A Study on the Formation of Magnetic Refrigerant $La(Fe,Si)_{13}$ Compounds by Spark Plasma Sintering

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ABSTRACT

The phase formation of magnetic-refrigerant $La(Fe,Si)_{13}$ compounds with a $NaZn_{13}$-type structure has been investigated using an electron probe micro analyzer (EPMA) and X-ray diffraction (XRD). The structure of a sample synthesized by solid-state reaction of fine elemental powders using a spark plasma sintering (SPS) technique was compared with that synthesized by conventional methods including a melt and solidification process. The conventional methods, namely, arc-melting and melt spinning, easily caused segregation of the Fe-rich phase. On the other hand, the remarkable $NaZn_{13}$-type structure was observed in the SPS sample. These experimental results indicate that homogenous distribution of the elements and short-range atomic diffusion are important for forming the $NaZn_{13}$-type structure efficiently.

INTRODUCTION

Magnetic refrigeration using permanent magnets is attractive as an alternative cooling technology to conventional gas-compression cycle refrigeration. This is because it does not use toxic or environmentally harmful substances such as chlorofluorocarbons, and moreover, its cooling performance is estimated to be highly efficient.[1-3] Recently, Fe-based compounds with a cubic $NaZn_{13}$-type structure such as $La(Fe,Si)_{13}$ have been proposed as suitable for magnetic refrigeration applications.[4-6] These compounds have at least three advantages. First, they exhibit a large value of magnetic entropy change in low magnetic fields. Second, it is easy to control their Curie temperatures. Finally, they consist of low-cost elements. However, the $NaZn_{13}$-type structure is rarely generated in ingots prepared by a conventional method such as arc-melting, because the Fe-rich phase is likely to segregate by passing through a melt and solidification process. This phenomenon is due to the dissolution between La and Fe. Accordingly, a long annealing time (ten days to one month) is necessary to form the $NaZn_{13}$-type structure in these compounds. Very recent studies reported that the generation of the $NaZn_{13}$-type structure is enhanced by melt spinning.[7] Melt spinning has a high quenching speed and is widely known to result in a fine microstructure. However, it is very difficult to completely suppress the segregation of the Fe-rich phase even by rapid quenching performed with melt spinning; this is because it includes a melt and solidification process that is the principal factor causing the segregation of the Fe-rich phase. To our knowledge, investigations of the formation of the $NaZn_{13}$-type structure are limited from a metallurgical point of view. In the present study, the effect of a solid state reaction to form the $NaZn_{13}$-type structure is investigated and compared with conventional methods, namely, arc-melting and melt spinning.

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EXPERIMENTS

Ingots of $La(Fe_{0.88}Si_{0.12})_{13}$ were prepared by arc-melting in an Ar atmosphere using La, Fe and Si of higher than 99.9% purity and melted several times to ensure homogeneity. Subsequently, one specimen was wrapped with Ta foil and annealed in a vacuum quartz tube for 10 days at 1323K. The other one was induction melted and rapidly quenched by a single roll technique with a Cu roll in an Ar atmosphere. The surface speed of the Cu roll was 40 m/s. On the other hand, the solid state reaction was performed as described in the following. First, elemental powder were blended with a stoichiometric amount of $La(Fe_{0.88}Si_{0.12})_{13}$ and mixed sufficiently. The starting materials are higher than 99.9% in purity and under 5 μm in particle size. Subsequently, the mixed powder was sintered in a cylindrical graphite die in vacuum using the SPS system. The conditions for sintering were as follows: temperature 1273-1423K, pressure 40 MPa and holding time 5 min. The crystal structure analysis of the samples was carried out using X-ray diffraction (XRD) with CuK α radiation. The microstructure and the element distribution mapping were performed using a scanning electron microscope (SEM) and an electron probe micro analyzer (EPMA), respectively.

RESULTS AND DISCUSSION

Arc-melting

The element distribution mapping of arc-melted and annealed samples is shown in Figure 1: (a) as-cast, (b) annealing for 5 days at 1323K, and (c) annealing for 10 days at 1323K, respectively. The typical dendritic structure, which separated into an Fe-rich phase and La-rich phase, was observed in the arc-melted sample as Fig. 1 (a) shows. The dendrite width of the Fe-rich phase is estimated to be about 10-30 μm. The Fe-rich phase decreased with increase in annealing time (Fig. 1 (b)) and it was not observed in the annealed sample (Fig. 1 (c)). The powder X-ray diffraction patterns of the above-mentioned samples are shown in Figure 2. It appears that the main phase in the arc-melted sample is α-Fe, and the diffraction peak of the $NaZn_{13}$-type structure was hardly detected (Fig. 2 (a)). The amount of the $NaZn_{13}$-type structure was increased by subsequent annealing, and an almost single phase of the $NaZn_{13}$-type structure was obtained in the sample annealed for 10 days (Fig. 2 (c)). These facts suggested that the coarse α-Fe dendrites make the formation speed of the $NaZn_{13}$-type structure slow because of long-range diffusion of the elements.

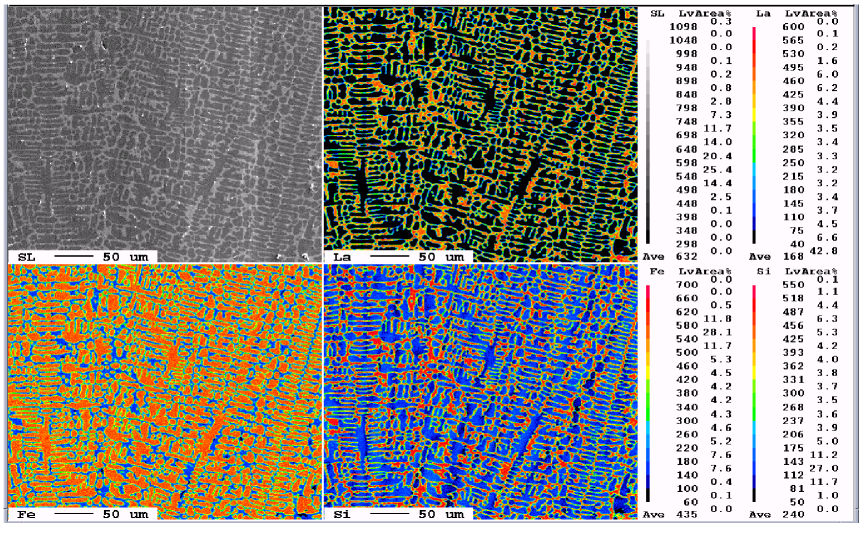

Figure 1 (a). EPMA image of arc-melted $La(Fe_{0.88}Si_{0.12})_{13}$ (as-cast).

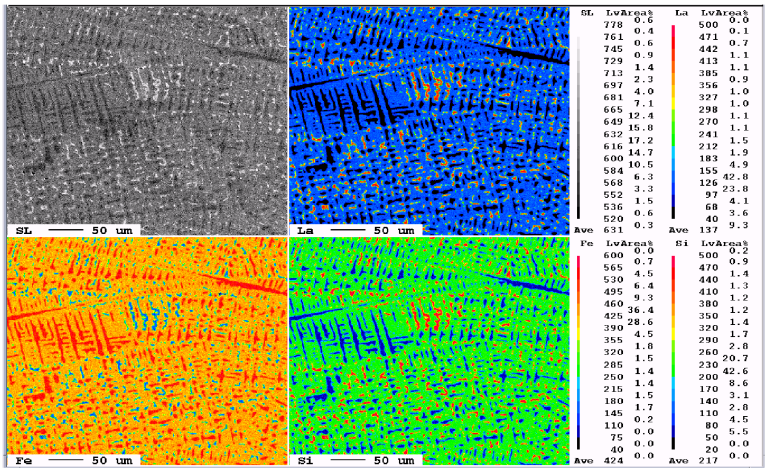

Figure 1 (b). EPMA image of arc-melted La($Fe_{0.88}Si_{0.12}$)$_{13}$ after a annealing (1323K / 5 days).

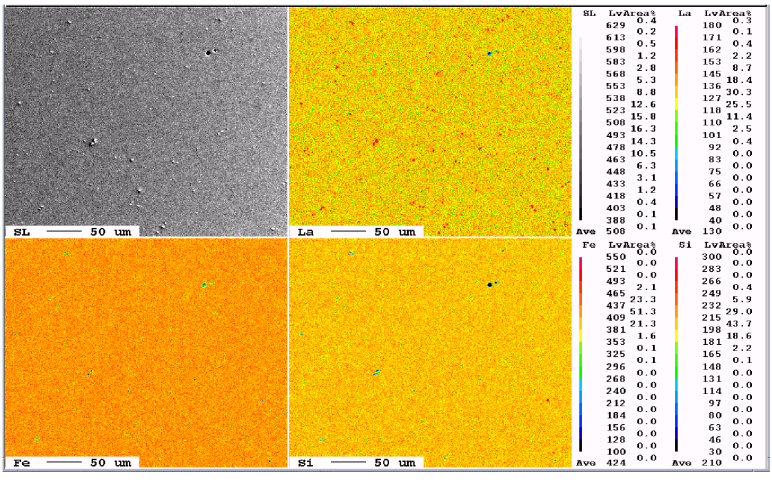

Figure 1 (c). EPMA image of arc-melted La($Fe_{0.88}Si_{0.12}$)$_{13}$ after a annealing (1323K / 10 days).

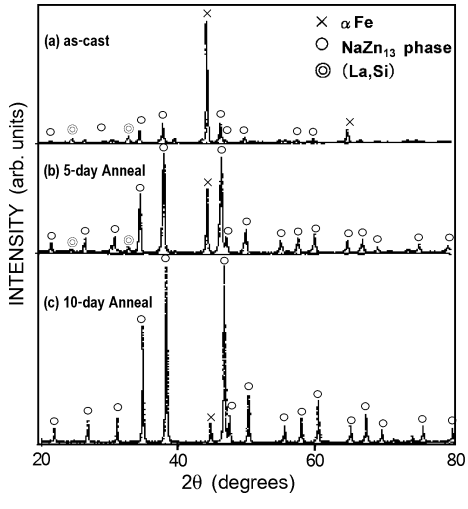

Figure 2. XRD patterns of arc-melted La($Fe_{0.88}Si_{0.12}$)$_{13}$: (a) as-cast, (b) after annealing 5 days at 1323 K, (c) after annealing 10 days at 1323 K.

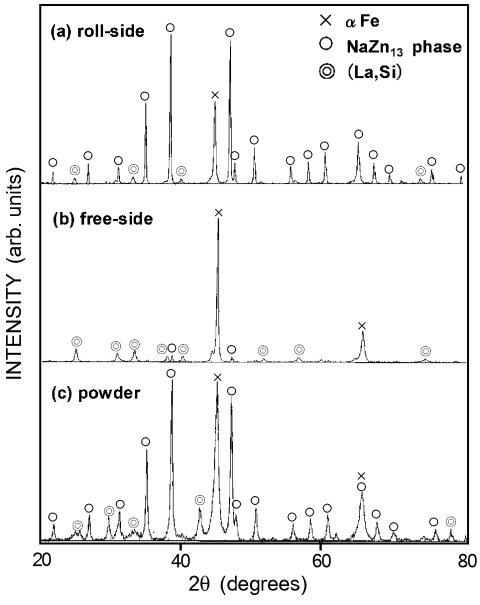

Figure 3. XRD patterns of melt-spun $La(Fe_{0.88}Si_{0.12})_{13}$: (a) roll-side surface, (b) free-side surface, (c) powdered ribbon

Melt-spinning

The X-ray diffraction patterns of melt-spun ribbon are shown in Figures 3(a) to (c); (a) roll-side (contact side) surface, (b) free-side surface, and (c) powdered ribbon. X-ray analysis revealed that the $NaZn_{13}$-type structure was formed at the roll-side surface without annealing. In contrast to the roll-side surface, a Fe-rich phase was still dominant at the free-side surface, which was the same as in the case of arc-melted samples. The EPMA images of the roll-side surface and the cross-sectional view are shown in Figure 4. Homogenous distribution of the elements was observed at the roll-side, the homogeneity of which decreases toward the free-side surface. A fine microstructure was observed at the roll-side surface from the SEM investigation as Figure 5 shows. The microstructural change corresponded to the homogeneity enhancement of the element distribution of the ribbon.

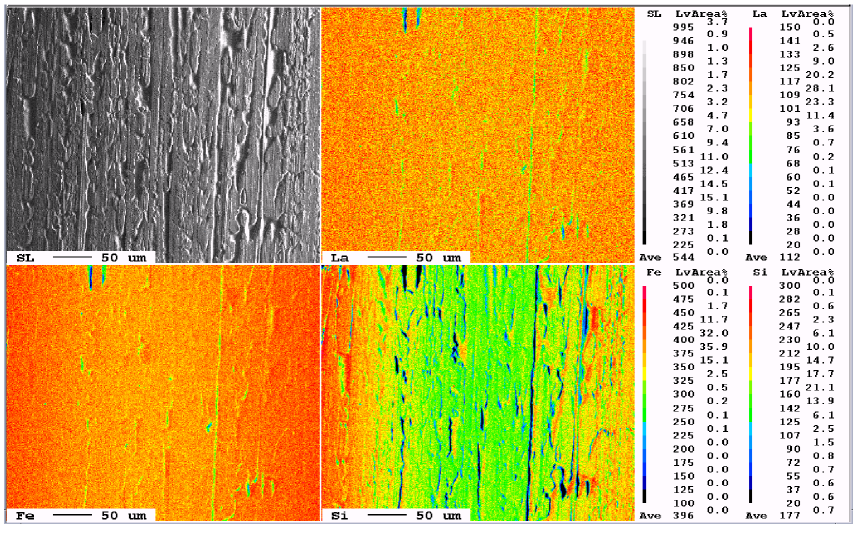

Figure 4(a). EPMA images of melt-spun $La(Fe_{0.88}Si_{0.12})_{13}$ (Roll-side surface)

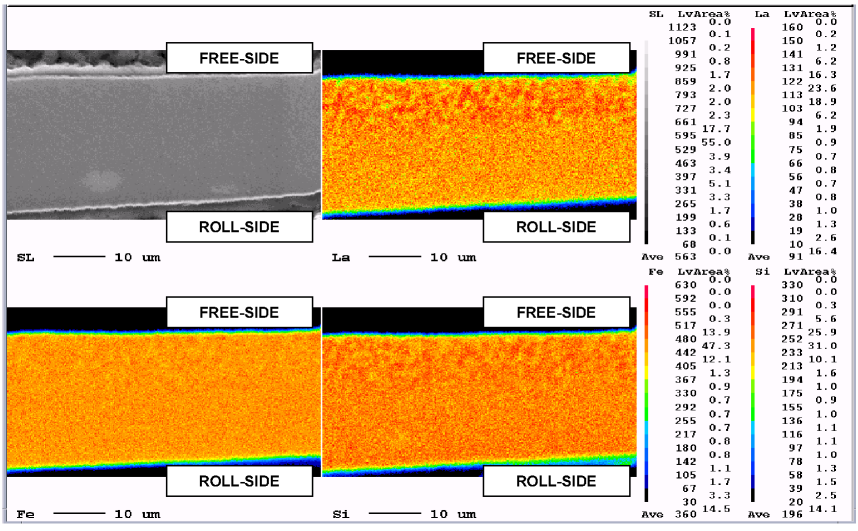

Figure 4 (b). EPMA images of melt-spun La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ (Cross-section).

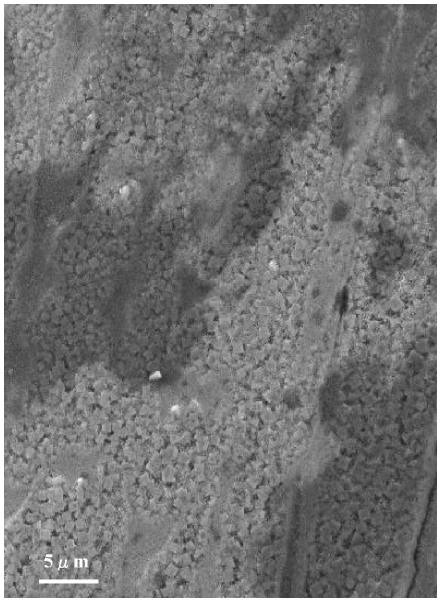

Figure 5. Microstructure of melt-spun La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ at roll-side surface

The findings as stated above lead to the preliminary conclusion that efficient forming of the NaZn$_{13}$-type structure proceeds as follows: (1) short range atomic diffusion of the elements, (2) homogeneous elements distribution.

Spark plasma sintering

Next, we investigated the formation of the NaZn$_{13}$-type structure by a solid state reaction using the SPS technique. It should be noted that we used fine elemental powders that have particle size in the size-range 3-5 μm, which is smaller than the dendrite width of the α-Fe phase in the arc-melted bulk alloy, and the specimens have sufficient homogeneity due to thorough mixing. The XRD patterns and the EPMA images of SPS samples are shown in Figure 6 and 7, respectively. In spite of a sintering of only 5 minutes, the NaZn$_{13}$-type structure was formed sufficiently. Moreover, the ele-

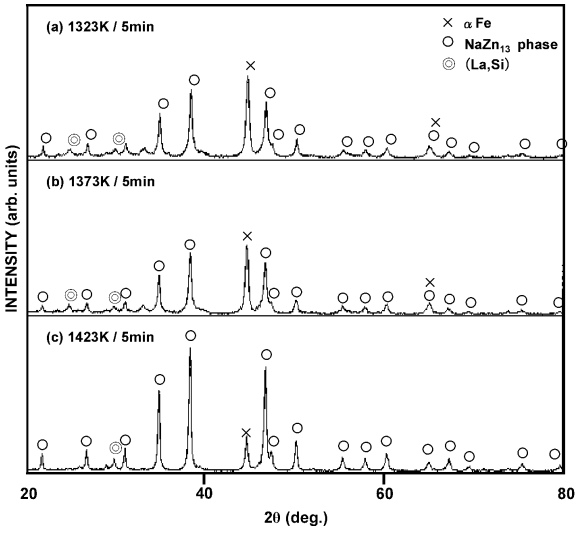

Figure 6. XRD patterns of spark plasma sintered $La(Fe_{0.88}Si_{0.12})_{13}$

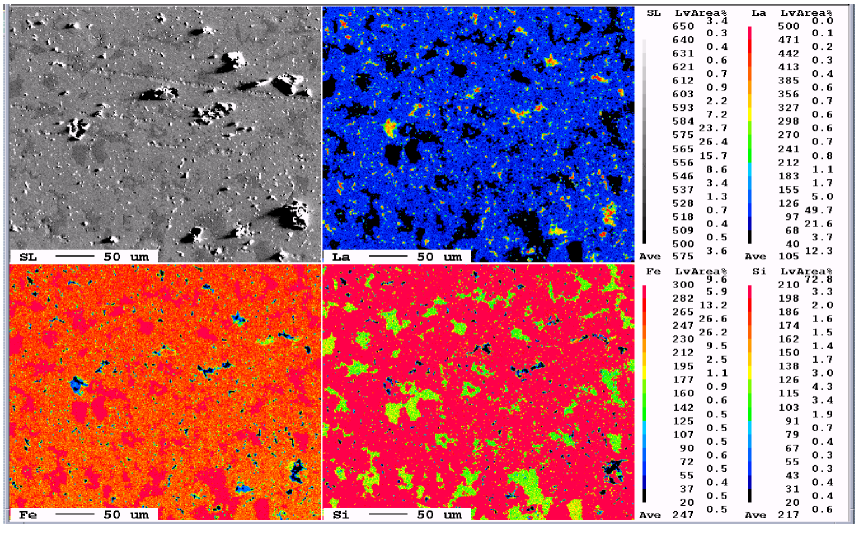

Figure 7. EPMA images of spark plasma sintered $La(Fe_{0.88}Si_{0.12})_{13}$

ment distribution of the samples changed little during the sintering process, suggesting that the sufficient homogeneity of fine elemental powders led to short-range atomic diffusion that caused rapid formation of the $NaZn_{13}$-type structure.

CONCLUSIONS

The novel formation of the $NaZn_{13}$-type structure was investigated and compared with formation by conventional fabrication methods. Short-range atomic diffusion of the elements and homogeneous distribution of the elements enhance the formation of the $NaZn_{13}$-type structure. We have shown that the $NaZn_{13}$-type structure can be formed by solid-state reaction using fine elemental powder. Our method consists of only one process and does not require melting, annealing, grinding, or molding.

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