Journal of Alloys and Compounds 724 (2017) 249–257

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Nitridation enhancement of $TiSi_2$ powders by addition of nickel

J. Roger*, L. Nouvian, Y. Le Petitcorps, L. Maillé

Université de Bordeaux, CNRS, Laboratoire des Composites ThermoStructuraux, UMR 5801, 33600, Pessac, France

ARTICLE INFO

Article history:
Received 10 April 2017
Received in revised form
27 June 2017
Accepted 4 July 2017
Available online 5 July 2017

Keywords:
A. ceramics
B. Gas-liquid reactions
C. Catalysis
C. Kinetics
E. thermodynamic properties
D. Thermal analysis

ABSTRACT

The nitridation enhancement of a $TiSi_2$ powder by nickel addition was examined. The quantities of the added metal were comprised between 2.5 and 25mol.%, the balance being $TiSi_2$. The isothermal heat treatments were made at 1100 °C for durations up to 40 h under normal pressure and continuous flow of pure nitrogen. Comparing to pure $TiSi_2$ powder, an improvement of the conversion in TiN and Si_3N_4 is obtained for compositions containing 10.0; 12.5 and 15.0 mol.% of nickel. According to the quaternary Ti-Si-Ni-N phase diagram, nickel was found to form $Ni_4Ti_4Si_7$ compound. Thermogravimetric analysis of these three compositions showed the existence of three successive stages during the conversion. First, an initiate reaction occurred with a very weak weight gain. Then, the second stage exhibited an acceleration of the weight gain. Those two stages are both controlled by nucleation and growth, as represented by the kinetic equation $[-\ln(1-\alpha)]^{1/2} = k.t$. Finally, the reaction is limited by three-dimension diffusion, as represented by the kinetic equation: $[1-(1-\alpha)^{1/3}]^2 = k.t$. From this behavior, an activation mechanism is proposed.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Materials based on silicon nitride are one of the more promising materials for use in high-temperature applications thanks to their high heat resistance, refractoriness, hardness, durability, thermal shock resistance, and chemical resistance. They have a high potential in the practical utilization not only as a structural material but also as a functional material. Understanding of the silicon nitridation process has evolved significantly over the past decades, and the effects of many of the reaction variables on the reaction kinetics and product morphology are well documented [1–18]. In addition to monolithic ceramics, some works have also focused on using reaction-bonded silicon nitride as a composite matrix [19,20]. But, this way requires long durations and temperatures that exceed 1400 °C. This is problematic for composite applications because the whiskers or fibers used as reinforcements could be degraded at elevated temperatures. The formation of Si_3N_4 from pure silicon generates a low volume expansion of 22%. So, full densification implies an initial powder compactness of about 82%. This starting value is unrealistic and full densification is then not possible by this way. An alternative possibility is to use an intermetallic compound as $TiSi_2$. Indeed, the reaction to form Si_3N_4-TiN composite from $TiSi_2$ is accompanied by a 60% volume expansion which occurs in the void space of the compact, such that complete nitridation should fully densified a 62.5% dense $TiSi_2$ body. Titanium nitride is an interesting compound which is widely used to prepare metal ceramic, cutting tools, molds, coatings because of its high strength, high hardness, thermal stability, high electrical conductivity, good wear and corrosion resistance. The conventional synthesis of TiN involves direct nitridation, laser cladding, self propagating high-temperature synthesis and mechanical milling [21,22]. The combustion synthesis of TiN was investigated by several authors and was found relatively easy to proceed [23–27]. M. Ade and J. Hauβelt [28] reported that the maximum conversion (90%) of a pure $TiSi_2$ powder with a mean grain size less than 2 μm was obtained for a temperature close to 1400 °C, probably because of the formation of liquid silicon ($T_{melting}(Si) = 1414$ °C). The exothermicity of this reaction and the formation of liquid silicon could be detrimental in the case of fibrous composites. In a previous work, we focused our attention on the nitridation of pure $TiSi_2$ compacts at lower temperatures (1000–1200 °C) to produce the matrix of a fibers-reinforced composite [29]. Accordingly to previous papers [30–33], it was found that the nitridation is sluggish in these conditions because of diffusional limitations. Indeed, the titanium nitridation is easily but silicon reacts very slowly due to the formation of a TiN layer at the surface of the grains. This TiN layer behaves as a diffusion barrier towards nitrogen and silicon [30,31,34]. To circumvent this pitfall, it is required to set up a

* Corresponding author.
E-mail address: jerome.roger@lcts.u-bordeaux.fr (J. Roger).

http://dx.doi.org/10.1016/j.jallcom.2017.07.031
0925-8388/© 2017 Elsevier B.V. All rights reserved.

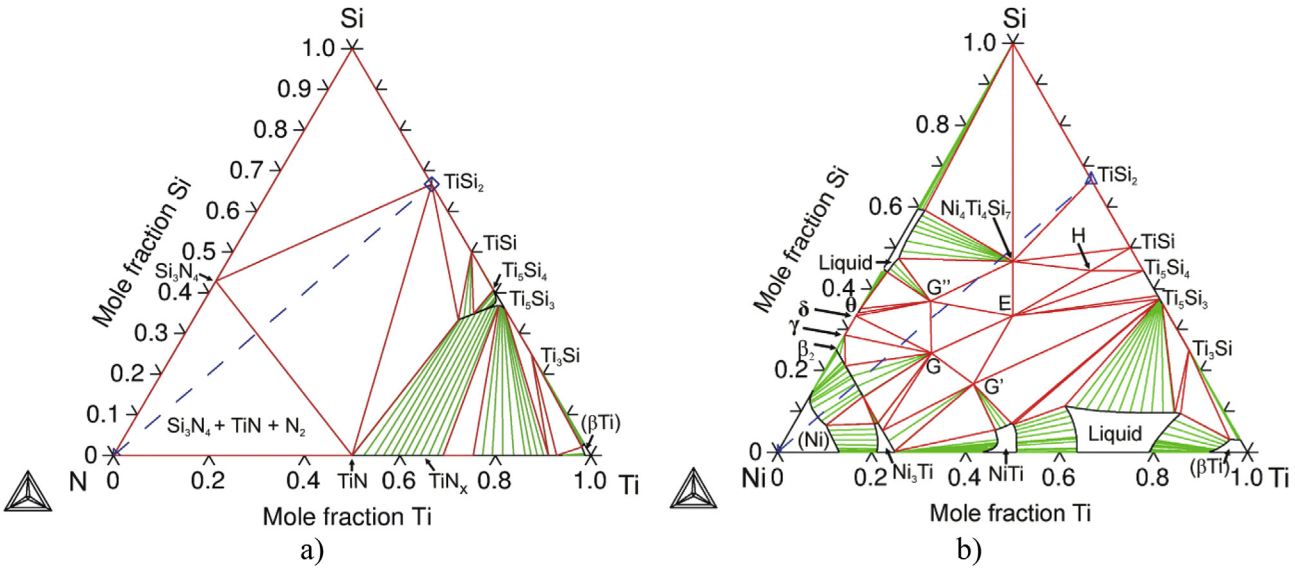

Fig. 1. Equilibrium diagrams simulated at 1100 °C with ThermoCalc software [42]: a) N-Ti-Si [43] and b) Ni-Ti-Si [44].

strategy to enhance the nitridation of $TiSi_2$, this is the objective of the present work. It has been known that transition metals can regulate kinetics of silicon nitridation as well as the phases formation [3,12,35–37]. Since sintering additives are always used in the fabrication of materials from silicon nitride powder, the nitridation enhancement role of minor additions of common metals in the starting Si powder is well established [12,35,36,38–41]. Especially, it was shown that Fe, Ni or Al addition promotes the formation of nitrides [36–38]. These metals should promote the crystallization and the disruption of the amorphous native silica layer located at the surface of the grains. Another explanation suggested that metals form a liquid phase by reacting with silicon to form a eutectic. On this way, we examine the effect of adding a metal powder to a $TiSi_2$ powder to improve nitridation. Several metals were considered to promote nitridation at a temperature as low as 1100 °C. Based on the hypothesis that the formation of a liquid phase should enhance atomic mobility and consequently nitridation rate, the attention was focused on nickel because of the low-temperature eutectic NiSi-$NiSi_2$ (956 °C). In the present work, the synthesis of Si_3N_4-TiN-based composite has been studied by the nitridation of $TiSi_2$ and Ni powders mixtures under nitrogen atmosphere.

2. Thermodynamic analysis of the Ti-Si-Ni-N system equilibrium

Prior to experimental investigation, a preliminary thermodynamic analysis of the equilibrium in the Ti-Si-Ni-N system was performed with the help of the ThermoCalc software [42]. The relevant thermodynamic descriptions of the Ti-Si-N and Ti-Si-Ni systems reported by S. Sambasivan et al. and T. Tokunaga et al., respectively, were used for these calculations [43,44]. The so-calculated equilibrium diagrams at 1100 °C are shown in Fig. 1a and b. The particularity of the Ti-Si-Ni system is the formation of a Si-rich ternary liquid phase at this temperature. This liquid phase originates from the NiSi-$NiSi_2$ eutectic reaction at only 956 °C, as shown in Fig. 2 [45]. The phases stability diagrams for the (1-x) $TiSi_2$ + x Ni mixtures were calculated as a function of nitrogen content at 1100 °C for x = 0.025; 0.100; 0.150 and 0.250. The so-obtained diagrams are shown in Fig. 3. In each case, the formation of TiN and Si_3N_4 nitrides is announced. Depending on the nitrogen quantity, nickel generates first the ternary compound $Ni_4Ti_4Si_7$, then the ternary liquid and finally binary nickel silicides in equilibrium with gaseous nitrogen. This means that the formation of the liquid phase is possible at the interface with the atmosphere, what is favorable to nitrides formation by improving atomic diffusion. When looking at the variation of the nickel activity versus nitrogen content shown in Fig. 4-a, one note that the lower Ni-activity value corresponds to the TiN+Si_3N_4+$Ni_4Ti_4Si_7$+$TiSi_2$ and TiN+Si_3N_4+$Ni_4Ti_4Si_7$ equilibriums. So, one could expect that the equilibrium TiN+Si_3N_4+$Ni_4Ti_4Si_7$ should be favored as a further nidridation implies an increase of nickel activity whereas nitrogen activity increases during the conversion (Fig. 4-b). The expected reaction is (Reaction 1):

$$TiSi_2 + x\,Ni + \left(\frac{11}{6} - \frac{5}{3}x\right)N_2 \Rightarrow (1-x)\,TiN + \left(\frac{2}{3} - \frac{7}{12}x\right)Si_3N_4 + \left(\frac{x}{4}\right)Ni_4Ti_4Si_7$$

The Gibbs free energy that varies with the progress of this reaction was also calculated. This reaction is favorable as it implies a large negative Gibbs free energy and decreases with the progress of the reaction as shown in Fig. 5.

3. Materials and experimental procedures

The starting $TiSi_2$ powder (99.95%, d_{50} = 44 μm, Neyco) used in these experiments was analyzed by spectrographic analysis (S.C.A.-C.N.R.S., Villeurbanne, France) to determine the impurities content: 1.64% O, 0.43% C and 0.48% Fe in mass. The nickel powder was supplied by Strem Chemicals (99.9%, d_{50} = 5 μm). The two raw powders were milled together during 1 h in ethanol with a vibratory mixer mill (Retsch MM200) (WC-milling-bowl and -balls) to

Download English Version:

https://daneshyari.com/en/article/5460090

Download Persian Version:

https://daneshyari.com/article/5460090

Daneshyari.com