

Preparation of Fe₇₃Cr₁₈Ni₉ Alloy Powder from Nano-Fe₇₃Cr₁₈Ni₉ Composite Oxide by Hydrogen Co-reduction Process

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Abstract. In this paper, Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was prepared by chemical co-precipitation method taking FeSO₄ 7H₂O, CrCl₃ 6H₂O, NiSO₄ 6H₂O and NaOH as raw materials. Its particle size was about 50nm. Then Fe₇₃Cr₁₈Ni₉ alloy powder was obtained by hydrogen co-reduction process taking advantage of active nano-characteristics of Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder at 1000°C after 1.5h of co-reduction. Its particle size was about 300nm.

Introduction

Nano-oxide powder(1~100nm) has some unique properties, such as small particle size, large specific surface area, quantum size effect, macroscopic quantum tunneling effect, which has some new characteristics compared with common oxide powder. Therefore, the preparation, properties and further application of nano-oxide powder have attracted extensive attention recently [1-15].

Metal oxide nano-powder has many advantages ,such as small size, incomplete crystal structure on the surface, many active sites, which greatly improved its reaction activity. Because of the large specific surface area, the hydrogen reduction reaction speed of nano-metal oxide powder has increased. There have been some reports on the microtherm preparation of metal, alloy and composite metal powder taking advantage of the high activity of nano-metal oxide and nano-metal composite oxide powder[16-19].

However, it is difficult to obtain metallic chromium by direct reduction of high valent chromium oxide. So the preparation of Cr powder by direct hydrogen reduction of nano-Cr₂O₃ powder has scarcely been reported so far, and the same thing happens to the preparation of Fe₇₃Cr₁₈Ni₉ alloy powder from Fe₇₃Cr₁₈Ni₉ nano composite oxide powder.

Fe₇₃Cr₁₈Ni₉ alloy powder is the raw material of Cr₁₈Ni₉ stainless steel powder, which is widely used in powder metallurgy, corrosion coating, filter material and other industries[20-22]. The most frequently used methods to obtain stainless steel powder include mechanical alloying[23], gas-solid flow atomization method[24], supersonic gas atomization[25] and high energy milling method[26], etc.

Hydrogen is a kind of renewable, clean energy which can be used as a reducing agent and could gradually replace carbon. As the problems of resources depletion, environment and global warming become serious, it is of great significance to study the process of hydrogen reduction.

In this paper, Fe₇₃Cr₁₈Ni₉ alloy powder was obtained by directly reducing Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder with hydrogen at 1000°C by taking advantages of high activity of nano-powder.

Experiment

Experimental apparatus: drying oven, acidmeter, electric blenders, vacuum pump, and closed cycle hydrogen reduction furnace, etc.

Chemical reagents: NiSO₄ 6H₂O, CrCl₃ 6H₂O, FeSO₄ 7H₂O, NaOH, anhydrous ethanol, all of which are chemical pure; hydrogen, nitrogen.

Preparation of the aqueous solution of FeSO₄-CrCl₃-NiSO₄: Some FeSO₄ 7H₂O, CrCl₃ 6H₂O,

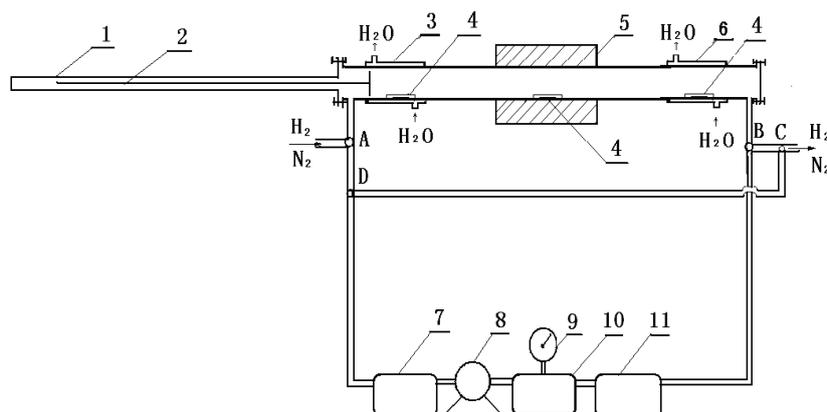
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Fe:Cr:Ni= 73:18:9, wt%) were dissolved in a certain amount of deionized water. After removing the insoluble impurities by filtration, $\text{FeSO}_4\text{-CrCl}_3\text{-NiSO}_4$ mixtures solution of 0.1 mol L⁻¹ was obtained.

Preparation of aqueous solution of NaOH: NaOH solution of 4 mol L⁻¹ was achieved by solving some NaOH into a certain amount of de-ionized water and the successively filtrating of insoluble impurities.

Preparation of $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ composite oxide nano-powder: 500mL of 0.1 mol L⁻¹ $\text{FeSO}_4\text{-CrCl}_3\text{-NiSO}_4$ mixed solution was put in a beaker, and then 4 mol L⁻¹NaOH solution was dripped with a strong stir. The pH value of the end of the reaction was 11. By dropping the deposit into alcohol for several hours, the $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ composite oxide nano-powder was obtained.

Preparation of $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ nano-powder: The $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ composite oxide nano-powder placed in a porcelain crucible was put into cooling zone (the 3 condensator in Fig.1) of the closed cycle hydrogen-reduction furnace. The three-way valve was placed in the status of gas replacement, and N_2 gas was using for the elimination of air. Hydrogen was pumped in, and the whole system was set on the closed circulation status, then hydrogen would pass through the system, during which hydrogen and nitrogen was circulated in the system by gas pump. After the reduction furnace was heated to desired constant temperature, the $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ composite oxide nano-powder was reduced in constant temperature zone. The pressure change was also recorded in the system. The reaction is over when the pressure of the system would not decrease. The reduced powder was quickly pushed to cooling zone (the 6 condensator in Fig.1), and then take out when it was cooled down to room temperature.

Samples examination: The samples were examined by X-ray diffractometer (XRD), scanning electron microscope (SEM) and Transmission electron microscope (TEM).



1-Latex sheath, 2- push sample implement, 3and 6-condensator, 4-porcelain crucible and sample, 5-reduction furnace of temperature controller, 7 and 10-buffer bottles, 8-gas pump, 9-manometer, 11-moisture removing apparatus, A, B, C, D- the three-way valve. A→4→B→8→D→C was path of the system gas replacement; A→4→B→8→D→A was path of the system closed circulation.

Fig. 1 Schematic diagram of the closed circulation-hydrogen reduction system

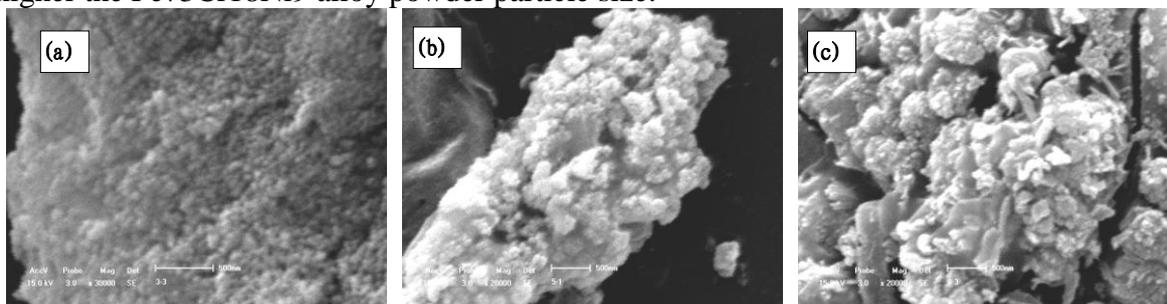
Results and Discussions

Influence of Particle Size of $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ Composite Oxide Powder on the Hydrogen Co-reduction Process

The $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ composite oxide nano-powder was prepared by co-precipitation. The reaction conditions were as follows: reaction temperature of 25°C; reaction time of 35min; stirring speed of 1000rpm; PH value of 11 for terminal reaction; drying time of 48h; drying temperature of 25°C,100°C,150°C, respectively. The SEM analytic results were shown in Fig.2. The $\text{Fe}_{73}\text{Cr}_{18}\text{Ni}_9$ alloy powder was prepared at 1000°C after 1.5h of co-reduction. The SEM and XRD pattern of the final reduction products was shown in Fig.3 and Fig.4.

The Fig.2(a)~2(c) shows that with the increase of drying temperature, the particle size of Fe₇₃Cr₁₈Ni₉ composite oxide powder was increased.

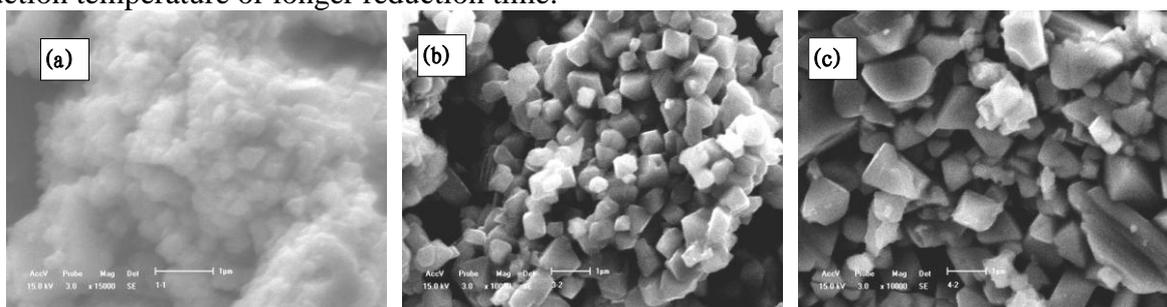
The Fig.3(a)~3(c) shows that the higher the Fe₇₃Cr₁₈Ni₉ composite oxide powder particle size, the higher the Fe₇₃Cr₁₈Ni₉ alloy powder particle size.



(a)25°C dryness 48hour, (b)100°C dryness 48hour, (c)150°C dryness 48hour

Fig.2 SEM image of Fe₇₃Cr₁₈Ni₉ composite oxide powder

It indicated that the lower the temperature, the fewer the diffraction peaks of XRD. The Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was obtained at drying temperature of 25°C. The Fe₇₃Cr₁₈Ni₉ alloy powder was prepared at 1000°C after 1.5h of co-reduction. As the drying temperature increased, the particle size of the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder increased, which resulted in lower reduction rate. Sample (b) and sample (c) were needed higher reduction temperature or longer reduction time.



The Fe₇₃Cr₁₈Ni₉ composite oxide powder dryness temperature was (a)25°C, (b)100°C, (c)150°C

Fig.3 SEM image of Fe₇₃Cr₁₈Ni₉ alloy powder

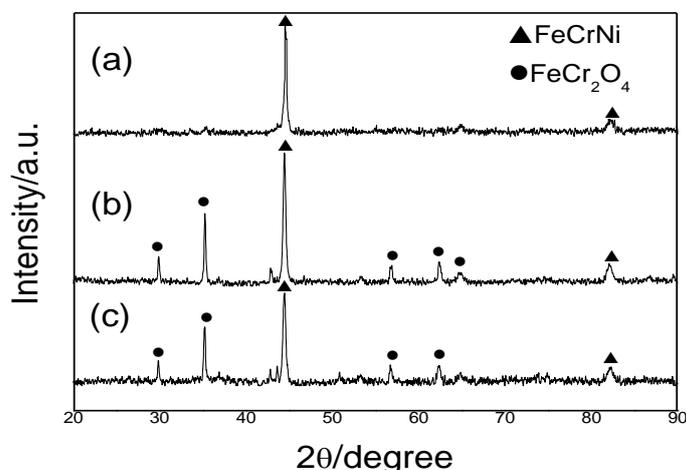


Fig.4 XRD pattern of the final reduction product obtained by 2h of reduction at 1000°C from the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder dried at (a) 25°C, (b) 100°C and (c) 150°C, respectively

Influence of Reaction Temperature on the Hydrogen Co-reduction Process

The Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was placed in a porcelain boat, and pushed into the closed reduction furnace cooling zone. When the temperature reached 800 °C, 900 °C and 1000 °C respectively, and another 5 minutes was kept to make temperature of the system homogenous, the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was pushed into the constant temperature zone quickly to reduce the oxide powder by hydrogen. After 1.5h reaction, the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was moved to the cooling zone of the reduction furnace.

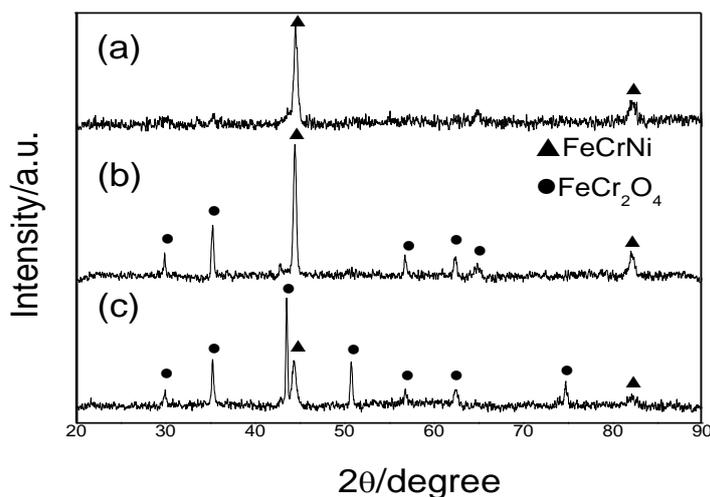


Fig.5 XRD patterns of the products obtained by hydrogen reduction of the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder for 2h at (a) 1000°C, (b) 900°C and (c) 800°C, respectively.

Fig.5 was the XRD patterns of the reduction products at 800°C, 900°C, 1000°C, respectively. The results showed that the Fe₇₃Cr₁₈Ni₉ alloy powder was obtained at 1000 °C after 1.5h of co-reduction. When the reaction temperature increased, the impurities in the product decreased, and hydrogen reduction of the oxide powder was more complete.

Influence of Reaction Time on the Hydrogen Co-reduction Process

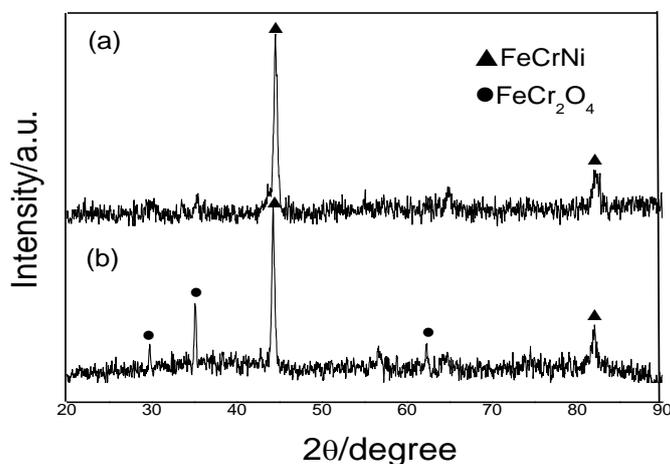


Fig.6 XRD patterns of the products obtained by hydrogen reduction of the Fe₇₃Cr₁₈Ni₉ composite oxide powder at 1000°C for (a) 1.5h and (b) 1h, respectively.

The Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was placed in a porcelain boat, and pushed into the closed reduction furnace cooling zone. When the temperature reached 1000 °C and another 5 minutes was kept to make temperature of the system homogenous, the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder was pushed into the constant temperature zone quickly to reduce the oxide powder by hydrogen. After 1h, 1.5h of reaction respectively, the porcelain boat was moved to the cooling zone of the reduction furnace. Fig.6 was XRD patterns of the reduction product.

Fig.6 shows that the Fe₇₃Cr₁₈Ni₉ alloy powder was obtained at 1000 °C after 1.5h of co-reduction. When the reaction time increased, the impurities in the product decreased, and hydrogen reduction of the oxide powder was more complete.

Influence of Temperature System on the Hydrogen Co-reduction Process

Sample (a): The Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder in a small porcelain boat was placed in the cooling zone of the furnace. When the temperature reached 1000 °C, another 5 minutes was successively kept, then the porcelain boat was pushed into the constant temperature zone for 1.5h of hydrogen reduction. XRD pattern was shown in Fig.7(a).

Sample (b): The Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder in a small porcelain boat was placed in the constant temperature zone, and the furnace was heated to 1000 °C at a rate of 15 °C •min⁻¹ for 2h of hydrogen reduction, whose XRD pattern was presented in Fig.7(b).

Sample (c): The Cr(OH)₃ nano-powder was prepared by the method of precipitation at following conditions: reaction temperature of 25 °C, reaction time of 35min, stirring speed of 1200rpm, PH value of 11 for terminal reaction, drying temperature of 25 °C, drying time of 48h and using CrCl₃ 6H₂O, NaOH as raw materials. The powder was reduced by hydrogen under in the same conditions to those in the preparation of sample (c). The XRD analysis of the reduction product was shown in Fig. 7(c).

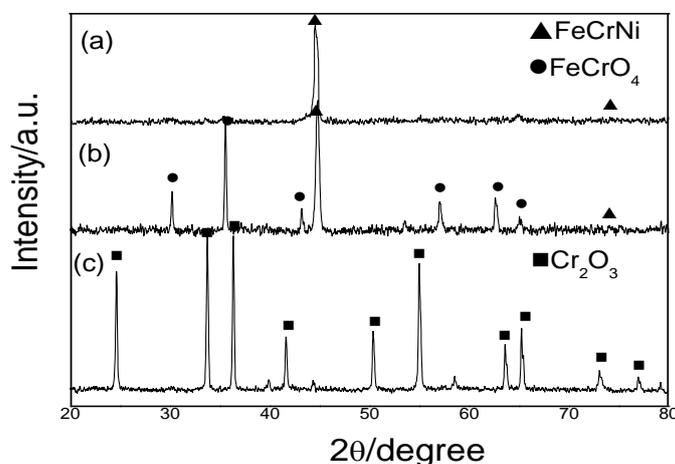


Fig.7 XRD pattern of the final reduction product in (a) sample A, (b) sample B and sample C, respectively

The Fig.7(c) shows that Cr(OH)₃ can not be reduced by hydrogen. According to Eq.1, the theoretical temperature for the reduction of Cr₂O₃ is about 4610.48 °C under the standard state.



The Fig. 7(a) shows that at the same experimental conditions, the composite oxide nano-powder, including Fe, Cr, Ni three elements, was quickly pushed into 1000 °C constant temperature zone to

take 1.5 h reduction reaction, and was reduced to Fe₇₃Cr₁₈Ni₉ alloy powder.

The composite oxide nano-powder along with the reduction furnace was heated to 1000°C with the rate of 15°C•min⁻¹, and was reduced for 1.5 hours. FeC₂O₄ was still in reduction products. Reduction reaction was incomplete. This shows that Fe₇₃Cr₁₈Ni₉ composite oxide powder's particle size was increased at rise temperature process.

Conclusions

The Fe₇₃Cr₁₈Ni₉ composite oxide powder was prepared at the reaction end point of pH of 11, the reaction time of 35min, the stirring rate of 1200rpm, the reaction temperature of 30°C, NaOH solution concentration of 4 mol L⁻¹, FeSO₄-CrCl₃-NiSO₄ mixed solution concentration of 0.1 mol L⁻¹ and the dropping rate of NaOH solution of 50 ml min⁻¹. Its particle size was about 50nm. With the increase of drying temperature, the particle size of Fe₇₃Cr₁₈Ni₉ composite oxide powder was increased.

Then Fe₇₃Cr₁₈Ni₉ alloy powder was obtained by hydrogen co-reduction process taking advantage of active characteristics of Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder at 1000°C after 1.5h of co-reduction. Its particle size was about 300nm. The particle size of the Fe₇₃Cr₁₈Ni₉ composite oxide nano-powder increased, the Fe₇₃Cr₁₈Ni₉ alloy powder particle size was increased, reduction rate was slower.

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