

# Latest Developments in Carbon Block for Blast Furnace

Yawei Li, Shaobai Sang, Xilai Chen, Tianbin Zhu, Yiwei Li

High thermal conductivity (TC), excellent micropore structure (MS) and molten iron erosion resistance (MIE) are required for high-performance carbon block to achieve the longer service life of blast furnace (BF). Firstly, the micropore structure and properties of carbon block could be improved by optimization of processing parameters. For example, the MS can be further optimized by the addition of microsilica besides incorporating Si powder and reactive alumina. Also, directly adding carbon nanotubes as an additive or in situ forming phases, e.g. finer SiC whiskers,  $Al_4C_3$  and AlN phases is an alternative approach to improve the TC of carbon block. Meanwhile, MIE resistance combining with optimized micro-porous structure and higher thermal conductivity can be improved by the decomposition of zircon micropowders in the matrix of carbon block at high temperature. Secondly, ceramic-bonded carbon (CBC) technique could be used to prepare high performance carbon block. In this paper, the latest developments in carbon block for BF are summarized.

## 1 Introduction

The blast furnace (BF) is a very important vehicle of carbothermal reduction of iron oxide ores into hot metal in the metallurgical process. It has the established consensus that the life of BF is mainly determined by the rate of erosion and corrosion of hearth and bottom carbon block [1, 2]. Based on the investigations of the blown-out blast furnace, the penetration into the pores by molten iron or alkali and carbon dissolution into hot metal are regarded as the main reasons for the deterioration of carbon block [3–8]. Hence, in order to hinder those damages, it is required for the BF carbon block that the pore be made small enough to reduce the infiltration of molten iron and reactive gases and the thermal conductivity (TC) be high enough to reduce the thermal stresses. Currently, to optimize the microporous structure (MS), increase the TC and improve the excellent molten iron erosion (MIE) resistance is the development direction of carbon block for BF.

Generally, the mean pore diameter and  $<1\ \mu\text{m}$  micropore volume ratio of open pores are used to evaluate the MS besides apparent porosity of carbon block. The micropore structure in carbon block is characterized with the mean pore diameter in the range of 0.1–0.5  $\mu\text{m}$  or less and  $<1\ \mu\text{m}$  pore volume ratio of open pores being accumulated more than 80 %. So, adding metallic silicon and decreasing the particle size of the fillers such as alumina powder, are popularly adopted to improve the MS in carbon block. Meanwhile, there are two processing routes to increase TC of carbon block, namely, one is to increase the amount of high TC phases, such as adding raw materials with high TC or in situ forming phase compositions, another is to enhance the thermal network connection, such as increasing the amount of high TC whiskers and compacting carbon block. Furthermore, TiC,  $TiO_2$  and  $ZrO_2$  [2] compositions are used or impregnated into carbon block to improve the MIE resistance. Of course, the impregnation tech-

nology of the latter can also optimize the MS in carbon block.

Similarly, some work on how to improve the properties and performance (especially MS, TC and MIE resistance) of carbon block for BF has been done in our research group in the past several years. For instance, the addition of appropriate silicon content along with its particle size [9–11], electrically calcined anthracite aggregates [12], aluminum powder [13], reactive alumina [14] and microsilica [15] can be favorable for optimization of MS. Also, it was found that ex situ adding or in situ forming substances with high TC such as carbon nanotubes [16], metallic Al [13], reactive alumina [14] etc. are toward increasing the TC of carbon block.

With respect to the MIE resistance, zircon micropowders were incorporated into carbon block to improve the MIE resistance [17].

In this paper, some main results based on the additions of  $SiO_2$  micropowders, Al powder, multi-walled carbon nanotubes and zircon micropowders into carbon block

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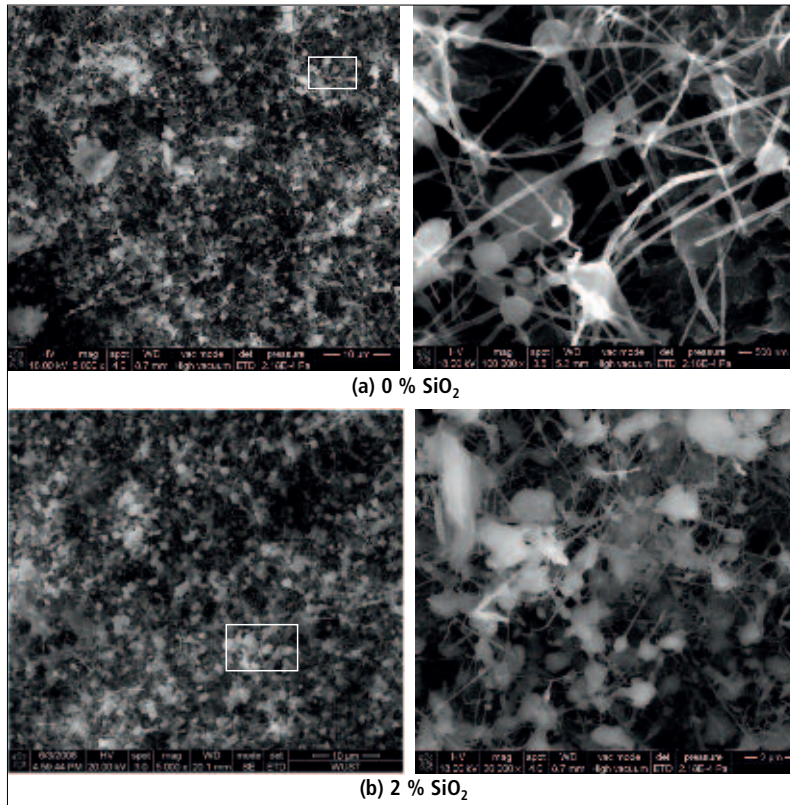
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**Tab. 1** Properties of microsilica containing carbon block coked at 1400 °C

Specimen	SiO <sub>2</sub> Micropowders			
	0	1	2	3
Mean pore diameter [μm]	0,46	0,49	0,35	0,31
<1 μm pore volume [%]	57,1	66,4	76,8	88,1
TC [W/m·K], 600 °C	13,2	12,6	11,7	11,3



**Fig. 1a–b** SEM morphologies of microsilica containing carbon block specimens coked at 1400 °C

for BF will be summarized below. Also, ceramic-bonded carbon (CBC) technique is adopted to prepare high performance carbon blocks.

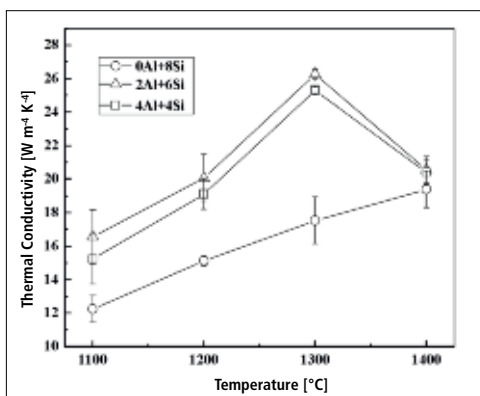
## 2 Microsilica

In the production of carbon blocks, reactive alumina powder is commonly used as an additive. Microsilica (97 % SiO<sub>2</sub>, Elkem/NO)

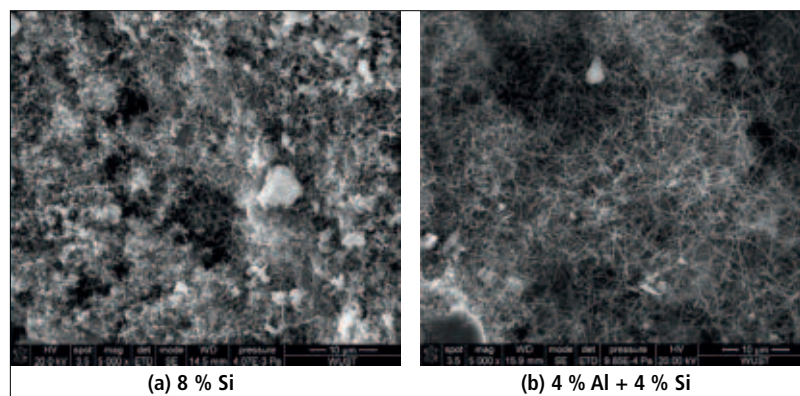
is added to fill in the smaller pores to further improve the MS [15]. Properties of microsilica containing carbon block coked at 1400 °C are illustrated in Tab. 1. As can be seen, alumina powder is gradually substituted by microsilica with finer size, thereafter, the MS is increasingly improved. For instance, the mean pore diameter straightly decreases from 0,46 to 0,31 μm respectively, correspondingly the <1 μm pore volume increased from 57,1 to 88,1 % as 3 % microsilica was added into the carbon block. However, the TC of the specimens coked decreases with the increase of microsilica, 13,2 W/m·K for no SiO<sub>2</sub> specimen and 11,3 W/m·K for 3 % SiO<sub>2</sub> containing specimen. The fractured surface SEM morphologies of carbon block specimens without or with SiO<sub>2</sub> coked at 1400 °C are shown in Fig. 1. It was found that the SiO<sub>2</sub> containing specimen had more SiO<sub>2</sub> microballs and much shorter SiC whiskers, which results in finer pore diameter, higher <1 μm pore volume, and lower TC of the specimens.

## 3 Metallic aluminum powder

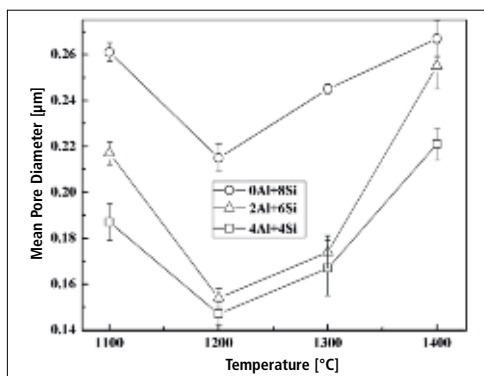
The results mentioned above showed that much ball-like cristobalite formed in the matrix, which deteriorated the properties (especially TC) of samples as only silicon powder was added or combined with microsilica [9–11]. Thermodynamically, the cristobalite phase can be easily formed than SiC at coking temperatures. So, Al powder was added into carbon block to control the oxygen partial pressure and to promote the formation of high thermal conductive SiC phase instead of cristobalite [13]. For all the samples with Al addition, their TC is higher than that of the sample with only addition of 8 %



**Fig. 2** TC of with or without Al powder containing carbon block



**Fig. 3a–b** SEM morphologies of Al containing carbon block coked at 1300 °C

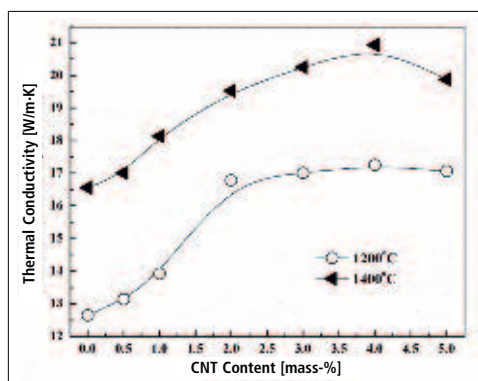


**Fig. 4** Mean pore diameter of with and without Al containing carbon block

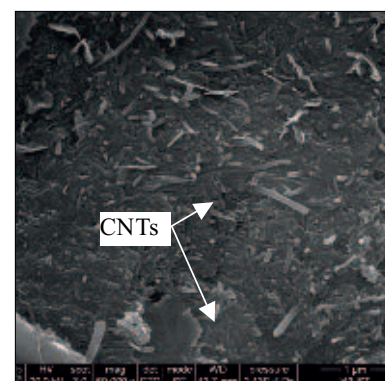
Si and reached the maximum value at 1300 °C (Fig. 2). It can be seen that Al in the samples can effectively increase TC, which is attributed to the fact that much more SiC whiskers (Fig. 3), Al<sub>4</sub>C<sub>3</sub> and AlN are formed in the carbon block matrix. Meanwhile, the mean pore diameter for the samples with addition of Al powder was lower than that of the sample without Al powder and reached a minimum value at 1200 °C (Fig. 4).

#### 4 Multi-walled carbon nanotubes (MWCNTs)

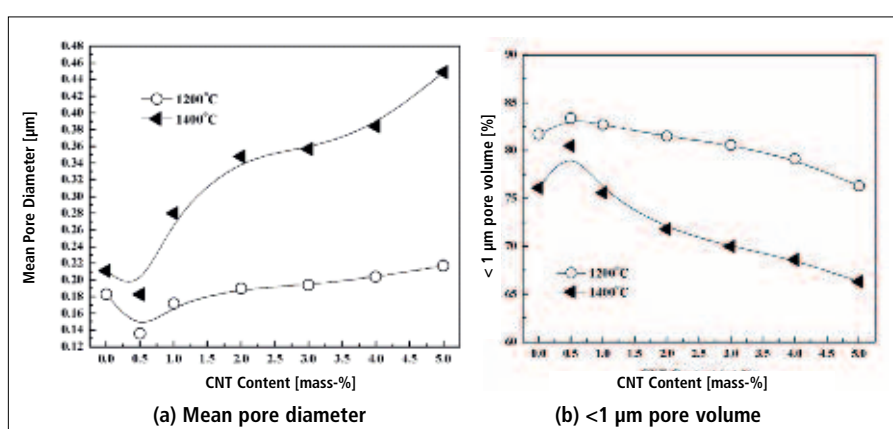
In the past decades, the incorporation of CNTs in polymer- and ceramic-based composites could lead to significant improvements in thermal properties due to CNTs excellent TC (6600 W/m·K for individual SWCNT and >3000 W/m·K for individual MWCNT) [18, 19]. Also, MWCNTs was incorporated into the carbon block to investigate its effect on TC as well as MS of the BF carbon block [16]. The variation of TC (25 °C) against addition of MWCNTs is shown in Fig. 5. The TC of specimens coked at 1200 and 1400 °C respectively increased with the addition of MWCNTs up to 4 %. For example, at 1400 °C, the TC is 16,5 W/m·K for the no-CNT specimen, and 20,8 W/m·K for the 4 %-CNT specimen. However, TC decreases slightly as it exceeds 4 % MWCNTs. It is supposed that the addition of CNTs promote the formation of SiC in the presence of residual CNTs (Fig. 6), which can increase the TC of specimens. Excess of MWCNTs deteriorated the packing structure, which is perhaps related to high specific surface area of MWCNTs. As a consequence, it will damp the effect of CNTs on TC of specimens. In addition, Fig. 7 shows the variations of MS against the adding amount of CNTs. The mean pore



**Fig. 5** TC as a function of MWCNTs content



**Fig. 6** MWCNTs in the matrix



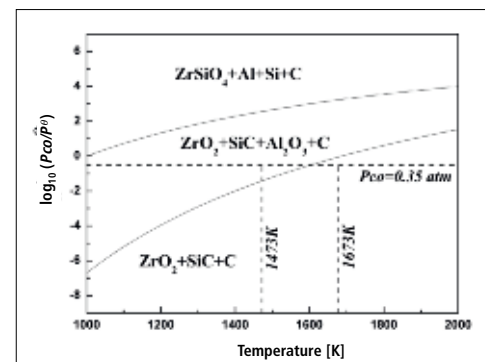
**Fig. 7a–b** The variations of MS as a function of CNTs content

diameter for the coked specimens decreases by the addition of 0,5 % CNTs, but it increases gradually again by subsequent addition of CNTs, e.g., at 1400 °C, from 0,18 µm for 0,5 % CNTs to 0,44 µm for 5 % CNTs. Correspondingly, the trend of <1 µm pore volume was opposite to that of mean pore diameter, e.g., at 1400 °C, from 80,8 % for 0,5 % CNTs to 66,7 % for 5 % CNTs. It seemed that fewer amounts of CNTs can be dispersed in the matrix; much more ones lead the agglomerate of CNTs.

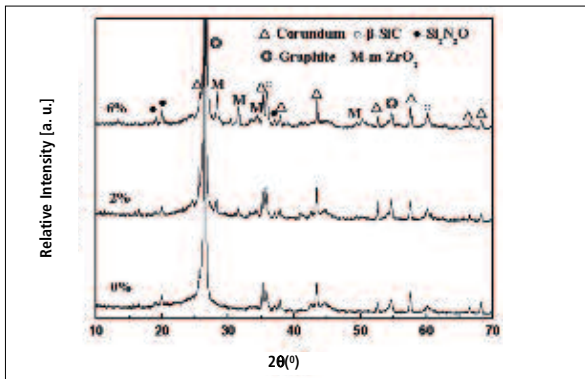
#### 5 Zircon powder

As it is known, zircon can decompose into ZrO<sub>2</sub> and amorphous SiO<sub>2</sub> at high temperature. On the one hand, ZrO<sub>2</sub> can enhance the corrosion resistance of materials [20, 21]. On the other hand, high reactive SiO<sub>2</sub> formed may react with C (s) or CO (g), and then form SiC in a CO-N<sub>2</sub> atmosphere (Fig. 8 and Fig. 9), which can be favorable for the improvement of a series of properties and performance of carbon block [17]. TC and MS as a function of zircon powder are pre-

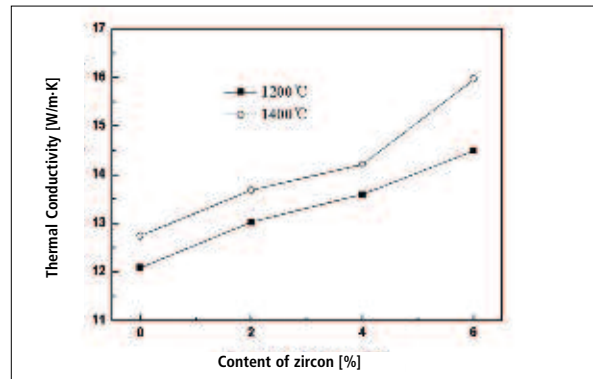
sented in Fig. 10 and Fig. 11. The TC increases with increased amount of zircon powder. For instance, at 1400 °C, the TC is enhanced from 12,74 W/m·K for the specimen without zircon additions to 15,97 W/m·K for the 6 % zircon powder specimen. However, the mean pore diameter of open pores for the coked specimens decreases with increasing in zircon powder, e.g., at 1200 °C, from 0,159 µm for speci-



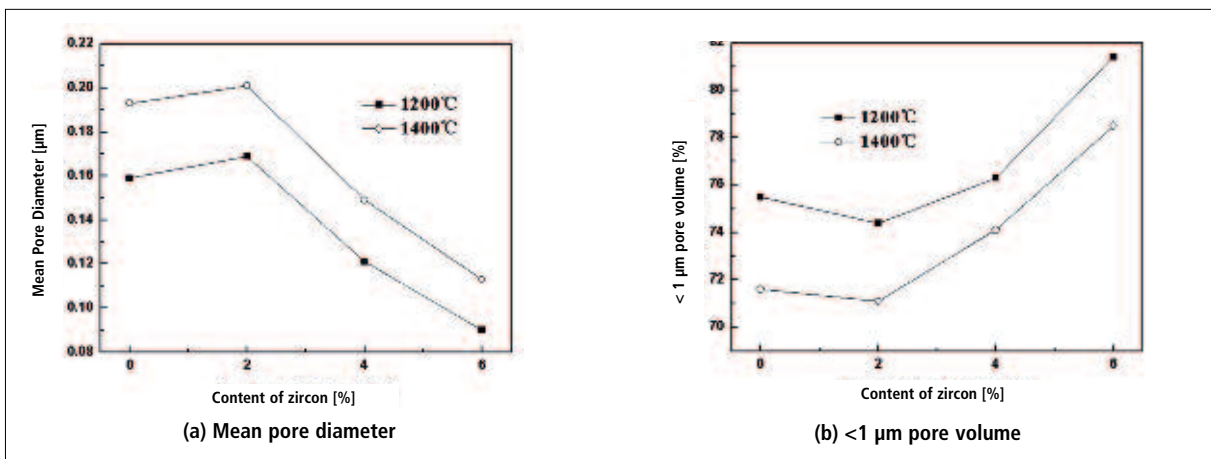
**Fig. 8** Stability domain of condensed phases in the Si-Zr-Al-C-O system



**Fig. 9** XRD patterns of specimens containing 0,2 % and 6 % zircon coked at 1400 °C



**Fig. 10** TC as a function of the zircon content



**Fig. 11a–b** MS as a function of the zircon content

mens without zircon additions to 0,09 μm for 6 % zircon powder specimens. Correspondingly, the trend of <1 μm pore volume is opposite to that of mean pore diameter, e.g., from 75,5 % for specimens without zircon additions to 81,4 % for 6 % zircon powder specimens. The enhancement of TC and MS might be explained by the in situ formation of much more SiC whiskers. Moreover, the MIE index decreases with the increasing of the zircon powder addition [17].

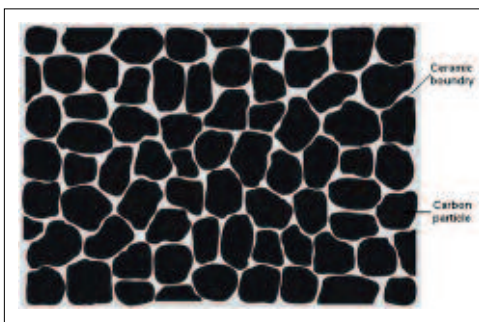
### 6 Ceramic-bonded carbon block

Ceramic-bonded carbon (CBC) is a new composite of carbon and ceramics [22]. It has a unique microstructure of carbon particles bonded with a three dimensional network of ceramic boundary layers (as illustrated in Fig. 12). Similarly, CBC technique could be used to prepare the carbon block of the hearth for blast furnace with high performance [23]. This kind of carbon block may be constructed as such model that graphite aggregates are covered/bonded with three-dimensional ceramic structure, herein defined as CBC carbon blocks. In that case carbon block is granted good erosion/corrosion resistance to hot metal from ceramics structure and high thermal conductivity from graphite aggregates (40,65 W/m·K at 873 K [600 °C]) [12].

The ceramic phases covered with graphite aggregates are designed and produced in two aspects, one is to incorporate micron-sized reactive Al<sub>2</sub>O<sub>3</sub> powder directly in mixing process, and the other is to in situ form

SiC phase in matrix from silicon powder together with addition of aluminum powder into the mixing process, where metal aluminum powder is adopted to avoid the formation of cristobalite phase instead of SiC phase at high temperature [13].

The properties of CBC samples were listed with common carbon block samples (ECA) as a reference in Tab. 2. Compared with sample ECA, sample CBC has higher density, 1,90–1,91g/cm<sup>3</sup> and lower porosity, 2,9–3,0 % owing to high amount addition of alumina. Also, it has much higher thermal conductivity, depending on whichever direction it was measured, lower mean pore size and higher <1 μm pore volume. At 1473 K (1200 °C) it has thermal conductivity no less than 39 W/m·K and <1 μm pore volume of 88,43 %. With the increasing of coking temperature, both thermal conductivity increased and <1 μm pore volume was up to 90 %, correspondingly, it has higher cold crushing strength. Also, CBC samples had already achieved better hot metal corrosion resistance and cold crushing strength than



**Fig. 12** A concept of ceramic-bonded carbon (CBC)

**Tab. 2** Properties of CBC carbon blocks in comparison with common carbon blocks (ECA)

Samples	Coking Temperature	Bulk Density	Apparent Porosity	Thermal Conductivity		Mean Pore Size	<1 $\mu\text{m}$ Pore Volume	Hot Metal Corrosion	Cold Crushing Strength
	[K]	[g·cm <sup>-3</sup> ]	[%]	[W/m·K] (573 K [300 °C])		[nm]	[%]	[%]	[MPa]
				Perpendicular	Parallel				
CBC	1473	1,91	3,0	41,96	39,44	70,9	88,43	/	/
	1673	1,90	2,9	52,79	41,20	71,3	90,04	4,0	32,3
ECA	1473	1,54	4,7	10,31	10,34	701,7	55,54	/	/
	1673	1,55	6,4	11,95	9,94	423,6	59,94	4,2	17,4

that of ECA. That's because a large amount of ceramics filled and in-situ formed in interfacial boundaries between carbon aggregates to protect them from molten iron corrosion and increase the strength of CBC samples.

## 7 Conclusions

Nowadays the longer servicelife of blast furnace (BF) requires high-performance carbon block with high thermal conductivity (TC), excellent micropore structure (MS) and molten iron erosion resistance (MIE). Based our research work, firstly, the micropore structure and properties of carbon blocks could be improved by optimization of processing parameters, e.g. microsilica, zircon powder, carbon nanotubes as additives to improve the TC, MS and MIE. Secondly, some new techniques could be adopted to prepare high performance carbon blocks, e.g. the ceramic-bonded carbon (CBC) technique.

## Acknowledgement

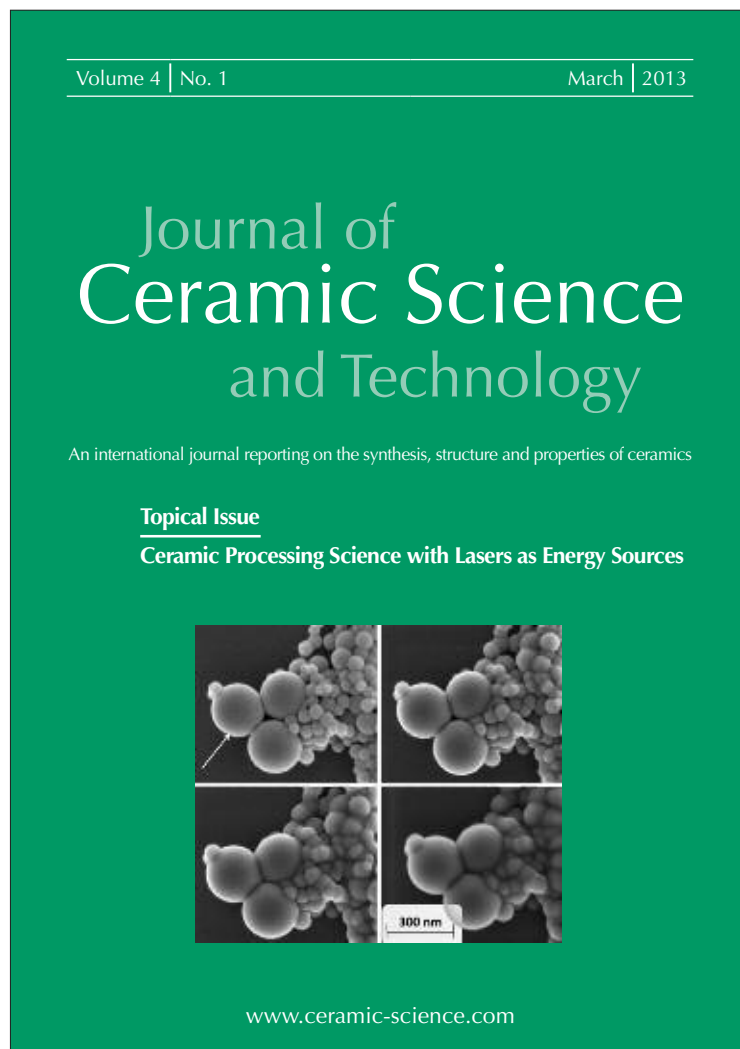
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