Studies on the Preparation of TiNi Alloy by Combustion Method*

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Abstract: The metal oxides, obtained by combustion method at 500 ℃, were used as precursors to synthesize intermetallic compound TiNi with reduction-diffusion method. XRD studies on the product showed that the TiNi phase together with the $TiNi_3$ phase appeared when precursors were reduced by CaH_2 at 800 ℃ for 2 hours. If elevate the reduction temperature from 800 ℃ to 1100 ℃ or append NaCl etc as flux to the reduction process, the TiNi phase and $TiNi_3$ phase were also coexistent. It was difficult to obtain a single phased TiNi alloy by combustion method in the experiment.

Key words: TiNi alloys; combustion method; reduction-diffusion method
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The hydrogen storage alloys which have been used as electrode are Laves phase series, La-Ni series and Ti-Ni series. Among them, the Ti-Ni alloy is a competitive material with low relative gravity and large capacity and excellent oxidation resistance performance. There was complex Ti-Ni alloy with capacity of 320 $mA \cdot h \cdot g^{-1}$ reported[1].

Generally, the Ti-Ni alloy was prepared by ball mill, hydrogenation grind or reduction-diffusion method directly. By these methods, special equipment was needed. In this experiment we tried to prepare Ti-Ni alloy by combustion method as we prepared La-Ni series alloys by the method before[2]. The result indicated that the TiNi phase and $TiNi_3$ phase were coexistent under any condition. It was difficult to obtain a single phased TiNi alloy by combustion method in the experiment.

1 Experiment

1.1 Instrument and reagent

MASL-XD2 X-ray powder diffraction instrument. Reagent: $Ni(NO_3)_2 \cdot 6H_2O$ (AR), $TiOSO_4$ (AR), CaH_2 (AR).

1.2 Preparation of nano-meter mixed metallic oxide precursors

$Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in water to dispense Ni^{2+} solution, then titrated it accurately.

Firstly, $TiOSO_4$ and Ni^{2+} solution were taken into a crucible according to their stoichiometric proportion, then complexing and reducing agent was added and mixed uniformly. After the complex reaction was complete, the mixture was put into a furnace with the temperature of 500 ℃. Several minutes later, combustion reaction took place. It took 5 minutes to obtain black pluffy small particle. In order to remove organic matter that did not burn out, the reaction continued for half an hour.

1.3 Preparation of TiNi alloy by reduction diffusion

Nanometer metallic oxide precursors and CaH_2 with double doses were mixed by rubbing inside a glove-box that was dried by silica gel. When the mixture was uniform it was placed in a stainless steel tube, then the tube was introduced into a tube furnace. It was treated at 850 ℃ in flowing H_2 for 2 hours to reduce the precursors. The sample was taken out when it dropped to room temperature.

The alloy powder was washed intensely by de-ionized water firstly and then treated by immersing in 5% acetic aid for 12 hours to remove dense CaO, afterwards it was washed by de-ionized water till the lotion was neutral, finally it was washed by C_2H_5OH. After it was naturally dried or dried in vaccum, alloy powder was obtained.

2 Result and discuss

2.1 Combustion process

In combustion process, the Gly was used as complexing and reducing agent with NO_3^- used as oxidizing agent. We can control the flame temperature and air current by change the ratio of Gly/NO_3^-. In the experiment, the Gly/NO_3^- ratio of 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 were adopted. As a result, when the ratio of Gly/NO_3^- was less than 0.6, the combustion

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reaction was not complete or could not take place at all. When the ratio of Gly/NO_3^- was 0.8 or 0.9, the product was bulky with small size. If the ratio of Gly/NO_3^- was more than 1.0, the product was difficult to be collected because of flying over. Therefore, the Gly/NO_3^- ratio of 0.8 or 0.9 was optimal.

2.2 Reduction-diffusion process

The mixture of combustion reaction product and excessive CaH_2 was placed in a tube furnace to proceed reduction-diffusion reaction. The reaction underwent at 700, 800, 900, 1000, 1050 and 1100 ℃, respectively for 2 hours. Fig. 1 was the XRD patterns of product at different temperature. From the figure we can conclude that TiNi phase did not appear at 700 ℃. The TiNi phase was present when precursors were reduced by CaH_2 at 800 ℃ for 2 hours, together with the $TiNi_3$ phase. If elevate the reduction temperature from 800 to 900, 1000, 1050, or 1100 ℃, the TiNi phase and $TiNi_3$ phase were also coexistent.

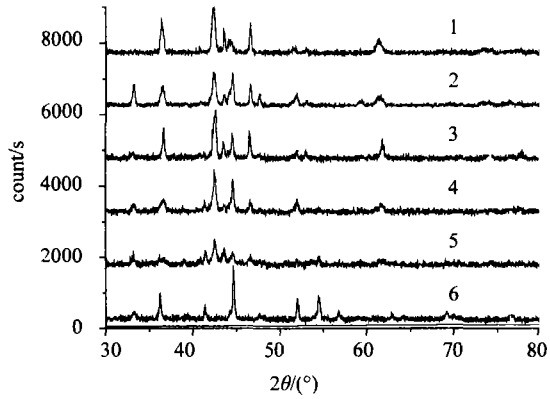

Fig.1 XRD patterns of alloys at various temperature
1:700 ℃;2:800 ℃;3:900 ℃;
4:1000 ℃;5:1050 ℃;6:1100 ℃

If append NaCl + $CaCl_2$ (melting point 500 ℃) as flux to the reduction process at 650 ℃, or Li_2CO_3 (melting point 618 ℃) at 750 ℃ or NaCl (melting point 801 ℃) at 850 ℃, the TiNi phase and $TiNi_3$ phase were also coexistent in product(Fig.2).

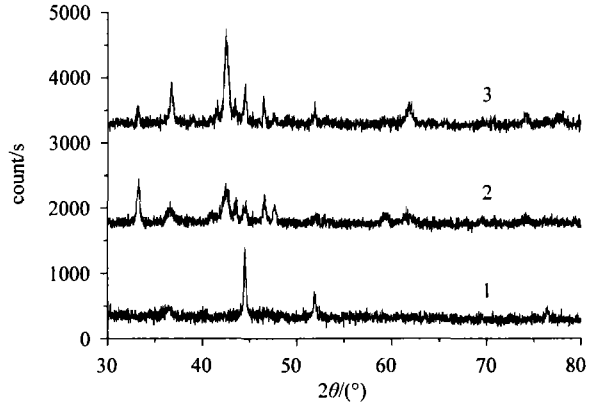

Fig.2 XRD patterns of alloys at various flex
1:NaCl + $CaCl_2$ as flex;
2:Li_2CO_3 as flex;3:NaCl as flex

3 Conclusions

It was difficult to obtain a single phased TiNi alloy by combustion method from the experiment.

References:

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[2] ZHANG J X, et al. *Chinese J Inorganic Chemisty*, 2002, 18 (2).

燃烧法制备 TiNi 合金的研究

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摘 要:首先运用燃烧法在 500 ℃制得金属氧化物前驱体,再将前驱体与 CaH_2 在一定温度下进行还原扩散反应制备 TiNi 金属间化合物。实验结果表明当还原扩散反应在 800 ℃下进行 2 h 就有 TiNi 相生成,同时也有 $TiNi_3$ 相存在。如果改变反应温度或加入助熔剂,产物中 TiNi 相与 $TiNi_3$ 相总是并存。本实验运用燃烧法没有得到纯相的 TiNi 合金。

关键词:TiNi 合金;燃烧法; 还原扩散方法
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