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IMPROVEMENT OF BASIC CARBON REFRACTORIES BY TITANIUM-BASED ANTIOXIDANT

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Preliminary Note - Prethodno priopćenje

Possibility of the preparation of the titanium-based antioxidant from Ti-scrap materials. Thermodynamic conditions and theoretical aspects of its application in magnesia carbon bricks. Laboratory tests oriented on the efficiency of this application. The finger corrosion tests of bricks from different sorts of magnesia clinkers

Key words: *refractory, carbon, periclase, titanium, antioxidant*

Poboljšavanje bazičnog ugljičnog vatrostalnog materijala antioksidantom zasnovanim na titanu. Mogućnosti pripremanja titanskog antioksidanta iz otpadnog titana. Termodinamički uvjeti i teoretski aspekti njegove primjene u magnezijsko-ugljičnim opekama. Cilj laboratorijskih ispitivanja je pronalaženje učinkovitog načina takve primjene. Ispitivanje opeka na koroziju dodirom prsta napravljenih od raznih vrsta magnezijskog klinkera.

Ključne riječi: *vatrostalni materijali, ugljik, periklas, titan, antioksidant*

INTRODUCTION

Generally speaking antioxidants are metals and non-metals with higher affinity to oxygen than graphite and with oxidation products without negative influences on refractories. To provide their distributions in to pores and surface of MgO to create a protective oxide-layer they need a high vapour pressure in a work conditions. As antioxidants are frequently used metal powders for instance Mg, Al, Si and B and non-metals compounds as SiC, SiB_6, B_4C and BN. Their theoretical efficiency can by calculated through stoichiometry as amount of reduction 1 kg CO to carbon [1]. This value is the lowest for the boron (0.26 kg) and B_4C (0.33 kg). Because of the price, in the industry the most frequently used is Al sometimes with Si addition [2]. On the other side and because of high quality of the melted protective layer of B_2O_3, very often also B and B_4C are used in spite of 10 times higher price [3].

Titanium powder seems not to be very advantageous antioxidant. Its price is 2-4 times higher and its theoretical efficiency (0.85 kg) is lower that of Al (0.64 kg). But its useful properties can be very interesting if the powder Ti - antioxidant is made from Ti - scraps materials which is not suitable for remelting to pure metallic Ti [4]. The most of Ti - scraps are Ti - alloys with content of Ti is above 90 mass % and the main admixture is mostly Al.

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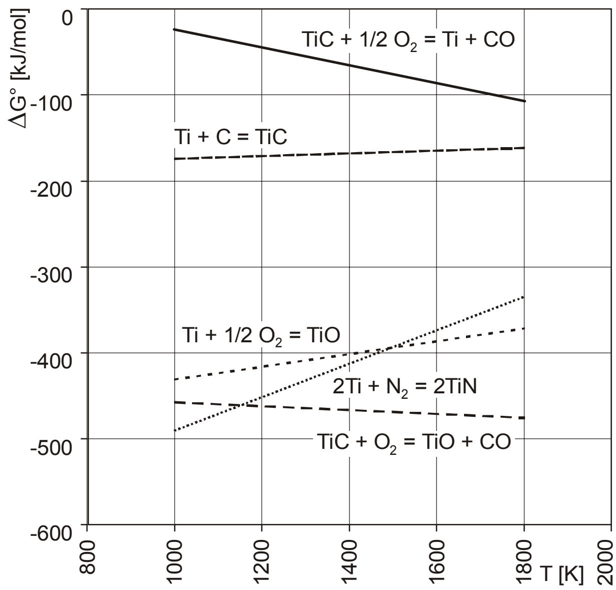

Figure 1. **Standard Gibbs free energy versus temperature**
Slika 1. **Standardna Gibbsova slobodna energija prema temperaturi**

The thermodynamic conditions of the antioxidation processes were calculated from the standard Gibbs free energy [5]. From the calculated diagrams on Figure 1. and Figure 2. it is assumed that TiN and TiC are stable in reducing atmosphere and TiO in CO-CO_2 atmosphere.

The most stable TiO like SiO has a high vapour pressure which facilitates it transport to the surface of MgO.

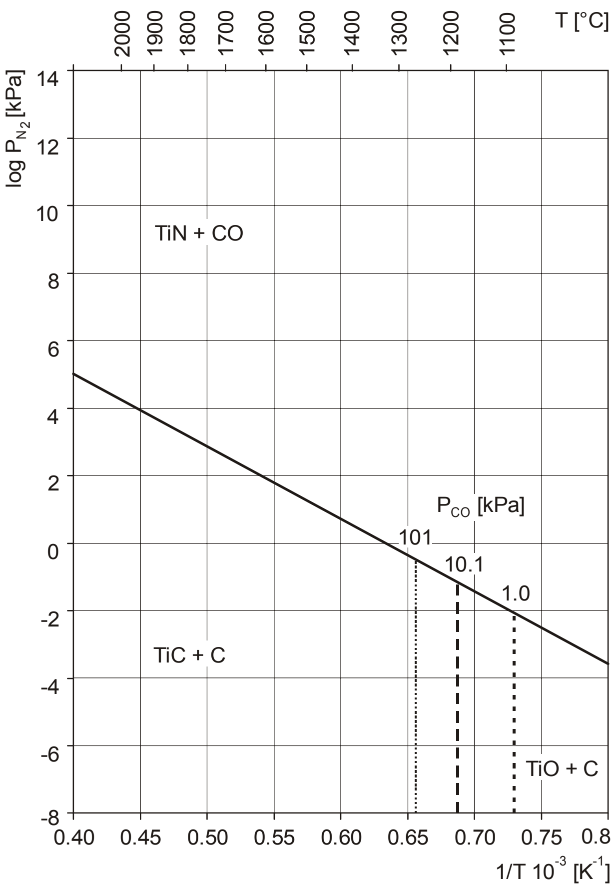

Figure 2. **Predominance area diagram of the system Ti-C-N**
Slika 2. **Dijagram predominancije površine sustava Ti-C-N**

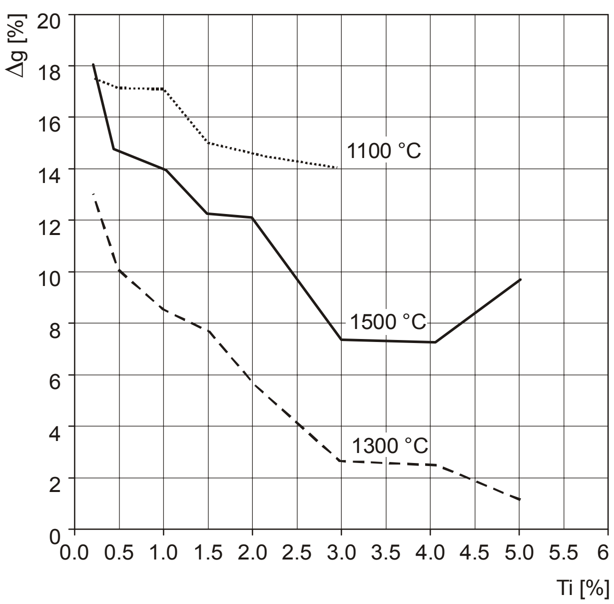

Figure 3. **Mass decrease of samples made without resin binders in air**
Slika 3. **Ovisnost smanjenja mase uzoraka, napravljenih bez smolastih vezivnih tvari, o slobodnom pristupu zraka**

EXPERIMENTAL RESULTS AND DISCUSSION

To confirm the efficiency of the Ti antioxidant, samples of MgO - sinter has been prepared by mixing with 20 mass % of graphite and 0.25 - 5.0 % of Ti- powder produced by the HDH process [6]. Pellets with diameters of 10mm prepared by pressing at 200 MPa were annealed for two hours in air at 1100, 1300 and 1500 °C. The dependence of mass decrease of samples is shown in Figure 3..

Experiments using epoxy binder FERNAL and Ti - antioxidant prepared by a modified process [4], (using cheaper then hydrogen natural gas) were performed with samples prepared from HAMAG sinter MgO. The mass decrease at annealing temperature 1100 °C is shown in Figure 4..

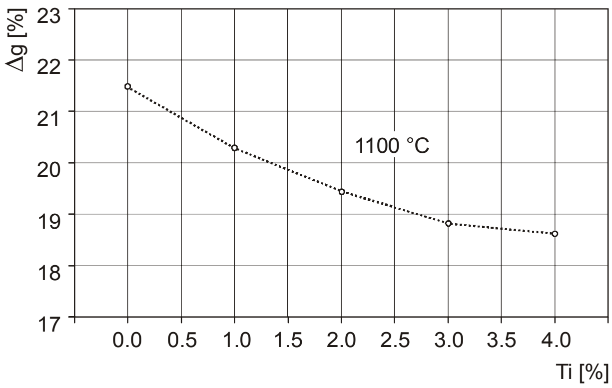

Figure 4. **Mass decrease of samples made with resin binder FERNAL in air**
Slika 4. **Ovisnost smanjenja mase uzoraka, napravljenih od smolastih vezivnih tvari FERNAL, o slobodnom pristupu zraka**

The samples for one-hour corrosion test were prepared from six type of magnesite with and without 2 mass % additive of Ti - antioxidant prepared by the same modified process [4]. The chemical composition of the testing sinter MgO and its bulk density are listed in Table 1.. Test

Table 1. **Chemical composition of the testing magnesite**
Tablica 1. **Kemijski sastav ispitivanog magnezija**

	Type of the magnesite	SiO_2 [%]	Fe_2O_3 [%]	Al_2O_3 [%]	CaO [%]	MgO [%]	bulk density [gcm^{-3}]
A	Jelšava (SR)	0.43	7.74	0.12	2.57	89.07	3.33
B	Molten chinese C/S=1	0.82	0.59	0.12	0.77	97.70	3.52
C	Turkish	0.49	0.19	0.06	2.24	97.00	3.45
D	Hačava (SR)	0.20	0.29	0.06	0.07	99.02	3.30
E	Molten chinese C/S=2	0.32	0.49	0.06	1.26	97.87	3.50
F	Korean	1.23	1.09	0.06	1.03	97.33	3.52

of modelling was carried out by dynamic corrosion of refractories in the steel - slag melt at the temperature of 1600 °C [7]. The results of test and the mass decrease as mass % is shown in Figure 5. and Figure 6..

The corrosion finger tests at 1600 °C confirm the efficiency of the Ti-antioxidant (Figure 5. and 6.). The best results are obtained with tested brick from magnesite with low content of Fe_2O_3 (Hačava and Chinese sinters).

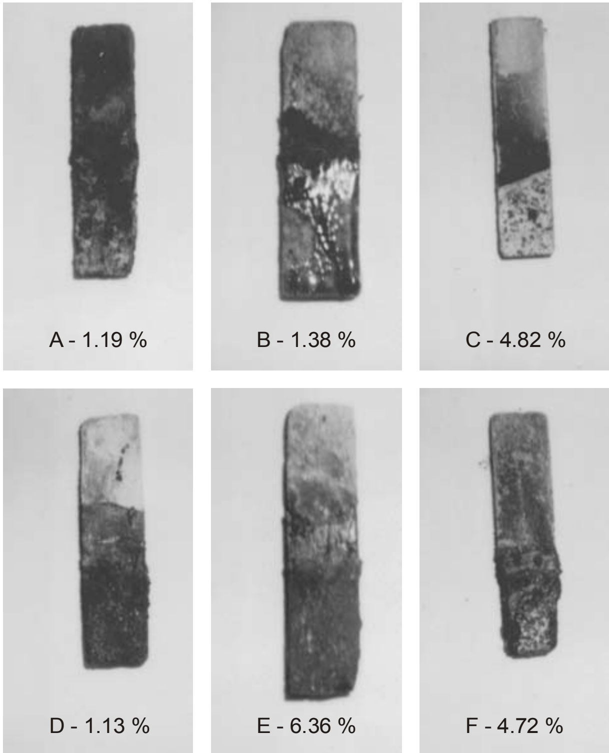

Figure 5. **MgO-C samples after finger test**
Slika 5. **Uzorci MgO-C nakon ispitivanja prstom**

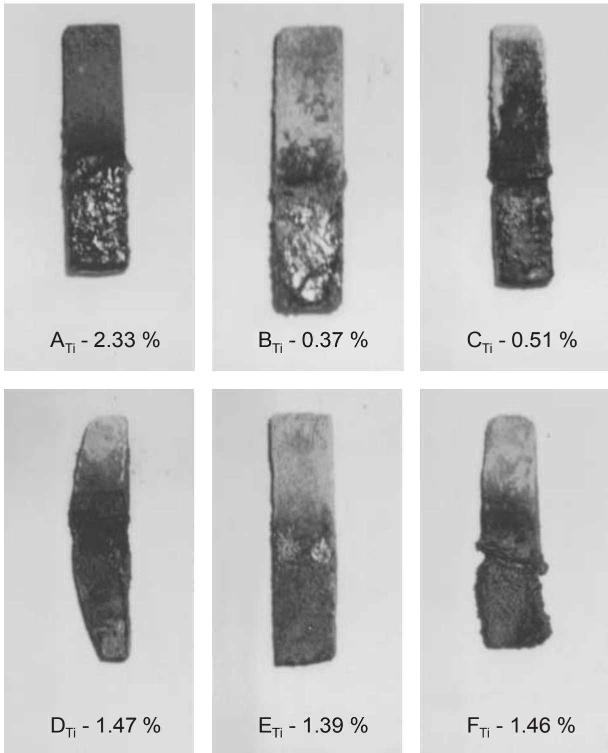

Figure 6. **MgO-C samples with Ti after finger test**
Slika 6. **Uzorci MgO-C s dodatkom Ti nakon ispitivanja prstom**

CONCLUSION

Both titanium powders made by HDH [6] and by modified process [4] confirm their suitability as antioxidants for periclase-carbon refractories. Ti-scraps treatment with the reducing gas can be ground to powder - 0.5 mm. TiO covers the titanium powder surface and the amount of impurities depend of the Ti-scrap quality. The thermodynamic calculation shows that the antioxidation effect is due to reactions producing TiO up to 1200 °C and TiC at the higher temperature. The optimal addition of Ti-antioxidant without resin binders is 3 mass %, as shown in Figure 3.. The dependence of samples mass decrease at 1500 °C can be related to oxidation of TiC and the higher velocity of carbon oxidation. The samples of tested magnesite (Table 1.), prepared with a resin binder has not the optimal content of addition as it can be see from experimental results at 1100 °C in Figure 4..

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