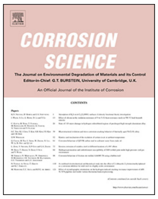
Corrosion Science 141 (2018) 97–108

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Accelerated oxidation behavior of $NbSi_2$ coating grown on Nb substrate at 600–900 °C

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ARTICLE INFO

Keywords:
A. Intermallics
B. SEM
B. TEM
B. XRD
C. Oxidation

ABSTRACT

Isothermal oxidation of $NbSi_2$ coating formed on Nb substrate was investigated in air at 600–900 °C, which exhibited the complex and accelerated kinetics at intermediate temperatures and failed due to either the cracking of the $NbSi_2$ coating or the oxide layer formed. This complex oxidation behavior was governed by the balance between the stress generated by the forming of oxide phases and the subsequent stress relaxation processes. Pesting-induced accelerated oxidation at 700 °C was affected by extrinsic factors such as pre-existing defects in $NbSi_2$ coating. Accelerated oxidation originated from the oxide layer cracking at 750 °C was intrinsic to $NbSi_2$.

1. Introduction

Niobium disilicide ($NbSi_2$), Nb-base alloys, and Nb silicide-based in-situ composites are potential candidates for high temperature structural materials because of their low density, high melting points, excellent creep strength and low-temperature damage tolerance [1–3]. However, poor oxidation resistance at elevated temperatures limits their use, and many attempts were made to make alloys capable of forming protective oxide scale at high temperatures [4–8]. Only few satisfactory results from alloying have been reported, mainly because of the degradation of high temperature mechanical properties [9,10].

An alternative approach is to employ $NbSi_2$ protective coating on Nb-based alloys by combining the oxidation resistance of $NbSi_2$ coating with the mechanical properties of Nb or Nb alloys [11–16]. Even with this approach, the phenomenon of pest oxidation poses a serious problem, limiting usage in high temperature structural applications [17–27]. It is known that, due to low vapor pressure of Nb_2O_5, $NbSi_2$ forms the mixed oxides of silica and Nb_2O_5 during oxidation as shown in Eq. (1).

$$4NbSi_2(s) + 13O_2(g) \rightarrow 8SiO_2(s) + 2Nb_2O_5(s) \tag{1}$$

With this reaction, bulk $NbSi_2$ sometimes disintegrates into powder when oxidized at around 750 °C, and this is known as “pest oxidation” [13,17–27]. Pest oxidation of $NbSi_2$ was first reported by Rausch [20] and later confirmed by Pitman and Tsakiropoulos who showed that the $NbSi_2$ ribbons prepared by melt spun of arc melted ingots had completely disintegrated, leaving a white powder after 10 h at 750 °C in air [21].

Pest oxidation of $NbSi_2$ is attributed to significant internal stress produced by the large volume expansion (Pilling-Bedworth ratio [28] of Eq. (1) = 3.18 as shown in Table 3) caused by the formation of mixed oxides of amorphous SiO_2 (a-SiO_2) and Nb_2O_5. This leads to the premature failure of $NbSi_2$ through preexisting structural defects, such as pores, microcracks and/or grain boundaries in bulk materials and coatings during oxidation at 727–1000 °C [8,21–27]. Berztiss et al. reported that pesting was always preceded by accelerated oxidation which was a necessary, but insufficient condition for pest oxidation to occur [29]. Accelerated oxidation is defined as a phenomenon that a faster oxidation rate is observed at certain low temperatures than at higher oxidation temperature range [30]. Researchers investigated how structural defects impacted accelerated and pest oxidation, but no clear determination was made concerning their origin or mechanism.

According to the literature, experimental results on the accelerated, high temperature oxidation behavior of bulk $NbSi_2$ and $NbSi_2$ coating are summarized in Table 1, and apparent inconsistencies must be noted. First, the two experiments on $NbSi_2$ coating show oxidation temperatures and incubation periods that are quite different from each other. Similarly, for bulk $NbSi_2$, specimens made by arc melting show only pest oxidation. Second, the oxidation kinetics of pest oxidized $NbSi_2$ follows a parabolic rate law during the initial stage until an abrupt increase in the oxidation rate becomes observable during the later oxidation stage. But accelerated oxidation without pesting shows the

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https://doi.org/10.1016/j.corsci.2018.07.001
Received 9 October 2016; Received in revised form 29 June 2018; Accepted 3 July 2018

Table 1
Comparison of previous experimental results on the accelerated isothermal oxidation behavior of $NbSi_2$ in air.

Authors	Crystal type	Sample preparation	Relative density (%)	Oxidation temperature (°C)	Oxidation kinetics	Oxidation time (hr)	Pest oxidation	Oxide products
Pitman et al. [21]	Ploy	AM & Melt spun		(750)		10	Y	Powders (Nb_2O_5 + a-SiO_2)
Majumdar et al. [22]	Poly	Coating		800–1300 (800 – 8 h, 1000 – 17 h)	$\alpha\, t^{1/2}$ & abrupt increase	24	Y	Powders or small particles (Nb_2O_5 + a-SiO_2)
Zhang et al. [23]	Poly	AM	97	(750 – 3 h)	$\alpha\, t^{1/2}$ & abrupt increase	4	Y	Powders (Nb_2O_5 + a-SiO_2)
		SPS-1	93.8	(750)	$\alpha\, t$	89	N	Nb_2O_5 + a-SiO_2
		SPS-2	95		$\alpha\, t$	89	N	
	Single	FZM	99.3		$\alpha\, t$	89	N	
Murakami et al. [24]	Poly	HPS		(750)	$\alpha\, t$	100		Nb_2O_5 + a-SiO_2
Song et al. [25]	Poly	HPS	$>$ 97	550-850 (750)	$\alpha\, t$	120	N	Multilayer Oxide (Nb_2O_5 + a-SiO_2)
Kurokawa et al. [26]	Poly	SPS	98-99	500-1300 (800)	$\alpha\, t$	100	N	Porous oxide (Nb_2O_5 + a-SiO_2)
Yamada et al. [27]	Poly	Coating		827-1427 (727)		10	Y	Powders

AM : Arc melting, SPS : Spark plasma sintering, FZM : Floating zone melting, HPS : Hot press sintering, Y : Yes, N : No, Temperature and time in bracket mean an accelerated oxidation temperature and the incubation time for the initiation of pest oxidation.

linear oxidation kinetics. Obviously, there is no clear explanation or clarification of the differences between accelerated oxidation with pesting and accelerated oxidation without it.

Many researchers reported that the accelerated oxidation of metal silicides such as $NbSi_2$ or $MoSi_2$ depends on various factors like composition, density, processing methods, temperature, atmosphere and preexisting structural defects such as pores, cracks, grain boundaries, etc [23,26,29–36]. However, they did not explain the origin or detailed microscopic process behind accelerated oxidation with or without pest oxidation. Therefore, the purpose of this study is to investigate the oxidation kinetics of $NbSi_2$ coating formed on Nb substrate, as well as the growth behavior and microstructure of oxide scale formed at a temperature range of 600–900 °C. In order to improve the poor oxidation resistance of $NbSi_2$ at these temperatures, it is therefore essential to investigate how oxidation of $NbSi_2$ coating proceeds on a macro scale, how the microstructure of oxide scales evolve with respect to oxidation temperatures and times, and what microscopic process leads to pest and/or accelerated oxidation.

2. Experimental procedures

2.1. Preparation of $NbSi_2$ coating

Nb metal (Nilaco Co., 99.95% purity) was cut into rod-shaped specimens (5 mm in diameter and 15 mm in length) and ground with a series of SiC papers up to grit 4000#. The specimen's edges were rounded off to prevent crack formation at sharp corners. The Nb specimens were ultrasonically cleaned in acetone, alcohol, and distilled water, and dried afterwards. The $NbSi_2$ coating was prepared by the pack siliconizing process of the Nb substrate. Pack powders with a composition of 40 wt.% Si-5 wt.% MgF_2-bal Al_2O_3 were used. Pure Si powder (-325 mesh, 99.5%, Alfa Co.) and MgF_2 powder (-200 mesh, 99.9%, Cerac Co.) were used as the master alloys, with the halide salt serving as an activator. Al_2O_3 powder (-325 mesh, 99%, Cerac Co.) was the inert filler used. The powders were weighed, blended and mixed in a ball mill for 24 h. To eliminate moisture, the mixed packs were dried at 200 °C for 5 h. The Nb substrate was embedded in the pack powders within an Al_2O_3 crucible. The crucible packs were heated in a horizontal Inconel 600 tube furnace for isothermal heat treatment at 1100 °C for 7 h in an argon atmosphere, which produced $NbSi_2$ coating with a thickness of 110 μm. Ar gas was used after purification by an Ar purifier (2G-100-SS, Centorr Co.).

2.2. Oxidation test

Isothermal oxidation tests were conducted using a high temperature thermogravimetric analyzer (TGA-51, Shimadzu) at a temperature range of 600–900 °C A sample was placed in a quartz crucible and loaded into a vertical alumina tube furnace. The sample was heated to oxidation temperatures in the high purity Ar atmosphere at a rate of 10 K/min and then maintained in flowing air. Upon completion of the oxidation test, the power and flowing air was turned off so that the samples were cooled to room temperature in an Ar atmosphere.

2.3. Characterization of $NbSi_2$ coating and oxidation products

Standard metallographic techniques were used to polish the sample through 0.04 μm Al_2O_3. The microstructure of the $NbSi_2$ layer and oxidation products were observed using field-emission scanning electron microscopy (FE-SEM, S-4200, Hitachi) operated at 15 kV, as well as cross-sectional transmission electron microscopy (XTEM, Tecnai F20, FEI) operated at 200 kV. Kroll's reagent (20 ml HNO_3, 4 ml HF, and 76 ml distilled water) was used for 30–60 s to etch the $NbSi_2$ coating. In order to observe the microstructure of oxide scales at a specific location via TEM, a focused ion beam (FIB, NOVA Nano Lab 600, FEI) was used. Platinum was deposited on the surface of oxide scales, and the sample was bonded to a metal ring for thinning via an FIB apparatus. Finally, the chosen part of the sample was thinned to less than 100 nm, and the microstructure of oxide scales was observed via TEM. A Rikagu diffractometer was also employed for X-ray diffraction (XRD) studies of the oxidation products at an operating voltage of 30 kV, using Cu-K_α radiation.

3. Results

3.1. Oxidation kinetics of $NbSi_2$ coating

The etched cross-sectional secondary electron (SE) image of Nb-silicide coating formed on Nb substrates via pack siliconizing is shown in Fig. 1a. Chemical analysis and XRD (Fig. 1b) identified the deposition product as the $NbSi_2$ layer. This layer exhibited a typical columnar morphology perpendicular to the Nb substrate. While cooling from coating temperature to room temperature, many vertical cracks formed along the $NbSi_2$ coating's columnar grain boundaries. A mismatch in the coefficient of thermal expansion (CTE) between the $NbSi_2$ coating