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Segregation control for the preparation of rare earth based hydrogen storage alloys

S.E. Hsu*, M.T. Yeh, I.C. Hsu, J.Y. Wang, V. Beibutian
R/D Center, HYTEC Co. Ltd., 80 Erh-Cha Road, Ying-Keh, Taipei-Hsian, Taiwan, China

Abstract

This study investigated the effect of a segregation control process on micro-structural change in the rare earth based hydrogen storage alloy. Micro-structural analysis correlating with $P–C–I$ data revealed that segregation in rare earth based intermetallics after conventional solidification was crucial. In order to minimize the effect of segregation, a new process, SMQ, in which the spontaneous reaction synthesis (SRS) is combined with vacuum induction melting (VIM) and immediately followed by spin-off quenching (SOQ) was developed in this work. Examination of micro-structural changes showed that segregation was obviously controlled by the new process. As a result, hydrogen absorption capacity as well as the electrochemical characteristics for MH electrode was improved.

Keywords: Segregation control; Rare earth based hydrogen storage alloys; Spontaneous reaction synthesis; Spin-off quenching

1. Introduction

The rare earth based metal hydrides have attracted widespread attention in the last several years due to their cost effectiveness and massive application in rechargeable Ni/MH batteries [1]. The final metal hydride electrode must be processed in mass production with high volume equipment which produces high quality electrodes having the characteristics of hydrogen absorption as well as electrochemical properties. There are two main requirements that directly affect the success of production: (1) environmental control for the reduction of corrosion; and (2) segregation control for quality consistency.

Segregation is an avoidable phenomenon during conventional solidification. It can be minimized or averted by controlling the cooling rate during casting, or by a process of long periodic homogenization at elevated temperatures [2]. The influence of segregation in certain circumstances is tolerable, for instance, the dendritic structure in the single crystal growth for structural applications. However, it becomes a serious problem in the case of a functional application such as hydrogen storage alloys used as electrodes for Ni/MH second batteries. In serious cases, segregation is equivalent to the enhancement of phase decomposition during solidification. Most R.E. based intermetallics, especially La–Ni systems, exhibit a peritectic reaction during cooling. Phase separation is usually followed by segregation.

Many efforts have been devoted to improve segregation by controlling the cooling rate [3]. In the production of hydrogen storage alloys, melting should be processed in a vacuum furnace. Alloys cast with different cooling rates depend on the various casting technique such as: (1) ingot casting; (2) flat pancake casting; (3) ingot bundle casting; (4) melt spin casting; (5) inert gas atomization casting etc. Each one exhibits advantages but also retains certain disadvantages. Alloys are normally heat-treated to homogenize the segregated structure before pulverization. A dramatic cost saving could be achieved if this homogenization step could be eliminated.

An alternative processing technique is presented in this paper which combines three processes (synthesis, melting and quenching, hereafter we call it SMQ-processing) together in one system. The equipment is designed such that the process of spontaneous reaction synthesis (SRS) [4] is combined with vacuum induction melting (VIM) and then immediately followed by spin-off quenching (SOQ). With this process, the experimental data showed that segregation was effectively controlled. As a result, the homogenization step is actually not necessary.

*Corresponding author. Corresponding address: MRL, ITRI, Hsinchu, Taiwan, China.

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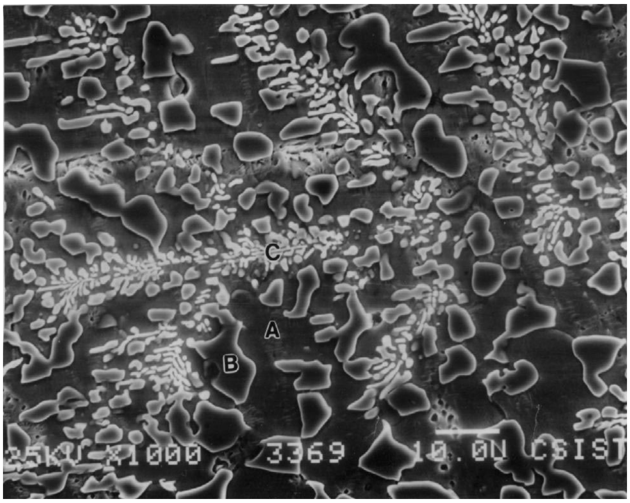

Fig. 1. SEM micro-structure of the $Lm(NiMnCoMo)_5$ which was prepared by conventional VIM melting and followed by pancake casting.

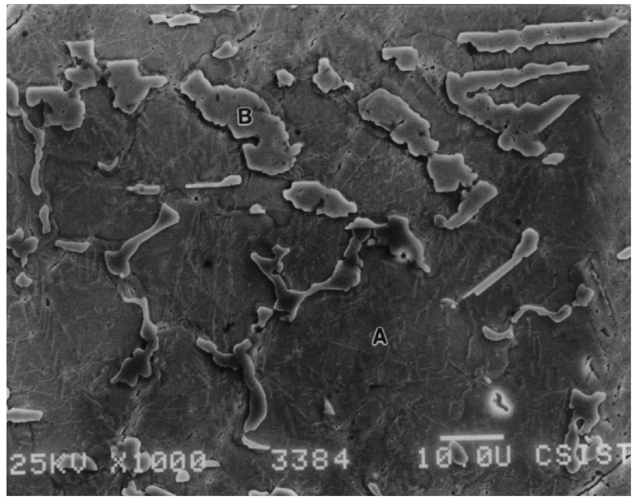

Fig. 2. Same as Fig. 1, but with higher magnification, note that spot A was taken from the matrix and spot B was taken from a dendritic second phase.

2. Experimental details

The material studied is $Lm(NiM)_5$ where Lm denotes La-rich misch-metal and M denotes Mn, Mo, Co and Al. The alloys were separately prepared either by conventional VIM melting or by the new technique, SMQ-processing. With this new process, the powder billet containing the designated composition was first synthesized [4] in an induction coil, melted and finally poured onto a fast rotating water cooled conical drum surface. Via the inclined drum surface, the molten drops were spun-off and hit a vertical wall. The solidified drops became flake-shaped before falling into the pre-cooled container. The alloys, either by VIM or by SMQ-process, were mechanically pulverized to an average particle size of 40 microns. The particle size and powder distribution was measured using a HORIBA laser scattering particle size analyzer.

The micro-structures of the alloys were analyzed using XRD and SEM equipped with an electron probe micro-analyzer (EPMA).

Hydrogen absorption/desorption characteristics were performed by use of a fully automatic P–C–I monitor (GfE product). The calculated C/D capacities were compared with the electrochemical experimental data. The preparation procedures for the electrodes of the open-cell can be found in the standard literature [5].

3. Results and discussion

Figs. 1 and 2 show the SEM micro-structures of $Lm(NiM)_5$ where M denotes Mn, Mo, Co and Al which were prepared using conventional VIM followed by flat pancake casting with a cooling rate of about 50°C/s. Figs.

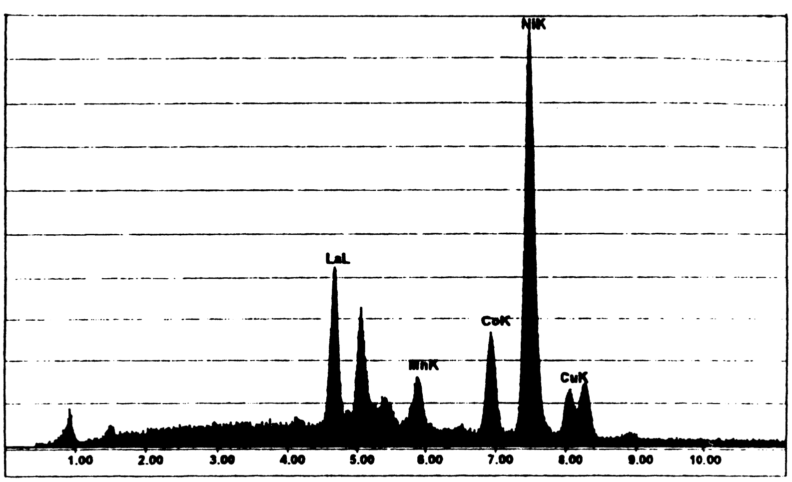

Fig. 3. EDS spectra taken from spot A in Fig. 2.

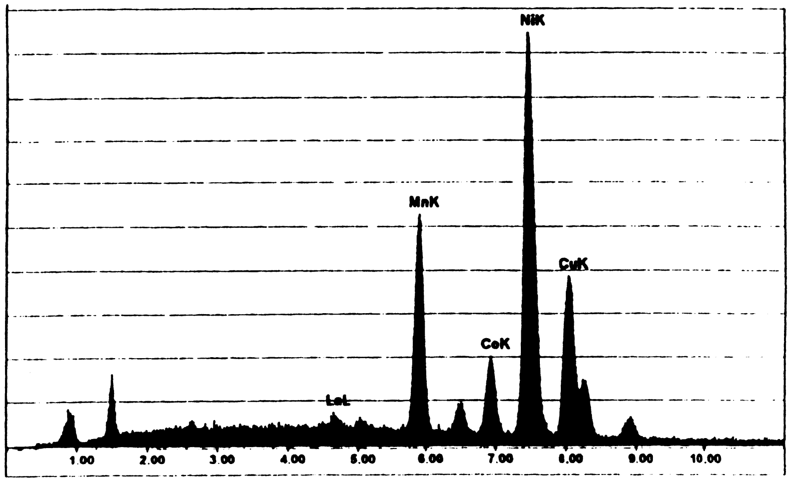

Fig. 4. EDS spectra taken from spot B in Fig. 2.

3 and 4 illustrate two EDS spectra which were taken from two different spots, A and B, as indicated in Fig. 2. XRD quantitative analysis showed that the composition distribution at spots A and B are also different as listed in Table 1.

The selection area diffraction pattern (SADP) from TEM at spots A and B are shown in Figs. 5 and 6. SADP in Fig. 5 was taken along $[11\bar{1}]$ zone axis of the $LaNi_5$ structure. It was observed that the 'rel.-rod' shaped diffraction spots were due to the laminate structure of $LaNi_{5.}$ While in the SADP in Fig. 6, a regular array of tiny diffraction spots was found in the matrix. It is believed that some precipitation of the second phase $MoCo_3$ formed along the grain boundaries during cooling [6]. From these qualitative and quantitative analyses, it is concluded that the segregation in the multi-component alloys during conventional casting is fundamental and serious. In order to remove the segregation, a lengthy homogenization process is needed. However, the dramatic costs of such a process is a production obstacle.

In order to control the segregation, an alterative SMQ-process, as described in the experimental details, was developed in this study. With this process, the molten drops are spun-off via an inclined conical surface. Under the high compression pressure executed by the centrifugal force, the liquid drops are pressed into flakes before falling into the container. The thickness of the flakes (as illustrated in Fig. 7) is an inverse function of the spin-off force, proportional to the revolution speed of the drum. As an example, the flakes are about 1 mm in thickness at about 200 RPM rotation speed. A photograph of the optical micro-structure of the $Lm(NiMnMoCoAl)_5$ system is shown in Fig. 8. As seen in this picture, the morphology of the cell structure is presented on the surface of the flakes. The flakes are so brittle that they can be mechanically pulverized without any difficulty.

Table 1
EDS quantitative analysis at spots A and B

Spot A (matrix)	Spot B (dendrite phase)
Ni>La>Co>Mn>Mo	Ni>Co>Mn>Mo>La

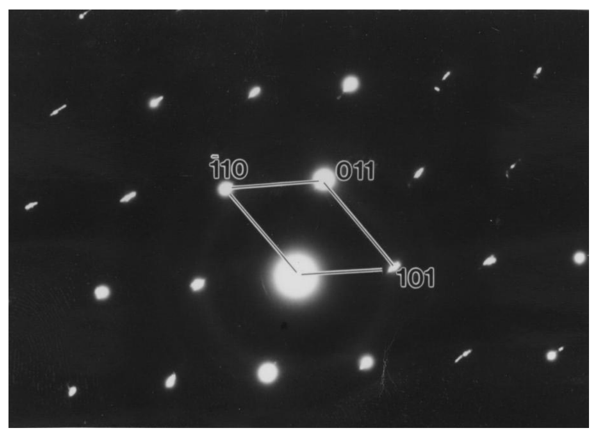

Fig. 5. SADP, taken from spot A as indicated in Fig. 2.

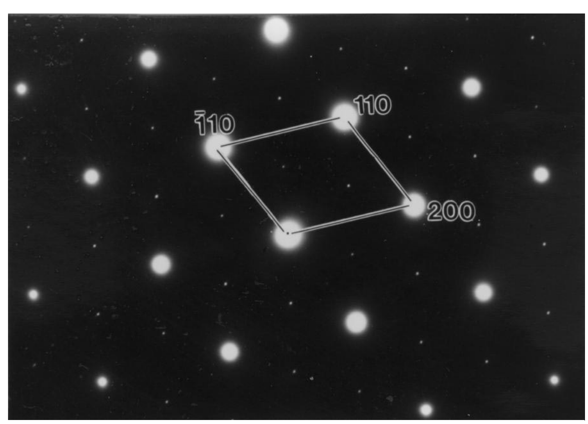

Fig. 6. SADP, taken from spot B as indicated in Fig. 2, the tiny diffraction spots illustrated the precipitation of $MoCo_3$ dispersed along the grain boundaries.

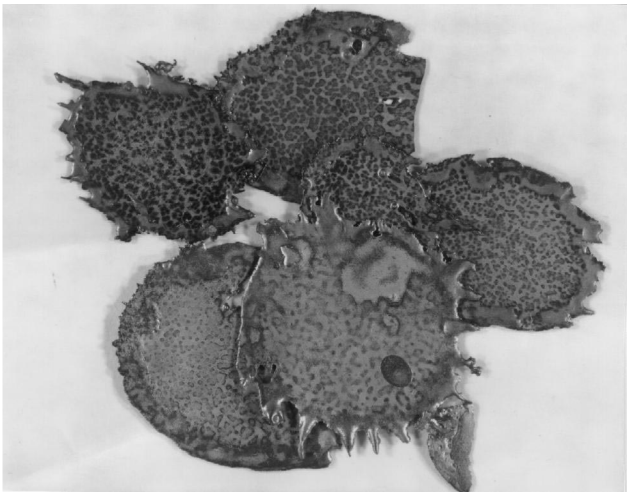

Fig. 7. Optical photograph shows the flakes that were prepared by the new process, SMQ.

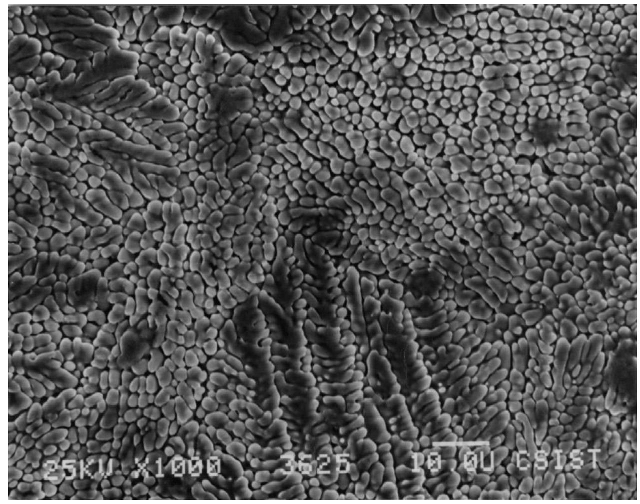

Fig. 8. SEM micro-structure shows the surface morphology of the flake which was prepared by the new process, SMQ.

Fig. 9 depicts two *P–C–I* curves for H_2-absorption both tested at 40°C. In this figure A-019 alloy was prepared using the conventional VIM process, while A-024 alloy was prepared with the new SMQ process. In comparing these two curves it is seen that the hydrogen absorption capacities are almost the same, however, the obvious difference between these two curves are the slopes. A high slope value indicates that a second phase or segregation is present in the matrix of the hydrogen storage alloy even if the alloy has experienced a lengthy homogenization process. On the other hand, a horizontal plateau pressure represents the degree of homogenization, indicating that the SMQ process exhibits a sufficient ability to control segregation even without further heat treatment. To compare electrochemical capacity data with charge/discharge cycle life, it was found that the electrochemical capacity of 300 mAh/g for the alloy HY#4 prepared by both processes used for MH electrode application made no difference. It is concluded that the SMQ process is an effective process for segregation control.

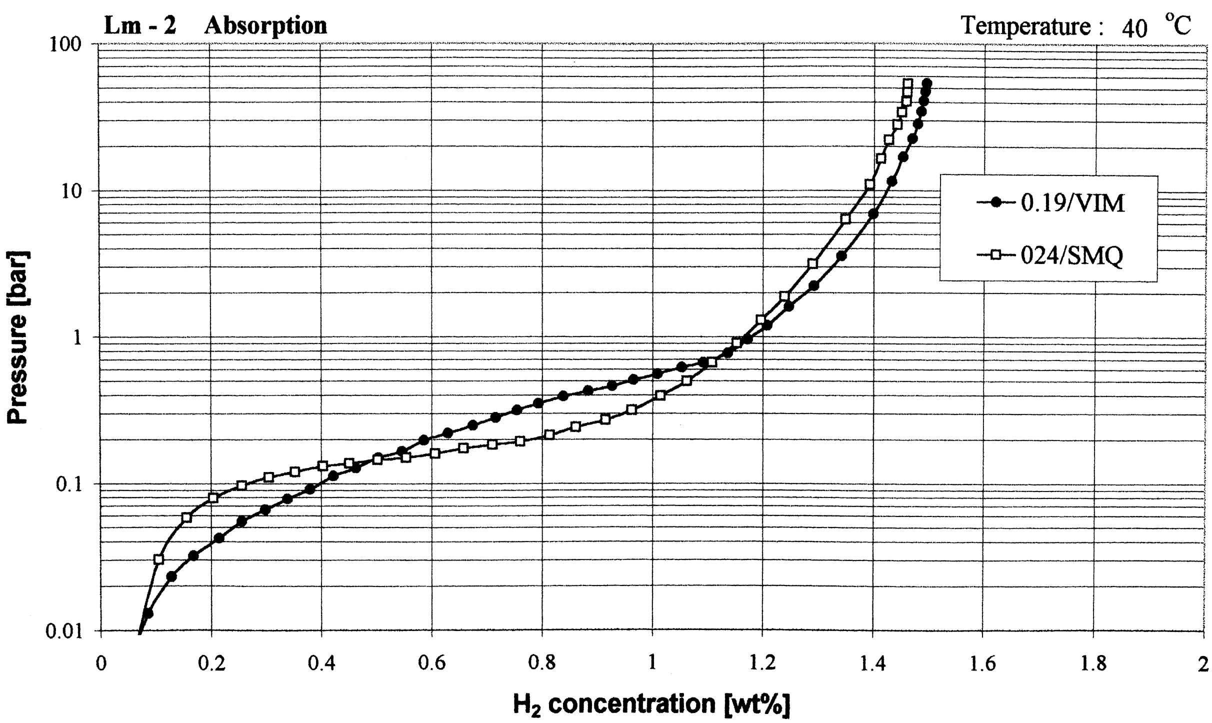

Fig. 9. *P–C–I* curves of two hydrogen storage alloys, alloy A-019 was prepared by the conventional VIM process and alloy A-024 was prepared by the new process, SMQ.

4. Conclusions

From the qualitative and quantitative micro-structural analyses, it was found that the segregation is fundamental and unavoidable in conventional solidification. The results in this work demonstrate that preparation of $Lm(NiM)_5$ type hydrogen storage alloys can be achieved using the newly developed SMQ process. SMQ processing is considered to be a very effective technique not only for segregation control but also for obtaining a uniform material without further homogenization.

Acknowledgements

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