

## RESEARCH

### EFFECT OF NICKEL NITRATE ON PHASE CHANGES IN MULLITE AND MULLITE - CORUNDUM REFRACTORIES WHEN HEATED IN OXIDIZING AND REDUCING CONDITIONS

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The speeding up of high-temperature processes is largely connected with an extension of the use of reducing gases. The production of hydrogen and carbon monoxide from natural gas in a number of cases is accomplished in conversion equipment which is lined with refractories. The plant is filled with refractory checkers impregnated with nickel catalysts.

The plant operates cyclically: 30 min on conversion at 1250-1300°C (reducing atmosphere), and 30 min heating to 1450°C (oxidizing atmosphere) [1]. The reaction catalyst for decomposing the natural gas is metallic nickel, which during heating is oxidized, with the formation of oxide or another compound [2]. This paper deals with a study of the reaction between mullite refractory and nickel catalyst in oxidizing and reducing atmospheres.

The starting materials for preparing the checker products consisted of commercial alumina, electrocorundum, and Novoselitsk kaolin (Table 1). The catalyst consisted of nickel nitrate  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The chamotte was made from 50% commercial alumina and 50% Novoselitsk kaolin. The commercial alumina was premilled in a ballmill to obtain a powder having a residue on a screen with 10,000 apertures/cm<sup>2</sup> of not more than 2%. The kaolin was dried to a moisture content of 9.5%, ground to pass completely through a screen having apertures of 2 mm, and then blended with the commercial alumina. The prepared mixture was moistened to 27.5%, and passed through a pugmill. After drying to 12% the briquette was fired at 1650°C with a soak of 10 h. The water absorption of the chamotte was 2-3%; the chemical composition was 73%  $\text{Al}_2\text{O}_3$ , 25%  $\text{SiO}_2$ , and the remainder impurities.

The body for making the checker products consisted of 60% chamotte fractions 3-0.2 mm, 32% electrofused corundum with grain sizes of less than 50  $\mu$ , and 8% kaolin.

During impregnation of the refractory with nickel nitrate it is difficult to investigate the influence of the quantity of catalyst on the change in the phase composition of the refractory. In connection with this the body, at a pressure of 500 kg/cm<sup>2</sup>, was pressed into specimens containing additions of 1, 10, 25, and 50%

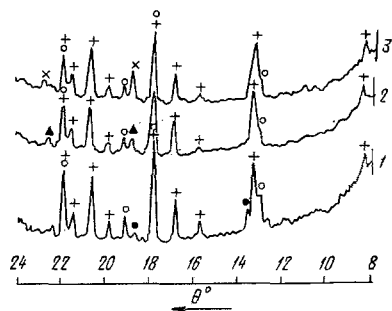


Fig. 1. Diffractograms for mullite-corundum specimens containing 10%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  unfired (1) and after firing in air at 500°C (2) and 1300°C (3): ○) corundum; +) mullite; ●)  $\alpha$ -quartz; ▲) NiO; x)  $\text{NiAl}_2\text{O}_4$ .

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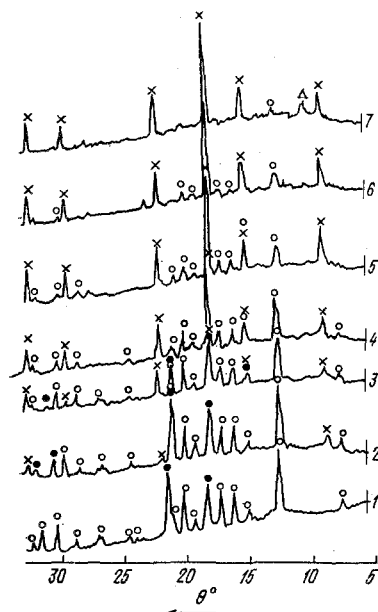


Fig. 2. Diffractograms for mullite specimens recorded at different temperatures. 1) Room temperature; 2) 1000°C; 3) 1100°C; 4) 1300°C; 5) 1500°C (I heating); 6) same; 7) 1500°C (II heating); 2, 5) before soaking; remainder – after soak at temperature for 1 h; ●) NiO; ○) mullite; x)  $\text{NiAl}_2\text{O}_4$ ; Δ)  $\beta$ -cristobalite.

nickel nitrate. The specimens were then fired in an oxidizing atmosphere at 500, 900, 1000, 1100, 1200, 1300, and 1500°C, and subjected to investigation.

The mineral composition of the specimens after firing is shown in Table 2. The specimens containing 1% nickel nitrate heated to 1500°C contained no nickel oxide or its compounds. The specimens containing 10% nickel nitrate after heating to 500°C acquired a light gray color. The grains of chamotte consist chiefly of mullite and cryptocrystalline substance, and the bonding mass is of corundum. The x-ray pattern shows lines for NiO (Fig. 1). With an increase in temperature to 900°C the bond of the specimen is pale blue colored as a result of the formation of very fine grains of NiO. As seen from Table 2, with an increase in the firing temperature, the mullite concentration is increased from 8-10 to 40-45% on account of the reduction in the cryptocrystalline substance.

In the specimens heated to 1100-1500°C nickel spinel is formed, and its quantity increases with an increase in temperature. A similar, but clearer picture for the formation of NiO and spinel is noted in specimens containing 25% nickel nitrate. Petrographic studies show that after firing at 1300°C the specimens contain a large quantity of colorless anisotropic new formations, sometimes in the form of short prisms possessing direct extinction, a positive sign in the main zone; refractive indices  $N_g = 1.694 \pm 0.002$ ,  $N_p = 1.630 \pm 0.002$ . Apparently, the new compounds are nickel  $\beta$ -alumina ( $\text{NiO} \cdot 5\text{Al}_2\text{O}_3$ ) [3]. The quantity of spinel and the rate of its formation increase with an increase in the nickel nitrate concentrations in the specimens, and with the firing temperature.

According to data in [4], above 1300°C there is rapid formation of solid solutions between  $\text{NiAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$ , and at the moment of fusion within the limits of the solid solution there is more than 80% (mole)  $\text{Al}_2\text{O}_3$ . From a study [4] of the system  $\text{NiO}-\text{Al}_2\text{O}_3$  the authors obtained a compound,  $\text{NiO} \cdot 13\text{Al}_2\text{O}_3$ , which is classified as the type  $\beta$ -alumina.

In view of the fact that the investigated specimens consist mainly of mullite and corundum, it was not possible to establish the influence of the catalyst on the behavior of the mullite during heating. To resolve this problem mullite was synthesized, and a fine powder of it was made into tablets of diameter 10 mm. The composition of the specimens was 50% (mole) mullite and 50% (mole) NiO.

To study the phase formation in the system  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{NiO}$  directly during heating the authors used a heating attachment to the diffractometer URS-50I [5]. The specimens were placed in the heater of the diffractometer, heated for a time, and then x-ray patterns were taken at temperatures up to 1500°C. After reaching each prescribed temperature a photograph was taken (in a period of 30 min) and then the specimen was maintained at this temperature for 1 h, and another x-ray pattern recorded. After this, the cycle was repeated at a higher temperature.

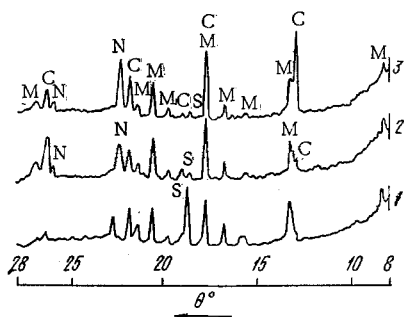


Fig. 3. Diffractograms of mullite-corundum specimens fired in different media. 1) 1300°C in air; 2) 1400°C in the silicon carbide filling; 3) 1400°C in hydrogen; C) corundum; M) mullite; S) spinel  $\text{NiAl}_2\text{O}_4$ ; N) Nimet.

The x-ray pattern of the original specimen at room temperature consists of a collection of crystallographic lines for mullite and  $\text{NiO}$ . At 500, 800, 900°C before and after soaking the x-ray patterns also exhibited lines for mullite and  $\text{NiO}$ . At 1000°C before and after soaking weak lines developed for spinel  $\text{NiO} \cdot \text{Al}_2\text{O}_3$  (Fig. 2). At 1200°C before and after soaking the x-ray pattern, in addition to mullite and spinel, exhibits lines which are classified as  $\beta$ -cristobalite.

The phase composition of the specimens after heating to 1300-1500°C consisted of mullite, spinel, and small quantities of  $\beta$ -cristobalite. During repeat heating to 1500°C before and after soaking the x-ray patterns for the specimen indicate that it is spinel. There were also weak lines for mullite and  $\beta$ -cristobalite. The results of the studies showed that during soaking at 1500°C the content of spinel increases on account of the reduction in the quantity of mullite. With an increase in the temperature and soaking time, we observe increases in the lines for spinel, and a reduction in the intensity of the lines for  $\text{NiO}$  and mullite. The formation of  $\beta$ -cristobalite occurs owing to the decomposition of the mullite. However, the intensity of the lines for  $\beta$ -cristobalite is very low. This suggests that part of the  $\text{SiO}_2$  is amorphous to x-rays, and is

TABLE 1. Chemical Composition of Starting Materials, %

Material	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	Alkalis
Commercial alumina . . .	0,04	99,49	0,01	0,05	0,02	0,01	0,38
Electrocorundum . . .	0,29	98,76	<0,02	0,39	0,08	0,01	0,45
Novoselitsk kaolin * . . .	52,07	45,11	1,43	0,69	0,44	0,08	0,17

\* Loss on ignition 13,4%.

TABLE 2. Mineral Composition of Specimens after Firing

Firing temperature, °C	Color	Composition, %			
		cryptocrystalline substance	mullite	corundum	NiO *
With an addition of 1% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$					
500	Light gray	60—65	8—10	25—30	—
900	"	60—65	8—10	25—30	—
1100	"	45—50	15—20	30—35	—
1200	"	40—45	20—25	30—35	—
1500	"	10—15	45—50	35—40	—
With addition of 10% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$					
500	Whitish	60—65	8—10	25—30	—
900	Pale blue	60—65	8—10	25—30	1—2
1100	"	45—50	15—20	30—35	1—2
1200	"	40—45	20—25	30—35	1—2
1300	"	25—30	35—40	30—35	1—2
1500	Same, in places blue	15—20	40—45	35—40†	—
With addition of 25% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$					
500	Gray	60—65	8—10	25—30	—
1300 †	Greenish-blue	20—25	20—25	30—35 ‡	1—2
1500 ‡	"	15—20	25—30	35—40 ‡	—

\* Content of  $\text{NiO}$  established with insufficient accuracy.

† At 1300°C contains 15-20%, at 1500°C 20-25%  $\beta$ - $\text{NiO} \cdot 5\text{Al}_2\text{O}_3$ .

‡ Corundum colored a greenish color.

contained in the specimen in the form of glass. The formation of spinel in the system  $\text{NiO}-\text{mullite}$  commences at  $1000^{\circ}\text{C}$ , while in the system  $\text{NiO}-\text{Al}_2\text{O}_3$  it commences at  $900^{\circ}\text{C}$ . This suggests that the reaction for the formation of nickel spinel occurs more rapidly during the reaction of  $\text{NiO}$  with corundum, and not with mullite. The spinel in the system  $\text{NiO}-3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  forms as a result of the decomposition of mullite by nickel oxide, which commences at  $1000^{\circ}\text{C}$ .

Special experiments were conducted to study the phase composition of high-alumina specimens containing an addition of nickel-containing catalyst during heating in reducing conditions. The specimens were prepared from high-alumina body, the composition of which is given above. The nickel nitrate was added in amounts of 25%. The specimens were fired at  $1300^{\circ}\text{C}$  in oxidizing conditions to form aluminonickel spinel, and then subjected to secondary firing at  $1400^{\circ}\text{C}$  in a reducing atmosphere for 30 min. The specimens were fired in hydrogen or a silicon carbide mixture.

Under the microscope it is seen that they consist of chamotte and gray-colored bond. The grains of chamotte are composed mainly of isometric mullite, and small quantities of corundum. The bond body is slightly transparent, and in immersion preparations it is seen that it consists of glassy substance, mullite, and corundum.

Among the new formations in reflected light we observed very small quantities of metal buttons. On the x-ray patterns there were lines of mullite, corundum, and nickel. The  $\text{NiAl}_2\text{O}_4$  is present in small quantities (Fig. 3), and furthermore the specimens fired in the hydrogen contain less nickel spinel than the specimens fired in the silicon carbide filling. Consequently, the reduction of the spinel occurs more rapidly when heated in hydrogen.

The study showed that with short heating (30 min) in hydrogen even at  $1400^{\circ}\text{C}$  a small quantity of spinel is preserved, that is, some of the nickel is located in the bonded form. In corundum specimens in similar conditions the spinel is completely destroyed.

## CONCLUSIONS

During heating in oxidizing atmospheres of mullite-corundum specimens with an addition of nickel nitrate at  $500-900^{\circ}\text{C}$ ,  $\text{NiO}$  is formed, and an increase in temperature from 900 to  $1500^{\circ}\text{C}$  is characterized by the development of nickel spinel,  $\text{NiAl}_2\text{O}_4$ , the quantity of which increases with an increase in the content of the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and the firing temperature.

The high temperature diffractometric method showed that in the system  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2-\text{NiO}$  heating in oxidizing conditions, and commencing at  $1000^{\circ}\text{C}$ ,  $\text{NiO}$  decomposes the mullite with the formation of aluminonickel spinel, whose quantity rapidly increases with further temperature rise. At  $1500^{\circ}\text{C}$  the mullite is preserved in small quantities.

The nickel spinel, formed as a result of heating to  $1300^{\circ}\text{C}$  the mullite-corundum refractory containing 25%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  during firing in the silicon carbide mixture and in the hydrogen atmosphere at  $1400^{\circ}\text{C}$  for 30 min, in the main decomposes with the separation of metallic nickel and corundum. However, x-ray patterns confirm that in these conditions the nickel spinel is not completely decomposed.

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