SYNTHESIS OF Al₂O₃-Ni COMPOSITE POWDERS BY CO-PRECIPITATION METHOD

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Received: August 2016 Accepted: March 2017

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Abstract: The synthesis of micro-sized, uniformly distributed Al₂O₃-15Vol% Ni powders were studied through three
step co-precipitation of hydroxides mixtures from proper solution, calcination at air atmosphere and final step of
calcined powders in a carbon bed. Al and Ni hydroxide and amorphous phase were first obtained from their salt’s
solutions through chemical co-precipitation method by adjusting pH. The precipitated powders were then calcined to
obtain a mixture of their oxides as NiO and NiAl₂O₄ which were reduced in a carbon bed at various temperatures up
to 1300°C. Proper temperature for calcination in air was determined through TG analysis; 900°C. SEM observation
of powders after reduction, revealed micro-sized Ni particles, along with fine distribution of Ni and Al₂O₃ elements.
XRD analysis of the calcined sample showed the presence of NiAl₂O₄ and NiO and the same analysis for the reduced
sample confirmed the formation of Al₂O₃ and Ni.

Keywords: Composite, Al₂O₃-Ni, Carbon Bed, Carbon Bed, Co-Precipitation, NiAl₂O₄

1. INTRODUCTION

Alumina is a widely used ceramics for structural applications because it has high mechanical properties, thermal stability and
corrosion resistant properties[1]. However, alumina ceramics are brittle with regard to fracture toughness. It well recognized that the
fracture toughness of brittle ceramic materials can be increased by the addition of a dispersed second phase such as a ductile metal[2, 3]. The
metallic phase can be either continuous or in the form of particulates homogeneously dispersed in the ceramic matrix. Furthermore, a
microstructure with a highly-interconnected ceramic and metal network might offer some unique characteristics, since the continuous metal and
ceramic phase could lead to improved fracture toughness and creep resistance respectively. Typically, ceramic-metal
composites have been produced by dry mixing of ceramic and metal powders followed by hot pressing or sintering. This process is often
difficult to control resulting in non-uniform dispersion of the components. In contrast, chemical techniques offer several advantages
compared with traditional powder processing techniques such as greater control over stoichiometry and microstructure. In addition,
some chemical techniques have the advantage of simplicity and low cost, and they can be readily scaled up[4]. Although a small-scale
homogeneity can be obtained using the sol-gel rout, the relatively high cost of some reactants and the difficulty to control the gel-drying step
are drawbacks of the method[5]. The results of some studies, have demonstrated that the heterogeneous precipitation method is able to
overcome difficulties in the second phase dispersion in matrix. Based on this method, two different salts precursors are utilized to produce the
hydroxide or other composition of cation [6]. The literature on Al₂O₃-Ni composites prepared by the chemical method are few, so the present
study aimed at synthesizing Al₂O₃-20vol%Ni submicron powders by chemical rout and produce a homogenously dispersed powder with
a narrow size range. Understanding and optimizing the precipitation process to achieve this was objective of the study as little is known
for the Al₂O₃-Ni system in that regard.

2. EXPERIMENTAL

The precursor of Al₂O₃ and Ni were aqueous solutions which were prepared by separately
dissolving 33.15 gr of Al(NO₃)₃·3H₂O (99.0% purity, china) and 12.92 gr of NiSO₄·6H₂O (99.0% purity, china) salts in the 150 ml and 125 ml distilled water, respectively. Concentration of Al and Ni ions was based on the stoichiometric proportions to produce a final Al₂O₃·20vol%Ni powder. The two precursor solutions were then mixed together and heated on a stirrer hot plate at 60°C. To adjust the pH to 8.8, ammonia solution was drop wise added and stirred for 2 h, in order to have desirable precipitated. The precipitate was separated by filtering and the remained solution was analyzed by ICP-OES determine any residual reactant elements. The precipitants were rinsed with water for several times and then dried at 110°C for 24 h. Qualitative information about the different stretching and bending bonds at co-precipitation powders was studied with Fourier transformed infra-red spectrometry (FTIR, model Perkin Elmen) In order to determine the appropriate calcination temperature, the dried sample was subjected to thermogravimetry analysis (TG) up to 1200°C with a heating rate of 10°C/min(model D-32609 Hullhorst). Then the dried sample was calcined in an electrical muffle furnace at 900°C for 4 h in air to obtain oxide powders. The temperature for complete reduction of oxide phases in a carbon bed was determined by heating samples at various temperature ranges from 1000°C up to 1300°C at the rate of 10°C/min in a carbon bed. The products were analyzed by XRD (Siemens-Germany, Cu-Kα) to identify the present phases. The microstructure and morphology of the reduced powder and also their homogeneity were studied by scanning electron microscope (VEGA TESCAN Environmental SEM). Al and Ni distribution of material in different stages were investigated by elemental mapping using Energy-dispersive spectroscopy (EDS, model EPMH-8705Q_H₂).

3. RESULTS AND DISCUSSION

3. 1. Precipitation

The color of the precursor salts of Al and Ni were white and green, respectively. The nickel salt NiSO₄·6H₂O is dissolved in water by ionizing to Ni²⁺ and SO₄²⁻ resulting in an acidic solution. The aluminum salt Al(NO₃)₃·3H₂O is dissolved in water by ionizing to Al³⁺ and NO₃⁻, according to reactions.

\[
\text{Al(NO}_3)_3\cdot3\text{H}_2\text{O} \rightarrow \text{Al}^{3+} + 9\text{NO}_3^- + 3\text{H}_2\text{O} \quad [7] \quad (1)
\]

\[
\text{NiSO}_4\cdot6\text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + \text{SO}_4^{2+} + 6\text{H}_2\text{O} \quad [8] \quad (2)
\]

After ionizing reactions, hydrolysis reactions have been occurred due to the following reactions[7, 8];

\[
\text{Al}^{3+} + 6\text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O})_6]^{3+} \quad (3)
\]

\[
\text{Ni}^{2+} + 6\text{H}_2\text{O} \rightarrow [\text{Ni(H}_2\text{O})_6]^{3+} \quad (4)
\]

In second step, ammonia was added to the mixture solution to change the pH of the environment. The dissolution of ammonia in water produce OH⁻ and NH₄⁺ ions. In this case, Al precipitate as Al(OH)₃ and Ni precipitate as Ni(OH)₂ and NiOOH. The pH of the solution after adding adequate ammonia was about 8.8 and the color of the precipitates were light green. Equations (5-11) represent the suggested reactions[9-11];

\[
[\text{Al(H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3(\text{H}_2\text{O})_3 + 3\text{H}_2\text{O} \quad (5)
\]

\[
\text{Al(OH)}_3(\text{H}_2\text{O})_3 \rightarrow \text{Al(OH)}_3 + 3\text{H}_2\text{O} \quad (6)
\]

\[
[\text{Ni(H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightarrow [\text{Ni(NH}_3)_6]^{2+} + 6\text{H}_2\text{O} \quad (7)
\]

\[
[\text{Ni(NH}_3)_6]^{2+} \rightarrow \text{Ni}^{2+} + 6\text{NH}_3 \quad (8)
\]

\[
\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \beta-\text{Ni(OH)}_2 \quad (9)
\]

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} \quad (11)
\]

The residual Ni and Al in the remained solution after filtering the precipitate was analyzed by ICP which showed 1.2 and 0.85 ppm respectively. By these results it can be concluded that the chemical co-precipitation method has been successful in extracting Ni and Al from their solutions when pH is about 8.8. The XRD pattern of the precipitants is illustrated in Fig. 1. The
**Fig. 1.** XRD pattern of precipitated powders after drying at 110°C.

**Fig. 2.** The FTIR spectra of precipitated powders after drying at 110°C.
precipitates consist of nickel and aluminum hydroxides including: Ni(OH)$_2$, NiOOH, Al(OH)$_3$ and with high amount of amorphous phase, as shown in background of XRD peaks. The FTIR profile of dried sample illustrated in Fig. 2, includes some absorption peaks related to the bonds between O, H, Ni and Al as hydroxide and oxide compounds. Detailed study on the bonds showed that there is a strong wide and deep absorption band in 2800-3700 cm$^{-1}$ that can be attributed to aqua (O-H-O) bending. This peak could be an indication of Ni(OH)$_2$ as well. The bonds around 390 cm$^{-1}$ is assigned to Ni-O stretching vibration mode.[12]

3. 2. Calcination

The thermogravimetric analysis of the dried samples performed between 20°C - 1200°C in air. Fig. 3 illustrates the TG curve of the dried precipitated powder. The TG curve presents two well defined mass loss steps which culminate at 220-450°C and 750-900°C. The first 52% mass loss corresponds to decomposition of Al and Ni hydroxides. Generally Ni(OH)$_2$ and Al(OH)$_3$ are converted to NiO and transition form of Al$_2$O$_3$ at 350°C and 300-500°C respectively[1,15]. The second 15% mass loss corresponds to transition of aluminum transition form to drier form and removal of OH and probably residual sulfate composition. There are 34% OH phase in transition alumina that exit from structure above 500°C [13]. As it can be seen any appreciable weight loss when the sample was heated above 900°C and it was considered as calcination temperature.

Fig. 4 shows the XRD pattern of the powder after calcination at 900°C in air atmosphere for 4 h. NiO and NiAl$_2$O$_4$ peaks are clearly observed. Reaction of NiO and Al$_2$O$_3$ begin between 700-900°C according to particle size and activity of raw material[17]. Due to solubility of Al$_2$O$_3$ in Ni Al$_2$O$_4$, excess Al$_2$O$_3$ were not observed at calcined powders[7,12].

![TG curve](https://example.com/tg.png)

**Fig. 3.** The TG curve of dried sample with the rate of 10 °C/min in air.
**Fig. 4.** The XRD pattern precipitated powders after calcination at 900°C for 4h in air atmosphere.

**Fig. 5.** The XRD pattern of calcined powders after reduction in carbon bed at different temperature for 3h.
3.3. Reduction

The XRD pattern of calcined powder heated in a carbon bed at various temperatures are shown in Fig. 5. As reported by Toshihiro Isobe, decomposition of NiAl$_2$O$_4$ and formation of NiO and Al$_2$O$_3$ occur above 700°C in reduction atmosphere and this NiO was reduced to Ni metal above 800°C [14]. Al$_2$O$_3$, which was formed by decomposition of spinel was transformed to $\alpha$-Al$_2$O$_3$ at $\geq$1300°C, and the obtained sample is consisted of $\alpha$-Al$_2$O$_3$ and Ni[19].

Fig. 6 shows the SEM micrograph of reduced sample in two different temperatures. It appears from elemental map that Ni particles are bright and Al$_2$O$_3$ particles are gray ones. SEM images shows uniform distributed Ni particles.

4. CONCLUSION

Aluminum and nickel hydroxides such as Al(OH)$_3$, Ni(OH)$_2$, NiOOH, and amorphous phases were coprecipitated from solution of aluminum nitrate and nickel sulfate at 60°C and pH 8.8. A mechanism for the formation of the precipitates was deduced based on the characterization of precipitates. After calcination of dried precipitated powders at 900°C for 4 hours NiAl$_2$O$_4$ spinel and NiO were obtained. After reduction of calcined powders composite powders at 1300°C for 3 hours, alumina nickel composite was obtained that showed uniformly dispersed micro-sized nickel in alumina matrix.

REFERENCES


