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Manufacture of Raney Ni catalyst with metastable Ni_2Al_3 by high-energy milling①

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Abstract: The Ni-Al alloy containing Cr, Fe additives were prepared as Raney Ni catalyst by high energy milling. The size and surface state of Ni-Al alloy powder were studied by particle size analyzer and sanning electron microscopy, the structure was analyzed by XRD and Mössbauer methods. The results showed that after a high-energy milling (HEM), the Ni-Al alloy transforms to a nano-scale NiAl structure with rich Al. By annealing the alloy, a metastable Ni_2Al_3 phase can be obtained.

Key words: Raney nickel catalyst; nano-crystal; high-energy; milling **Document code:** A

1 INTRODUCTION

Raney Ni catalyst, whose component is Ni-Al alloy, is a fine powder known as hydrogenation catalyst. According to the chemical reaction, some times Raney Ni catalyst must be filled with some mircroelements of catalyst-accelerator such as Cr, Cu, Co, Mn, Fe, etc. The skeleton nickel catalyst is produced by leaching out Al element from Ni-Al alloy in aqueous solution with 12% sodium hydroxide before it is used. This newborn nano-crystalline sponge nickel with high specific surface is provided with extreme catalyst activity.

The traditional technology of producing Raney Ni catalyst is casting the Ni-Al binary alloy with Ni_2Al_3 and $NiAl_3$ phases and then annealing the Ni-Al alloys obtained. The experimental results have proved that the crystalline grain of Ni obtained by leaching out Al element from Ni_2Al_3 is smaller than that obtained by leaching out Al element from $NiAl_3$[1]. Because the crystalline grain size is reduced, the defects of catalytic surface are increased, and the activity of catalyst is increased. The high-energy milling(HEM) is widely used to produce amorphous[2], crystalline[3], oversaturated solid solution[4] and nano-crystalline[5,6] materials etc. In present work, a new method of producing Raney Ni catalyst by HEM is investigated.

2 EXPERIMENTAL

The Ni-Al alloy that consists of high purity Ni(99.9%) 48.5%, Al(99.7%) 49.95% and microelement Cr (98.5%) 1.2%, Fe (99%) 0.45% was produced by vacuum induction furnace. After crushing, the alloy was treated with commonly milling, high energy milling and quenching respectively. The line speed of roller is 26 m/s. The rotating speed of milling jar is 720 r/min and the milling jar was filled with Ar gas during milling. The analytical samples of phase and particle size were taken out in 15 h interval. The analysis of phase was carried out by RIGAKU MAX/RB X-ray diffractometer (CuK_α(λ=0.15406 nm)). The analysis of par-

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ticle size was performed by SA-CP3 particle analyzer. The JSM 6400 SEM analyzer was used to analyze the particle size and surface morphology of particle. The Mössbauer was measured at room temperature.

3 RESULTS AND DISCUSSION

3.1 Particle size and surface morphology of NiAl during HEM

During the initial period of high-energy milling, the particle size is rapidly decreased. After several hours of high-energy milling, the particles size increases and then reaches a peak after about 60 h. When continuing milling, the particles size is decreased again. The relation between particle size and high-energy milling time is shown in Fig.1.

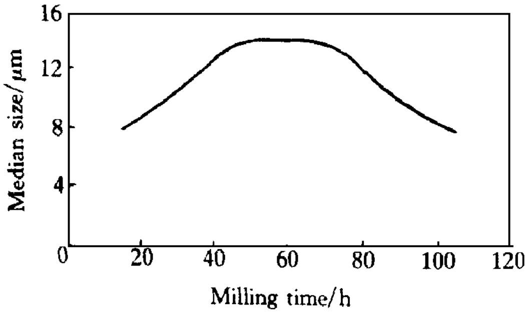

Fig.1 Variation of median size with milling time

The morphology of particles was observed by scanning electron microscopy during high-energy milling (Fig.2). During high-energy milling, the particles exist two kinds of trends of breaking and welding. It is considered that the big particles tend to breaking, but the small particles tend to welding, because some micro-crackles are distributed in the particles and the critical crackles exist more possibly in the big particles than in the small particles[7]. During high energy milling of Ni-Al alloy, when the welding process exceeds the breaking process, the particle growth is along with increasing time of high energy milling.

3.2 Structure characteristic of NiAl after HEM

The X-ray diffraction patterns of the alloy in different states are shown in Fig.3. After 45 h commonly milling, the component of phase is co-incided with original alloy. But after high-energy milling, the X-ray diffraction patterns have obvious changes. The layer structure of the particle surface (in Fig.2) is caused by slippage of a good many dislocations under high energy milling. The Ni_2Al_3 phase is hexangular crystalline system and $NiAl_3$ phase is rhombic crystalline system. Because the slippage coefficient is small in the Ni_2Al_3 and $NiAl_3$ phases, a large number of defects are produced during milling. When the time of high energy milling is increased, the defect density in the Ni_2Al_3 and $NiAl_3$ phases is increased and at the same time the free energy is also increased. The Ni_2Al_3 and $NiAl_3$ phases easily transform into NiAl phase with cube structure and many slip planes. When $NiAl_3$ phase transforms into NiAl phase, a large number of defects such as crystal boundaries and phase boundarys are produced. When the defect density in the cutting-change band comes up to critical value ,the grain is broken. This process is repeated continuously, so the grain is broken into very fine till nano-crystalline. According to Scherrer formula ,the grain-size is about 11 nm after 75 h high-energy milling. The widening of X-ray diffraction pattern is caused by the grain refinement and the strain in crystal lattice. The grain-size computed out by Scherrer formula includes the strain energy. This grain-size is called "the effective grain-size". The effective grain-size is bigger than the true grain-size. When the metastable NiAl phase is heated, the material tends to produce the mixture of the $NiAl_3$ and Ni_2Al_3 phases. The production and growth of the new phase needs diffusion of solute element. But this process is very slow. The metastable Ni_2Al_3 with rich Al can preferentially produce when NiAl with rich Al is heated (see X-ray diffraction pattern E in Fig.3).

3.3 Mössbauer spectra of high-energy milling Ni-Al alloys

Because X-ray diffiraction patterns of Ni_2Al_3 and NiAl alloys are overlapped, X-ray

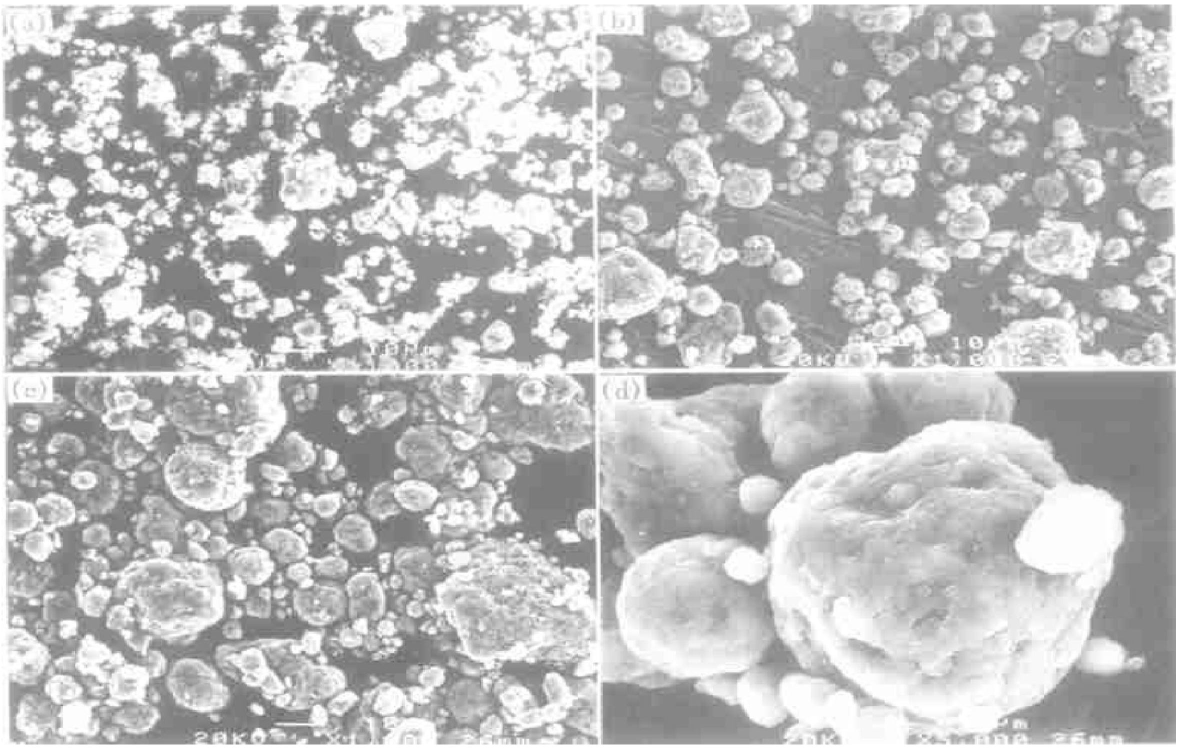

Fig.2 Powder size distribution after different milling time
(a) —15 h; (b) —30 h; (c) —60 h; (d) —75 h

Fig.3 X-ray diffraction patterns

diffraction patterns can't discriminate phase transformation. Mössbauer spectrum is used because it offers peculiar information on the very local environments around Fe atoms. The element Fe which is catalyst-accelerator in Raney Ni can be used as probe. When phase transformation occurs, the change of symmetry electron structure in crystalline field can cause change in Mössbauer spectra of Ni-Al alloy. A, B, C, D in Fig.4 are respectively the spectrum of as-cast, as-quench, 60 h and 105 h high energy milling Ni-Al alloy. Gros studied the distribution of the trace element Fe in the Ni-Al alloy of casted and quenched states[8], the results showed that Fe is concentrated on Ni_2Al_3 phase. From Fig.4 it can be discovered that $NiAl_3$, Ni_2Al_3 and NiAl phases always exist in Ni-Al alloy of casted or quenched state, so the Mössbauer spectra of A and B almost do not change, which means that Fe is concentrated on Ni_2Al_3 phase of casted or quenched states. After the high energy milling, the Mössbauer spectra change obviously. After 60 h high-energy milling, the change of Mössbauer spectra is caused by phase transformation, from Ni-Al alloy to NiAl phase. The X-ray diffraction pattern declared that X-ray diffraction peak moves to smaller angle[9]. It is caused by the increased crystal lattice constant of NiAl alloys containing excessive Al after $NiAl_3$

and Ni_2Al_3 was transformed into NiAl. When continuing high energy milling, the change of Mössbauer spectra is caused by the increased crystal lattice defect and the increased Fe that exists around defects.

Fig.4 Mössbauer spectra of differents states specimens
A—As-cast; B—As-quench;
C—After high energy milling for 60 h;
D—After high energy milling for 105 h

Because the difference of melting point of Ni and Al is great, Ni-Al alloy produced by smelting has great segregation of component, and at the same time a few NiAl phase which has no catalyst activity is firstly separated. The influence of catalyst-accelerator elements on the catalyst activity is performed through the change of electron construction of active matter and the arrange of surface atoms. The peritectic reaction of transforming NiAl phase into Ni_2Al_3 and the uniform distribution of alloying element require the condition of heat-treatment at high temperature and long time. This condition of heat-treatment certainly causes oxidation of Ni-Al alloy. During high-energy milling the solute element is mixed by atom each other to eliminate segregation, therefore NiAl alloy treated with high energer milling and heat-treatment can be obtained with Ni_2Al_3 construction.

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