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Towards the improvement of the oxidation resistance of Nb-silicides *in situ* composites: A solid state diffusion approach

S. Mathieu [a,*], S. Knittel [b], M. François [a], L. Portebois [a], S. Mathieu [c], M. Vilasi [a]

[a] Université de Lorraine, Institut Jean Lamour, UMR7198, Boulevard des Aiguillettes, BP70239, 54506 Vandoeuvre-lès-Nancy Cedex, France
[b] Snecma (Safran), site d'Evry-Corbeil, rue Henri Auguste Desbruères, 91003 Evry Cedex, France
[c] Service Commun de Microscopies Electroniques et de Microanalyses X, Université de Lorraine, BP 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France

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ABSTRACT

The present study focuses on the oxidation mechanism of Nb-silicide composites and on the effect of the composition on the oxidation rate at 1100 °C. A theoretical approach is proposed based on experimental results and used to optimise the oxidation resistance. The growth model based on multiphase diffusion was experimentally tested and confirmed by manufacturing seven composites with different compositions. It was also found that the effect of the composition has to be evaluated at 1100 °C within a short time duration (50 h), where the oxide scale and the internal oxidation zone both grow according to parabolic kinetics.

1. Introduction

Progress in the field of gas-turbine engines for aircraft is controlled by the availability of structural materials able to withstand the higher-temperature hostile environments (very significant flow conditions containing aggressive elements such as oxygen, water vapour, and volcano ashes at more than 1150 °C). Niobium silicide composites should be capable of operating under these severe conditions [1]. Their Si concentration is in the range of 16–24 at.% for optimum oxidation resistance and creep behaviour [2,3]. The microstructure of these composites consists of a niobium solid solution, which will be defined as $(Nb,Ti)_{ss}$ in the following, and of various silicides with different crystal structures and stoichiometries (α, β, γ-M_5Si_3 and/or M_3Si). Elements such as titanium, hafnium, chromium and aluminium are present in the most promising compositions of these niobium alloys [1]. The addition of these elements is necessary to obtain the physico-chemical properties (room temperature fracture toughness, low creep rate and oxidation resistance) required for the targeted high-temperature applications. The role of Ti, Hf, Cr and Al was mainly to improve the oxidation resistance of the niobium solid solution [2,4,5]; the real effects of these additional elements on the oxidation resistance are not clearly defined, although the effects of these additions on the microstructure have been studied [6–10].

We recently focused our attention [11] on the oxidation mechanism of a Nb-silicide composite of the MASC family (Metal And Silicide Composite [12] with composition Nb–25Ti–8Hf–2Cr–2Al–16Si) both at an intermediate temperature of 815 °C and at 1100 and 1200 °C. Indeed, the oxidation resistance evaluation has to be made in two ranges of temperature: 600–900 °C, where Nb–Si composites suffer from pesting that consists in the fast fragmentation of the specimens during isothermal oxidation [13], and 1000–1300 °C, where the oxidation resistance is generally slightly better because niobium silicides become ductile and thus are not subject to pesting anymore.

At all temperatures, a substantial difference between the oxidation behaviour of the $(Nb,Ti)_{ss}$ phase and γ-$(Nb,Hf)_5Si_3$ was observed [11]. Oxygen diffused quickly through the niobium solid solution but was hindered in it by the reactive elements (Hf, Ti, Al). Those elements formed small-sized precipitates within the solid solution. The corresponding zone affected by this precipitation will be called the “internal oxidation zone” in this paper. The oxidation rates of both the silicides and some constituents (Nb and Cr) of the $(Nb,Ti)_{ss}$ were observed to be lower than those of the Al, Hf and Ti constituents of the $(Nb,Ti)_{ss}$. Consequently, it was suggested that the composition of the silicide phase controlled the partial pressure at the metal–oxide interface.

This finding is highly relevant for the optimisation of Nb-silicide composites and will be further described in the first part of this paper dedicated to the theoretical description of the oxidation

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[*] Corresponding author. Tel.: +33 (0) 383684670; fax: +33 (0) 383684611.
E-mail addresses: stephane.mathieu@univ-lorraine.fr (S. Mathieu), stephane.knittel@snecma.fr (S. Knittel), michel.francois@univ-lorraine.fr (M. François), leo.portebois@univ-lorraine.fr (L. Portebois), sandrine.mathieu@scmem.uhp-nancy.fr (S. Mathieu), michel.vilasi@univ-lorraine.fr (M. Vilasi).

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mechanism of the Nb-silicide composite. The first objective of this paper is to give a comprehensive approach to the oxidation mechanism of Nb-silicide composites, based both on solid state diffusion theory and on experimental evidences.

The experimental study that is presented hereafter was performed to ascertain the oxidation mechanism. The work consisted of the manufacturing and the assessment of the oxidation resistance of seven Nb-silicide composites with various Ti, Al and Si contents. The study of the influence of the Nb-silicide composite composition assumed that the oxidation resistance of tested specimens was not affected by the microstructure. Thus, all samples were synthesised through the same manufacturing route to limit this effect. The assessment of the chemical effect on the oxidation resistance was only performed at 1100 °C. This peculiar choice will be argued in the following section.

2. Theoretical statements

First, the authors invite the reader to refer to paper [11] prior to reading this paper to better follow the development given hereafter. For a complete understanding of the relevance of the oxidation results obtained in [11] and to better appreciate the experimental work performed in the present study, let us first summarise some important experimental results obtained on the oxidation of Nb-silicide composite (MASC):

1. It was found that the weight gain recorded during thermogravimetry corresponded mainly to oxygen uptake in the internal oxidation zone (after 100 h in air at 815 °C, oxygen in the internal oxidation zone represented more than 70% of the recorded mass gain).
2. The oxygen concentration in each layer was well-defined (C_O^{ox} = 68 at.% for the oxide scale, C_O^{int} = 38 at.% for the internal oxidation zone, C_O^{sub} < 1 at.% for the substrate).
3. The growth of the oxide scale and the internal oxidation zone followed the same kinetic laws (diffusion-controlled in the present case).
4. Both layers (the oxide scale and the internal oxidation zone) grew mainly by inward oxygen diffusion, *i.e.* the oxygen flux was several orders of magnitude higher than that of metallic species from the bulk. The X-ray mapping performed (Fig. 6 in [11]) strongly demonstrated that the diffusion of metallic elements in the alloy was very slow compared with that of oxygen at 815 °C.
5. The growth process was continuous for the duration of the oxidation tests, which suggests that steady state conditions exist at the phase boundary between two contiguous layers and that local equilibrium was attained at the phase boundaries.
6. The oxide/internal oxidation zone boundary (hereafter referred to with the superscript *x*) moved only once the silicide was completely consumed. Thus, the oxygen partial pressure at this boundary ($P_{O_2}^{x}$) was fixed by the oxygen partial pressure of the Si/SiO$_2$ equilibrium (Eq. (1)):

$$\mathrm{Si}_{\mathrm{composite}} + \mathrm{O}_2 = \mathrm{SiO}_2 \qquad (1)$$

for which the equilibrium constant is $K_1 = \dfrac{a_{\mathrm{SiO}_2}}{a_{\mathrm{Si}} \cdot P_{O_2}^{x}}$ (2)

7. The internal oxidation zone/substrate boundary (hereafter referred to with the superscript *x*′) moved once the titanium of the (Nb,Ti)$_{ss}$ was completely transformed into TiO$_2$. Thus, the oxygen partial pressure at this boundary ($P_{O_2}^{x'}$) was fixed by the oxygen partial pressure of the Ti/TiO$_2$ equilibrium (Eq. (3)):

$$\mathrm{Ti}_{\mathrm{composite}} + \mathrm{O}_2 = \mathrm{TiO}_2 \qquad (3)$$

for which the corresponding equilibrium constant is

$$K_3 = \frac{a_{\mathrm{TiO}_2}}{a_{\mathrm{Ti}} \cdot P_{O_2}^{x'}} \qquad (4)$$

.

Thus, given this set of data, the typical cross section (Fig. 1) resulting from the oxidation of the MASC composite at 815 °C can be simply described as the result of a diffusion couple experiment between air, for which $P_{O_2}^{atm}$ = 0.2 atm, and the substrate, for which the oxygen partial pressure was very low (lower than the partial pressure of the Hf/HfO$_2$ equilibrium, where Hf presents the highest affinity for oxygen in this system). This diffusion couple experiment is shown schematically in Fig. 2, where the parameters defined above were used (C_O^{ox}, C_O^{int}, C_O^{sub}, x, x', $P_{O_2}^{x}$, $P_{O_2}^{x'}$). The diffusion fluxes for oxygen in each layer were defined as J_O^{ox}, J_O^{int}, and J_O^{sub} for the fluxes in the oxide scale, the internal oxidation zone and the substrate, respectively.

It is now clear from this scheme that the boundary displacements are mathematically easy to formulate to this polyphase diffusion system [14]. If we consider the flux of oxygen from left to right, the displacement rates of the oxide/internal oxidation zone and the internal oxidation zone/substrate boundaries, respectively, are given with the mass balance at the boundary by:

$$\frac{dx}{dt} = \frac{J_O^{ox} - J_O^{int}}{C_O^{ox} - C_O^{int}} \qquad (5)$$

$$\frac{dx'}{dt} = \frac{J_O^{int} - J_O^{sub}}{C_O^{int} - C_O^{sub}} \qquad (6)$$

The growth rate of the internal oxidation zone can be rigorously written as

$$\frac{dL^{int}}{dt} = \frac{dx'}{dt} - \frac{dx}{dt} = \frac{J_O^{int} - J_O^{sub}}{C_O^{int} - C_O^{sub}} - \frac{J_O^{ox} - J_O^{int}}{C_O^{ox} - C_O^{int}} \qquad (7)$$

where L^{int} is the thickness of the internal oxidation zone.

In addition, we know from the experimental mass balance results [11] for short oxidation duration (<100 h) that the displacement d*x* occurring during the interval of time d*t* is much lower than the displacement d*x*′ during the same d*t*. Thus, for this demonstration, the growth rate of the internal oxidation zone can be rewritten by assuming that the second term of Eq. (7) is negligible:

$$\frac{dL^{int}}{dt} = \frac{J_O^{int} - J_O^{sub}}{C_O^{int} - C_O^{sub}} \qquad (8)$$

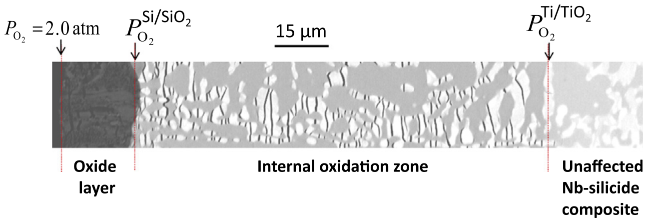

Fig. 1. SEM cross-sectional observation in back-scattering mode for the MASC oxidised for 100 h at 815 °C showing, from left to right, the oxide scale, the internal oxidation zone and the unaffected Nb-silicide composite.