DEVELOPMENT OF MgO-C REFRACTORIES DOPED WITH CARBON NANOFIBERS

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ABSTRACT.

This work presents the development and characterization of a new family of magnesia-carbon bricks (MgO-C) bonded with a new coal-tar pitch modified by the addition of carbon nanofibers (CNFs), thus producing a MgO-C-CNF refractory.

Steel makers and refractory suppliers rely on MgO-C bricks for some of the most aggressive refractory applications. This research, by fully characterizing a reference formulation, suggests that the use of a CNF doped coal-tar pitch, while maintaining its characteristics as a binder and source of carbon, increases MgO-C fracture toughness. The explanation offered is that CNF doping modifies the pitch microstructure, and hence the refractory microstructure, introducing a number of new mechanisms for stress absorption.

KEYWORDS.

Magnesia-carbon bricks, coal-tar pitch, carbon nanofibers.

INTRODUCTION.

This article summarizes the design, study and characterization of a new family of magnesia-carbon refractory bricks (MgO-C-CNF) bonded with a coal-tar pitch modified by the addition of carbon nanofibers (CNFs).

MgO-C bricks manufacturing started in the 1970s, initially replacing compositions based on dolomite, which suffered heavy corrosion by CaO in the slag. However, it was not until the mid-1980s that MgO-C started to be used in the Japanese steel industry. Even if the first industrial experiences had taken place in North America, the use of this new family of refractory materials was consolidated in Japan^{[2] [3]}. Thus, at the first International Refractory Conference (UNITECR) in Tokyo (Japan) in 1983, the decisive importance of graphite for the Japanese refractory industry was recognized ^{[1] [2]}. The Conference devoted a specific session to the problems related to MgO-C materials and other oxide-graphite mixes^[4].

Since then this family of refractories underwent rapid developed around the world. By 1984, at the International Refractory Colloquium in Aachen (Germany) fifty percent of the works submitted on MgO-C were European. The research interest continued through the 1980s and 1990s. Today steel makers heavily rely on MgO-C bricks for some of the most aggressive industrial applications, such as the slag line in steel ladles or the lining of converters and arc furnaces, all subjected to strong chemical attack ^{[5] [6]}.

MgO-C bricks are composed basically of magnesia (MgO) and natural graphite (C), bonded together by either coal tar pitch or phenolic resins. The final product has low porosity and, depending on the specific application, aggregates up to 10 mm grain size. Different types of magnesia^{[5][7]} can be used, varying in origin, nature (sintered or electro-fused), purity and primary crystal size. Also different types of carbon sources are used; they are classified according to their purity (carbon content), shape and size (flake, amorphous or carbon black). The percentage of graphite added varies between 10 and 20 ^W/_o, thus obtaining a wide range of properties. Graphite confers greater resistance to oxidation than amorphous carbon, the latter resulting from the carbonization of resin binders, while coal-tar pitch produces a more graphitic carbon. From the thermomechanical point of view, graphite, by limiting the ceramic bond MgO-MgO, reduces the stiffness of the refractory and increases its thermal conductivity, improving the resistance to thermal shock.

This research suggests that the introduction of CNFs in MgO-C pitch bonded materials, achieved in this case by doping CNF in the coal-tar pitch, while maintain the positive effects brought about by the pitch as source of carbon, increases the resulting material fracture toughness. Given the MgO-C extensive use and importance, the perspective of a significant improvement in service life of these materials may lend substantial industrial interest to this work.

The experimental results point to some microstructural alterations in the MgO-C-CNF pitch bonded materials, induced by the presence of carbon nanofibers in the binding system, as responsible for delivering higher structural integrity and some new mechanisms of stress absorption.

EXPERIMENTAL.

Materials.

Tab. 1 shows the raw materials, additives and the range of compositions employed to formulate a base MgO-C coal-tar pitch bonded MgO-C refractory. The formulation incorporates four magnesia grain fractions, flake graphite, carbon black and coal-tar pitch, and was designed following Alfred's model with a "q" value 0,45 and a maximum grain size of 6 mm^{[8][9]}.

Raw materials and additives	Range $(^{W}/_{0})$
Fused magnesia / 2-5 mm	35-50
Fused magnesia / 0-2 mm	30-40
Fused magnesia / 0-100 µm	5-10
UF magnesia (QMAG)	0,5-5
Flake graphite (SV94)	8-10
Carbon Black (Thermal)	1-3
Coal tar pitch	<5.0

Tab. 1. Raw materials, additives and range composition

The carbonaceous binder used to bond the refractory formulations, was a coal-tar pitch (BPR) produced by Industrial Química del Nalón, S.A. (Spain).

The carbon nanofibers (GANF F2001 S1) incorporated in the pitch are produced by Grupo Antolín (Spain) through process of chemical deposition in vapour phase on floating catalyst ^[10] and are traded as GANF (Grupo Antolín Nano Fibers).

These carbon nanofibers present a heterogeneous aspect and relatively large range of diameter sizes (Fig. 1).



Fig. 1. GANF morphology and diameter sizing

Pitch modification.

Two coal-tar pitches were used: i) a reference anthracene pitch (manufactured from anthracene oil, a by-product of coal tar distillation) and ii) a conventional coal-tar pitch. Tab. 2 shows the main characteristics of these two binders. The anthracene derived pitch was used as reference since it lacks the confounding quinoline insoluble fraction, thus allowing a better observation of CNF dispersion.

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DITCH	Softening	Insolubl	Carbon				
псп	point(°C)	Quinoline	Toluene	Fixed(^W / ₀)			
Anthracene	105,0	0,4	27,2	44,9			
Coal tar	89,3	8,8	28,7	48,8			

It is well known that the main handicap to develop top performing nanoparticle reinforced composites is the difficulty to disperse the nanoparticles, since these tend to agglomerate in the form of clusters or tangles (as seen in Fig. 2).

Both artifacts, clusters and tangles, worsen the uniformity of the microstructures obtained and, therefore, the properties of the resulting materials. Even when nanoparticles are added dispersed and suspended in fluids, the artifacts described tend to increase their viscosity and thus hinder dispersion. The approach followed in this work was to initially disperse the carbonaceous nanostructures, in this case carbon nanofibers (CNFs), in the coal-tar pitch later used as binder. Fig. 2 shows an initial unsuccessful dispersion trial of CNFs in the reference anthracene pitch, where a CNF agglomerate is clearly visible.



Fig. 2. Detail of a tangle of CNFs in anthracene pitch doped with $1^W\!/_0$ CNF

Proper dispersion was achieved by chemically modifying the CNF surface, and then incorporating the CNFs in the pitch through intensive mixing.

Fig. 3 to 6 are SEM images of the reference anthracene pitch fracture surfaces showing good dispersion for 1% and $3^{W}/_{0}$ CNFs additions.



Fig. 3. Reference Anthracene pitch + $1^{W}/_{0}$ CNF



Fig. 4. Reference Anthracene pitch + 1^W/₀ CNF



pitch + $3^{W}/_{0}$ CNF

pitch + $3^{W}/_{0}$ CNF

In order to evaluate the effect of different percentages of CNF addition to the pitch, fixed carbon analysis (according DIN 51905) and exhaustive XRD studies were carried out after coking at 1000° and 1500°C.

Magnesia-carbon bricks preparation.

The MgO-C-CNF pitch bonded refractory masses were mixed in a high intensity mixer (Eirich, Germany) at a maximum speed of 360 rpm. These masses were then shaped by pressing at 200 MPa in a double-acting uniaxial hydraulic machine (OnaPress P01164). The bricks obtained were dried and tempered at 280°C following a typical industrial schedule (Tab. 3). Coking was carried out following EN 993-3.

Tab. 3. MgO-C tempering programme

Treatment temperature (°C)	Heating rate (°C·min ⁻¹)	Hold (h)	
280	0,5	10	

Once thermally treated, bricks were fully characterized. Room temperature cold crushing strength was carried out according to EN 993-5. Room and high temperature modulus of rupture testing (MOR, HMOR) followed EN 993-6 and 993-7 respectively. Thermal expansion was measured following EN 993-19 and fracture toughness values obtained from the tensiondeformation curves following ASTM D-5045.

RESULTS AND DISCUSION.

Pitch characterization.

BPR pitch +

0,5% CNF

BPR pitch +

1,0% CNF

Tab. 4 presents the characterization of the coal-tar pitch BPR doped with different CNF weight percentages.

Insoluble (^W/₀) Soft. Carbon PITCH+CNF point(°C) Quinoline Toluene Fixed(^W/₀) Undoped 89,3 8,8 28,7 48,8 **BPR** pitch BPR pitch + 92,3 9,1 29,3 49,4 0,1% CNF

9,5

10.9

29,4

29.5

49,4

50.3

Tab. 4. Characterization of BPR + CNF dispersions

93,9

96.8

As	can	be	observ	ed	in [Гаb.	4,	CNF	additio	on	proc	luced	an
inc	remei	nt iı	n fixed	car	rbon	val	ues,	whic	h was	hig	gher	than	the
per	centa	ge c	of CNF	intr	oduc	ced.							

Fig. 7 shows general and detailed diffractograms of BPR coaltar pitch-CNF dispersions coked at 1500°C, in a reducing atmosphere and a heating rate of 5°C min⁻¹, which are compared to the diffractogram of pure graphite.



Fig. 7. Diffractograms for BPR pitch-CNF dispersions coked at 1500°C and reference graphite.

The inset in Fig. 7 details the XRD patterns of the different BPR pitch-CNF dispersions. It indicates that CNF incorporation into BPR coal-tar pitch intensifies the 002 plane graphite reflection after coking at 1500°C. Once coked all pitch-CNF dispersions showed higher 002 plane intensities that the un-doped BPR pitch (the lower curve in the inset). A maximum was reached for 0.5% CNF addition.

Magnesia-carbon bricks characterization.

Regarding the characterization after different thermal treatments (tempering at 280°C, coking at 1000°C and coking at 1500°C) of the MgO-C-CNF bricks, bonded with coal-tar pitch doped with different percentages of CNFs, Tab. 5 shows the values obtained for apparent density (AD), open porosity (OP), cold crushing strength (CCS) and total carbon content (C).

Tab. 5. Characterization of MgO-C-CNF materials as a function of percentage of CNF doping in the BPR binding pitch

Composition	Thermal treatment	AD (g·cm ⁻³)	OP (%)	CCS (MPa)	С (^W / ₀)
MgO-C	280°C	3,11	4,0	35,5	9,6
(BPR pitch +	1000°C	3,07	7,5	40,0	
0% CNF)	1500°C	3,05	8,5	40,0	
MgO-C (BPR pitch	280°C	3,09	4,6	33,5	9,8
	1000°C	3,06	8,1	44,5	
0,1%CNF)	1500°C	3,02	9,0	36,5	
MgO-C (BPR pitch + 0,5%CNF)	280°C	3,09	4,4	32,0	9,9
	1000°C	3,07	8,1	44,5	
	1500°C	3,02	9,0	37,5	
MgO-C	280°C	3,09	4,4	33,5	9,4
(BPR pitch	1000°C	3,06	8,1	44,5	
1,0%CNF)	1500°C	3,02	8,9	37,5	

Other than the total carbon content in the case of MgO-C-CNF bonded with BPR pitch with 1% wt CNF addition, which was lower than expected, the results in Tab. 5 were all consistent.

Fig. 8 shows two micrographs of a MgO-C-CNF brick bonded with a 0.5% CNF doped BPR pitch, corresponding to the microstructure after coking at 1000°C. The magnesia aggregates (zones 1) are well distributed in the matrix, as are the graphite flakes (zone 3) and the coke generated from the binding pitch. Moreover, the coke formed shows a distinctive densified aspect (zone 2). These characteristics have been common to all MgO-C-CNF bricks processed with CNF doped BPR coal-tar pitch; either tempered at 280°C or coked at 1000°C and 1500°C.



Fig. 8. Optical micrograph of a MgO-C-CNF, bound with 0,5% CNF doped BPR pitch, after coking at 1000°C

Fig. 9 shows a comparison of the thermal expansion curves of all tested MgO-C-CNF compositions, processed using BPR pitch doped with different CNF percentages as binder. The inset details the curves between 1200°C and1650°C. At around 1300°C a fall in thermal expansion is observed in Fig. 9 for the MgO-C-CNF material bound with BPR pitch doped with 0,1 and 0,5 W_{0} CNF. This drop is associated to a softening effect on the bricks' matrix which would explain some other findings.



Fig. 9. Thermal expansion of MgO-C-CNF materials as a function of percentage of CNF doping in the BPR binding pitch

Bricks tempered at 280°C showed better fracture toughness values for lower CNF contents: 0.1% and 0.5%. A $1^{w}/_{0}$ CNF addition resulted in a fracture toughness value similar to that of the undoped reference (Fig. 10).

After coking at 1000°C fracture toughness was improved with CNF additions in the pitch, reaching a maximum for 1% CNF (Fig. 11).

For bricks coked at 1500°C there was no improvement. Variations from the undoped reference value were small: a 0.1% CNF addition in the pitch (Fig. 12) showed no influence, while 0.5% and 1^{w}_{0} CNF additions presented slightly lower values.



Fig. 10. Fracture toughness of tempered at 280°C MgO-C-CNF materials as a function of percentage of CNF doping in the BPR binding pitch



Fig. 11. Fracture toughness of coked at 1000°C MgO-C-CNF materials as a function of percentage of CNF doping in the BPR binding pitch



Fig. 12. Fracture toughness of coked at 1500°C MgO-C-CNF materials as a function of percentage of CNF doping in the BPR binding pitch

CONCLUSIONS.

CNF additions to the BPR coal-tar pitch used in this work increased the pitch softening point by 4% for $0.1^{w}/_0$ CNF and 8.5% for $1^{w}/_0$ CNF (Tab. 4). CNF addition also produced an increment in fixed carbon values, which was higher than the percentage of CNF added. This result has been attributed to the CNFs capacity to catalyze the aromatic condensation of the pitch, assisting its graphitization.

After coking at 1500°C, XRD analysis of all BPR coal-tar pitch dispersions incorporating CNFs showed graphite's 002 plane reflection intensity peaks higher than that obtained for the undoped BPR pitch. A maximum was reached at 0.5% CNF addition. This result proves the capacity of CNFs to assist pitch graphitization.

The MgO-C-CNF refractory formulations presented a well densified microstructure. It is proposed that CNFs are responsible for the higher fracture toughness values obtained after tempering at 280°C for MgO-C bonded with $0.1^{w}/_0$ and $0.5^{w}/_0$ CNF in BPR pitch. However, the mechanism apparently reaches a saturation limit, since the fracture toughness value for the bricks bonded with BPR pitch with $1^{w}/_0$ CNF falls back to that of MgO-C bonded with undoped pitch.

The toughening mechanism of CNF additions remains active even for bricks coked at 1000°C, where fracture toughness still reaches a maximum at $1^{w}/_0$ CNF addition in the pitch. However, for bricks coked at 1500°C the mechanism is no longer active, since no positive effect was detected with CNF addition to the pitch.

A most interesting effect was observed in the characterization of the thermal expansion of the MgO-C-CNF formulations, where, at around 1300°C, a significant variation in thermal expansion takes place for the MgO-C-CNF materials bonded with BPR pitch doped with 0,1 and $0.5^{w}/_0$ CNF (Fig. 9). The effect disappeared for BPR pitch with $1^{w}/_0$ CNF addition.

The proposed explanation is that CNFs produce a softening effect on the binder derived matrix of the MgO-C-CNF pitch bonded bricks which would be behind both observations: toughening at 280 and 1000°C and thermal expansion variation from 1300°C.

Therefore, the main conclusion of this work is that a certain amount of CNFs in the pitch binder improves MgO-C-CNF microstructural evolution, promoting graphitization and possibly introducing a relaxation mechanism active even at high temperature. Further work is needed to fully characterize the mechanism at work.

ACKNOWLEDGEMENTS.

The authors want to thank RHI Refractories for supporting this work, carried out under CDTI project IDI-20111499, in association with ArcelorMittal, Arciresa, Industrial Química del Nalón and Ferroatlántica.

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