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Original Research

# Oxidation behaviours of Nb–22Ti–15Si–2Al–2Hf–2V–(2, 14)Cr alloys with Al and Y modified silicide coatings prepared by pack cementation

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## Abstract

Al and Y modified silicide coatings on the Nb–15Si–22Ti–(2,14)Cr–2Al–2Hf–2V alloys (where the alloy with 2 at% Cr or 14 at% Cr is hereafter referred to as 2Cr and 14Cr alloy, respectively) was prepared by pack cementation. The microstructural evolution and the oxidation behaviours of the coating 2Cr and 14Cr samples at 1250 °C were studied. The 2Cr alloy consists of Nb solid solution ($Nb_{SS}$) and α-$Nb_5Si_3$ silicide, while the Laves C15–$Cr_2Nb$ phase arised in the 14Cr alloy. The coating structure of the coating 2Cr sample contained the outer (Nb, X)$Si_2$ + (Nb, X)$_5Si_3$ layer, the middle (Nb, X)$_5Si_3$ layer and the inner undeveloped intermetallic (Nb,Ti)$_3$(Al,X) layer; the structure of the coating 14Cr sample consisted of the outer single (Nb, X)$Si_2$ layer, the middle (Nb, X)$_5Si_3$ layer, the transition (Nb,Ti) (Cr,Al) layer and the inner (Cr, Al)$_2$(Nb,Ti) layer. The coating 14Cr sample exhibited better oxidation resistance than the coating 2Cr sample. With an outer single (Nb, X)$Si_2$ layer, a compact oxide scale consisting of $SiO_2$ and $TiO_2$ formed on the coating 14Cr sample, which can efficiently prevent the substrate from oxidising. For the coating 2Cr sample with an outer (Nb, X)$Si_2$ + (Nb, X)$_5Si_3$ layer, the oxide scale of the $SiO_2$, $TiO_2$, $Nb_2O_5$ and $CrNbO_4$ mixture generated, and the scale spalled out from the surface of the sample, resulting in disastrous failure.

*Keywords:* Nb–Si based alloys; Pack cementation; Silicide coating; Oxidation behaviour

## 1. Introduction

Nb–Si based alloys with a dual-phase Nb/$Nb_5Si_3$ microstructure have considerable potential to be high-temperature structural materials due to their low density, high melting points, excellent creep strength and acceptable room-temperature fracture toughness [1–9]. In the dual-phase Nb/$Nb_5Si_3$ microstructure, the room-temperature toughness and the high-temperature strength and creep resistance can be supplied by the ductile Nb phase and the stiffening $Nb_5Si_3$ silicide, respectively; however, both of them exhibit poor oxidation resistance because their parabolic constants of the oxidation kinetics curves are as high as $2.06 \times 10^4$ $\mu m^2/h$ [10]. This poor oxidation resistance results in disastrous consequences when the Nb/$Nb_5Si_3$ alloys are in service in an oxygen atmosphere at high temperatures.

To improve the oxidation resistance, alloying the Nb–Si alloys by Cr, Al, Hf, Sn and B [11–13] is an effective approach. The addition of Cr to Nb–Si based alloys inhibits the oxidation of the Laves $Cr_2Nb$ phase and reduces the oxygen diffusion and solubility in Nb, thereby enhancing the environmental stability of Nb–Si-based alloys at high temperatures [11–13]. A short-term goal of a material thickness loss of 200 μm in 10 h of air exposure at 1370 °C has been successfully achieved for Nb–Si–Cr ternary-based alloys with a tri-phase Nb/$Nb_5Si_3$/$Cr_2Nb$ microstructure [14–16]. Therefore, the Nb, $Nb_5Si_3$ and $Cr_2Nb$ phases are the basic phase constituents for a designed Nb–Si based alloy. Subsequently, optimisation of the microstructure and determination of the properties dependent on the Nb, $Nb_5Si_3$ and $Cr_2Nb$ fractions become urgent issues in developing Nb–Si-based alloys with a balance of room-temperature toughness, high-temperature strength and oxidation resistance. The Cr-free Nb–Si based alloys with no $Cr_2Nb$ phase were reported to show the mass gain above 250 mg/cm$^2$ at 1250 °C for 100 h [17], and they were found to be usually exhausted in several hours. Comparatively, the mass gain of a Nb–22Ti–14Si–2Hf–2Al–*x*Cr alloy oxidised at 1250 °C for 100 h decreased from 200 mg/cm$^2$ to 60 mg/cm$^2$ when the Cr content increases from 2 at% to 17 at%

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[18]. This improvement in the oxidation resistance by higher Cr content is due to the higher amount of the $Cr_2Nb$ phase.

Unfortunately, this improvement was still far from the requirement of actual high-temperature applications in the oxidising environments, and we cannot unboundedly increase the fraction of the $Cr_2Nb$ phase because more $Cr_2Nb$ may decrease the fracture toughness of the bulk alloys [17]. Manufacturing approaches of protective coatings that can form dense, adherent and slow-growing oxide scales, such as pack cementation, are the most promising approaches to improve the environmental stability of the Nb–Si based alloys at high-temperatures and have been developed to augment alloying [19–21]. A report in the literature indicated that an $NbSi_2$ coating formed at the surface when silicon was deposited onto the Nb–Si substrate and the protective glassy $SiO_2$ scale was formed on the $NbSi_2$ coating, stopping the oxygen diffusion from the atmosphere further into the substrate [20]. Such pack cementation silicide coatings further modified with Ge, Al, B, Cr and Y [22–24] have also been found to be beneficial in improving their oxidation resistance of the Nb–Si based alloys. To date, two types of the Nb–Si based alloys with typical $Nb_{SS}$/$Nb_5Si_3$ and $Nb_{SS}$/$Nb_5Si_3$/$Cr_2Nb$ microstructures have been developed. The two-phase $Nb_{SS}$/$Nb_5Si_3$ microstructure has a balance of the room temperature toughness and high temperature strength [1–9], whereas the $Nb_{SS}$/$Nb_5Si_3$/$Cr_2Nb$ microstructure shows better oxidation resistance [14–16,18]. In the present work, the above two microstructures were used as the substrates on which the coatings have been prepared using the Si, Al and $Y_2O_3$ co-deposition pack cementation technique. We will focus the effect of the substrate composition on the coating structures and their oxidation behaviours. This comparative investigation considers the universality of the oxidation behaviours of different Nb–Si substrates under the same pack cementation mixture and processing parameters, which may guide the composition and microstructure design of the Nb–Si based substrates with balanced properties of strength, toughness and oxidation resistance.

## 2. Material and methods

### 2.1. Specimen preparation

Button ingots of the Nb–Si based alloys with nominal compositions of Nb–15Si–22Ti–(2,14)Cr–2Al–2Hf–2V(at%) (where alloy with 2 at% Cr or 14 at% Cr is hereafter referred to as 2Cr or 14Cr alloy, respectively), each with a mass of 1500 g, prepared by vacuum non-consumable arc-melting (VCAM) through five or six cycles in an argon atmosphere, were used as substrates for the coating tests. The purity of all the raw elements was 99.9% (by mass) or higher. The ingots were subsequently heat treated at 1350 °C for 50 h in a high vacuum heat treatment furnace to stabilise the microstructure. Isothermal oxidation specimens of 10 mm × 10 mm × 3 mm cubes were cut from the heat-treated ingots using an electro-discharge machine. The specimens were then mechanically polished using 1000-grit SiC paper with water, followed by ultrasonic cleaned in acetone before coating preparation. Note that the sharp increase in the nominal Cr contents from 2% to 14% is to form Nb–Si based alloys with typical two-phase Nb/$Nb_5Si_3$ and three-phase Nb/$Nb_5Si_3$/$Cr_2Nb$ microstructures.

### 2.2. Processing of the coatings

Pure Si, Al, $Y_2O_3$, NaF and $Al_2O_3$ powders were used as donor sources, activator and filler of the pack cementation mixture. The pack cementation mixture was composed of 10 wt% Si, 10 wt% Al, 2 wt% $Y_2O_3$, 5 wt% NaF and 73 wt% $Al_2O_3$, which were homogenised through tumbling a ball mill for 4 h. Packs were made by burying the substrates in a pack powder mixture in a cylindrical alumina retort of 20 mm in diameter and 35 mm in length, which was then sealed with an alumina lid and cement. Next, the packs were loaded into an alumina tube furnace circulated with argon. The furnace temperature was raised to 1150 °C at a heating rate of 5 °C $min^{-1}$ and sustained for 10 h, followed by cooling of the furnace to room temperature and keeping the argon gas flowing. The coated specimens were retrieved from the packs and then cleaned in an ultrasonic water bath to remove any residual powders on their surfaces. The coated 2Cr and 14Cr alloys are hereafter referred to as coating 2Cr sample and coating 14Cr sample, respectively.

### 2.3. Oxidation tests

Isothermal oxidation tests were conducted at 1250 °C in an open-ended tube furnace filled with static air. The specimens were removed from the furnace to cool at room temperature for weight measurements at intervals of 1, 7, 10, 20, 40, 60, 80, and 100 h, and then put into the furnace for the oxidation tests. The total period of the oxidation experiment was 100 h. The mass gains of these specimens were measured continuously using a precision analytical thermal balance (Model CPA225D, Germany) with an accuracy of $10^{-5}$ g. To obtain the average mass gains, three measurements of each coating/substrate specimen were conducted at each oxidation time.

### 2.4. Analysis methods

X-ray diffraction (XRD) analysis was performed to identify the phase constitutions using Cu Kα ($\lambda = 0.15405$ nm) radiation at 40 kV and 40 mA (Rigaku D/Max 2500PC). Back-scattered electron (BSE) images were taken to investigate the microstructures of the substrates and the coating scale before and after oxidation using a scanning electron microscope (SEM, QUANTA600). Phase compositions were determined using energy-dispersion X-ray spectroscopy (EDS) (EDX, Oxford Instruments, UK).

## 3. Experimental results

### 3.1. Microstructures of substrates and coatings

Typical back-scattered SEM images of the heat-treated 2Cr and 14Cr samples are shown in Fig. 1. Two types of phases with clear contrast were found in the 2Cr alloy, in which the