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Synthesis of magnetocaloric LaFe$_{11.6}$Si$_{1.4}$ alloy by spark plasma sintering

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Abstract. LaFe$_{11.6}$Si$_{1.4}$ alloys have been successfully fabricated by spark plasma sintering (SPS). An annealing study of the SPS LaFe$_{11.6}$Si$_{1.4}$ alloys at different temperatures ranging from 1373 to 1523 K for annealing times from 30 minutes to 72 hours was carried out. This annealing study showed that LaFe$_{11.6}$Si$_{1.4}$ samples annealed at 1473 K (for annealing times between 30 minutes and 6 hours) have a significantly higher amount of the NaZn$_{13}$-type phase compared to samples annealed at other temperatures. Thus the critical annealing temperature which enhances the formation of the NaZn$_{13}$-type phase in SPS LaFe$_{11.6}$Si$_{1.4}$ compounds is 1473 K. A second study investigated the effect of different particle sizes of the starting powders on the formation of the NaZn$_{13}$-type phase. This study found that the samples synthesized using larger sized powder particles exhibited a significantly higher amount of the NaZn$_{13}$-type phase compared to samples synthesized using smaller sized powder particles, for the same heat treatment.

1. Introduction

Magnetocaloric (MC) materials are candidate materials for solid state refrigeration, due to their theoretical cooling efficiency being 60% of the Carnot engine. Prototype devices have been demonstrated including the Haier wine cooler, launched in January 2015 [1], used MnFeP$\text{SiGe}$ for the MC component. One of the industrially preferred MC material is LaFe$_{11.6}$Si$_{1.4}$ (La(Fe,Si)$_{13}$) in the NaZn$_{13}$-type phase. This is because the change in the magnetic entropy ($-\Delta S_M$) is 20-25 J kg$^{-1}$K$^{-1}$ for La(Fe,Si)$_{13}$, which is one of the highest of the MC materials with the Curie Temperature ($T_c$) near room temperature [2], plus it is non-toxic and consists of relatively cheap elements. La(Fe,Si)$_{13}$ alloys disadvantages include the $T_c$~187 K and the difficulty in achieving the NaZn$_{13}$-type phase. The first is solved by chemically doping with either Co or H, which shifts $T_c$ up to ~270 K and maintains $-\Delta S_M$ at 10-20 J kg$^{-1}$K$^{-1}$, as required for applications [2,3].

For the second, the main method of fabricating La(Fe,Si)$_{13}$ involves using conventional casting methods (arc-melting and induction melting) [3] followed by annealing at 1373 K for up to 14 days, to allow the correct NaZn$_{13}$-type phase to be achieved. One method of producing MC materials in a shorter time frame is melt-spun ribbons. Lyubina et al [4] investigated melt-spun La(Fe,Si)$_{13}$ ribbons, and determined that only a short annealing time of 1 hr at 1273 K was required to achieve 90% 1:13 phase within the samples. The La(Fe,Si)$_{13}$ ribbons had no thermal hysteresis as a function of magnetic field, but still had a first order transition. The main disadvantage of melt-spun La(Fe,Si)$_{13}$ ribbons was that they were brittle, so tended to break under magnetic cycling. Thus further investigations into different synthesis routes are required, so to reduce the production time, while maintaining the large $-\Delta S_M$.

Spark plasma sintering (SPS) is becoming a popular method for fast synthesis of a range of materials from metals to ceramics [5]. The process involves applying a high pressure at the same time as an electric
current to a powder sample within a die, at a holding temperature for a short period of time (5 – 30 mins) [5]. This produces dense samples as well as control of the grain size. Further annealing can take place after the SPS synthesis. Both Patisser et al. [6] and Shamba et al. [7] have used SPS to successfully sinter the NaZn$_{13}$-type phase in La(Fe,Si)$_{13}$. In this paper, we present two studies of how the annealing temperature and particle size influences the amount of NaZn$_{13}$-type phase present in La(Fe,Si)$_{13}$ synthesized using SPS.

2. Experimental Procedure

5g of high purity (99.9% or higher) La, Fe and Si elemental powders were mixed in the required stoichiometric ratio using a speedmixer (Speedmixer DAC 800 FVZ) for 20 minutes. The thoroughly mixed powders were introduced into a 20mm graphite die under argon atmosphere and consolidated using spark plasma sintering (FCT Systeme GmBH SPS system, type HPD 1050). The variation of the sintering parameters for the 12 samples studied are given in Table 1. The sintering parameters varied included the particle sizes of the starting materials from 5 - 800µm, the applied pressure from 41-51MPa, and the holding time from 5-15 minutes. After the SPS process the samples were polished to remove the graphite coatings, wrapped in tantalum foil and place in evacuated quartz tubes, then annealed at different temperatures ranging from 1373-1523K.

Analysis of the samples crystal structure was carried out using x-ray diffraction (XRD) with Cu K$_\alpha$ radiation using a Siemens D5000 diffractometer. A scanning electron microscope (SEM), (FEI Inspect F (FEI, Netherlands)) was used to investigate the microstructures of the SPS La(Fe,Si)$_{13}$ alloys including elemental mapping using energy dispersive spectroscopy (EDS). The magnetization measurements were carried out using a Quantum Design Physical Property Measurement system (PPMS) at 0.02T, varying the temperature from 100 – 350K.

| Sample | Starting particle size (µm) | Applied pressure (MPa) | Holding time (mins) | Holding Temp (K) | Annealing temp (K) | Annealing time (hrs) |
|--------|--------------------------|------------------------|---------------------|------------------|-------------------|---------------------|
| Sample 1 | 45 - 800 | 41 | 5 | 1423 | 1373 | 72 |
| Sample 2 | 45 - 800 | 41 | 10 | 1423 | 1373 | 72 |
| Sample 3 | 45 - 800 | 41 | 15 | 1423 | 1373 | 72 |
| Sample 4 | 45 - 800 | 45 | 5 | 1423 | 1373 | 72 |
| Sample 5 | 45 - 800 | 51 | 5 | 1423 | 1373 | 72 |
| Sample 6 | 45 - 800 | 51 | 5 | 1423 | 1373 | 72 |
| Sample 7 | 45 - 74 | 41 | 5 | 1423 | 1523 | 6 |
| Sample 8 | 45 - 74 | 41 | 5 | 1423 | 1473 | 0.5 |
| Sample 9 | 45 - 74 | 41 | 5 | 1423 | 1473 | 6 |
| Sample 10 | 45 - 74 | 41 | 5 | 1423 | 1373 | 72 |
| Sample 11 | 45 - 74 | 41 | 5 | 1423 | 1373 | 72 |
| Sample 12 | 5 - 74 | 41 | 5 | 1423 | 1373 | 72 |

3. Results and Discussion

In this work, we investigated the effects of various high-temperature annealing times from 1373-1523K on the phase formation of the SPS La(Fe,Si)$_{13}$ compounds. For the La(Fe,Si)$_{13}$ material system, the NaZn$_{13}$-type structure phase (known as the 1:13 phase), whose three strong diffraction peaks are at 20 = 27, 35 and 38.5° is the phase that exhibits promising MC properties. The α-Fe phase has strong diffraction peaks at 20 = 45 and 65° (Fig. 1a) and is detrimental to the MC properties. From the XRD patterns of the SPS La(Fe,Si)$_{13}$ samples, it is clearly observed that samples 6, 8 and 9 exhibit a significant amount of the 1:13 phase as compared to the rest of the samples, as the 1:13 phase XRD peaks have a higher intensity suggesting an increase in its volume fraction. Table 1 shows that samples 6 and 8 were annealed at 1473K for 30 minutes, whilst sample 9 was annealed at 1473K for 6 hours. The differing
amounts of the 1:13 phase in samples 6, 8 and 9 can be attributed to the different particle sizes of the starting powders (Table 1). Sample 6 which was synthesized using larger La powder particles (800 µm) exhibited a significantly higher amount of NaZn$_{13}$-type phase compared to samples 8 and 9, which were synthesized using smaller sized La powder particles (74 µm), but for different annealing times.

It is also observed in Fig. 1a that samples 1-5 and samples 10-12, which were annealed at 1373K for 72 hours consisted mainly of the $\alpha$-Fe phase suggesting that annealing La(Fe,Si)$_{13}$ compounds at lower temperatures for longer times independent of particle size does not significantly increase the formation of the 1:13 phase. While sample 7 was annealed at 1523K for 6 hours, it also consisted mainly of the $\alpha$-Fe phase, which suggests that annealing La(Fe,Si)$_{13}$ compounds at temperatures above 1500K for longer times also does not increase the formation of the 1:13 phase. Thus the XRD confirms that short time annealing at 1473K causes homogenization of the La(Fe,Si)$_{13}$ alloys by enhancing the formation of the 1:13 phase, thereby suggesting that 1473K is the critical temperature for obtaining the 1:13 phase.

Fig 1b shows the backscattered SEM micrograph of the SPS La(Fe,Si)$_{13}$ sample 6 alloy in the unpolished condition. The different phases in these alloys were identified by EDS (Fig. 2a). Fig. 1b shows that the SPS La(Fe,Si)$_{13}$ alloy has a texture with grains of various diameters ranging from 5 to 17 µm. The main grey phase within the grains contains La, Fe and Si, which corresponds to the 1:13 phase.
phase. The presence of a cracked appearance of the SPS La(Fe,Si)$_{13}$ alloy can be attributed to the short annealing time (30 minutes) which prevented full densification. The composition distribution in these La(Fe,Si)$_{13}$ alloys was investigated by SEM and EDS experiments. Fig. 2a shows the element mappings of the La(Fe,Si)$_{13}$ sample 6, in which the La, Fe, Si C elements were scanned to enable distributions of these elements to be obtained. The element mappings do not show significant inhomogeneity. As expected, carbon is observed in the entire sample, which is due to contamination from the SPS graphite die. Fu et al [8] investigated arc-melted La(Fe,Si)$_{13}$ doped with carbon, and found that the carbon diffused through the microstructure. They also found that the carbon lowered the optimum annealing temperature and accelerated the formation of the 1:13 phase by improving the nucleation rate. Thus the present of the die carbon, could be beneficial to the synthesis process and explain why a shorter annealing time gives the preferential phase.

Fig 2b shows the temperature dependence of the magnetization for the La(Fe,Si)$_{13}$ sample 6 measured in the zero field cooled (ZFC) and field-cooled (FC) process under a magnetic field of 0.02T over a temperature range from 100K to 350K. $T_c$ is defined as the temperature at which the $dM/dT$ (fig. 2b inset) of the heating $M$-$T$ curves is at a minimum. For the SPS La(Fe,Si)$_{13}$ sample 6, $T_c = 230K$, compared to an arc-melted La(Fe,Si)$_{13}$ sample $T_c = 186K$. The SPS sample $T_c$ is higher, due to a larger amount of residual $\alpha$-Fe impurity phase. This $\alpha$-Fe impurity phase was confirmed by the residual magnetization to be $\sim 4.5emu/g$ after the phase transition (Fig. 2b). Fig 2b, also shows the broadened FM-PM transition of the SPS La(Fe,Si)$_{13}$ alloy with no thermal hysteresis. This broadening of the $M$-$T$ curve is an indication of a 2nd order magnetic transition of this compound. The MC properties as well as other magnetic properties of the SPS La(Fe,Si)$_{13}$ alloy are discussed in details elsewhere [7].

4. Conclusions

The optimisation of SPS conditions for the synthesis of La(Fe,Si)$_{13}$ alloys has been investigated in detail by varying sintering parameters such as the applied pressure and holding times. An annealing study has shown that the optimum annealing temperature which results in the highest yield of the NaZn$_{13}$-type phase is 1473K. Results from this work show that the particle size of the starting powders play an important role in optimising the yield of NaZn$_{13}$-type phase. This study found that samples synthesised using larger La sized powder particles exhibited a significantly higher amount of the NaZn$_{13}$-type phase compared to samples synthesised using smaller La sized powder particles after undergoing the same heat treatment.

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