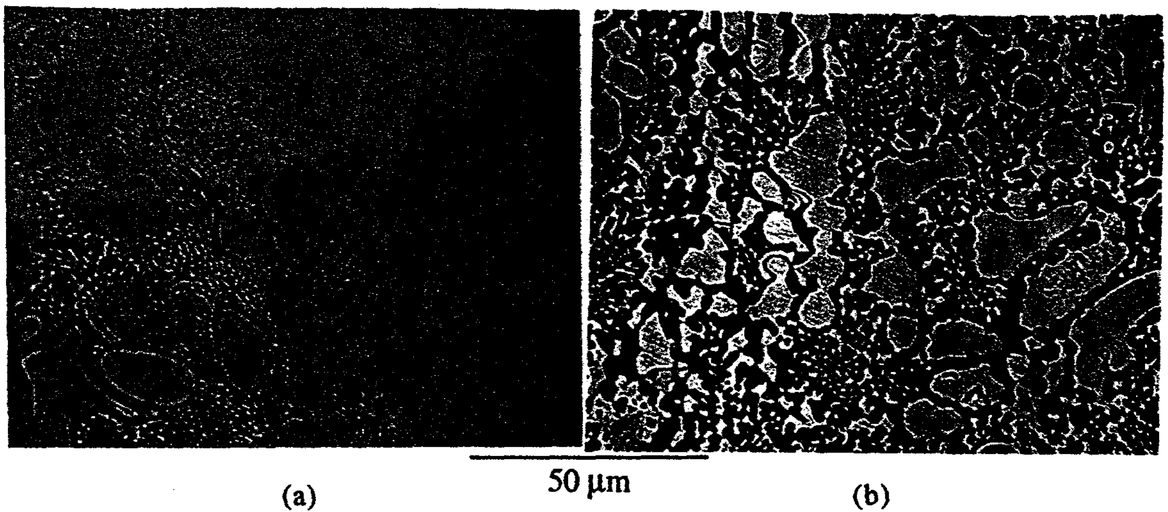
Preparation of CN alloys using elemental powders has just been initiated. In this case, the powders were mixed completely to give the correct alloy compositions and then placed inside molybdenum cans. The filled cans were then degassed in a vacuum chamber and sealed by electron-beam welding. They were hot extruded at 1480°C to produce CN alloys. Initial results indicate the as-extruded bars contained many foreign particles which were identified as aluminum and niobium oxides by energy dispersive x-ray spectroscopy (EDS). The amount of the oxide phase depended on the way the powders were prepared prior to insertion into the molybdenum cans. Significant recent progress was made in decreasing the amount of the oxide phases by reducing interstitial contamination during the powder processing.

MICROSTRUCTURAL ANALYSIS

Alloying additions, heat treatment, and material processing all strongly affect the microstructure of Cr(Nb)-Cr_2Nb alloys. Figure 1 compares the as-cast microstructure of two alloys, CN-96 and -97 containing 12% Nb and other alloying additions. (All compositions are at.% unless otherwise noted.) The compositional difference of the two alloys is that CN-97 had 0.1 wt% of a minor alloying addition (designated as X5). As shown in Fig. 1, the base alloy CN-96 exhibits a typical lamellar-type eutectic structure (Fig. 1a) while the doped alloy CN-97 shows blocky particles in the eutectic structure. In these photos, the Cr-rich phase appears as light gray while the Cr_2Nb is darker. The primary Cr-rich patches precipitated out fine Cr_2Nb particles after annealing at 1200 to 1300°C (as shown in Fig. 2 for CN-103).

Hot extrusion at 1450 to 1500°C was apparently effective in breaking the interconnected Cr_2Nb phase in the eutectic structure. This is shown in Fig. 3 for CN-90 containing 6% Nb and other alloying additions. The coarse Cr_2Nb plates that formed around primary Cr-rich patches (Fig. 3a) were broken into blocky particles (Fig. 3b) after hot extrusion at 1480°C.

The alloys CN-80, -85, and -87 were examined by transmission electron microscopy (TEM). All the alloys were hot extruded at 1480°C and annealed for 3 d at 1200°C. Alloy disks were prepared by ion milling at 6 kV and were examined in a Philips CM30 at 300 kV. Figure 4 is a TEM micrograph showing Cr_2Nb particles observed in CN-85 which was annealed for 3 d at 1200°C. The blocky particles contain numerous microtwins. This may be due to the C14 → C15 transformation. The study of the crystal structure of these particles



(a) (b)

Fig. 1. Optical micrograph of as-cast (a) CN-96 and (b) CN-97 containing 12 at.% Nb and other alloying additions. The difference in composition is that CN-97 has 0.1 wt% X5.

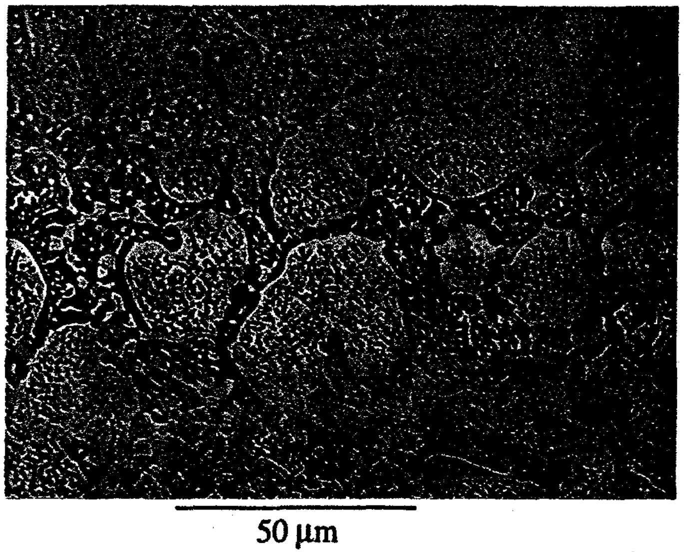


Fig. 2. Optical micrograph of CN-103 containing 10 at.% Nb and 0.1 wt% X5. The alloy was annealed for 1 d at 1300°C and 2 d at 1200°C.

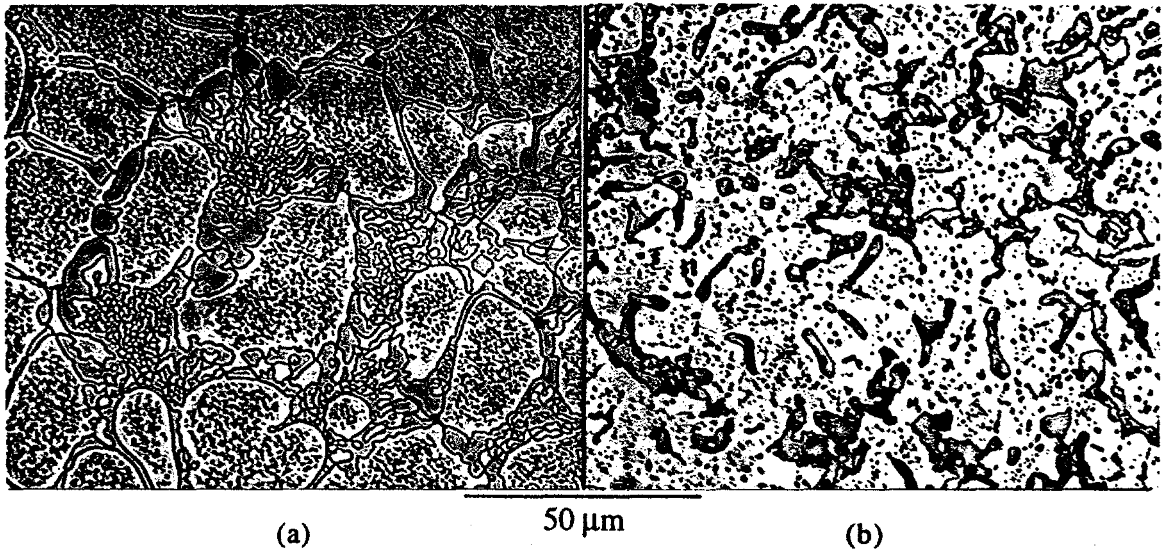


Fig. 3. Comparison of optical micrograph of CN-90 in (a) as-cast plus 1 d at 1200°C anneal and (b) hot extrusion at 1480°C plus 1 d at 1200°C anneal.

is in progress. Dislocations and dislocation networks are generally observed in the Cr-rich phase, but they are very seldom observed in Cr_2Nb particles.

An EDAX 9100 spectrometer was used to perform EDS in conjunction with the TEM studies. The EDS analyses were made on precipitates that intersected the ion milling perforations, thereby minimizing the contributions from surrounding matrix material. The results were averaged and are shown in Table 1. Here X1, X2, X3, and X4 represent the beneficial elements added to the Cr-Nb alloys. X1 was added for refining the coarse eutectic structure, X2 was for improving oxidation resistance, X3 for enhancing the high-temperature strength, and X4 for ease of fabrication. The Cr-rich solid solution (that is, the matrix phase)

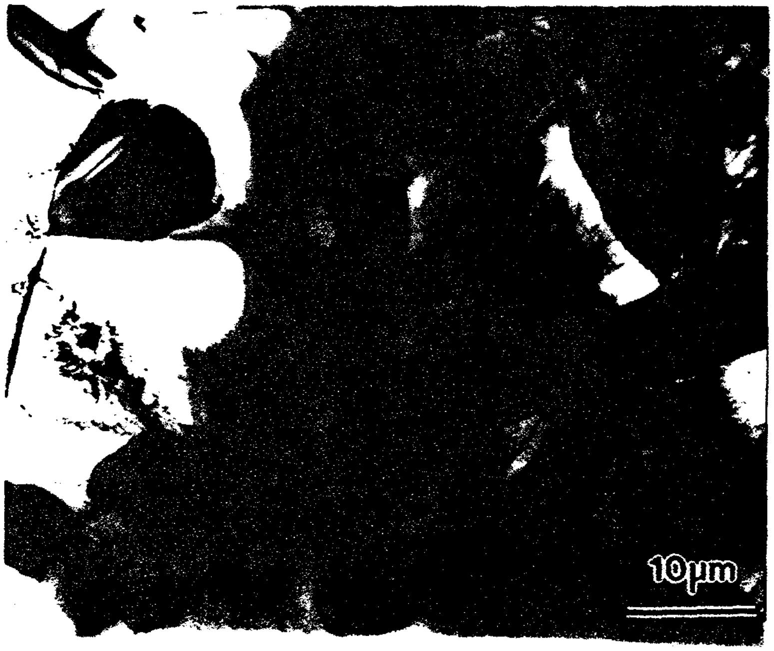


Fig. 4. TEM micrograph of CN-85 (Cr-Nb-1.5Al-5X1-4X2) hot extruded at 1480°C.

Table 1. Partitioning of Alloying Additions in CN Alloys* as Determined by EDS/TEM

Alloy (at. %)	Cr_2Nb Phase (at. %)	Cr-rich Matrix (at. %)
CN-80: Cr-12Nb-1.5Al-6X1	Nb = 33	Nb = 1
	Cr = 59	Cr = 90
	X1 = 6	X1 = 8
	Al = 2	Al = 1
CN-85: Cr-6Nb-1.5Al-5X1-4X2	Nb = 32	Nb = 1
	Cr = 51	Cr = 90
	X1 = 7	X1 = 6
	X2 = 10	X2 = 1.5
	Al = 0	Al = 1.5
CN-87: Cr-8Nb-1.5Al-5X1-4X2-20X4	Nb = 27	Nb = 0.4
	Cr = 27	Cr = 73.5
	X1 = 10	X1 = 4.8
	X2 = 10	X2 = 2.3
	X4 = 24	X4 = 16.5
	Al = 2	Al = 2.5

*The alloys were fabricated by hot extrusion at 1480°C and annealed for 1 to 3 d at 1200°C.

in CN-80, -85, and -87 dissolves a small amount (≤1%) of niobium. The Cr_2Nb-type phase, on the other hand, contains more than 27% Nb, and the exact amount of niobium in this phase depends on the partitioning of alloying additions in the CN alloys. The element X1 partitions more or less equally in the Cr_2Nb and the Cr-rich phases in CN-80 and -85, and preferentially in the Cr_2Nb phase in CN-87 (containing 20% X4). A careful examination of the Cr_2Nb compositions suggest X1 essentially occupies the chromium subsites. The element X2 in CN-85 and -87 partitions strongly in the Cr_2Nb-type phase, as shown in Table 1. The element X4 was distributed roughly equal in the two phases in CN-87. The partitioning behavior of these alloying elements could not be rationalized by considering both reactivity and atomic size of the alloying elements.

TENSILE PROPERTIES

Button-type tensile specimens with gage dimensions 0.31 cm diam x 0.95 cm long were machined by electro-discharge machining, followed by grinding. The tensile specimens were polished by "0"-grade Emery paper and tested in an Instron testing machine at room temperature in air and at 1200°C in vacuum at a crosshead speed of 0.25 cm/min. Since the tensile properties are sensitive to defects in the alloys, the CN alloys at room temperature were tested using different fabrication conditions to show the defect effect. Table 2 summarizes the tensile results for CN alloys in as-cast, directionally solidified, hot-isostatically pressed (HIPped), and hot extruded conditions. Note that all the specimens were annealed 1 to 3 d at 1200°C prior to tensile testing.

The alloy Cr-5.6Nb-1.5Al-6X1 prepared by arc melting showed a fracture strength at room temperature of 143 MPa. The fracture strength increased to 294 MPa when the alloy was prepared by directional solidification via levitation-zone remelting at the University of Tennessee. The strength further increased to 399 MPa when the arc-cast material was HIPped at 1480°C at 413 MPa (60 ksi). HIPping was used to reduce cast defects in the CN alloys. The best fracture strength at room temperature was obtained for a specimen produced by hot extrusion at 1480°C, which supposedly further reduced cast defects and refined the cast microstructure in CN alloys. A fracture strength as high as 548 MPa was obtained for hot-extruded Cr-12Nb-1.5Al-6X1 (CN-80).

At 1200°C, the CN alloys exhibited significant plastic deformation in tension, with 23% elongation for CN-80, which also had excellent strength at this temperature (see Table 2). For comparison, the strength of Ni-base superalloys, the state-of-the-art high-temperature materials, drops to almost nil at 1200°C. The strength appeared to increase with the niobium

Table 2. Effect of Processing and Alloy Composition on Tensile Properties of CN Alloys

Alloy Composition	Processing*	Fracture Strength (MPa)	Yield Strength (MPa)	Elongation (%)
	Room Temperature			
Cr-5.6Nb-1.5Al-6X1	AM	143		
Cr-5.6Nb-1.5Al-6X1	DS	294		
Cr-5.6Nb-1.5Al-6X1	HIP	399		
Cr-6.0Nb-1.5Al-5X1-4X2 (CN-90)	HE	435		
Cr-12Nb-1.5Al-6X1 (CN-80)	HE	548		
	1200°C			
Cr-6.0Nb-1.5Al-5X1-4X2-2X3 (CN-90)	HE	384	302	13.4
Cr-10Nb-1.5Al-5X1-4X2 (CN-89)	HE	269	238	1.6
Cr-12Nb-1.5Al-6X1 (CN-80)	HE	388	290	23.0

*AM = arc melt; DS = directional solidification; HIP = hot isostatic pressing; HE = hot extrusion at 1480°C.

concentration (or the amount of the Cr_2Nb phase). The data suggest that alloying with 2% X3 significantly increases the strength of CN alloys at 1200°C.

The fracture mode of CN-80 was examined by scanning electron microscopy (SEM). The alloy showed a mixture of both brittle cleavage fracture and intergranular fracture at room temperature. On the other hand, it exhibited a ductile fracture with a dimple appearance at 1200°C. It is known that Cr-based alloys can be embrittled by as little as 100 ppm (or less) of nitrogen or oxygen.[12,13] In order to detect segregation of these interstitial elements in CN-alloys, CN-80 was fractured in an ultra-high vacuum and analyzed by Auger electron spectroscopy (AES). Limited analyses gave no indication of nitrogen or oxygen segregated to grain-boundary facets or cleavage planes in this alloy.

FRACTURE TOUGHNESS

The fracture toughness of CN-87 (Cr-8Nb-1.5Al-5X1-4X2-20X4) hot extruded at 1480°C was determined by three-point bend testing of Chevron-notched specimens. The alloy exhibited a fracture toughness of 7.6 MPa$\sqrt{m}$ at room temperature. The toughness increased substantially with temperature, to 18.3 and 24.4 MPa$\sqrt{m}$ at 800 and 1000°C, respectively. The alloy was so ductile at 1200°C that it could not be fractured by bend testing. The fracture toughness of CN-87 at room temperature is comparable to that of a Cr_2Hf/Cr alloy reported recently by Kumar and Miracle.[12] Figure 5 shows the crack growth modes in CN-87 at room temperature and 800°C. The alloy exhibited a mixed fracture mode at room temperature (Fig. 5a) and a more ductile fracture with Cr-rich patches necking down to a chisel point at 800°C (Fig. 5b).

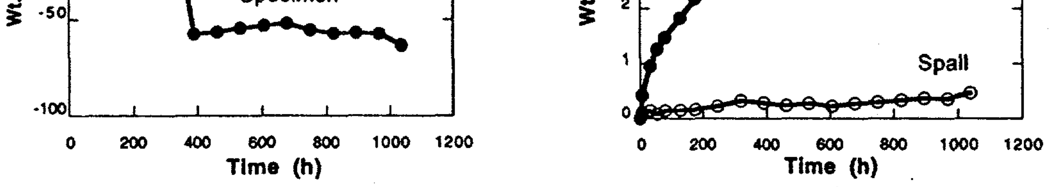
(a) (b)

Fig. 5. SEM fractographs of CN-87 hot extruded at 1480°C and fractured by bend testing at (a) room temperature and (b) 800°C.

HIGH-TEMPERATURE OXIDATION BEHAVIOR

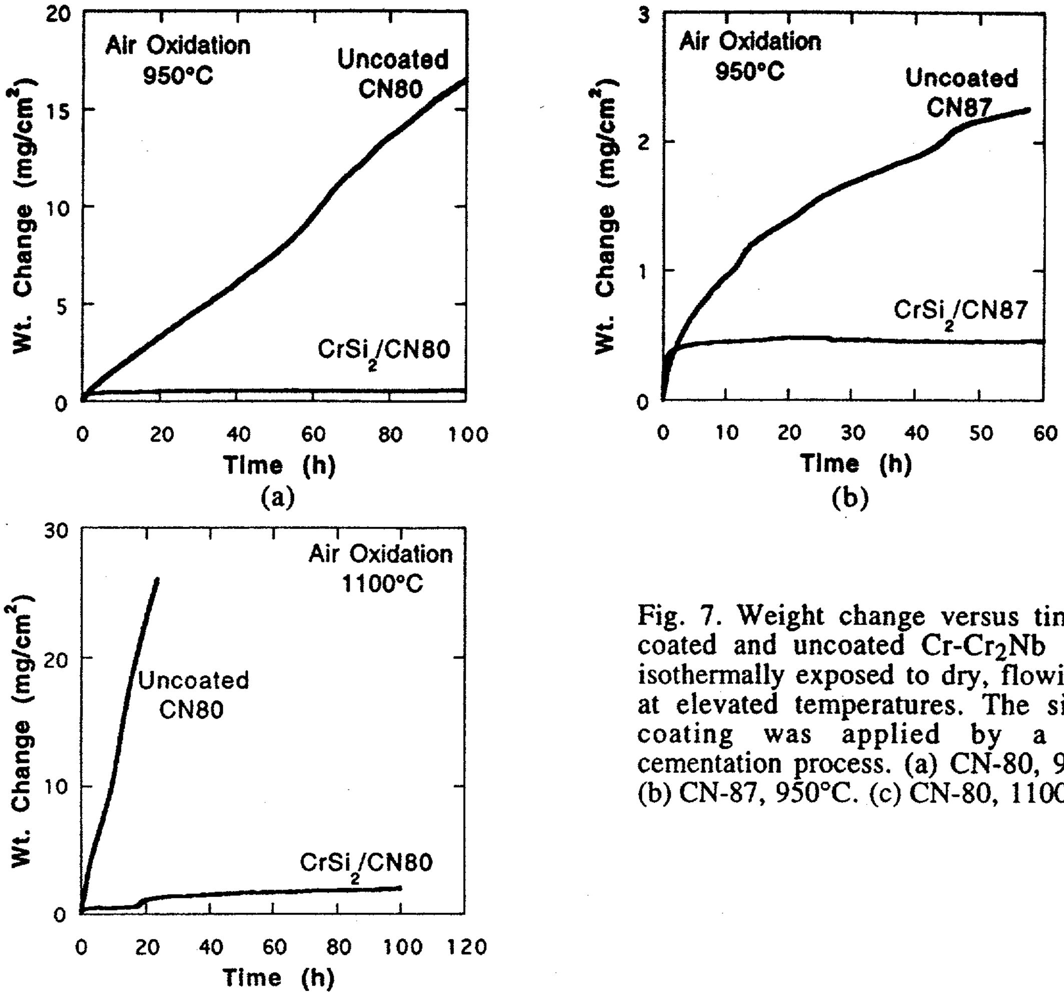
It has been previously demonstrated[9] that the presence of significant concentrations of element X1 substantially increased the isothermal oxidation rates and spallation susceptibilities of $Cr-Cr_2Nb$ alloys, while the addition of X2 completely offset these deleterious effects. The presence of this latter element resulted in the best overall oxidation behavior of all $Cr-Cr_2Nb$ compositions.[9] The effects of X2 were manifested as relatively low weight gains, substantially reduced scale cracking and spallation, and elimination of the dependence of oxidation behavior on niobium content (that is, on the relative amounts of the Cr-rich and eutectic phases). Its beneficial influence was attributed to improvement in the oxidation resistance of the Cr-rich regions (despite its partitioning to the Cr_2Nb phase),[9] which otherwise showed preferential susceptibility to degradation upon exposure to high-temperature air.[8,14] Recent work has shown that the positive effect of X2 on oxidation resistance is maintained under the more severe oxidation conditions associated with thermal cycling. This is shown by the cyclic oxidation results in Fig. 6: the alloy containing X2 (CN-87, see Table 1) showed relatively low weight gains and significantly improved spallation resistance (as characterized by the weight of spalled material) when compared to a Cr-Cr_2Nb composition containing X1 (CN-80).

Element X2 continued to impart a beneficial effect on the rate of isothermal weight gain and spallation resistance up to 1100°C, as shown by comparison of the curves for uncoated CN-80 and -87 in Fig. 7a and b, respectively. However, the oxidation rate at this temperature was still relatively high (as it is for all chromia-formers). Therefore, it was deemed necessary to examine the possibility of using coatings to reduce the oxidization at higher temperatures. To this end, some preliminary experiments were conducted by depositing a germania-doped silicide coating on CN-80 and CN-87 by pack cementation at The Ohio State University.[15] The details of the coating process for these alloys are described elsewhere.[16] In isothermal microbalance exposures in dry air, specimens coated in this manner exhibited very low weight gains at 950 and 1100°C (Fig. 7). The oxidation rate was essentially controlled by the



(a) (b)

Fig. 6. Weight change versus time for specimens cyclically oxidized in air at 950°C. Each point represents one thermal cycle. Closed and open symbols represent weight changes of the specimen and spalled material, respectively. (a) CN-80 (b) CN-87



(a)

(b)

(c)

Fig. 7. Weight change versus time for coated and uncoated Cr-Cr_2Nb alloys isothermally exposed to dry, flowing air at elevated temperatures. The silicide coating was applied by a pack cementation process. (a) CN-80, 950°C. (b) CN-87, 950°C. (c) CN-80, 1100°C.

coatings as there was little difference between the 950°C gravimetric results for coated CN-80 and CN-87 (compare Fig 7a with 7b) despite the significant differences in their oxidation rates when uncoated.

While these initial results with coated Cr-Cr_2Nb are quite encouraging, particularly as the coatings have not yet been optimized for these substrates,[16] the influence of thermal stresses produced during cyclic oxidation on the integrity and adherence of these surface layers, and of the oxide scales that formed on them, must be assessed in some detail. In one microbalance experiment, the exposure was twice interrupted by cooling to room temperature with subsequent reheating to the oxidation temperature. The results, shown in Fig. 8, indicated an abrupt weight gain (probably due to cracking of the scale on the coating) after a thermal cycle, but a rapid healing of any cracks such that the same low oxidation rate was quickly reestablished. While final conclusions regarding the utility of this approach for

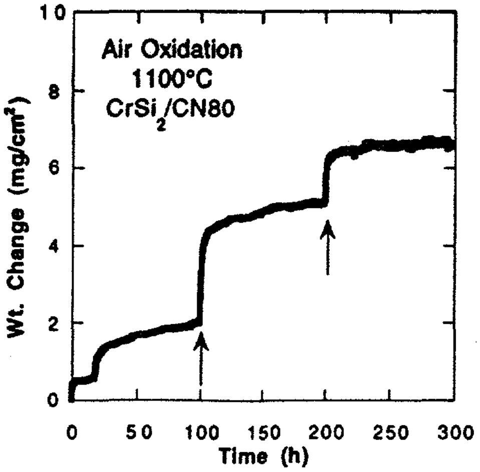


Fig. 8. Weight change versus time for silicide coated CN-80 isothermally oxidized in air at 1100°C. Arrows indicated times at which specimen was cooled to room temperature and then reheated to the exposure temperature.

corrosion protection of these alloys await more rigorous cyclic oxidation testing and coating optimization, the present results indicate that such surface treatments offer excellent promise as effective routes to oxidation resistance for temperatures (such as 1100°C) where the superior strength of Cr-Cr_2Nb alloys can be exploited.

SUMMARY AND CONCLUSIONS

Two-phase Cr-Cr_2Nb alloys (designated as CN alloys) were prepared by arc melting, followed by directional solidification, HIPping, or hot extrusion at 1450 to 1500°C. The secondary processing was used to reduce cast defect structures in CN alloys.

The microstructure of CN alloys containing 6 to 12% Nb depended strongly on alloying addition, heat treatment, and material processing. Hot extrusion at 1480°C was most effective in reducing as-cast defects and refining the cast Cr-Cr_2Nb eutectic structure.

Several beneficial alloying elements have been identified. Element X1 refined the coarse eutectic structure but reduced oxidation resistance. X2 substantially improved both isothermal and cyclic oxidation resistance. X3 strengthened CN alloys at high temperatures. X5 is used to control the morphology of the eutectic structure.

Tensile properties were sensitive to defects in CN alloys. The best results were obtained from hot-extruded CN-80 (Cr-12Nb-1.5Al-6X1) which showed a fracture strength of 548 MPa at room temperature, and an ultimate tensile strength of 388 MPa, with an elongation of 23%, at 1200°C.

The alloy CN-87 fabricated by hot extrusion at 1480°C showed a fracture toughness of 7.6 MPa$\sqrt{m}$ at room temperature. The toughness increased substantially with temperature and reached 24.4 MPa$\sqrt{m}$ at 1000°C.

A silicide coating applied by a pack cementation process substantially improved the oxidation resistance of the Cr-Cr_2Nb alloys at 950 and 1100°C. Such surface layers offer the potential to afford corrosion resistance to these alloys at temperatures (such as 1100°C) at which thermally grown oxides on CN compositions are not protective and, thus, may allow the superior strength of Cr-Cr_2Nb alloys to be exploited.

ACKNOWLEDGMENTS

The authors thank C. G. McKamey and S. J. Pawel for their reviews of the manuscript. This research was sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U. S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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