Isothermal nitridation kinetics of TiSi₂ powders

Jérôme Roger, L Maillé, Marie-Anne Dourges

► To cite this version:

Jérôme Roger, L Maillé, Marie-Anne Dourges. Isothermal nitridation kinetics of TiSi₂ powders. Journal of Solid State Chemistry, 2014, 212, pp.134-140. 10.1016/j.jssc.2014.01.021 . hal-01323667

HAL Id: hal-01323667

<https://hal.science/hal-01323667>

Submitted on 2 Jun 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Isothermal nitridation kinetics of TiSi₂ powders

J. Roger*, L. Maillé, M.A. Dourges

Université de Bordeaux, CNRS, Laboratoire des Composites ThermoStructuraux,

UMR 5801, 33600 Pessac, France

* Corresponding author: e-mail: roger@lcts.u-bordeaux1.fr, phone number: +33 5 56 84 47

36, fax number: +33 5 56 84 12 25

Abstract

The aim the present work is to determine the reaction kinetics between a TiSi₂ powder with gaseous nitrogen. Isothermal nitridation of TiSi₂ powders with fine (1.4μm) and medium (4.5μm) particle size has been studied in pure nitrogen atmosphere ranging from 1000 to 1200°C for duration up to 50 hours. The isothermal nitridation kinetics of TiSi₂ powders were investigated by thermogravimetry. The nitridation rate strongly depends on the particle size and temperature. The smaller particle size exhibits the higher nitridation rate due to its larger surface area. The conversion process is complex with nucleation and growth of TiN at the surface of the grain and Si₃N₄ inside the grain promoted by Kirkendall effect with an influence of the volume increase.

Keywords: nitridation; kinetic law; isothermal; powder; nucleation.

1. Introduction

During the last decades, important progress has been made in the development of engineering ceramic materials, particularly the technical ceramics which are expected to be used in the structural components for high temperature applications. Previously, the synthesis of silicon nitride Si_3N_4 by the reaction between silicon and nitrogen has received much attention in the attempt to exploit the high-strength, heat-resistant properties of this material [1-7]. One of the attractive methods for the synthesis of Si_3N_4 ceramics is the nitridation of silicon powder compacts but this requires high temperatures treatments and induces a relative low volume increase of only 21.6%. The effects of the main controlling factors on the nitridation of silicon powders were examined in several previous studies: temperature [8-10], particle shape and size [8], impurities in the sample and in the atmosphere [11-13], composition of the atmosphere [14,15]. On this way, synthesis of silicon nitride and titanium nitride phases by direct nitridation of a TiSi_2 powder has the advantage to generate of more economical generation a ceramic. Indeed, $\text{TiN-Si}_3\text{N}_4$ composites represent an interesting combination with specific properties: high strength, low density, electrical conductivity [16]. This kind of composite can be easily obtained by self-propagating high temperature synthesis (SHS) under nitrogen atmosphere [17]. Previous studies undertaken on the nitridation of TiSi_2 powders demonstrated that the nitridation of this compound is a two stepped mechanism [18-20]. The influence of the temperature factor was also reported with a noticeable acceleration of the kinetics above 1100°C . Up to now, the observed limitations of this process were not clearly identified and no evaluation of the kinetic variations with temperature was made [20]. It was then especially interesting to realize our experiments around 1100°C . At this relative low temperature, the main difficulty is the requirement of long time for complete nitridation [21-23]. According to the Ti-Si-N phase diagram at 1100°C (Fig. 1) from Ma et al. [24], the

complete nitridation of the initial powder leads to the formation of TiN and Si₃N₄ phases according to the Reaction [1]:

This reaction would occur by a theoretical weight gain of 50% and a theoretical volume gain of 59% [24]. Extensive and complete studies of the kinetic analysis of silicon nitridation were previously realized and would be compared with titanium silicide nitridation [13,25]. So, the purpose of the present work is a study of the nitridation mechanism and kinetic of TiSi₂ powders with different grain sizes. In order to examine the effect of time and temperature parameters, the study was performed under normal atmosphere of N₂ at different temperatures between 1000 and 1200°C for durations up to 50 hours.

2. Materials and experimental procedures

The TiSi₂ powder (99.95%, 44 μm, Neyco) used in these experiments was analyzed by spectrographic analysis (S.C.A.-C.N.R.S., Villeurbanne, France) to contain 1.64% O, 0.43% C and 0.48% Fe in mass. The presence of some percents of iron is known as having a catalytic effect on Si reactivity [26]. Due to the very low quantity of iron in the TiSi₂ powder and the relative low working temperature we could consider it as having a negligible effect. The raw powder was milled by two different ways: with a vibratory mixer mill (Retsch MM200), or with a planetary ball mill (Fritsch Pulverisette 7). By these ways, two types of powders were obtained and used in the present work. The powders exhibit the following characteristics: d₅₀=4.5μm, d₉₀=10μm for the powder milled with a vibratory mill and d₅₀=1.4μm, d₉₀=1.9μm for the powder milled with a planetary ball mill. The grain size distributions of the powders were determined with the help of a Fritsch Analysette 22 Nanotec plus granulometric analyser. The mass variation measurements were performed in a thermogravimetric analyser

(Setaram TAG24) by heating from 20°C to the treatment temperature at a heating rate of 10°C/min by applying the isothermal treatment for various durations up to 50 hours. The measurements of mass gain at 1150°C and 1200°C were limited to 12.5 hours of nitridation because of technical limitations due to the volatility of silicon. Moreover, weight gains of about 30% were estimated as sufficient for a kinetic analysis. The two kinds of nitridation experiment were realized at normal pressure under a continuous nitrogen gas flow (50mL/min) to have a nitrogen excess. The experimental deviation of mass variation was estimated to be about 0.5%. The gaseous nitrogen used contains 2 ppm of oxygen as impurity, what was considered as having a low impact on the experiments. The powder masses used for thermogravimetric analysis were comprised between 100 and 110 mg for each sample, the mass conversion degree (α) of reaction at a time t was estimated according to Equation 1:

$$\alpha = \frac{(w_i - w_0)}{(w_f - w_0)} \quad (1)$$

where w_0 , w_i , w_f are the initial, intermediate and final sample masses for complete conversion of TiSi₂ according to Equation 1. Some powders were also treated in a tubular furnace at 1000 or 1100°C in order to obtain sufficient quantities of matter for X-ray diffraction (XRD) measurements. Indeed, these diffraction experiments were used for phase identification and quantitative phase determination in samples of sufficient size (200 mg) which permitted accurate powder diffraction profiles to be obtained [27]. Each pattern was analyzed using the Rietveld [28] whole profile fitting method with the software Fullprof [29]. XRD experiments in Bragg-Brentano geometry were performed with a Bruker D8 Advance diffractometer using a Cu K α radiation fitted with a one-dimensional position sensitive silicon strip detector (Bruker, Linxeye). XRD patterns were recorded using a step size of 0.01° for 2 θ range 10-90° and a counting time of 0.3 second per step. Sections of nitrided TiSi₂ grains were 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 5 kV (interaction volume of roughly 150 nm wide in this condition).

3. Results and discussion

3.1 Effect of temperature and grain size on the nitridation

Figures 2 and 3 shows the conversion curves $\alpha = f(t)$ obtained from thermogravimetric analyses on the two powders at nitridation temperatures of 1000, 1050, 1075, 1100, 1150 and 1200°C. From these figures it appears that the particle size and the operating temperature have noticeable effects on the reaction kinetic of TiSi_2 with nitrogen. Faster reaction rates and greater overall conversions are generally observed with increasing temperature. Atkinson et al. [30] carried out nitridation of silicon at temperatures between 1523 and 1633 K. Their results also indicated that a higher conversion rate was obtained by increasing temperature. Pigeon and Varma [31] reported the same tendency during the nitridation of silicon in the range from 1473 and 1623 K. In Figures 2 and 3, all curves have the same shape. Indeed, the initial part of the curves is approximately linear with high slopes, and the latter part is approximately parabolic. This illustrates the fact that the formation of a nitride layer during the reaction rapidly covers the grain surface and consequently decreases the reaction rate. This phenomenon is observable in the Figure 4-a) where a thin layer of TiN is formed at the entire surface of the grain after only a nitridation at 1100°C during 5h. But after a heating of 50 hours, Si_3N_4 nucleates inside the grain thanks to porosities promoting the interaction between silicon and gaseous nitrogen within the grain as shown in the Figure 4-b). The porosities are due to a Kirkendall effect because of the faster diffusion of titanium to the surface of the grain. The values of the conversion rate α after 10 hours of nitridation are given in Table 1. It is clear that increasing temperature and decreasing the grain size promote the

conversion into nitrides. This is not really surprising by considering the fact that finer powders also have larger specific surface areas per mass unit, what improves the interaction between TiSi_2 and nitrogen and induce an increase of apparent reaction rates. This kind of behavior has already been reported previously about the nitridation of silicon powders [31-33]. It is worth noting that all the values of α for the coarser powder are lower than the corresponding ones for the finer powder except the value at 1200°C. This behavior at 1200°C could be explained by a limitation of the reaction at the bottom of the powder. After 10 or 50 hours of nitridation, the conversion rates are relatively low at any temperatures and far from the full conversion. The best values in each case are obtained at 1200°C after 12.5 hours of nitridation leading to interesting values equal to 81.8% and 60.9% for the coarser powder and for the finer one, respectively. Half conversion rate is only attained after 10 hours for samples heated at 1150 and 1200°C.

3.2 Isothermal nitridation kinetics analysis

Three types of kinetic models can be proposed for solid state reactions corresponding to three main mechanisms [34]:

- 1) controlling step is diffusion of reactants or diffusional models,
- 2) administrated mechanism is chemical reaction at the interphase of reactant-product,
- 3) reaction rate is determined by nucleation and growth.

In order to identify the appropriate reaction mechanism, the classic kinetic models were tested to the experimental $\alpha = g(t)$ curves [35,36]. Among these kinetic models, no one was able to fit correctly the curves. The initial quasi-linear shape is approximately described by an Avrami-Erofeev model (A2) corresponding to a one- or two-dimensional growth of nuclei. The equation of this model is expressed by the Equation 2:

$$k'.t = [-\text{Ln}(1-\alpha)]^{1/2} \quad (2)$$

with t the time and k' the reaction rate constant. Figure 5 shows the variation of the calculated k' factors with temperature for the two powders. First, it can be noticed that the k' coefficients are higher for the finer powder. The values increase regularly with temperature between 1050 and 1150°C. But stronger variations are observed between 1000 and 1050°C and between 1150 and 1200°C. In the first case, there is a stronger increase whereas in the second case there is an unexpected decrease. The durations of the steps are nearly equal to 30 minutes between 1000 and 1150°C in the both cases. Their durations are higher at 1200°C; 40 minutes for the powder with the higher granulometry and 80 minutes for the finer one. This step corresponds to the speedy formation of a continuous layer of TiN at the surface of the grain but with a variation of the mechanism probably induced by an evolution of the phenomenon limiting the reaction. Finally, the use of the Johnson-Mehl-Avrami (JMA) equation was found appropriate to determine the kinetics of the decelerating part of the curves, which defines the conversion limitation [37-38]. So, our examination is mainly focused on this stage. The JMA model describes a wide variety of isothermal solid state transformations and it is helpful to determine the characteristics of nucleation-growth processes [39,40]. The JMA model is relevant for homogeneous or heterogeneous nucleation at randomly dispersed second phase particles and the growth rate of this new phase is controlled by temperature and is dependant upon time, what is in good agreement with the observations made on the grains [41]. Hence, the JMA model was applied for modeling the kinetic of the second part of the conversion process. The equation corresponding to the JMA model expresses the fact that conversion mechanisms depend on a broad variety of solid state reactions; it is expressed by Equation 3 [42]:

$$\alpha(t) = 1 - e^{-(kt)^n} \quad (3)$$

where t is time, n the Avrami exponent which depends on the growth mechanism and the geometry of powder [42]. The value of n depends on the conversion mechanisms involved

during the phase transformation, providing that the phase conversion proceeds by nucleation and growth models [43]. k is the reaction rate and is constant for a given temperature. Hence, the values of n and k depend on the kind of reaction mechanisms which control the transformation. Equation 3 is generally used to evaluate experimental data by means of a logarithmic plot of $\text{Ln}[-\text{Ln}(1-\alpha)]$ versus $\text{Ln}(t)$. This curve is called the Avrami plot. The slope and intercept of the resulting straight line are n and $n.\text{Ln}(k)$, respectively. Avrami plots of each sample are shown in Figure 6. The slightly deviation from linearity observed particularly on the curves at temperatures higher than 1100°C for the $d_{50} = 4,5 \mu\text{m}$ can be explained by the grain size dispersion. The calculated values of n and k are listed in Table 2. All the values of n are less than 2.5, which indicates that the nucleation-growth process is limited by the diffusion within the grain [44-46]. Also, at any constant temperature the values of n and k increase by increasing milling efficiency. The apparent activation energy of transformation was calculated using the Arrhenius equation of reaction rate constant in the logarithmic form:

$$\text{Ln}k = \text{Ln}k_0 - \frac{E_a}{R.T} \quad (4)$$

where k_0 is a constant called frequency factor, E_a is the apparent activation energy, R is the gases constant, T is the absolute temperature. Figure 7 displays the variation of $\text{Ln}(k)$ as a function of $1000/T$ for each sample. E_a is determined from the slope of lines in each temperature range. The estimated values of apparent activation energy of the nitridation reaction in various conditions are listed in Table 3. Figure 7 shows changes of the slopes around 1100°C for the two kinds of powder. The diminution of the slopes reveals a modification of the nitridation mechanism at this temperature. The apparent activation energies are nearly the same below 1100°C with values equal to 964.33 kJ.mol⁻¹ for the powder with $d_{50} = 1.4 \mu\text{m}$ and 920.82 kJ.mol⁻¹ for the powder with $d_{50} = 4.5 \mu\text{m}$. It can be deduced that the nucleation-growth mechanism is the same in both cases. At temperatures higher than 1100°C, the activation energies are lower than below 1100°C and the value with

the finer powder is half of the value for the other powder, the values being equal to 245.13 kJ.mol⁻¹ and 594.45 kJ.mol⁻¹, respectively. This important difference can only be attributed to the different kind of milling, whereas there is no evidence of such an effect below 1100°C. This demonstrates that decreasing the grain size of the powder influences the reaction mechanism at the higher temperatures. Nevertheless, the values of the frequency factors k_0 given in Table 4 indicate that the frequency factor of the finer powder is a little higher below 1100°C comparing to the other powder. The same remark is applicable to the values of the Avrami coefficients n (Table 2). The values of the Avrami coefficients are lower than the values expected in classical cases, comprised between 1.5 and 4. The range of calculated values for n is comprised between 0.150 and 0.765, it was previously identified for complex mechano-chemical syntheses [47,48]. In the present case, this is probably induced by the Kirkendall effect which generates complex solid-gas diffusion phenomenon. Despite the difficulties to interpret the values from the JMA theory, this result tends to confirm the fact that decreasing the grain size promotes the reaction by increasing the number of nucleation-growth sites, the apparent activation energy staying the same. In both cases, a decrease of the frequency factor values is observed above 1100°C. The variation is particularly noticeable for the finer powder. As a consequence, above 1100°C, the decrease of the apparent activation energy of the finer powder could promote the reaction but in the same time the strong decrease of the frequency factor indicates a great limitation of the reaction. It could be considered that this limitation is attributable to a rapid decrease of the porosity into the powder and/or to the formation of a coating at the surface of the sample. The mass percentage variations of the different phases during nitridation at 1000 and 1100°C for durations up to 100 hours are given in Figure 8, they were measured X-ray diffraction and Rietveld analysis on powders heat treated in tubular furnace. Those analyses were based in each case on a unique sample by successive samplings and by incrementing the heating times. Between each

sampling, the samples were homogenized by crushing. By this way the nitridation cannot be limited by gas diffusion. The mass variations of all the phases identified (TiSi_2 , Si, TiN and Si_3N_4) are given in the Figure 8. It appears that the TiSi_2 reaction kinetic is obviously higher for the smaller particles. It is also clear that the nitridation of titanium is easier than the nitridation of silicon. Indeed, even if the kinetics depend on temperature and grain size, in all cases the TiN mass percentages reach rapidly high values of about 50%. Contrarily to the nitridation of silicon that appears very slow since the reached values after some dozen of hours are less than 10% in mass, except at 1100°C for the finer powder but after several dozens of hours of treatment. From those results, it can be deduced that in all cases the nitridation of TiSi_2 powders proceeds in two processes corresponding to the rapid nitridation of titanium by forming TiN at the surface of the grain and to the slow nitridation of silicon by forming Si_3N_4 within the grain. These results agree well with the observations realized about the nitridation of TiSi_2 by Córdoba et al. [20]. The kinetics of these steps strongly depend on the temperature but also on the grain size. In the first times, the formation of TiN is the predominant reaction. This is not the case for the formation of Si_3N_4 even if its formation is accelerated by higher temperatures. The use of smaller powders facilitates the reaction between silicon and nitrogen especially at 1100°C so much so that free silicon is no more detectable by X-ray diffraction experiments after 50 hours at 1100°C . In the same time, the cumulative mass fractions of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ reaches a total of 51.4 mass% which is a value largely higher than the other ones obtained for this duration. The corresponding value for the powder with the higher grain size is only of 16.1 mass% with 33.3 mass% of silicon. It should be remarked that the finer powder heated at 1100°C during 100 hours is practically fully converted. Indeed, it contains 44.0% of TiN and 56% of Si_3N_4 in mass, the full conversion leading to a mass ratio of 40/60. This result is largely higher than the corresponding TGA sample which exhibits only a conversion rate equal to 60%. This

difference can be justified by the fact that the powders used for the X-ray analyses were homogenized by crushing between each sampling in order to promote the powder/gas interaction.

3.3 Kinetic model of TiSi_2 powders nitridation

The nitridation process of TiSi_2 can be partially compared to the nitridation behavior of silicon powders studied by Pigeon and Varma [13]. In their work these authors demonstrate that the nitridation of silicon consists of a reaction-bonding process divided into three stages. During the first stage, silicon exposed at the surface of the powder is converted into silicon nitride nuclei which are at the origin of a seeding effect inducing the second stage with a fast and massive nitridation rate. During this second stage, nitrogen is able to diffuse freely in the macropores. However, the volume gain induced by the particle nitridation decreases the permeability and consequently slows down the conversion kinetics, what corresponds to the third stage of the silicon conversion process. Nitridation of TiSi_2 is more complex because of the presence of titanium that influences the nitridation kinetics of silicon. The main difference between the present study and the one of Pigeon et al. [13] is that the nitridations of titanium and silicon are obtained by different mechanisms. Moreover, full nitridation of TiSi_2 is characterized by a volume gain equal to 59%. Compared to the corresponding value for pure silicone that is 21%, the volume increase during TiSi_2 conversion is very larger and could generate a decrease of the permeability of the powder and consequently an intense slowdown of the mass gain. This is the situation identified for the finer powder from 1100°C. According to the experimental observations, the reaction between TiSi_2 and nitrogen is composed of two main steps with different rates: the first one is mainly attributable to the rapid formation of a continuous TiN layer at the surface of the grains; the second step is slower. As the thickness of the TiN layer gradually increases, the nitridation rate decreases and the nucleation-growth

reactions are mainly controlled by diffusion. Concretely, silicon atoms cannot react with nitrogen because of the formation of the TiN layer, they react thanks to the formation of Kirkendall porosities that promote the diffusion of nitrogen molecules and their reaction with silicon atoms inside the grains. This conversion mechanism is complex and involves two different chemical reactions at different times and locations and by different ways as represented in the Figure 9. Thermal and milling activations increase Avrami exponent and reduce diffusion barriers effect, except at 1150 and 1200°C (Table 2). Indeed, lowering the grain size by milling increases the surface area and the structural defect, what accelerates the conversion [6]. Hence, larger number of nucleation sites and shorter diffusion routes enhance the nitridation reaction. Above 1100°C, the Avrami coefficients are notably lower for the finer powder. This is attributable to the apparition of a limitation for this powder at the highest temperatures because of the rapid formation of a dense layer at the surface of the powder obtained by volume increase. In fact, decreasing grain size promotes the reaction but in the same time the reaction occurs essentially at the surface of the powder. This volume gain influences the kinetic by obstructing the macroporosities between the grains, as reported by Pigeon and Varma. Therefore, the diffusion of nitrogen is made more difficult and leads up to an inhomogeneous nitridation of the whole powder. By this way, reducing grain size is deleterious for temperature above 1100°C. Analysis of the results also proposes that the phase conversion could partially depend on a powder-gas interface controlled growth [14,24].

This mechanism can be detailed as follows:

- a) nitrogen molecules are chemisorbed onto the powder surface. Nuclei of titanium nitrides are formed on the grains surface in the initial stage of the nitridation,
- b) titanium atoms diffuse to the surface of the nuclei to continue the nitridation reaction. A continuous layer composed of TiN is gradually formed at the surface of the grains, as shown on Figure 4-a),

c) when the TiN layer has thickened to cover the grain surface completely, the reaction rate decreases and is controlled by the diffusion of titanium and nitrogen through the TiN layer. In the same time, silicon begins to react with gaseous nitrogen infiltrated in the grain (Fig. 4-b)). Owing to volume increase, those reactions are also dependent upon the gas diffusion in the macroporosities of the powder that can be reduced at the surface.

As already expressed, the nitridation of titanium is the faster reaction and consequently is predominant. At the last stage, the conversion rate is relatively low but strongly depends on the particle size. Indeed, a reduction of the mean size of the powder makes possible to reach a conversion rate largely higher because of a more important area of contact between powder and the gas and also because of a reduction of the diffusion distances. In our case, this effect appears to be insufficient to reach rapidly a full conversion. As reported by Pigeon et al. [13], the compact effects dominate with the formation of a dense product layer on the outer side of the powder. The full conversion is consequently difficult in the case of large sized samples. More clearly, the global conversion rate and the final conversion value also depend on the quantity of matter to react.

4. Conclusion

The purpose of this study is to identify chemical mechanisms and the effect of temperature and grain size on the nitridation of TiSi_2 by pure nitrogen at temperatures comprised between 1000 and 1200°C for durations up to 50 hours. Nitridation behavior of TiSi_2 powders has been evaluated by kinetics investigations. The degree of nitridation strongly depends on both temperature and grain size. X-ray powder diffraction indicated that the nitridation of titanium to TiN is clearly the fastest phenomenon at any temperatures. This nitride forms a continuous layer at the surface of the grain. Nitridation of silicon is slower and highly dependent upon the temperature and grain size. This nitride is formed within the grain via a Kirkendall effect

which promotes the reaction between silicon and gaseous nitrogen. So, the nitridation kinetic of TiSi_2 powders exhibits two processes with a rapid crystallization of TiN at the surface of the grain accompanied and substituted in time by a slow nucleation-growth process of Si_3N_4 in the grain that obeys to the Johnson-Mehl-Avrami model. For the two powders, the activation energies were estimated. In any cases, the full nitridation is not reached even for long time treatments. The TiSi_2 powders nitridation process can be described by three different steps:

- a) Nuclei of TiN are rapidly formed on the grains surface in the initial stage of the nitridation.
- b) A product layer of TiN is gradually formed at the surface of the grains by diffusion of titanium and nitrogen.
- c) TiN synthesis decreases because of a thickened layer of products that completely covers the grain surface. In the same time, owing to Kirkendall porosities, free silicon can react with nitrogen coming from porosities. This mechanism is particularly complex and its kinetic is generally low.

The difficulty to reach a homogeneous and full conversion also comes from a lowering of the powder permeability because of the high volume increase which generates a noticeable limitation to gaseous nitrogen diffusion. This effect is largely influenced by temperature and grain size. A decrease of the grain size and an increase of temperature promotes a rapid and a high level of nitridation especially at the surface of the powder. This limits the interest of using low grains-sized at high temperature because the grains at the top of the powder react rapidly contrary to the grains at the bottom. The main inconvenient is a possible sealing at the top of the powder preventing its homogeneous conversion. The research of solutions to promote and to facilitate the full and homogenous conversion should be shortly examined.

Acknowledgement

The authors wish to express their thanks to Pr. Yann Le Petitcorps, from the University of Bordeaux, for his scientific assistance and for critical reading of the manuscript. Thanks go also to Christine Picard for all her technical assistance and TGA measurements.

References

- [1] H. Lange, G. Wötting, G. Winter, Silicon nitride-From powder synthesis to ceramic materials, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1579-1597.
- [2] F. Riley, Preparation and properties of silicon nitride based materials, *Mater. Sci. Forum* 47 (1989) 70-83.
- [3] H.M. Jennings, B.J. Dalgleish, P.L. Pratt, Reactions between silicon and nitrogen, *J. Mater. Sci.* 23 (1988) 2573-2583.
- [4] G. Ziegler, J. Heinrich, G. Wötting, Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride, *J. Mater. Sci.* 22 (1987) 3041-3086.
- [5] H.M. Jennings, On reactions between silicon and nitrogen, *J. Mater. Sci.* 18 (1983) 951-967.
- [6] A.J. Moulson, Reaction-bonded silicon nitride: its formation and properties, *J. Mater. Sci.* 14 (1979) 1017-1051.
- [7] M.J. Hoffmann, G. Petzow, Silicon Nitride Ceramics Scientific and Technology Advances, in: I.W. Chen, P.F. Belcher, G. Petzow, T.S. Yeu (Eds.), *Materials Research Society Microstructure design of Si₃N₄ based ceramics*, Pittsburgh, 1993, pp. 3-14.
- [8] A. Atkinson, P.J. Leatt, A.J. Mouslon, The role of nitrogen flow into the nitriding compact in the production of reaction-sintered silicon nitride, *Proc. Brit. Ceram. Soc.* 22 (1973) 253-274.
- [9] F. Wang, X. Qin, G. Jin, X. Guo, Temperature-controlled synthesis of Si₃N₄ nanomaterials via direct nitridation of Si powders, *Physica E* 42 (2010) 2033-2035.
- [10] M. Maalmi, A. Varma, Intrinsic nitridation kinetics of high-purity silicon powder, *AlChE Journal* 42 (1996) 3477-3483.

- [11] C.E. Bouldin, E.A. Stern, M.S. Donley, T.G. Stoebe, Iron impurities in Si_3N_4 processing, J. Mater. Sci. 20 (1985) 1807-1810.
- [12] W.R. Moser, D.S. Briere, R. Correia, G.A. Rossetti, Kinetics of iron-promoted silicon nitridation, J. Mater. Res. 1 (1986) 797-802.
- [13] R.G. Pigeon, A. Varma, Quantitative kinetic analysis of silicon nitridation, J. Mater. Sci. 28 (1993) 2999-3013.
- [14] H. Kim, C.H. Kim, The effects of second-component gases on the transport properties of silicon nitriding atmosphere, J. Mater. Sci. Letters 3 (1984) 199-200.
- [15] H. Kim, C.H. Kim, The influence of the various transport properties of the nitriding atmosphere on the formation of reaction-bonded Si_3N_4 , J. Mater. Sci. 20 (1985) 149-156.
- [16] C.C. Liu, J.L. Huang, Effect of the electrical discharge machining on strength and reliability of $\text{TiN}/\text{Si}_3\text{N}_4$ composites, Ceram. Int. 29 (2003) 679-687.
- [17] H. Wanbao, Z. Baolin, Z. Hanrui, L. Wenlan, Combustion synthesis of Si_3N_4 -TiN composite powders, Ceram. Inter. 30 (2004) 2211-2214.
- [18] L. Maillé, M.A. Dourges, S. Le Ber, P. Weisbecker, F. Teyssandier, Y. Le Petitcorps, R. Pailler, Study of the nitridation process of TiSi_2 powder, Appl. Surf. Sci. 260 (2006) 29-31.
- [19] J. Roger, L. Maillé, M-A. Dourges, Effect of temperature and grain size on TiSi_2 nitridation, ICCM19 proceeding, (2013) p2653-2660.
- [20] J.M. Córdoba, M.D. Alcalá, M.J. Sayagués, M.A. Avilés, C. Real, F.J. Gotor, Nitriding study of titanium silicide intermetallics obtained by mechanical alloying, Intermetallics 16 (2008) 948-954.
- [21] M. Wittmer, Self-aligned diffusion barrier by nitridation of TiSi_2 , Appl. Phys. Lett. 52 (1988) 1573-1575.

- [22] J. Perez-Rigueiro, C. Jimenez, L. Vazquez, R. Perez-Casero, J.M. Martinez-Duart, Nitridation of TiSi_2 thin films by rapid thermal processing, *Surf. Coat. Technol.* 80 (1996) 72-75.
- [23] A. Kamgar, F.A. Baiocchi, A.B. Emerson, T.T. Sheng, M.J. Vasile, R.W. Haynes, Self-aligned TiN barrier formation by rapid thermal nitridation of TiSi_2 in ammonia, *J. Appl. Phys.* 66 (1989) 2395-2401.
- [24] X. Ma, C. Li, W. Khang, The thermodynamic assessment of the Ti–Si–N system and the interfacial reaction analysis, *J. Alloys Compd.* 394 (2005) 138-147.
- [25] F.W. Chang, T.H. Liou, F.M. Tsai, The nitridation kinetics of silicon powder compacts, *Thermochimica Acta* 354 (2000) 71-80.
- [26] D. Kusano, Effects of impurity iron content on characteristics of sintered reaction-bonded silicon nitride, *Int. J. Appl. Ceram. Technol.* 10 (2013) 690-700.
- [27] R.G. Pigeon, A. Varma, Quantitative phase analysis of Si_3N_4 by X-ray diffraction, *J. Mater. Sci. Lett.* 11 (1992) 1370-1372.
- [28] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.* 2 (1969) 65-71.
- [29] J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B* 192 (1993) 55-69.
- [30] A. Atkinson, A.J. Moulson, E.W. Roberts, Nitridation of high-purity silicon, *J. Am. Ceram. Soc.* 59 (1976) 285-289.
- [31] R.G. Pigeon, A. Varma, A.E. Miller, Some factors influencing the formation of reaction-bonded silicon nitride, *J. Mater. Sci.* 28 (1993) 1919-1936.
- [32] R. Pompe, L. Hermansson, Characterization of silicon powders for the production of Si_3N_4 , *Mater. Sci. Eng.* 71 (1985) 355-362.

- [33] B.W. Sheldon, J. Szekely, J.S. Haggerty, Formation of reaction-bonded silicon nitride from silane-derived silicon powders: macroscopic kinetics and related transport phenomena, *J. Am. Ceram. Soc.* 75 (1992) 677-685.
- [34] A. Khawam, D.R. Flanagan, Solid-State Kinetic Models: Basics and Mathematical Fundamentals, *J. Phys. Chem. B* 110 (2006) 17315-17328.
- [35] A.K. Galwey, M.E. Brown, Thermal decomposition of ionic solids, Amsterdam, Elsevier, 1999, pp. 75-110.
- [36] ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, S. Vyazovkina, A.K. Burnhamb, J.M. Criadoc, L.A. Pérez-Maquedac, C. Popescud, N. Sbirrazzuolie, *Thermochimica Acta* 520 (2011) 1–19.
- [37] M. Avrami, Granulation, phase change and microstructure: Kinetics of phase change (III), *J. Chem. Phys.* 9 (1941) 177-184.
- [38] W.A. Johnson, P.A. Mehl, Reaction kinetics in processes of nucleation and growth, *Trans. Am. Inst. Metall. Pet. Eng.* 135 (1939) 416-458.
- [39] J.P. Braganti, O. Held, F.A. Kuhnast, E. Illekov, Kinetic study of isothermal crystallization in amorphous $\text{Al}_{33}\text{Ni}_{16}\text{Zr}_{51}$ produced by mechanical alloying, *Thermochimica Acta* 362 (2000) 71-78.
- [40] M.A. Bab, L. Mendoza-Zélis, L.C. Damonte, Nanocrystalline HfN produced by mechanical milling: kinetic aspects, *Acta Mater.* 49 (2001) 4205-4213
- [41] J. Malek, The applicability of Johnson-Mehl-Avrami model in the thermal analysis of the crystallization kinetics of glasses, *Thermochimica Acta* 267 (1995) 61-73.
- [42] J.W. Christian, The theory of transformation in metals and alloys. Oxford (UK): Elsevier Ltd., 2002.
- [43] A. Narlikar, Studies of high temperature superconductors: Advances in research and applications. Nova Publishers, Technology & Engineering, 2001, pp.48.

- [44] Y. Shen, H.H. Hng, J.T. Oh, Formation kinetics of Ni-15%Fe-5%Mo during ball milling. *Mater. Lett.* 58 (2004) 2824-2828.
- [45] H. Sheu, L. Hsiung, J. Sheu, Synthesis of multiphase intermetallic compounds by mechanical alloying in Ni-Al-Ti system, *J. Alloys Compds.* 469 (2009) 483-487.
- [46] L.E. Levine, K. Lakshmi Narayan, K.F. Kelton, Finite size corrections for the Johnson–Mehl-Avrami-Kolmogorov equation, *J. Mater. Res.* 12 (1997) 124-132.
- [47] C. Suryanarayana, E. Ivanov, V.V. Boldyrev, The science and technology of mechanical alloying, *Mater. Sci. Eng. A304-306* (2001) 151-158.
- [48] S. Sheibani, A. Ataie, S. Heshmati-Manesh, Kinetics analysis of mechano-chemically and thermally synthesized Cu by Johnson–Mehl–Avrami model, *J. Alloys Compds.* 455 (2008) 447-453.

|

Figure 1. Calculated isothermal Ti-Si-N diagram at 1373 K [24].

Figure 2. Mass conversion degree of reaction of the powder with $d_{50}=1.4\mu\text{m}$ for nitridation time up to 50 hours at temperatures between 1000 and 1200°C.

Figure 3. Mass conversion degree of reaction of the powder with $d_{50}=4.5\mu\text{m}$ for nitridation time up to 50 hours at temperatures between 1000 and 1200°C.

Figure 4. Backscattered electrons image of a transverse TiSi_2 grain nitridated at 1100°C :
a) during 5h, b) during 50h.

Figure 5. Plots of k' coefficients versus temperature for the two powders between 1000 and 1200°C .

Figure 6. Avrami plot of $\text{Ln}[-\text{Ln}(1-\alpha)]$ versus $\text{Ln}(t)$ for the powder between 1000 and 1200°C with a) $d_{50}=1.4\mu\text{m}$ and b) $d_{50}=4.5\mu\text{m}$.

a)

b)

Figure 7. Arrhenius plot $\text{Ln}(k) = f(1000/T)$ for nitridation of the powder between 1000 and 1200°C with a) $d_{50}=1.4\mu\text{m}$ and b) $d_{50}=4.5\mu\text{m}$. The blue and red dotted lines are the linear fits of the two behaviors.

a)

b)

c)

d)

Figure 8. Phases quantifications by Rietveld method during nitridation of TiSi_2 powders: a) powder with $d_{50}=1.4\mu\text{m}$ at 1000°C, b) powder with $d_{50}=4.5\mu\text{m}$ at 1000°C, c) powder with $d_{50}=1.4\mu\text{m}$ at 1100°C, d) powder with $d_{50}=4.5\mu\text{m}$ at 1100°C.

Figure 9. Schematic representation of the three main stages of the conversion: at the beginning TiSi_2 powder is in presence of gaseous nitrogen, then nitrogen reacts with titanium atoms to form a layer of TiN at the surface of the grain by generating a silicon sublayer. Owing to Kirkendall effect, porosities appear within the grain. Si_3N_4 is formed at the surface of the porosities.

Table 1. Values of the mass conversion rate α for the two powders with mean grain sizes of 1.4 and 4.5 μm after 10 hours of nitridation at 1000, 1050, 1100, 1150 and 1200°C.

		T (°C)					
	Mean grain size (d_{50})	1000	1050	1075	1100	1150	1200
α (%)	1.4 μm	25.7	30.1	34.5	41.8	55.5	59.1
($\pm 1\%$)	4.5 μm	25.7	28.1	31.0	36.9	51.6	76.2

Table 2. Calculated values of nitridation kinetics parameters (k , n) and of the corresponding reliability factors (R^2) for the two powders between 1000 and 1200°C.

T (°C)	Powder with $d_{50} = 1.4\mu\text{m}$			Powder with $d_{50} = 4.5\mu\text{m}$		
	k (min^{-1})	n	R^2	k (min^{-1})	n	R^2
1000	3.66×10^{-7}	0.150	0.992	1.47×10^{-7}	0.125	0.997
1050	7.90×10^{-6}	0.195	0.991	5.77×10^{-6}	0.191	0.979
1075	4.23×10^{-5}	0.230	0.994	1.45×10^{-5}	0.200	0.992
1100	3.08×10^{-4}	0.317	0.995	9.75×10^{-5}	0.257	0.998
1150	6.35×10^{-4}	0.188	0.995	5.29×10^{-4}	0.237	0.975
1200	1.32×10^{-3}	0.252	0.996	3.35×10^{-3}	0.765	0.989

Table 3. Apparent activation energies of nitridation for the two powders between 1000 and 1200°C.

Activation energy E_a (kJ.mol^{-1})		
Temperature range	1000-1100°C	1100-1200°C
Powder with $d_{50} = 1.4\mu\text{m}$	964	245
Powder with $d_{50} = 4.5\mu\text{m}$	921	594

Table 4. Frequency factors of nitridation for the two powders between 1000 and 1200°C.

Temperature range	Frequency factor k_0 (min ⁻¹)	
	1000-1100°C	1100-1200°C
Powder with $d_{50} = 1.4\mu\text{m}$	1.18×10^{33}	6.46×10^5
Powder with $d_{50} = 4.5\mu\text{m}$	9.65×10^{30}	3.85×10^{18}