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Thermal expansion of $CaAl_4O_7$-based refractory compositions containing MgO and CaO additions

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Abstract

Various compositions of recently developed $CaAl_4O_7$-based ceramics are mentioned with special reference to those called “nonexpansive refractories” (=NER). The observed effect of deep depression of their thermal expansion is mainly ascribed to the creation of a specific microstructure resulting from high temperature reactions of $CaAl_4O_7$ with MgO or CaO additives yielding a $CaAl_2O_4$-based liquid. Some details characterizing the phase composition of the reaction zone are given. The effect of the calculated approximate content of $CaAl_2O_4$ in the specimens is interpreted graphically. Basing on the results of changes in the $CaAl_4O_7$ single crystal dimensions presented in comparison with some other expansion data, the presumable nature of the specific behavior of NER bodies on heating up to 500 °C is discussed. The NER products fired at 1620 °C are characterized by high strength and low open porosity.

Keywords: Refractories; Thermal expansion; $CaAl_4O_7$

1. Introduction

Criado and de Aza[1,2] have disclosed a formerly unnoticed feature of the refractory phase $CaO\cdot 2Al_2O_3$ – its astonishingly low thermal expansion. Later, evidence has been brought that some two-phase composites based on a calcium dialuminate (=CA_2) matrix continue to show this feature in spite of the addition of granular components other than CA_2, characterized by much higher thermal expansion coefficients α.[3,4] Among these, compositions of special bimodal grain size distribution could be elaborated, showing α values even lower than those of CA_2 itself. As coarse components were added to the matrix highly refractory phases. $MgO\cdot Al_2O_3$ and $CaO\cdot ZrO_2$; this last compound has been dealt with in a number of publications by Japanese authors, also recently;[5,6] following this line, we have investigated bodies containing MgO clinker grains embedded in a CA_2 matrix. During these experimental series a novel phenomenon was observed: a range of negative α values on heating these bodies up to 200–300 °C. Overall expansion remained at close-to-zero values up to 400–500 °C. Accordingly, the term “nonexpansive” refractory compositions (=NER) has been proposed for this type of CA_2-based bodies. The observed effect was obviously connected with a special microstructure in the interaction zone between periclase grain surface and the surrounding dialuminate, developed following the high temperature reaction:[7]

$$CaAl_4O_7 + MgO = CaAl_2O_4 + MgAl_2O_4 \qquad (1)$$

In the present study, further data concerning the microstructure of the products of the above reaction were obtained. Taking into account the role played by calcium monoaluminate $CaAl_2O_4$ (=CA), a compound melting at around 1600 °C, in the formation of the special NER microstructure, another reaction:

$$CaAl_4O_7 + CaO = 2CaAl_2O_4 \qquad (2)$$

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was considered promising as the source of the said compound. Consequently, as a next step, powdered additions of MgO and CaO to finegrained CA_2 materials were tried-out and it was noted that specimens fired to temperatures exceeding 1600 °C (yielding thus the reaction product CA in the form of a melt) again showed the nonexpansive behavior.

In an attempt to gain insight into the nature of the observed phenomena of shrinkage on heating of some of the CA_2-based bodies, a series of crystallographic measurements of calcium dialuminate monocrystal samples was also carried out. It was expected to display the large differences in the dimension changes on heating along the particular axes of the dialuminate crystal. The phenomenon of anisotropic thermal expansion of this compound was recently dealt with by Fukuda and Yamaguchi.[8]

2. Experimental procedures and results

The specific microstructure of the MgO/CA_2 interaction layer was previously[9] studied and is further examined during this study in order to help corroborate the finding of $MgAl_2O_4$ crystalization as a product of the reaction (1). It is present as a result of penetration of the CA_2 matrix by a MgO-bearing high temperature liquid forming at the interface around a periclase grain during firing the specimen up to 1650 °C, held for half an hour. In Fig. 1 a small crystal of this spinel, of EPMA spot composition given in Fig. 2, is shown surrounded by CA_2 crystals. Spot analyses of both the calcium aluminates present in the interaction layer are shown in Figs. 3 and 4. The three crystalline phases expected to be found in the material after the completion of reaction (1) and cooling down to room temperature were identified by the X-ray diffraction analysis.

The mean thermal expansion coefficients of CA_2 specimens containing additions of MgO and CaO (admixed in the form of $CaCO_3$) were measured in the temperature range 20–900 °C, with heating rate 10 °C/min. A high temperature dilatometer with quartz glass elements (Linseis Messgeräte) was used. The results are listed in Tables 1 and 2, respectively. As mentioned above, these additives were used to promote reactions (1) and (2) yielding $CaAl_2O_4$ liquid as a precondition for the formation of the “nonexpansive” microstructure. The calcium dialuminate used in the experiments was previously synthesized by mixing chemically pure reagents, prefiring followed by regrinding and final firing at 1650 °C, similarly to the procedure described earlier.[3] The compositions with magnesia and lime additions being described here were prepared by common grinding the additives with the prepared

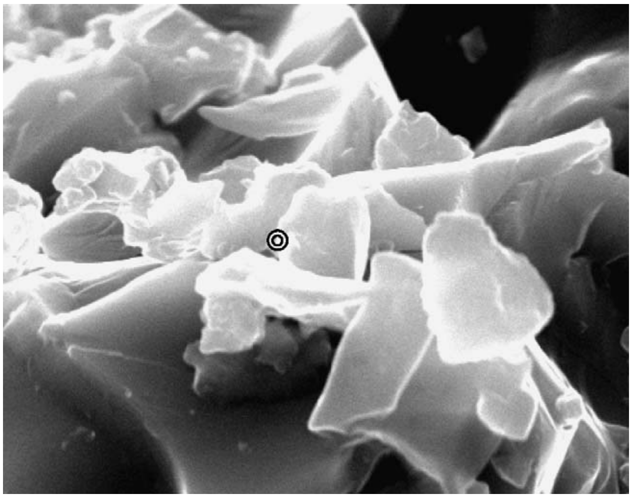

Fig. 1. SEM picture of a fragment of CA_2 body penetrated by MgO-rich liquid, showing an equant spinel crystal in the centre.

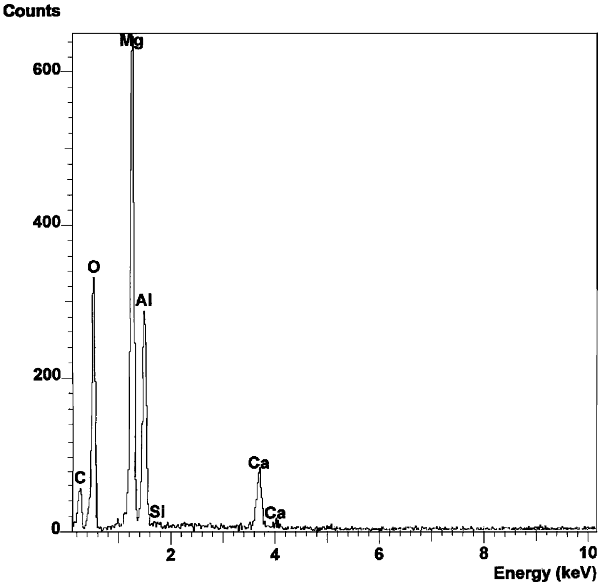

Fig. 2. EPMA spot analysis of the $MgAl_2O_4$ crystal shown in Fig. 1.

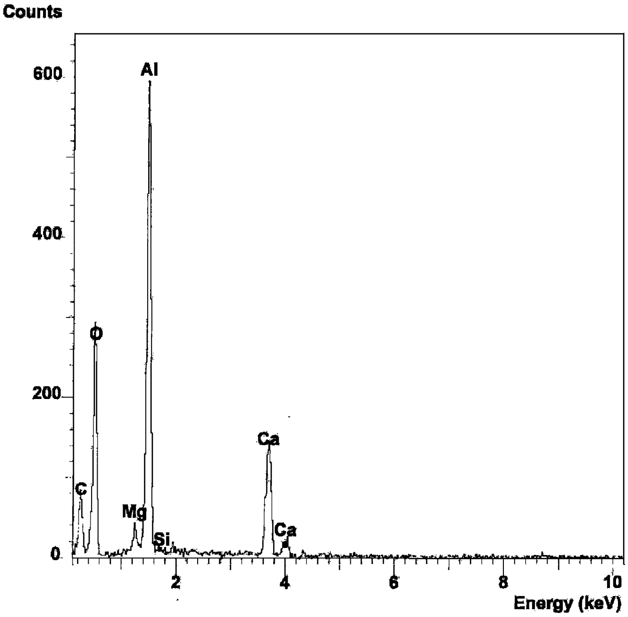

Fig. 3. EPMA spot analysis of a $CaAl_4O_7$ crystal.

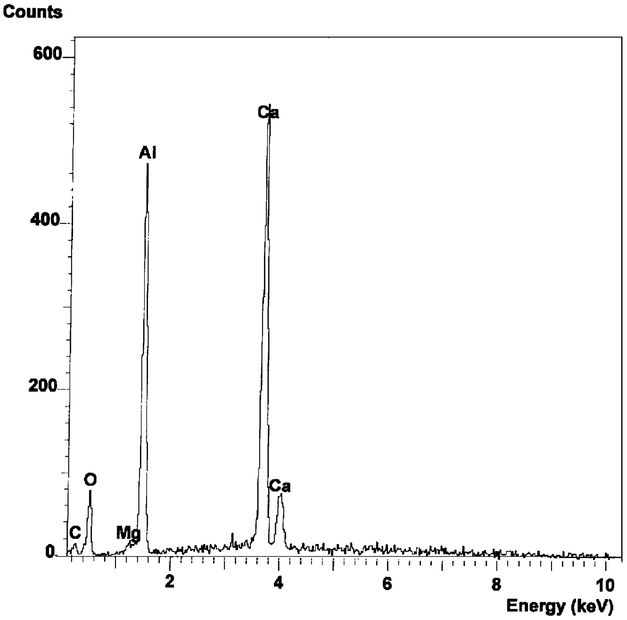

Fig. 4. EPMA spot analysis of a point in the interaction layer containing $CaAl_2O_4$.

earlier synthesized dialuminate and then compacting the mixtures under uniaxial 40 MPa pressure into cylindrical specimens of 7 mm diameter and ca 20 mm height. These were then fired to maximum temperature 1620 °C (held 1/2 h). This temperature of firing ensured the appearance of an equilibrium liquid in the CA_2–RO compositions.

In order to measure the changes of crystallographic dimensions (cell parameters) on heating $CaAl_4O_7$ monocrystal samples up to 500 °C, a KUMA KM4CCD X-ray difractometer equipped with a heating unit was used. The results, based on Mo K_α radiation, are given in Table 3. In Table 4 some properties of specimens of selected compositions (regarded as those near-optimum) are presented. The apparent (open) porosity and bulk density were determined by conventional method (boiling and weighing), using kerosene to avoid hydration.

3. Discussion

As can be seen from data presented in Tables 1 and 2, the additions of just a few percent of MgO and/or CaO to calcium dialuminate can bring about a deep depression in the measured α values - even a shrinkage behavior on heating the fired specimens. The precondition for the attainment of such effects is to expose samples to a firing temperature exceeding 1600 °C - an operation starting the sequence of chemical recombinations according to reactions (1) and (2), where pore penetration by the CA-based liquid occurs leading to the formation of a specific microstructure; this is shown in Figs. 1–4 and 7.

The small amounts of the reaction product CA present after firing among the CA_2 crystals in the finegrained compositions of Tables 1 and 2 are difficult to determine experimentally, but can be directly calculated from additive percentages. The dependence of α-data upon the stoichiometrically established CA content in the specimens after reaction is shown in Fig. 5, for some temperatures of measurement. The occurrence of a rather regular composition range of the lowest (even negative) thermal expansion data can be correlated with MgO and CaO additive contents - those believed to be near-optimum from the technological point of view. This range, similar for compositions containing both MgO and CaO, can be ascribed, as indicated above, to the role played by the CA-based liquid. According to the $CaO–MgO–Al_2O_3$ phase diagram,[10] this liquid will first appear somewhat earlier before reaching the firing temperature, at the invariant point 1550 °C. In the case of reaction (2), the recently published version of the $CaO–Al_2O_3$ phase

Table 1
Thermal expansion data for calcium dialuminate specimens containing MgO additions

Percent weight addition of MgO (above 100% CA_2)	Mean linear thermal expansion coefficient ($\bar{\alpha} \times 10^6\ {}^\circ C^{-1}$) from 20° up to temperature (°C)								
	100	200	300	400	500	600	700	800	900
0	2.3	3.1	3.5	3.8	4.0	4.1	4.2	4.3	4.5
1	2.8	3.5	3.9	4.1	4.2	4.3	4.4	4.6	4.7
2	−0.1	0.8	1.2	1.5	1.8	2.1	2.4	2.7	2.9
3	−0.3	0.1	0.4	0.8	1.2	1.5	1.9	2.3	2.6
4	−0.2	0.0	0.5	0.8	1.3	1.6	2.0	2.4	2.6
5	0.4	0.6	0.9	1.2	1.6	1.8	2.2	2.5	2.9

Table 2
Thermal expansion data for calcium dialuminate specimens containing CaO additions (introduced as $CaCO_3$)

Percent weight addition of CaO (above 100% CA_2)	Mean linear thermal expansion coefficient ($\bar{\alpha} \times 10^6\ {}^\circ C^{-1}$) from 20° up to temperature (°C)								
	100	200	300	400	500	600	700	800	900
~2.2 (4% $CaCO_3$)	−0.1	0.1	0.3	0.5	0.6	1.0	1.4	1.8	2.2
~2.8 (5% $CaCO_3$)	−0.5	0.1	0.4	0.7	1.2	1.5	1.9	2.3	2.6
~3.4 (6% $CaCO_3$)	0.0	0.5	0.8	1.1	1.4	1.7	2.2	2.5	2.9

Table 3
Change of crystallographic dimensions of a $CaAl_4O_7$ monocrystal on heating to 773 K (500 °C)

Temperature (K)	Crystallographic axis dimensions (Å)			β angle (°)	Cell dimensions (V)	Dimension changes on heating			
	a	b	c			$\Delta a/a_{300}$	$\Delta b/b_{300}$	$\Delta c/c_{300}$	$\Delta V/V_{300}$
300 (=27 °C)	5.43483	8.85301	12.43260	97.96993	592.41				
340 (=67 °C)	5.43793	8.85972	12.43175	97.86422	593.31	0.0570	0.0758	−0.0068	0.1519
375(=102 °C)	5.43526	8.85075	12.43534	97.82083	592.65	0.0079	−0.0260	0.0220	0.0405
473 (=200 °C)	5.43496	8.87515	12.41867	97.64590	593.70	0.0024	0.2501	−0.1120	0.2178
573 (=300 °C)	5.43940	8.88753	12.42982	97.59110	595.63	0.0841	0.3899	−0.0220	0.5435
673 (=400 °C)	5.43552	8.88535	12.42595	97.54007	594.94	0.0127	0.3653	−0.0530	0.4271
773 (=500 °C)	5.43718	8.89885	12.42805	97.43128	596.28	0.0432	0.5178	−0.0370	0.6533

Table 4
The effects of firing of selected compositions of Tables 1 and 2

Oxide addition to 100% CA_2	Forming pressure (MPa)	Weight loss on firing (%)	Firing shrinkage (% lin.)		Apparent porosity (%)	Bulk density (g/cm^3)	Crushing (compressive) strength (MPa)
			Diameter	Height			
4% MgO	20[a]	9.2	14.4	12.4	0.7	2.17	323
4% MgO	40	5.4	14.1	12.7	1.1	2.08	397
4% MgO	60	5.6	12.0	13.1	0.7	2.13	405
3% MgO	40	4.5	13.8	12.5	0.3	2.14	230
2.2% CaO	40	8.2	12.2	9.9	2.2	2.05	214
As above		7.1	12.5	11.2	2.2	2.05	232
3.4% CaO	40	7.2	13.8	11.4	1.7	2.08	179

[a] Formed with some excess of polyvmyl alcohol binder in the raw mix.

diagram is helpful in showing the incongruent melting of CA at 1604 °C in contact with CA_2.[11]

In order to account for the negative α values observed with some compositions and temperature ranges, the data of Table 3, presenting the behavior of a single crystal CA_2, may be analysed. The measured effects are believed to predominantly arise from dimension changes of the c axes – as can be concluded from column $\Delta c/c_{300}$.

The expansion of the individual crystals might not be fully projected onto the external dimensions of the polycrystalline specimens. This presumption is based on the possibility of some local rearrangements of crystals (to which the β-angle changes indicated in the table might contribute) and/or some elastic deformation under compression following expansion on heating. At the same time, the shrinkage effects occurring mainly due to the behavior along the c axis (column $\Delta c/c_{300}$) would probably have much more chance of being fully measurable at the macroscale, along the specimen's external dimensions. This chance is believed to arise from the above mentioned special microstructure, that was developed on firing as a result of the penetration of the CA liquid into space among the CA_2 crystals. If such a penetration would not occur, the planes of adherence of crystal faces responsible for shrinkage (those along the "c" axes of two CA_2 crystals in direct contact) could become prone to rupture under tensile stresses emerging on heating the samples. This would create microcracks preventing shrinkage of the sample as a whole. The mechanism of separation of these planes of adherence by crystallizing CA films would be able to avoid such cracking and thus help preserve the shrinkage effects, owing to the mentioned microstructure. Thus, with

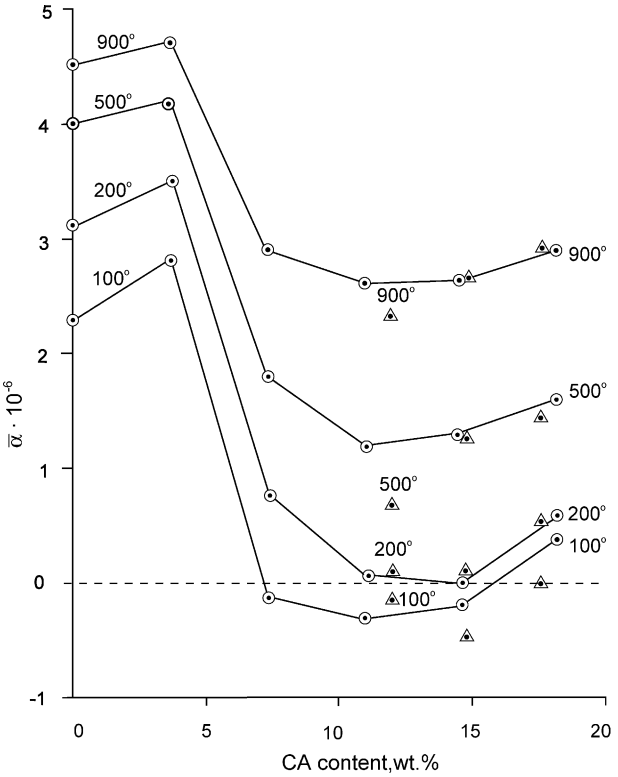

Fig. 5. Graph showing the dependence of the mean α values on the calculated $CaO \cdot Al_2O_3$ (=CA) content in $CaAl_4O_7$ (=CA_2) fired specimens containing MgO and CaO additions, on heating to temperatures: 100, 200, 500 and 900 °C. (⊙): Compositions with MgO additions, points connected by solid line and (▲): compositions with CaO additions (introduced to the batch as $CaCO_3$).

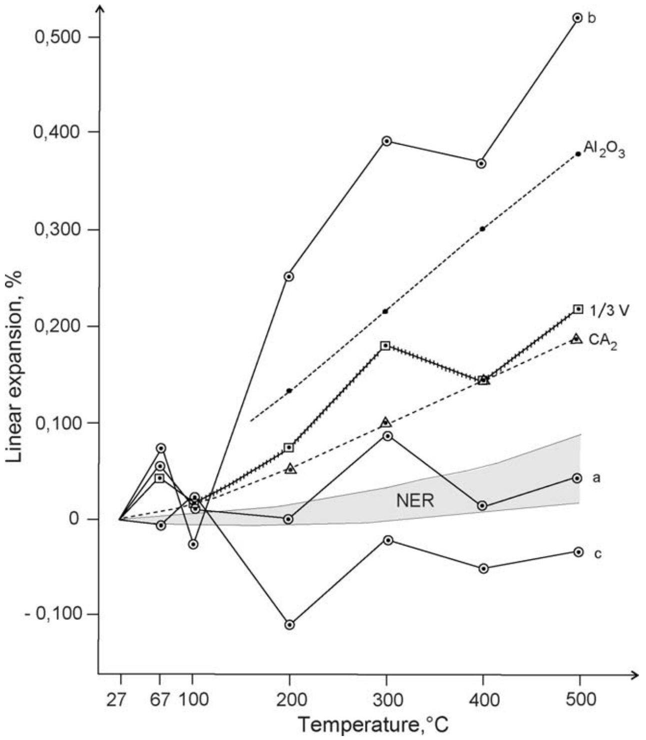

Fig. 6. Per cent linear expansion curves up to 500 °C of crystallographic dimensions of monocrystal $CaAl_4O_7$ (=CA_2) according to data of Table 4 (axes *a*, *b*, *c* and 1/3 cell volume *V*), compared with those of CA_2 polycrystalline specimens, Al_2O_3[2], and the range of typical NER (nonexpansive refractory) compositions (dotted area).

some compositions, the overall shrinkage effects could practically prevail over those of expansion, in spite of the very high elongation along the *a* axis. It must be stressed, however, that there is so far no experimental proof for this presumed mechanism.

These considerations, including data of Table 3 and some previous test results, are reflected graphically in Fig. 6. There are shown changes of the dimensions (1/3 volume) of the elementary cell of CA_2 monocrystal on heating to 500 °C, in comparison with those of the dimensions along the a, b and c axes. Also given are linear thermal expansion data calculated from *a* values for polycristalline Al_2O_3 and CA_2 specimens without MgO or CaO additions compared with those covering the range of NER compositions.

As evidenced in Table 4, the fired NER bodies are characterized by high strength and low open porosity; this can be correlated with the appreciable firing shrinkage, showing no distinguishable dependence on the level of forming pressure. The rather low bulk densities would indicate the presence of rather high closed pore volumes in the obtained materials. The pores of this type can be noticed on the micrograph in Fig. 7; the crystalline components are mostly equant.

From among the publications which might be correlated with the subject matter of this paper, that surveying materials of very low thermal expansion[12] may be indicated; also, the description of a ceramic showing partly negative α coefficients[13] is worth consideration.

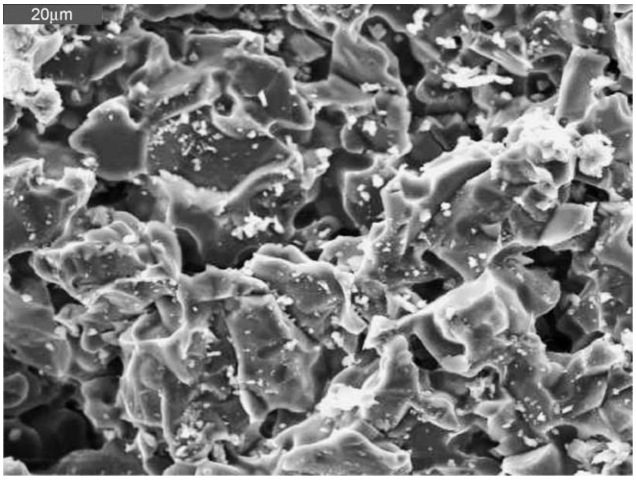

Fig. 7. General SEM picture of the MgO/CA_2 interaction microstructure.

4. Conclusions

Refractory compositions based on $CaAl_4O_7$ with MgO and CaO additions show deeply depressed thermal expansion values – even shrinking behavior on heating specimens previously fired at temperatures above 1600 °C. These compositions are referred to in this report as “nonexpansive refractories” (=NER). The occurrence of the NER effect is mainly ascribed to the creation of a specific microstructure developed as a result of high temperature reactions between $CaAl_4O_7$ (=CA_2) and MgO or CaO yielding a $CaAl_2O_4$-based (=CA) liquid capable of penetrating the body as a whole. There seems to exist an optimum content of the monoaluminate reaction product CA corresponding to a range of lowest expansion data on heating the NER specimens up to various temperatures within the 100–900 °C range. For further description of the nature of the thermal expansion behavior of the studied compositions, single crystal $CaAl_4O_7$ samples were prepared and the changes of their crystallographic dimensions on heating up to 500 °C were measured using a specially equipped difractometer. Basing on the obtained data concerning the expansion and/or shrinkage of the particular axes of the CA_2 monocrystalline structure, the presumable behavior of polycrystalline NER bodies which could account for the observed specific phenomena on heating is presented. After firing at 1620°, the NER specimens showed favorable physical properties: high strength and low open porosity.

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