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ON THE MECHANISM OF SILICON NITRIDATION IN THE PRESENCE OF ZrO₂

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Résumé- Le présent travail concerne les réactions entre Si et ZrO₂ susceptibles d'intervenir pendant la nitruration du silicium et pouvant affecter les produits de réaction. Les essais d'analyse thermique, de dilatométrie et de diffraction des rayons X montrent que Si réagit avec ZrO₂ pour donner ZrSiO₄ et ZrSi_{2-x}:



Ultérieurement, la nitruration peut mener à une apparition de ZrN, Zr₇O₁₁N₂ et Si₃N₄. Certains de ces composés (par ex. ZrN et Zr₇O₁₁N₂) pourraient diminuer la résistance à l'oxydation du matériau fritté.

Abstract - The present work addresses the interaction between Si and ZrO₂ which may occur during the nitridation stage of silicon and can affect the final reaction products. Using the thermoanalytical methods combined with X-ray diffractometry it has been shown that the Si, parallel to the nitride formation, disproportionates in the presence of ZrO₂ forming ZrSiO₄ and ZrSi_{2-x} according to



It is shown further that these reaction products form ZrN, Zr₇O₁₁N₂ and Si₃N₄ during the nitridation. ZrO₂ thus affects the nitridation so that less desirable by-products are introduced (i.e. ZrN, Zr₇O₁₁N₂) which may cause a decreased oxidation resistance of the sintered body.

I - INTRODUCTION

Increasing attention has been given in recent years to improving the strength and fracture toughness of ceramics by providing crack arresters in the ceramic matrix. Zirconia systems appear to be the most promising ones to study these phenomena. In partially stabilized zirconia (PSZ) the metastable tetragonal phase will transform to the monoclinic phase in the stress field of propagating cracks. This stress-induced transformation is assumed to provide the principal toughening mechanism in the PSZ. Zirconia is also being considered as a sintering aid for the fabrication of dense Si₃N₄-based ceramics. The emerging techniques (Sintered Reaction Bonded and Nitrided

Pressureless Sintered Silicon Nitride (SRBSN and NPS-technique))^{1,2/} for fabrication of complex shapes of dense Si_3N_4 -based ceramics involve use of Si powder in the starting powder materials. In these new techniques it is of interest to mix the Si powder, before nitridation, with the sintering and/or toughening aids to get dense Si_3N_4 -based ceramics without posttreatments. In this work the interaction between ZrO_2 and Si has been studied in both Ar and N_2 atmosphere to elucidate the reaction sequence in this system.

II - EXPERIMENTAL METHODS

The characteristics of the starting powders are given below.

Origin	Impurities (wt.%)	BET Spec. Surface area (m^2/g)
Si Kema Nord AB	0.40 Fe ; 0.23 Al; 0.02 Ca	2.3
ZrO_2 Kebo Grave AB	p.a.	6.5

The powders were mixed in molar ratios $\text{ZrO}_2:\text{Si} = 1:2 - 1:3$ in anagate mortar and powder compacts then were formed by uniaxial and isostatic pressing. Mettler thermoanalyzer TAI (TGA) and Harrop Dilatometer TD716 (TDA) were used to determine the mass and volumetric change, respectively. The dilatometric (TDA) curves were electronically compensated for the expansion of the alumina holder. The characteristic parameters were as follows: TGA sensitivity/range: 0.05 mg/100 mg; TDA sensitivity/range: $2 \cdot 10^{-4}$ mm per mm rec./1% per inch; gases used: N_2 -SR, Ar-SR (nominal impurity content: less than 15 ppm); flow rate: ca 5 l/h. The phases were identified by X-ray powder diffractometry (XRD).

III - RESULTS AND DISCUSSION

1. Dilatometry, thermogravimetry and XRD.

Fig. 1 shows a dilatometric (TDA) curve for a $\text{ZrO}_2/2.5$ Si powder compact in an argon atmosphere. Above about 980°C the compact is seen to start shrinking but at ca. 1200°C the shrinkage is altered to expansion which recedes slowly up to 1450°C . The minimum on the TDA curve coincides with the $m \rightarrow t$ - ZrO_2 phase transition temperature ($1175^\circ\text{C}/3$).

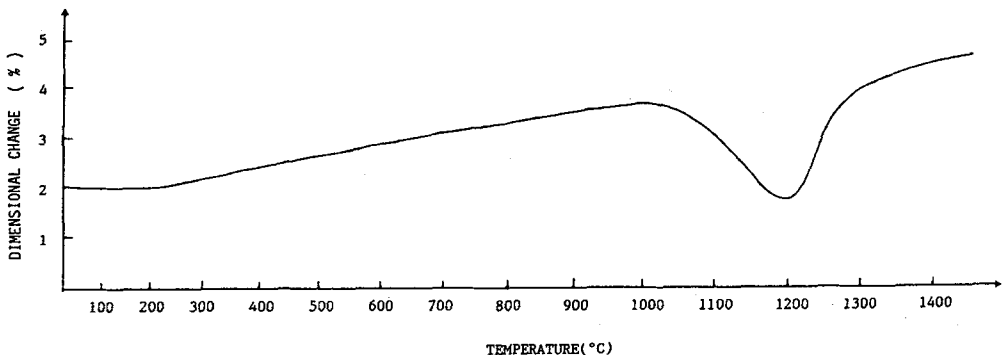
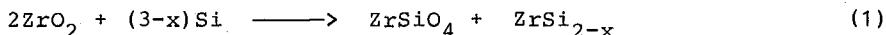
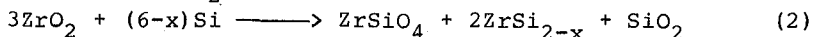


Figure 1. Dilatometric (TDA) curve for a $\text{ZrO}_2/2.5$ Si (molar ratio) powder compact heated at $5^\circ/\text{min}$ in an argon atmosphere.

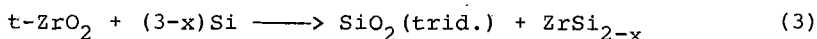
This change coincides with (a) the appearance of SiO_2 as an intermediate phase and (b) the $m \rightarrow t\text{-ZrO}_2$ phase transition ($T_{eg} \sim 1175^\circ\text{C}$). The chemical equation for the phases formed below 1200°C (Table 1) is



and corresponds to a change of molar volume $\Delta\bar{V} \sim -9.0\%$ (for $x = 0$) and thus is consistent with the observed contraction. Above 1200°C formation of SiO_2 occurs. The summary equation of



leads to $\Delta\bar{V} \sim -6.4\%$, ($x = 0$) while, instead, an expansion is observed (Fig.1). Considering only the partial process of



the $\Delta\bar{V} \sim 0$ for $x = 0$ and will change to expansion for $x > 0$ unless a significant contraction of the ZrSi_{2-x} lattice occurs as a result of non-stoichiometry. No such evidence has been apparent from the XRD spectra. The expansion as observed in Fig.1 above 1200°C will certainly be assisted by the transformation of $m\text{-ZrO}_2$ to the $t\text{-ZrO}_2$ of lower \bar{V} . (The above \bar{V} values are based on room temperature data and a significant difference of expansion coefficients for the phases involved may also be of importance in a rigorous treatment).

2.2 Free enthalpy changes

Table 2 below shows the thermodynamic data for the total reaction (1) and the partial reaction (2) with the intermediary SiO_2 formation.

T(K)	$\Delta H(\text{cal/mol})$		$\Delta S(\text{cal/mol K})$		$\Delta G(\text{cal/mol})$	
	(1)	(2)	(1)	(2)	(1)	(2)
298	$1.0 \cdot 10^3$	$7.5 \cdot 10^3$	-0.4	0.9	$1.1 \cdot 10^3$	$7.2 \cdot 10^3$
1400	$-0.9 \cdot 10^3$	$4.1 \cdot 10^3$	-3.2	-4.1	$3.6 \cdot 10^3$	$9.8 \cdot 10^3$
1600	$-3.8 \cdot 10^3$	$-0.3 \cdot 10^3$	-5.2	-7.1	$4.5 \cdot 10^3$	$11.1 \cdot 10^3$

Table 2. Thermodynamic data obtained /5/ for reaction (1) and (2).

As is apparent the ΔH and ΔS value for the total reaction is positive and negative, respectively, over the temperature range of 298-1600 K (25-1327°C). Thus according to the tabulated data there is no driving force for the reaction (1). For the reaction (2) including the formation of SiO_2 the ΔH is negative only at 1600 K but ΔS is still negative thus giving positive ΔG (but much less positive than for the reaction (1)). The reaction (2) however still takes place. To an extent this discrepancy certainly reflects the lack of accuracy in the tabulated data but, at the same time, suggests that the driving force for this reaction is very low. This is consistent with the results of XRD showing that the reaction is never complete - residual Si and ZrO_2 is always present in a relatively significant amount.

Besides, if the reaction (2) gives ZrSi_{2-x} with $x > 0$ the entropy on the left side will be lower and the entropy on the right side will be increased by a configurational term, due to the non-stoichiometry of ZrSi_{2-x} . Thus the total ΔS term may turn positive and give a negative ΔG already at the temperature of the observed start of the ZrSi_{2-x} formation (980°C (1253K), Fig. 1).

Formation of non-stoichiometric ZrSi_{2-x} is also consistent with the observed expansion above about 1200°C (Fig.1).

IV - CONCLUSION

Pure zirconia reacts with silicon, the reaction being already initiated below 1000°C. This reaction seems to start at a lower temperature or occurs parallel to the silicon nitride formation. The products formed, $ZrSiO_4$ and $ZrSi_{2-x}$, give ZrN , $Zr_7N_{11}O_2$ and Si_2N_2O as by-products of nitridation. The introduction of these by-products may destroy the oxidation resistance of Si_3N_4 materials sintered with ZrO_2 .

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