JOURNAL OF MATERIALS SCIENCE 31 (1996) 90–94

# The effects of additives on the properties and structure of hot-pressed aluminium titanate ceramics

LIU ZHIEN, ZHAO QINGMIN, YUAN JIANJUN
*Department of Inorganic Materials, East China University of Science and Technology, Shanghai 200237, People's Republic of China*

The effects of additives ($MgO$–$Al_2O_3$–$SiO_2$, $Al_2O_3$–$SiO_2$, $Si_3N_4$, SiC) on the properties and structure of hot-pressed aluminium titanate ceramics were studied. The results showed that the bending strength of aluminium titanate ceramics with additives was improved greatly, while the thermal expansion coefficient was also increased due to the change of structure for aluminium titanate ceramics. The results of X-ray diffraction patterns showed that a solid state reaction occurred between the additives and aluminium titanate, and a solid solution was formed.

## 1. Introduction

Aluminium titanate is a well-known ceramic with a low thermal expansion coefficient ($\alpha_{RT\text{-}1000} \leqslant 15 \times 10^{-7}\,°C^{-1}$) and a high melting point (1860 °C). Since the near-zero thermal expansion coefficient of a material minimizes thermal stresses in a body, it has potential use in thermal shock applications. For example, it can be used as a support of a catalyst at high temperatures, diesel engine cylinder liners etc. [1, 2]. However, poor mechanical strength caused by extensive microcracking and its tendency to decompose into component oxides below 1250 °C limit its application in industry. In the study of aluminium titanate ceramics, it is difficult to keep it having both high mechanical strength and low thermal expansion. Because the thermal expansion coefficient of aluminium titanate crystal is anisotropic, and the values are (up to 1000) $\alpha_a = 11.8 \times 10^{-7}\,°C^{-1}$, $\alpha_b = 19.4 \times 10^{-7}\,°C^{-1}$, $\alpha_c = -2.6 \times 10^{-7}\,°C^{-1}$, respectively [3] from which the calculated thermal expansion coefficient of polycrystalline titanate ceramic is $94 \times 10^{-7}\,°C^{-1}$. In fact, aluminium titanate ceramic has a thermal expansion coefficient as low as $15 \times 10^{-7}\,°C^{-1}$. The reason is that there exist extensive microcracks in ceramics resulting from high thermal stress during cooling due to the anisotropy in expansion. When heating, the healing of microcracks compensates for the expansion of aluminium titanate crystal. Therefore, researchers are trying to prepare aluminium titanate ceramics with both a low thermal expansion coefficient and high mechanical strength.

In this paper, by adding oxide and non-oxide additives into aluminium titanate ceramics, the effects of additives on properties and structure of hot-pressed aluminium titanate ceramics were studied.

## 2. Experimental procedure

### 2.1. Preparation of aluminium titanate ceramics

The $\alpha$-$Al_2O_3$ (purity 99.0%) $TiO_2$–rutile (purity 98.0%) and $Fe_2O_3$ powders (purity 98.0%) were used to synthesize $\beta$-$Al_2TiO_5$ powders. The batch of the composition with $Al_2O_3$:$TiO_2$:$Fe_2O_3$ = 53.5:43.3:3.4 (weight ratio) was calcined at 1380 °C for 4 h. Then single $\beta$-$Al_2TiO_5$ phase was formed; $Fe_2O_3$ is the stabilizer. It can be substituted for Al ions during calcining to form $\beta$-$Al_{2(1-x)}$ $Fe_{2x}TiO_5$ solid solution, which is more stable than $\beta$-$Al_2TiO_5$. The additives used in this study were all prepared in the laboratory. The $Si_3N_4$ and SiC powders were supplied by Shanghai Institute of Ceramics, Academia Sinica; $MgO$–$Al_2O_3$–$SiO_2$ (MAS, cordierite composition), $Al_2O_3$–$SiO_2$ (AS, mullite composition) and $Li_2O$–$Al_2O_3$–$SiO_2$ [7] (LAS) glass–ceramic powders were fabricated in our laboratory by chemical methods.

Aluminium titanate ceramics were prepared by the hot-pressing method. First, the additives were added to the synthesized $\beta$-$Al_2TiO_5$ powders, then mixed by ball-milling, finally hot-pressing the mixture at 1300–1500 °C for about 30 min after drying.

### 2.2. Characterization

The bulk density and apparent porosity of the ceramics were measured by Archimedes' method. The calculating equation is as follows

bulk density: $D_b = D_w\, m_1/(m_3 - m_2)$

apparent porosity:

$$Pa = (m_3 - m_1)/(m_3 - m_2) \times 100\%$$



0022–2461 

TABLE I The constitution of ceramics with SiC or $Si_3N_4$ additive

| No. | Constitution (wt %) | Hot-pressing conditions[a] |
|---|---|---|
| ATC-0 | 100AT[b] | 1300 °C 17 MPa |
| ATC-1 | $9Si_3N_4 \cdot 1LAS \cdot 90AT$ | 1400 °C 10 MPa |
| ATC-1-2 | $4.5Si_3N_4 \cdot 1LAS \cdot 94.5AT$ | 1400 °C 10 MPa |
| ATC-3 | $5SiC \cdot 95AT$ | 1400 °C 10 MPa |
| ATC-3-2 | $2.5SiC \cdot 97.5AT$ | 1400 °C 8 Mpa |

[a] Hot-pressing time is 30 min for all samples.
[b] AT-β-$Al_2TiO_5$.

where $m_1$ is the weight of dried sample, $m_2$ is the weight of samples soaked with water when measuring in water, $m_3$ is the weight of samples soaked with water when measuring in air and $D_w$ is the density of water at temperature when measuring.

The bending strength of the ceramics was determined from three-point bend tests using an Instron 1195 universal materials-testing machine. The samples were cut and ground into the form of 2.5 × 5 × 30 mm. The span was 20 mm and the loading speed was 0.5 mm $min^{-1}$. The crystalline phases of ceramics were determined by X-ray diffractometry (Rigaku D/max-II). A scanning electron microscope (Cambridge Stereoscan 250-MK3) was used to observe the microstructure of aluminium titanate ceramics.

## 3. Experimental results

### 3.1. The effects of non-oxide additives on the properties of aluminium titanate ceramics

In non-oxide ceramics, SiC and $Si_3N_4$ are widely used due to their excellent performance. Therefore, SiC and $Si_3N_4$ additives were selected in this study for their perfect mechanical properties and low thermal expansion coefficients. The constitution and properties of ceramics with non-oxide additives are shown in Tables I and II, respectively. Small amounts of LAS powders were added to sample ATC-1 and ATC-2, the purpose of which is to decrease the sintering temperature. From Table II it can be seen that the bending strength of aluminium titanate ceramics was greatly improved after adding SiC and $Si_3N_4$. Particularly for the sample with 2.5 wt % SiC, the bending strength is as high as 270 MPa, about 26 times as much as that of pure aluminium titanate ceramic. When $Si_3N_4$ additive was added, a ceramic with high bending strength could be easily obtained. For samples with low SiC and $Si_3N_4$ additives the flexural strain is more than 1%, which indicated that those samples might have good fracture toughness, while the thermal expansion coefficient of ceramics with non-oxide additives also increased noticeably. The values are in the range $62 \times 10^{-7}\,°C^{-1}$ to $82 \times 10^{-7}\,°C^{-1}$.

### 3.2. The effects of oxide additives on the properties of aluminium titanate ceramics

The oxide additives used in this study are amorphous MAS and AS powders. The constitution and properties of the ceramics are shown in Tables III and IV. The bending strength of aluminium titanate ceramics increased with increasing MAS content, and reached the maximum values of 279 MPa when MAS content was 20 wt %. The thermal expansion coefficient of the ceramics with MAS additives also increased compared with pure aluminium titanate ceramics. The sample ATC-4-2 has a minimum value of $58 \times 10^{-7}\,°C^{-1}$. However, the thermal expansion coefficient and the bending strength of the ceramics decreased noticeably after being heat-treated at 1200 °C. The bending strength was much lower for ceramics with AS additives than that of ceramics with MAS additives. There were probably a large amount of closed pores in sample ATC-5-2-1, so it has an extremely large thermal expansion coefficient. However, the ceramic with thermal expansion coefficient of $15 \times 10^{-7}\,°C^{-1}$ and bending strength of 109 MPa could be obtained by exactly controlling the hot-pressing technical parameters (ATC-5-2-2 in Table IV).

## 4. Discussion

From the experimental results it can be seen that the bending strengths of hot-pressed aluminium titanate ceramics were obviously improved after adding oxide or non-oxide additives. However, the thermal expansion coefficient of aluminium titanate ceramics also increased simultaneously. Fig. 1 is the SEM photographs of aluminium titanate ceramics with and without additives. It shows that there are large amounts of microcracks inside the crystalline grains and at the grain boundaries in pure aluminium titanate ceramic (Fig. 1(a)) which resulted in the very low thermal expansion coefficient and flexural strength of aluminium titanate ceramics. The microcracks were much less for sample ATC-4-2 (Fig. 1(b)) than ATC-0. Therefore, the decreasing of microcracks and the enhancing of the bulk density are the main reasons for the increase of thermal expansion coefficient for

TABLE II Properties of aluminium titanate ceramics with SiC or $Si_3N_4$ additive

| No. | Apparent porosity (%) | Bulk density ($g\,cm^{-3}$) | Thermal expansion coefficient ($\alpha_{RT\text{-}500} \times 10^7\,°C^{-1}$) | Bending strength (MPa) | Flexural strain (%) |
|---|---|---|---|---|---|
| ATC-0 | 0.7 | 3.61 | 12 | 55 | 0.19 |
| ATC-1 | 1.0 | 3.55 | 62 | 215 | 0.27 |
| ATC-1-2 | 1.1 | 3.27 | 71 | 200 | 1.43 |
| ATC-3 | 3.3 | 3.18 | 70 | 106 | 0.19 |
| ATC-3-2 | 4.8 | 3.18 | 82 | 270 | 1.93 |

TABLE III Constitution of aluminium titanate ceramics with oxide additives

| No. | Constitution (wt %) | Hot-pressing conditions[a] |
|---|---|---|
| ATC-4-1 | 5MAS·95AT | 1300 °C 8 MPa |
| ATC-4-2 | 10MAS·90AT | 1350 °C 8 MPa |
| ATC-4-3 | 20MAS·85AT | 1350 °C 5 MPa |
| ATC-4-4 | 30MAS·70AT | 1350 °C 10 MPa |
| ATC-5-1 | 15AS·85AT | 1350 °C 8 MPa |
| ATC-5-2-1 | 30AS·70AT | 1300 °C 8 MPa |
| ATC-5-2-2 | 30AS·70AT | 1300 °C 17 MPa |

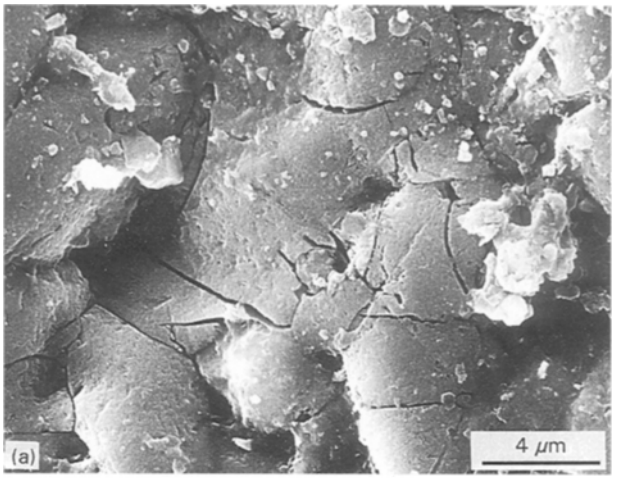
[a] Hot-pressing time is 30 min for all samples.

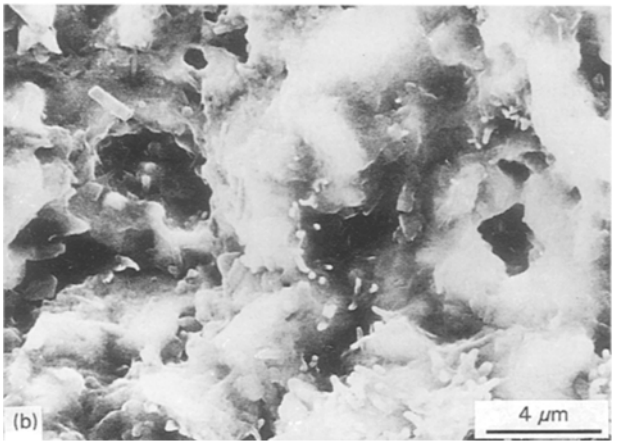
aluminium titanate ceramics with MAS and non-oxide additives. There was also a certain amount of microcracks in sample ATC-5-2-2. However, flake mullite grains about 1–2 μm in size (white phase in Fig. 1(c)), which acted as a reinforcer, existed at the boundaries of crystalline grains and made part of the microcracks heal (see grain A in Fig. 1(c)). Thus, an aluminium titanate ceramic-based composite with better strength and low thermal expansion coefficient was obtained.

Fig. 2 shows the X-ray diffraction patterns of aluminium titanate ceramics with different additives. The purpose of adding additives is to reinforce aluminium titanate ceramic by forming a multiphasic ceramic system with it. X-ray diffraction patterns indicate that the sample with AS powder is a β-$Al_2TiO_5$–mullite diphasic ceramic, while the samples with MAS powder still are β-$Al_2TiO_5$–mullite diphasic ceramic other than β-$Al_2TiO_5$–cordierite diphasic ceramic. The peak intensity of the mullite phase increases with increasing MAS content. At the same time the peak of β-$Al_2TiO_5$ phase shifts to the direction of small angle degrees which indicates that ionic substitution occurred in the β-$Al_2TiO_5$ crystal lattice [3, 4]. The mullite phase disappeared in sample ATC-4-2 after being heat-treated at 1200 °C for crystallization, and new aluminium titanate solid solution and a small amount of impurities of α-$Al_2O_3$ and $TiO_2$–rutile was formed. The following solid solutions can be formed for aluminium titanate:

1. Three $Si^{4+}$ ions are substituted for four $Al^{3+}$ ions and form a cation vacancy (□): $Al_{2(1-2x)}Si_{3x}\square_xTiO_5$

   The concentration of Si ions in the solid solution can be as high as 10 mol %.



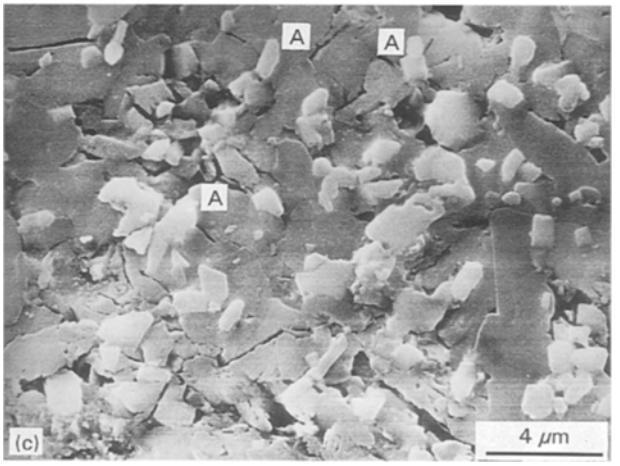




*Figure 1* SEM photographs of aluminium titanate ceramics (a) ATC-0; (b) ATC-4-2; (c) ATC-5-2-2.

TABLE IV The effects of oxide additives on the properties of aluminium titanate ceramics

| No. | Apparent porosity (%) | Bulk density (g $cm^{-3}$) | Thermal expansion coefficient ($\alpha_{RT\text{-}500} \times 10^7\,°C^{-1}$) | Bending strength (MPa) | Flexural strain (%) |
|---|---|---|---|---|---|
| ATC-4-1 | 1.3 | 3.50 | 68 | 75 | 0.8 |
| ATC-4-2 | 0.3 | 3.45 | 58 | 110 | 1.1 |
| ATC-4-3 | 0.3 | 3.43 | 64 | 279 | 1.3 |
| ATC-4-4 | 0.3 | 3.45 | 64 | 233 | 0.5 |
| ATC-5-1 | 18.3 | 2.80 | 58 | 68 | 1.0 |
| ATC-5-2-1 | 20.7 | 2.72 | 97 | 110 | 1.6 |
| ATC-5-2-2 | 5.3 | 3.52 | 15 | 109 | 0.2 |
| ATC-4-2B | – | – | 47 | 60 | 1.1 |

ATC-4-2B is the sample of ATC-4-2 crystallized at 1200 °C for 2 h.

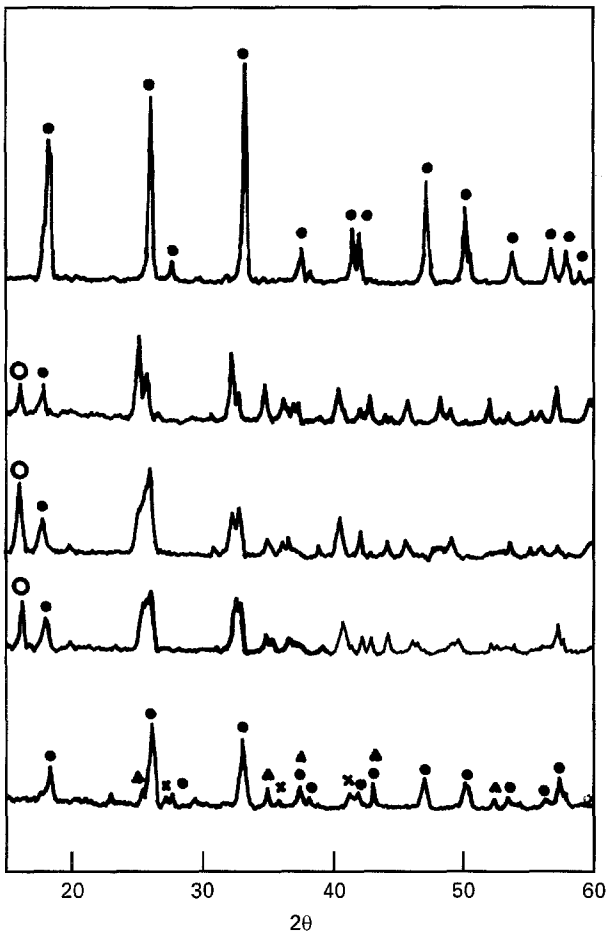



*Figure 2* X-ray diffraction curves of aluminium titanate ceramics with oxide additives. ● β-$Al_2TiO_5$; ○ mullite; ▲ α-$Al_2O_3$; *x* rutile.

2. $Mg^{2+}$ and $Si^{4+}$ ions are substituted for two $Al^{3+}$ ions: $Al_{2(1-x)}Mg_xSi_xTiO_5$, where $x$ is in the range 0.1 to 0.4.

A small amount of the first kind of solid solution occurred in ATC-5 samples while the two kinds of solid solution existed in the ATC-4 samples. Only small amounts of α-$Al_2O_3$ and $TiO_2$–rutile (except for β-$Al_2TiO_5$) phase formed in the crystallized ATC-4-2 sample, and no phases containing MgO or $SiO_2$ are detected. Therefore the existence of the mullite phase (the thermal expansion coefficient of mullite is $\alpha_{RT\text{-}500} = 47 \times 10^{-7}\,°C^{-1}$) in samples adding oxide additives is another reason resulting in the increasing of the thermal expansion coefficient of aluminium titanate ceramics. The thermal expansion coefficient and bending strength of crystallized ATC-4-2 sample decreased obviously due to the disappearance of mullite phase and the relaxation of the structure (the growth of the grains is oriented in some degree under the hot-pressing).

Fig. 3 shows that both SiC and $Si_3N_4$ in samples with non-oxide additives disappeared and new phases of mullite, TiC and TiN formed. The reason is that the following solid state reactions occurred under hot-pressing conditions

$$3Al_2TiO_5 + 3SiC \rightarrow 3TiC + 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \quad (1)$$

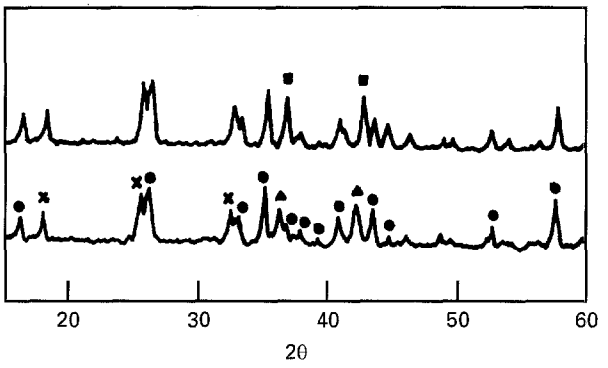



*Figure 3* X-ray diffraction curves of aluminium titanate ceramics with non-oxide additives. × β-$Al_2TiO_5$; ● mullite; ▲ TiC; ■ TiN.

$$3Al_2TiO_5 + Si_3N_4 + O_2 \rightarrow 3TiN + 3Al_2O_3 \cdot 2SiO_2 + SiO_2 + NO_2 \quad (2)$$

The first reaction (Equation 1) can be divided into the following two reactions in order to calculate easily

$$3SiC + 3TiO_2 + 3Al_2O_3 \rightarrow 3TiC + 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \quad (3)$$

$$Al_2O_3 + TiO_2 \rightarrow Al_2TiO_5 \quad (4)$$

The relationship of Equations 1, 3 and 4 can be expressed as

$$(1) = (3) - 3 \times (4)$$

thus

$$\Delta G°(1) = \Delta G°(2) - 3 \times \Delta G°(3)$$

The equilibrium constant of Equation 1 can be calculated

$$\ln K_{f,(1)} = \Delta G°_{(1)}/RT$$

The standard Gibbs' function change of Equation 3 can be obtained from the thermodynamic data of related compounds [5, 6], that is

$$\Delta G°_{(3),T} = \Sigma \Delta G°_{f,T\,(resultants)} - \Sigma \Delta G°_{f,T\,(reactants)}$$

The standard Gibbs function change of Equation 4 can be calculated from the following equation

$$\Delta G°_{(4),T} = \Delta H°_{298} - T\Delta S°_{298} + T\Delta C_p[\ln(298/T) + 1 - 298/T] \quad (5)$$

where $T$ is temperature (K). The results obtained from Equation 5 are shown in Table V. The standard Gibbs function change of Equation 2 is also calculated, that is, $\Delta G_{298,(2)} = -104$ kJ. From the above calculation, it can be seen that SiC–$Al_2TiO_5$ and $Si_3N_4$–$Al_2TiO_5$ system are thermodynamically unstable having the tendency to form new phases. However, Equations

TABLE V Thermodynamic data and equilibrium constant for Equation 1

| $\Delta G°_{298}$ (kJ) | $\Delta G°_{1273}$ (kJ) | $\Delta G°_{1773}$ (kJ) | $\ln K_{f,298}$ | $\ln K_{f,1273}$ | $\ln K_{f,1773}$ |
|---|---|---|---|---|---|
| −216.0 | −174.7 | −151.2 | 87.2 | 16.5 | 10.3 |

1 and 2 were controlled by kinetics at low temperatures, and could not react. The diffusion speed of ions increased with the increasing temperature and these reactions were controlled by thermodynamics. Therefore, Equations 1 and 2 became possible. From Fig. 3 SiC and $Si_3N_4$ basically reacted under hot-pressing temperatures into TiC and TiN, respectively. No $SiO_2$ phase was detected in both sample ATC-1 and ATC-3. The reason is that $SiO_2$ formed a solid solution with $\beta$-$Al_2TiO_5$. So the samples ATC-1 and ATC-3 are composed of $\beta$-$Al_2TiO_5$, mullite and TiN and $\beta$-$Al_2TiO_5$, mullite and TiC phases, respectively. Owing to the higher thermal expansion coefficient of TiN ($\alpha_{RT\text{-}500} = 90 \times 10^{-7}\,°C^{-1}$) and TiC ($\alpha_{RT\text{-}500} = 74 \times 10^{-7}\,°C^{-1}$), the samples with non-oxide additives have higher thermal expansion coefficients than the samples with oxide additives.

## 5. Conclusions

The mechanical properties of aluminium titanate ceramics can be greatly improved by adding suitable amounts of oxide or non-oxide additives. However, the thermal expansion coefficient increased simultaneously due to the increasing of bulk density and decrease of microcracks. Therefore, it is highly important to make a certain amount of microcracks to exist in aluminium titanate ceramics by controlling the preparing process to get the ceramic with high strength and low thermal expansion. Only mullite additive can form a stable diphasic ceramic system with $\beta$-$Al_2TiO_5$ in the four kind of additives used in this study.

## References


1. FUKUSHIMA TATSUTO, *Jpn Kokai Tokkyo Koho, JP* 04,124,070 (1992).
2. KATO HIROMICHI, NAKADA KATSUHISA and TABATA KAZUHITO, *ibid.* 04,124,063 (1992).
3. H. A. J. THOMAS and R. STEVENS, *Br. Ceram. Trans. J.* **88** (1989) 184.
4. M. KAJIRSARA, *ibid.* **86** (1987) 77.
5. YE DALUN, "Practical handbook of thermodynamics for inorganic compounds" (Metallurgical Industry Press. Beijing, 1981).
6. LIN CHUANXIAN and ZHZNG ZHERU, "Thermodynamic handbook of minerals and relating compounds" (Science Press, Beijing, 1985).



*Received 22 December 1994*
*and accepted 2 May 1995*