Corrosion behavior of Fe25Mn6Si5Cr shape memory alloys modified with rare earth in a NaCl solution

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The Fe-Mn-Si based shape memory alloys (SMAs) have undergone significant development in recent years [1–6]. They are expected to be used as a material for tighteners or pipe couplings on a large scale due to the advantages of low cost and good workability. Several efforts have been made to improve the shape memory effect (SME) and corrosion resistance through various alloying methods with substitutional elements Cr, Ni [2] and/or interstitial atoms of N [3].

In early 1998, Hsu [7] suggested that a rare earth (hereafter, RE stands for rare earth elements) addition might lower the stacking fault energy and T_N temperature of FeMnSi based alloys and therefore improve the SME. Zhou *et al.* [5] and Zhao [8] then proved such a beneficial effect by adding a blend of RE or Ce respectively. Recently, a systematical study [6] on the effect of RE, over a wide range of RE-content, indicated that appropriate amounts of RE, 0.02–0.3 wt%, cannot only lower the stacking fault energy but also strengthen the austenite and a FeMnSiCr-0.16RE alloy achieves almost 100% shape recovery after only two training cycles with 4% prestrain. However, a question still remains whether the corrosion resistance of such alloys will be deteriorated due to adding RE, which has to be considered when they are used practically, for instance, in water-pipe system. Therefore, the corrosion behavior of the Fe25Mn6Si5Cr based alloys containing various contents of RE in 3.5 wt% NaCl aqueous solution that approximately simulates the sea water was investigated by using potentiodynamic polarization measurement and immersion tests. An 18-8 stainless steel was taken as reference material for comparison.

Three alloys with nominal compositions Fe-25Mn-6Si-5Cr-xRE ($x = 0$, 0.16 and 0.30 wt%) were prepared by vacuum induction melting using high purity iron, manganese and silicon and a blend of RE elements (mainly La and a small quantity of Ce). Their analyzed compositions, together with that of the reference 18-8 stainless steel, are listed in Table I. The ingots were homogenized at 1373 K for 10 hrs, and then forged and hot-rolled into 1–2 mm plates.

Potentiodynamic scanning measurements were conducted using a Solatron SI1260 electrochemical interface. A conventional three-electrode cell was employed, in which a saturated calomel electrode (SCE) was used as reference, and a large platinum foil served as the auxiliary electrode. Electrochemical tests were carried out in a glass cell filled with ~200 ml of aqueous solution maintained at room temperature. To avoid interference from crevice corrosion, the mounted electrodes were painted on the resin-alloy interface with an alkyd varnish. Alloy samples with an exposed surface area of ~1 cm^2 were wet ground with 800-grit SiC paper, washed in distilled water and rinsed in acetone prior to polarization. The samples were immersed in 3.5 wt% NaCl aqueous solution for 20–30 min until a stable open circuit penitential (OCP) was attained. Then, polarization was initiated at ~200 mV negative to OCP, followed by scanning toward the noble direction.

Immersion tests were also carried out on the investigated alloys, by adapting the GB10124-88 standard [9], in the same solution as described above. The total exposure time was 120 hrs for the weight loss measurements and the corrosion rate was then calculated.

Light microscopy (LM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to observe the microstructures of the investigated alloys.

The measured results of the weight loss in immersion tests are shown in Fig. 1. It is seen that the corrosion rates of the tested alloys can be ranked as below:

1# alloy > 3# > 2# > 18-8 steel;

One can see that the 2# alloy containing 0.16 wt% RE shows quite low corrosion rate compared to the others. It is worth noting that this alloy was found to be the best in SME [6]. That is to say, by carefully controlling the RE-content a good combination of both the SME and corrosion resistance was achieved.

Fig. 2 shows the potentiodynamic scanning (PDS) curves of the sample in 3.5 wt% NaCl solution at a sweeping rate of 0.5 mV/s, between −0.2 V from OCP and +1 V from OCP.

The measured data of the PDS curves shown in Fig. 2 is summarized in Table II where R_P, I_O and E_O are the polarization resistance, corrosion current and corrosion potential respectively. Polarization resistance was calculated as the inverse of the slope of the I vs. E curve measured at the E close to the open circuit potential. A higher value of R_P implies better corrosion resistance

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TABLE I Analyzed composition (wt%) and grain size of the alloys investigated

Alloy	Mn	Si	Cr	RE	Ni	Ti	Fe	Grain size (μm)
1#	25.11	5.95	5.34	–	–	–	Balance	51
2#	25.82	5.63	5.27	0.16	–	–	Balance	16
3#	24.60	6.44	5.34	0.30	–	–	Balance	13
18-8	1.05	0.39	18.2	–	9.7	0.56	Balance	

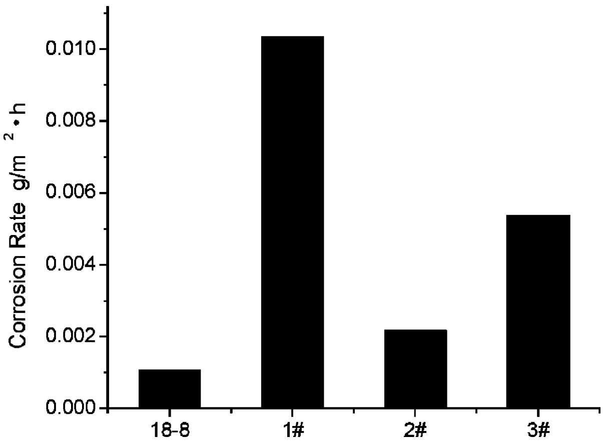

Figure 1 Corrosion rates in 3.5 wt% NaCl aqueous solution.

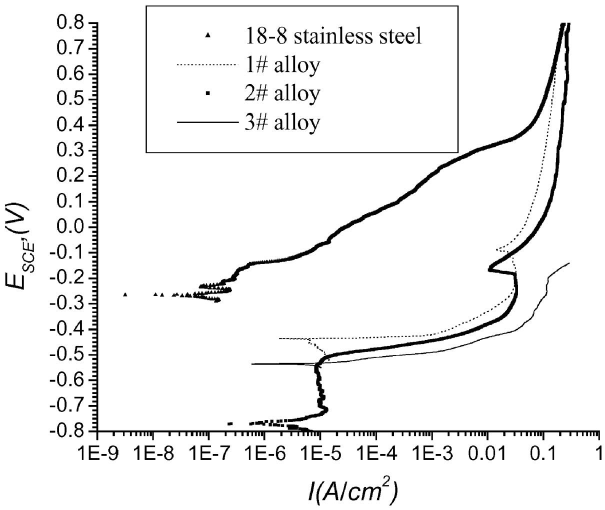

Figure 2 The potentiodynamic scanning curves in 3.5 wt% NaCl aqueous solution.

TABLE II The measured data of the PDS curves in 3.5 wt% NaCl aqueous solution

Alloy	R_P (Ω/cm^2)	I_O (A/cm^2)	E_O (V)
18-8	8235.9	3.1675E-6	−0.29914
1#	38.83	6.7182E-4	−0.43883
2#	3623	7.2003E-6	−0.76906
3#	447.36	5.8314E-5	−0.53773

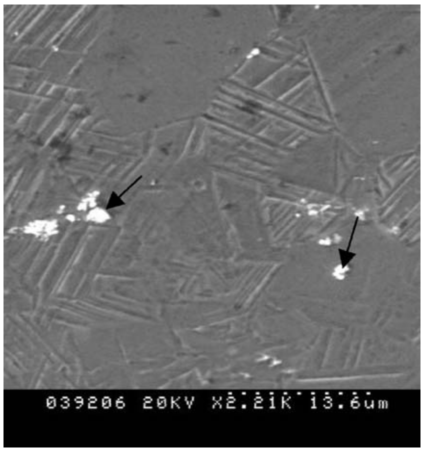

Figure 3 SEM micrograph of the 3# alloy.

of the material. It is clearly shown that their ranking orders are in good agreement with the weight loss results.

The grain size of the investigated alloys is listed in Table I, showing that the addition of rare earth elements can strongly refine austenite grains. SEM observations revealed second phase particles of 2–3 μm size at grain boundaries and within grains in alloy 3# as marked by arrows in Fig. 3, while no evidence was found of such particles in the alloys 1# and 2#. By EDS analysis, they were identified as compound(s) containing the rare earth element La.

The above results indicated that the corrosion resistance of alloy 2# with 0.16 wt% RE, which is below the concentration limit for its solid-solution in matrix (and thus no RE-containing precipitate was found), is remarkably improved. In neutral NaCl solution, the factor controlling the corrosion reaction of Fe based alloys is the diffusion of oxygen [10]. Rare earth atoms are believed to preferentially segregate at faults such as dislocations and grain boundaries. The bond strength between RE and oxygen atoms is very strong, and this forms a protective film which inhibits the oxygen diffusion into the interior of the alloys so that the velocity of the corrosion reaction is reduced.

Furthermore, it is seen that with excessive amounts of RE, which results in the precipitation of second phase particles, e.g., in alloy 3#, the corrosion resistance will always be decreased though not so seriously. Rare earth elements and their compounds are chemically active, and therefore the particles of RE-compound are dissolved preferentially, which causes the corrosion resistance of the alloy 3# to degrade.

Based on experimental results, relatively small amounts of RE, addition can greatly enhance the corrosion resistance of FeMnSiCr alloys in 3.5 wt% NaCl aqueous solution. The alloy containing 0.16 wt% RE exhibits the best behavior among the investigated Fe-based shape memory alloys. But when the FeMnSiCr alloys contain second phase particles due to an excessive RE addition, e.g., 0.3 wt%, their corrosion resistance will definitely be decreased, but will still be better than that without RE.

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