AN ACCURATE APPROACH OF THE NITRIDATION PROCESS OF TiSi₂ POWDER

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Abstract

A work based on the study of nitrogen diffusion in a micrometer-sized powder of TiSi₂ is reported in this paper. In order to provide accurate information about the various reaction mechanisms involved with the transformation process of this powder, TiSi₂ is treated under nitrogen flow, at 1100°C, during various nitridation times. The structure of this powder is characterized by X-Ray Diffraction (XRD). Transverse sections of grains, prepared using ion polishing system (Cross Polisher JEOL Ltd), are observed with an Environmental Scanning Electron Microscope (SEM) whereas the chemical composition is analyzed by Energy dispersive X-ray spectroscopy. All these analyses have underlined that under a nitrogen flow, TiSi₂ is transformed into nanograins of TiN at the extreme surface, surrounding silicon inside the grain. These results are discussed in term of various diffusion limitation phenomena: nitrogen through TiN and titanium through silicon, according to phases equilibria. During oxidation of nitridated TiSi₂, the less resistance phase and the more exposed phase to oxygen supply TiN and Si, are oxidizing in TiO₂ and SiO₂. This latter part is demonstrated in-situ using the SEM.

Introduction

Titanium and its alloys are attractive to the aerospace and chemical industries because they possess superior specific strength and a good corrosion resistance [1]. Titanium disilicide (TiSi₂) is also used in microelectronic industry on account of its low electrical resistivity, high thermal stability, and chemical and structural compatibility (small lattice mismatch) with silicon substrate [2-4]. TiSi₂ powder can also be introduced in ceramic matrix composite (CMC) fabrication route. In order to be competitive on civil aeronautic market, low cost CMC processing as liquid phase route including polymer impregnation/pyrolysis were developed. But an inherent shrinkage is observed after pyrolysis of the polymer, even when powders are inserted in the matrix. P. Greil suggested overcoming this problem with addition of active fillers, which react during pyrolysis to form oxides, carbides or nitrides leading to volume expansion [5-15]. Titanium disilicide (TiSi₂,
density = 4.01 g/cm$^3$) has been identified as an interesting active filler. Indeed, under nitrogen atmosphere, TiSi$_2$ can form TiN (d = 5.43 g/cm$^3$) and Si$_3$N$_4$ (d = 3.19 g/cm$^3$); going with a 57% volume increase. Some studies are performed in our group to prepared ceramic composites with a smaller size powder obtained by ball-milling$^{[16-17]}$. To control the process, nitridation of TiSi$_2$ must be well known. In this paper, we explore the influence of temperature and time on the nitridation rate of a micrometer-sized TiSi$_2$ powder. Oxidation behavior of nitrided TiSi$_2$ is presented too.

**Materials and experimental procedure**

A high purity micrometer-sized TiSi$_2$ powder (C-54 stable phase, 99.95% in purity, ~45µm, Neyco) is used in this work. A study of XRD patterns shows the presence of 8.6%wt of free silicon and 91.4% wt of TiSi$_2$ phase. This powder is heated under nitrogen atmosphere at a ramping rate of 10°C/min up to 1000 °C and 1100°C, and maintained at this temperature during 45 min or 5h. Nitridation is performed in a thermogravimetric analyser (Setaram TAG24) or in a furnace using alumina crucibles. The crystallographic structure of samples is studied by X-Ray Diffraction (XRD) in Bragg-Brentano geometry, with a Bruker D8 Advance apparatus, using Cu Kα radiation. XRD patterns are recorded using a step size of 0.01° for the 2θ range 10-90°, and a counting time of 0.3s per step. Sections of nitrided TiSi$_2$ grains are prepared using ion polishing system (Cross Polisher JEOL Ltd). These sections are observed with an Scanning Electron Microscope (SEM) Quanta 400 FEG microscope whereas the chemical composition is analyzed by Energy Dispersive X-ray spectroscopy (EDX), operated at 5kV (resolution: around 2 nm in this condition). In such a microscope the oxidation of nitrided powder can be studied in situ by heating samples, at 900°C, during 10 minutes at a pressure of 140 Pa, with an O$_2$ flow rate equal to 10 sccm. During the experiment, an image is captured every three seconds.

**Results and discussion**

**Nitridation process**

According to the Ti-Si-N phase diagram$^{[18-19-20]}$, the whole nitridation of titanium inside TiSi$_2$ is resumed by equation 1 and respectively the complete nitridation of TiSi$_2$ by equation 2.

\[
2 \text{TiSi}_2 (s) + N_2 (g) \rightarrow 2 \text{TiN (s) +4 Si (s)} \quad \text{(reaction 1)}
\]

\[
6 \text{TiSi}_2 (s) + 11 N_2 (g) \rightarrow 6 \text{TiN (s) + 4 Si}_3\text{N}_4 (s) \quad \text{(reaction 2)}
\]
XRD patterns of nitried TiSi₂ during 45 minutes at 1000°C and 1100°C reveal the formation of TiN and Si when TiSi₂ reacts with nitrogen. More TiSi₂ reacted with nitrogen at 1100°C compared to 1000°C (thermo-activated reaction), for the benefit of the TiN formation. The presence of crystallized Si₃N₄ is not shown through XRD patterns. Sections of nitried TiSi₂ grains are observed by SEM (figure 1). EDX measurement also confirms the growth of TiN and Si, as the XRD characterization. TiN is located at the extreme surface of the grain. It is composed of nanograins, with approximately 15 nm of diameter. Free metallic silicon seems to coalescence at the grain periphery. In the bulk of the grain, the TiSi₂ phase is still present, with the right stoichiometry. Elsewhere porosities are created in the TiSi₂ phase, surrounded by TiN. These porosities increase with the nitridation temperature, as a phenomenon close to pitting. The weight gain of these samples is around 2% and 4% for nitridation temperature, respectively equal to 1000°C and 1100°C.

Figure 1. SEM images of transverse sections of grains nitride during 45 min at a) 1000°C and b) 1100°C.

Figure 2 presents SEM images of grain TiSi₂ powder treated under nitrogen during 5h at 1000°C and 1100°C.

The same phenomena are observed as the samples nitried during 45 minutes. The same reaction mechanism seems to be maintained with nitridation TiSi₂. Only TiSi₂, TiN and Si phases are observed, with XRD patterns and EDX analysis of Si/Ti/N. The presence of crystallized Si₃N₄ is not shown through XRD patterns. A thick film is identified as TiN surrounds the grain. SEM shows that the TiN thickness is around 60 nm. TiN is also located along the porosity surface inside the grain. The silicon is located at the grain periphery, between the TiSi₂ (observed by SEM in the center) and the TiN. Free silicon embeds TiSi₂ and is respectively covered by TiN layer. Only the 3 µm in diameter grain would completely react with nitrogen according to the reaction 1.

The porosity of grains increases with the nitridation temperature and with duration of thermal treatment, as it was shown on the figure 1 and 2, nitrided
45 min and 5h respectively. The reaction with the nitrogen is the origin of this pitting phenomenon. The hypothesis is supported by the SEM observation of the presence of TiN near to the porosity. In conclusion, the process of nitridation explored at 1000 and 1100°C during 45 min and 5 hours is in agreement with the reaction mechanism 1, and the data published ².

**Figure 2.** SEM images of transverse sections of nitrided grain during 5 h at a) 1000°C and b) 1100°C.

In order to verify the existence of the Si₃N₄ phase, a TiSi₂ powder has been nitrided at 1100°C during 50h. XRD confirms the presence of the TiN phase and of a slight quantity of the Si₃N₄ phase. Figure 3 presents transverse sections of a TiSi₂ grain observed by SEM, after a nitrogen thermal treatment during 50h at 1100°C.

**Figure 3.** SEM images of a section of a grain nitrided during 50 h at 1100°C.
The kinetic of transformation of free silicon in Si₃N₄ is very low. The volume expansion of TiSi₂ powder during nitridation is also checked through this experiment. TiSi₂ may be used to avoid skrinkage during pyrolysis of polymer when nitridation is done in the same time. In over work, it has been shown that a close nanoscale size of grains, the formation of Si₃N₄ occurs earlier at the same low temperature [16-17].

**Oxidation behavior**

TiSi₂ powder, nitrided at 1100°C during 5 hours, has been studied in order to understand the oxidation behavior. This study is realized in-situ using the SEM during 10 minutes, at 900°C, at 140 Pa, under a O₂ gas flow rate equal to 10 sccm.

![Figure 4. SEM images of a TiSi₂ grain nitrided during 50 hours at 1100°C (a) and after an in-situ oxidation at 900°C during 10 minutes (b-c).](image)

During oxidation of nitrided TiSi₂, nanograins of TiN and free Si are oxidized in TiO₂ and SiO₂ (figure 4). SiO₂ is an amorphous phase, whereas TiO₂ is in the crystallise rutile phase. This latter phase is present as constituted of nanograins with 500nm of diameter (figure 4-c).

**Conclusions**

The nitridation of a micrometer-sized TiSi₂ powder is reported in this paper at 1000°C and 1100°C for various times. Nanograins of TiN and free silicon are formed in the presence of nitrogen. We demonstrate that it is possible to grow Si₃N₄ at 1100°C, for long times of nitridation. TiN formation takes place before the formation of Si₃N₄. An in-situ oxidation study by SEM of nitrided TiSi₂ shows the growth of TiO₂ nanograins and of SiO₂ amorphous phase.

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References