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JOURNAL OF RARE EARTHS
JOURNAL OF RARE EARTHS, Vol. 31, No. 12, Dec. 2013, P. 1163
www.re-journal.com/en/

Refrigeration effect of $La(FeCoSi)_{13}B_{0.25}$ compounds and gadolinium metal in reciprocating magnetic refrigerator

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Received 16 April 2013; revised 14 September 2013

Abstract: The $LaFe_{11.9-x}Co_xSi_{1.1}B_{0.25}$ with x=0.9 and x=0.82 compounds were synthesized from commercial purity raw materials. The magnetic property of $LaFe_{11.9-x}Co_xSi_{1.1}B_{0.25}$ and Gd particles were tested on the reciprocating refrigerator at the same condition in order to compare the cooling capacity of the two materials. The results showed that the cooling velocity of Gd was obviously higher than that of $LaFe_{11.9-x}Co_xSi_{1.1}B_{0.25}$. The maximum temperature span was 12.7 ºC for $LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$, 14.9 ºC for Gd metal whose mass is the same as that of $LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$, 8.1 ºC for Gd metal whose volume is the same as that of $LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$. Series connection of $LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$ and $LaFe_{11.08}Co_{0.82}Si_{1.1}B_{0.25}$ had the maximum cooling temperature span of 15.3 ºC.

Keywords: magnetic refrigeration; magnetic temperature span; magnetic entropy change; adiabatic temperature change; rare earths

Magnetic refrigeration is a kind of cooling technology by using the magnetocaloric effect (MCE) materials which emit heat in the condition of isothermal magnetization and absorb heat in the condition of adiabatic demagnetization. It is a green cooling technology with the character of high efficiency, low energy dissipation and non-pollution etc. compared with the traditional gas refrigeration.

Magnetic refrigerant as an important part of magnetic refrigeration, the magnetocaloric effect value of the refrigerant is a key factor of the magnetic cooling technology. The magnetocaloric effect materials have been widely studied these years. Giant magnetocaloric effect material $Gd_5Si_2Ge_2$ with first order transition was discovered by Jr K.A. Gschneidner and V.K. Perchsky in Ames Lab of America in 1997[1–3]; Giant magnetocaloric effect material $MnAs_{1-x}Sb_x$ was discovered by Wada and Tanabe of Tokyo University in 2001[4]; Fengxia Hu and Baogen Shen from Chinese Academy of Sciences found giant magnetocaloric effect material $La(Fe_{1-x}Si_x)_{13}$ with $NaZn_{13}$ phase in 2001[5–9]; O. Tegus et al. found the large magnetocaloric effect material $MnFeP_{1-x}As_x$ with Fe_2P phase in Amsterdam University in 2002[10,11]. For the giant magnetocaloric effect, non-toxic and relatively cheap $La(Fe_{1-x}Si_x)_{13}$ series materials are considered to be the most promising room temperature magnetic cooling material and are widely researched[12–15]. Saito et al. prepared $La(Fe,Co,Si)_{13}$ sphere particles with the diameter of 0.1–1.2 mm by the revolving electrode method successfully[16]. Katter et al. prepared various kinds of $LaFe_{13-x-y}Co_xSi_y$ plates by sintering method[17]. Although the isothermal magnetic entropy of $La(Fe,Co,Si)_{13}$ compound is larger than that of Gd metal, the adiabatic temperature change of the compound is smaller than that of Gd. Whether the large isothermal magnetic entropy could lead to large cooling capacity has to be further studied. There are few reports about the $La(Fe,Co,Si)_{13}B_x$ compound and Gd metal prepared to the same shape and tested on the magnetic refrigerator at the same condition. We researched the synthetical refrigeration effect of the above mentioned two materials in application in this paper.

1 Experimental

1.1 Sample preparation

According to the large numbers of experiment results, we designed $LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$ (BS1001, T_c=291 K) and $LaFe_{11.08}Co_{0.82}Si_{1.1}B_{0.25}$ (BS1002, T_c=279 K) with different magnetic transition points. Cylindrical ingots of the above mentioned compounds were synthesized using induction furnace. The starting materials with commercial purity were mixed in stoichiometric proportion, the purity of La is 98% and the purity of the rest metals is 99%. The prepared ingots were annealed at 1070 ºC for

Foundation item: Project supported by National High Technology Research and Development Program of China (2011AA03A404), International Cooperation Program (2011DFA53230), National Natural Science Foundation of China (51261001) and Science Foundation of Inner Mongolia (2011MS0801)

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DOI: 10.1016/S1002-0721(12)60421-9

10 h. Irregular particles with the size of 0.42–0.85 mm of BS1001, of BS1002 and of Gd metal of commercial purity were prepared by the jaw crusher.

X-ray diffraction (XRD) showed that the samples possessed the $NaZn_{13}$-type structure.

1.2 Magnetocaloric effect characterization

We analyzed the phase structure of the alloy by XRD (Philips PW-1700). We measured the thermal magnetic curve (*M-T*) and the isothermal magnetization curve (*M-H*) of the sample by a vibrating-sample magnetometer (VSM-Lakeshore7407 type) and calculated the magnetic entropy ΔS_m by Maxwell relation. We used the self-produced XHY type adiabatic temperature change test device[18] to test the adiabatic temperature change ΔT_{ad}.

1.3 Application in reciprocating magnetic refrigerator

To compare the practical cooling capacity of $LaFe_{11.9-x}Co_xSi_{1.1}B_{0.25}$ and Gd, we measured the samples in the 2nd self-produced reciprocating magnetic refrigerator (the principle graph shown in Fig. 1), which employed H type Nd-Fe-B permanent-magnet system (Fig. 1(1)) with the magnet length of 200 mm, the out diameter of 150 mm, magnet space diameter of 37 mm and the magnet field of 1.5 T. The field reciprocated on the two test benches (Fig. 1(2)) with the effective length of 400 mm and effective volume of 157 cm^3. The cold end (Fig. 1(3)) and the hot end (Fig. 1(4)) were made from red copper pipe. The Na(OH) solution with the concentration of 1% was used as heat transfer medium to prevent oxidation of Gd. The mixture solution of Na_2MoO_4, Na_3PO_3, $NaCr_2O_7$ and Na_2SiO_3 was used as heat transfer medium to prevent oxidation of $La(FeCoSi)_{13}B_x$.

The particles of BS1001 (580 g), Gd metal (785 g) and series connection of BS1001 (390 g) and BS1002 (190 g) were put into the three benches. To compare the cooling capacity of BS1001 and Gd in the condition of the same weight, particles of Gd (580 g) were put into the special benches. The porosity of the material in the test benche was 43.2%. The maximum of the cooling temperature span of the four benches were tested at the same running conditions at room temperature.

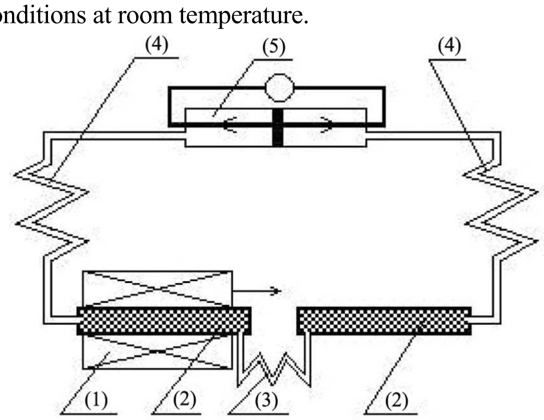

Fig. 1 Sketch of structure of reciprocating refrigerator
(1) Magnet; (2) Test benches; (3) Cool end; (4) Hot end; (5) Pump

2 Results and discussion

2.1 Magnetocaloric effect of materials

Fig. 2 shows that the max magnetic entropy ΔS_m is 5.2 J/KgK for BS1001, 3.5 J/KgK for Gd at 0–1.5 T which were calculated from the measured *M-T* curves and *M-H* curves. The maximum magnetic entropy ΔS_m of BS1001 is larger than that of Gd. In order to evaluate the magnetic refrigeration effect of the two materials, the relative cooling power (RCP) is calculated by the following expression:

$$RCP=-\Delta S_{m,max}\times\delta T \quad (1)$$

Where $\Delta S_{m,max}$ and δT are the negative maximum value and the full width of half maximum of the max magnetic entropy, respectively. According to the data of Fig. 2 the calculated RCP is 176.8 J/Kg for BS1001, 101.5 J/Kg for that of Gd. The RCP of BS1001 is lager than that of Gd obviously.

Fig. 3 shows the adiabatic temperature change ΔT_{ad} of BS1001, BS1002 and Gd metal measured by XHY type adiabatic temperature change test device. The results show that the maximum ΔT_{ad} is 3.5 K for Gd with T_c=294 K, 2.3 K for BS1001 with T_c=291, and 2.4 K for BS1002 with T_c=279 K. The Curie temperature of BS1001

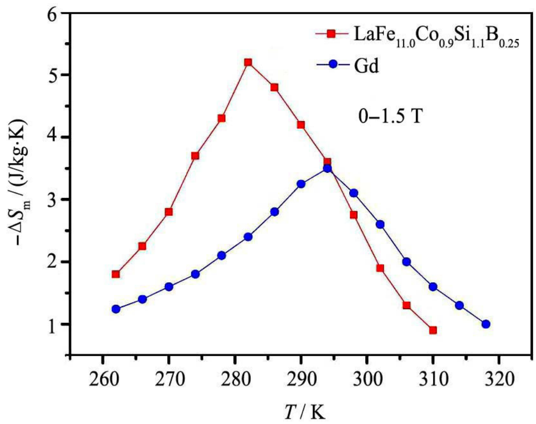

Fig. 2 Temperature dependence of the magnetic entropy change of BS1001 ($LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$) and Gd metal for a field variation of 1.5 T

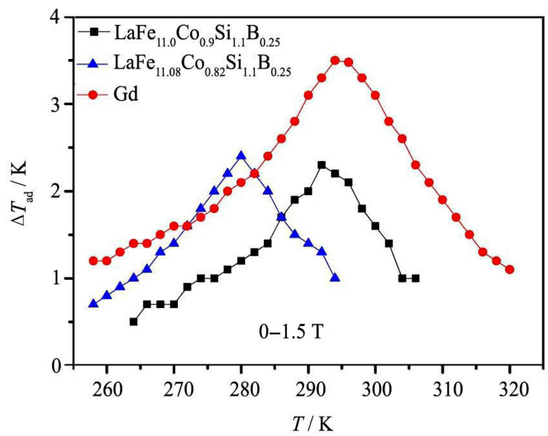

Fig. 3 Temperature dependence of the adiabatic temperature change of BS1001 ($LaFe_{11.0}Co_{0.9}Si_{1.1}B_{0.25}$), BS1002 ($LaFe_{11.08}Co_{0.82}Si_{1.1}B_{0.25}$) and Gd for a field variation of 1.5 T by direct measurement