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THE INFLUENCE OF CARBON MATERIALS ON THE PROPERTIES OF MgO REFRACTORIES

VPLIV DODATKOV OGLJIKA NA LASTNOSTI OGNJEVZDRŽNIH GRADIV MgO

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Results of an on-going investigation into the properties of a MgO refractory with a low carbon content and without phenol resin binders are presented. To improve the strength, erosion resistance and to decrease phenol evaporation at heating, a preliminary treated coal-tar pitch with a higher melting temperature and a lower content of volatile component were investigated. The samples were treated with heating at 1000 °C and the tensile strengths were determined at room temperature. The domestic pre-treated coal-tar pitch showed the best results.

Keywords: pitch, resins, carbonization, basic refractories, benz(a)pyrene, carbon binder

Predstavljeni so rezultati o raziskavi ognjevzdržnega materiala MgO z majhno vsebnostjo ogljika in brez fenolovega veziva. Za povečanje trdnosti, odpornosti proti eroziji in za zmanjšanje izhlapevanja fenola med segrevanjem je bil raziskan predobdelan premogov ter z visokim tališčem in majhno vsebnostjo hlapnih snovi. Vzorci so bili ogrevani pri 1000 °C in določene so bile raztržne lastnosti pri sobni temperaturi. Domač predobdelan premogov ter je pokazal najboljše rezultate.

Ključne besede: ter, smola, karbonizacija, ognjevzdržna gradiva, benzopiren, ogljikovo vezivo

1 INTRODUCTION

The application of basic refractory materials (RMs) containing carbon has become widespread in steel-making processes, and a summary of the properties and the use of such materials was presented in a paper at UNITECR '99[1]. The further development of pitch and resin-bonded RM is aimed at decreasing the presence of environmentally harmful components, such as benz(a)pyrene (BaP), monocyclic aromatic hydrocarbons (MAH), polycyclic aromatic hydrocarbons (PAH) as well as the products of resin binders (phenol and formaldehyde). Minimizing their content to an environmentally acceptable level can be practically achieved by the application of thermally treated (hard) pitch having a low content of volatile, environmentally unacceptable components or by the application of advanced bonding materials with a low content of volatile components[2], free of BaP[3] and good binders, flowing and sintering properties and improved resistance against corrosion and thermal shock.

The discussion on the suitability of the application of pitch binders for the preparation of MgO-C and Al_2O_3-MgO-C refractory materials is a long way from a final conclusion. The application of resinous synthetic binders undoubtedly brings new, progressive elements into the technology of the carbon-containing production of RM. The opinions about their optimum properties depend on the authors' views[4]. The use of resinous synthetic binders is approximately 10 % smaller and the production costs are about four times higher. Pitch-bonded RM can undergo graphitization more easily, and their pyrolysis takes place in the liquid phase. In this way the distribution of graphite leads to better resistance against oxidation and corrosion by the slag phase. Pitch-bonded RM shows a greater thermal shock resistance. The analysis of their qualitative properties from the point of view of their environmental friendliness was described by Altpeter-Lechner[5].

From the economic point of view, the optimal solution is the application of so-called mesophase bonding materials that are being used in carbon preparation, i.e., fibre composites[6]. Mochida[7] was the first to use these materials in the preparation of MgO-C refractory materials. The application of powder pitch binders produces an increased porosity of the materials and the deterioration of the strength at a temperature above 700 °C, even if the precursors' grain size was below 0.075 mm[7].

The application of advanced bonding materials for the preparation of MgO-C refractories was introduced in 1966[2,7]. However, the substitution of resin bonding materials with the so-called "new carbon bonding" containing low[3] or zero content[7] of environmentally harmful components has not been described in detail in the quoted references.

The combination of pitch and resin-bonding materials also extends the lifetime of refractory lining. It is achieved by the impregnation of the magnesite products with molten pitch in vacuum or with the addition of pitch to MgO-C refractories with resin-bonding material. The MgO-C refractories show better resistance to corrosion, to thermal shocks and increased strength without a change of the modulus of elasticity.

2 EXPERIMENTAL

Laboratory experiments were carried out to verify the bonding characteristics of different kinds of hard pitch materials with Chinese iron-free magnesium oxide. Its chemical composition was 97.15 % MgO; 0.96 % CaO; 0.88 % SiO_2; 0.22 % Al_2O_3; 0.49 % Fe_2O_3. The weight loss was 0.21 % and the bulk density was 3.45 g cm^{-3}. The experimental samples contained 70 % of the grain fraction 0.5–1.04 mm and 30 % of the fine fraction <0.045 mm. To this mixture 5 % of the bonding material was added. The pitch materials were tested by thermal analysis in an inert atmosphere to determine the softening temperature and the volatile fraction with a Derivatograph MOM Q1500D. The carbon content and the temperature of the maximum oxidation rate were determined with a LECO RC-412.

The experimental samples were prepared in the form of compressed tablets, 2 cm in diameter, using the method proposed by Mochida[7]. After blending and homogenizing, the mixture was compressed in a metallic die by applying (75, 100, 125 and 150) MPa. After that the samples were thermally treated in nitrogen gas. The samples were held at softening and carbonization temperatures of (450, 700) °C and 1000 °C for two hours. Finally, the apparent porosity and the perpendicular tensile strength of all samples were determined.

3 RESULTS AND DISCUSSION

In **Table 1** the chemical and thermal properties of the used pitches are shown. The Svit pitch was first diluted with hydrogenated oil, then the solid carbon residue was removed by centrifuge and the content of the volatile components reduced to 24.7 % by heating at 400 °C in an inert atmosphere. The pitch of Japanese provenience contained 41 % of volatile components. The pitch of German provenience is a commercial product from Poschel Erzkontor, Löbeck. It has a relatively broad temperature range of softening, contained several fractions as was revealed by DTA, with 42 % of volatile components. About 90 % of it had a grain size below 0.075 mm. The Gillsonite pitch was a natural one and did not undergo any thermal treatment. For comparison, one sample was prepared with 5 % of NOVOKOL E-20 resin as a bonding material. Moreover, a silicon antioxidant was added to the Svit pitch bonded sample.

Table 1: Chemical and thermal properties of the pitches
Tabela 1: Kemijske in toplotne lastnosti terov

Pitch	Softening temperature interval t_m/°C	Carbon content w/%	Oxidation temperature t_{ox}/°C
Svit	228–290	93.9	582
Japan	314–380	62.8	568
Germany	200–427	63.4	536
Gillsonite	278–318	91.5	453

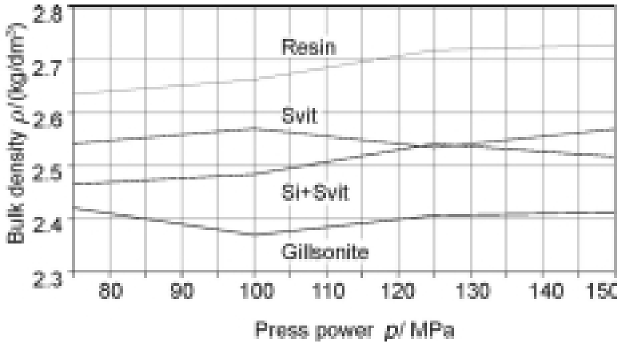

Figure 1: Effect of pressure on the bulk density
Slika 1: Vpliv pritiska na volumensko gostoto

The effects of pressure on the bulk density and the apparent porosity are presented in **Figure 1** and **Figure 2**.

It is clear that the best pressing results were obtained for the samples containing molten resin. The Gillsonite pitch was found to be the least suitable among the bonding materials tested, since it contains an unacceptable amount of amorphous carbon that is difficult to press, and with pressing properties similar to those of soot. Gillsonite pitch has the lowest ignition point for carbon (453 °C), as shown by the LECO analysis results in **Table 1**. A pressure between 100 MPa and 125 MPa seems to be sufficient because increasing the pressure did not affect the apparent porosity.

The results of the carbonization process carried out at (450, 700) °C and 1000 °C were analyzed in six samples compressed at 100 MPa. The results of both the apparent porosity and the perpendicular tensile strength (PTS) are presented in **Figures 3** and **Figure 4**, respectively.

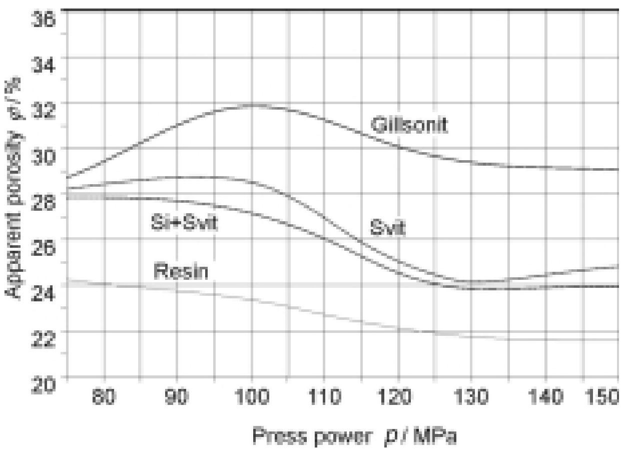

Figure 2: Effect of pressure on the apparent porosity
Slika 2: Vpliv pritiska na navidezno poroznost

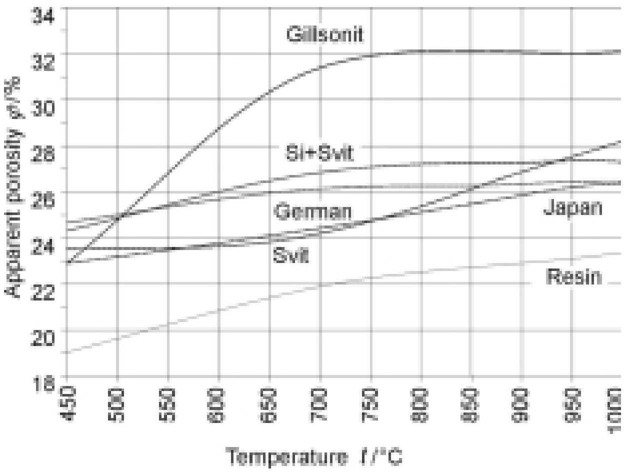

Figure 3: Effect of the annealing temperature on the apparent porosity
Slika 3: Vpliv temperature žarjenja na navidezno poroznost

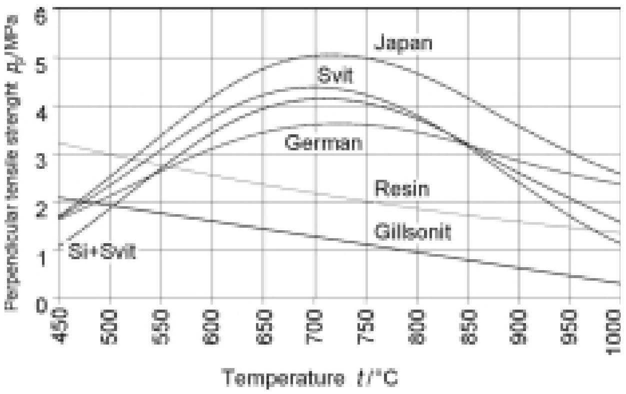

Figure 4: Effect of the annealing temperature on the perpendicular tensile strength
Slika 4: Vpliv temperature žarjenja na pravokotno natezno trdnost

The apparent porosity decreased when the sample was carbonized at 450 °C because of the rearrangement of particles after the melting of the bonding material as well as the elimination of volatile components. The carbonization at this temperature was still incomplete. The samples containing Gillsonite and resin carbonized at 700 °C or 1000 °C showed an increased apparent porosity. In both cases the product of the carbonization was an amorphous carbon, the presence of which lowered the strength, as shown in **Figure 4**. The decrease in the strength at temperatures above 700 °C, shown in **Figure 4,** is the result of the networking of carbon chains for all the other materials. This process takes place in both isotropic and anisotropic (mesophase) pitch bonding materials that are used for making oxide or non-oxide refractories[7,8] as well as for making carbon products[9].

4 CONCLUSION

The laboratory testing of the bonding characteristics of the selected powder pitch materials shows that the apparent porosity of the samples, when compared to the initial values, was increased. The explanation is in the unequal distribution of the powder bonding particles in the sample material as well as the high content of volatile components. This was confirmed by the microscopic observation of a cross-section of polished samples as well as by EDX analysis. The best results were obtained for the case of additions of German pitch, which has the smallest particle size. Other samples were only ground to a particle size below 0.1 mm. As the individual MgO grains were not covered by bonding material, it is necessary to improve the milling with a thinner in order to solve this problem. The relative amount of bonding material that will be used in the preparation of the refractory materials will also have to be increased.

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