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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 1473K (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 1473K. 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 MnFePSiGe 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 $Jkg^{-1}K^{-1}$ 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~187K 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 ~270K and maintains $-\Delta S_M$ at 10-20 $Jkg^{-1}K^{-1}$, 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 1373K 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 1273K 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_α 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.

Table 1. The fabrication and annealing parameters for the SPS $La(Fe,Si)_{13}$ samples

	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	41	5	1423	1473	0.5
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 2θ = 27, 35 and 38.5° is the phase that exhibits promising MC properties. The α-Fe phase has strong diffraction peaks at 2θ = 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

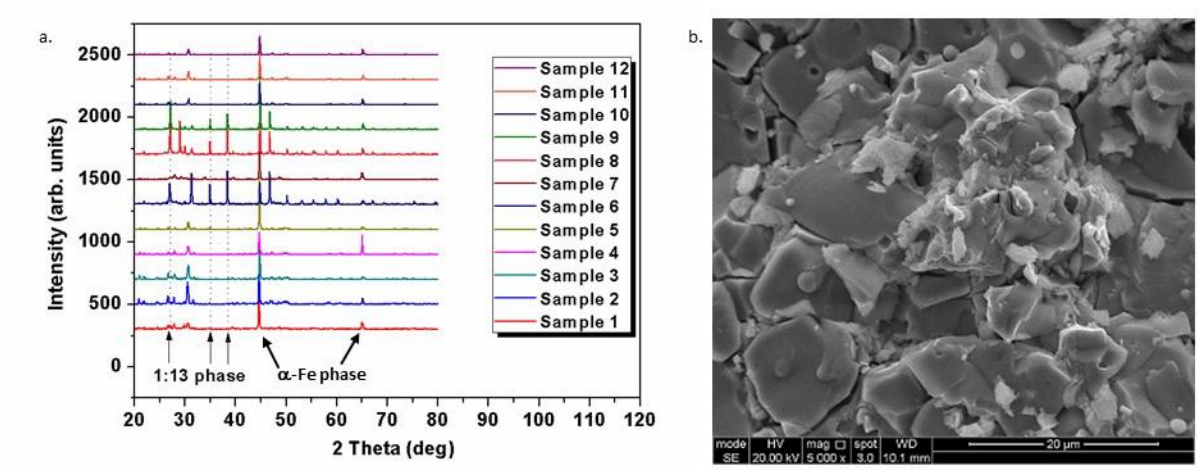

Figure 1a. XRD of the different SPS La(Fe,Si)$_{13}$ alloys. **1b**. Backscattered SEM micrograph of La(Fe,Si)$_{13}$ sample 6.

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 (800µm) 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 (74µm), 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 α-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 α-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 17µm. The main grey phase within the grains contains La, Fe and Si, which corresponds to the 1:13

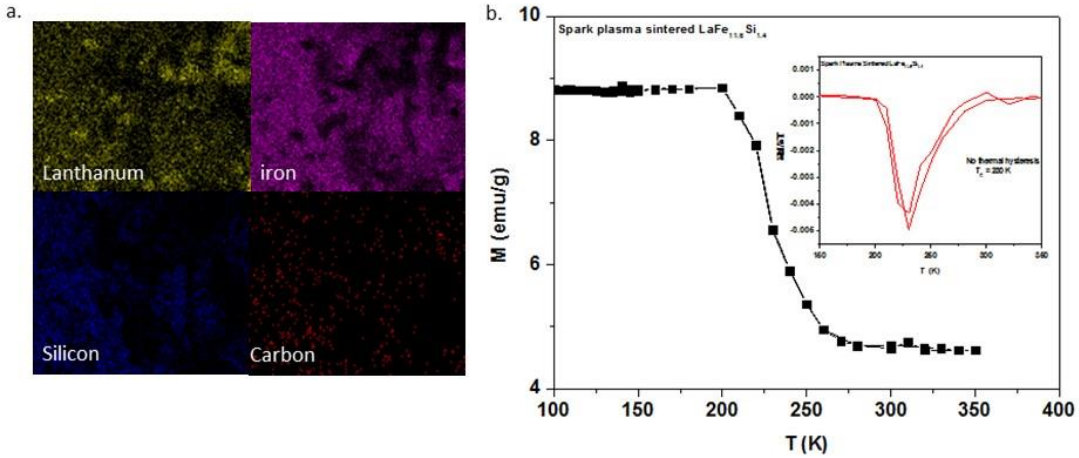

Figure 2a. EDS elemental mapping of the La(Fe,Si)$_{13}$ sample 6. **2b**. Magnetisation as a function of temperature of sample 6 $\mu_0 H$ = 0.02 T. **Inset:** *dM/dT* of La(Fe,Si)$_{13}$ sample 6.

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 α-Fe impurity phase. This α-Fe impurity phase was confirmed by the residual magnetization to be ~ 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* cuvre 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.

Acknowledgements

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