



Microstructure, Corrosion Resistance, and Magnetic Properties of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) Compounds after Corrosion in Distilled Water

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Abstract

Corrosion tests were carried out by immersion the $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) compounds in distilled water for different times. The effect of corrosion is systematically studied in terms of morphology, microstructure, corrosion resistance, and magnetic properties. The results show that after 30-min corrosion, obvious corroded spots appeared on the surface of all compounds. It was also found that Si has an adverse effect on corrosion resistance. With the increase of Si content, the corroded spots are connected. The E_{corr} decreased from -0.57 to -0.65 V while I_{corr} increased from 3.91 to 5.08 $\mu\text{A}/\text{cm}^2$ with increasing the Si content from 1.3 to 1.5. In continuing to extend the corrosion time to 7 days, a large-scale corrosion area appeared, accompanied by the peeling of the main phase as anode and the retention of $\alpha\text{-Fe}$ phase as cathode. Meanwhile, the magnetic entropy change of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds decreased from 8.1 to 7.7 J/(kg K) when the corrosion time increased from 0 to 7 days. After 21-day corrosion, the sample surface was completely covered by corrosion products. Furthermore, long-time corrosion has a significant effect on magnetic properties. The Curie temperature increased from 289 to 314 K for 0-day and 21-day corrosion of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds, respectively. Significantly, the magnetic entropy change curves showed two peaks in the ΔS - T_c curves. Magnetic stability was decreased after long-time corrosion.

Keywords $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ magnetic refrigeration material · Corrosion behavior · Magnetic properties

1 Introduction

$\text{La}(\text{Fe},\text{Si})_{13}$ compounds with cubic NaZn_{13} -type structure (1:13 phase) are promising materials for magnetic refrigeration due to their excellent soft ferromagnetism, high magnetization, abundant resource reserve, and low cost [1–3]. As we all know, the 1:13 phase is the magnetocaloric phase of $\text{La}(\text{Fe},\text{Si})_{13}$ alloys [4]. However, it is very difficult to obtain

a single 1:13 phase because of the intrinsic characteristics of peritectic reaction $\text{Fe} + \text{LaFeSi} \rightarrow \text{La}(\text{Fe},\text{Si})_{13}$ [5]. A certain amount of secondary phases are retained in most annealed $\text{La}(\text{Fe},\text{Si})_{13}$ compounds [6–8]. Multiphase structure and large corrosion potential difference between phases lead to poor corrosion resistance [9–11]. From previous literature, the maximum magnetic entropy change of $\text{La}(\text{Fe}_{0.94}\text{Co}_{0.06})_{11.7}\text{Si}_{1.3}$ decreased about 16% after 15-day corrosion in distilled water [12]. Corrosion will shorten the service time of magnetic refrigerator, and corrosion precipitate will deteriorate the heat exchange performance. The corrosion resistance can be enhanced by partial substituting Co, Cr, B for Fe and reducing dissolved oxygen concentration in aqueous solution [13–16]. The magnet can also be isolated from the corrosive medium by surface treatment to improve the corrosion resistance. Zhao et al. [17] reported the corrosion behavior and magnetocaloric effect of $\text{LaFe}_{11.6}\text{Si}_{1.4}/\text{Sn}$ with FeNi coatings by hot pressing. The high-permeability FeNi permalloy can enhance the corrosion resistance and magnetocaloric effect. The $\text{LaFe}_{11.5}\text{Si}_{1.5}$ particles with Cu coatings prepared by electroless plating method also can have

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better corrosion resistance and lower magnetic hysteresis loss [18]. You et al. [19] demonstrated that the compressive strength and corrosion resistance can be significantly increased with Cu coating by magnetron sputtering machine. However, no matter what kind of anti-corrosion method is adopted, it is necessary to understand the corrosion behavior to carry out effective corrosion protection. What's more, it is very important for application to investigate the influence of corrosion on magnetic properties. In this paper, we studied the corrosion behavior of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ magnets when the Si content changed from 1.3 to 1.5 and investigated the impact of corrosion on the magnetic properties by

immersing the $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds in the distilled water for different times.

2 Experimental Details

$\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) ingots used in the present experiments were systematically investigated previously [20]. The ingots were annealed at 1373 K for 4 days.

A DX-2600 X-ray powder diffractometer (Cu-K radiation) was used to determine phase constitution and crystal structure. The microscopic surface morphologies and elemental

Fig. 1 Surface morphology of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) compounds after being immersed in distilled water for different times **(a)** Backscattered electron image of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ before corrosion; **(b-d)** Backscattered electron image of the different compounds after being immersed for 30 min: $\text{LaFe}_{11.05}\text{Co}_{0.65}\text{Si}_{1.3}\text{C}_{0.15}$ **(b)**, $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ **(c)**, $\text{LaFe}_{10.85}\text{Co}_{0.65}\text{Si}_{1.5}\text{C}_{0.15}$ **(d)**; **(e-f)** Second electron image of the different corrosion zone for $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ after being immersed for 7 days; **(g-h)** Second electron image of the different corrosion zone for $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ after being immersed for 21 days

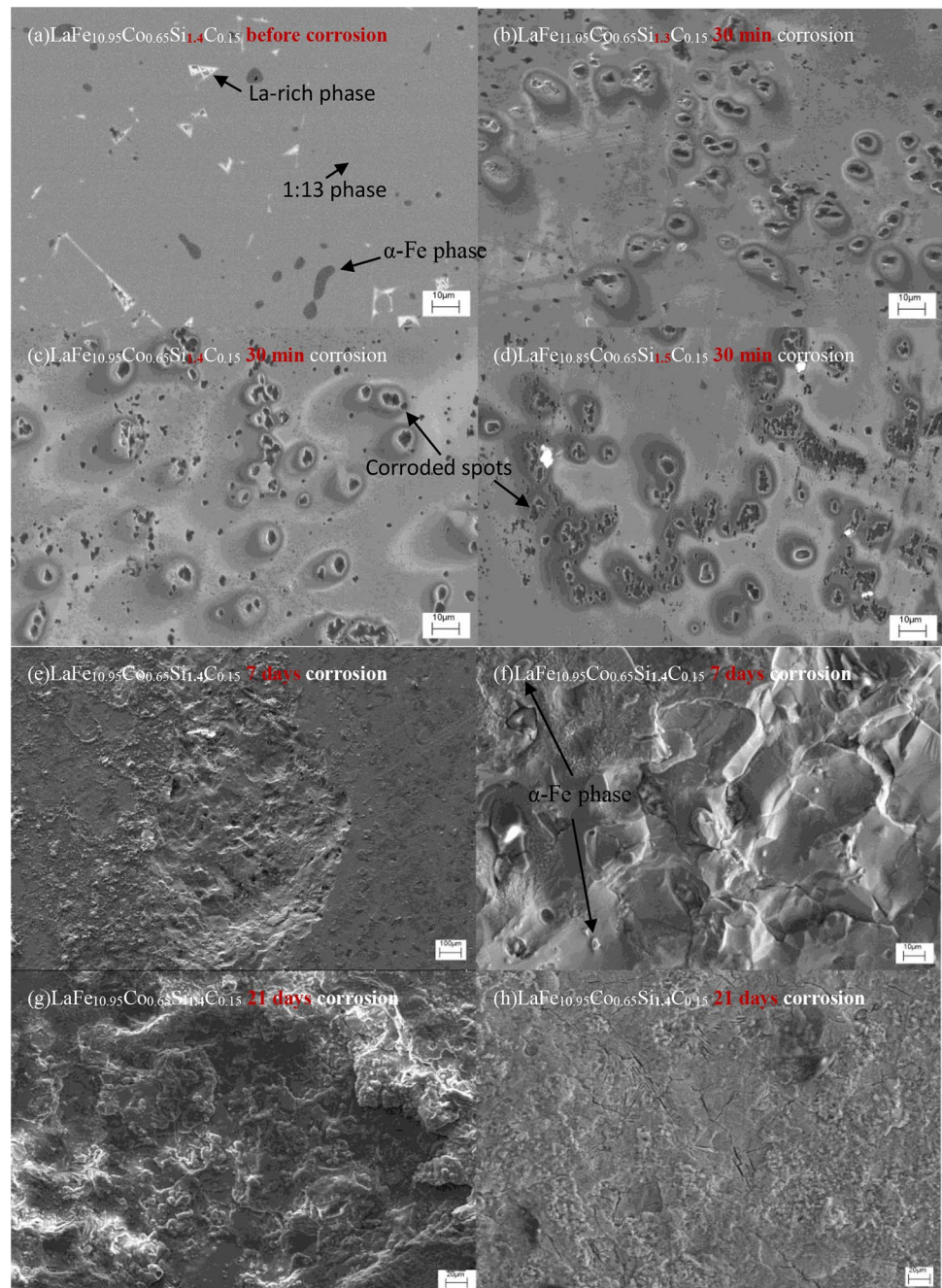
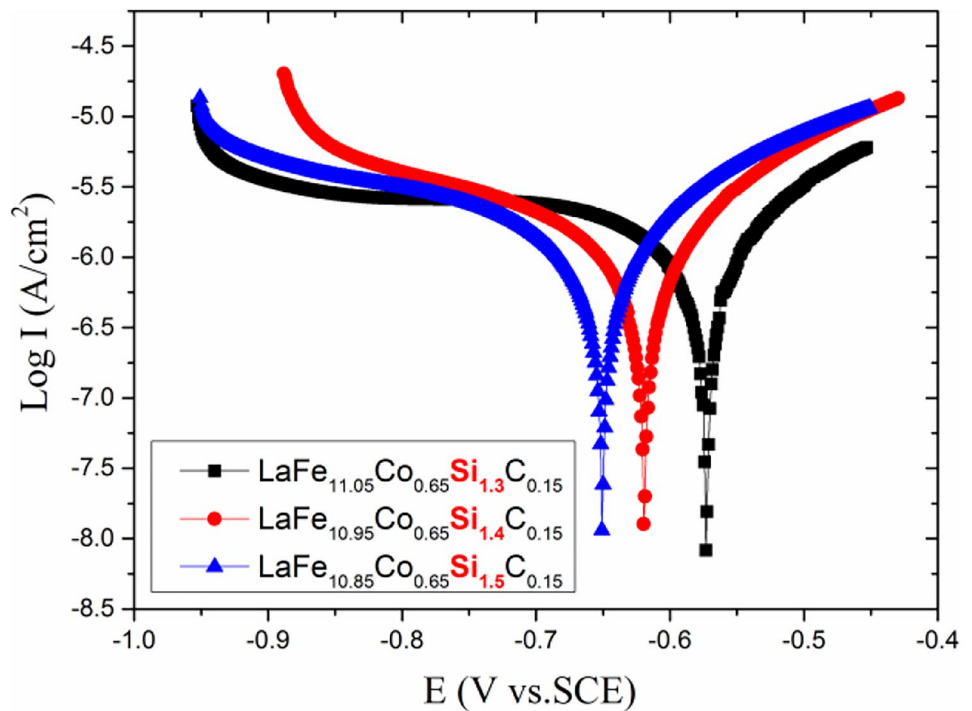


Fig. 2 Polarization curves of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x=1.3, 1.4, 1.5$) compounds



compositions were carried out using a scanning electron microscope (SEM) with energy-dispersive spectrometry (EDS). Electrochemical tests were conducted by VersaSTAT MC electrochemical analyzer/workstation. Each measurement was performed in a standard three-electrode cell consisting of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ working electrode, saturated calomel reference electrode (SCE), and a Pt counter electrode. Polarization curves for specimens in the test solution were recorded at a sweep rate of 1×10^{-3} V/s. All the corrosion studies were carried out in distilled water in an air environment at room temperature. The employed amplitude of the sinusoidal signal was ± 5 mV and the tested frequencies ranged from 100 kHz to 100 mHz. Magnetic properties of the samples were measured by Quantum Design VersaLab with a vibrating sample magnetometer (VSM) option. The magnetic entropy change was calculated from magnetization data by using the Maxwell relation.

3 Results and Discussion

To study the corrosion behavior of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x=1.3, 1.4, 1.5$) compounds, the surface morphology of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ compounds after being immersed in distilled water for different times (Fig. 1) was obtained. Figure 1a shows SEM image of the $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compound before corrosion. The black areas, white areas, and gray areas represent α -Fe phase, La-rich phase, and 1:13 phase, respectively (analyzed by EDS). The number of secondary phases is small. The XRD results also showed that all samples were mainly composed of the NaZn_{13} -type phase

(not shown here). Figure 1b–d show the surface morphology of the compounds with different Si content after immersion for 30 min. After a short time of corrosion, all compounds show obvious corroded spots, and the number of corroded spots does not change significantly with the different Si content. However, it should be noted that with the increase of Si content, the corroded spots show a connecting trend on the surface. Figure 1e–h present the surface morphology of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds after being immersed in distilled water for different time. As can be seen from these

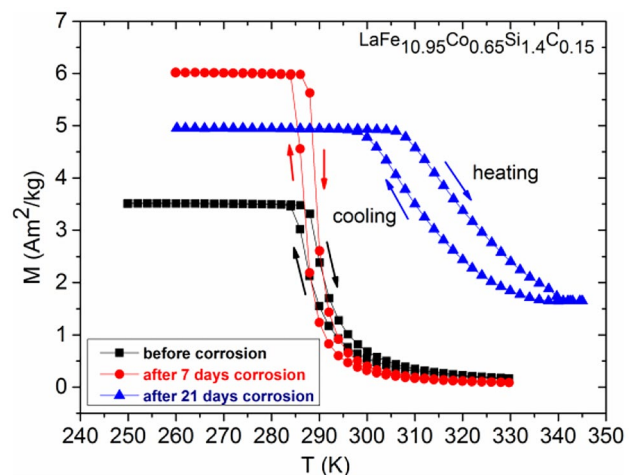
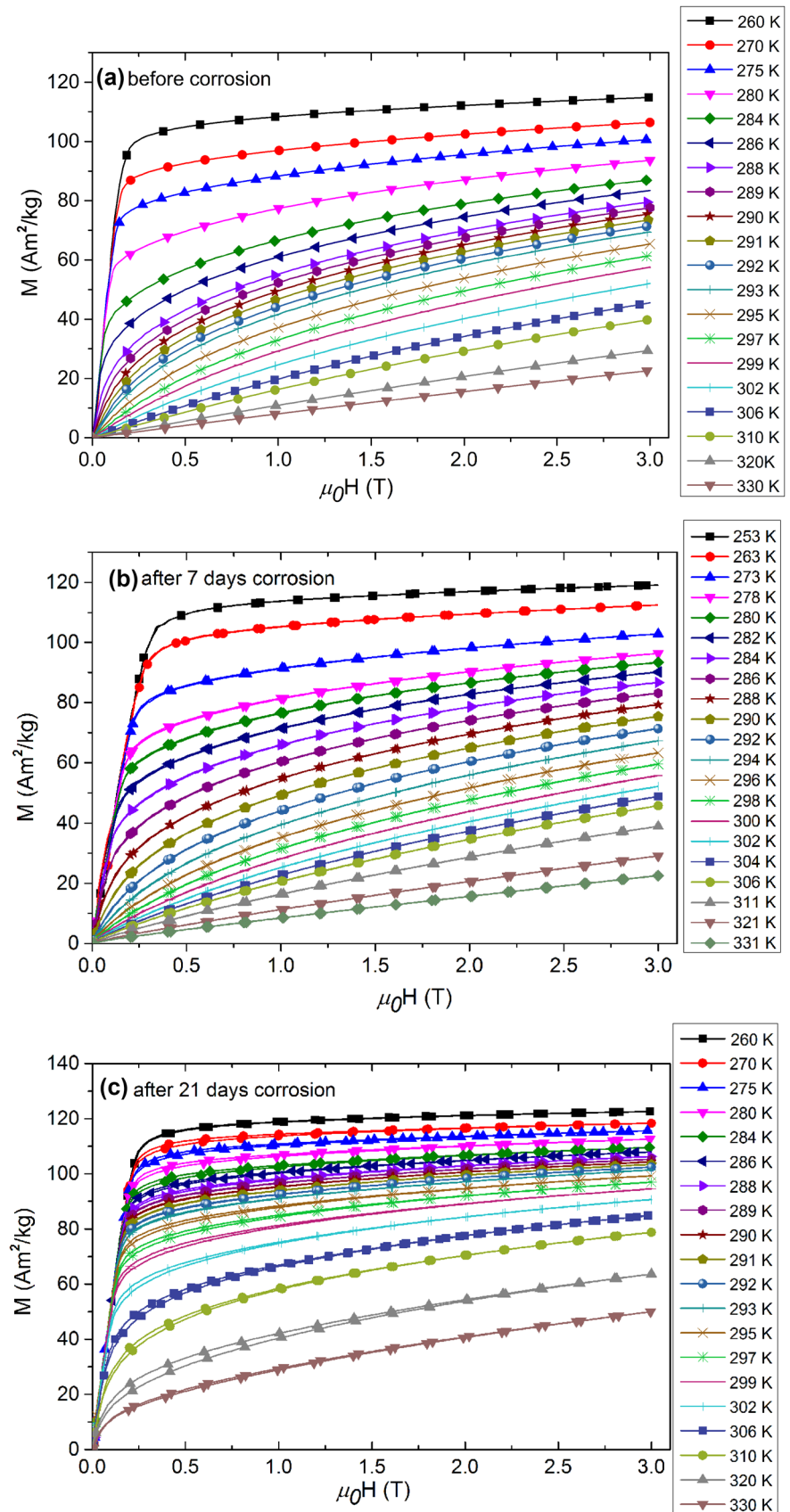


Fig. 3 Magnetization versus temperature for $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds after immersed in distilled water for different time under a magnetic field of 0.01 T

Fig. 4 Magnetization isotherms of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds measured at various temperatures around T_c and in the magnetic field 3 T (a) M-H curves of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compound before corrosion; (b) M-H curves of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ after being immersed for 7 days; (c) M-H curves of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ after being immersed for 21 days



figures, a large range of corrosion zone has been formed on the surface of the compound after 7-day corrosion (Fig. 1e). The corrosion product film is relatively loose, and the 1:13 phase particles are spalled off obviously. A small amount of α -Fe phase is observed in and around the corroded spots after the 1:13 phase falls off (Fig. 1f). After 21-day corrosion, the compounds have been completely covered by corrosion products (Fig. 1g). The corrosion product film becomes denser than that after 7 days, but also has many cracks (Fig. 1h).

To further understand the effect of Si on corrosion behavior, the electrochemical behaviors were systematically investigated. Figure 2 shows the potentiodynamic polarization curves for $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) compounds in distilled water. The results show that the anodic reaction of all samples exhibited active dissolution. This behavior indicates that the corrosion product film does not provide sufficient protection for the compound. With the increase of Si content, the polarization curves were shifted to the lower potential region, and the anodic and cathodic sections of the polarization curves were shifted to the region of higher current density. As Si content increased from $x = 1.3$ to 1.5, E_{corr} decreased from -0.57 to -0.65 V while I_{corr} increased from 3.91 to 5.08 $\mu\text{A}/\text{cm}^2$, indicating that the corrosion resistance of the compound became worse with the increase of Si content. This is probably because the corroded spots of the compound with high Si content are easier to connect, the corrosion product film is not suitable to form, resulting in faster corrosion rate.

Figure 3 shows the temperature dependence of the magnetization for $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds after corrosion compared to the parent sample (before corrosion). The Curie temperature T_c , defined as the temperature at the minimum of dM/dT of the heating M - T curves, are 289 K,

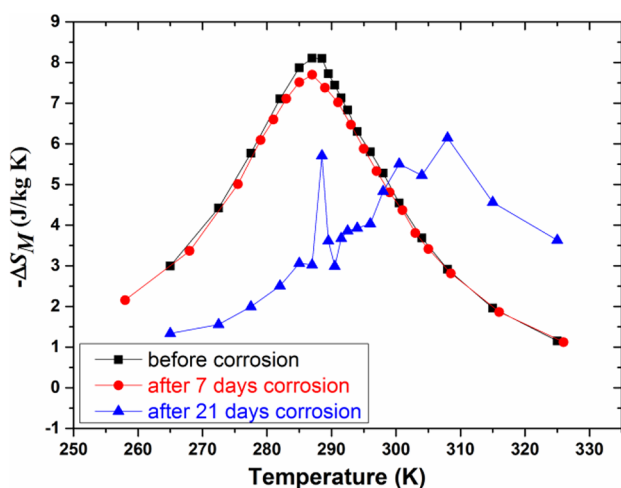


Fig. 5 Temperature dependence of the magnetic entropy changes of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds after corrosion in distilled water for different time under 0–3 T field change

290 K, and 314 K for 0-day, 7-day, and 21-day corrosion, respectively. The maximum magnetization of the sample varies irregularly because the low applied magnetic field cannot make the sample reach saturation state. There is no significant difference in T_c between 0-day and 7-day corrosion. Therefore, 7-day corrosion has little effect on T_c . However, after 21-day corrosion, the T_c increased significantly. The ferromagnetic paramagnetic transitions of the 0-day and 7-day corroded compounds are completed in a narrow temperature zone, while the transition temperature zone of the sample corrosion for 21 days becomes wider, and there is an obvious thermal hysteresis phenomenon. The M - T curve of the compound after 21-day corrosion shows that the residual magnetization in the high-temperature zone is much higher than zero, indicating the existence of residual magnetization of α -Fe phase. It can also be seen from the above scanning photos that after a long time of corrosion, the 1:13 main phase was corroded as the anode, leaving a certain number of α -Fe phases as the cathode.

The isothermal magnetization curves of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds corroded for 0 days, 7 days, and 21 days are shown in Fig. 4a–c, respectively. Figure 4a, b display an excellent reversible behavior in the magnetic cycle, and almost no magnetic hysteresis during the increase and decrease of fields. However, there is an obvious hysteresis phenomenon in Fig. 4c. Furthermore, M - H curves of Fig. 4c have bending phenomena in the low field range when temperatures are higher than T_c of 1:13 phase. It is due to the contribution of soft magnetic α -Fe phase, which is remained as cathode during corrosion.

Figure 5 shows the variation curve of magnetic entropy change with temperature of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds before and after corrosion. After only 7-day corrosion, the maximum magnetic entropy change decreased by 5%. The magnetic properties of $\text{La}(\text{Fe},\text{Si})_{13}$ magnet are closely related to its microstructure. As the main source of magnetic entropy change of magnets, the 1:13 phase was corroded and peeled off after 7-day corrosion, as shown in Fig. 1. After 21-day corrosion, not only the magnetic entropy change but also the stability of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ compounds decreased. Two peaks (at 289 K and 308 K) appeared in the ΔS - T_c curves. Rare earth elements have a strong affinity for hydrogen atoms. Soaking the compound in non-deoxygenated water will lead to hydrogen absorption behavior. The non-uniform hydrogen absorption in the corrosion process of the compound leads to the instability of magnetism.

4 Conclusions

In summary, we studied the corrosion behavior of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$) compounds in distilled water for different times. It was found that the

corrosion resistance decreased with the increase of Si content. More importantly, corrosion has a great influence on the morphology, microstructure, and magnetic properties. Only after 30-min corrosion, a large number of corrosion spots appear on the surface of $\text{LaFe}_{12.35-x}\text{Co}_{0.65}\text{Si}_x\text{C}_{0.15}$ ($x = 1.3, 1.4, 1.5$). After 7-day corrosion, the main phase as anode peeled off. A wide range of corrosion zone appeared in the $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$. After 21-day corrosion, the $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ was all covered by corrosion film. However, the film was not dense enough and there were many cracks, so it could not effectively protect the compounds. Short-time corrosion caused the decrease of magnetic properties. After 7-day corrosion, the maximum entropy change of $\text{LaFe}_{10.95}\text{Co}_{0.65}\text{Si}_{1.4}\text{C}_{0.15}$ decreased about 5%. Long-time corrosion not only reduces the magnetic entropy change, but also leads to the instability of magnetic properties. After 21-day corrosion, two peaks (at 289 K and 308 K) appeared in the magnetic entropy change curve due to the heterogeneous hydrogen absorption. From the perspective of practical application, the corrosion behavior deserves sufficient attention in the use of $\text{La}(\text{Fe},\text{Si})_{13}$ as magnetic refrigerant.

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