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Influence of rotating magnetic field on the microstructure and phase content of Ni–Al alloy

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ABSTRACT

Rotating magnetic field is introduced in the production process of Ni–Al precursor alloy of skeletal Ni catalyst. The results showed that the big dendrites of Al_3Ni_2 disappeared, the size of Al_3Ni_2 decreased from 64.5 μm to 37.2 and 35.5 μm, phase content of Al_3Ni_2 decreased while Al_3Ni increased after applying field current of 80 A and 140 A, respectively. The change of phase content is probably caused by the increase of surface area between the Al_3Ni_2 phase and fluid which is favorable to the peritectic reaction.

1. Introduction

Raney nickel is a widely used catalyst for hydrogenation reactions [1,2]. It is obtained by leaching 50 wt% Ni–Al alloy particles in aqueous sodium hydroxide. The soluble aluminum is selectively dissolved, leaving behind a finely divided nickel. Because of its highly porous sponge-like structure, it is also referred to as skeletal nickel catalyst [1].

It is generally agreed that the performance of skeletal nickel catalyst is strongly affected by the production procedure of precursor alloy and the leaching process [3]. Besides, suitable activation conditions are required in the leaching process to obtain the best catalytic activity when different precursor alloys are used. From this point of view, the production procedure of precursor alloy becomes a crucial factor. Different phases have various strengths and leaching resistance and lead to different catalytic activities [1,3]. Therefore, many alloy production technologies which can change the alloy structure, such as mechanical alloying [4–8], rapid solidification [9–16] and adding alloying element combined with previous procedure are used to produce precursor alloys. Better skeletal catalysts are obtained, but many factors which affect the catalytic performance are mixed together. For example, rapidly quenched alloys have not only smaller grain size but also different phase content compared with those prepared by traditional cast and crush process. In order to get a better understanding of the relationship between structure and catalytic performance, it is worth producing alloys with only one factor changed.

Electromagnetic fields have been widely used in materials processing for a long time [17–21]. And extensive researches have been carried on to investigate the role of rotating magnetic field (RMF) in non-directional and directional solidification process, such as in the production of copper hollow billets [22,23], superalloy ingots [24–26] and Sn–Bi alloy [21]. It is well known that the liquid metal in the rotating magnetic field is subjected to electromagnetic stirring, and the electromagnetic stirring has the advantages of refining the internal structures of the ingot, increasing the fraction of equiaxed grains and reducing the segregation and shrinkage cavity [21,24,27]. However, the available literature data concerning Al–Ni peritectic alloy in a rotating magnetic field during the non-directional solidification process are very limited. Furthermore, it is possible to produce Al–Ni alloys with same composition, same phase content but different grain size, and then with these alloys the single influence of grain size on the final catalytic performance can be investigated.

2. Experimental details

Ni–Al alloy of 50 wt% Ni was produced from constituent elements, specifically commercial purity aluminum and electronic nickel, by medium frequency induction

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Table 1
Magnetic field intensity (without load) in the rotary electromagnetic stirrer.

Current intensity	Magnetic field intensity (mT)	
	Center	Near the inner side
80 A	43.81	40.79–60.95
140 A	71.70	67.29–100.04

melting. Since the evaporation pressure of Al is higher than that of Ni. It was expected that the loss of Al would be much higher than that of Ni. Therefore, extra 2% Al of aluminum was added to compensate its loss. There were two steps in the procedure of melting. First step was carried out in air. Al was first melted and when temperature reached up to 850 °C Ni was added. A graphite rod was used to stir the melt to ensure homogeneity and detect whether the Ni pieces were melted completely or not. When Ni was melted completely, induction power was turned down to let the surface of melt solidify. Next step was to degas the melt in order to minimize the influence of gas on the microstructure. Vacuum system was turned on, and induction power was turned up slowly to avoid melt splash. The temperature was kept at about 1500 °C for 10 min. The melting temperature of 50 wt% Ni–Al alloy is about 1300 °C. But the melt flow ability is poor. So the pouring temperature was set to 1470 °C. When the melt was poured into the mould, electromagnetic stirring with 50 Hz frequency was started immediately and lasted for several minutes. The intensity of RMF was controlled through adjusting the value of the alternating current inputted into the electromagnetic stirrer. Current intensities (I) of 80 A and 140 A were used in the experiments. The magnetic field intensity in the rotary electromagnetic stirrer without load was measured using Gauss/Teslameter (Model 7030, Sypris Test & Measurement), as shown in Table 1. The rotation of the melt in mould could be seen clearly from observation window. For comparison, the ingot without RMF was also produced.

It should be emphasized that only the lower center part of alloys (vide infra) can be used for comparison, avoiding the influence of cooling effect of mould wall on solidification and shrinkage porosity and cavity on the top side. Cooling condition plays a very important role in the phase transformation. The transformation from Al_3Ni_2 to Al_3Ni can be suppressed if the cooling rate is too fast. And too many shrinkage porosities can influence the analysis of phase content and the following catalytic test. The composition of the alloys was analyzed on X-ray fluorescence spectrometer (XRF-1800). After being polished the specimens were etched in 20% NaOH aqueous solution for 3 min. The etched surface was examined by optical microscope (OM). Size of Al_3Ni_2 phase was estimated by Image Pro-Plus 6.0 software. Alloy powders which passed 400-mesh were characterized by X-ray diffraction (XRD) performed at room temperature, using a Shimadzu XRD-6000 X-ray diffractometer with a Cu Kα target. And weight fraction of each phase was quantitatively analyzed by Rietveld method [28] using Fullprof computer code [14,29].

3. Results and discussion

3.1. Photomacrograph and microstructure

The ingots produced were vertically sectioned, as shown in Fig. 1. The bottom edges were crushed when the ingots were pushed out from the mould since the alloys are brittle. It can be seen that there are many shrinkage porosities in alloy with no RMF applied in Fig. 1(a). When 80 A RMF was applied the shrinkage porosities were reduced apparently in Fig. 1(b). This phenomenon is consistent with the study of Jin et al. [24]. It can be seen in Fig. 1(c) that a big cavity was formed after applying 140 A RMF. It is because the electromagnetic force is too big to allow the melt to feed. The specimens were sampled from the rectangle area.

The microstructure of Al–Ni alloys can be seen in Fig. 2. Al_3Ni_2 phase is light grey. (Al) and Al_3Ni phase are prone to react with OH^- and become darker than Al_3Ni_2 phase. Big dendrites (in the ellipse) of Al_3Ni_2 can be easily found in the alloy without RMF in Fig. 2(a). While there are no big dendrites can be found after imposing RMF, as shown in Fig. 2(b) and (c). The size of Al_3Ni_2 phase at different field currents is shown in Fig. 3. Without RMF, the average grain size of Al_3Ni_2 phase is about 64.5 μm. It becomes 37.2 and 35.5 μm with field current of 80 A and 140 A, respectively.

As well known, the melt is subjected to electromagnetic body force caused by the interaction of the eddy current and RMF [30]. In the present study, Al_3Ni_2 phase forms preferentially and grows until the peritectic temperature is reached. The Al_3Ni_2 dendrites on the solid–liquid interface are disturbed by the temperature and concentration fluctuation, and the roots of the dendrites are easy to be fused off. The compulsive convection caused by RMF generates shearing force, and plenty of dendrites are broken off as new nucleation center [22]. Therefore, Al_3Ni_2 phase can be finely divided in the alloy.

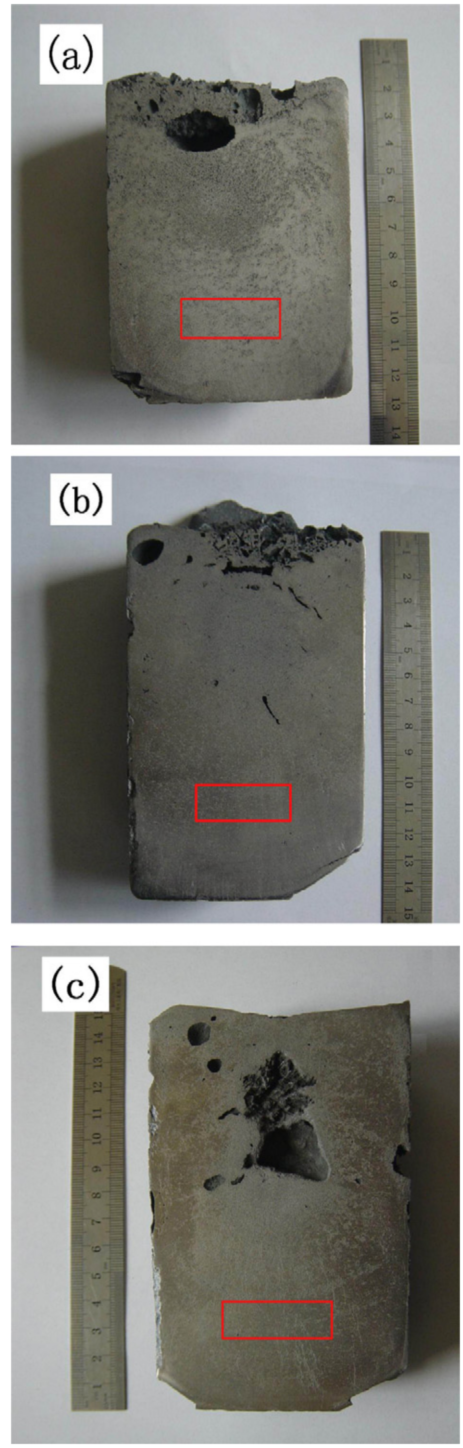

Fig. 1. Photos of vertical sections of three ingots: (a) without RMF, (b) with 80 A RMF, (c) with 140 A RMF. The specimens for analysis were sampled from the rectangle position.

3.2. Composition and phase analysis

The Ni contents of the ingots are 56.23%, 56.29% and 56.78% when I = 0 A, 80 A and 140 A, respectively. The content of Ni is higher

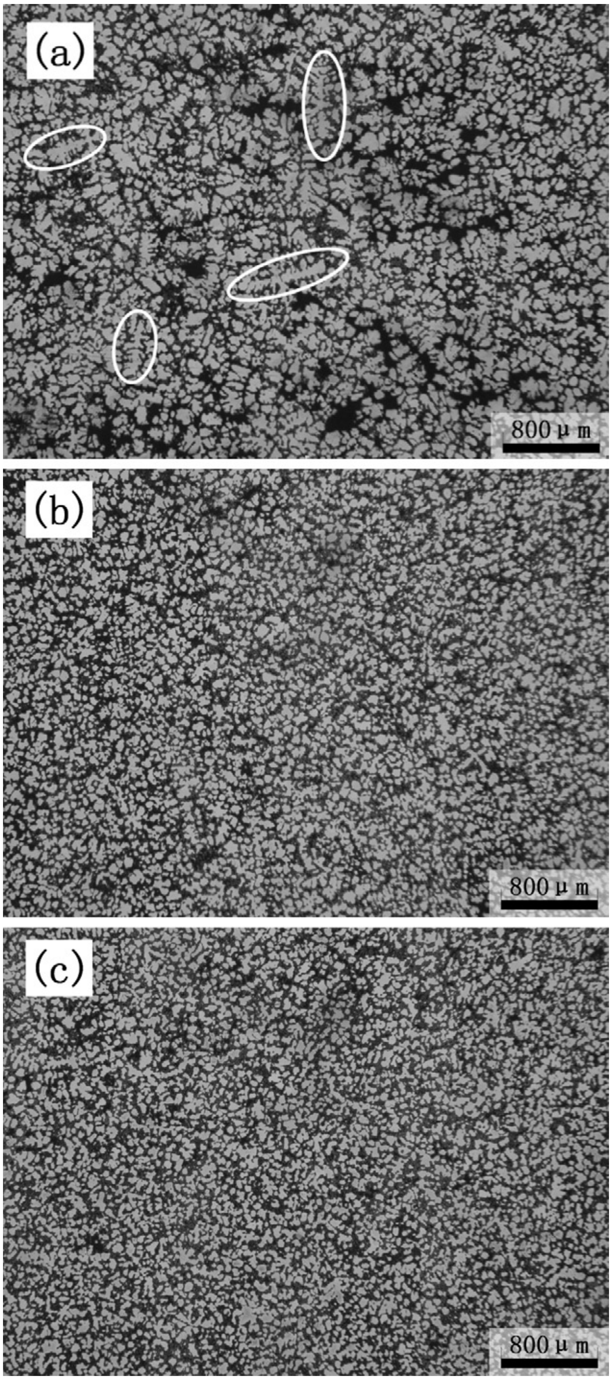

Fig. 2. Metallographs of Al–Ni alloys at different field currents: (a) 0 A, (b) 80 A, (c) 140 A. Al_3Ni_2 (light grey) and Al_3Ni (black). (Etched in 20% NaOH aqueous solution for 3 min.)

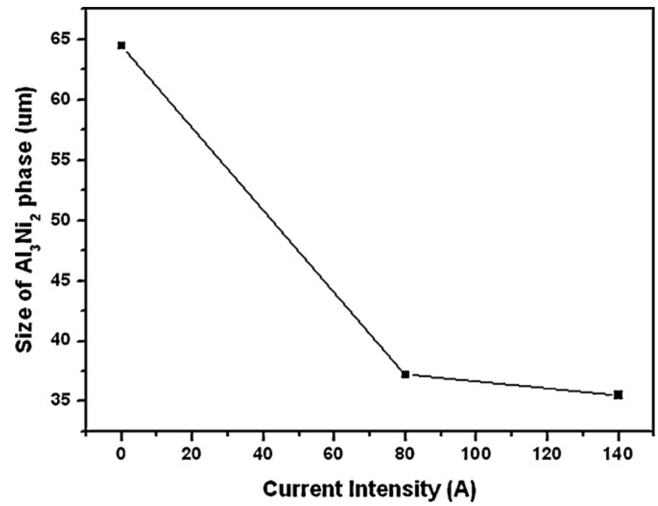

Fig. 3. Size of Al_3Ni_2 at different field currents.

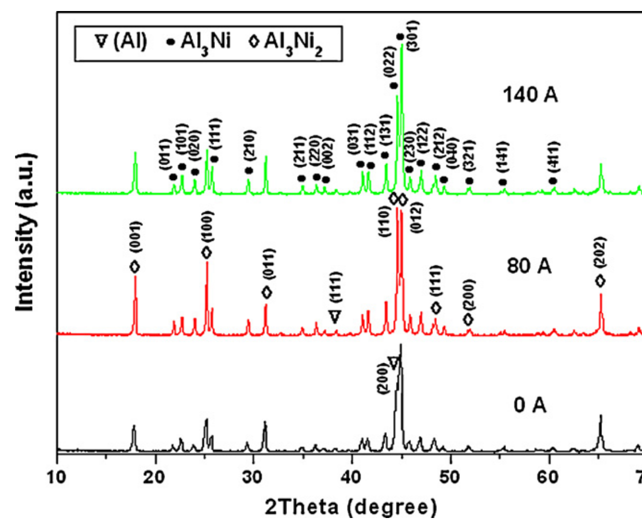

Fig. 4. XRD patterns of Al–Ni alloy powders.

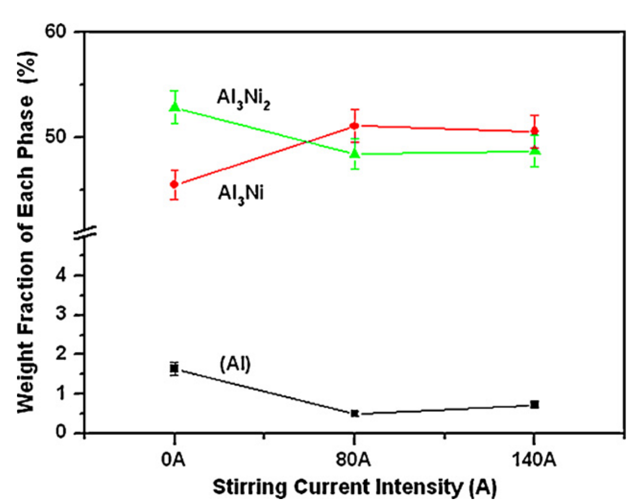

Fig. 5. Phase contents in Al–Ni alloy produced at different filed current of rotating magnetic stirring.

than the nominal composition (50 wt% Ni) since Al is prone to evaporate. This reminds us that some white powders formed at the top of the crucible during the melting process. The white powder was tested by X-ray diffraction and it was Al_2O_3. Although extra aluminum was added, it did not compensate its loss. However, the composition of three samples is still almost the same. So the comparison among them is reasonable.

XRD patterns of Al–Ni alloy powders are shown in Fig. 4. It can be seen that the investigated powders contains two main phases: Al_3Ni and Al_3Ni_2, with a small amount of (Al), as expected from the Al–Ni phase diagram [31]. Weight fractions of each phase are plotted in Fig. 5. When 80 A field current was applied, the content of Al_3Ni_2 phase decreased while Al_3Ni phase increased slightly. Specifically, the weight fraction of Al_3Ni_2 changed from 52.9% to 48.4% and Al_3Ni changed from 45.5% to 51.1%. The alloys produced by applying 80 A and 140 A field current have almost the same phase content. The content of (Al) is always less than 2%.

To explain the above phenomenon, we should first consider the macro-segregation caused by the effect of secondary flow in many eutectic alloy systems. If the macro-segregation took place, the composition at different position of the alloys should be different. Accordingly, the composition of same position of three alloys should also be different. However, the composition of three alloys is almost the same before and after applying RMF at the same examined position. Therefore, the change of phase content should be attributed to other reason. Then we notice that the solidification process is mainly a peritectic reaction. The factors which can influence the peritectic reaction should be considered. Interface area of liquid and Al_3Ni_2 plays a very important role in the formation of Al_3Ni. Al_3Ni can form readily at the interface of liquid and Al_3Ni_2 by the peritectic reaction of them. However, when Al_3Ni isolates Al_3Ni_2 from the liquid, the peritectic transformation becomes slower and slower. In present study, the interface area increases after the big dendrites are broken into many small dendrites. They are well dispersed in the melt. The fracture zones are new produced surface area compared with the one without applying RMF. That is to say, applying RMF on the solidification of melt makes the peritectic reaction go further. One may say that the low temperature which can suppress the peritectic reaction may be obtained after compulsive heat convection of the melt by electromagnetic body force. It is true that temperature is an important factor in the peritectic reaction, but low temperature can also enhance nucleation of Al_3Ni_2 which provide more and more surface area for peritectic reaction.

Compared with alloys in this paper, those prepared by mechanical alloying and rapid solidification have more factors which can influence the performance of the final skeletal catalyst besides the grain size and phase content. As well known, many defects and sometimes metastable phase exist in the alloys prepared by mechanical alloying and rapid solidification. And those defects play a very important role in accelerating the following dealloying process [12]. Moreover, metastable phases [5] have different leaching resistance and leave specific structure compared with Al_3Ni and Al_3Ni_2. Actually, alloying elements such as Fe [5], P and B [10] were added in most of the above procedures. In that case, the situation is more complex and the analysis of relationship between alloy structure and catalytic performance is less reliable since the synergistic effect caused by many intertwined factors.

4. Conclusions

Rotating magnetic field was introduced into the solidification of Al–Ni peritectic alloy. The results showed that the big dendrites of Al_3Ni_2 disappeared and Al_3Ni_2 were finely divided in the alloy after applying RMF. Phase content of Al_3Ni_2 and Al_3Ni also changed. Although the expected alloys with only grain size changed is not precisely obtained using electromagnetic stirring, it is still valuable to learn its catalytic performance because of its big differences with the alloys prepared by mechanical alloying and rapid solidification.

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