

MODIFIED IN SITU SPINEL-ALUMINA CASTABLES

SUNANDA MUKHOPADHYAY, P.K. DAS PODDAR*

*College of Ceramic Technology, 73 A C Banerjee Lane, Kolkata-10, India***University of Calcutta, Dept. of Chemical Technology, 92 A P C Road, Kolkata-9, India*

E-mail: msunanda_cct@yahoo.co.in

Submitted February 18, 2003; accepted July 15, 2004

Keywords: Sol-gel process, Electron Microscope, Coprecipitation, Spinel Refractories

Modified in situ spinel-alumina castables were prepared by using 8.0 wt.% of calcined hydrated magnesium aluminate additives synthesized via facile sol gel and coprecipitation routes. These additives were characterized by particle size analysis and transmission electron microscopy. The castables prepared by them were compared in terms of bulk density, apparent porosity, cold crushing strength and spalling resistance to identify the excellent performance of the sol gel additive having nanocrystalline feature. The quality of castable was illustrated again by comparing it with the same prepared by commercially available spinel fines having well established performance. Scanning electron microscopy, energy dispersive spectroscopy, pore size distribution and X-ray diffraction analysis were used to examine selected fired samples. It appeared that the spinel-alumina castable prepared by the sol gel additive can be a potential candidate for application in steel plants.

INTRODUCTION

Steel being an abundantly used engineering material requires special attention for its production and for obtaining highest quality clean steel several ladle metallurgical operations are undertaken [1]. These quick and efficient secondary refining processes extend the period of contact of superheated steel with the ladle refractories in a corrosive atmosphere in presence of extremely aggressive slags and metals [2]. Consequently it became essential for refractory producers and researchers to opt for suitable high performance monolithic castables to cater for the needs of today and tomorrow [3,4]. In the modern ladles, spinel-bonded high alumina based castables with desired service life are extensively used because of the appreciated qualities of magnesium aluminate ($MgAl_2O_4$) spinel especially its chemical resistance [5]. Commercially available preformed spinels are widely used in this regard [6-8] in spite of the stringent steps associated with their production (namely, precalcination, co-grinding, drying, sintering at $\sim 1900^\circ C$, granulating, sieving etc) raising the price of the material. The alternative trend is the fabrication of in situ spinel -alumina castables[9] where magnesia powder taken in the batch reacts with alumina fines to result in spinel on due course of heating at service temperature of the site keeping a special precaution for hydration and volume expansion [10-11]. Some researchers reported another way of preparing in situ spinel-alumina castable [12-18] by incorporating hydrated spinels (prepared via cost effective chemical routes) in the batch to get the advantages of homogeni-

ty, temperature, time and thermal shock resistance. However this process too is associated with volume expansion and the additives when used beyond a certain limit affect green strength and installation flexibility of the castable [14].

The present investigation attempts to prepare and characterize a modified version of in situ spinel-alumina castables with partly calcined ground gels synthesized by sol gel and coprecipitation routes from relatively cheaper ingredients. Firstly, the shortcoming of gel-bond castable compared to the preformed one has been discussed in brief together with the advantage of the former in regards spalling resistance. In the second and major part of the work, the characteristics of the modified and improved in situ spinel additives were studied to correlate their influences in the newly formulated castables at elevated service temperatures. The performance of the best modified in situ castable was also compared with that of conventional spinel-alumina castables utilized in commercial practice.

EXPERIMENTAL

Table 1 is the composition of the original spinel free castable. Its packing efficiency was optimized by the q-value (distribution modulus) determined from several constituents of castables [19], namely fused alumina (6-16, 16-30, 30-60 and < 100 mesh BS grades) with other microfines. Table 2 is the composition of newly formed modified castable batch. The typical characteristics of hydrated spinel gels applied to the

100% batch of castable (table 1) from outside, i.e. sol-gel (G) and coprecipitate (C) types, have been shown in table 3. These in situ spinels were synthesized in laboratory from cheaper precursors (e.g. nitrates, chlorides etc) that have been reported in our previous articles [12–18] together with the categorical determination of their special properties. The amount of hydrated C and G precursors added to the castable batch shown in table 1 was increased twice in each five successive stages (i.e. 0.25, 0.5, 1.0, 2.0 and 4.0 wt.%) until it resulted in a detrimental effect in green strength and installation flexibility of castables [20]. It has also been reported [21] that such kind of gel mass is effective in small quantity when added to a bulk ceramic body. The spinel bonded high alumina based monolithic mass, with requisite amount of deflocculant and water was cast in cube moulds (25.4 mm), gently tamped by hands with no extra mechanical vibration applied from outside. Extensive curing and drying stages were maintained in humid atmosphere, dry air and oven. Finally the samples were heated to 110, 900, 1200 and 1500°C with a soaking for 2 hr at each temperature. The pore size distribution in

terms of pressure vs. delta volume intrusion patterns of the fired castables (1500°C) formulated with hydrated in situ (G type) and preformed alumina-rich (~ 90 %, R type, table 4) spinel additives were compared to clarify the better thermal shock resistance of gel-bonded specimens. This experiment was done in a Mercury Porosimeter Instrument (Model Poremaster-33, Quantachrome, version 4.01).

In the second phase of this work another new castable batch was formulated (table 2) to estimate the feasibility of industrial application of a newer version of in situ spinel additives. In this regard the semidried gels (G and C) were ground in agate for 1 h [22–24] and then partly calcined to 900°C for 2 hr [25]. Finally these were again comminuted for 1h in laboratory by agate (without recourse to expensive instrument like ball mill or vibro-grinder) to sieve them through 200 mesh (BS) i.e. a fineness below around 75 µm. These were termed as modified in situ additives. The transmission electron microscope studies of modified in situ additives were performed in the instrument Hitachi H-600 bright field electron microscope with an accelerating voltage 50 kV. Two commercially available preformed spinel powders known to be rich in alumina e.g.~ 78 % (P) and ~90 % (R) were also collected and characterized in detail (table 4) to observe their influences to the same castable batch[15-18]. All these four type powders (G,C,P and R types)were utilized one at a time in the new castable batch (table 2) in same quantity (8.0 wt.%) to fabricate

Table 1. Batch composition of original low moisture spinel-free castable and its physical properties after firing at 1500°C/2 h.

constituents	content (wt.%)
white fused alumina	77
microfine alumina	8
micro silica	5
high alumina cement	6
white tabular alumina	4
shmp (deflocculant)	0.05
water	5-7 %
bulk density (g/cm ³)	2.97
apparent porosity (%)	15
cold crushing strength (at 1500°C, kg/cm ²)	1400
PLC (%), 1500°C, 2 h	+0.2

Table 2. Formulation of modified in situ spinel-alumina castable batch.

	constituents	amount (wt.%)
aggregate →	white fused alumina; coarse, medium, fine.	75.0
matrix ↗ ↘	micro silica, micronized alumina, refractory high alumina cement.	17.0
	modified in situ spinel powder (CN or GN type, one at a time)	8.0
		Total = 100

Table 3. Physicochemical properties of two types of hydrated spinel precursors.

Characteristics	Co-ppt spinel (C)	Sol gel spinel (G)
solid content	~10 %	10 %
pH	6-7	3-4
average particle size	6 µm	11 nm
MgAl ₂ O ₄ (wt.%) in calcined additive at 1500°C	> 99.8 %	>99.8 %
amount added to castable (wt.%)	0.25, 0.5, 1, 2, 4.0	0.25, 0.5, 1, 2, 4.0

Table 4. Characteristics of preformed magnesium aluminate spinel fines.

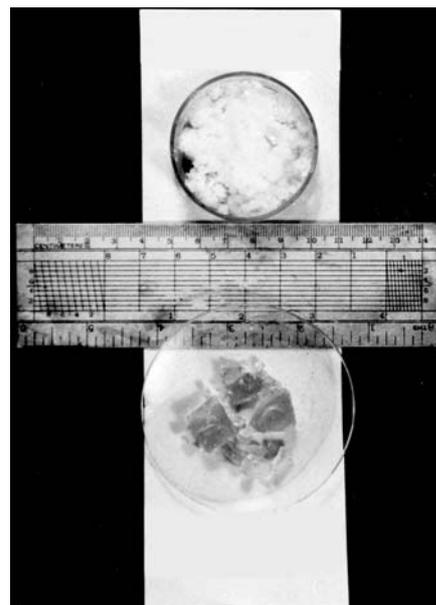
	R type	P type	
major constituents ↗ ↘	Al ₂ O ₃	> 90.0	> 77.0
	MgO	> 8.9	> 22.0
bulk density (g/cm ³)	~3.29	~3.26	
average fineness (µm)	< 45	< 45	

new spinel-alumina castable batches (100%) and represented respectively as GN, CN, PN and RN types. All these four categories of castables were prepared by the same procedure as discussed in the last paragraph and fired at different elevated temperatures even upto 1600°C without any deformation of the materials. It should also be mentioned that the microsilica content of the newly formed castable batch (table 2) was kept significantly low (~ 1.0 wt.%) to avoid the low melting phases generated in the materials prepared earlier (table 1) having greater quantity of silica fines [14,26]. The chemical analysis of raw materials shown in tables 1 and 2 have been mentioned in our previous article [14]. The particle size distribution of the modified additives was studied in Mastersizer, E Ver. 1.2.b model. Bulk density (BD), apparent porosity (AP) and cold crushing strength (CCS) were determined by standard methods [14]. The thermal shock resistance of pre-fired castables (1500°C) was estimated in terms of percent residual strength (% RS) which is the CCS value retained by the samples after 5 cycles of thermal shock, where each cycle included heating the samples at 800°C for 10 minutes followed by quenching them in water in room temperature for another 10 minutes. The XRD patterns of GN type castables were taken by using Ni filtered $\text{CuK}\alpha$ at 40 kV/20 mA. Some selected samples were subjected to SEM and EDS test by the instruments JEOL JSM 5200 and Hitachi S-2300 models.

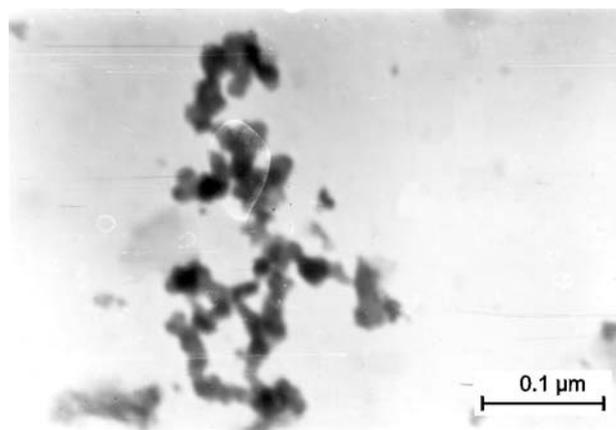
RESULTS AND DISCUSSION

Characteristics of gel-bond in situ and conventional preformed spinel-alumina castables

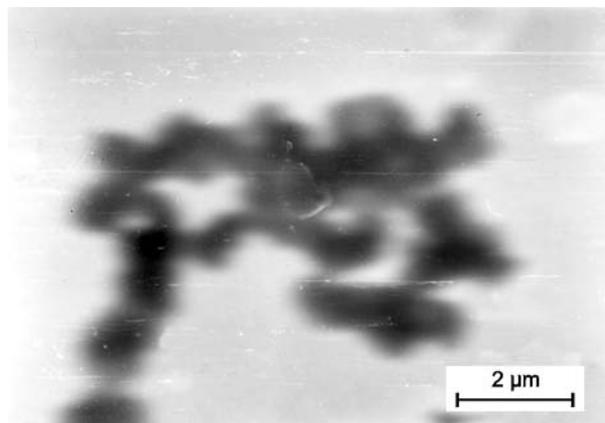
Figure 1a shows the photograph of hydrated spinel gels (G and C) prepared by sol gel and coprecipitation routes respectively. It has been reported (from the respective XRD and IR patterns presented) in our earlier communication [14-18] that the sol gel material shows spinel evolution at a temperature 450°C while the coprecipitated gel at around 900°C. It has also been shown that the sol gel precursor possesses particles lying within nano-fine range while that of coprecipitated one is within micron ranges (table 3). It is once again corroborated from the TEM of the same powders in the modified form (figure 1b and 1c). The beneficial effect of sol-gel additive is related to its tremendously high surface area, which has been explained in our previous articles [13,14,16] while the coprecipitate is somewhat agglomerated. Those TEM figures clearly reveal that the sol-gel additive maintains its nanocrystalline feature while the coprecipitate is highly aggregated. The coar-



a)



b)



c)

Figure 1. a) Photograph of semidried sol-gel (G) and coprecipitated (C) hydrated spinel precursors; b) TEM of modified G additive; c) TEM of modified C additive.

ser scale mixing of the coprecipitate probably led to such agglomeration while the flexible sol gel route helped in atomic scale mixing of the precursor and as such seems to manifest its nanofineness till after modification of the ultimate particles. The additional benefits achieved from this sol gel additive applied in monoliths is the improved thermal shock resistance of in situ spinel bonded castable in comparison to the preformed spinel bonded material. It has been shown in some papers [14,16] that the same batch of a refractory castable when separately bonded with hydrated in situ and presintered spinel additives, the former performs better in terms of spalling resistance. It has been suggested [14] that a series of micro-bubbles released from sol-gel additive inside the refractory at higher temperature created distributed pores and flaws that hinder the extension of cracks [27]. This is further demonstrated in figure 2a, which corroborates that the volume intrusion (done by Hg-porosimetry with increasing pressure) progressively goes on to a wider range due possibly to the presence of fine micro-sized voids and cracks distributed throughout the in situ spinel alumina castable originated from the volatiles released at elevated temperature from the hydrated sol-gel precursor. On the contrary, figure 2b shows that the range of volume intrusion with pressure is narrow in preformed spinel-bonded castable due to the absence of those microbubbles and conse-

quently the chances of crack closure during spalling is very much less there. However the other properties (BD, AP, CCS) of the prereacted spinel bonded castable are exceedingly well [15-18] and for this reason such kind of preformed additive, specially alumina rich, is popularly used in high alumina based castables [28]. This is observed from figure 3a, the SEM micrograph of fired castable bonded with alumina rich spinel (~ 90 %, table 4), which reveals a very much compact and interlocking morphology. However this is also an established fact that when microsilica content in the castable batch is high enough (as in table 1), it generates some low melting phases to affect the hot properties of castable [29]. This is evident from figure 3a, which shows some detrimental CaO-Al₂O₃-SiO₂ (C-A-S phase) possibly generated due to ~ 5 % fine silica present in batch that could deteriorate the refractoriness of the dense network under load. That phase is confirmed by the EDS pattern of the indicated region as shown in figure 3b.

Characteristics of modified in situ and conventional spinel-alumina castables

As reported earlier [12-18] these hydrated in situ additives suffer from three drawbacks. Firstly, the spinel forming reaction itself being volume expansive, is further triggered by the reactivity of the gel precursors. Secondly, the solid content of gels being 10 % by weight, the amount of them (0.25–4.0 wt.%) used in castable introduces enormous porosity after firing.

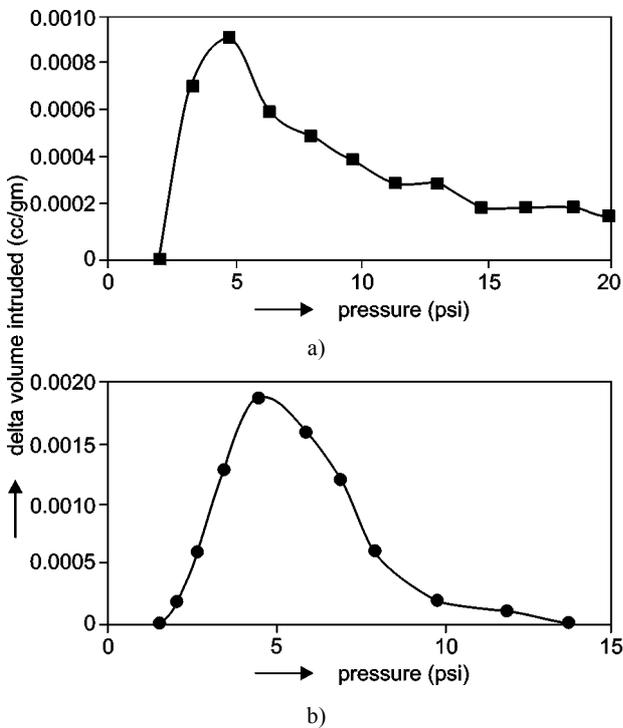


Figure 2. Pore-size distribution pattern in terms of pressure vs. volume intrusion of fired castable (1500°C, table 1) bonded with different spinel sources; a) hydrated sol-gel precursor, b) preformed (R type) powder.

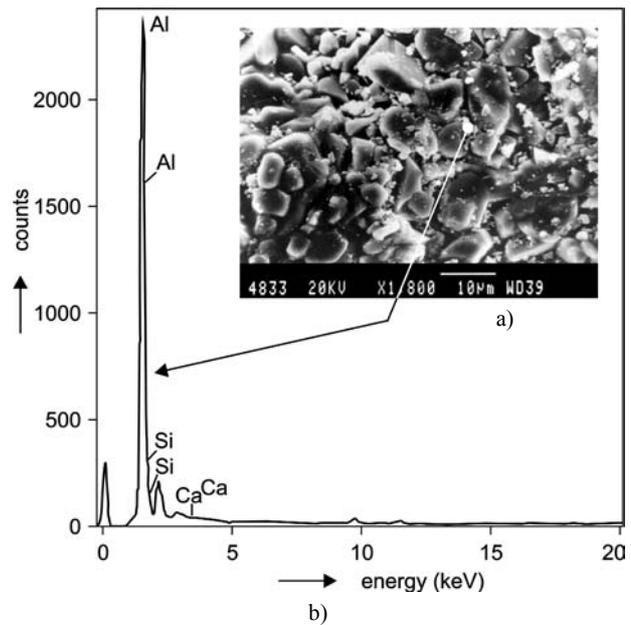


Figure 3. a) Micrograph of R-type spinel bonded castable fired at 1500°C/ 2 h; b) EDS trace of the indicated region in SEM micrograph.

Although pores are beneficial for thermal shock resistance, but an excessive porosity must adversely affect the strength and corrosion resistance of castables. Due to this reason, in this second phase of investigation (as mentioned in the Experimental part) the gel precursors (G, C types) were calcined and ground in laboratory easily to a fineness below $75\ \mu\text{m}$ (figure 4a). We suggest that the grinding of semidried gels for 1h before calcination partially assisted the homogeneity and activation of the same as usually observed in mechanochemical synthesis [22-24]. The optimized calcination was done to generate reactive spinel [25] as studied by Bratton, considering the tradeoff between surface area and relative density. Here some part of the free energy change that drives the decomposition during calcinations, possibly creates an additional surface free energy. After calcination, the grinding might have also been facilitated by the topotactic orientation relationship [30] and large molar volume difference between the hydrated parent salt and calcined oxide that produces a high degree of coherency strain associated with the particles. Moreover the residual OH-groups present after calcination in modified additives [31] provides further homogeneity during comminution to result in better quality additives in an energy efficient way.

Thus a newer batch of castable (table 2) was formulated with an equal quantity of calcined additives (i.e. G,C added separately) and its packing efficiency was found satisfactory from q-value calculation as shown in figure 4b [19]. The third drawback of hydrated gel precursors was the restriction of their amount used in castable. During a two-fold increase with their additions (0.25, 0.5, 1.0, 2.0 and 4.0 wt.%) it was observed that at the last stage, the green strength of castable falls miserably [20]. This is observed from figure 4c that indicates a practical inconvenience towards installation flexibility of castables bonded with such precursors beyond a certain limit. The initial slab of 0.25% practically rendered no effect to the properties of spinel-free castable (table 1). Therefore, the region of interest was fixed between 0.5–2.0 wt.% as communicated before [14]. But as the net solid content coming out from the gels (table 3) lie within the range 0.05–0.2% in the castable matrix, it was obviously difficult to compare them judiciously with the presintered spinels, which are frequently applied in much higher quantities [32-35]. Considering all these aspects, the gel precursors were pre-calcined at $900^\circ\text{C}/2\ \text{h}$ to reduce the volume expansion and excess water. Consequently these modified versions also overcame the restriction of their amount (0.5–2.0 wt.%) used in castables as encountered during the first phase of this work.

The better performance of sol gel additives can also be related to its excessive reactivity to generate spinel phase earlier [12,14]. As a consequence, the chance of

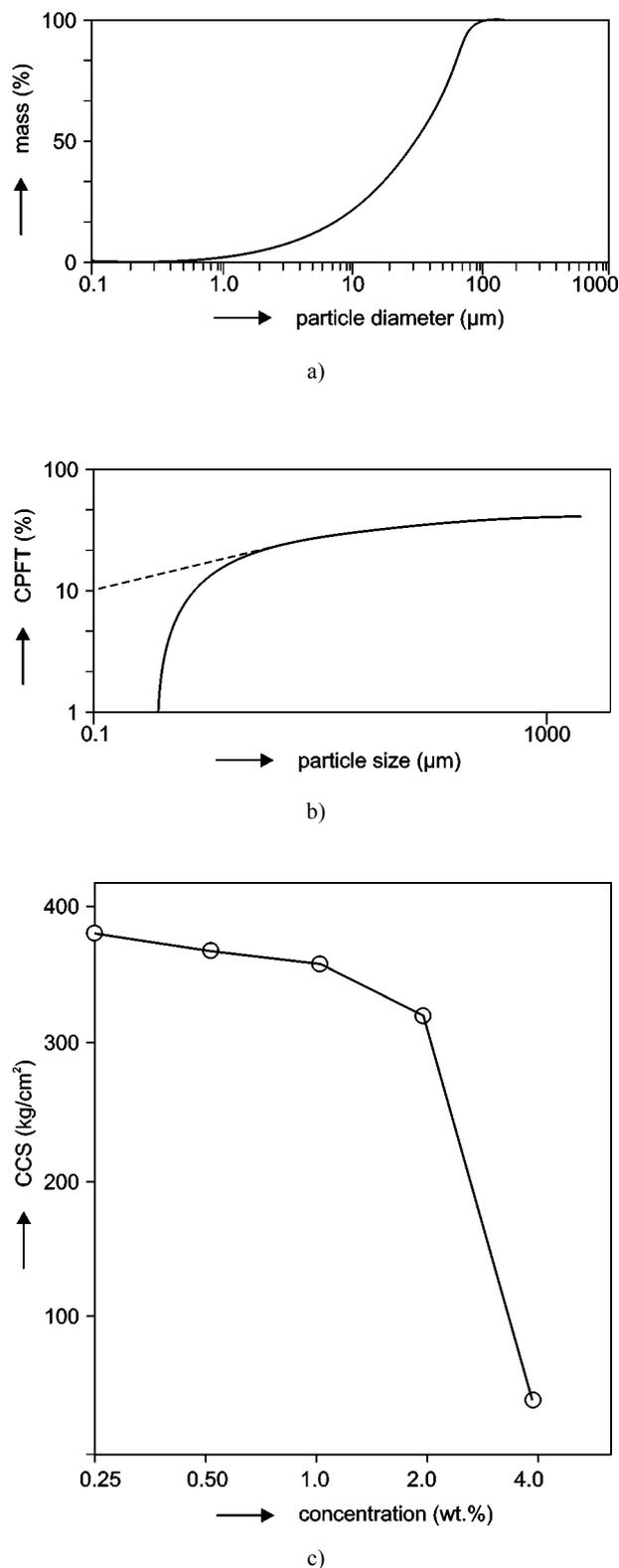


Figure 4. a) Particle size distribution curve of G-type modified in situ spinel additive; b) Particle size distribution of modified in situ spinel-alumina castable (table 2) in terms of cumulative percent finer than (CPFT) vs. particle diameter; c) Variation of green strength (CCS) of original castable (table 1) with progressive addition of G type hydrated precursor.

volume stress rendered by them in castable as compared to the coprecipitated additives should be far less. The appearance of pores therefore should also be less conspicuous in castables bonded with sol gel additives. For the same reason, the sinterability of coprecipitated spinel additive was found to be less as mentioned afterwards. It has been corroborated in our earlier articles [15-18, 31] by the IR patterns of G and C additives that the relative intensity of the spinel forming peaks is more prominent in the reactive former gel (G) while the latter (C) is more complex in nature with a lot of additional peaks. It has also been clarified from the IR pattern of C type that it still possesses a considerable amount of entangled and entrapped hydroxyl, amide and amine groups in its calcined state and these volatiles are liberated at further higher temperature to create voids and cracks in the matrix of castable due to generation of substantial amount of stress. The non-uniformity and uncontrolled precipitation is thus found here to be a noticeable limitation of the coprecipitation route.

Figure 5 is the comparison in properties (BD, AP, %RS) with increasing temperature between GN and CN type castables. It is apparent that GN again excels over CN while spalling resistance of the latter is better might be due to the advantage of enhanced porosity as described before [27]. The better BD and AP values of GN are substantiated by figure 6, the XRD patterns of the same at 110°C and 1600°C, and the latter reveals that sufficient amount of spinel and hibonite phases [28, 35,36] have been produced inside the modified castable. Figure 6a clearly supports the presence of spinel crystallites in the matrix. Figure 7, the micrographs of the GN and CN type castables confirm an extremely compact and interlocking texture between aggregates and matrix. The evolution of desirable spinel, hibonite and C-M-A-S (M = MgO) in appreciable quantity is again very much conspicuous in GN which provides a strong indication of better BD and AP values of the GN type castable [7-9]. The same kind of morphology is also observed in figure 7b for CN, although a bit of agglomeration and abnormal grain growth at several places is prominent may be due to relatively coarser and less dispersed particles present in the respective hydrated precursor material (table 3). As the G additive completes the evolution of spinel phase at comparatively lower temperature than C, it is likely that the chances of volume stress in GN is less and the generation of CMAS phase is more convenient in the same matrix. The modified spinel additive prepared by the ultrafine solgel precursor seemed to confer nanostructuralisation in some parts of castable (figure 7a). Very fine grain size distribution has been possible due to the controlled reactivity of partly calcined sol-gel additives. These fine spinel crystallites directly bonded to corundum as well as CA_n grains and between their interfaces presumably demon-

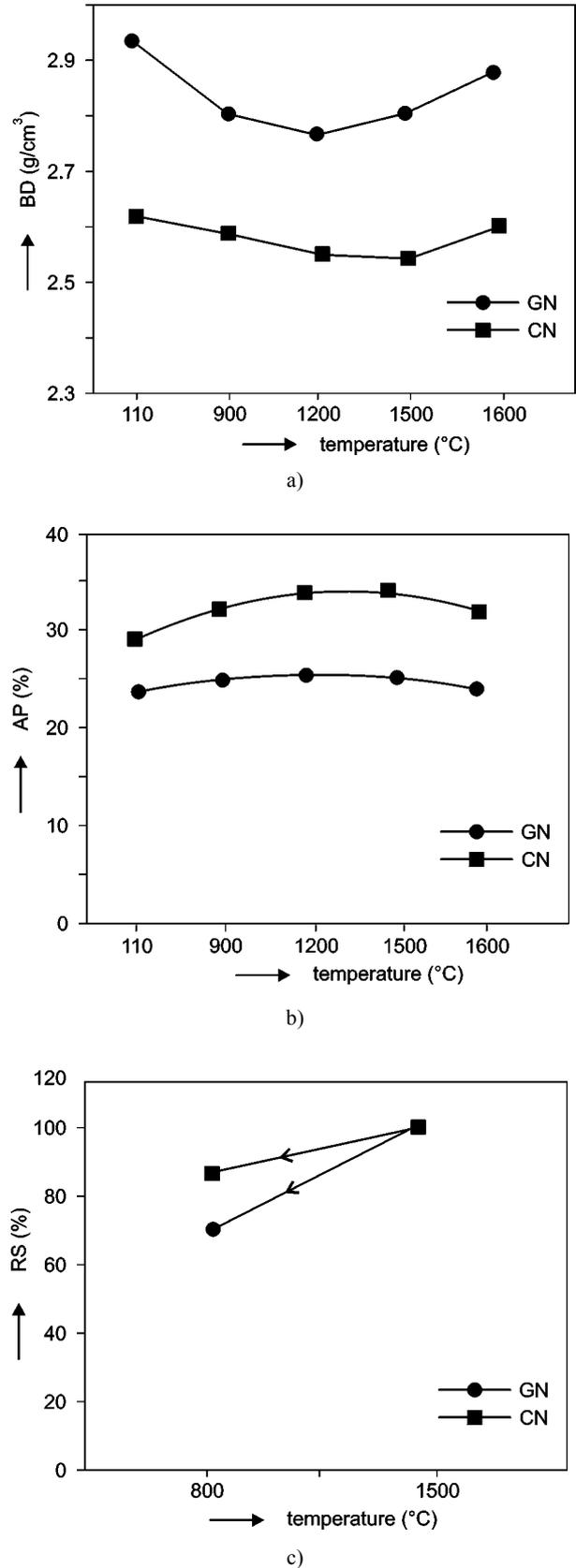


Figure 5. Comparison of change in properties with temperature between GN and CN type modified in situ spinel-alumina castables; a) BD; b) AP; c) % RS.

strated unique mechanical properties. The high surface to volume ratio of such crystallites also might enhance densification in a more pronounced manner. However for both the cases there is practically no sign of low melting C-A-S phase, which has been avoided [26] possibly by reducing the microsilica content in the modified batch (table 2). This also made it possible to raise the service temperature to 1600°C without any distortion of the fired material retaining the integrity of the structure. It should be mentioned that in the former batch (table 1), it was difficult to raise the temperature beyond 1500°C [14-17] because of the deformation of castable cubes might be due to enormous liquid C-A-S phases generated within the material [29].

Figure 8 is the comparative study between BD, AP and % RS of PN and GN type castables separately prepared by the same amount (8.0 %) of spinel powders added to the same batch (table 2). In the former (PN), commercially available costly alumina rich spinel

(~ 78 %, table 4) was used having fineness below 45 µm (figure 9). It is revealed that the BD, AP values are little better in PN while the thermal shock resistance is improved in GN. A slight decrease of BD and AP of GN may possibly take place due to the particle size effect [32] and porosity arising from the residual OH groups [31] present in the partly calcined sol-gel derived spinel fine. The specific gravity of calcined G additive has been found to be around 17 % less than the presintered spinel (P) powder, which obviously makes the BD and AP of GN to be a bit inferior. Nevertheless in GN, the spinel powders had average fineness below 75 µm (figure 4a), done easily in laboratory by agate while that of PN (45 µm) was achieved by exhaustive vibrogrinding and milling process done in industry with a possibility of escalation of price factor. It is well reported that [30] conventional milling methods are basically energy intensive and less efficient consuming very less (below 15 %) of the total energy supplied for size reduc-

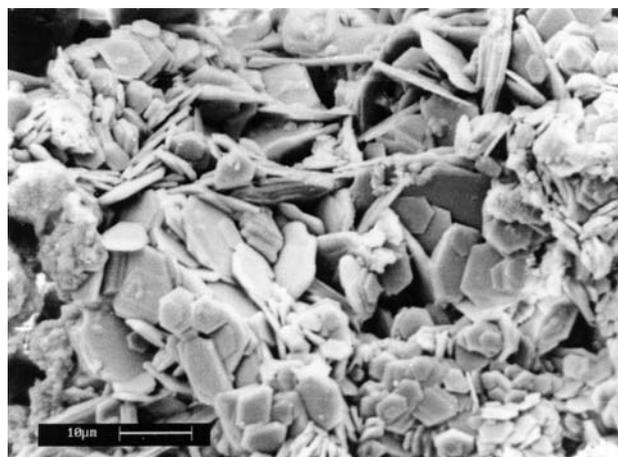
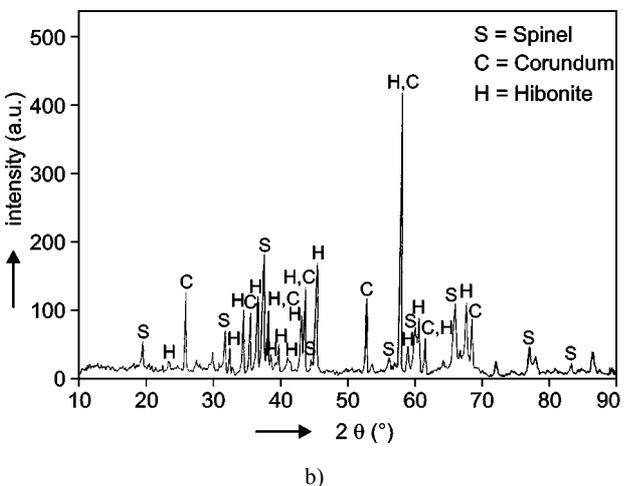
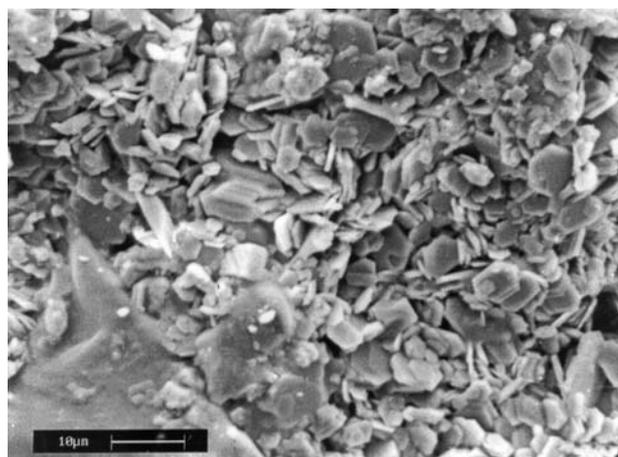
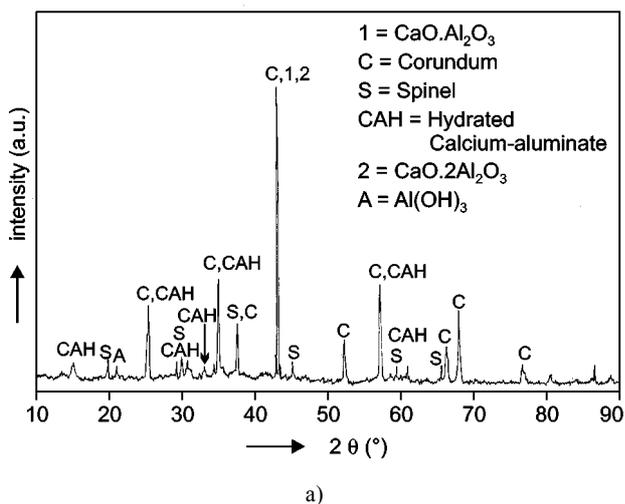


Figure 6. XRD pattern of GN type castable heated at a) 110° C/2 h and b) 1600° C/2 h.

Figure 7. SEM micrographs of a) GN and b) CN type castables after 1600° C/2 h.

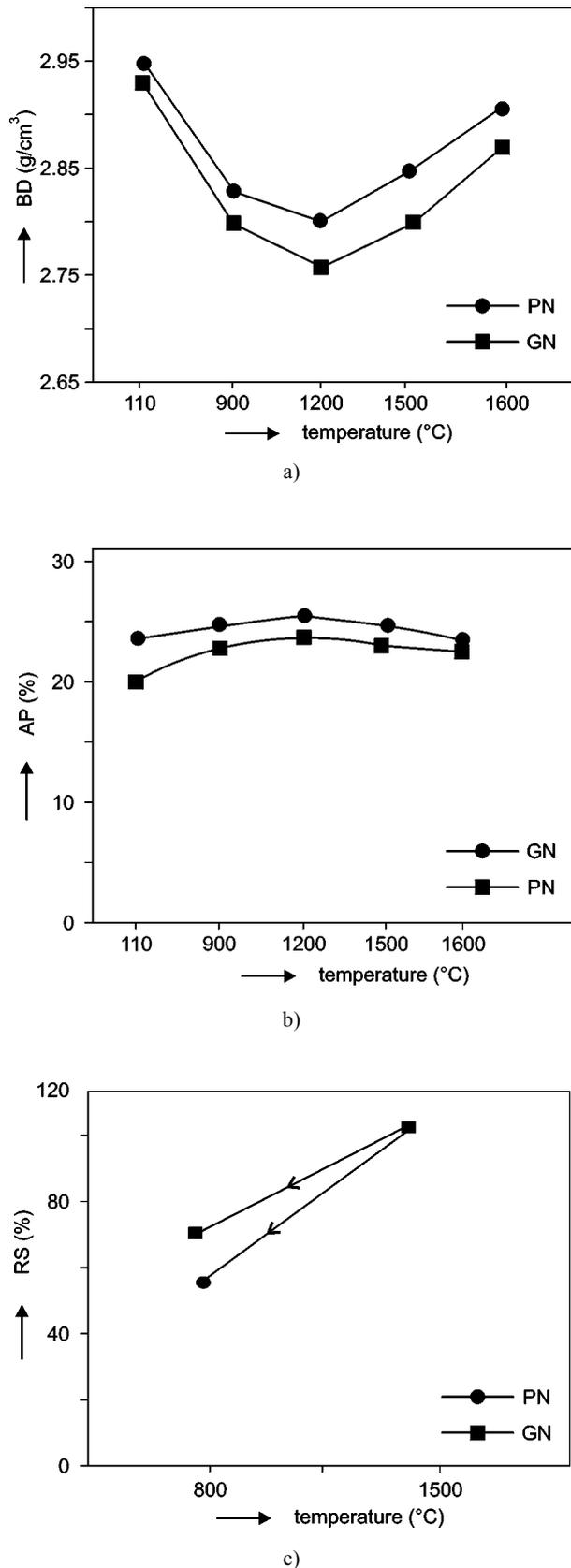


Figure 8. Comparison of change in properties with temperature between GN and PN type castables; a) BD; b) AP; c) % RS.

Wet milling is advantageous than dry milling but it introduces a variety of pitfalls to the ground material in the form of impurities like surfactants, binders and sintering aids. But the optimally calcined additives used here were friable porous agglomerates and as such easily subdivided by agate to result in reactive spinel fines having activated surfaces [37]. However as the fragmentation proceeded the required fracture stress increased so much that some plastic deformation could occur [30]. For this reason, the limit of fineness was limited to below 75 μm not to allow the chance of particle reaggregation on prolonged crushing. The little decrease in BD due to the residual pores present in GN can be sacrificed if this porosity is utilized to prevent the propagation of microcracks to upgrade the spalling resistance. Moreover, the nanofine sol-gel additive (table 3) being extremely reactive, generates spinel at remarkably low temperature range (450–600°C) [12, 14] that might have assisted to yield the desirable C-M-A-S phase when applied to castable. Furthermore, as the hydrated sol gel spinel used here was prepared by cheaper starting materials (e.g. nitrates instead of alkoxides often used for sol gel processing), it may be strongly suggested that this additive holds a strong prospect for being utilized in high performance castables required for secondary refining of steel without a significant rise in cost.

The agreeable performance of GN type might further be correlated to its microstructural features as again displayed in figure 10 (a and b). Those SEM pictures show microfine pores and vents in GN that possibly stood beneficial for spalling and corrosion resistances [31]. It is suggested that the residual pores must be designed carefully in castables and it may be possible by the pliancy of the sol-gel route. That additive enables tuning of such pore size distribution within castable matrix by expelling the remnant OH-groups present in it. Otherwise an extensive amount of pores with bigger diameters would agglomerate to form larger flaws to deteriorate the castable quality. The optimum calcina-

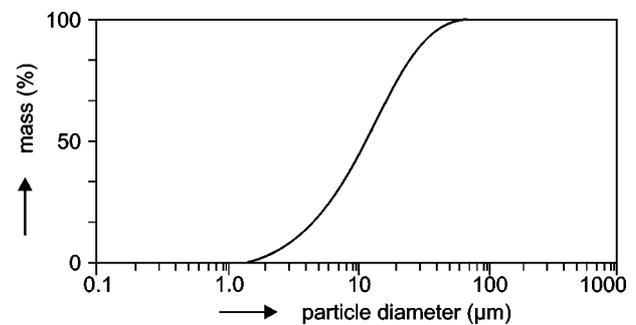
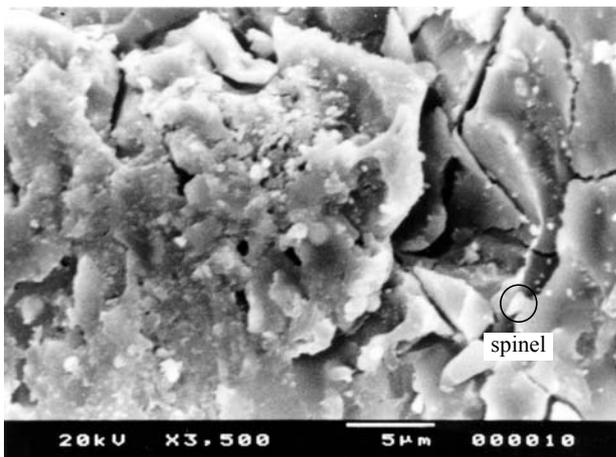
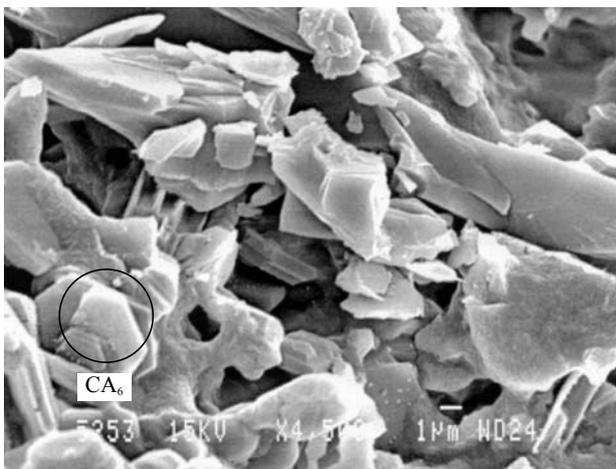


Figure 9. Particle size distribution curve of P type preformed spinel powder.

tions of precursor, in this respect, is very much important to partly reduce the fugitive volatiles in them which give rise to series of microbubbles by extended pyrolysis [14, 18]. Recently the advantage of nanostructures in the matrix of refractories had been reported by some researchers [38] and the sol-gel route, in this context, might be considered as a useful tool [39, 40] to prepare nanofine refractory additives at relatively mild conditions with such versatile positive influences. The spinel and hexagonal CA_6 (calcium hexa-aluminate) crystallites, visible in those micrographs opine tangibly that the required slag corrosion properties [8, 28, 35] of the GN castable must be excellent as been confirmed in our other paper [31]. The spinel composition was found slightly rich in alumina (80 wt.%) as per EDS reports and that of CA_6 was with alumina content around 87 %. It seems that some alumina from matrix was taken by



a)



b)

Figure 10. SEM micrographs of selected regions of GN type castable after firing at 1600°C/2 h.

reactive spinel to extend the solid solution and some microflaws have been generated. The better spalling resistance of GN than PN (commercial type) might arise also due to such flaws [27].

CONCLUSIONS

From the present investigation, it may be concluded that,

- 1) Magnesium aluminate gels prepared via sol-gel and coprecipitation methods from cost effective starting materials can conveniently fabricate modified in situ spinel-alumina refractory castables. Of these two, the superior nanofine sol-gel precursor possesses high potential in averting the expenditure of excess energy and time required to fabricate a preformed spinel-alumina castable, when used in equal quantity (8.0 %) as calcined powder to the same batch. However the sol-gel precursor in gelatinous form can not be used beyond a certain limit (4.0 %) while the preformed continued to retain its excellence at till higher doses.
- 2) The drawbacks of hydrated in situ gels, namely the uncontrolled volume expansion, extended pyrolysis and restriction of amount used in castable, can be remarkably reduced when they are modified by partly calcining at 900°C and grinding without much effort to below 75 µm in laboratory. The thermal shock resistance of castables prepared by these modified in situ additives keep their excellence and they hold a strong prospect to prepare tailor made matrix if done scalable economically.
- 3) Curtailment of microfine silica content to ~ 1.0 wt.% in the new modified castable batch helped to raise the working temperature to 1600°C without any sign of low melting liquid phase detrimental for hot properties of refractory.

References

1. Chesters J.H.: *Refractories for Iron and Steel Making*, p. 322-57, The Metals Society, London 1974.
2. Kudrin V.: *Steel Making*, p. 257-79, MIR Publishers, Moscow 1985.
3. Lee W.E., Moore R.E.: *J.Am.Ceram.Soc.* 81, 1385 (1998).
4. Mori J., Watanabe W., Yoshimura M., Oguchi Y., Kawakami T., Matsuo A.: *Am.Ceram.Soc.Bull.* 69, 1172 (1990).
5. Chiang Y.M., Birnie D.P., Kingery W.D.: *Physical Ceramics: Principles for Ceramics Science and Engineering*, p. 50, John Willey and Sons Inc., New York 1997.
6. Chan C.F., Ko Y.C.: *Interceram* 47, 374 (1998).

7. Simonin F., Olagnon C., Maximilien S., Fantozzi G.: *J.Am.Ceram.Soc.* 83, 2481 (2000).
8. Vance M.W., Kriechbaum G.W., Henrichsen R.A., Maczura G., Moody K.J., Munding S.: *Am.Ceram.Soc. Bull.* 73,70 (1994).
9. Fuhrer M., Hey A., Lee W.E.: *J.Euro.Cer.Soc.* 18, 813 (1998).
10. Evans R.M.: *Am.Ceram.Soc.Bull.* 72, 59 (1993).
11. Hwang K.H., Oh K.D., Bradt R.C. in: *Proc.UNITECR*, Vol-3, p.1575, New Orleans 1997.
12. Mukhopadhyay S., Ghosh S., Mahapatra M.K., Majumdar R., Barick P., Gupta S., Chakraborty S.: *Ceramics International* 28, 719 (2002).
13. Ghosh S., Majumdar R., Sinhamahapatra B.K., Nandy R.N., Mukherjee M., Mukhopadhyay S.: *Ceramics International* 29, 671 (2003).
14. Mukhopadhyay S., Sen S., Maiti T., Mukherjee M., Nandy R.N., Sinhamahapatra B.K.: *Ceramics International* 29, 857 (2003).
15. Mukhopadhyay S., Chatterjee I., Mukherjee R., Nath S.K., Sarkar S., Mondal S., Bhowmik S.: *Industrial Ceramics* 23, 198 (2003).
16. Mukhopadhyay S., Daspothdar P.K.: *Ceramics International* 30, 369 (2004).
17. Mukhopadhyay S., Daspothdar P.K.: *Industrial Ceramics* 24, 33 (2004).
18. Mukhopadhyay S., Daspothdar P.K.: *Industrial Ceramics*, in press.
19. Bonadia P., Studart A.R., Pileggi R.G., Pandolfelli V.C.: *Am.Ceram.Soc.Bull.* 78, 57 (1999).
20. Studart A.R., Ortega F.S., Innocentini M.D.M., Pandolfelli V.C.: *Am.Ceram.Soc.Bull.* 81, 41 (2002).
21. Bhattacharya H., Samaddar B.N.: *J.Am.Ceram.Soc.* 61, 279 (1978).
22. Temujin J., Okada K., Mackenzie K.J.D.: *J.Euro. Ceram.Soc.* 18, 831 (1998).
23. Temujin J., Okada K., Mackenzie K.J.D.: *Ceramics International* 25, 85 (1999).
24. Kawai S., Yoshida M., Hashizume G.: *J.Ceram.Soc.Jpn.* 98, 669 (1990).
25. Bratton R.J.: *Am.Ceram.Soc.Bull.* 48, 1069 (1969).
26. Ko Y.C. in: *Proc.UNITECR*, p. 22-25, Berlin 1999.
27. Hasselman D.P.H.: *J.Am.Ceram.Soc.* 52, 600 (1969).
28. Maczura G., Madono M., Kriechbaum G.W., Sewell B. in: *Proc UNITECR*, Vol.3, p.179, Kyoto, Japan 1995.
29. Chan C.F., Huang F.J., Ko Y.C.: *Interceram* 46, 86 (1997).
30. Schneider Jr. S.L., Lampman H.F., Wheaton N.D.: *Engineered Materials Handbook, Vol-4, Ceramic & Glasses*, p. 75-78, ASM International, The Materials Information Society, New York 1991.
31. Ghosh S., Maiti T., Sen S., Mukhopadhyay S.: *Ceramics International*, in press.
32. Ko Y.C., Chan C.F.: *J.Euro.Ceram.Soc.* 19, 2633 (1999).
33. Ko Y.C.: *Ceramics International* 27, 501(2001).
34. Mukhopadhyay S., Daspothdar P.K., Banerjee G. in: *Proc. UNITECR 2003*, p. 158-161, Osaka, Japan 2003.
35. Korgul P., Wilson D.R., Lee W.E.: *J.Euro.Cer.Soc.* 17, 77 (1997).
36. Khalil N.M., Jawrah M.F.M.: *Brit.Ceram.Trans.* 100, 110 (2001).
37. Ye G., Troczynski T., Oprea G. in: *Proc. UNITECR 2003*, p. 168-171, Osaka, Japan 2003.
38. Tamura S., Ochiai T., Kanai T., Nakamura H. in: *Proc. UNITECR 2003*, p. 521-524, Osaka, Japan 2003.
39. Nalwa H.S.: *Handbook of nanostructured materials and nanotechnology*, Vol. 1, p. 216-388, Academic Press, New York 2000.
40. Goldstein A.N.: *Handbook of nanophase materials*, p.44, Marcel Dekker Inc., New York 1997.

ODLÉVATELNÉ HMOTY Z Al_2O_3
MODIFIKOVANÉ SPINELEM

SUNDAN MUKHOPADHYAY, P.K. DAS PODDAR*

*College of Ceramic Technology,
73 A C Banerjee Lane, Kolkata-10, India
*University of Calcutta, Dept. of Chemical Technology,
92 A P C Road, Kolkata-9, India*

Odlévatelné hmoty z Al_2O_3 modifikované spinelem byly připraveny přidávkem 8% žíhaného hydratovaného spinelu získaného metodou sol-gel a spolusrážením. Spinelová aditiva byla charakterizována analýzou velikostí částic a transmisní elektronovou mikroskopií. Připravené odlévatelné hmoty byly srovnávány podle jejich objemové hustoty, zdánlivé porozity a odolnosti k drcení za studena a k drolení s cílem nalézt co nejlepší vlastnosti sol-gelového aditiva s nanostrukturálními vlastnostmi. Kvalita odlévatelných hmot byla dále srovnávána s hmotami s osvědčenými komerčně dostupnými spinelovými drtěními. Vybrané žíhané vzorky hmot byly analyzovány řádkovací elektronovou mikroskopií, energiově disperzní spektroskopií, distribucí velikostí pórů a rtg difrakcí. Ukázalo se, že spinelem modifikované odlévatelné hmoty z Al_2O_3 jsou vhodné k použití v ocelárnách.