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Experimental study of the solid-liquid phase equilibria at the Si-rich region of the Cr-Nb-Si system

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ABSTRACT

High temperatures solid-liquid equilibria in the Cr-Nb-Si system are poorly known in the Si-rich area (> 20% at Si). In this study, twenty-two as-cast samples were prepared and fully characterized using X-ray diffraction, scanning electron microscopy and quantitative energy dispersive spectrometry. Obtained results lead us to propose a new schematic layout of the liquidus projection of this system.

1. Introduction

Niobium silicide based composites are potential candidates for replacing nickel-based superalloys in aerospace applications [1]. These materials are also known to possess poor oxidation resistance at high temperatures [2]. Elements such as titanium, hafnium, chromium and aluminium are present in the most promising compositions of these niobium alloys. Addition of these elements is necessary to reach the physico-chemical properties required for the targeted high-temperature applications. The role of Ti, Hf, Cr and Al is mainly to improve the low oxidation resistance of the niobium solid solution phase [3]. Therefore, previous work focused on the Nb-Si sytem and results were extended to more complicated systems including Cr, Hf, Ti and Al as alloying elements [4,5]. Cr appears to be an efficient alloying element to prevent oxidation [6] as it promotes the stabilization of the $CrNb_2$ Laves phases (C14 and C15 structures) [5]. Cr is also used to elaborate protective coatings by pack cementation process [7–10]. Therefore, the determination of the Cr-Nb-Si system was the purpose of several previous studies.

The Cr-Nb-Si ternary system was firstly investigated by Goldschmidt et al. [11], but the results were claimed by Zhao et al. [5] as being not relevant because equilibria were not reached. These authors produced the main experimental work on this system, focused on the 1000 and 1150 °C isothermal sections. Three ternary phases were evidenced: CrNbSi, $(Cr, Nb)_6Si_5$ and $(Cr, Nb)_{11}Si_8$. The first one is stoichiometric whereas the other two exhibit intersolubility of Nb and Cr in the metal sites (at constant Si at%). The Cr_2Nb (C14) Laves phase appears to be stabilized with addition of Si. Further work [12] evidenced a three phase equilibria region (Nb)-Cr_2Nb(C14)-Nb_5Si_3 at 1000 °C and 1500 °C instead of (Nb)-CrNbSi-Nb_5Si_3 as proposed by [5]. The only experimental work involving the liquid phase was published by Bewlay et al. [13]. It consists of a partial liquidus projection in the (Nb, Cr)-rich area of the Cr-Nb-Si system (< 30 at% Si). Bewlay et al. report the stability of a new ternary phase - $Cr_3Nb_9Si_2$ also designated by $Nb_9(Cr, Si)_5$, which forms a small primary solidification region close to its ideal stoichiometry [13]. Another remarkable feature of their results is a very large primary solidification region for the β-Nb_5Si_3 phase, extending from the Nb-Si to the Cr-Si binary borders. Some other works evidenced the existence of other ternary phases: $CrNb_4Si_3$ [14], $Cr_2Nb_3Si_3$ which is considered as metastable [9] and the high temperature phase $Cr_3Nb_2Si_3$ (T > 1250 °C) [8]. All the phases are listed in Table 1.

Two thermodynamic modeling of the Cr-Nb-Si ternary system were proposed in the literature by Shao [15] and David et al. [16]. Shao used experimental data of annealings from [11] and of diffusion couples from [5] at temperatures up to 1150 °C for his assessment, while David et al. also considered equilibrium experiments at 1200 °C and the enthalpy of formation $(Cr, Nb)_6Si_5$ measured by direct-synthesis calorimetry at 1200 °C. Shao [15] proposed also a calculated liquidus projection. Despite its prospective nature, the results of Bewlay et al. [13] agree well with it except for the extension of the primary solidification area of the β-Nb_5Si_3 phase and the existence of for the high temperature new phase $Cr_3Nb_9Si_2$.

The present work is an experimental study of the solid-liquid

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Table 1
Crystal structures of phases, system Cr-Nb-Si sytem [5,8,14,15].

Phase	Pearson symbol	space group
Cr	cI2	$Im\bar{3}m$
Nb	cI2	$Im\bar{3}m$
Si	cF8	$Fd\bar{3}m$
Cr_3Si	cP8	$Pm\bar{3}n$
βCr_5Si_3	hP16	$P6_3/mcm$
αCr_5Si_3	tI38	$I4/mcm$
CrSi	cP8	$P2_13$
$CrSi_2$	hP9	$P6_222$
Nb_3Si	tP32	$P4_2/n$
βNb_5Si_3	tI32	$I4/mcm$
αNb_5Si_3	tI32	$I4/mcm$
$NbSi_2$	hP9	$P6_222$
Cr_2Nb (C14)	HP12	$P6_3/mcm$
Cr_2Nb (C15)	cF24	$Fd\bar{3}m$
CrNbSi	HP9	$P\bar{6}_2m$
$CrNb_4Si_3$	tI32	$I4/mcm$
$Cr_2Nb_3Si_3$	tI32	I4/ mcm
$Cr_3Nb_2Si_3$	hP16	$P6_3/mcm$
$(Cr, Nb)_6Si_5$	oI44	$Ibam$
$(Cr, Nb)_{11}Si_8$	OP76	$Pnma$
$Cr_3\ Nb_9Si_2$		$I4/mcm$

equilibria in the Cr-Nb-Si system and focuses on the Si-rich area (> 20 at% Si). Twenty-two as-cast samples were prepared and their microstructures were characterized combaining X-ray diffractometry, scanning electron microscopy and quantitative energy dispersive spectrometry.

2. Experimental procedure

22 as-cast samples were prepared with compositions chosen in order to be a complement to the study of Bewlay et al. [13]. These compositions are summarized in Tables 2 and 3 and their corresponding localization on the Gibbs triangle are shown on Fig. 1.

Samples were manufactured by triple melting mixture of the pure elements (purity higher than 99.9%) under Ti-gettered argon atmosphere in an arc melting furnace using a non-consumable tungsten electrode and a water-cooled copper crucible. Rapid solidification of the samples was achieved by abrupt interruption of the arc during melting in order to define the primary phase and the solidification path.

For each sample, phases in the microstructure were determined by X-ray diffraction (XRD) on fine powders using a Cu anticathode ($\lambda_{k\alpha1}$=1.54056 Å) and by matching the characteristic XRD peaks against the ICDD data. A Philips X′Pert Pro diffractometer equipped with a fast X′Celerator detector was used to perform the measurements.

Phase compositions were obtained by scanning electron microscopy (JEOL JSM7600F) in association with an Energy Dispersive X-ray spectrometer (EDS) and a wavelength dispersive spectrometer (WDS, wave oxford). JEOL JSM7600F is a schottky field emission Scanning Electron Microscope (SEM). This SEM provides a stable current which is measured by a faraday cup.

A X-Max[20 mm^2] Silicon Drift Detector (Oxford Instruments) with INCA software was used for analysis. The experimental condition was 15 kV to 1.5 nA with polished samples. A calibration was performed before each session using $NbSi_2$ (for Nb) and $CrSi_2$ (for Cr and Si) standards.

INCA software uses the XPP matrix correction scheme developed by Pouchou and Pichoir [17]. This is a Phi-Rho-z approach which uses exponentials to describe the shape of the $\varphi(\rho z)$ curve. The atomic number and absorption effects are included by integrating a model for $\varphi(\rho z)$. Since the correction factors are dependent on the composition of the sample (which is what we trying to determine), the true concentrations have to be derived using an iterative procedure.

Table 2
Phases present in the as-cast microstructures (DRX and EDS measurements), samples 1–10.

Samples (at%)	Primary phase	Other phases
1- Nb10Cr30Si60	**$NbSi_2$**	**$NbSi_2$** $(Cr, Nb)_6Si_5$ CrSi2
2- Nb20Cr20Si60	**$NbSi_2$**	**$NbSi_2$** $(Cr, Nb)_6Si_5$ $CrSi_2$
3- Nb30Cr10Si60	**$NbSi_2$**	**$NbSi_2$** $(Cr, Nb)_6Si_5$ $CrSi_2$
4- Nb5Cr20Si75	**$NbSi_2$**	**$NbSi_2$** $CrSi_2$ Two phases equilibria: ($CrSi_2$/Si)
5- Nb5Cr37Si58	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** CrSi2 ternary eutectic: [$(Cr, Nb)_6Si_5$/CrSi/$CrSi_2$]
6- Nb6Cr43Si51	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** CrSi ternary eutectic: [$(Cr, Nb)_6Si_5$/CrSi/$CrSi_2$]
7- Nb7Cr50Si43	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** Cr5Si3 CrSi CrSi2
8- Nb18Cr37Si45	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** Cr_5Si_3 ternary eutectic: [$(Cr, Nb)_6Si_5$/CrSi/$CrSi_2$]
9- Nb22Cr25Si53	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** $NbSi_2$ $CrSi_2$
10- Nb38Cr8Si54	**$(Cr, Nb)_6Si_5$**	**$(Cr, Nb)_6Si_5$** $NbSi_2$ $CrSi_2$

3. Results and discussions

All results (XRD and EDS) are summarized in Tables 2 and 3. They lead to propose a new schematic layout of the liquidus projection of the system (Fig. 1). Almost all phases, binary or ternary identified by [5,15,16] present a field of primary crystallization. CrNbSi and $(Cr, Nb)_{11}Si_8$ are the only ones who were not observed as primary phase during our investigations. We believe that the primary phase region of $(Cr, Nb)_{11}Si_8$, if it exists, is really thin. Phases compositions are presented in online Supplementary material.

3.1. $NbSi_2$ primary phase region

$NbSi_2$ is the primary phase in 4 samples (1–4). Its primary phase field is much larger than the one proposed in [15]. $NbSi_2$ is the primary phase when Si is about 60 at% (samples 1, 2 and 3). Fig. 2a is an optical micrograph of sample 2 and the microstructure reveals that the precipitation of $NbSi_2$ (white phase) is followed by the solidification of $(Cr, Nb)_6Si_5$ (grey phase) and then by $CrSi_2$ (dark phase).

The as-cast microstructure of sample 4 is slightly different (Fig. 2b) and the last liquid to solidify reaches the binary eutectic L=$CrSi_2$+Si. It's not obvious to know the nature of the invariant reaction involving $NbSi_2$, Si and $CrSi_2$. There are two options for the solidification path -i) if the $NbSi_2$ / $CrSi_2$ equilbria line joins the Si/$NbSi_2$ equilibria and then reach the binary eutectic $CrSi_2$/Si or, -ii) if the $NbSi_2$/$CrSi_2$, Si/$NbSi_2$ and Si/$CrSi_2$ equilibria lines join to form a ternary eutectic Si/$NbSi_2$/$CrSi_2$. In Fig. 1, we consider the ternary eutectic L=Si+$NbSi_2$+$CrSi_2$ as existing.

3.2. $(Cr,Nb)_6Si_5$ primary phase region

$(Cr, Nb)_6Si_5$ is the primary phase in 6 different samples (5–10). The primary phase field is also extended. Thus, $(Cr, Nb)_6Si_5$ is the primary