Metal Synthesis

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Sol–Gel Autocombustion Synthesis of Metals and Metal Alloys**

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The development of technology for the synthesis of metals and alloys continues to be one of the most important challenges in materials science. A general method for the synthesis of metals is to reduce metal oxides with hydrogen or carbon at high temperature. Pure metals are then used as starting materials to synthesize alloys by a melting method. There are some existing methods used to synthesize metals and alloys that have improvement of their capabilities.[1–3] However, the reduction of energy costs in the synthesis process is one of the critical factors for making the overall products cost-effective. Autocombustion is a self-sustaining method for heat generation from its own exothermic reaction.[4,5] In addition, the sol–gel technique has been widely used for the synthesis of a variety of metal oxides by mixing of different elements at the atomic level.[6–13]

Herein, we describe a versatile new strategy for producing pure metals and alloys by combining the sol–gel method and autocombustion; similar methods have been successfully used for the synthesis of metal oxides.[14,15] We used metal nitrate, citric acid, and ammonia as starting materials; the dried gels were prepared through a routine sol–gel approach. The autocombustion was activated at 300 °C in a tube furnace. The resulting materials were characterized by X-ray diffraction (XRD) with $\mathrm{Cu_{K\alpha}}$ radiation. This method has the following features: 1) simple apparatus with inexpensive raw materials; 2) a relatively simple synthesis process with fine and highly homogeneous powder products; and 3) a very low temperature is required to activate the reaction, and importantly the combustion can then continue without extra energy supply.

Pure metals are important materials that are extensively used for their unique properties (such as magnetic, catalytic, superconducting). Furthermore, atoms of pure metals can be used as building blocks in the construction of different kinds of alloys. As shown in Figure 1, pure Co, Ni, Cu, Ag, and Bi were identified. The morphologies of the synthesized metals were characterized by transmission electron microscopy (TEM), which showed that the metals and alloys were composed of nanoparticles of size from several nanometers to 100 nm.

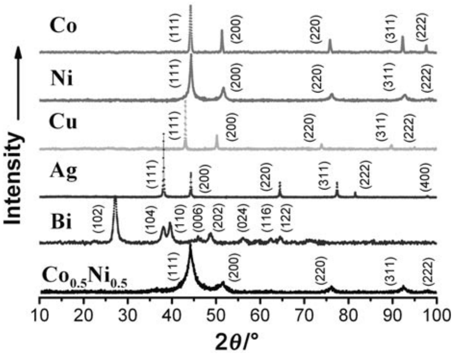

Figure 1. XRD patterns of the products from sol–gel autocombustion. All the peaks can be indexed to the corresponding metals and alloy with no impurities detected.

Figure 2 shows a typical TEM image of the metallic nickel. The inset of Figure 2 is a high-resolution TEM image of one grain. The distance between two fringes is 2.03 Å, which fits very well to the *d* spacing of the (111) plane in nickel. From this image it is estimated that the grain size of nickel is about 10 nm. TEM images of the metals Co, Cu, Ag, and Bi and $Co_{0.5}Ni_{0.5}$ alloy can be found in the Supporting Information.

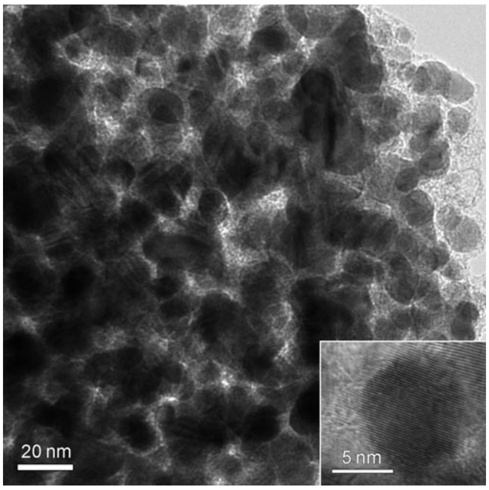

Figure 2. TEM image of the prepared nickel metal. Inset: high-resolution TEM image of one grain. The particle size is estimated as between 10 and 25 nm. The grain size of the nickel is about 10 nm.

In addition to the synthesis of pure metals, we have demonstrated the successful synthesis of a series of Co_xNi_{1-x} ($x = 0.2$, 0.4, 0.5, 0.6) alloys. The XRD pattern of $Co_{0.5}Ni_{0.5}$ is shown in Figure 1 (see the Supporting Information for other XRD patterns). The (111) peak shifts to a higher angle with an increase of the ratio of the Ni atom. As the crystalline unit

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cell parameter of Ni metal is a little smaller, this result indicates the formation of Co–Ni alloys.

To obtain a good understanding of the sol–gel autocombustion process in the synthesis of metals and alloys, we characterized the gel for metallic Ni by using thermogravimetry (TG) and differential thermal analysis (DTA). The experiments were carried out at up to 600 °C at a heating rate of 4 K min^{-1} under an argon atmosphere. Figure 3a shows that the weight loss started around 50 °C, and the corresponding endothermic peak (arrow A) can be assigned to the evaporation of the remaining water in the gel. The weak weight loss at 130 °C (arrow B) arises from desorption of chemically absorbed water. Another endothermic peak at 170 °C (arrow C) may come from the decomposition of NH_4NO_3 formed during the pH adjustment of the solution mixture. The TG curve shows an abrupt weight loss from 220 to 245 °C, which indicates the combustion of the gel. The strongest exothermic peak is at about 244 °C, which is related to burning. No more weight loss was seen after combustion. The TG–DTA studies showed that the sol–gel combustion reaction was finished at about 244 °C.

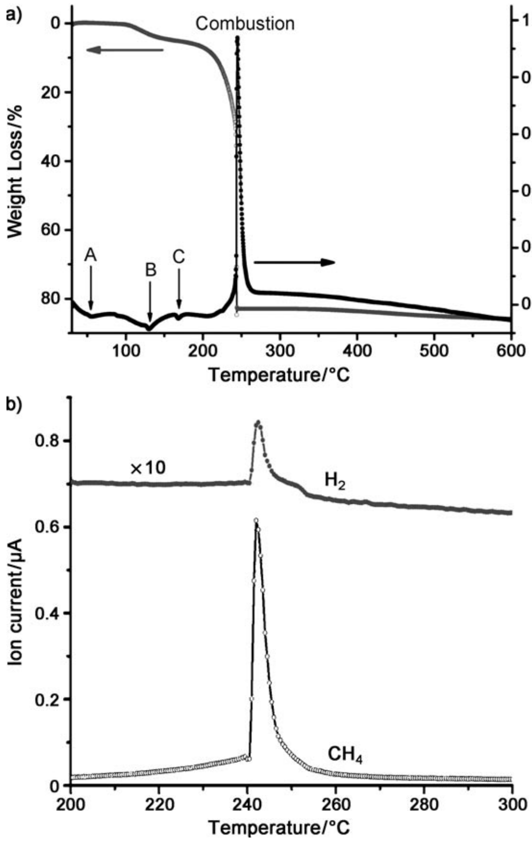

Figure 3. a) TG and DTA curves of Ni gel. The abrupt drop in the TG curve represents the violent combustion of the gel. The three endothermic peaks (marked with arrows A–C) indicate the evaporation of the remaining water, the desorption of chemically absorbed water, and the decomposition of NH_4NO_3 in the gel, respectively. The exothermic peak at about 244 °C results from the combustion of the gel. b) Mass spectrometry of the Ni gel, from which H_2 and CH_4 can be detected near the combustion temperature.

To dissociate and analyze the resulting molecules while heating the gel, we used mass spectrometry to record the ion currents released from the gel. The results show that H_2, H_2O, CH_4, NO, CO_2, NH_3, and NO_2 species were identified near the combustion temperature. H_2 and CH_4 are reducing agents that can be used in the redox reaction for synthesizing metals from oxides. The mass spectrometric data for H_2 and CH_4 near the combustion temperature (Figure 3b) illustrate the release of reducing gas during combustion.

Based on the data obtained from the TG–DTA and mass spectrometry analysis, we speculated that there might be five reactions occurring during burning of the gel at high temperature: 1) exothermic reaction between fuel and oxidant; 2) the formation of metal oxide(s) through decomposition of the nitrate(s); 3) generation of CH_4 and H_2 by the decomposition of CH_x-containing groups of citric acid; 4) exothermic reaction between CH_4/H_2 and oxidant; and 5) reduction of metals from their corresponding metal oxides by CH_4 and H_2 in nascent form.

As others have shown, many oxides were synthesized by the autocombustion method with high temperature (even more than 1000 °C) from the exothermic reaction between fuel and oxidant during the combustion process.[15,16] In our work, citric acid is used as the fuel and the nitrate ion is used as an oxidant. Various ratios between fuel and oxidant led to a variety of maximum temperatures of the reaction, which would affect the composition of the gas and thus play an important role in forming the product. Deshpande et al.[16] reported that the temperature in an inert atmosphere would be high when the ratio between fuel and oxidant was low. Although a high temperature would be helpful for reduction of metal oxides, superfluous oxidant would constrict this reduction. However, when the ratio was too high, the temperature would be decreased and thus not be favorable for the reduction of metal oxides.

The appropriate ratio between fuel and oxidant is critical for the synthesis of metals by sol–gel autocombustion. We optimized the reaction by varying the ratio between fuel and oxidant; the optimization of nickel synthesis is demonstrated here. Six samples were synthesized with a $C_6H_8O_7/Ni(NO_3)_2$ stoichiometric ratio of 0.3:1, 0.5:1, 0.8:1, 1:1, 1.2:1, and 1.5:1. The XRD patterns of the samples are shown in Figure 4.

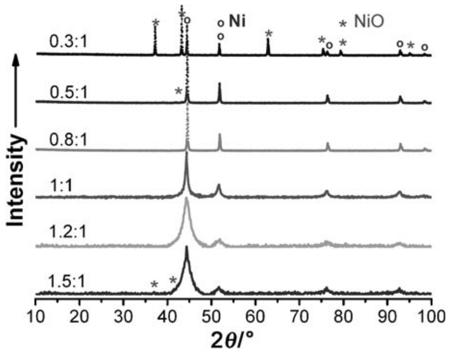

Figure 4. XRD patterns of the products from sol–gel autocombustion with different fuel/oxidant ratios as indicated. The NiO peaks are marked with * and the peaks belonging to Ni metal are marked with ○. The optimized fuel/oxidant ratio is around 1:1.

There was a very strong XRD signal from NiO in the sample with the ratio of 0.3:1. By carefully analyzing the XRD data, we concluded that when the ratio is higher than 1.5:1 or lower than 0.5:1, nickel oxide is formed in the products. For the synthesis of nickel metal, the optimized ratio is from 0.8:1 to 1.2:1. The fuel/oxidant ratio was 1:1 in the synthesis of the metals and metal alloys.

We also noticed from the XRD patterns that the peak becomes sharper with increasing oxidant content, which suggests an increase of the reaction temperature. This result fits well with the analysis of the influence of fuel/oxidant ratio on the reaction.

In summary, the technique described herein offers a convenient way for the synthesis of metals and alloys. We believe this technique will find broad application as a versatile and energy-efficient method for synthesizing magnetic materials, catalysts, and conducting colloids, and be useful in the metallurgy field.

Experimental Section

Metal nitrates and citric acid ($C_6H_8O_7{\cdot}H_2O$) were used as starting materials. The gel was prepared by a routine sol–gel method. In the cases of Co, Ni, and Cu, the pH value of the aqueous solution was adjusted to 7 by ammonia. In the cases of Ag and Bi, the metal nitrates were first dissolved in dilute nitric acid, then an appropriate amount of citric acid was added, and finally the pH value was adjusted to around 3 with ammonia. In the case of Co_xNi_{1-x} ($x = 0.2$, 0.4, 0.5, 0.6) alloy, cobalt nitrate and nickel nitrate with stoichiometric ratio $x/(1-x)$ were dissolved in aqueous solution, then the pH value was adjusted to 7 by ammonia. The resultant solution was poured into a beaker and heated at 95°C to develop a dried gel. Under the protection of inert gas (such as argon or nitrogen), these dried gels were heated to the preset temperature to activate combustion. Then, the gel was combusted violently and a large amount of white gas was released. After cooling to room temperature, the metals were obtained in the remaining loose powder. The activation temperature for sol–gel autocombustion in a tube furnace was 300°C.

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