To Study the Effect of Addition of Nano-Ni Particles as Catalyst on Microstructure and Properties of MgO-C Refractory

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Abstract— Magnesia-carbon (MgO-C) refractory bricks have been used in the slag line of ladles due to its superior slag penetration resistance and excellent thermal shock resistance at high temperatures. However, the life of this bricks has become limited on prolonged use due to its poor oxidation resistance as well as low strength at high temperatures. Thus, the physical and chemical properties of MgO-C refractories could be improved by the use of nanotechnology and addition of suitable additives nano range. Metallic nano-Ni particles has been recognized as one of the most effective nanomaterial to be used in MgO-C refractory as it has large surface area and density which lead to the development of various in-situ ceramic phases in the refractories which enhances its properties. Hence, the present work deals with the improvement of the physical and chemical properties of MgOC refractories with the addition of nano-Ni particle as catalyst. In this work, a set of experiments was carried out in order to standardize amount of nano-Ni addition in MgO-C refractory system. Here nano sized metallic Nickel particles are added in different amount (2,4,6 and 8 wt.%) in MgO-C refractory with fixed content of graphite (12 wt.%) and antioxidants B4C and metallic aluminum powder each (1wt.%). So that only the effect of nano-Ni variation in the MgO-C refractories can be evaluated. Total five compositions has been made by varying the composition of nano-Ni from (0-8 wt.%) and then compare the properties of nano-Ni added MgO-C brick with the conventional MgO- C brick, which contain 12wt.% graphite only, there is no nickel added in it. Out of the different samples containing nano-Ni in MgO-C brick, MC6 sample (containing 6 wt.% nano-Ni) exhibits better compaction, so has high bulk density (BD), cold crushing strength (CCS) and hot modulus of rupture (HMOR).

Keywords: Nano-Ni Particles, MgO-C Refractory, BD, CCS, HMOR

I. Introduction

With the rapid economic and infrastructural development in India, the demand of Steel has seen substantially increased and is expected to increase further in the future as embarks to become a $5 trillion economy by 2024. The government has taken various steps to boost the sector including the introduction of National Steel policy 2017 that aims to increase the per capita steel consumption to 160 kg by 2030 from its current low of 72 kg per capita.

The ASTM C71 defines the refractories as "nonmetallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000 0F (538 0C)".

MgO- C bricks are used in Slag lining of ladles as they possess excellent slag penetration resistance and good thermal and corrosion resistance at elevated temperature due to non-wetting property of carbon with slag, low thermal expansion, high thermal conductivity and high toughness.

Addition of nano-particles (size < 100nm) in MgO-C refractory led to increase in various properties of refractory brick include the durability, thermal shock resistance, spalling resistance, corrosion resistance, erosion resistance and oxidation resistance of brick Nano-particles having finer size, helps to fill the void space of magnesia grains and increases the compactness, results in better strength. Antioxidant metal powders play an important role in improving the properties of refractory. Thus it is interesting to study the physical and chemical properties of MgO-C bricks with the addition of nano- Ni particle.

II. Experimental Work

A. A. Raw material for nano-nickel added MgO-C brick.

Commercially available high quality fused magnesia (FM) fine powder (MgO 97 wt.%), natural flakes graphite(<147 µm, C 95 wt.%), Al-metal powder (< 90 µm Al 98.5 wt.%), boron carbide powder as antioxidant were used to maintain the granulometry of the mixture and thermosetting liquid phenolic resin were taken as binder to base raw material for the fabrication of MgO-C refractory brick.

In this present work, high purity magnesia, FM 97 was taken as the raw material for fused magnesia, considering the selection criteria like purity, CaO/SiO2 ratio, and low Fe2O3 content and large crystals in the range of 500-1500 µm. High purity graphite, 95 FC, was selected as a raw material for carbon and liquid phenolic resin was used as binder. The physical and chemical properties of magnesia, flake graphite, liquid resin and nano nickel are given in tables below.

Raw materials	Flake graphite
Carbon (%)	95.1
Volatile matter (%)	0.80
Ash (%)	4.1
Surface area (m2/g)	5.34

Table 1: Physical and chemical analysis of flake graphite:

Raw material (chemical composition)	Fused magnesia
MgO	97.20
Al2O3	0.08
SiO2	0.40
CaO	1.40
Fe2O3	0.50
Na2O	0.50

Table 2: Chemical composition in percentage of fused magnesia:

Powder	Nano-Ni
Purity (%)	40
Size (nm)	40-46

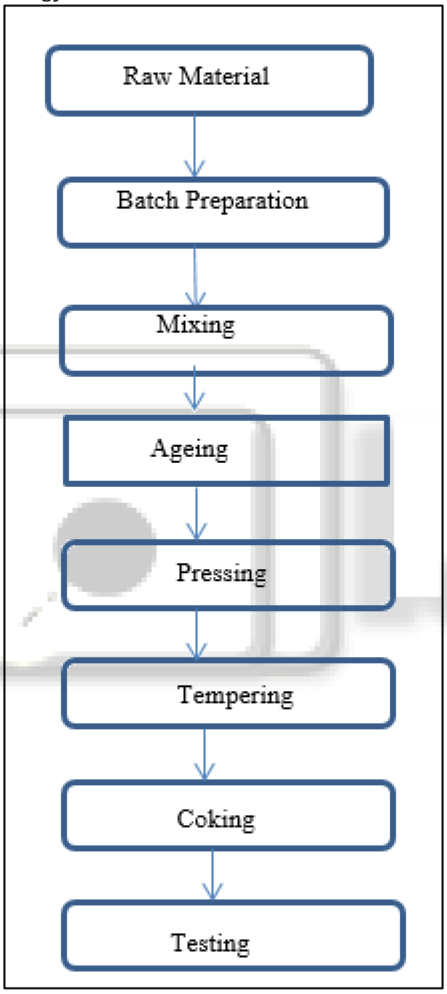
SSA (m^2/g)	>60
True density (gm/cm^3)	3.9
Color	White

Table 3: Characteristics of Ni-nanoparticles:

- Aluminum Powder: % of Aluminum = 98.5. Particle size:100% passing through 150 mesh, 60-70% passing through 300 mesh BSS.
- Boron Carbide: % B4C= 95%, Total Boron=77 wt.%, Total Carbon= 22 wt.%,(Fe2O3, B2O3) traces. Particle size= 100 BS=100% min,200 BS=95wt.% min, 300BS=75% min.

B. Fabrication of nano-Ni containing MgO-C bricks

1) Methodolgy



III. RESULTS AND DISCUSSIONS

A. Physical and chemical properties of Nano- Nickel particle added to MgO-C bricks.

A. AP, BD and CCS (before and after coking) AP, BD and CCS of MgO-C refractories before and after coking with the addition of nano-Ni with varying amount from 0 to 8 wt.% are given in Table 4, Table 5 and Table 6, respectively.

Composition	Nano-Ni amount wt.%	AP before coking	AP after cooking at 1400 °C
MC	0	7.20	13.26
MC2	2	6.80	11.45
MC4	4	6.24	10.99
MC6	6	5.75	10.12
MC8	8	6.04	10.91

Table 4: AP before and after coking at 1400°C temperature in MgO-C refractories with the addition of Nano-Ni particle.

The effect of addition of nano-Ni in MgO-C refractories is studied and found that Apparent porosity (AP) the samples decreases 7.20% to 6.04% as the nano- nickel content is increases. better compaction occurs which lead to the filling up of intergranular voids between MgO and graphite grains. As a result the bulk density (BD) of the samples increases from 2.98g/cm3 to 3.31 g/cm3 due to the higher true density of Nickel (8.9 g/cm3), in comparison to the graphite (2.26 g/cm3) and MgO (3.58g/cm3) or may be because of a possible new phase formation, such as MgAl2O4 (3.64 g/cm3), AlN (3.26 g/cm3), Al4C3 (2.36 g/cm3).

Composition	Nano-Ni amount wt.%	BD before coking	BD after cooking at 1400°C
MC	0	2.98	2.89
MC2	2	3.12	3.10
MC4	4	3.18	3.12
MC6	6	3.25	3.19
MC8	8	3.31	3.26

Table 5: BD before and after coking at 1400°C temperature in MgO-C refractories with the addition of Nano-Ni particle.

Composition	Nano-Ni amount wt.%	CCS before coking	CCS after cooking at 1400°C
MC	0	352	217
MC2	2	375	223
MC4	4	387	219
MC6	6	414	245
MC8	8	395	221

Table 6: CCS (Kg/cm2) before and after coking at 1400°C temperature in MgOC refractories with the addition of Nano-Ni particle.

The cold crushing strength (CCS) of the MC sample is lowest and as the content of Nano-Ni increases in the samples the value of the CCS increases and is highest for the sample containing 6wt.% nano- Ni after which the value CCS decreases due to the mis-match in the thermal expansion coefficient of the various phases formed at 1400°C.

B. Hot Modulus of rupture.

Composition	MC	MC2	MC4	MC6	MC8
HMOR (kg/cm2) at 1400 °C	28	35	42	40	36

Table 7: shows the HMOR as a function of different amounts of nano-Nickel added in MgO-C refractories. Higher HMOR was observed in nano-Ni added MgO-C refractories than conventional MgO-C refractories (MC) at 1400°C.

C. Oxidation resistance before and after coking.

The oxidation resistance value of the nano-Ni containing samples in MgO-C refractories are shown on the Table 8. Increase of nano-nickel content in the samples shows an increase in the oxidation resistance of the MgO-C refractories brick.

Composition	MC	MC2	MC4	MC6	MC8
Oxidized (%)	19.5	16.5	14.5	14	13.75

Table 8: Effect of nano-Ni on improvement of oxidation resistance of samples at 1400 °C.

Diameter-wise oxidation has been reduced from 19.5% for MC composition to 13.75% for MC8 composition. Nano-nickel being very reactive in nature produces faster and greater extent of Mg vapor, which led to the formation of in-situ magnesia-spinel $MgAl_2O_4$ in the samples. Formation of spinel modifies the pore size distribution i.e. reduces the number of large and channel pores, thereby hinders the entrance of oxygen into the matrix which ultimately results in high carbon retention.

D. Static slag corrosion resistance.

Fig.1: shows the effect of nano-Ni addition on the slag corrosion resistance of specimens. It revealed that with the increasing the amount of nano-nickel content in MgO-C refractory brick, the depth of slag penetration decreased. Also, the amount of slag penetration decreasing is more for sample contain nano-nickel. Generally, the reasons of corrosion resistance improvement of samples by adding nano-nickel are:-

Formation of in-situ spinel phase ($MgAl_2O_4$) which have high corrosion resistance.

The changing state of free-graphite in samples and the formation of carbide and nitride phases which led to preventing of graphite oxidation.

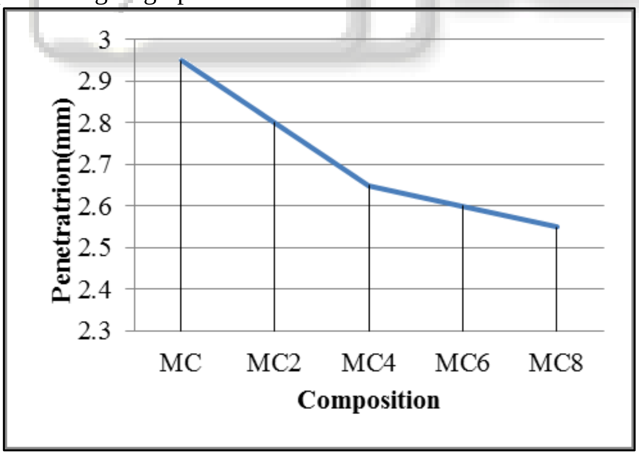


Fig.1: Effect of nano-Ni on penetration depth of samples after slag corrosion test.

E. Thermal shock resistance.

The thermal shock resistance of different samples is shown in Table 9. MC contains 12% graphite shows highest thermal shock resistance than Sample of compositions MC2, MC4, MC6 and MC8 which contains 2wt.%, 4wt.%, 6wt.% and 8wt.% nano-nickel respectively. As nano-nickel content increases the distribution of nickel in the matrix increases results in homogeneous mixing of nickel takes place with MgO which increases the catalytic formation of carbide, nitrides and magnesia-spinel $MgAl_2O_4$ in the sample. This is due to the high surface area and high volume of the nanoparticles of nickel which led to the mis-match in the thermal expansion coefficient of different phases so formed in the sample of MgO-C refractory.

Compositions	MC	MC2	MC4	MC6	MC8
No. of cycles	12	12	9	8	6

Table 9: Table of thermal shock resistance.

The thermal expansion coefficient of MgO is 13.5× 10^{-6}/ ^{0}C, Graphite =1.2-8× 10^{-6}/^{o}C , Nickel =13-20× 10^{-6} / ^{o}C, $MgAl_2O_4$= 7.5×10^{-6}/ ^{0}C, Al_4C_3= 8× 10^{-6}/ ^{0}C and AlN= 7.3× 10^{-6}/ ^{0}C. This differential thermal expansion coefficient between different phases present in the sample leads to formation of peripheral micro-cracks that lowers the thermal shock resistance of MgO-C refractories.

IV. CONCLUSIONS

The present work deals with the improvement of physical and chemical properties of MgO-C bricks with the addition of metallic nano- Ni powder in MgO-C refractories significant findings of this work are:-

Utilization of nickel nanoparticles enhanced physical, mechanical, and thermochemical characteristics of MgO-C refractories by the generation of $MgAl_2O_4$, Al_4C_3, and AlN phase which have higher oxidation resistance.

For improving the performance of MgO-C nanoparticles utilization have a good impact due to the specific properties of nanoparticles such as significant surface effect, size effect, and higher activity.

Nano-Ni addition promotes the densification and reduces apparent porosity of MgO-C refractory to 6 wt. % and progresses cold crushing strength due to the formation of $MgAl_2O_4$, Al_4C_3, and AlN phases.

Graphite retention and corrosion resistance has been improved by many folds with the addition of nano-Ni as compared to without nano-Ni containing bricks (MC) which was clearly observed from optical micrographs.

Nano-Ni particles leads to the formation of spinel ($MgAl_2O_4$) whiskers at 1200^{0}C.The Ni-particles accelerate the reaction between MgO and C and generate a certain amount of Mg-vapor, which plays a key role in the growth of spinel whiskers. Through dissolution and precipitation spinel crystals directly nucleate and grow into whiskers from the catalytic droplets of nano-sized metallic Ni particles. The growth of $MgAl_2O_4$ spinel whiskers follows a typical V-L-S mechanism.

Graphite retention and corrosion resistance has been improved by many folds with the addition of nano-Ni as compared to without nano-Ni containing bricks (MC) which was clearly observed from optical micrographs.

Finally, this research work clearly shows the potential of nano-sized metallic Nickel particles addition in MgO-C bricks for the application in the slag lines of ladle metallurgical furnace.

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