Improving Corrosion Behaviour of Magnesia-chrome Refractories by Addition of Nanoparticles

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This article reports the results of a study on mag-chrome refractories including nanoparticles of Cr_2O_3, Fe_2O_3, TiO_2 and boehmite. Nanoparticles were introduced into refractory body through primary batch and via slurry impregnation into fired body. The penetration of fayalitic slag was studied by cup test. The microstructural observation was carried out by SEM. It was found that nano-Cr_2O_3 and nano-Fe_2O_3 both improved corrosion resistance by strengthening the matrix to aggregate bonding. The impregnated nano-species improved the penetration resistance by increasing the viscosity of slag locally in the penetration frontier. It seems the small nano-species are dissolved in attacking slag and change the viscosity. The penetration indexes are correlated to microstructural observations.

1 Introduction

High thermal stability, strong erosion-corrosion resistance and low thermal expansion makes magnesia-chromite bricks vital material for non-ferrous industries, cement and secondary metallurgy applications [1–5]. Though, environmental concerns lead to use chrome-free refractories such as magnesia-spinel.

Conventional magnesia-chromite bricks are still used as a basic refractory in copper smelting due to stability in the harsh working conditions [4, 6, 7]. Of course, the hexa-chrome formation in mag-chrome spent refractories a negative point of using them [7, 8]. Therefore, it is necessary to improve the life span of refractory lining in order to minimize the refractory scrap.

To improve life span of refractories it is obvious that the microstructure should be modified [9]. For example, the weak point of refractory texture which is the bonding between fine matrix and aggregate should be improved. Therefore, direct bonding in magnesia-chrome must be encouraged. Alternatively, if the slag aggression on refractory is reduced, the corrosion would decrease and refractories would survive for a longer time.

Using nano-species in refractories has a history of about 10 years [9]. This issue has always had two types of objections namely the difficulties of mixing nanoparticles into refractory coarse particles without agglomeration and using expensive nanomaterial in a rather cheap refractory media. Despite of these obstacles, research was carried out in different parts of the world due the demand of life improvements of refractories in sever condition.

The research in nano-refractories has absorbed many scientists in different parts of the world. *Roungous et al.* have published several papers on MgO–C and Al_2O_3–C refractories reinforces by nano-species [10–12]. *Nouri et al.* has reviewed the nano-bonded refractory castables [13]. *Zargar et al.* reported on the effect of nano-Cr_2O_3 on solid solution assisted sintering of MgO refractories [14, 15]. *Mariana Braulio et al.* have intensively studied the effect of magnesia grain size on in situ spinel formation in castables [16–18].

Introducing nanoparticles into refractories, their rather high cost and tendency towards severe agglomeration has been an important issue in refractory technology during last 10 years [9]. The nanoparticles can encourage the desired phase formation and therefore decrease the sintering temperature [1]. Additionally, the nano-species, if well-dispersed and accommodated into refractory pores, may encounter with penetrating slag and subsequently change its viscosity. In this scenario, the slag penetration will be retarded and the corrosion rate can be decreased. The nano-species also may influence the wettability of refractory texture and develop new phases locally in the corrosion frontier. These types of postulation have not been fully understood and of course require further studies. In this study, the authors report the effect of nanoparticles employment in mag-chrome refractories where they compare the effect of nano-species as primary additive as well as in the post-fired impregnation.

2 Experimental procedure

The so called nano-refractories were prepared via two different routes. In the first method nano-iron oxide supplied by *Nanoamor Co./*US and Cr_2O_3 supplied by *ionic liquids technologies GmbH & Co/*DE after being dispersed were added to the fine portion of the conventional mag-chrome batch. In the second method nano-MgO

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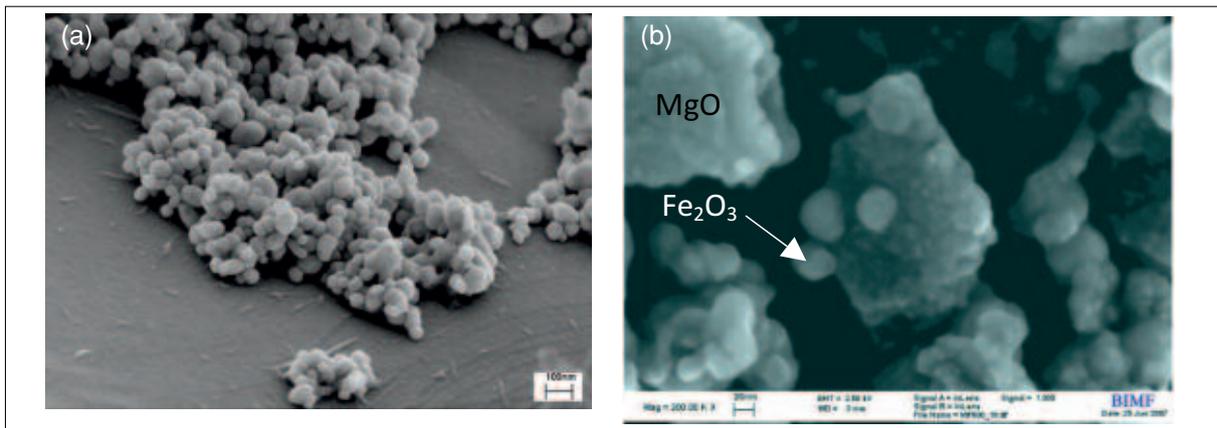E-mail: golestanifard@iust.ac.ir

Fig. 1 a–b (a) Agglomerates of as-received nano-Fe$_2$O$_3$, (b) mixture of dispersed nano-Fe$_2$O$_3$ and fine MgO aggregates

Tab. 1 Physical and mechanical properties of nano-containing bricks and reference brick

HMOR [MPa]	CCS [MPa]	AP [%]	BD [g/cm³]	Sample Code
8,9	47,6	17,1	3,09	Nano-Cr$_2$O$_3$ (1 %)
9,5	46,1	17,0	3,10	Nano-Fe$_2$O$_3$ (1 %)
11,0	46,9	16,7	3,11	Reference

(ionic liquids technologies GmbH & Co), TiO$_2$ (*AEROXIDE* TiO$_2$ P25), and boehmite (*SASOL companies*) were impregnated into a sintered magnesia-chrome body under a mild vacuum of 10^{-1} torr. The batch formulation was processed in an industrial site similar to ordinary mag-chrome bricks. The nano-containing batch was shaped in NF1 bricks and fired along with ordinary bricks in an industrial kiln at 1700 °C.

The impregnated laboratory size samples were cup corrosion tested at 1550 °C by a fayalitic slag received from the copper convertor. The slag contained 22,56 mass-% SiO$_2$, 65,58 mass-% Fe$_2$O$_3$, 1,66 mass-% Al$_2$O$_3$, and 4,24 mass-% SO$_3$. Phase and mi-crostructural evaluations were examined by XRD and SEM, respectively.

3 Results and discussion

3.1 Nano-species in the primary batch

Agglomeration of nanoparticles is a big barrier for using nanomaterials. Nano-Fe$_2$O$_3$ could not be dispersed in ordinary ultrasonic bath sonication as shown in Fig. 1 a, where a cluster of nanoparticles is demonstrated. The agglomerates were broken by sonication with probe ultrasonic using 400 W power. This lab procedure was scaled-up to semi-industrial level where NF1 bricks could be formed. Fig. 1 b shows the dispersion and mixing of iron oxide nanoparticles with MgO fine grains after using of probe sonication.

3.2 Adding nanoparticles to the primary formulation

Tab. 1 gives the physical and mechanical properties at room temperature and hot modulus of rupture (HMOR) of samples at 1400 °C. Differences in bulk density (BD) and cold crushing strength (CCS) are insignificant due to very little addition of nanoparticles. The reference is a conventional mag-chrome product of the company *Pars Refractory Company* located in Yazd/IR.

On the other hand, CCS of nano-Cr$_2$O$_3$-containing sample shows the highest value. However, the HMOR values show that nano-Cr$_2$O$_3$ and nano-Fe$_2$O$_3$ have slightly decreased the high temperature mechanical behavior of the bricks. This phenomenon requires a deeper study but the phase diagrams indicate that both iron and chromium oxide can decrease the softening points re-
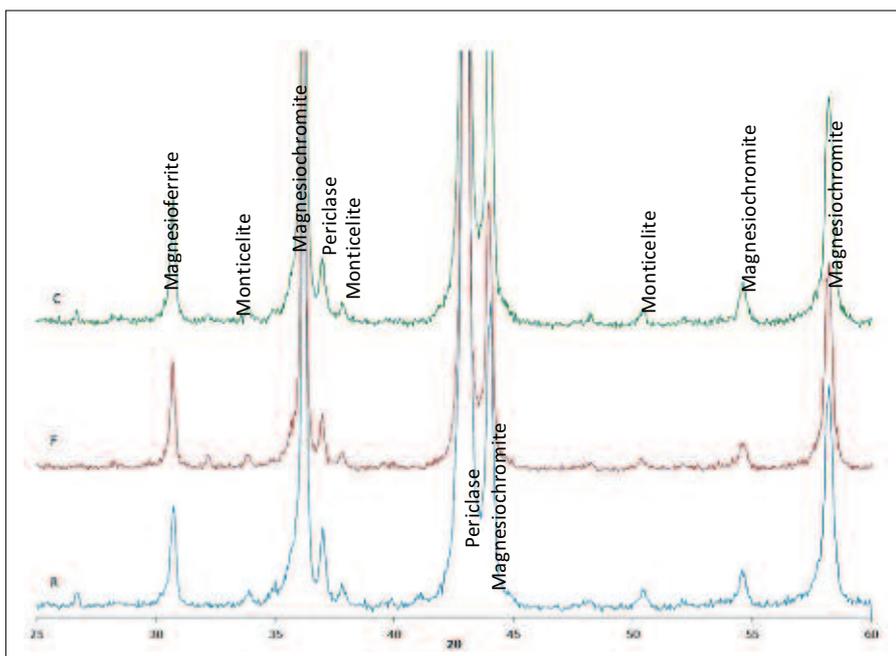

Fig. 2 X-ray diffraction pattern of produced bricks, reference sample (R), nano-chromium oxide (C) and nano-iron oxide (F)
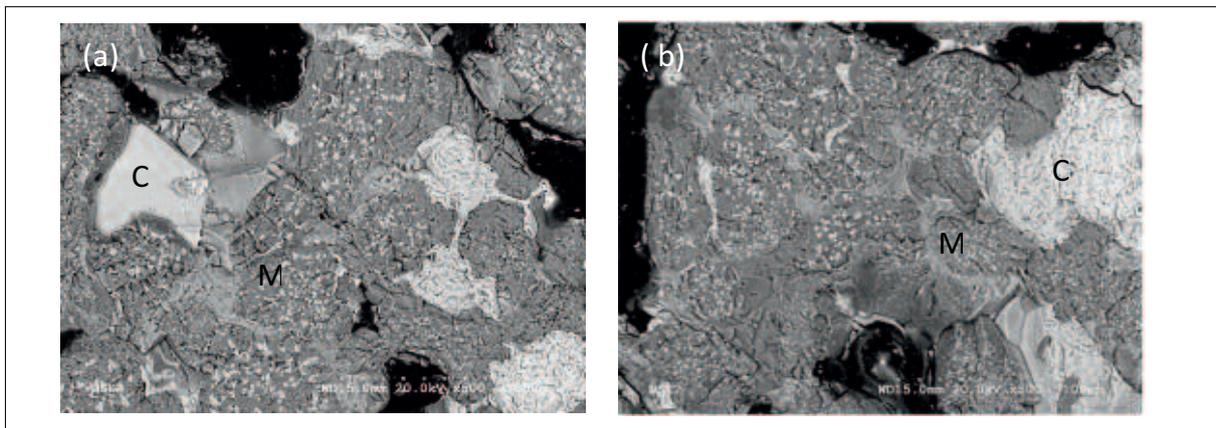
Fig. 3 SEMs of a conventional magnesia-chrome brick (a), and of a Cr_2O_3-nanoparticles-containing brick (b) (M: magnesia, C: chromite)
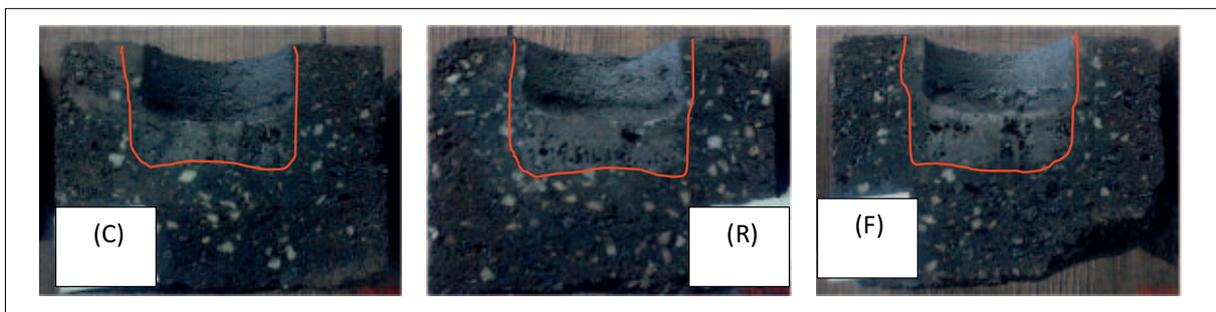

Fig. 4 Photograph of a corroded brick section: nano-chromium oxide (C), reference sample (R), and nano-iron oxide (F)
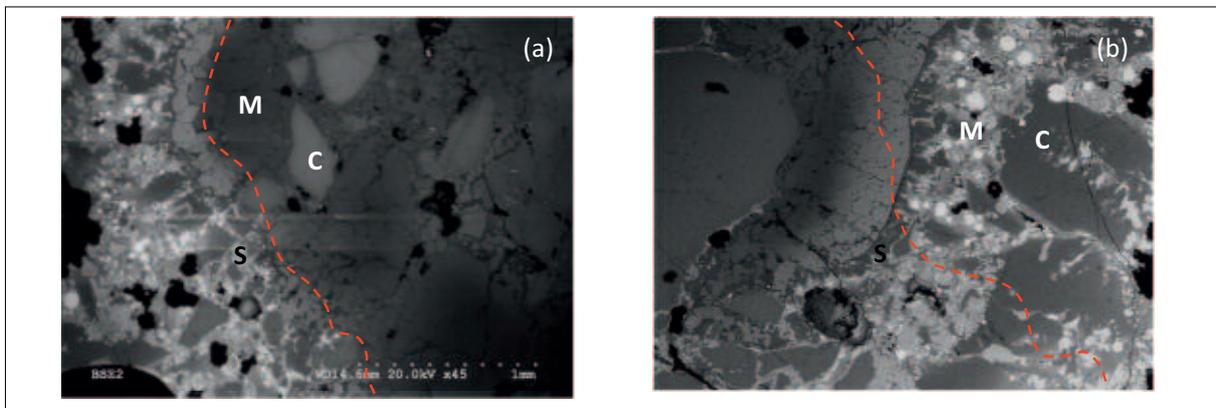

Fig. 5 SEM images and corresponding boundary curves of polished section of corroded conventional and nanoparticle-containing brick: (a) nano-Cr_2O_3-containing brick, and (b) reference brick (M: magnesia, C: chromite, S: slag)

ferring to the silicate bond in magnesia-chrome refractories.

Comparison of phase structure of the two samples, nano-containing and reference, shows that all bodies are virtually the same due to insignificant change in brick formulation by adding small amounts of nanoparticles. The XRD patterns in Fig. 2 confirm a similar phase composition in all fired bodies. SEM images of the nano-Cr_2O_3-containing and the reference brick are given in Fig. 3. The microstructures are almost the same in lower magnifications. However, the amount of spinel formed in nano-iron and chrome bodies is higher than in the reference one. The formation of better direct bonding was observed in nano-iron bearing bodies [2]. In the nano-chrome containing microstructure it was difficult to trace the direct chromite-magnesia bonding.

Digital photos of cross section of cups after the corrosion test at 1550 °C are given by Fig. 4. Area of slag penetration measured by image analyzing methods was taken to measure the corrosion index. As shown in Fig. 4, the depth of slag penetration in reference and nano-iron oxide containing bricks is roughly the same. However, for the nano-chromium oxide containing sample the depth is about 20 % less.

Fig. 5 presents SEM micrographs of reference samples after corrosion test at brick-slag interface, reaction area and cold zone. Slag penetrated through the porosity and grain boundaries, and reacted with magnesia; then, wash out periclase grains get into
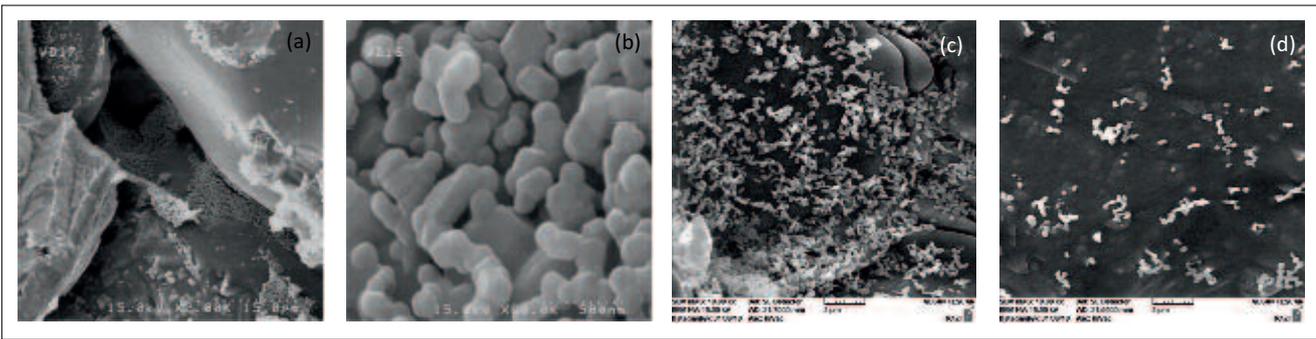
Fig. 6 SEM images of sections of specimens after impregnation by nano MgO and TiO$_2$ at different places (a) and (b), nano-MgO (c), and nano-TiO$_2$ (d)
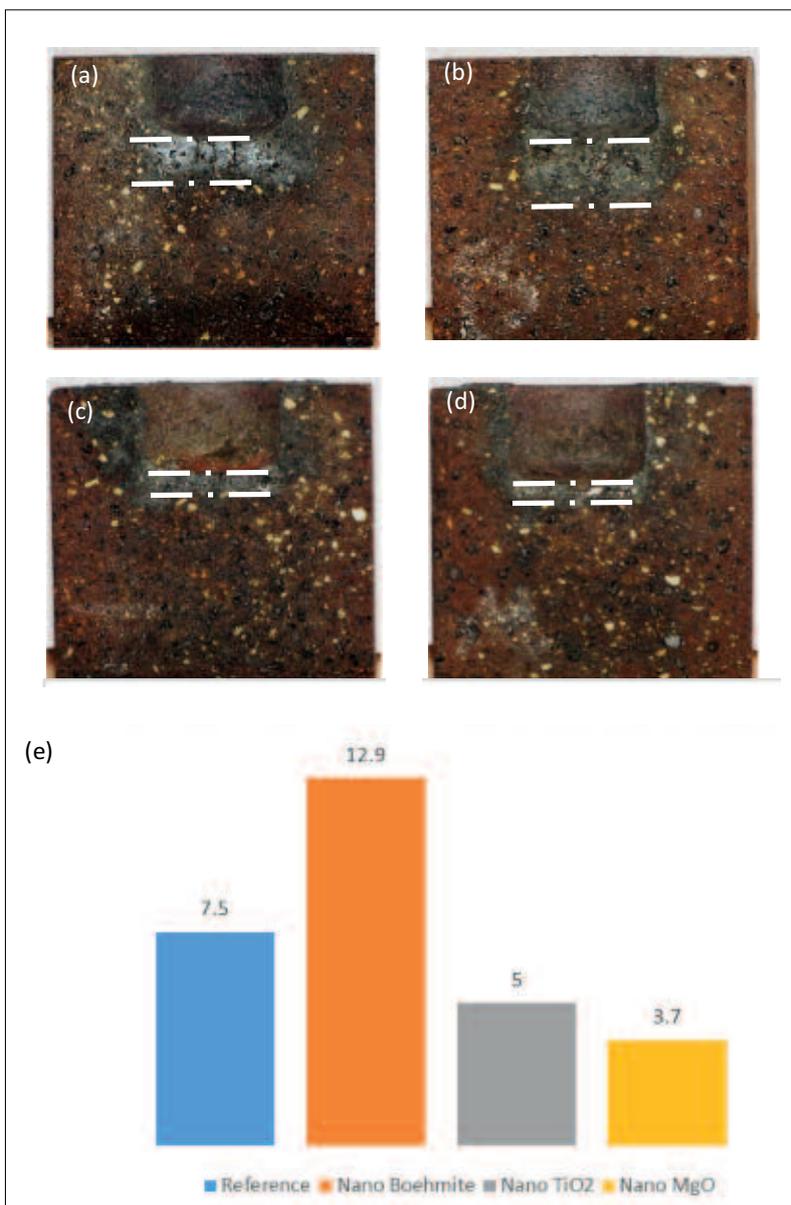

Fig. 7 Photographs of corroded sample sections: (a) untreated sample; (b) impregnated by nano-boehmite; (c) impregnated by nano-TiO$_2$, (d) impregnated by nano-MgO after exposure to copper converter slag; (e) slag penetration index of magnesia-chrome brick for as received and after impregnation

slag. In Fig. 6 b surrounded magnesia by slag is presented. Slag solved intergranular phases like monticilite and pull-out periclase grains form the refractory matrix. As corrosion test is conducted by static method soon after solution of refractory components, the slag is saturated and the affinity of reaction is reduced, so reaction between slag and refractory is limited. Therefore, there is no change between the microstructure of corroded and uncorroded bricks at 17 mm from the bottom of the cup.

3.3 Nanoparticles impregnation into refractory body

Impregnation of a slurry containing nanoparticles of TiO$_2$, MgO and boehmite was carried under vacuum. Primary experiences indicated that applying vacuum was very influential for encouraging the particles to travel deep into the refractory body. In fact, without vacuum one only could see the presence of particles in a few millimeters below the surface.

Fig. 6 shows the existence of nano-MgO and TiO$_2$ particles impregnated in a depth of about 10 mm. As shown, nanoparticles are still agglomerated but could fill the pores. Nano-TiO$_2$ was found to be more difficult to penetrate into the bodies apparently due to a bigger particle size and less tendency to agglomeration in primary slurry.

The process of impregnation repetition of dried bodies was also found to be useful in terms of pushing the nanoparticles to a deeper level. However, this process could work only after 3 repetitions after which the pore throats were blocked. It is important to note that having a proper dispersed slurry plays a key role in success of impregnation. Therefore, the chemistry of slip employing proper surfactants is very important.
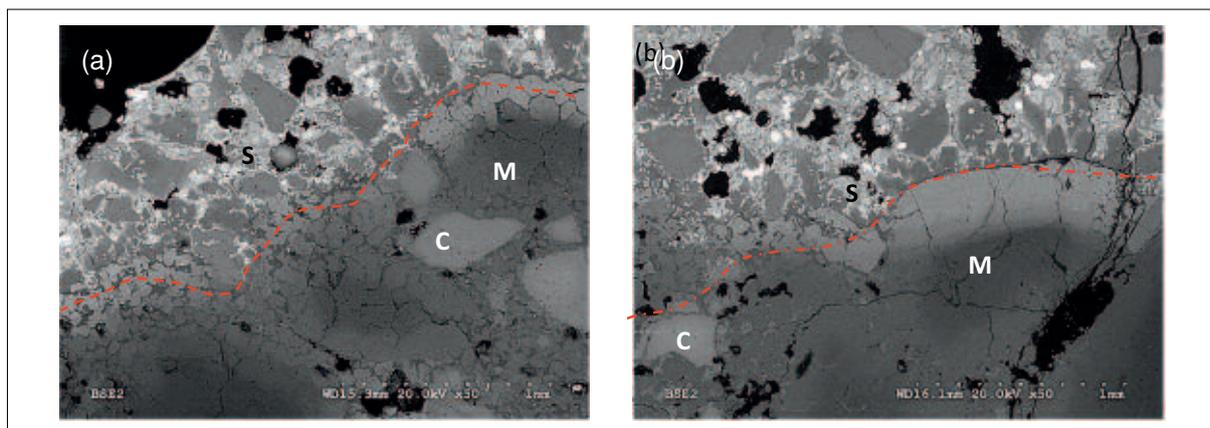
Fig. 8 SEM images and corresponding boundary curves of polished section of corroded nano-TiO$_2$ and MgO impregnated at frontier of slag penetration: (a) nano-TiO$_2$, and (b) nano-MgO (M: magnesia, C: chromite, S: slag)

The corrosion test was carried out as cup test and the penetration zone was measured by image analysis (Fig. 7). It shows typical corrosion test results, where the cross section of cups and depth of slag penetration as penetration index are demonstrated. The reference sample (conventional magnesia-chrome) and impregnated bodies by boehmite, MgO and TiO$_2$ were compared in terms of impregnation zone area.

It is obvious that compared to the reference sample boehmite-containing body, the samples show less resistance against slag. The TiO$_2$- and MgO-containing samples, however, demonstrated improved resistance. Fig. 7 e shows the penetration index for different samples. It shows that MgO-nanoparticles had a significant effect in hindering the slag penetration while boehmite had the negative effect. Titania-containing samples also demonstrated a slight improvement.

Fig. 8 shows the slag penetration frontier in MgO- and TiO$_2$-containing samples. In both cases, a smooth frontier could be distinguished which indicates a mild aggression of slag. Comparing these penetration line with the reference brick sample (Fig. 5 b), demonstrates the effect of nanoparticles. In the reference sample with no nanoparticles, the slag is very aggressive and the penetration line is very rough where in nano-containing bodies slag could not penetrate through pores and wash out the MgO particles.

A sample impregnated by nano-Cr$_2$O$_3$ was also compared to the reference brick body while both were cup-tested at 1300 °C. Fig. 9 shows a cross section of both samples.

It is clear that the Cr$_2$O$_3$-impregnated sample resists in front of slag penetration significantly. Previous reports on slag viscosity study show that Cr$_2$O$_3$, TiO$_2$ and MgO addition to fayalitic slag increases its viscosity while Al$_2$O$_3$ has opposite effect [19]. On this basis the authors may suggest that nanoparticles are dissolved in slag melt then increases the viscosity locally and subsequently decrease its penetration power. There are other possibilities for decrease of penetration including the effect of wettability and pore clogging. Nanoparticles while sticking on pore surface may alter the surface wettabili-
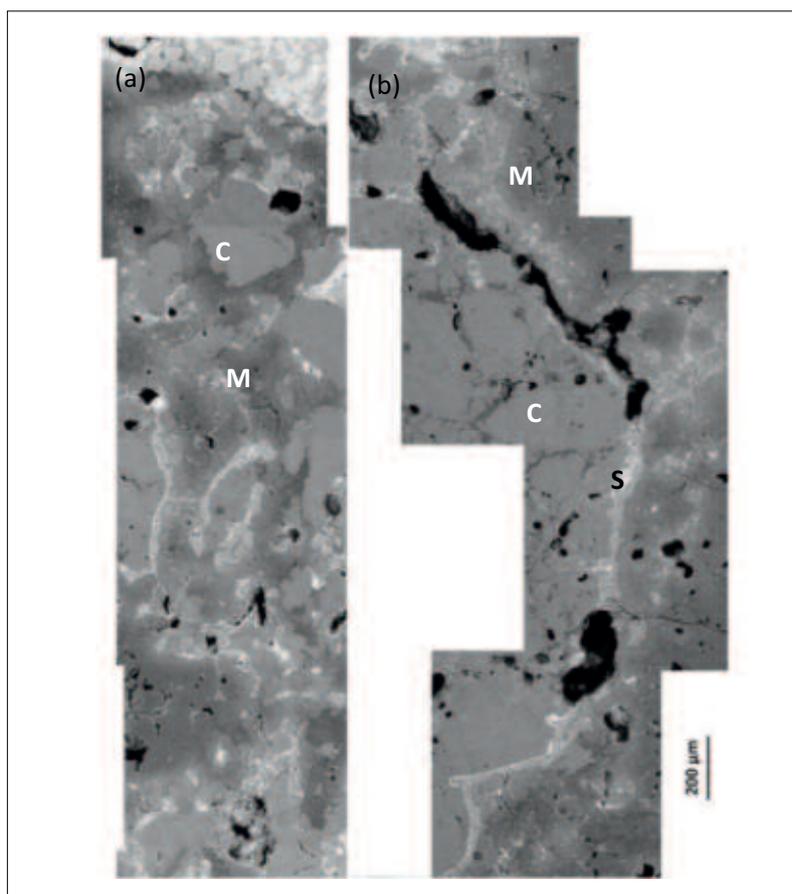

Fig. 9 SEM images polished section of slag penetration path of corroded unimpregnated and nano-chromium oxide impregnated: (a) unimpregnated, and (b) nano-chromium oxide (M: magnesia, C: chromite, S: slag)

ty by slag. This effect has not been studied and not very clear at this moment. Clogging of pores throat by nano is also a possibility. If this is the dominant effect, all nanoparticles, including nano-boehmite should have done the same while we explained there was a big difference between nano-boehmite and nano-MgO. So, at this stage it is more possible that the dissolution of nanoparticles into slag and subsequent viscosity change in the frontier plays the vital role in slag penetration.

4 Conclusion

1. Addition of nano-Fe_2O_3 and nano-Cr_2O_3 into primary batch of magnesia-chrome refractories was found to improve the matrix-aggregate bonding and improve the corrosion resistance.
2. Impregnation of nano-MgO, Cr_2O_3, and TiO_2 containing slurries into fired magnesia-chrome bricks improved the slag penetration resistance of the refractory brick. Nano-boehmite, however, had a negative effect.
3. Nano-addition to refractory, either through primary batch or slurry impregnation, can have positive influence only if the nanoparticles are well-dispersed mechanically or chemically.
4. The mechanism of nanoparticles in improving the corrosion resistance is not clearly understood and requires further studies.

Acknowledgments

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