DEVELOPMENT OF SÖDERBERG CARBON ELECTRODES BONDED WITH A CARBON NANOFIBER REINFORCED COAL-TAR PITCH

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ABSTRACT
Electric arc furnace (EAF) operation relies on the use of different types of carbon electrodes. Most are subjected to thermal treatments before use, but Söderberg electrodes are formed in situ, their carbon paste resulting fully transformed under furnace operation conditions. In general terms Söderberg paste is composed of calcined anthracite and petroleum coke, using pitch as binder. This work evaluates the incorporation of carbon nanofibers (CNF) to the coal-tar pitch used as binder in the production of Söderberg paste. Initially the effects of CNFs have been evaluated on the coal-tar pitch itself, and later on the Söderberg paste.
A hypothesis is formulated which explains the effects of CNFs on the paste behavior. This theory was verified by processing and fully characterizing a reference Söderberg paste formulation.

Keywords:
Söderberg electrodes, Coal-tar pitch, Carbon nanofibers

INTRODUCTION

Söderberg type electrodes were developed in 1917 by Elkem. They have been used in submerged electric arc furnaces (EAF) and other electrode based furnaces [1]. Thermal treatment of the Söderberg electrode paste takes place during the operation of the furnace itself [2,3,4]. As can be seen in Fig. 1, heat dissipated by Joule effect transforms the paste until forming a conventional graphite electrode. Although Söderberg electrodes have only been used in the steel industry under emergency situation, times of military conflicts when no graphite electrodes were available, its main application today lies in electric arc furnaces for ferrosilicon, ferromanganese and ferrochrome production, and as electrodes in electrolytic cells for aluminium production [2].

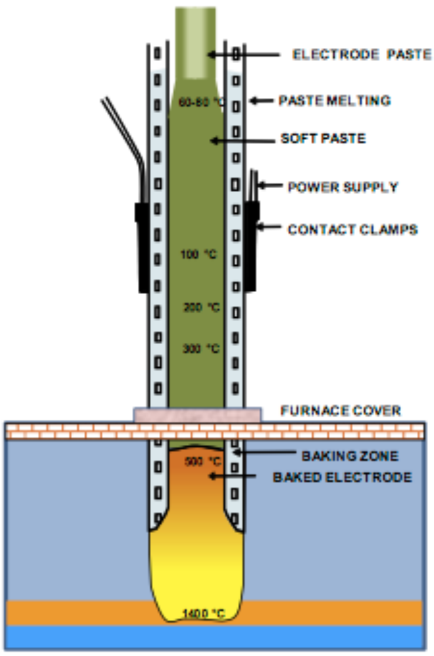

Fig. 1. Scheme of a Söderberg type electrode[5].

Söderberg electrodes are shaped placing the paste just described in a thin metal case which acts as formwork (Fig. 1). Each metal sheet composing the case is welded and some orifices are left on the steel plates to allow paste degassing during heating.

The most common cause of Söderberg electrode failure is fracture, which is classified in two categories: soft and hard [6]. Soft fracture is rather uncommon. It takes place when the baking zone position, well above its theoretical location, coincides with that of the electric current clamps. Under these circumstances the metal case may melt, and the lower part of the electrode will slip inside the furnace. The volatile gases then released catch fire inside the furnace and may even cause an explosion. Hard fractures are more common. They occur when an already coked part of the electrode loosens from the rest of the piece; their cause is an uncontrolled baking process, which, when not fatal, also causes low mechanical strength or excessive thermal shock.
The flow behaviour of the Söderberg paste is one of the most important properties conditioning its performance. If the paste is too fluid their components may segregate. Conversely, if viscosity is too high it leads to poor compaction. In both cases the probability of the electrode fracturing increases, while its performance is reduced. This research suggests that the introduction of CNFs in the coal-tar pitch used to bond the Söderberg paste may influence its rheological behaviour and, therefore, be key to improve its performance.

EXPERIMENTAL

Materials

Tab. 1 shows the raw materials and range of compositions employed to formulate a reference Söderberg paste, which was used to investigate the effect of different amounts of CNFs in the coal-tar pitch used as binder.

Carbon nanofibers (GANF F2001 S1) were supplied by Grupo Antolín (Spain), while coal tar pitch was supplied by Industrial Química del Nalón, S.A. (Spain).

Tab. 1. Raw materials and range of compositions of the reference formulation.

Raw Material	Range ($^w/_0$)
Coal-tar pitch	20 - 30
Calcined anthracite	35 - 50
Petroleum coke	25 - 40

The CNFs were produced by vapour phase chemical deposition on floating catalyst and are traded as GANF by Grupo Antolín NanoFibers [7].

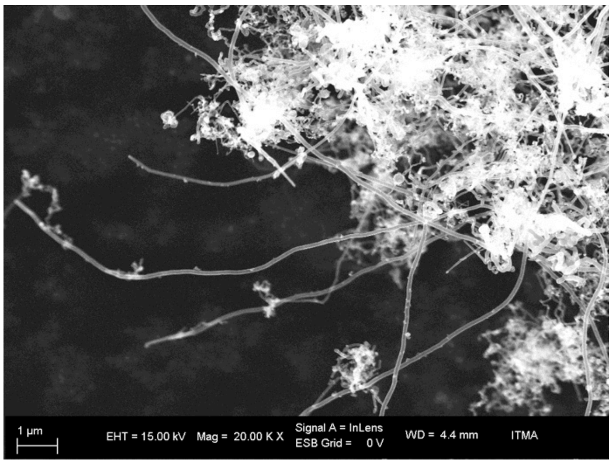

Fig. 2. SEM images showing the morphology of GANF nanofibers (x20 000, SE).

Coal-tar pitch doping

When developing nanoparticle reinforced composites one of the main problems is nanoparticle dispersion. Nanoparticles tend to agglomerate, forming tangles or clusters. Fig. 3 shows one of the initial CNF dispersion trials in coal tar pitch. Tangles and clusters can be seen on the pitch fracture surface. Optimal dispersion was obtained functionalizing the carbon nanofibers surface before incorporating them into the pitch through intense mixing.

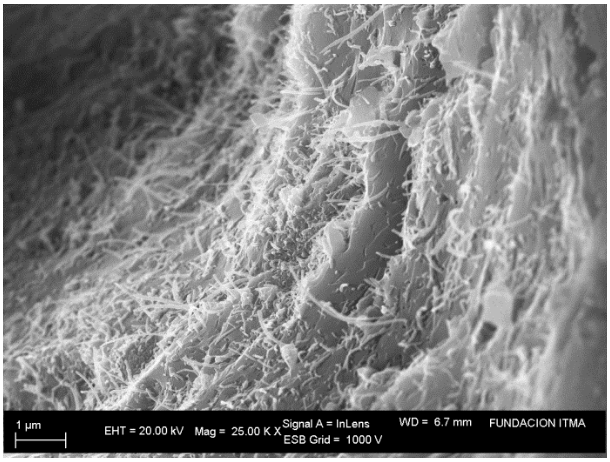

Fig. 3. Detail of a CNF agglomerate in a CNF doped coal-tar pitch fracture surface (x25 000, SE).

Söderberg paste preparation

Mixing of the raw materials for the preparation of Söderberg paste was carried out using a high intensity mixer (Eirich, Germany) at a maximum speed of 360 rpm. Raw materials were preheated above the softening point of the coal-tar pitch, between 250ºC and 350ºC. Once mixed, the paste was cast in metallic molds, vibrated for 60 seconds and cooled with water. Fig. 4 shows the aspect of the crude Söderberg paste obtained.

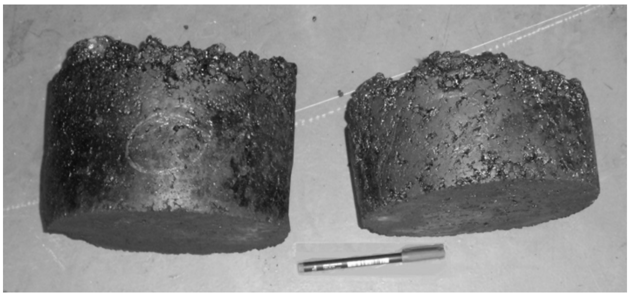

Fig. 4. Crude samples of Söderberg paste.

RESULTS AND DISCUSSION

Pitch characterization

The coal-tar pitch, with and without the CNFs addition, was characterized measuring its Mettler softening point (ASTM D3104-14), quinoline insoluble (ASTM D4746), toluene insoluble (ASTM D4072) and fixed carbon (ASTM D3172).

Tab. 2. Properties of the coal-tar pitch un-doped and doped with CNFs.

	CNF content ($^w/_0$)			
	0%	0.1%	0.2%	0.5%
Mettler Softening Point / ºC	69.0	75.0	74.3	84.5
Quinoline Insoluble / $^w/_0$	26.9	28.6	29.5	30.0
Toluene Insoluble / $^w/_0$	9.9	11.3	11.4	13.7
Fixed carbon / $^w/_0$	48.7	51.5	51.1	52.5

According to Tab. 2, the addition of CNFs to the pitch induced higher softening points and fixed carbon values. In fact, fixed carbon values increased more than the quantity of CNF added.

Physical properties of Söderberg paste

Bulk density (EN 993-1) and Modulus of Rupture at room temperature (EN 993-6) were determined for the paste, both crude and thermally treated at 500ºC for 5 hours (heating rate 30 ºC h^{-1}). Cylindrical stainless steel molds (300 mm height and 150 mm diameter) were used to contain the paste. No segregation of the components of Söderberg paste was observed after thermal treatment. As it has been mentioned before, segregation takes place when the flowability of the paste is too high and would result in reduced mechanical properties and performance of the paste.

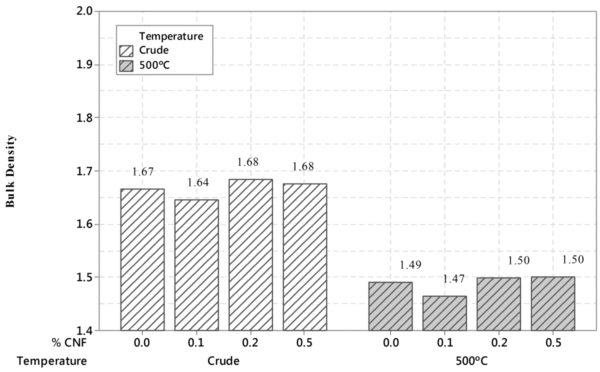

Fig. 5. Bulk density of crude and thermally treated (at 500ºC) Söderberg paste.

Fig. 5 and Fig. 6 show respectively the bulk density and the apparent porosity of the crude and treated Söderberg paste of reference. After treatment at 500ºC the coal-tar pitch has already been partially carbonized, releasing in the process volatile gases that reduce density and increase open porosity.

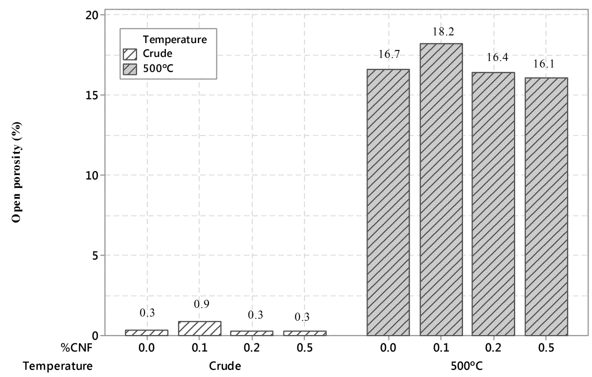

Fig. 6. Apparent porosity of crude and thermally treated (at 500ºC) Söderberg paste.

Fig. 7 shows the modulus of rupture of the reference Söderberg paste. The results indicate a reduction of mechanical properties after thermal treatment at 500ºC. This reduction of mechanical properties is certainly due to the release of volatiles during carbonization.

The different CNF contents in the coal-tar pitch did not show any significant effect on either the paste bulk density or its apparent porosity other than the observation that open porosity is higher and the bulk density is lower for the 0,1% CNF addition.

Regarding flexural strength, for the crude paste the lowest value corresponds to the 0,1% CNF addition. However, after treatment at 500ºC a maximum was reached precisely at 0.1% of CNF addition. For a 0.5% addition MOR values returned to those of the undoped paste. Compared to the undoped pitch, 0.1% and 0.2% CNF additions resulted in strength increments of 42% and 50% respectively.

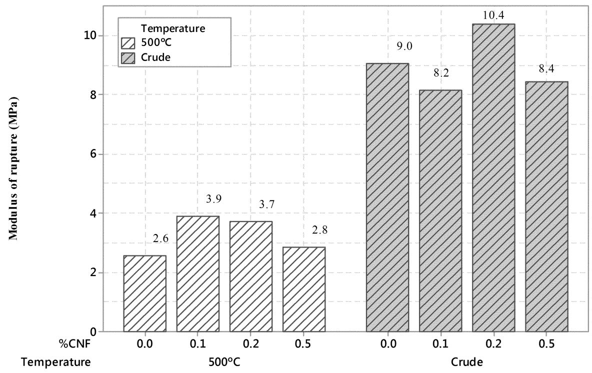

Fig. 7. Modulus of rupture of crude and thermally treated (at 500ºC) Söderberg paste.

Flow test of the Söderberg paste

Söderberg paste flowability was measured using cylindrical test specimens, 50 mm height and 50 mm diameter, shaped by pressing. The specimens were heated up to 305ºC (heating rate 60 ºC h^{-1}) resting for 1 hour on a graphite paper. Flowability was calculated, according to (1), from the initial (d_0) and final (d_f) diameters of samples having undergone such treatment.

$$F_V = 100\,(d_f - d_0) / d_0 \qquad (1)$$

Fig. 8 shows the results, obtained as the mean value of five determinations, and plotted versus the CNF content in the coal-tar pitch.

The flowability value for the reference paste, without CNFs, was about 56%, increasing to more than 70% when 0.1% to 0.2% of CNFs by weight were incorporated to the pitch. However, for a CNFs content of 0.5% a significant reduction of flow was observed, falling to values about 66%, but still higher than those measured for the undoped paste.

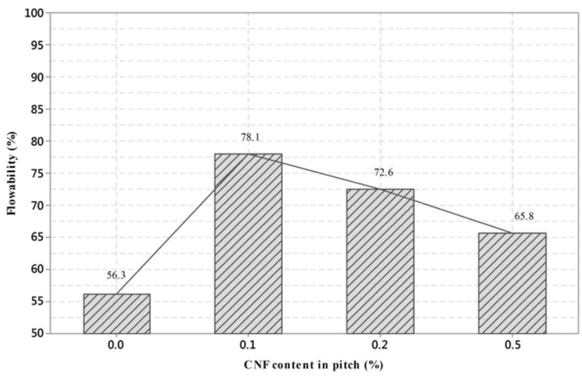

Fig. 8. Flowability results for a Söderberg paste as a function of CNFs content in the coal-tar pitch.

These results are in stark contrast with those obtained for the Mettler softening points of same coal-tar pitch used as binder (Tab. 2), where CNFs increasing additions resulted in corresponding higher softening points. A priori this would mean lower pitch flowability of the paste, but what we have observed (Fig. 8) was the opposite: an increment in paste flowability, which must be attributed to the effect of CNFs.

Rheology of the coal-tar pitch

Viscosities of undoped and 0.2% CNF doped coal-tar pitch was determined by rheometry (TA Instruments DHR-2) with a parallel, 40 mm diameter, plate's geometry. Viscosity curves (Fig. 9) were obtained at 125 and 150ºC and shear rates between 10^{-2} and 10^{2} s^{-1}.

A clear dependency between viscosity and shear rate was observed. Shear rates higher than 10^{1} s^{-1} resulted in an approximately constant viscosity for both CNF doped and undoped pitch. Therefore, coal-tar pitch behaviour in that shear rate region and tested temperatures is approximately Newtonian.

At each temperature there is a critical shear rate, determined by the intersection between the curves for the doped and undoped pitch, from which, at higher shear rates, the viscosity of the doped pitch is higher than that of the pitch without carbon nanofibers. To the left of such intersection, that is, for lower shear rates, the viscosity of the CNF doped pitch is significantly lower. To the right there is a transient viscosity hike for CNF doped pitch.

In the case of the 0.2% CNF doped pitch at 125ºC this shear rate critical value is approximately 0.05 s^{-1}. Below that shear rate value, such 0.2% CNF doped-pitch would flow more easily than the undoped one. At higher shear rates the opposite would occur.

At 150ºC the behaviour of the un-doped and doped pitch follows the trend already described. For shear rates below the intersection shear rate (in this case 0.09 s^{-1}) viscosity of the doped pitch is much lower than that of the undoped. As shear rate increases the flowability of the undoped pitch becomes higher than that of the doped pitch. There is a transient viscosity hike between approximately 10^{-1} and 10^{0} s^{-1} shear rate, while above 10^{1} s^{-1} shear rates the viscosity of both pitches presents an asymptotically decreasing tendency.

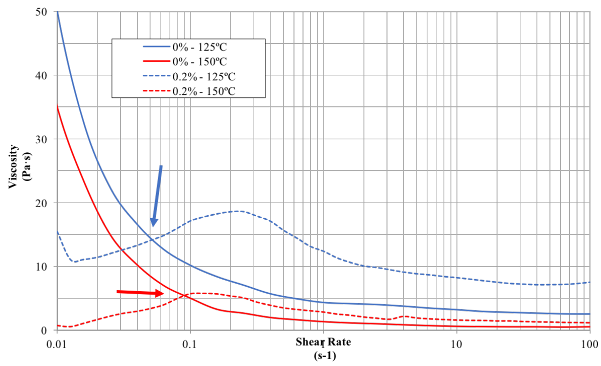

Fig. 9. Viscosity versus shear rate charts for the undoped and 0.2% CNF doped pitch at 125ºC and 150ºC.

This set of results indicates that the addition of CNFs to the coal-tar pitch produces a shear thinning effect at very low shear rates (below 10^{-1}). As the shear rate increases there is a transient thickening effect and at even higher shear rates (higher than 10^{1} s^{-1}) viscosity values then to lower but never reach those of the undoped pitch.

This type of effect on fluids viscosity is generally attributed to the geometry of the additives. In our specific case, the explanation would be that at low shear rates the cylindrical shaped carbon nanofibers would acquire a configuration offering less resistance to flow. However, as shear rate increases the network of nanofibers probably becomes entangled, causing an increment in the resistance to flow and therefore increasing the viscosity of the pitch. Even higher shear rates would break the tangles of nanofibers, but their presence would keep viscosity higher than that of the undoped coal-tar pitch. As seen in Fig. 9, the intensity of the CNF effects is also temperature dependent.

CONCLUSIONS

The use of a carbon nanofiber (CNF) doped coal-tar pitch as binder of a reference Söderberg paste improved its flowability, while no component segregation was observed.

For the reference Söderberg paste tested in this study, flexural strength after treatment at 500ºC was increase for 0.1% and 0.2% CNF additions to the coal-tar pitch used as binder.

These results have been explained as due to the modification of the rheological behaviour of the pitch itself, induced by the presence of CNFs.

At low shear rates (approximately below 10^{-1}), CNF doped pitches show higher flowability that the undoped ones. Such effect may constitute a desirable feature for Söderberg paste compaction, for instance under its own weight in the formwork, and will possibly also allow an easier release of volatiles.

A transient thickening behaviour of the CNF doped coal-tar pitch was also observed at intermediates shear rates (10^{-1} to 10^{0} s^{-1} shear rate). This circumstance could be of technological use since it may help preventing paste segregation.

The effect of CNFs on coal-tar pitch, and therefore on the Söderberg paste, can be attributed to an “internal structuration” of the pitch delivered by the CNFs presence, geometry and high length-to-diameter ratio.

At low shear rates, below the critical point described in this work, CNFs would facilitate pitch flow. At intermediate shear rates CNFs would get entangled, resulting in a transient increment in the pitch´s resistance to flown and therefore higher viscosities.

If shear rate is even further increased, CNFs tangles may be broken, facilitating flow and thus lowering viscosity. Further work is needed to fully characterize the mechanisms at work.

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REFERENCES

[1] European Commission. Integrated pollution prevention and control (IPPC). Reference document on best available techniques in the non ferrous metals industries; 2001.

[2] Guerra E, Berciano J. Monografías sobre tecnología del acero. Parte I acería eléctrica, 2009.

[3] Salgado P. Mathematical and numerical analysis of some electromagnetic problems, application to the simulation of metallurgical electrodes”, PhD Thesis 2002.

[4] Karuppannan C, Prabhakar R. Analysing of Söderberg cell technology performance and possibilities. Manufacturing engineering, 2009(2): 5-9.

[5] Müller, G. (2000). Euromat 99, Ceramics. Wiley-VCH.

Roos, H. (2011). Thermomechanical analysis of raw materials used in the production of Söderberg electrode paste/Roos H.

[6] Invaer, R., “A status for the Söderberg smelting electrodes”, Elkem Carbon. Electrotech 92, Montreal 1992.

[7] Merino C. Fabricación y caracterización de nanofibras-nanotubos de carbono mediante la técnica de catalizador flotante. Tesis Doctoral. Universidad de Madrid, 2006.