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ARTICLE

In-situ Cr-doped Alumina Nanorods Powder Prepared by Hydrothermal Method

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Abstract: Cr-doped ammonium aluminum carbonate hydroxide nanorods were prepared by a hydrothermal method, with $Al(NO_3)_3\ 9H_2O$, $Cr(NO_3)_3\ 9H_2O$, and urea as raw materials and PEG-20000 as surfactant. In-situ Cr-doped alumina nanorods powder was obtained through calcining its precursors (Cr-doped ammonium carbonate hydroxide nanorods) at 1200 ℃. The crystal composition, the structure and the morphology of the as-prepared products were characterized by XRD, SEM and FTIR. Besides, the color performances of the products were analyzed by UV/Vis/NIR spectrometer and automatic color measurement. Results show that the precursors of Cr-doped alumina nanorods powder prepared by the hydrothermal method are composed of uniform nanorods. After its calcinations at 1200 ℃, the in-situ doping of Cr in the alumina substrate is achieved. In the Cr-doped alumina nanorods powder, a continuous solid solution of Cr_2O_3 and Al_2O_3 is formed, which has a corundum crystal structure. With the increasing Cr content, Cr-doped ammonium aluminum carbonate hydroxide nanorods gradually become short, and the melting phenomenon occurs in calcined products. UV-Vis spectroscopy analysis shows that Cr-doped alumina nanorods powder has three strong absorption bands at 562, 406 and 372 nm, thus leading to a pink color for samples which is in agreement with chromatic data. In the present study, Cr-doped alumina nanorods powder prepared by the hydrothermal method can reduce the formation temperature of corundum crystal structures and resolve the problem of mixing homogeneity of Al_2O_3 and Cr_2O_3, which will contribute to the preparation and the application of alumina-chrome refractory, pink corundum abrasive and ceramic pigment.

Key words: chromium doping; alumina; hydrothermal method

In recent years, chromium-alumina solid solutions have received special attention due to their wide applications in ceramics industry. For example, alumina-chrome refractories have been applied in various forms, such as castables and shaped refractory in blast furnaces, electric arc furnaces, fiber glass furnaces, gasification melting furnaces and various corrosion resistance refractories because of their superior mechanical properties, low solubility, chemical stability, corrosion resistance, and thermal shock resistance [1-4]. The powder of the so-called pink corundum, a solid solution of Al_2O_3 and Cr_2O_3, is a common and useful abrasive in grinding wheels owing to its superior hardness and thermal shock resistances[5]. The addition of chromium oxide to alumina has been found to increase the hardness and the tensile strength of alumina, and improve its resistance to thermal shock and its corrosion behavior[6,7]. Besides, the Cr-doped α-Al_2O_3 powder, chromium presenting in the octahedral site of the corundum lattice, is a kind of traditional pink pigment used at high temperatures[8]. Due to the high toxicity and sustainability of this pigment, lately the research on ceramic pigments has been dedicated to improve traditional color systems from an environmental point of view and maintain their color performance. Moreover, the ceramic pigment must meet the growing demands of fine ceramics decoration.

The conventional preparation of chromium-alumina solid solutions by a solid state route is based on an interdiffusion reaction between the reagents. The high temperature and mixing homogeneity of Al_2O_3 and Cr_2O_3 used for its synthesis restrict the preparation, the investigation, and the application of this kind of solid solution[9,10]. Therefore, there is a growing interest

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in "nonconventional" methods of synthesis that can be achieved under lower temperature conditions. Of the chemical methods, the hydrothermal method gives rise to homogeneous nucleation and growth in aqueous solution, and produces the materials with controllable particle sizes and high purity at low temperature[11]. In the present study, we proposed a hydrothermal method to prepare the precursors (Cr-doped ammonium aluminum carbonate hydroxide) of Cr-doped alumina nanorods powder. In-situ Cr-doped alumina nanorods powder could be obtained through calcining its precursors at 1200 ℃. The crystal composition, the structure and the morphology of the as-prepared products were characterized by XRD, SEM and FTIR. Also, the color performances of the products were analyzed by UV/Vis/NIR spectrometer and automatic color measurement.

1 Experiment

All chemicals were analytical-grade regents without further purification. In a typical synthesis, 0.4 mmol of poly-glycol (PEG)-20000 was dissolved in 35 mL deionized water to form a clear solution, in which 2.0 mmol $Al(NO_3)_3$ $9H_2O$ and an appropriate amount of $Cr(NO_3)_3$ $9H_2O$ (Cr^{3+}/Al^{3+}=0~0.2) were added. After the aluminum and chromium salts were totally dissolved to form a green solution, 0.36 mmol of urea was added. Further, the mixed solution was magnetically stirred for 3 h. Then the solution was transferred into a Teflon-lined autoclave and placed in an oven at 120 ℃ for 24 h. After cooling to room temperature, the gray precipitation was collected and washed several times with deionized water and ethanol to remove the impurities and then dried at 80 ℃. To obtain Cr-doped alumina nanorods powder, the products were calcined at 1200 ℃ for 2 h in a muffle electrical furnace.

The crystal structures of the samples were characterized using X-ray diffraction (XRD-D/max 2200pc, Japan) with Cu Kα radiation of wavelength λ=0.154 18 nm. The microscopic features of the samples were characterized with a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) operated at 5 kV. Fourier transform infrared (FT-IR) spectrometer (JASCO FT/IR-470, Janpan) was used for detecting the precursor of Cr-doped alumina nanorods powder. The diffuse reflectance spectrum of products was analyzed using an UV/Vis/NIR spectrometer (Perkin Elmer, Lambda 950, USA). The colors of products were evaluated according to the Comission Internationale de l'Eclairage (CIE) using an automatic color measurement (ADCI-60-C, Beijing). In this system, L^* is the color lightness (L^*=0 for black and L^*=1 for white), a^* is the green (−)/red (+) axis, and b^* is the blue (−)/yellow (+) axis.

2 Results and Discussion

2.1 XRD analysis

The XRD patterns of the precursors of Cr-doped alumina nanorods powder are shown in Fig.1. It can be seen that the XRD pattern of 10%Cr-samples precursors are very similar to that of the virgin samples, and all of the diffraction peaks can be indexed to crystalline ammonium aluminum carbonate hydroxide (AACH, JCPDS card No.42-0250). The high intensities and sharp peaks in Fig.1 indicate that the phase of the precursors synthesized in the present work is well crystallized. No other diffraction peaks are detected, suggesting that no impurities exist in the precursors of Cr-doped alumina nanorods powder, and that the Cr which is in-situ doped in the precursor is achieved by the hydrothermal method.

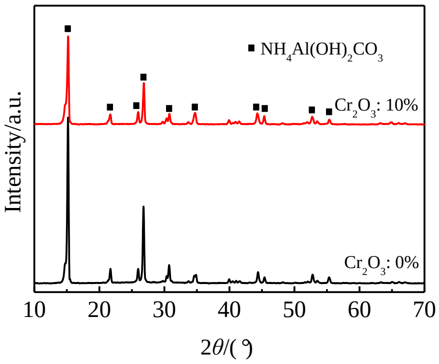

Fig.1 XRD patterns of the precursors of Cr-doped alumina nanorods powder

Fig.2 shows the XRD patterns of Cr doped alumina nanorods powder after calcining the precursors at 1200 ℃. According to XRD results, $Al_{2-x}Cr_xO_3$ is the main phase of the samples. The Al_2O_3-Cr_2O_3 system is a continuous solid solution in which the solute is completely incorporated in the lattice [12,13]. Hence, it shows the single phase XRD patterns of $Al_{2-x}Cr_xO_3$, which has a corundum crystal structure. The only difference in the XRD patterns is that the location of peaks are shifted due to expansions of the lattice, which can be seen from the (104) crystal face of the enlarged XRD pattern (Fig.3). As the ionic radius of Cr^{3+} (0.0615 nm) is larger than that of Al^{3+} (0.0535 nm) [14], the corresponding peaks of the samples shift from higher angles to lower angles with increasing of Cr content. The lattice constants *a* and *c* calculated from the Rietveld refinement versus Cr concentration are plotted in Fig.4, showing the linear dependence of both lattice constants

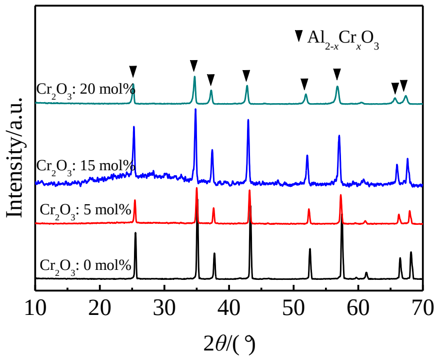

Fig.2 XRD patterns of Cr-doped alumina nanorods powder after calcining the precursors at 1200 ℃

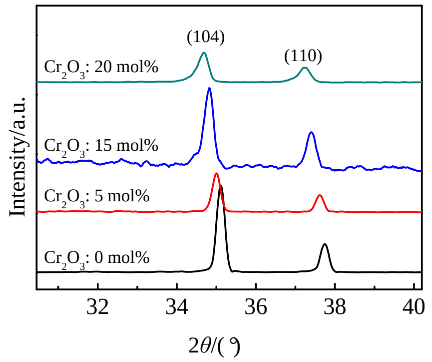

Fig.3 Partially enlarged XRD patterns of Cr-doped alumina nanorods powder ((104) crystal face)

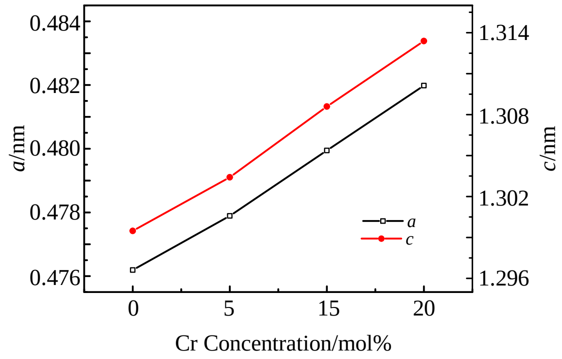

Fig.4 Lattice constants of Cr-doped alumina nanorods powder

on Cr concentration. The Vegard's law works well in this case, which further illustrates the formation of solid solutions.

2.2 Morphology analysis

Fig.5 shows SEM morphologies of the precursors and Cr-doped alumina nanorods powders obtained after calcining the precursors at 1200 ℃. The precursors prepared by the hydrothermal method are composed of uniform nanorod. With increasing Cr content, the length of the nanorods becomes shorter. When the concentration of Cr doped in alumina is 20%, the lengths of the nanorods in precursors are 1~1.5 μm and the diameter is about 300 nm. After calcining the precursors at 1200 ℃, the morphologies of Cr-doped alumina nanorods powder are similar to those of their precursors, but the nanorods shrink and some become broken. This is associated with the decomposition of AACH in the calcinations process, releasing CO_2, NH_3, and H_2O. With increasing Cr content, melting of nanorods occurs in samples, which is associated with the action of fluxing and decreasing of sintering temperature of Cr_2O_3 added to Al_2O_3.

2.3 FT-IR analysis

The FT-IR spectra of the precursors and Cr-doped alumina nano-powder obtained after calcining the precursors at 1200 ℃ were performed by a FT-IR spectrometer (Fig.6). Fig.6a is the FT-IR spectrum of the precursors of 5%Cr-doped alumina nanorods powder. It shows that the broad band is around 3446 cm^{-1}, which is assigned to stretching vibration of adsorbed water[15]. The weak peak at 1637 cm^{-1} is assigned to the $\delta(H_2O)$ bending vibration of the absorbed water from the air in the sample preparation process. The bands at 1452 and 1539 cm^{-1} are attributed to asymmetric stretching modes of CO_3^{2-}. The split of this double degenerate peak exhibits that the CO_3^{2-} in the AACH belongs to the structural carbonate group. The weak peak at 1390 cm^{-1} is due to the asymmetric stretching vibration of NH_4^+. The peak at 981 cm^{-1} belongs to the CH_2-stretching vibration, which originates from the PEG sur- factant. The peaks at 1127, 620 and 482 cm^{-1} belong to the Al-O and Cr-O stretching vibrations. In the spectrum of calcined products shown in Fig.6b, the peaks at 1637 cm^{-1} and in the region 3415~3551 cm^{-1} are due to the bending and stretching vibration of absorbed water from the air in the sample

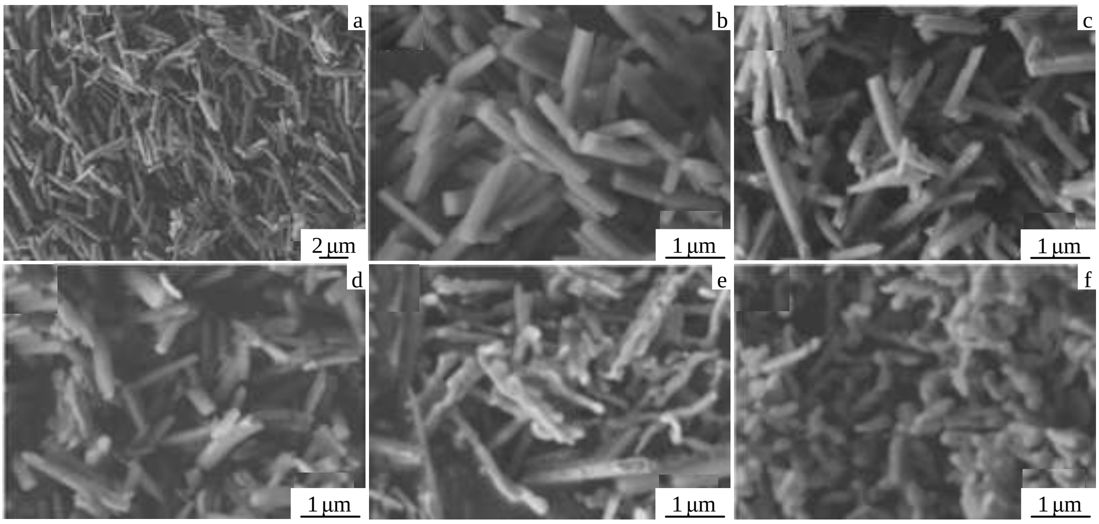

Fig.5 SEM images of the precursors with the contents of 10%Cr (a) and 20%Cr (b); Cr-doped alumina nanorods powder with the content of 0%Cr (c), 5%Cr (d), 10%Cr (e), and 20%Cr (f)

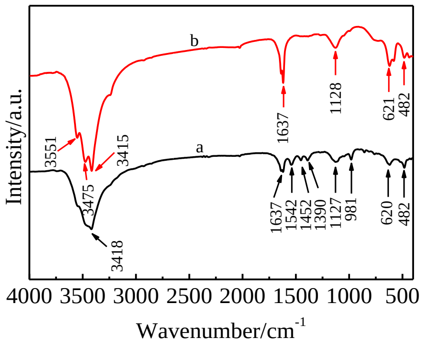

Fig.6 FT-IR spectra of the precursors (a) and 5% Cr-doped alumina nanorods powder

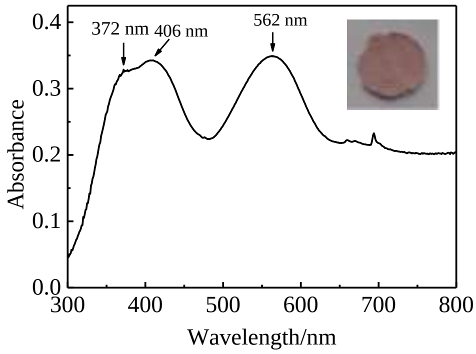

Fig.7 Diffuse reflectance spectrum and color of Cr-doped alumina nanorods powder

preparation process. The peaks at 1128, 621 and 482 cm^{-1} are assigned to the Al-O and Cr-O stretching vibrations. Compared to the FT-IR spectrum of the precursors, all absorption peaks of carbonate, ammonium and organic groups vanish, indicating complete decomposition of AACH and the formation of Cr-doped alumina nanorods powder.

2.4 Diffuse reflectance spectra and chromaticity data

In order to study the surrounding of the Cr^{3+} chromophore in the solid solution, 20% Cr-doped alumina nanorods powder, a representative of Cr-doped alumina nanorods powder, was analyzed by UV-vis spectroscopy diffuse reflectance. The spectrum is presented in Fig.7. It shows that the powder has three strong absorption bands at 562, 406 and 372 nm, which is related to d-d electronic transitions of Cr^{3+}. The theory of the Ligand field for a Cr^{3+} in an octahedral coordination predicts the existence of three absorption bands. These three absorption bands are attributed to the energies of electronic spin allowed transitions, which are described as follows:

$$^4A_{2g}\rightarrow{}^4T_{2g(F)} \qquad (1)$$

$$^4A_{2g}\rightarrow{}^4T_{1g(F)} \qquad (2)$$

$$^4A_{2g}\rightarrow{}^4T_{1g(P)} \qquad (3)$$

The energies of the first two electronic spin allowed transitions correspond to visible light energies, whereas the energy of the third spin allowed transition corresponds to ultraviolet light that does not affect the color. Depending on the Ligand field created by the oxide ions, the position of these bands can be modified, resulting in a variation in the observed coloration. According to Ref.[6], the absorption bands of pure Cr_2O_3 appear at 445 and 590 nm. Yet, we can observe in Fig.7 that these two absorption bands for the measured sample appear at wavelength values lower than that of the pure Cr_2O_3 ones. This shift can be attributed to an increase in the intensity of the Ligand field due to a decrease of the Cr-O distances produced by the substitution of Al^{3+} by larger Cr^{3+} in the corundum structure. In the spectrum, the pink shade is associated with the absorption bands at 562 and 406 nm, which explains the existence of this coloration and agrees with chromatic data (Table 1). In the case of low Cr concentration (≤20 mol%), the samples exhibit pink tonalities. With increasing Cr concentration, the a^* values of samples gradually decrease, and the color of samples becomes gray. If the Cr content is continuously increased, the products will become the Cr_2O_3-Al_2O_3 green ceramic pigment based on a $Cr_{2-x}Al_xO_3$ solid solution.

2.5 Formation mechanism of Cr-doped alumina nanorod

In the solution reaction process, urea is used as a dual-role agent, not only as a source of carbonate, but also as a slow-released pH adjusting agent. At the initial stage, the pH value of the synthesis system is about 2.8, and it is observed that the synthesis system remains transparent before the hydrothermal treatment. As the hydrothermal treatment goes on, urea begins to decompose with the onset of the following reaction:

$$CO(NH_2)_2+H_2O\rightarrow CO_2\uparrow+2NH_3 \qquad (4)$$

$$\begin{aligned}&Al(NO_3)_3/Cr(NO_3)_3+4NH_3+CO_2+3H_2O\rightarrow\\&\quad NH_4[Al(OOH)HCO_3]/NH_4[Cr(OOH)HCO_3]\downarrow\\&\quad +3NH_4NO_3\end{aligned} \qquad (5)$$

$$CO(NH_2)_2+3H_2O+CO_2\rightarrow 2NH_4HCO_3 \qquad (6)$$

Combining the above reactions yields an overall reaction:

$$\begin{aligned}&Al(NO_3)_3/Cr(NO_3)_3+3CO(NH_2)_2+8H_2O\rightarrow\\&\quad NH_4[Al(OOH)HCO_3]/NH_4[Cr(OOH)HCO_3]\downarrow\\&\quad +3NH_4NO_3+2NH_4HCO_3\end{aligned} \qquad (7)$$

In the calcination process, the AACH is converted to Cr-doped alumina by release of H_2O, NH_3 and CO_2 with the elevating temperature, as described in the following equation:

$$\begin{aligned}&NH_4[Al(OOH)HCO_3]/NH_4[Cr(OOH)HCO_3]\rightarrow\\&AlOOH/CrOOH+CO_2+NH_3\end{aligned} \qquad (8)$$

$$AlOOH/CrOOH\rightarrow Cr_xAl_{2-x}O_3+H_2O \qquad (9)$$

Combining the above reactions yields an overall reaction:

$$\begin{aligned}&NH_4[Al(OOH)HCO_3]/NH_4[Cr(OOH)HCO_3]\rightarrow\\&\quad Cr_xAl_{2-x}O_3+CO_2+NH_3\end{aligned} \qquad (10)$$

Table 1 Chromatic data of Cr-doped alumina nanorods powder

Cr content/mol%	L^*	a^*	b^*
5	89.00	7.88	3.88
10	84.99	6.13	2.19
15	80.91	5.62	2.01
20	78.91	5.35	2.78

Bai and co-workers reported the formation mechanism of alumina microfibers synthesized by homogeneous precipitation using PEG as surfactant. We propose that the growth process of Cr-doped alumina nanorods is similar to the formation of alumina microfibers. Initially, the AACH nanocrystals are formed through the above proposed reactions because of the homogeneous increase in pH in the system with urea decomposition. These AACH nanocrystals are adsorbed on the PEG micelles and undergo a surfactant induced fiber formation (SIFF) mechanism to produce the AACH/PEG nanofibers. Then the resulting AACH/PEG nanofibers aggregate into AACH/PEG nanorods through a layer-by-layer self-assembly mechanism. Further the growth of the nanorods may proceed through Ostwarld ripening, during which large AACH/PEG nanorods become larger while smaller AACH/PEG nanorods and AACH nanocrystals disappear. Then the AACH processor is conveniently converted into the Cr-doped alumina nanorods followed by a calcination process without deformation of the microstructures.

3 Conclusions

1) Cr-doped ammonium aluminum carbonate hydroxide nanorods can be prepared by the hydrothermal method. After calcination at 1200 ℃, Cr-doped alumina nanorods powder is obtained, which has a continuous solid solution of Cr_2O_3 and Al_2O_3 with a corundum crystal structure.

2) With increasing Cr content, Cr-doped ammonium aluminum carbonate hydroxide nanorods gradually become short, and the melting phenomenon occurs in calcined products.

3) Cr-doped alumina nanorods powder has three strong absorption bands at 562, 406 and 372 nm, thus leading to a pink color for samples, which is in agreement with chromatic data.

4) The in-situ doping of Cr in the alumina substrate improves mixing homogeneity of Al_2O_3 and Cr_2O_3, which will be contributed to the preparation and the application of alumina-chrome refractories, pink corundum abrasive and ceramic pigment.

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原位铬掺杂氧化铝纳米棒的水热合成

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摘　要：以 $Al(NO_3)_3\ 9H_2O$、$Cr(NO_3)_3\ 9H_2O$ 和尿素为原料，PEG-20000 为表面活性剂，采用水热法合成了铬掺杂碳酸铝铵纳米棒，经 1200 ℃煅烧后，成功制备原位铬掺杂氧化铝纳米棒。利用 XRD、SEM 和 FTIR 对产物晶相组成、结构和形貌进行了表征，采用 UV-Vis 光谱和全自动测色色差计对产物的呈色性能进行测试。结果表明：铬掺杂碳酸铝铵纳米棒经 1200 ℃煅烧后，实现了铬在氧化铝基体中的原位掺杂，两者形成了完全固溶体，固溶体晶体结构为刚玉型。随着铬掺杂量的增加，所制备的碳酸铝铵纳米棒长度变短，煅烧后的产物出现熔融现象。样品的紫外可见吸收光谱结果表明，制备的铬掺杂氧化铝基纳米粉体分别在 372，406，562 nm 存在较强的吸收峰，因而样品会呈现淡红色，这与全自动测色色差计测得的色度值相一致。利用水热合成原位铬掺杂氧化铝纳米棒提高了铬与氧化铝的混合均匀度，在较低温度下生成了刚玉相，有助于刚玉型耐火材料、刚玉磨料和铬铝红颜料的制备与应用。

关键词：铬掺杂；氧化铝；水热法

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