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A New Non-silicate Refractory of Low Thermal Expansion

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Abstract: Preliminary experiments were conducted aimed at developing refractory ceramics of low thermal expansion based on calcium dialuminate $CaAl_4O_7$. This compound was synthesized by a specific cycle of calcination, regrinding and firing (finally at 1450°C), the emerging phases having been identified by X-ray diffraction. The obtained product was combined in various proportions with the highly refractory calcium zirconate $CaZrO_3$; also,$CaAl_4O_7$ specimens were impregnated with SiC using the chemical vapour deposition (CVD) technique. Thermal expansion up to 900°C and porosity data were established for a number of compositions. The obtained microstructures were shown as scanning electron microscope pictures. From among the potential applications, the continuous casting of steel is indicated, the composites containing $CaZrO_3$ and vapour deposited SiC being regarded as promising materials for submerged nozzles. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Failure due to thermal shock constitutes a major problem in many applications of refractory ceramics. A significant factor in this troublesome behaviour is the high thermal expansion of the material's constituents—such as the commercially important basic oxides of very high melting points: MgO and CaO. These substances, as well as a number of refractory orthosilicates, show thermal expansion coefficients α near that of steel. Lower values, but still involving a risk of excessive thermal stresses, are characteristic of some other common components of refractory products: alpha-Al_2O_3, the spinels, and ZrO_2 which, in addition, requires stabilization. A conveniently moderate thermal expansion is characteristic of two high-melting silicates: mullite and zircon, as well as of the fairly common non-oxide ingredients of refractory composites: graphite and SiC. Substances of very low coefficients used in some kinds of technical ceramics: cordierite, Li-aluminosilicates and silica glass are either non-refractory or undesirable in many refractory applications because of specific reactions of SiO_2.

Recently, a new low-expansion, non-silicate ceramic was elaborated[1] based on one of the refractory aluminates—$CaAl_4O_7$ (CA_2, melting at 1750°C). This compound is a common component of refractory cements; however, its impressively low thermal expansion (a unique feature among the 7 phases of the CaO-Al_2O_3 system) has not so far been given the attention it deserves from the technological point of view. The appropirate α values were indicated by Criado and De Aza[2] in their paper on calcium hexaluminate, the reported data reaching back to their experiments conducted in the 1970s.

The present work was undertaken following our preliminary tests corroborating in general the mentioned Spanish data about the low level of the thermal expansion coefficient of CA_2 (especially at lower temperatures). An attempt was made to work out composites combining the merits of calcium dialuminate (low thermal expansion irrespective of its non-silicate nature) with those of a ZrO_2-based phase—calcium zirconate $CaZrO_3$ (CZ). This compound shows a very high melting point (2345°C), crystallographic stability in contrast to

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zirconia and can easily be synthesized. CA_2 and CZ are compatible at high temperatures according to the $CaO–Al_2O_3–ZrO_2$ subsolidus phase diagram.[3]

In addition, a specific technological operation was tried out in the present work: chemical vapour deposition (CVD) of SiC on CA_2 specimens. This measure was meant to impart to the new material the feature of reduced wettability by oxide-type slags, while advantage was taken of some previous experiments along this line.[4]

2 EXPERIMENTAL

2.1 Materials

The powders $CaO·2Al_2O_3$ (CA_2) and $CaO·ZrO_2$ (CZ) were prepared from chemically pure reagents: $CaCO_3$ and Al_2O_3 for CA_2 synthesis and $CaCO_3$ and ZrO_2 for CZ synthesis. Mixtures of the starting materials corresponding to the stoichiometric compositions were wet milled in isopropyl alcohol in a Fritsch ball mill for 8 h, then dried and pelletized. To obtain fully synthesized compounds, two- (CZ) or three-step (CA_2) calcination was carried out, successively at 1200, 1300 and 1450°C (CA_2). After the first and the second thermal treatment the pellets were pulverized and pressed again. The difference in the heat treatment for CA_2 and CZ was adopted taking into account the dissimilarity of their behaviour on heating (reflected in the relevant publications): the necessity of mutiple firing to synthesize the first [2] and the ease of the synthesis of the second.[5,6]

The phase compositions of the synthesized materials were checked by X-ray diffraction analysis, using the XRD-7 device.

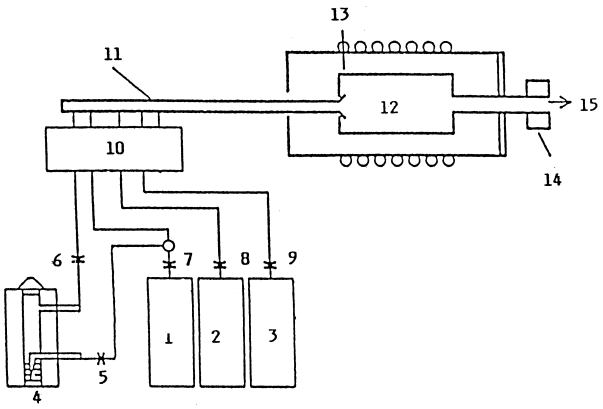

Fig. 1. Schematic outline of the CVD device used for impregnating the CA_2 specimens with SiC: 1,2,3—gas bottles Ar, $Ar+H_2$, NH_3; 4—CH_3SiCl_3 dosage system; 5–9—valves; 10—electric gas flow control system; 11—gas reagents mixer; 12—rotary furnace; 13—heating system; 14—electric motor; 15—gas exhaust.

In the CA_2 powder only the reflexes connected with this aluminate were clearly identified; however, some peaks of weak intensity which may indicate a few per cent content of $CaAl_2O_4$ (CA) were also recorded. No traces of the other five phases of the $CaO–Al_2O_3$ system: CaO, $3CaO·Al_2O_3$, $12CaO·7Al_2O_3$, $CaO·6Al_2O_3$ or Al_2O_3 could be detected.

Crystals other than $CaZrO_3$ were not found in the CZ powder; the peaks of this phase were somewhat shifted on the diffraction pattern, which might signal some non-stoichiometry.

True densities of fine powders of both the synthesized materials were determined using the Micrometrics Acc-pyc 1330 device.

2.2 Preparation and examination of fired specimens

The semi-products CA_2 and CZ were ground under 10 μm, pressed into rods of 7 mm diameter and ca 20 mm height and sintered at 1450°C (held during 0.5 h). Some specimens were prepared as composite mixtures: 50 wt% $CA_2+50\%$ CZ and 20% $CA_2+80\%$ CZ, designated 50/50 and 20/80, respectively.

The thermal expansion coefficients of the specimens thus prepared were measured in the temperature range 20–900°C, using a high temperature dilatometer (Linseis Messageräte) with quartz glass elements.

Apparent porosities and bulk densities of the examined rods were determined in kerosene according to the Polish standard method PN-64/H-04185.

CVD impregnation of the sintered CA_2 specimens (rods of the dimensions indicated above) was carried out using reactive mixtures $CH_3SiCl_2+Ar+10\%H_2$. The classical CVD apparatus was equipped with a rotating reactor which enables one to attain a homogeneous uniform impregnation of several specimens in a single operation (Fig. 1). The parameters of the process are given in Table 1 (adopted according to previous experience).[4,7–9]

Selected fragments of both the sintered semi products and the composite mixtures, as well as the CVD impregnated specimen were surveyed under a scanning electron microscope (Philips xL 30 Link Iris).

3 RESULTS

The characteristics of the synthesized materials obtained in this work are summarized in Table 2.

Table 1. CVD process parameters applied in SiC impregnation of the specimens

Pressure Ar (kPa)	Pressure H_2 (kPa)	Pressure CH_3SiCL_3 (kPa)	Temperature (°C)	Time (min)
91.69	9.12	0.51	1150	30

The linear thermal expansion coefficients measured over the ranges from ca 20° up to the indicated temperatures are given in Table 3.

For three temperature ranges of α values of the four compositions investigated the obtained data are depicted graphically in Fig. 2.

The results of the determinations of apparent porosity, bulk density and estimated closed pore volume of the specimens, including that having undergone CVD impregnation, are given in Table 4.

Typical microstructures of the compositions considered in this study after firing at 1450°C are shown in Fig. 3(a)–(f).

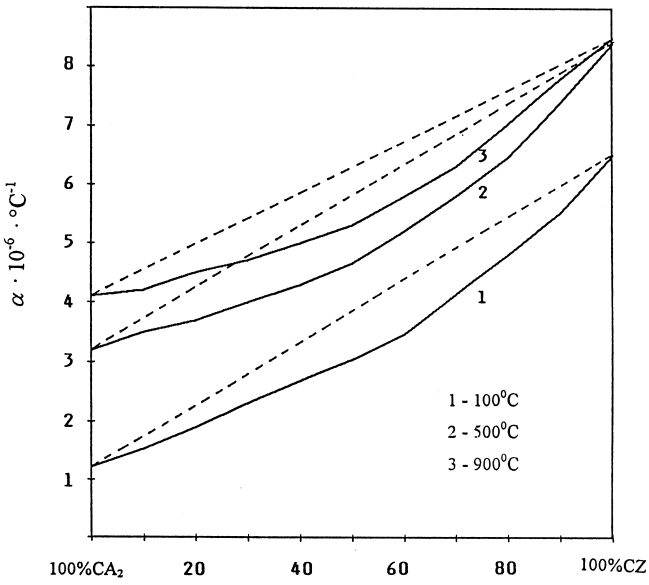

Fig. 2. Mean thermal coefficient values of compositions of Table 3, for three selected temperature ranges: 1 = 20–100°C; 2 = 20–500°C; 3 = 20–900°C.

4 DISCUSSION

There were differences in the course and effects of the preparation procedures of the two semi-products used in this work: the calcium dialuminate required repeated firing and regrinding operations while the zirconate was easy to synthesize. Accordingly, some residual amounts of the intermediate reaction products (possibly $CaAl_2O_4$) may have survived in the obtained CA_2 semi-product which also remained porous after the last 1450°C firing—in contrast to the densely sintered CZ. These differences were to some extent reflected in the microstructures.

The exceptionally low thermal expansion of calcium dialuminate, evidenced earlier by the Spanish authors, could once more be confirmed on the material synthesized in this work, while less intensive heat treatment had been applied. The α values of calcium zirconate established in our experimental

Table 2. Characteristics of the synthesized materials

Designation	Chemical formula and melting point	X-ray diffraction data		True density, g cm^{-3}
		Phases detected	Remarks	
CA_2	$CaAl_4O_7$ 1750°C	CA_2, some CA	No other aluminates or Al_2O_3 present	3.19
CZ	$CaZrO_3$ 2345°C	CZ	Peaks somewhat shifted	4.95

Table 3. Mean thermal expansion coefficient values of fired specimens of single components and composite-mixtures

Designation	Composition	Mean linear thermal expansion coefficient [$\alpha\ 10^{-6}\ °C^{-1}$] up to temperature, °C								
		100	200	300	400	500	600	700	800	900
CA_2	Single component $CaAl_4O_7$	1.2	2.1	2.5	2.9	3.2	3.4	3.7	3.9	4.1
CZ	Single component $CaZrO_3$	6.5	7.7	8.2	8.3	8.4	8.5	8.5	8.5	8.5
50/50	Composite 50% $CaAl_4O_7$ +50% $CaZrO_3$	3.4	4.0	4.4	4.6	4.9	5.0	5.2	5.3	5.4
20/80	Composite 20% $CaAl_4O_7$ +80% $CaZrO_3$	4.9	5.7	5.9	6.4	6.6	6.7	6.8	6.9	6.9

Table 4. Apparent porosities, bulk densities and closed porosities of the fired specimens (compositions as in Table 3)

Designation	Apparent porsity, vol%	Bulk density, g cm^{-3}	Estimated closed porosity, vol%
CA_2	25.1	2.34	under 1
CZ	1.2	4.59	6
50/50	6.7	3.50	6
20/80	6.5	4.04	7
CA_2/CVD	19.9	2.40	—

series are similar to those given in Ref. 5. Other data reported in the literature for $CaZrO_3$ are somewhat higher.

Thermal expansion of the composite specimens made from mixtures of the two semiproducts turned out to be lower than the intermediate values which could be suggested merely from their weight proportions in the samples (cf dashed straight lines in Fig. 2). This can obviously be ascribed to the much lower true density of the CA_2 powders. In

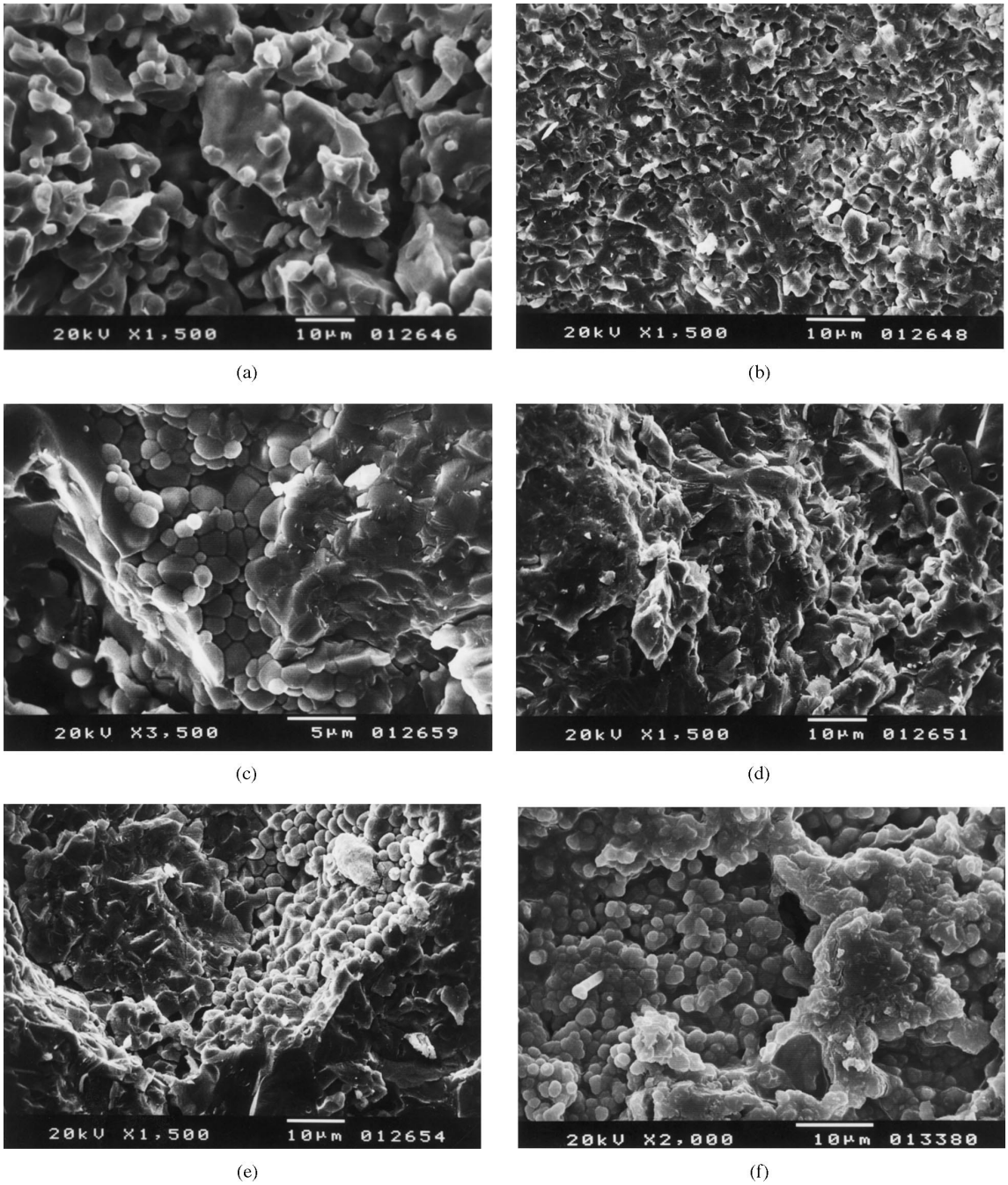

Fig. 3. Scanning electron microscope pictures of fired specimens showing typical fragments of microstructure: (a) CA_2. Small (of micron-order size) oval isometric crystals, often sticking to shapeless matter. Open pores; (b) CZ. High degree of densification. Very small (sometimes of submicron size) closed pores inside the densely sintered crystalline body; (c) 50/50. The two-component character of the material is shown; both small crystal agglomerations and larger sintered grains can be seen; (d) 20\80 Both dense (left) and more porous (right) fragments of the composite are shown; (e) 20/80. A fragment of the composite showing a concave surface of the matrix (with accumulated small crystals), presumably exposed after a sintered grain had been broken off; (f) CA_2/CVD. Small, ball-like (sometimes elongated) beta-SiC crystals deposited in the pore space of the CA_2 body.

addition, a favourable microstructure of the composites with CA_2 matrix surrounding the sintered CZ grains may also play a role in this effect. The high apparent porosity of the fired CA_2 specimens can be considered insignificant once the material has been ground to prepare the composite mixtures.

For a more general assessment the obtained data were recalculated to draw per cent expansion curves of the four compositions as a function of final temperatures to which the specimens were brought-up; so were the results of the measurements by Criado and De Aza.[2] This is shown in Fig. 4 in comparison with a typical curve from among those reported for stabilized zirconia. It is evident that both CA_2 and the composite products show the advantage of a spectacularly low thermal expansion as compared with ZrO_2. This applies as well to comparisons with other common non-silicate refractories—those based on MgO, Al_2O_3, $MgAl_2O_4$ and Cr_2O_3. Composites containing 50% and more CZ embedded in a CA_2 matrix will presumably keep the character of highly refractory bodies while their thermal shock resistance should favourably contrast with that of stabilized zirconia (not to mention the ZrO_2 products developing cracks on cooling). The features of the new materials can further be improved by purposefully influencing their microstructures. The micrographs in Fig. 3 yield only a general information in this aspect, showing fine-crystalline bodies built-up of equant particles and some specific differences in the pore structure of CA_2 and CZ. The morphological peculiarities and grain arrangement appearing in the composite specimens on the presented micrographs should become the subject of more systematic studies, along with technological development.

The apparent porosities of the composites are low; these bodies also show closed pore volumes characteristic of the densely sintered CZ material, in contrast to the texture of CA_2.

The advantageous effect of CVD impregnation is clearly seen from the micrograph in Fig. 3(f) which shows tiny SiC crystals filling the open pores in the CA_2 specimen. This is in accordance with the porosity decrease evidenced by the data given in Table 4. Although a similar or even greater densification could probably be attained by sintering CA_2 at higher temperatures, the significance of the shown microstructure lies in the anticipated non-wettability of its pore channels by slag owing to the presence of the non-oxide (SiC) deposits. This should be taken into account when considering such potential applications of the refractories described here as the ZrO_2-based submerged nozzles in continuous casting of steel. In publications discussing the service problems of this type of installations, both the introduction of $CaZrO_3$ (e.g. in Ref. 10) and non-oxide constituents other than graphite (e.g. in Ref. 11) have been postulated.

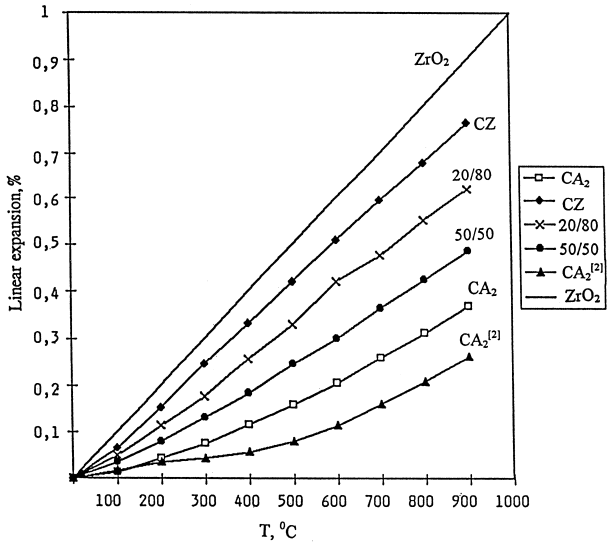

Fig. 4. Per cent linear expansion curves of various compositions as a function of temperature.

5 CONCLUSIONS

A new non-silicate refractory based on calcium dialuminate $CaAl_4O_7$ was elaborated, characterized by a low thermal expansion, especially at low temperatures. Composites combining $CaAl_4O_7$ with sintered $CaZrO_3$ and those containing SiC deposited by CVD technique are considered promising as fine-grained, dense, highly refractory materials resistant to thermal shocks.

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