INVESTIGATION OF TiO_2-ADDED REFRACTORY BRICK PROPERTIES FROM CALCINED MAGNESITE RAW MATERIAL

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This paper is the second part of a study on recycling magnesite and chromite ore (in the $0 – 10^{-3}$ m fraction) powder, which remains as a production process waste. In this work, 90% magnesite-10% chromite composition was used as a brick composition. Compaction pressure, sintering temperature, ratio of TiO_2 addition, and influence of bonding type on refractory properties were examined. In refractory brick production, one of the most important parameters that affects the properties of the product is the particle size distribution of the blend. Experiments show that using a magnesite particle size of $–10^{-3}$ m and a chromite particle size of $–63\times10^{-6}$ m affects the properties of the product in a positive way. Experiment blends with the particle sizes selected above were used. Magnesite ore was used in experiments after calcination at 1200°C for four hours. In the experiments we mention, $MgCl_2$ and $MgSO_4$ solutions were used as a bonding agent, as a result of which a 6% bonding ratio of $MgCl_2$ and $MgSO_4$ solutions was determined as optimum. The effect of compacting pressure on the refractory properties was studied, and the optimum compacting pressure was determined as 180 MPa. For bricks prepared using calcined magnesite, the optimum sintering temperature was found to be 1750°C. The positive effect of TiO_2 addition on the magnesite chrome refractory brick structure has been reported in the literature. Thus, 1, 3, 5, and 7 wt.% TiO_2 ratios were used in the blend, and the refractory properties were positively affected by the 3% TiO_2 addition. Taking the result of the $MgCl_2$ and $MgSO_4$ bonding solution into consideration, it is clear that the refractory properties of brick can be improved by using a mixture of $MgCl_2$ and $MgSO_4$ bonding solutions. In light of the above concept, bonding mixtures with 1:3, 1:5, and 1:10 ratios were prepared, and these bonding mixtures were studies as a bonding material. The experimental results show that the cold crushing strength (CCS) and volume density of bricks increase, whereas the porosity decreases when a 1:5 ratio of $MgCl_2$ and $MgSO_4$ in the bonding mixture and 3% TiO_2 addition were used. Microstructural study of the produced bricks was done using scanning electron microscope (SEM). In addition to this, the phases forming the structure of brick were examined via x-ray diagrams of the material. In bricks where a mixture of a 1:5 $MgCl_2$: $MgSO_4$ bonding solution was used as bonding agent and 3% TiO_2 was added, spinel (magnochromite ($MgCr_2O_4$)), magnesium orthotitanate (Mg_2TiO_4), monticellite ($CaMgSiO_4$), and forsterite (Mg_2SiO_4) phases were found. The perovskite phase was not observed during the experimental study.

INTRODUCTION

The aim of this study is to reuse the waste magnesite and chromite dust with particle size below $–10^{-3}$ m for refractory brick production. Magnesite ore is used in refractory production after being sintered, but due to the transport of dust to from the movement of gases coming out from the cold end of the rotary furnace, magnesite dust is not suitable for sintering in a rotary furnace [1]. Previous studies on calcination of magnesite have shown that calcination at low temperatures gives MgO, which is to moisture, and CO_2 is found in such a medium. To achieve physically and chemically stable magnesite, the most suitable calcination temperature has been found to be about 1200°C [2].

Chemically bonded refractory bricks are pressed with the addition of a chemical binder in order to strengthen them [3]. Magnesia binders are obtained from caustic magnesite [$Mg(OH)_2$], which are magnesium chloride and magnesium sulfate solutions [4].

In magnesite–chromite refractories, the periclase-chromite-spinel bond is stronger when the chromite particle size used is fine [5].

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Within increase in pressure, the contact area between the fine and thick particles increases, so the particles can be sintered better. The level of porosity in the material is also affected by the chromite content [6].

It is known that the size of crystals in sintered ceramics determines a number of important properties of the product such as strength, creep friction, thermal-shock resistance, etc. Several studies have demonstrated that rapid recrystallization of refractory oxides occurs at the final stage of sintering, and the size of the crystals is affected by the pore [7]. It is possible to control recrystallization by making certain additions. Additives entering into the magnesite-chromite composition contribute to the growth of Cr_2O_3 grains [7]. Studies show that the addition of TiO_2 contributes to the recrystallization of Cr_2O_3 [6, 7].

The $MgO–Cr_2O_3$ sintering rate depends on the sintering temperature. Sintering the specimens at 1450°C does not lead to the expected enlargement of the crystals. However, significant recrystallization is observed above 1600°C, resulting in the mation of $MgCr_2O_4$ spinel at the particle boundaries of the chrome oxide [7]. It was observed that open porosity was eliminated when magnesite-chromite bricks are sintered above 1750°C [8].

Gudilian, et al. (1984) indicate that during the cooling of specimens of $MgO–Cr_2O_3–TiO_2$ composition, decomposition of spinel's solid solution which are magnochromite ($MgCr_2O_4$) and magnesium orthotitanate (Mg_2TiO_4), take place. After that process, magnesium orthotitanate, reacting with molten monticellite, forms perovskite ($CaTiO_3$) and forsterite (Mg_2SiO_4) [9].

Kvyotovskii, et al. studied the phase composition of periclase-spinel refractories and determined that the $Me_2O_3–MgO–TiO_2$ phase diagram gives standard phase diagram information. They showed that the interaction between the titanium added for ease in sintering and magnesia (as periclase) — Chromite ores during the sintering process result in the formation of a solid solution of spinel having a high content of titanium ($MgCr_2O_4 \cdot Mg_2TiO_4$). They observed that during the cooling of the specimens, decomposition of the spinel's solid solution and dissolution of the intermediate spinel in the original spinel10 take place.

EXPERIMENTAL

Materials and Compositions

Magnesite obtained from the Konya region of Turkey (magnesite-sodur) was used as starting material, which was calcined at 1200°C for four hours. As the raw materials, domestic chromite from Etibank, Turkey was used in the experimental studies. The chemical compositions and particle size analyses of these ores are indicated in Tables 1 and 2.

The percentage of mixture used in the experiments is 90% magnesite and 10% chromite.

TABLE 1. Particle Size Analysis of the Magnesite and Chromite Ores, %

Sieve, μm	+1000	+500	+250	+100	+63	–63
Magnesite	10.80	34.70	20.80	19.10	3.40	11.20
Calcined magnesite	10.19	24.90	24.48	22.38	9.26	8.79
Chromite	11.40	25.60	27.1	22.80	5.63	7.80

TABLE 2. Results of Chemical Analysis of the Magnesite and Chromite Ores, %

Composition	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3	SiO_2	CaO	Δm_{prc}
Magnesite	47.73	0.05	–	0.27	1.43	0.63	49.89
Chromite	18.02	13.51	48.58	15.87	2.66	0.63	0.73

Preparation of Samples

The mixtures were prepared using ores whose particle size distribution was $–10^{–3}$ m magnesite and $–63\times10^{–6}$ m chromite. Binders of $MgSO_4$ and $MgCl_2$ were added to the mixtures prepared for the above particle distribution at a proportion of 6% [12 – 16]. The positive effect of $MgCl_2$ binding solution on the cold crushing strength is seen in the experiments. Because of this, 1:3, 1:5, and 1:10 mixtures of the $MgCl_2$ and $MgSO_4$ solutions were examined as binding material.

RESULTS AND DISCUSSION

Compaction Pressure

In order to study the effects of compaction pressure on the properties of the products and to specify the optimum pressure, mixtures with fine average particle size distribution were pressed between the range 90 – 180 MPa. The optimum pressing pressure of the materials containing calcined magnesite was 180 MPa at 1750°C.

The effect of compaction pressure on CCS and porosity values for the samples sintered at 1750°C is given in Fig. 1.

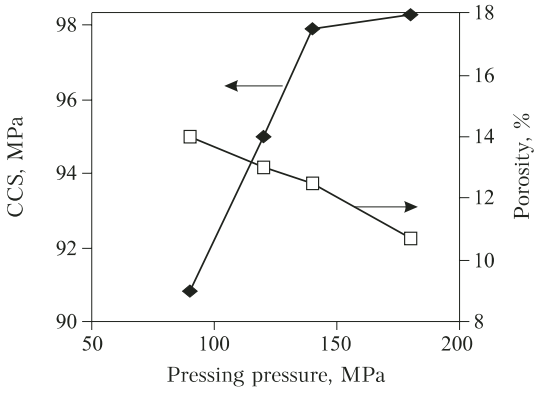


Fig. 1. Change in the values of the pressing pressure, porosity (%), and cold crushing strength (CCS) of samples.

Effect of Binder Type and TiO_2 Addition on Porosity and CCS Values

In the first stage of the experimental study, a mixture prepared by using $MgSO_4$ and $MgCl_2$ binders was pressed under a pressure of 180 MPa and sintered at 1750°C. The binder content was found to be 6% in a previous study [17].

In Table 3, in which $MgSO_4$ solutions were used as a binder, the experimental CCS values were found to be higher than $MgCl_2$ binder, and the apparant porosity values were found to be lower.

In order to study the effect of TiO_2 addition on the properties (P, %, and CCS) of the products and specify the optimum TiO_2 addition value, the mixtures were prepared by addition of 1, 3, 5, and 7 wt.% TiO_2 and sintered at 1750°C.

The effect of the TiO_2 addition on the CCS and apparent porosity values for the samples sintered at 1750°C is shown in Figs. 2 and 3.

The result obtained are given in Figs. 2 and 3, it can be seen from the figures that, as expected, CCS increases and porosity decreases with the 3% TiO_2 additions.

As the content of TiO_2 was changed from 1 to 3% in the mixtures, CCS was observed to increase and porosity to decrease, but when the content of TiO_2 was changed from 5 to 7 in the mixtures, CCS was observed to decrease and porosity to increase.

Thus, the optimum TiO_2 addition to the mixture was found to be 3%. Also $MgSO_4$ solution has been found to result in better properties than $MgCl_2$ solution.

The most improved properties of the refractory samples were found to be obtained by using a binder mixture of $MgCl_2 + MgSO_4$.

Binder mixtures of $MgCl_2 + MgSO_4$ with 1:3, 1:5, and 1:10 ratios were prepared for the TiO_2-added samples, which were sintered at 1750°C. The results of this series of experiments are given in Table 4.

The best properties were observed in the composition prepared with the 1:5 mixture 17.

TABLE 3. Variation in Refractory Properties with Type of Bond

Materials Compositions	CCS, MPa	Porosity, %	Bulk density, g/cm^3
90% Magnesite 10% Chromit 6% $MgSO_4$ solu.	98.3	10.7	3.15
90% Magnesite 10% Chromite 6% $MgCl_2$ solu.	84.5	23.5	2.75

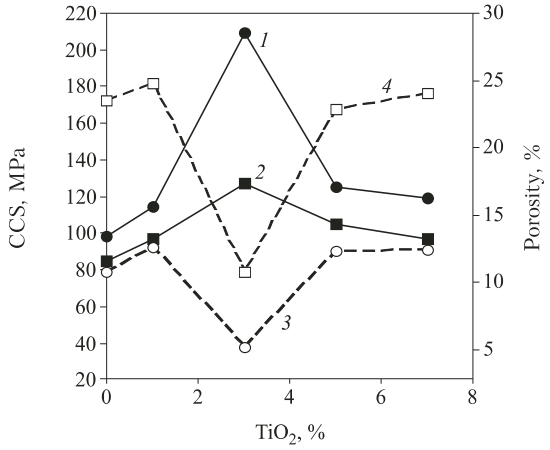


Fig. 2. Variation of porosity (%) and CCS values with TiO_2 additions.

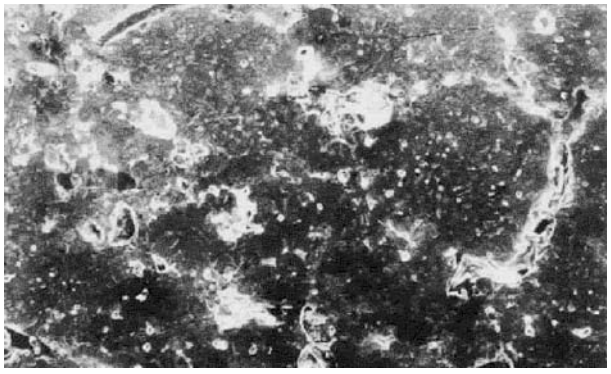


Fig. 3. Electron microscopic images (SEM) of the specimens with 6% $MgSO_4$ as the bonding agent and fired at 1750°C. ×100. SEM.

TABLE 4. Effect of Binder Composition on Porosity (%) and CCS Values at 1750°C

Materials compositions	CCS, MPa	Porosity, %	Bulk density, g/cm^3
90% Magnesite 10% Chromite 6% (1:3) ($MgCl_2$:$MgSO_4$) 3% TiO_2	117.2	1.30	3.14
90% Magnesite 10% Chromite 6% (1:5) ($MgCl_2$:$MgSO_4$) 3% TiO_2	> 210	0.5	3.24

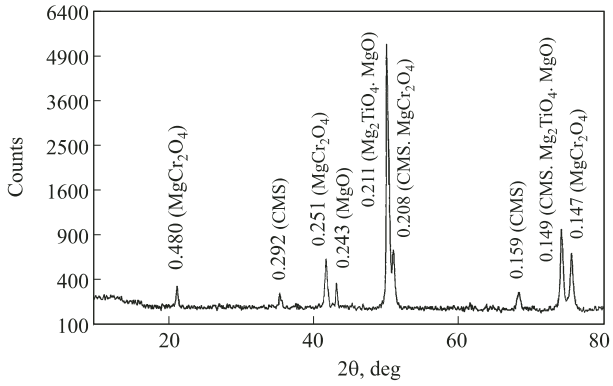


Fig. 4. X-ray diffraction diagram of bricks with 6% $MgSO_4$ as the bonding agent and 3% TiO_2 addition.

Effects of Binder Type and TiO_2 Addition on Microstructural Evolution

Electron microscopic images (SEM) of specimens (Fig. 3) show coarse periclase grains between the particle cavity and chrome spinel at the particle boundary.

The x-ray differaction diagram of bricks, with 6% $MgSO_4$ as the bonding agent (Fig. 4), displayed periclase (MgO), Monticellite (CMS), magnochromite ($MgCr_2O_4$), and magnesium orthotitanate (Mg_2TiO_4) peaks.

The x-ray differaction diagram of bricks with 6% $MgCl_2$ as the bonding agent is shown in Fig. 6.

As shown in Fig. 5, when using an electron microscope to analyze the image of the sample in which $MgSO_4$ acts as a bonding agent, it is observed that the chrome spinel has formed at the grain boundary. However, as shown in Fig. 7 where $MgCl_2$ acts as the bonding agent in the samples, due to the porosity of the structure it is seen that the spinel forms within the pore.

Although the two structures consist of similar phases (Figs. 4 – 6), following analysis using an electron microscope it may be noticed that samples in which $MgCl_2$ is used as a bonding agent have a fairly porous structure. This situa-

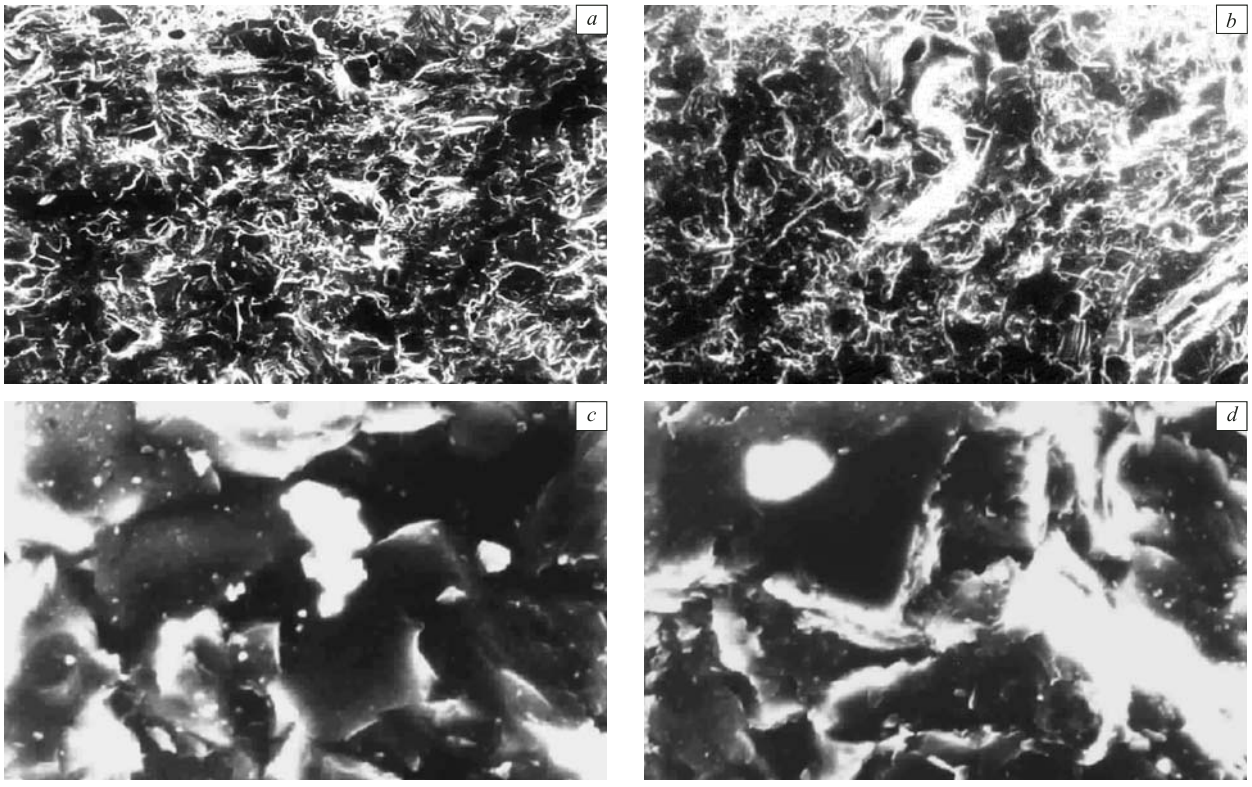


Fig. 5. Electron microscopic images (SEM) of the specimens with 6% $MgSO_4$ as the bonding agent and 3% TiO_2 addition: *a*) general image of microstructure (×100); *b*) pores (×100); *c*) silicates (monticellite) (×3500); *d*) solid solution of magnochromite $MgCr_2O_4$ with magnesium orthotitanate Mg_2TiO_4 (×3500).

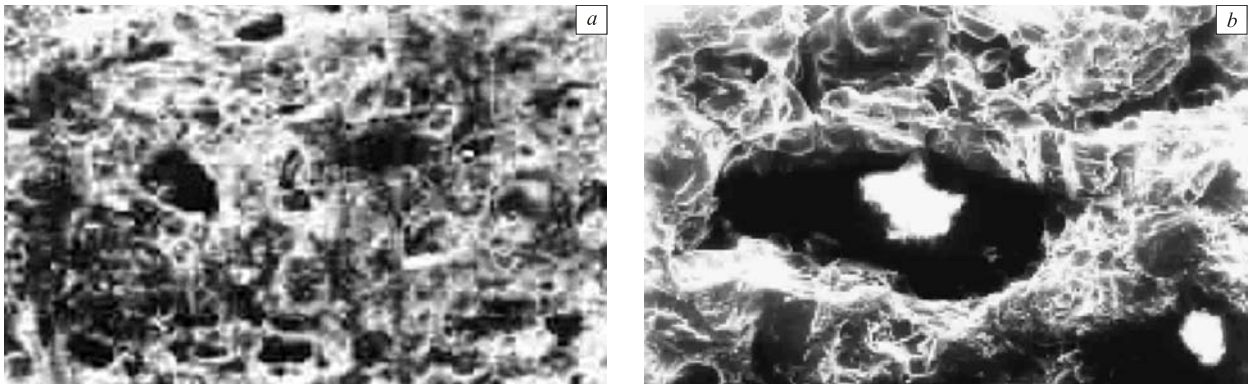


Fig. 6. X-ray diffraction diagram of bricks with 6% $MgCl_2$ as the bonding agent and 3% TiO_2 addition: *a*) general image of microstructure (×150); *b*) chrome spinel (inside of the cavity) at the boundary (×350). SEM.

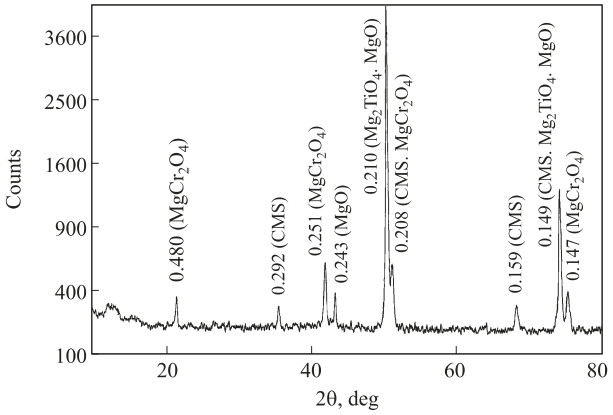


Fig. 7. Electron microscopic images of the specimens with 6% $MgCl_2$ as the bonding agent and 3% TiO_2 addition.

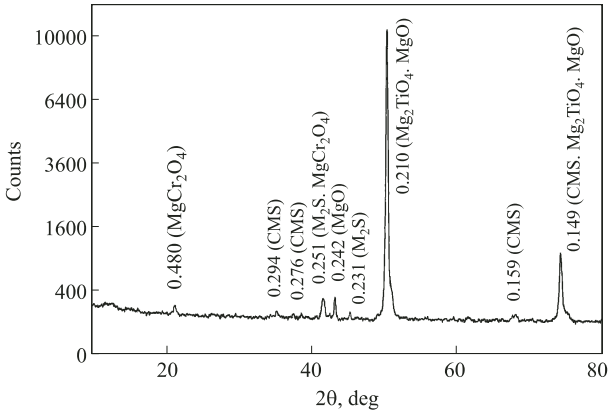


Fig. 8. X-ray diffraction diagram of bricks with 6% (1:5) ($MgCl_2$:$MgSO_4$) solution as the bonding agent and 3% TiO_2 addition.

tion was also shown by the application of a porosity designation. The MgO found in the magnesia of $MgCl_2$ reacts and causes an exothermic reaction, following which a magnesium oxychloride bond is formed. This exothermic reaction explains the porosity of the structure. The MgO found in the magnesia of $MgSO_4$ reacts, and as a result a magnesium oxysulfate bond is formed, which provides for the stability of the ceramic bond in bricks as well as aiding in the formation of MgO throughout the sintering process and helping to make the brick structure stronger.

The x-ray diffraction diagram of bricks with a 6% (1:5) ($MgCl_2$:$MgSO_4$) bonding solution and 10% chromite composition show that MgO, $MgCr_2O_4$, and Mg_2TiO_4 peaks are formed, but the intensity of the monticellite (CMS) and forsterite (M_2S) peaks was low (Fig. 8).

Electron microscopic images of a fragment of the polished surface are shown in Fig. 9.

As shown in Fig. 9, when using an electron microscope to analyze the image of the sample in which the $MgSO_4$ and $MgCI_2$ (1:5) mixture acts as a bonding agent, it is observed

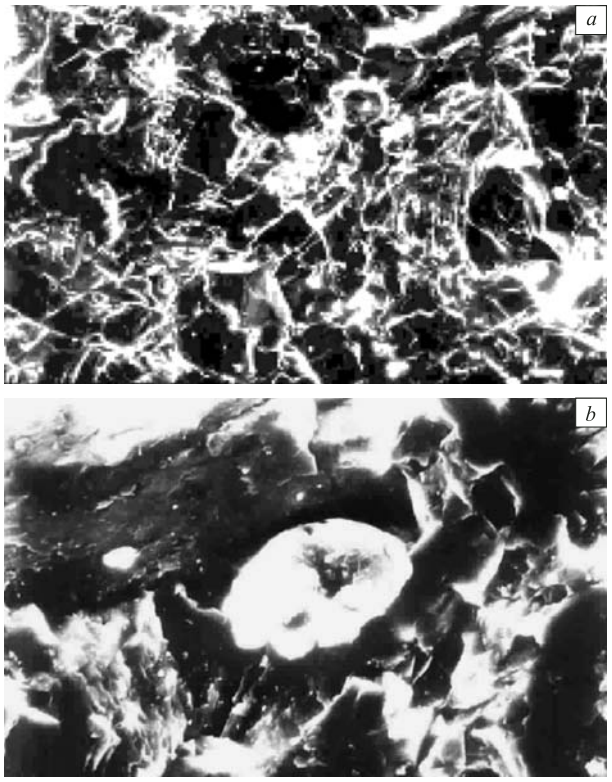


Fig. 9. Electron microscopic images of a fragment of the specimen with a 6% (1:5) ($MgCl_2$:$MgSO_4$) bonding solution and 3% TiO_2 addition: *a*) general image of microstructure (×350); *b*) chrome spinel (×2000).

that the porosity of the structure is fairly low and also that the chrome spinel has formed at the grain boundary.

CONCLUSION

1. The optimum compaction pressure for the 90% calcined magnesite – 10% chromite mixture was found to be 180 MPa.

2. For the 90% magnesite and 10% chromite composition, porosity % and CCS values using 3% TiO_2 addition and $MgSO_4$ binder were 5.1% and CCS 209.4 MPa, respectively.

3. When an x-ray analysis is made of samples in which 6% $MgCl_2$ is used as a bonding agent, it is observed that samples where 6% $MgSO_4$ is used as a bonding agent possess similar phases. The experimental results indicated that, as given in Table 3, the exothermic reactions of $MgCl_2$ binder with MgO caused cracks in the brick structure, and the CCS and especially porosity (%) values were found to be different. Thus, result, $MgSO_4$ is a better binding agent than $MgCl_2$ for magnesite-chromite refractory brick production.

4. Using a $MgCl_2$ and $MgSO_4$ binder composition for 10% chromite composition, we obtained a porosity as low as 0.5% and CCS higher than 210 MPa. This can be used for the production of MgO–Cr_2O_3 refractory brick.

5. It is observed that the microstructure and phase compositions display MgO (periclase), $MgCr_2O_4$ (magnochromite), Mg_2TiO_4 (magnesium orthotitanate), and $CaMgSiO_4$ (monticellite) phases when magnesite-chromite refractories in powdered form are sintered at 1750°C.

6. In the structures there are periclase solid solutions, and $MgCr_2O_4$ spinels are formed. $MgCr_2O_4$ spinel is formed at the particle boundaries of the chromium oxide.

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