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STUDY OF THE NITRIDATION PROCESS OF TiSi_2 POWDER

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This paper reports on the nitriding process of TiSi_2 micro/submicrometer-sized powders. TiSi_2 powders were treated under nitrogen flow, at 1100°C , during various durations. The composition and morphology of the nitride powders are characterized by X-ray diffraction and observed on cross-section, prepared using ion polishing system by scanning electron microscopy whereas the chemical composition is analyzed by energy dispersive X-ray spectroscopy. All these analyses revealed that under nitrogen flow, TiSi_2 grains are first transformed into a core-shell structure composed of TiN , surrounding by Si . Long nitriding treatments result in the complete transformation of Si_3N_4 . These results are discussed in terms of various diffusion limitation phenomena.

Keywords : CMC, milling, powder, XRD

INTRODUCTION

Ceramic Matrix Composites are developed for aeronautic and spatial applications [1]. Due to their refractoriness and their low density they are used in the hot parts of engines. These composites are usually elaborated by infiltrating a weaved preform by chemical vapor infiltration to form a ceramic matrix. Other processes can also be used to form the matrix. In particular ceramic processes in which a slurry impregnation including filler powder and liquid polymer impregnation can be used [2-7]. The active fillers are aimed at reducing the volume shrinkage resulting from the pyrolytic conversion of polymer to ceramic [8-9]. Titanium disilicide ($d=4.01\text{g/cc}$) is identified as interesting active filler: under nitrogen atmosphere, the nitridation of TiSi_2 starts in a temperature range around 1000°C to form TiN ($d=5.43\text{g/cc}$) and Si_3N_4 ($d=3.19\text{g/cc}$) [10]. This reaction generates a 57% volume increase. In this paper, we explore the influence of temperature and duration on the nitriding rate of a micro and submicrometer-sized TiSi_2 powder.

1. MATERIALS AND EXPERIMENTAL PROCEDURES

A high purity micrometer-sized TiSi_2 powder (C-54 stable phase, 99.95% in purity, $\sim 45\mu\text{m}$, Neyco) is used. The raw powder is milled with a vibratory mixer mill (Retsch MM200) and with planetary ball mill (Retsch PM200). Nitriding process is carried out in a thermogravimetric analyser (Setaram TAG24) or in a furnace using alumina crucibles. This powder is heated under a flow of nitrogen gas (50mL/min) from 20°C to 1100°C at a heating rate of 10°C/min , during various durations (45min, 5h, 50h). The crystallographic structure is studied by XRD in Bragg-Brentano geometry, with a Bruker D8 Advance diffractometer, using a copper anode (CuK_α) and a one-dimensional position sensitive silicon strip detector (Bruker, Linxeye). XRD patterns are recorded using a step size of 0.01° for the 2θ range $10-90^\circ$, 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 a FEI Quanta 400 FEG scanning electron microscope whereas the chemical composition is analyzed by EDX (EDAX Genesis XM4), operated at 5kV (interaction volume of roughly 150nm wide in this condition). Specific surface areas are determined by the BET method with an ASAP 2010 (Micromeritics); the samples are degassed by heating at 220°C during 4h immediately prior to measurements.

2. RESULTS AND DISCUSSION

2.1. Nitriding process of micrometer-sized TiSi_2 powder

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Powder is analyzed by XRD. Pattern is analyzed using the Rietveld [2] whole profile fitting method with the software Fullprof [3]. Results indicate that the powder is composed of 4.2(±0.7)% wt of free silicon (ICDD-PDF 04-001-7247) and 95.8% wt of TiSi₂ compound (ICDD-PDF 04-007-1144). A low specific surface area of 0.33m²/g was measured by the BET method.

According to the Ti-Si-N phase diagram [10-10], the partial nitridation of TiSi₂ is resumed by the equation 1 and respectively the complete nitridation of TiSi₂ by the equation 2.

The nitriding of powders are performed in a thermogravimetric analyser at three temperatures; 1100°C, 1200°C and 1300°C. The variations of mass gain versus time are presented on figure 1.

XRD patterns (figure 2) and mass gains revealed different behaviours in the different conditions. At 1100°C partial nitriding reaction occurs with a mass gain less than 13.5% and the presence of residual TiSi₂ is revealed by XRD analysis. The Eq. 1 formulates this partial reaction with formation of TiN and Si. Above 1200°C a higher mass gain is observed, due to a total nitriding reaction of TiSi₂ (Eq. 1) and partial nitriding reaction of silicon (Eq. 2) leading to the formation of both nitrides TiN and Si₃N₄. The amount of Si₃N₄ phase is probably too low to be revealed by the XRD pattern. This reaction is more efficient at 1300°C, with a higher conversion rate, peaks of Si₃N₄ are clearly observed by XRD analysis (figure 2). These results show a two-step nitridation of TiSi₂, as it was previously reported in literature [11-12].

Sections of nitrided TiSi₂ grains at 1100°C during 5h, are observed by SEM (figures 3a, b). EDX measurements also confirm the presence of TiN and Si. TiN is located at the extreme surface of the TiSi₂ powder. A thin discontinuous layer of around 60 nm is formed; it is composed of nanograins, of approximately 15 nm wide. TiN is also located along the porosity surface inside the grain. Free metallic silicon seems to precipitate at the grain periphery, between the TiSi₂ (observed by SEM in the center) and the TiN compounds. Free silicon embeds TiSi₂ and it is respectively covered by the TiN layer. Nevertheless, for smaller particules (diameter < 3µm), TiSi₂ is completely transformed according to the reaction 1 (figure 3b).

Some thermodynamic studies in the Ti-Si-N ternary system indicate that TiSi₂ can be nitrided into TiN and Si₃N₄ at 1100°C [4-10]. This assertion is not confirmed by our first experiments, even after 5h of nitridation at 1100°C. So, it has been decided to mill the as received powders, with the intention of getting close to a submicronic scale. We expected that the total nitriding reaction of milled powders can occur at lower temperatures in order to get Si₃N₄.

2.2. Milling study

The TiSi₂ commercially powders are milled with a vibratory ball mill or a planetary ball mill in order to get sub-micronic particles. Results are shown in Table 1.

Thermogravimetric analyses were then performed on these milled powders at 1100°C (figure 4). The milling improved significantly the nitridation rate, with a weight gain of 8.6% after 5h at 1100°C. Nitridation of planetary milled powder starts at a clearly lower temperature of 650°C, with a much steeper slope during the heating stage. Furthermore after planetary milling the weight gain of TiSi₂ nitriding reaction reached the value of 29.5% (5h at 1100°C). This indicated the formation of Si₃N₄. XRD analyses of the powders were performed on the powders treated within the thermogravimetric device (Figure 5). XRD patterns of all nitrided products indicate the presence of TiN and Si. The XRD pattern of the TiSi₂ powder nitrided after planetary milling also exhibits small peaks corresponding to the α-Si₃N₄ and β-Si₃N₄ phases.

3. CONCLUSION

Our experiments confirm that the complete nitridation of TiSi_2 at 1100°C is described by two steps: the precipitations of free silicon and TiN followed by the nitridation of the free silicon. It was observed that decreasing the grain size allows to lower the nitriding temperature to form Si_3N_4 . For instance in the case of raw powders, the formation of Si_3N_4 starts above 1200°C while for planetary milled powder the reaction begins at 1100°C after five hours of treatment.

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Figure 1. Thermogravimetric curves of TiSi_2 commercial powder heated at various temperatures within N_2 atmosphere

Figure 2. XRD patterns of the starting powder and after TGA experiments in N_2 .

(●) TiSi_2 (ICDD-PDF 04-007-1144); (Δ) Si (ICDD-PDF 04-001-7247) (■) TiN (ICDD-PDF 04-002-1925); ($\blacktriangle$) $\beta\text{-Si}_3\text{N}_4$ (ICDD-PDF 04-007-2386)

Figure 3. Backscattered electrons SEM images of transverse sections of two grains nitrided during 5 h at 1100°C

Figure 4. Thermogravimetric curves of TiSi_2 milled and raw powders heated to 1100°C into N_2 atmosphere

Figure 5. XRD patterns after TGA experiments at 1100°C in N_2 on raw and milled powders.

(●) TiSi_2 ; (Δ) Si ; (■) TiN ; ($\blacktriangle$) α and $\beta\text{-Si}_3\text{N}_4$

Table 1. Specific surface area and granulometry of raw powders and milled powders.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1

	commercial powders	vibratory ball milling powders	planetary ball milling powders
Specific area S (m ² /g)	0.3	2.0	41
Mean size d ₅₀	45 μm	2 μm	550 nm