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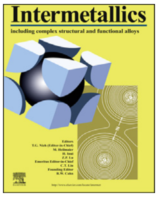

Effect of Cr on the evolution of microstructures in as-cast ternary niobium-silicide-based composites

Poulami Maji, R. Mitra, K.K. Ray*

Department of Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

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ABSTRACT

The aim of this report is to present the effect of chromium on the detailed microstructural evolutions in Nb-Si-Cr ternary alloys. The microstructural characteristics of as-cast Nb-Si-Cr ternary alloys with five different compositions have been studied using SEM and XRD. In addition, the lattice parameter and the microhardness of the constituent phases were also estimated. The microstructures of the investigated alloys primarily reveal the presence of three phases: $(Nb, Cr, Si)_{ss}$, $Nb_5(Si_x, Cr_y)_3$ and $Nb(Cr_x, Si_y)_2$. The nature, morphology and the amount of the phases, as well as that of the eutectic domains, are found to vary with the composition of the investigated alloys. The lattice parameter of the $(Nb, Cr, Si)_{ss}$ phase decreases, whereas that of the silicide phase first increases and then decreases with increasing concentration of Cr in the investigated alloys. The effect of Cr on the microhardness of $(Nb, Cr, Si)_{ss}$ is more significant compared to that of the adjacent silicide, or the laves phase or that of the eutectic domains.

1. Introduction

There have been continued efforts directed towards the development of refractory metal silicides like niobium silicide based alloys for high-temperature applications [1–5]. These refractory materials usually possess poor ductility and inferior fracture toughness at room temperature, as well as somewhat inadequate oxidation resistance. Several attempts have been made in the past to overcome these drawbacks by addition of suitable alloying elements like Al, Hf, Ti, Cr, Mo, W, V, Ga, Mg, etc. [2,4–8]. Of all these elements, chromium is known to improve the oxidation resistance of the alloys by forming a protective surface oxide layer [9]. But only scattered information is available on the effect of Cr on the evolution of microstructural features like the nature and volume fraction of the phases in different Nb-Si-Cr alloys.

In order to understand the evolution of the phases in Cr-added Nb-silicides, it is a-priori required to examine the binary Nb-Si as well as the available information related to ternary Nb-Si-Cr phase diagrams. The equilibrium Nb–Si phase diagram [10] shows that Nb_{ss} and Nb_3Si constituents form through the eutectic reaction at 1915 °C. On lowering the temperature to 1765 °C, the Nb_3Si phase decomposes leading to the formation of $Nb_{ss} + Nb_5Si_3$ mixture through a eutectoid reaction. The earlier attempts to examine Nb-Si-Cr system include thermodynamic modeling and generation of a few isotherms of this system [11–16].

Geng et al. [17] have reported studies on Nb–18Si–15Cr ingot in as-cast and heat-treated conditions and have identified Nb_{ss}, $NbCr_2$ (C14) and Nb_5Si_3 phases in its microstructures. On the other hand, Deal et al. [18] have identified Nb_{ss}, $NbCr_2$ and Nb_5Si_3 phases in the microstructure of Nb-8Cr-16Si alloy, and Nb_{ss}, $NbCr_2$ plus an unknown phase (possibly Nb_9Cr_4Si) in the microstructure of Nb-25Cr-12Si alloy. Liquid–solid phase equilibrium at the niobium-rich region of the Nb-Si-Cr system has been examined by Bewlay et al. [9] using a series of as-cast directionally solidified Nb-Si-Cr alloys. These investigators have shown: (a) six invariant reactions at the liquidus surface of the metal-rich region of the Nb-Si-Cr system, (b) existence of phases Nb_{ss}, Nb_5Si_3, and $NbCr_2$ (C14), as well as (c) presence of an additional ternary phase $Nb_9(Cr, Si)_5$ in the investigated alloys. The ternary phase $Nb_9(Cr, Si)_5$ reported by Bewlay et al. [9] in as-cast Nb–18Si–15Cr alloy is absent in a similar alloy reported by Geng et al. [17] indicating contradictory observations, which needs clarification. Further, the presence of eutectic domains in the Nb-Si based ternary alloys with both lamellar and non-lamellar morphology has been reported by Chattopadhyay et al. [4] and Kim et al. [6]. Chattopadhyay et al. have reported the

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* Corresponding author.
E-mail addresses: poulami@metal.iitkgp.ernet.in, poulamim2015@yahoo.in (P. Maji), rahul@metal.iitkgp.ernet.in (R. Mitra), kkrmt@metal.iitkgp.ernet.in, kalyankumarry@yahoo.com (K.K. Ray).

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influence of coarse eutectic on the fracture toughness of the alloys [4]. It is well known that interlamellar spacing of the eutectic constituents has direct influence on the property of the concerned alloys. So morphology of these phases and their distribution are expected to be important parameters that would control the performance of Nb-Si based alloys. But investigation related to the morphology of the eutectic constituents in the Nb-Si-Cr systems has not been explored so far. Cast materials are usually preferred for their inherent advantages of being cost effective and for the manufacture of structural components with intricate design. Thus study of cast structures is required, which provides the guideline to design materials possessing desirable mechanical properties with suitable microstructures.

This report deals with the influence of Cr on the morphology and the nature of the phases in five Nb-Si-Cr alloys, in which the compositions have been selected to represent both hypo- and hyper-eutectic domains corresponding to the Nb-Si system. The objective is to achieve a systematic understanding of the evolution of microstructure in Nb-Si-Cr alloy for a limited composition range.

2. Materials and experimental details

Five varieties of chromium added niobium-silicon based ternary alloys were prepared by arc melting using Cr (99%), Nb (99.7%), and Si (98.6%) powders with their purity in wt.% as shown in the parenthesis. The powders were thoroughly mixed in selected proportions in a ball mill for 3 h in acetone medium. Pellets of 10 mm diameter and approximate height of 10–12 mm were made by compaction at the pressure of ≈ 16 MPa. These were next subjected to arc-melting in argon atmosphere inside a water-cooled copper crucible with the help of non-consumable tungsten electrode. The ingots were turned and remelted at least five times inside the crucible to achieve chemical homogeneity. The compositions of the prepared alloys were estimated using bulk Energy Dispersive X-ray (EDX) analyses. The prepared alloys are referred to as CrA (Nb-15Si-32Cr), CrB (Nb-13Si-22Cr), CrC (Nb-18Si-23Cr), CrD (Nb-16Si-9Cr) and CrE (Nb-9Si-7Cr), where the numeric values indicate their compositions in approximate atomic percentages.

Samples for microstructural observations were fabricated from the arc-melted ingots using wire electro-discharge machining (EDM). Microstructural studies were carried out on metallographically polished and etched specimens of all the alloys; etching was done using a reagent comprising of 5 ml HNO_3, 10 ml HF, 15 ml H_2SO_4 and 50 ml distilled water. The microstructures were first examined using optical (Leica Microsystems, Germany, Model: Q550IW) and scanning electron microscopes (SEM) (Carl Zeiss, Germany, Model: Supra 40 FESEM) equipped with an energy dispersive X-ray (EDX) micro-analyzer (Oxford Instruments Ltd., UK Model: ISIS300). The SEM was operated at EHT = 20.00 kV and WD = 10–13 mm. The chemical compositions of the individual phases were analyzed using the EDX analyzer. Representative SEM microstructures were recorded for measuring volume fractions of the concerned phases in each of the alloys using point-counting analysis. For this measurement, a rectangular grid having 21×21 grid points was superimposed on the microstructure. The number of grid points falling on a phase of interest was counted to estimate the volume fraction of the concerned phase. In addition the volume fractions of the phases were also estimated using image analysis technique.

X-ray diffraction (XRD) analyses were done for identification of the phases with a diffractometer (BRUKER AXS, GERMANY, Model: D8 Advance), operated with the help of Cu K_α radiation; the X-ray source was operated with voltage of 40 kV and current of 40 mA. The diffraction angle was varied in the range of 20^o-140° at a fixed scan rate of $0.06^\circ\ s^{-1}$. The lattice parameters of the constituent phases of the Nb-Si-Cr alloys have been determined using Cohen's method [19]. Further microhardness of the major phases were measured with the help of a Leco microhardness tester (Model: LM700) operated at loads of 0.05 N for Nb_{ss} phase and at 0.1 N for other phase constituents in a way that an indentation remains well within the phases. At least ten indentations were made on each of the phase for the investigated alloys in order to estimate their average hardness values.

3. Results and discussions

Five Nb-Si-Cr base ternary alloys having low as well as high Cr compositions, representing nearly both hypo- and hyper-eutectic sides of the binary Nb-Si alloys, were prepared through the arc-melting process. The elemental losses of the ingredients during melting were of an uncertain amount, and hence trial and error approaches were employed to achieve the desired compositions. The compositions of the prepared alloys are shown in Table 1.

3.1. *Microstructure of the investigated alloys*

Microstructural examinations of the investigated alloys have been carried out using optical microscope, scanning electron microscope, EDX analyses of the distinguishable phases and XRD in order to reveal the nature, morphology and the amount of their various phase constituents. These examinations have been done to understand the effect of Cr addition on the relative amounts of the phases in the investigated Nb-Si-Cr alloys. It may be noted that the alloys, CrA, CrB and CrC contain higher concentration of Cr compared to the alloys CrD and CrE.

3.1.1. *High chromium alloys*

The phases present in the as-cast alloys, CrA, CrB and CrC, have been identified by XRD analyses, as shown in Fig. 1. XRD analyses indicate the presence of distinct peaks from (110) plane of Nb_{ss}, (213) plane of α-$Nb_5(Si, Cr)_3$, and (112) plane of hexagonal $Nb(Cr,Si)_2$ at θ positions closely corroborating to those of Nb, α-Nb_5Si_3, (C14) $NbCr_2$ as can be obtained from ICDD database (Fig. 1). At least five low-intensity peaks for each of above constituent phases could be distinguished from the X-ray line profiles, as shown in Fig. 1. The XRD patterns also exhibit the presence of a few additional low-intensity peaks, which do not correspond to any of the above-mentioned phase constituents; these peaks interestingly are found to represent the β-Nb_5Si_3. The observed peaks exhibit minor shifts in 2θ positions with respect to the ICDD data of Nb, α-Nb_5Si_3, (C14) $NbCr_2$ and β-Nb_5Si_3; the peak shifts are considered to originate from their Cr content in substitutional solid solution.

The microstructures of the alloys, CrA, CrB and CrC exhibit three major phases as distinguished by grey-scale contrast: bright, grey and dark grey (Figs. 2–4). The amount of the constituent elements in the phases of the high chromium alloys, as indicated by EDX analyses are shown in Table 2. The atomic percentages of the constituent elements (Table 2) suggest the chemical formulae of the phases to be niobium solid solution [$(Nb, Cr, Si)_{ss}$, bright phase], niobium silicide [$Nb_5(Si, Cr)_3$, grey phase] and the Laves phase [$Nb(Cr, Si)_2$, dark grey phase]. The niobium solid solutions in high chromium alloys consist of 12.7–14.7 at.% Cr and 2.1–3.4 at.% Si (Table 2). The obtained results are in tune with the maximum solubility of Cr (≈ 15 at%) and Si (≈ 3.5 at.%) in Nb_{ss} as expected from the binary Nb-Cr and Nb-Si phase diagrams, respectively. The stoichiometric ratio of at.% of Nb to at.% of (Cr + Si) as indicated by EDX analyses in the grey and the dark grey phases are found to be 5:3.3 and 1:1.7, respectively. These ratios are close to stoichiometric ratios of 5:3 and 1:2 for the silicide and the Laves phase, respectively, and hence the chemical compositions of the grey and dark