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A bimodal particle size distribution enhances mechanical and magnetocaloric properties of low-temperature hot pressed Sn-bonded $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ bulk composites

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ABSTRACT

We report a Sn-bonded $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ bulk composite with improved mechanical and magnetocaloric properties. $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ powders with a bimodal particle size distribution were mixed with a binder of Sn powder and hot pressed at a relatively low temperature of 423 K (150 °C). The use of bimodal size-distributed powder can reduce the non-magnetic Sn content. A bimodal particle size distribution of coarse particles (180–250 μm) and fine powders (< 45 μm) resulted in particle integrity even after hot pressing. The maximum values of magnetic entropy change ($-\Delta S_M$) and adiabatic temperature change (ΔT_{ad}) increased from 7.96 J/(kg·K) (2 T), and 2.05 K (1.4 T) to 8.71 J/kg and 2.14 K, respectively, due to this microstructure. The optimized composite exhibited an enhanced compressive strength of 224 MPa and a large $(-\Delta S_M)^{max}$ of 8.71 J/(kg·K) as well as an excellent thermal conductivity of about 8.05 W/(m·K).

1. Introduction

Another round of energy crisis is knocking at the door, which is awakening people's awareness of energy conservation and has stimulated extensive attention to energy efficient technologies. Magnetic refrigeration, based on the magnetocaloric effect (MCE) exhibited by solid magnetic refrigerants, can potentially replace conventional gas compression-based cooling. In recent years, applications of magnetic refrigeration include gas liquefaction systems [1], cryogenic applications [2] and ambient temperature refrigeration [3,4].

The $La(Fe,Si)_{13}$ compound with cubic $NaZn_{13}$-type structure has great advantages as a magnetocaloric material in terms of price, environmental friendliness and magneticaloric performance [4,5], relative to other high performance magnetic refrigerants such as Mn-based alloys [6] or $Gd_5Si_2Ge_2$ [7]. The large magnetic entropy change ($-\Delta S_M$) of $La(Fe,Si)_{13}$ is attributed to its large negative lattice expansion at its Curie temperature (T_C) and itinerant electron metamagnetic transition (IEMT) above T_C [8]. However, the microcracks can be caused by volume change in $La(Fe,Si)_{13}$ bulk material.

Although the $LaFe_{13-x}Si_x$ alloys exhibit a giant MCE, the magnetic entropy change ($-\Delta S_M$) peak usually appears at low temperatures (< 210 K) [4]. From the viewpoint of practical applications, it is highly desirable that the maximal ($-\Delta S_M$) of $NaZn_{13}$-type $La(Fe,Si)_{13}$-based alloys takes place near ambient temperatures.

The T_C of the $La(Fe,Si)_{13}$ alloys can be tailored to near room temperature by introducing hydrogenation, and the large MCE is retained [9]. However, it is inevitable that $La(Fe,Si)_{13}$-based compounds can be pulverized after hydrogenation due to their brittleness. The substitution of Fe by Co increases T_C [10,11]. But, the first-order magnetic transition (FOMT) becomes weak and the maximal ($-\Delta S_M$) decreases with increasing Co content in $La(Fe,Co)_{13-x}Si_x$ alloys [10,11]. Previous work has been reported [12–15] that partial substitution of La by RE (RE = Ce, Pr, Nd) in $La(Fe,Si)_{13}$ alloys enhances ($-\Delta S_M$) remarkably, the 1:13 phase is more easily formed, while T_C reduces monotonically due to lattice contraction. In order to increase the T_C and simultaneously maintain large MCE in $La(Fe,Si)_{13}$-based compounds, the effect

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of combined substitution of Co and Ce on the magnetic properties and magnetocaloric effect of La(Fe,Si)$_{13}$-type compounds has been previously studied [14,16]. Alloys prepared by the strip-casting method with a nominal composition of $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ ($T_C \sim 246$ K) were selected in this work.

The poor mechanical stability and cracking of these La(Fe,Si)$_{13}$ bulk alloys during magnetic field and thermal cycling can be restrained by introducing porosity to relieve the stress [17]. Powder sintering [18–21], epoxy bonding [22–25] and hot pressing (HP) with amorphous particles [26], Cu [27], Sn [28], and $Sn_{42}Bi_{58}$ [29] powders have been used to introduce porosity. Epoxy-bonded La(Fe,Si)$_{13}$ composites possess better mechanical properties compared with cast bulk material. However, epoxy severely reduces thermal conductivity, negatively impacting the performance of the composite [26–29].

Compaction of large La(Fe,Si)$_{13}$ particles within an amorphous Pd-based matrix at its glass transition temperature (T_g) keeps the particles intact [26]. However, Pd is very expensive, and the HP temperature only permits non-hydrogenated La(Fe,Si)$_{13}$ particles. The addition of 20 wt% Pd-based amorphous powders impairs the magnetic performance of the composite.

Hot pressed $LaFe_{11.6}Si_{1.4}$/Cu magnetocaloric composites revealed that the optimization of HP temperature is vital to produce composites with both large MCE and high strength [27]. Zhang, et al. [28] performed HP above the melting point of Sn (T_m = 505 K), molten Sn could easily fill the porous spaces, similar to liquid-phase sintering and showed no reaction among these elements. However, Sn exhibits a tetragonal to orthorhombic structural transformation at 434 K, the accompanying volume change can adversely influence the mechanical properties of the composite. $LaFe_{11.6}Si_{1.4}$ hydrides are chemically unstable above 423 K (150 °C) [4], hence the HP temperature is too high for the desired hydrogenated La-Fe-Si-H compound [28]. In our recent work [29,30], the influence of particle size on the mechanical and magnetocaloric properties were systematically investigated. Composites composed of large particles have larger values of stress and comparable strain compared to composites composed of small particles. The $(-\Delta S_M)^{max}$ values for composites with large particles are larger than those of composites with small particles, which is attributed to the effect of particle size on MCE [5,30–32].

The $(-\Delta S_M)$ of La(Fe,Si)$_{13}$ reduced with decreasing particle size [5,30–32]. Hence, small particle size was not much studied and there is few report of a bimodal particle size distribution. Here we report a La(Fe,Si)$_{13}$-based composite with a bimodal distribution particle size. The HP temperature was 423 K (150 °C), at this temperature stability of a hydrogenated La(Fe,Si)$_{13}$ is retained [33]. Our results showed that an appropriate mass ratio of bimodal distribution particles improves the mechanical and magnetocaloric properties of the composite. The precursor of the particles were obtained by the strip cast technique, confirming the feasibility of mass production of these magnetocaloric composites by HP.

2. Experiments

The flakes with nominal composition of $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ were produced by strip-casting. The structure of these flakes has been systematically investigated in our previous work [16]. The annealed flakes containing 93.5 wt% $NaZn_{13}$-type (1:13) majority phase (shown in Fig. 5 of Ref.[16]) were mechanically ground and distributed into two parts. The majority of the crushed flakes are coarse particles with a size of 180–250 μm, which are in the suggested range for good magnetocaloric performance [20]. The rest are fine powders under the size of 45 μm. To prepare bulk composites based on our previous work [29], 90 wt% $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ powders and 10 wt% Sn powders are mixed and pressed into bulk. For the $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ powders, fine particles with the weight proportion of 0, 5, 10, 20, and 30 wt% are used, these samples are denoted 0, 5, 10, 20, and 30 wt% fine powder sample, respectively. Non-magnetic Sn powders (> 99.9 wt % purity) with a size of 3–5 μm were employed as the binder. Before pressing, the $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ powders and Sn powders were homogenously mixed for 30 min by simple V-shape low-speed granulate powder mixing machine with speed of 24 r/min. Due to the low running speed of the mixing machine, the influence of external stress applied to the powders can be neglected and this mixing process does not affect the particle size. The homogenously mixed powders were pressed for 2 min at 423 K (150 °C) by a uniaxial stress of ~900 MPa into cylindrical pieces of Φ8 × 4 mm. The microstructure was investigated by scanning electron microscopy (SEM). The density of the composites was measured according to the Archimedes principle. The thermal conductivity was measured using the Quantum Design thermal transport option (TTO) for the Physical Property Measurement System (PPMS-9) at 300 K. The compression tests were conducted at ambient temperature using a universal materials testing machine. The adiabatic temperature change (ΔT_{ad}) was directly measured in a field change of 1.4 T using a home-built apparatus. The value of entropy change ($-\Delta S_M$) was deduced from the isothermal magnetization $M-H$ data according to the Maxwell relation.

3. Results and discussion

Fig. 1 shows the microstructures of the pressed samples. The white and grey areas represent Sn and $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ alloys, respectively. For sample without fine powder added, due to the large stress and limited Sn content, some coarse particles were crushed (marked by red ellipse) and many cracks appeared, as shown in Fig. 1(a). When fine powders were introduced, much less crushing was observed, as shown in Fig. 1(b)–(d). With increasing fine powder content, more micro-porosity was observed which was well distributed in the spaces between the coarse particles. From the enlarged boxed view in Fig. 1(f), these microporous regions (red boxed area in Fig. 1(e)) were found to consist of fine Sn powders and La-Ce-Fe-Co-Si powders, the Sn can buffer the stress due to its high ductility. During hot-pressing, the applied stress can be transferred and absorbed by these ductile microporous regions. As a result, the coarse particles are not broken. The porous structure could also reduce magnetic hysteresis loss by reducing internal strain and grain boundaries [17]. It should be noted that dark black holes in the microporous regions were caused by polishing.

Fig. 2 shows the density, porosity and thermal conductivity (λ) of the composites with different fine powder content. With increasing fine powder content from 0 to 20 wt%, the density of the composite increases. Based on Rietveld refinement, the theoretical density of the $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}$ alloy is 7.3 g/cm^3 and the density of β-Sn is 7.28 g/cm^3. Therefore, the theoretical density of the composites is about 7.3 g/cm^3. 20 wt% substitution of fine powders increased the density from 6.82 to 6.94 g/cm^3, the porosity of the composites decreased from 6.8 vol% to 4.9 vol% (20 wt% fine powder sample). This densification can be observed in Fig. 1. However, the addition of excessive fine powders is not beneficial to the density. As shown in Fig. 1(e), extensive microporous regions will decrease the density. Hence, the content of fine powders should not be higher than 20 wt%. The variation of thermal conductivity, shows a similar behavior as the density in Fig. 2(a). The composite with 20 wt% fine powders shows excellent thermal conductivity of about 8.05 W/(m·K), though it is smaller than that of bulk $LaFe_{11.6}Si_{1.4}$ (9.7 W/(m·K) at 300 K) [17], it is still higher than that observed in metal-bonded La(Fe,Mn,Si)$_{13}H_x$ composite material (7.5 W/(m·K)) [34]. Increasing fine powder content to 30 wt% leads to an undesirable drop in thermal conductivity, which is owing to the fact that the porosity does not decrease further, but increases instead. Obviously, the appearance of porosity in the composite sample causes the increase of thermal resistance and it is unfavourable to enhance the heat transfer ability [28]. However, it is an effective approach to decrease the porosity and significantly enhance