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Influence of Chromium-Containing Al$_2$O$_3$ Nanopowders on Structural Modifications in Aluminum Oxide Micropowders

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Influence of an additive of chromium-containing Al$_2$O$_3$ nanopowders on phase transitions in aluminum oxide micropowder (a waste from alumina production) is investigated. Aluminum oxide nanopowders were synthesized by shock-wave method. Chromium compounds were introduced during the synthesis as well as following annealing of powders. Main difference between obtained chromium-containing Al$_2$O$_3$ nanopowders was their phase composition. Mixtures of nanopowders and alumina macropowders were pressed and sintered. The additive of the Al$_2$O$_3$ nanopowder that was dopped with chromium ions during the synthesis and is characterized by the prevalence of θ-phase is demonstrated to be the most perspective for ceramics fabrication on the alumina base.

Keywords: aluminum oxide nanopowders, phase transition, corundum ceramics.

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Влияние добавок хромсодержащих нанопорошков Al₂O₃ на структурные изменения микропорошков оксида алюминия

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Исследовано влияние на фазовые превращения микропорошка оксида алюминия (отхода глиноземного производства) добавок хромсодержащих нанопорошков Al₂O₃. Нанопорошки оксида алюминия получали ударно-волновым синтезом, соединения хрома вводили как на стадии синтеза, так и при последующей термообработке порошков. Основное отличие полученных хромсодержащих нанопорошков Al₂O₃ заключалось в вариациях фазового состава. Смеси нанопорошков и микропорошка глинозема подвергали прессованию и спеканию. Показано, что для получения керамики на основе глинозема наиболее перспективно использование добавки нанопорошка оксида алюминия, легированного ионами хрома в условиях синтеза и характеризующегося преобладанием θ-фазы.

Ключевые слова: нанопорошки оксида алюминия, фазовые превращения, корундовая керамика.

Introduction

Nanopowders with various chemical compositions are widely applied as structure-forming additives for synthesis of composites and compacts. A type of the additive influence on properties of fabricated materials depends on number of factors including their synthesis method. It was shown that mechanical properties of the widely used corundum ceramics that is based on α-Al₂O₃ micropowder can be improved when a shock-wave synthesized nanopowder (NP) of aluminum oxide is used as an additive [1, 2]. These NPs are a fine fraction of products of the shock-wave pressurization of aluminum powder in the oxygen-containing atmosphere. An average particle radius is 38-40 nm with Al₂O₃ being in δ- and θ-modifications with a ratio of 7:1 [3]. NP additives lead to the reduction of grain size in ceramics. At early stages of sintering the most important factors are a phase composition of a NP [1] and, consequently, temperature ranges of phase transitions.

Earlier we demonstrated that the structure-forming additive of Al₂O₃ NP dopped by chromium ions during the synthesis allows to additionally improve properties of ceramics based on alumina powder (that is a flotation waste of alumina production) [4]. Corundum ceramics was produced by shock-wave compaction and sintering. The chromium-containing NP was obtained by the product fractionation after the shock-wave pressurization of a mixture of aluminum powder and ammonium dichromate (a precursor of trivalent chromium). Main differences of phase and chemical composition of these NPs from additives used in [1, 2] are the prevalence of θ-Al₂O₃ (65%) and the presence of α-Al₂O₃ (5%) and chromium of 1.2% both as a solid solution of Cr₂O₃ in α- and θ-Al₂O₃ and "free" Cr₂O₃ [5]. In comparison with undopped NPs the density of an obtained ceramics was increased by 15%, its microhardness grew by 10-15% [4] while its microstructure practically didn't change. Considering a low Cr₂O₃ content in

mixtures that were used in our experiments (0.18%), we presume that phase transitions in NPs and their influence on processes taking place during alumina sintering play a key role. However, the influence of the chromium oxide presence on the corundum formation in alumina can not be excluded as e.g. in [6] it was shown that the addition of 0.2% Cr_2O_3 to aluminum hydroxide accelerates the corundum formation (though it does not affect the temperature range of the phase transition).

We also obtained chromium-containing shock-wave synthesized NPs of aluminum oxide by the thermal processing of its mixture with ammonium dichromate. When such NPs are heated up to 1000°C δ-Al_2O_3 prevails, chromium partially incorporates to the lattice of α-phase and solid solution in θ-Al_2O_3 does not form. Therefore, the phase composition of Al_2O_3 and the chromium state in NPs differ for NPs that are dopped by Cr ions during synthesis and obtained by thermal processing of Al_2O_3 mixture with ammonium dichromate. The influence of additives of different chromium-containing NPs on phase transitions of alumina and properties of obtained ceramics have not been studied before.

The relevant issue of the rational usage of alumina production waste combined with a high efficiency of shock-wave synthesis of aluminum oxide nanopowders calls for studies focusing on the detection of factors that would enable to fabricate NP-based ceramics with improved properties.

In this work we investigated phase transitions in Al_2O_3 during annealing of chromium-containing shock-wave synthesized NPs and their mixtures with alumina micropowder that is a waste from alumina production (Achinsk alumina refinery).

Methods

Shock-wave synthesized nanopowders of aluminum oxide were studied: chromium-free NP-1, NP-2 with an additive of ammonium dichromate, NP-3 that was doped with chromium(III) ions during the explosion and their mixtures with alumina micropowders (an average particle radius of 2.6 micron). Mixtures of micropowders with 10% mass NP (a NP content is equivalent to the one used in [4]) were obtained by the ultrasonic dispersion of an ethanol suspension (UZDN-A, frequency of 22 kHz) followed by desiccation. Derivatographs Q-1500 и Netzsch STA 449 were used for differential thermal analysis (DTA). X-ray diffraction (XRD) was carried out at the powder diffractometer DRON-4 with monochromatic CuK_{α} emission. Data from [7] and the ASTM catalogue were used to identify phases. When a maximum intensity peak of one phase coincided with some reflexes of a different phase, the relative phase content was estimated by intensity values of single peaks as described in [5].

Compression of powder mixtures was carried out at a hydraulic press at the pressure of 1 GPa. 3% solution of polyvinyl alcohol was used as plasticizer. High-temperature furnace SVTP–1650 was used for thermal processing of powders and sintering. Ceramics microhardness was measured by Vickers hardness test (PMT-3M). The reported results were averaged by 3-5 parallel experiments.

Results and discussion

According to XRD data NP-1 contains only δ- and θ-Al_2O_3 with a ratio of 7:1. The same phase ratio is observed for NP-2 that differs only by chemical composition with 1.2% of chromium. The same amount of chromium is presented in NP-3 where θ-Al_2O_3 prevails and α-phase is observed: the ratio of θ-, δ- and α-Al_2O_3 is 13:7:1. According to the most wide spread literature data corundum formation with annealing of δ-Al_2O_3 that is presented in all NP samples goes via an intermediate stage of θ-phase (at 1050°C) and subsequent transition $\theta\rightarrow\alpha$ takes place at 1200°C [8]. Nevertheless, at

nonisothermic heating conditions with the rate of 15°C/min DTA curves for all NPs under investigation are characterized with the presence of the only peak with the maximum at temperatures above 1200°C with the narrowest one being observed for NP-3. Characteristic points of derivatogramms and calculated values of activation energies of Al_2O_3 phase transitions are listed in Table 1.

Calculated values of activation energies coincide within error limits for all the samples and they are close to the average one for the transition $\delta \rightarrow \theta$-$Al_2O_3$ when overlapped with the transition $\theta \rightarrow \alpha$: 669 kJ/mole [9]. Obviously, same overlapping is observed in our experiments as well. Comparison of DTA data for NP-1 and NP-2 (Table 1) demonstrates the Cr_2O_3 influence on the acceleration of corundum formation. A narrower exo-effect peak at the NP-3 DTA curve corresponds to the NP phase composition: prevailing of θ-phase and presence of α-Al_2O_3. DTA data for alumina micropowder are presented in Fig. 1.

Low- and high-temperature peaks on the DTA curve agree well with literature data for aluminum hydroxides: endothermic effects at 130–160°C are due to unbounded water [10], up to 400°C bounded or structural water is removed [11] and exothermic effect at temperatures above 1200°C is due to α-Al_2O_3 crystallization [10]. According to NMR-spectroscopical data [11] for temperatures of 400–600°C γ-Al_2O_3 forms and at 700°C δ- and θ-Al_2O_3 appear that are transformed to corundum under following heating.

A diffractogram of alumina powder demonstrated its low degree of crystallinity. The most pronounced peak corresponds to $2\theta \approx 67.3°$, but for this angle reflexes of γ-, κ-, θ-, δ-Al_2O_3 can be observed. Only presence of κ–phase can be reliably identified with a maximum at $2\theta \approx 42.6°$, as there is no overlapping with other phases.

Exo-effects at the DTA curve for temperatures above 800°C (Fig. 1) are due to phase transitions of Al_2O_3. XRD data (Fig. 2) shows that annealing of alumina micropowder at 800°C during 2 hours

Table 1. DTA results for NPs

Sample number	T_{init}, °C	T_{fin}, °C	T_{max}, °C	E_{act}, kJ/mole
NP-1	1262	1397	1300	686±25
NP-2	1150	1300	1225	685±31
NP-3	1150	1260	1220	689±36
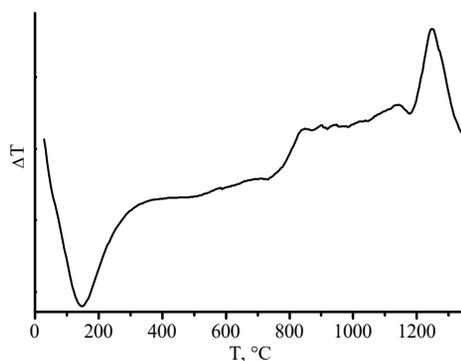
Fig. 1. DTA curve for alumina micropowder
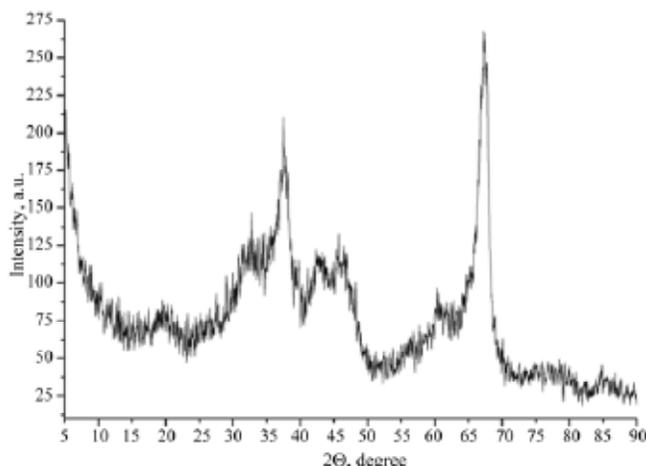
Fig. 2. Diffractogram of alumina micropowder after annealing at 800°C

results in a higher degree of crystallinity of the sample and arising of γ-phase that is identified by a reflex at $2\theta \approx 60.9°$. Calculated ratio of κ- and γ-Al_2O_3 was approximately 1:1.

DTA analysis reveals that the influence of additive of the aluminum oxide nanopowder NP-1 on alumina phase transition mainly results in a more pronounced exo-effect in the range between 730–1000°C, some decrease of the temperature of the maximum related to α-Al_2O_3 formation and a significant drop of the enthalpy of this process from 19 to 4 kJ/mole. According to XRD data after annealing at 800°C during 2 hours such mixture contains δ-Al_2O_3 (a peak at $2\theta \approx 34.5°$) and α-Al_2O_3 ($2\theta \approx 43.3°$) with the ratio of 5:1. We believe that the presence of δ-phase is related to the NP-1 phase composition (with prevailing δ-Al_2O_3) and corresponding stimulation of the transition from γ-Al_2O_3 to δ-phase in alumina. Heat release from this transition initiates corundum formation mostly from κ-Al_2O_3 that is characterized by a direct transition κ→α-Al_2O_3 [8]. Decrease of heat release above 1200°C is explained with the fact that a significant part of corundum has already formed before.

Presence of ammonium dichromate in this mixture (alumina with NP-2) results in a pronounced peak at DTA curves that corresponds to exo-effect in the temperature range 735–930°C with a maximum at 836°C. Apart from δ- and α-Al_2O_3 diffractogramms of these samples reveal the presence of θ-phase ($2\theta \approx 38.7°$) and traces of γ-Al_2O_3. The ratio of δ-, θ- и α-Al_2O_3 is around 6:3:1. We suggest that the presence of chromium oxide facilitates the crystallization of γ-Al_2O_3 from an amorphous alumina phase. This agrees well with data from [12] about influence of Cr_2O_3 on the decrease of crystallization temperature of γ-Al_2O_3 in powders that were obtained by thermal decomposition of aluminum hydroxide. Stimulating effect of Cr_2O_3 on formation of δ- и θ-Al_2O_3 under annealing of γ-Al_2O_3 was indicated in [13].

When compared with DTA data for these samples the mixture of alumina with NP-3 demonstrates less pronounced exo-effects in the medium-temperature range and there is no distinct peak with a maximum at 836°C. In the high-temperature range significant differences were not observed for characteristic points. For 750–950°C exo-effects are less pronounced also when compared with the alumina mixture with NP-1.

The main difference of phase composition of this powder mixture after annealing at 800°C and the alumina mixture with NP-2 is a slight increase of α-phase relative content when compared with other phases that is explained with the presence of α-Al₂O₃ in NP-3.

It is obvious that less pronounced exo-effects at 750–950°C are caused by significant decrease of δ-Al₂O₃ fraction in an original mixture: from ∼ 9% in mixtures with NP-1 and NP-2 down to 3%. This decrease of δ-phase that stimulates the transition γ → δ-Al₂O₃ in alumina results in corresponding decrease of γ-oxide that was transformed in this temperature range.

A stepped sintering regime was used for ceramics fabrication from mixtures of alumina micropowders with Al₂O₃ NPs according to DTA data. It included a linear heating with a rate of 15°C/min and isothermic stages: annealing at 400°C during 2 hours to remove unbounded and structural water completely, annealing at 800 and 1200°C during one hour for transformation accompanying phase transitions and one hour annealing at 1600°C. Microhardness measurements have shown practically identical (within the limits of experimental error) values of this property for sintered samples fabricated with NP-1 and NP-2 additives. Microhardness of NP-3 sample was higher by factor of 1.4–1.5.

Thus, the presence of small amount of chromium oxide in NP-2 additive nearly did not influenced microhardness of fabricated ceramics. The main factor of the microhardness increase for samples produced with NP-3 was a lower intensity of phase transitions at early sintering stages. Respectively, the local heating caused by their exo-effects was less steep. It could reduce the formation of closed pores that are "trapped" when particles are "baked". The density increase for samples with NP-3 additive when compared with sintered mixtures of alumina with NP-1 and NP-2 confirms this suggestion.

Conclusion

The additive of ammonium dichromate (precursor of Cr₂O₃) in amount that was considered in this work to shock-wave synthesized nanopowder of aluminum oxide practically does not influence microhardeness and density of ceramics that was sintered from alumina mixture with Al₂O₃ nanopowders. The increase of ceramics microhardeness and density that was obtained when aluminum oxide was dopped by chromium ions during shock-wave synthesis are mainly caused by differences of its phase composition and corresponding influence on alumina phase transition.

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