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Metastable bcc phase formation in the Nb-Cr system

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Abstract

Extended metastable bcc solid solutions of Nb-Xat.%Cr ($X = 35, 50, 57, 77, 82$, and 94) were synthesized by two-anvil splat-quenching. In addition, bcc(Nb-67at.%Cr) was prepared by mechanically alloying mixtures of niobium and chromium powders. The lattice parameters were measured by X-ray diffraction and the Young's moduli were measured by low-load microindentation. The composition dependence of the lattice parameters and elastic moduli show a positive deviation with respect to a rule of mixtures. During continuous heating at $15^{\circ}\text{C}/\text{min.}$, the metastable precursor bcc phases decomposed at temperatures above 750°C to uniformly refined microstructures.

1. Introduction

Alloys based upon NbCr₂ are being explored for high-temperature structural applications [1-3] because of the high melting temperature ($\sim 1730^{\circ}\text{C}$), reasonable oxidation resistance [4,5], appreciable creep resistance [4], and high-temperature strength [6] of the ordered intermetallic compound. In addition, the NbCr₂ Laves phase exhibits a relatively wide single-phase homogeneity range and forms a Laves/bcc two-phase field with both (Nb) and (Cr) on either side of the compound in the binary system. Composite structures of a C15 Laves phase and a bcc phase have been shown to improve the low-temperature toughness in the Nb-Cr [7] and other systems [8,9].

The Nb-Cr phase diagram has been investigated recently to resolve conflicting phase boundary and invariant eutectic compositions under equilibrium conditions [10] and is shown in Figure 1 along with the calculated $T_0(\text{bcc/liquid})$ [11]. Based upon the continuous $T_0(\text{bcc/liquid})$ between niobium and chromium, the formation of a continuous bcc solid solution appears possible. The objective of this study was to examine the formation of metastable bcc solid solutions in the Nb-Cr system by rapid

solidification and by mechanical alloying, as well as to explore the mechanical properties and the thermal stability of the metastable product in this high-temperature system.

2. Experimental procedure

The rapid solidification technique of two-anvil splat-quenching was employed on the nominal alloy compositions illustrated in Figure 1. The splat-quenching process started with the levitation melting of a 60-100 mg piece of an arc-cast ingot in an evacuated (10^{-3} Pa) and purged Ar environment (~ 0.5 atm). The falling molten droplet was splat-quenched between the two copper anvils at an estimated cooling rate of 10^5 to 10^8 K/s [12] in the resultant foil (~ 25 - $50\mu\text{m}$ thick). A Nb-67at.%Cr alloy powder was prepared by mechanical alloying (MA) elemental powder mixtures in a SPEX mill (model 8000) using a tungsten carbide vial and ball. The ball-mill resided in a glove box with a recirculated high-purity argon environment (< 0.1 ppm O_2 and < 1 ppm H_2O).

The purities of the Nb and Cr pieces used for arc-melting of the Nb-Cr ingots were 99.8% and 99.99%, respectively. After arc-melting, the ingots contained 0.002 wt.% oxygen and 0.004 wt.% nitrogen, as determined by inert-gas fusion analysis. The Nb and Cr powder used for MA was less than $44\mu\text{m}$ in diameter and had the same metal purity as the bulk metals. After processing, alloy compositions were determined with elemental standard-based energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) with Cu $K\alpha$ radiation was used to measure the lattice parameters [13], and the machine accuracy was calibrated using Nb and Cr standards to within 0.02%. The Young's modulus of the splat-quenched foils were evaluated with a low-load microindentation mechanical properties microprobe (MPM) [11,14,15].

3. Results

The XRD scans of the seven splat-quenched alloys are given in Figure 2. The niobium-rich and chromium-rich alloys show only diffraction peaks of the metastable bcc phase. The alloy compositions close to NbCr_2 show diffraction peaks for the metastable bcc phase at the nominal composition which formed during rapid quenching. In addition the patterns indicate diffraction peaks for the metastable C14 phase and the stable C15 Laves phases [10] which are in coexistence with the equilibrium bcc phases. The splat-quenched sample at the NbCr_2 composition exhibits no bcc diffraction peaks.

An etched cross-section of the splat quenched Nb-82%Cr alloy is shown in Figure 3a together with a schematic of the microstructure in Figure 3b. The microstructure consists of a mottled columnar-type growth of the bcc phase emanating from each anvil side of the foil and growing into the middle of the splat, where impingement of the two growth fronts occurs. Fine equiaxed eutectic grains are apparent in the middle of the splat. A proposed solidification pathway in the splat-quenched alloy which is consistent with the XRD results and microstructural development is given in Figure 3c. For example, to promote an extended bcc solid solution from the liquid of eutectic composition, a minimum liquid undercooling of $\sim 0.04T_m$ is required to reach the $T_0(\text{bcc/liquid})$ (dotted line). In fact, the liquid undercooling is probably significantly larger than $0.04T_m$ since the XRD peaks for the metastable bcc phase that forms have a higher intensity than the peaks for the bcc phase that is in equilibrium with the Laves phases. Upon recalescence, the initial solid formation approaches partitionless freezing, as shown by the vertical lines in the schematic (Fig. 3c). The schematic suggests that as recalescence proceeds, the solid formation partitions towards the Cr-rich extended solidus boundary, yielding the asymmetric skew towards larger 2θ values in the bcc diffraction peaks of curve (b) in Fig. 2. At the completion of recalescence, the final liquid composition should lie in the coupled eutectic region, accounting for the fine middle layer of eutectic grains in the splat foil microstructure.

Since the metastable bcc solid solution could not be detected after splat-quenching at the NbCr₂ composition, MA was utilized as an alternate processing method. In the mechanically alloyed Nb-67%Cr powder, EDS analysis showed that the composition of sample was very close to nominal. Elemental impurities of tungsten or cobalt were not detected, even after milling times up to 159 hours. The XRD plots for the powder as a function of ball-milling times are represented in Figure 4. Separate powder batches were mechanically alloyed for 5, 20, 45, and 159 hours. Broadening of the Nb and Cr diffraction peaks occurred after 5 hours of MA. After 20 hours of MA, the asymmetric skewing of the Nb diffraction peaks (towards higher 2θ values) and the Cr diffraction peaks (towards lower 2θ values) indicates the solubility of Cr and Nb into the respective bcc solutions. The Nb-rich and Cr-rich diffraction peaks start to overlap after 45 hours of ball-milling time. After 159 hours of MA, only one bcc phase was evident in the XRD trace.

To characterize the metastable product beyond XRD, MPM analysis was done on the splat-quenched Nb-50%Cr and Nb-82%Cr alloys and on pure niobium and pure chromium. Continuous regions of the metastable bcc phase existed through the majority of the alloy foils enabling consistent

and reproducible elastic modulus measurements of this phase. The Young's modulus values of the alloys were 215 and 300 GPa $\pm$ 5 GPa, respectively. The modulus for pure niobium and pure chromium were 105 GPa and 280 GPa, respectively, which agree to better than 1 % with the values quoted in the literature [16].

The lattice parameters (translated to average molar volumes) and moduli of the bcc solid solutions are plotted against the experimentally determined compositions in Figure 5. The solid circles representing molar volumes for compositions within the terminal solubilities (<24 % Cr and >94 % Cr) were obtained from quenching homogenized alloys from varying temperatures [10] whereas the solid circles for compositions outside these limits were from the rapidly quenched liquids. The molar volume of the metastable bcc phase formed by MA is shown by the open circle in the figure. The bcc phase moduli of chromium, 50%Cr, 82%Cr, and niobium are indicated on Fig. 5 with solid squares. The open square moduli were determined from MPM measurements on monolithic NbCr₂ ingots [11] and are shown for comparison. Both sets of data have empirically fitted lines drawn through them, displaying a positive deviation with respect to rule of mixtures.

After the metastable synthesis the thermal stability of the splat-quenched eutectic alloys and the mechanically alloyed sample was investigated by differential thermal analysis (DTA) using heating rates of 15°C/min. The Nb-50%Cr and Nb-82%Cr alloys decomposed at 885°C and 930°C, respectively. The Nb-67%Cr sample decomposed at 750°C. XRD analyses after decomposition of the splats showed the expected coexistence of equilibrium C15 Laves and bcc structures [10,17]. The ball-milled Nb-67%Cr powder decomposed to the Laves phase with no detectable bcc phases.

SEM micrographs (back-scattered mode) of the decomposed Nb-50%Cr and Nb-82%Cr splats are given in Figures 6a and 6b. The structure of the Nb-50%Cr alloy (Fig. 6a) shows a continuous dark matrix of NbCr₂ with isolated light dispersoids (approximately 1 μ m in size) of the Nb solid solution. The structure of the Nb-82%Cr alloy (Fig. 6b) consists of a continuous light matrix NbCr₂ with isolated dark dispersoids of the Cr solid solution, approximately 1 μ m in size.

4. Discussion

It is not surprising that the Nb-Cr system forms a continuous *metastable* solid solution since it obeys Hume-Rothery Rules for solid solubility. The normalized difference between the atomic radii of metallic Nb and Cr is 13.8%, and the elements have the same crystal structure (bcc) and display similar

electronegativities. Moreover, the measured bcc molar volumes show only a slight positive deviation with respect to Vegard's Rule which may be associated with the tendency for a positive heat of mixing [11]. In the analogous Ti-Cr system [18] a similar behavior is observed along with an indication of a molar volume decrease and hardness increase near TiCr_2 suggesting other localized atomic interactions may be operative at the intermetallic composition.

The metastable bcc solid solutions are relatively stable, with decompositions during continuous heating occurring at temperature close to 60% of the $T_0(\text{bcc/liquid})$. After decomposition of the splat-quenched metastable bcc solutions to the equilibrium phases, the resultant microstructures are dual phase alloys consisting of an NbCr_2 Laves phase matrix with isolated bcc dispersoids of either Nb or Cr solutions. The decomposition of a metastable precursor bcc phase produced with either rapid solidification or mechanical alloying contrasts to other in-situ multi-phase microstructure formation techniques (such as directional solidification or precipitation) in that the volume fractions of the phases can be designed to specific amounts. Therefore, considering the potential of NbCr_2 as a candidate high-temperature structural material, particularly in composite form, an effective microstructural tailoring scheme to produce controlled multi-phase microstructures of NbCr_2 -based materials has been demonstrated with rapid solidification processing.

5. Conclusions

Three main points are evident with the splat-quenching and MA of Nb-Cr alloys.

1. An extended metastable bcc solid solution can be produced between niobium and chromium.
2. The composition dependence of the lattice parameters and elastic moduli show a positive deviation with respect to a rule of mixtures.
3. Decomposition of the metastable bcc precursor phase offers an effective technique to prepare uniformly refined NbCr_2 -based microstructures.

Acknowledgments

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Figure Captions

Figure 1 - Nb-Cr phase diagram. Arrows indicate nominal compositions of alloys studied.

Figure 2 - XRD traces of splat-quenched Nb-Cr alloys for the nominal atomic percent compositions of a) 94%Cr, b) 82%Cr, c) 77%Cr, d) 67%Cr, e) 57%Cr, f) 50%Cr and g) 35%Cr

Figure 3 - Microstructural development in a splat-quenched Nb-82%Cr sample where a) SEM etched micrograph, b) schematic of microstructure, and c) proposed solidification pathway

Figure 4 - XRD traces of powder samples after progressively increasing MA times

Figure 5 - SEM micrographs (back-scatter image mode) of the splat-quenched and decomposed a) Nb-50%Cr and b) Nb-82%Cr samples

Figure 6 - Plots of Young's moduli and average molar volumes as a function of measured composition.

Fig. 1

Fig. 2

Fig 3

Fig. 4

Fig. 5

Fig. 6

a

b

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