Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 19(2009) 149−153
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effect of Cu addition on corrosion resistance and shape memory effect of Fe-14Mn-5Si-9Cr-5Ni alloy

HU Bao-quan(胡保全)[1, 2], BAI Pei-kang(白培康)[1, 2], DONG Zhi-zhong(董治中)[3], CHENG Jun(程　军)[1, 2]

1. School of Materials Science and Engineering, North University of China, Taiyuan 030051, China;
2. National Key Laboratory for Electronic Measurement Technology, North University of China, Taiyuan 030051, China;
3. School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

Received 10 March 2008; accepted 22 July 2008

Abstract: The modification of Fe-14Mn-5Si-9Cr-5Ni shape memory alloys(SMAs) by copper addition was carried out, aiming at further enhancing its corrosion resistance. The results of electrochemical potentiodynamic measurement and immersion test show that copper can remarkably improve the corrosion resistance in Cl^- solution. Otherwise, it is found that copper cannot markedly affect the mechanical properties nor the shape memory effect(SME). As for the effects of copper on Fe-Mn-Si based alloys, the austenite strengthening is one of the key factors to improve SME.
Key words: FeMnSiCrNi; shape memory effect; corrosion resistance; copper; austenite strengthening

1 Introduction

Fe-Mn-Si based shape memory alloys(SMAs) have drawn a lot of attention for over two decades due to their low cost, good shape memory effect, good mechanical properties, excellent workability, and wide transformation hysteresis[1−8]. Much effort has been done towards clarifying composition dependence of the shape memory effect and corrosion resistance behavior of Fe-Mn-Si based SMAs by addition of C, Cr, Ni, and Co etc[9]. Studies of physical and mechanical properties of these alloys together with microstructural observation on $\gamma\leftrightarrow\varepsilon$ transformation have been performed to develop new substitutives of the well used expensive NiTi-based SMAs. Among Fe-Mn-Si systems, two of them, namely, Fe-28Mn-6Si-5Cr with a fairly good SME but poor corrosion resistance and Fe-14Mn-5Si-9Cr-5Ni alloy with good corrosion resistance but poor shape memory effect(SME), are well developed. The former has been successively used as pipe coupling in oil field tubes[10]. However, it is necessary to improve the corrosion resistance of Fe-Mn-Si based SMAs, while maintaining their shape memory effect, to extend their utilization. In previous research, it was found that with suitable thermomechanical treatment, a very good SME could be obtained in Fe-14Mn-5Si-9Cr-5Ni alloy, which has been predicted to be one of the most potentially alternative materials as joining pipes in engineering.

Regarding such a potential use, corrosion problem is always an essential issue to be concerned, in particular in the case of Cl^- environment[11], and alloying is the most effective method to modify the composition of Fe-Mn-Si alloys. The function of nitrogen in shape memory alloys has been studied. For example, JIANG et al[12] got a slight improvement of SME in Fe-30Mn-6Si alloy with 0.047%N, but they also showed a discrepancy effect of N on the SME in the Fe-Mn-Si based SMAs. ARIAPOUR et al[13] reported that the SME of Fe-18Mn-13Cr-2Ni-5Si alloy decreased by 80% with 0.26%N addition. It seems that the effects of N on SME and corrosion resistance behavior are controversial. DONG et al[14] found that by involving Nb, the corrosion resistance of Fe-14Mn-5Si-9Cr-5Ni alloy has been enhanced. LI et al[15] added Cu in Fe-Mn-Si based alloys and a relatively good SME has been obtained in Fe-20Mn-5Si-7Cr alloy. However, the effect of Cu on corrosion resistance of Fe-Mn-Si based SMAs has not been reported. In this work, copper, as one of the effective elements to improve the corrosion resistance in

Corresponding author: BAI Pei-kang; Tel: +86-351-3557443; E-mail: baipeikang@nuc.edu.cn
DOI: 10.1016/S1003-6326(08)60243-5

stainless steels, especially in the sea water (with Cl^-), was added in Fe-14Mn-5Si-9Cr-5Ni alloy, to further improve its corrosion resistance behavior. The effect of alloying additions on shape memory effect and mechanical properties was discussed in order to clarify the correlation between shape memory capacity and thermomechnical treatment.

2 Experimental

Based on the principle of the design theory of austenite steel and the previous research[14,16], 0.8%Cu and 1.5% Cu were added in Fe-14Mn-5Si-9Cr-5Ni alloy. Three Fe-14Mn-5Si-9Cr-5Ni alloys with and without Cu were prepared by vacuum melting and cast under an argon atmosphere. After homogenization at 1 100 ℃ for 12 h, the ingots were hot rolled into *d* 15 mm round bars. In order to eliminate the influence of hot rolling, all samples cut from the bars were annealed at 950 ℃ for 2 h, followed by water quenching.

The corrosion resistance behaviors of the Fe-14Mn-5Si-9Cr-5Ni alloys were evaluated by immersion test and electrochemical potentiodynamic measurement, respectively. The mass loss rates were calculated by immersing samples of 20 mm×30 mm×50 mm in 6% $FeCl_3$ aqueous solution at 25 ℃ for 12 h. The potentiodynamic polarization curves were measured in 3.5% NaCl saline solution at 25 ℃ utilizing Monte Carlo Model with exposed surface of 10 mm×10 mm. The morphologies of the corroded surfaces were observed by Optical Microscopy and Philip Environment Scanning Electron Microscopy (ESEM).

The specimens of 0.5 mm×4 mm×150 mm were used to measure the shape memory recovery. All of these samples were 5.0% extended at room temperature, then heated up to 600 ℃ to evaluate the gauge change. The SME was given as $\eta=(l_1-l_2)/(l_1-l_0)$, where l_0, l_1, and l_2 are the gauge lengths before deformation, after deformation and after recovery, respectively. A D−3000 Atom Force Microscopy (AFM) was employed to observe the microstructure of the training samples in order to understand the mechanism of improving SME by training. The mechanical properties were measured by tensile test and impact test at room temperature. The tensile samples with gauge length of 50 mm and diameter of 10 mm were used to measure the strength and the elongation. The samples of 10 mm×10 mm×100 mm with a notch were employed to test the impact toughness.

3 Results and discussion

3.1 Corrosion resistance behavior

Fig.1 shows the grain sizes of the alloys without and with 1.5% Cu, in which all of samples were etched by H_2O_2+HCl+HNO_3 solution with volume ratio of 2:2:1. It can be seen that the grain sizes are almost the same for the two alloys, and the grain boundary of the Fe-14Mn-5Si-9Cr-5Ni alloy is more easily revealed than that of the Cu involved alloys in the same etching condition.

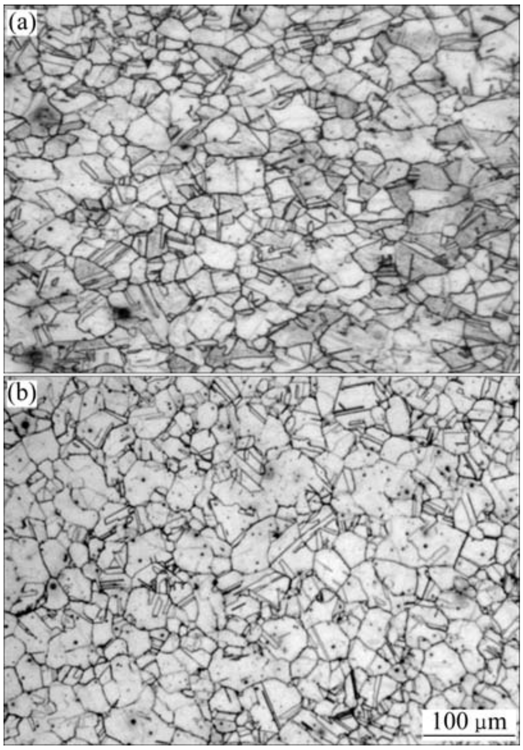

Fig.1 Grain size of Fe-Mn-Si SMAs after solution treatment at 1 050 ℃ for 10 h: (a) Fe14Mn5Si9Cr5Ni alloy; (b) Fe14Mn-5Si9Cr5Ni+1.5% Cu

Evaluation on corrosion resistance behavior of alloys was carried out by immersion test in various aqueous solutions. Table 1 lists the mass loss rates of the tested alloys in 6% $FeCl_3$ aqueous solution at 25 ℃ for 12 h. It is found that after adding Cu, the mass loss rate of Fe-14Mn-5Si-9Cr-5Ni alloy is remarkably decreased and the alloy with 1.5%Cu possesses the best corrosion resistance in such severe environment. In order to clarify the corrosion resistant difference, the surface morphologies of the immersed samples were observed by ESEM. Fig.2 shows the surface morphology of the eroded samples. It is shown that the eroded surface of the typical Fe-14Mn-5Si-9Cr-5Ni alloy is not smooth and there are some eroded pits and cracks on the surface. But after involving Cu, the surface of the alloy becomes uniformly corroded, especially for the case with 1.5%Cu, there are almost no corroded pits on the immersed surface. Since the eroded pits and cracks will cause the oxygen concentration difference and easily attract Cl^- anions due to the accumulation of metal cations[17], they

Table 1 Mass loss rates of Fe-14Mn-5Si-9Cr-5Ni alloys in 6% $FeCl_3$ solution at 25 ℃ for 12 h ($g \cdot m^{-2} \cdot h^{-1}$)

FeMnSiCrNi	FeMnSiCrNi+0.8%Cu	FeMnSiCrNi+1.5%Cu
76.60	44.78	32.54

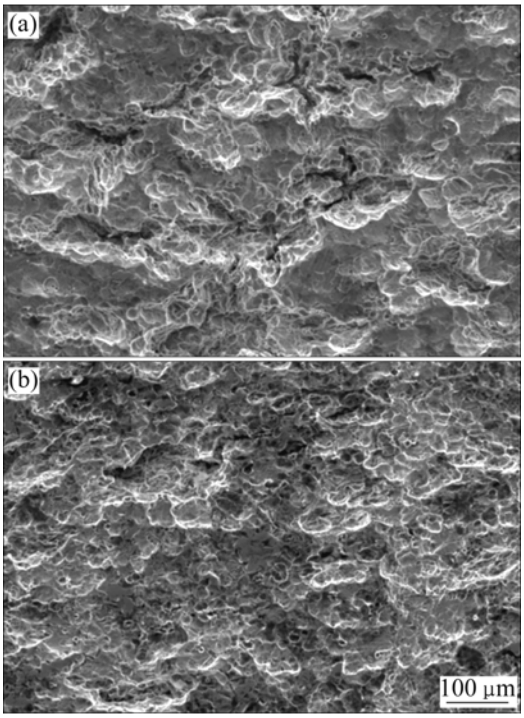

Fig.2 ESEM morphologies of Fe-Mn-Si SMAs after being immerged in 6% $FeCl_3$ for 12 h: (a) Fe14Mn5Si9Cr5Ni alloy; (b) Fe14Mn5Si9Cr5Ni +1.5% Cu

will act as the potential source of further corrosion. From this test in Cl^- environment, Cu is an effective element to enhance the corrosion resistance of Fe-Mn-Si alloys.

The improvement of corrosion resistant ability by Cu addition is also reflected in the electrochemical potentiodynamic measurement. Fig.3 shows the potentiodynamic polarization curves of three alloys in 3.5% NaCl

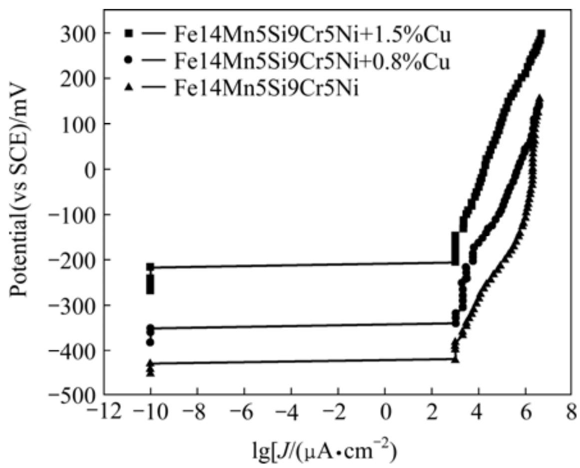

Fig.3 Polarization curves of Fe14Mn5Si9Cr5Ni alloys in 3.5% NaCl

solution. It is clearly seen that the positive potential of the alloy is remarkably increased after involving Cu, especially in the case of 1.5%Cu addition. At the same time, it can be found that the alloys have the feature of passivity in a relatively wide potential range and are pitting-attacked at chemical breakdown potential, at which the current density increases sharply. This means that similar to austenite stainless steel, pitting corrosion takes place for the Fe-Mn-Si-Cr-Ni alloys in solution with Cl^-.

3.2 Shape memory recovery

It is well known that the shape recovery of the Fe-Mn-Si based SMAS is due to the transformation of stress induced martensite ε(HCP) form austenite γ(FCC) and its reverse transformation by heating. Therefore, it is thought that, to get enough yield strength, the permanent slip should be avoided in the austenite matrix of Fe-Mn-Si based SMAs during the $\gamma \rightarrow \varepsilon$ transformation [3−5], which means that a shape change of a good SMA must be accomplished by stress-induced martensite but not by permanent slip. So one of the key points for achieving a good SME in Fe-Mn-Si based SMAs is to strengthen austenite and decrease the critical stress for stress-induced martensite transformation. Fig.4 shows the shape recovery of the alloys with and without Cu, in which all of samples were deformed by 5% at room temperature and heated up to 400 ℃. It can be seen that Cu does not markedly affect the SME, which is not the same as results of LI et al[15].

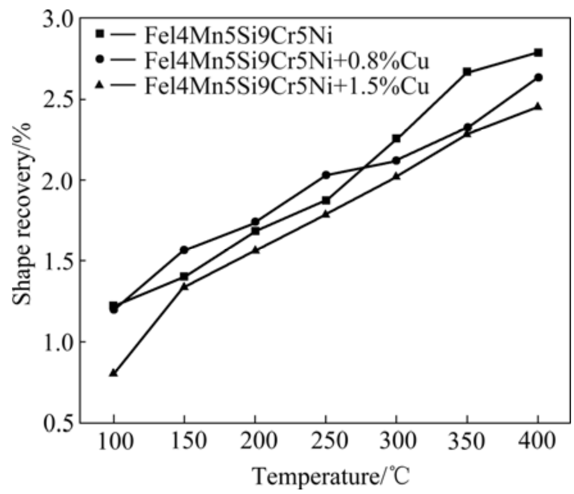

Fig.4 Shape recovery vs temperature under 5% deformation

In order to understand the mechanism of the shape recovery, the mechanical properties were investigated. It is found that the yield strength and tensile strength are a little decreased, and the elongation and the impact toughness are somehow increased by Cu addition. It seems to conform such a theory that the yield strength is one of the key factors correlative to the shape memory recovery of Fe-Mn-Si based SMAs.

The $\gamma\rightarrow\varepsilon$ transformation of Fe-Mn-Si based SMA is highly related to stacking faults and regular arrange of partial dislocations. YAKUBTSOV et al[18] proposed a method to estimate the stacking fault energy of FCC iron based alloys, $\eta=\eta_b+\eta_s+\eta_m$, where η_b is the stacking fault energy difference between FCC and HCP phase per unit area, η_s is the energy arising from the alloying element segregation to stacking faults and η_m is the magnetic contribution to the stacking faults energy. In this case, η_m is very small and the other two parts are mainly considered. In the view of stacking fault energy, the results infer that Cu seems to enhance the stacking fault energy. When the more amount of Cu is involved, η will increase due to the major effect of η_s and η_b contribution will play a major role to energy increase at relatively high levels of Cu. The difference between shape memory effect of Fe-14Mn-5Si-9Cr-5Ni alloy with and without Cu reflects the different influence on stacking fault energy.

It is found that the formation of lamellar martensite plates is the key factor to obtain good shape memory effect[8], and training is an essential process to get fine ε martensite. Fig.5 shows the shape memory recoveries of the alloys as a function of training cycles, in which specimens were deformed at room temperature to a plastic strain of 5.0%, followed by annealing at 870 K for 10 min per cycle. It can be seen that after 4-times trained, the maximum SME can be obtained. Fig.6 shows AFM image on the microstructure of 4-times training Fe-14Mn-5Si-9Cr-5Ni alloy, which confirms that the regularly oriented and uniformly distributed lamellar ε martensites are stress-induced after training. Obviously, such uniform fine and single-variant ε martensites are easy to reversely transfer along the same path of former transformation and therefore can improve the SME.

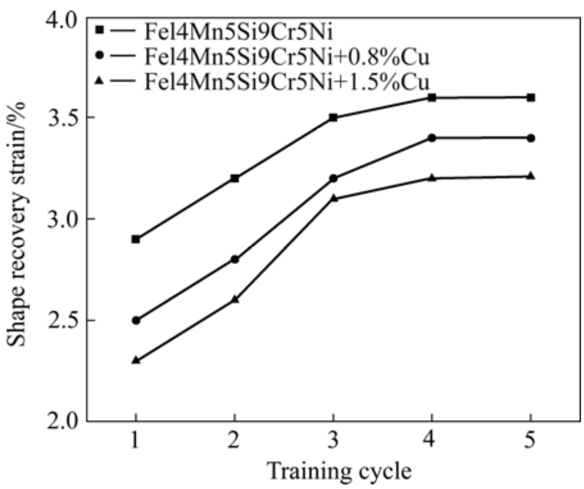

Fig.5 Shape memory recovery of Fe14Mn5Si 9Cr5Ni alloy vs training cycles

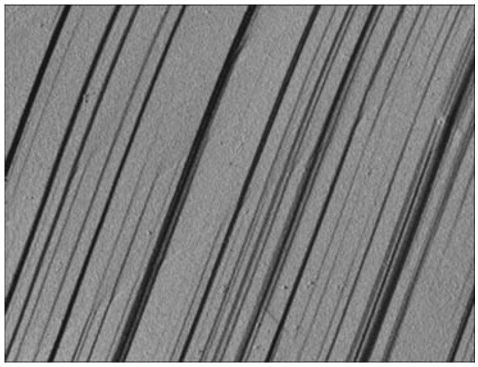

Fig.6 AFM image of 4-times trained sample of Fe14Mn5Si9Cr5Ni alloy

4 Conclusions

1) Electrochemical potentiodynamic measurement and immersion test show that the alloying element Cu can remarkably improve the corrosion resistance of Fe-14Mn-5Si-9Cr-5Ni alloy in solutions with Cl^-.

2) Mechanical properties and SME of Fe-14Mn-5Si-9Cr-5Ni alloy are not markedly influenced by Cu addition. With the amount of Cu increasing, the strength and SME are decreased very slightly, which correspondingly confirms that strengthening the austenite to improve yield strength is one of the key factors correlative with the shape memory recovery of Fe-Mn-Si based SMAs.

References

[1] SATO A, SOMA K, MORI T, hardening due to pre-existing ε-martensite in an Fe-30Mn-1Si alloy single crystal [J]. Acta Metall, 1982, 30: 1901−1904.

[2] SATO A, MORI T. Development of a shape memory alloy Fe-Mn-Si [J]. Mater Sci Eng A, 1991, 146: 197−200.

[3] INAGAKI H, METALLKD Z. Shape memory effect of Fe-14Mn-6Si-9CR-6Ni alloys [J]. Polycrystals, 1992, 83: 90−93.

[4] YANG J H, CHEN H, WAYMAN C M. Development of iron-based shape memory alloys associated with face-centered cubic-hexagonal close-packed martensitic transformations (Part I): Shape memory behavior [J]. Metall Trans, 1992, 23A: 1431−1434.

[5] GU Q, HUMBEECK J V, DELARY L, JANG W Y. Microscopic observation of γ-phase and ε and α'-martensite in Fe-Mn-Si based shape memory alloys [J]. Materials Characterization, 1995, 34: 67−71.

[6] JIANG B H, SUN L M, LI R C, HSU T Y. Influence of austenite grain size on γ-ε martensitic transformation temperature in Fe-Mn-Si-Cr alloys [J]. Scripta Metallurgica et Materialia, 1995, 33: 63−66.

[7] KAJIWARA S. Characteristic features of shape memory effect and related transformation behavior in Fe-based alloys [J]. Mater Sci Eng A, 1999, 273/275: 67−70.

[8] WANG D F, LIU D Z, DONG Z Z, LIU W X. Improvement of shape memory effect by ausforming in Fe-28Mn-6Si-5Cr alloy [J]. Mater Sci Eng A, 2001, 315: 174−177.
[9] WEN Y H, LI N, LI P H. The influence of carbon content on shape memory effect in different quenching Fe-MnSi-Cr-Ni-C alloys [J]. Heat Treatment of Metals, 1999, 3: 24−25.
[10] LIU D Z, WANG D F, JI W Y, LIU W X. Study of Fe-Mn-Si-Re alloy pipe coupling [C]// SMST-97, Proceedings of the Second International Conference on Shape Memory and Superelastic Technologies, Pacific Grove, California, USA, 1997. 356−359.
[11] LI. J C, LU X X, JIANG Q. Shape memory effects in an Fe14Mn6Si9Cr5Ni alloy for joining pipe [J]. ISIJ Inter, 2000, 40: 1124−1127.
[12] JIANG B H, QI X, ZHOU W M, ZHENG L X, XU Z Y. Comment on "influence of austenite grain size on γ→ε martensitic transformation temperature in Fe-Mn-Si-Cr alloys [J]. Scripta Materials, 1996, 34: 771−774.
[13] ARIAPOUR A, YAKUBTSOV I, PEROVIC D D. Effect of nitrogen on shape memory effect of a Fe-Mn-based alloy [M]. Mater Sci Eng A, 1999, 262: 39−41.
[14] DONG Z Z, LIU W X, CHEN J M, WANG D F. The influence and its mechanism of NbC precipitates on the shape memory effect of Fe-Mn-Si-Cr-Ni shape memory alloy [J]. J Phys IV, 2003, 112: 389−392.
[15] LI H J, DUNNE D, KENNON N. Factors influencing shape memory effect and phase transformation behavior of Fe-Mn-Si based shape memory alloys [J]. Mater Sci Eng A, 1999, 273/275: 517−520.
[16] XIAO J M. The metallurgical theory of stainless steel [M]. Beijing: Science Press, 1974: 110−122.
[17] LIN H C, LIN K M, LIN C S. The corrosion behavior of Fe-based shape memory alloys [J]. Corrosion Science, 2002, 44: 2013−2016.
[18] YAKUBTSOV I, ARIPOUR A, PEROVIC D D. Effect of nitrogen on stacking fault energy of f.c.c. iron-based alloys [J]. Acta Mater, 1998, 47: 1271−1274.

(Edited by YANG Bing)