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Effects of Electric Pulse Treatment on Shape Memory Effect and Microstructure in a Pre-deformation Fe13Mn6Si13Cr4Ni0.1C Alloy

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Abstract: Effects of electric pulse treatment on shape memory effect and microstructure of a pre-deformed Fe13Mn6Si13Cr4Ni0.1C alloy were investigated. The results indicate that electric pulse treatment can accelerate the migration of Cr and C atoms and the precipitation of $Cr_{23}C_6$ carbides, lower ageing temperature, shorten ageing time and induce the nucleation of $Cr_{23}C_6$ carbides. Therefore, the shape recovery ratio can be increased to 87.2% from 32% of a water-quenched alloy within 300 s for the Fe13Mn6Si13Cr4Ni0.1C alloy by 300 V, 1100 μF, 1 Hz electric pulse treatment after 10% tensile pre-deformation compared to alloys aged at 973 and 1073 K followed by the same pre-deformation.

Key words: shape memory effect; pre-deformation; electric pulse treatment; ageing; $Cr_{23}C_6$ carbide; nucleation ratio

Since Sato et al found that Fe-Mn-Si alloys exhibited an excellent shape memory effect (SME) in a single crystal in 1982[1], many studies have been carried out on these alloys because Fe-Mn-Si based shape memory alloys have good workability, good machinability and good weldability. However, Fe-Mn-Si alloys have got no important industrial applications. The main reason is that SME of Fe-Mn-Si alloys is not as significant as that in Ni-Ti alloys, except for some special cases such as single crystals or thin foils[2]. To obtain excellent SME of FeMnSi alloys, many factors affecting SME of FeMnSi alloys such as addition of the alloy elements[3], amount of pre-strain[4], deformation temperature[5], annealing treatment and thermo-mechanical training (the repetition of deformation and annealing)[6] have been studied. However, these methods can not greatly improve SME of FeMnSi alloys, and their technical process is very complex. Particularly, it is very difficult to conduct the production for the parts with complicated shape. The above mentioned cases significantly restrict their practical engineering applications.

The precipitation of second phase particles from FeMnSi alloys is another effective method for improving SME. The mechanism of increasing SME of FeMnSi alloys by this method has become a hot research topic. Kajiwara et al[7, 8] and Wen et al[9-11] found that addition of Nb/Cr and C element in Fe-Mn-Si-Cr-Ni based alloys could remarkably improve shape recovery ratio due to the precipitation of $NbC/Cr_{23}C_6$ carbides. However, their mechanism for improving SME of FeMnSi alloys is quite different. Kajiwara et al thought that NbC precipitate could increase the strength of austenite and reduce the occurrence of permanent slip, and the stacking faults near NbC particles could become crystal nuclei of transformation from austenite to martensite. But Wen et al found that $Cr_{23}C_6$ particles aligned inside austenite grains in an aged Fe-Mn-Si-Cr-Ni-C alloy after pre-deformation. They thought that there were three key reasons for great increasing SME: (1) directional $Cr_{23}C_6$ particles subdivided austenite grains into many smaller domains so that differently oriented martensite bands which formed in these smaller domains could avoid an intercrossing or a collision between them; (2) carbide precipitation or solute atom segregation could bring

greater back stress field for $\gamma \rightarrow \varepsilon$ reverse transformation; (3) martensite transformation starting temperature (M_s) of Fe-Mn-Si-Cr-Ni-C alloy rose closer to deformation temperature (T_d) because of the precipitation of $Cr_{23}C_6$ carbides from the austenite matrix[12]. It has been reported that electric pulse treatment, as a new potential approach for material processing and preparation, can accelerate the migration of atoms and the precipitation of intermetallic compounds[13]. Wen et al greatly improved SME within a short time via producing smaller NbC carbides in a pre-deformed Fe-Mn-Si-Cr-Ni-Nb-C alloy adopting electric pulse treatment[14]. Therefore, it can also be expected that electric pulse treatment can accelerate the migration of Cr and C atoms and induce the precipitation of $Cr_{23}C_6$ carbides in the pre-deformed Fe-Mn-Si-Cr-Ni-C alloy so that it can improve shape recovery ratio of these alloys more quickly.

Based on the ideas mentioned above, the effects of electric pulse treatment on SME and microstructure of pre-deformation Fe13Mn6Si13Cr4Ni0.1C alloy were investigated in the present paper.

1   Experiment

An experimental alloy ingot was prepared by induction melting in an argon atmosphere, using high purity iron, manganese, silicon, chromium, nickel and graphite as starting materials. After homogenization at 1373 K for 15 h, the ingot was hot forged into the bars of Φ15 mm at 1373 K, then they were swaged into wires of Φ3.5 mm and finally cold drawn into wires of Φ1.5 mm. The chemical composition of the alloy is as follows (mass fraction, %): 13.09Mn, 5.81Si, 13.28Cr, 4.38Ni, 0.10C and balance Fe. All specimens for measurement were cut from as-cold drawn wires of Φ1.5 mm. To remove the effect of ε martensite induced during cold drawn and setting the specimens in straight shape, the specimens were first straightened, and then annealed under constraint at 1323 K for 30 min, finally followed by a water-quenching. All specimens were deformed by 10% tensile strain at room temperature. Then the specimens were divided in three groups. The first group was directly subjected to electric pulse treatment by a special equipment, as seen in Fig.1. Peak voltage set for electric pulse generator was 300 V, electric capacity for capacitor 1100 μF, and its frequency 1 Hz. The second and the third groups of specimens were aged for different time at 973 and 1073 K, respectively. Finally, the shape recovery ratio for the first group of specimens was compared with those for the second and the third group of specimens, respectively.

The shape recovery ratio η was measured by the conventional bending techniques described in our previous paper[15]. The degree of bending deformation for all the specimens was approximately 5%, which was calculated by the formula $\varepsilon = t/d$, where t is the diameter of specimens and d the diameter of mould.

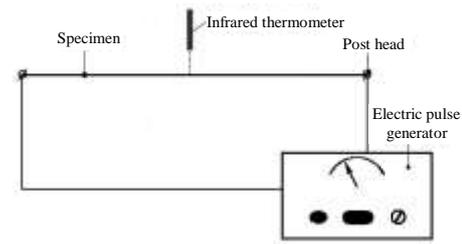The observation of microstructure was carried out by

Fig.1   Schematic drawing of the equipment for electric pulse treatment

HITACHI S-3400N scanning electron microscope (SEM). The microstructures of the specimens were studied by a JEM-2010 transmission electron microscope (TEM). In the preparation of foils for TEM observations, the samples were ground mechanically and then polished in a solution of sulphuric acid and methanol (1:4) at 253 K by a twin jet polisher.

2   Results and Discussion

2.1   Effect of ageing with different treatments after 10% tensile strain on shape recovery ratio

Fig.2 shows the effect of ageing with different treatment after 10% tensile strain on shape recovery ratio η of the alloy. SME of the alloy after water-quenching treatment was poor, and η is only 32%. Fig.2a shows the curve through electric pulse treatment by 300 V, 1100 μF, 1 Hz. When treated at 3 s
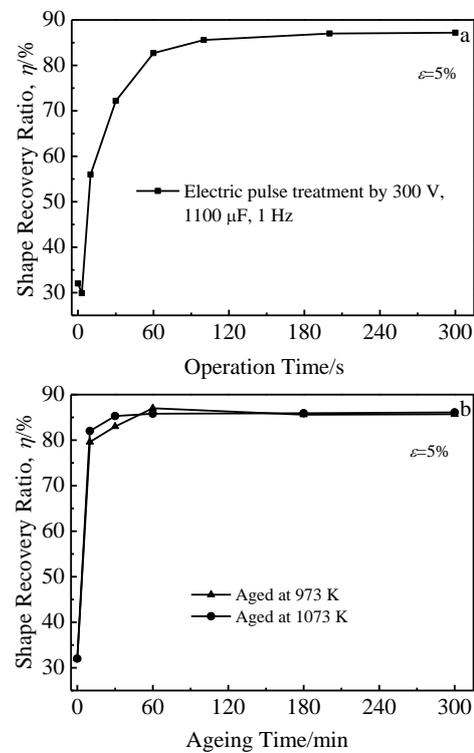

Fig.2   Effect of ageing with different treatments after 10% tensile strain on shape recovery ratio η of the alloy: (a) by electric pulse treatment of 300 V, 1100 μF, 1 Hz; (b) aged at 973, and 1073 K

by electric pulse, η slightly falls down to 29.9%. Then, η quickly rises. At 300 s, η rises up to 87.2%. For alloys aged at 973 and 1073 K, their η both drastically rise within 10 min, as seen in Fig.2b. Over 10 min, their η gradually increase. η for alloys aged at 973 K reaches 87%, the maximum value at 60 min. After that, η slightly decreases with the increase of ageing time. However, η for alloys aged at 1073 K gradually rises from 10 min to 300 min and is up to 86.1% at 300 min. From the above three treatments, time for electric pulse treatment is the shortest, and time for η to reach the maximum value should be over 300 s.

2.2 Effect of ageing with different treatment on $Cr_{23}C_6$ precipitation

Fig.3 shows SEM images of the specimens subjected to different treatments. In Fig.3a, the specimen was deformed by 10% tensile strain at room temperature after a water quenching. The matrix consists of austenite and stress induced ε martensite and some bulk of δ ferrite phase. And it can be seen clearly that the γ/ε interfaces inside the austenite grains are uniform along some special direction. When the pre-deformation alloy is treated by electric pulse for 3 s, stress induced ε martensites still exist and do not disappear, as seen in Fig.3b. This results in that shape recovery ratio is lower than 32% of a water-quenching alloy. This result is completely consistent with the curve in Fig.2a. With prolonging of treatment time, carbide particles start to nucleate and grow up, as shown in Fig.3c~3e. In this process, carbide nuclei become more and more. When treated for 14 s by electric pulse, the specimen has become reddish. By infrared thermometer, the temperature measured for the specimen is up to 1013 K at 20 s. Over 20 s, the temperature maintains at 1013~1023 K owing to balance of production of heat and loss of heat. Pits near carbide particles have already disappeared in Fig.3d compared to Fig.3f and Fig.3h. Effect of accelerating migration of Cr and C atoms by electric pulse could be seen here. And carbide particles in Fig.3e are more and smaller compared with ones in Fig.3g and Fig.3i. This is the result of increasing of nucleation ratio for carbide particles by electric pulse. Carbide particles mentioned above are $Cr_{23}C_6$ ones, as indicated in Fig.4e. Corrosion pits around $Cr_{23}C_6$ nuclei in Fig.3f is formed because gathering of Cr and C atoms there brings greater lattice distortion energy. Greater lattice distortion energy is favorable to $\gamma \rightarrow \varepsilon$ reverse transformation. This can explain that η reaches the maximum value in alloys aged for 60 min at 973 K. $Cr_{23}C_6$ particles in Fig.3i become bigger than those in Fig.3h, and the amount of carbide particles becomes more. This can explain that shape recovery ratio η continuously increases during ageing at 1073 K.

Fig.4 shows TEM images of specimens subjected to 5% tensile deformation after different treatments followed by 10% tensile strain. For the alloy indicated in Fig.4a, $Cr_{23}C_6$ carbides have nucleated and grown up. At the same time, the amount of $Cr_{23}C_6$ particles is large while particles remain at small size.
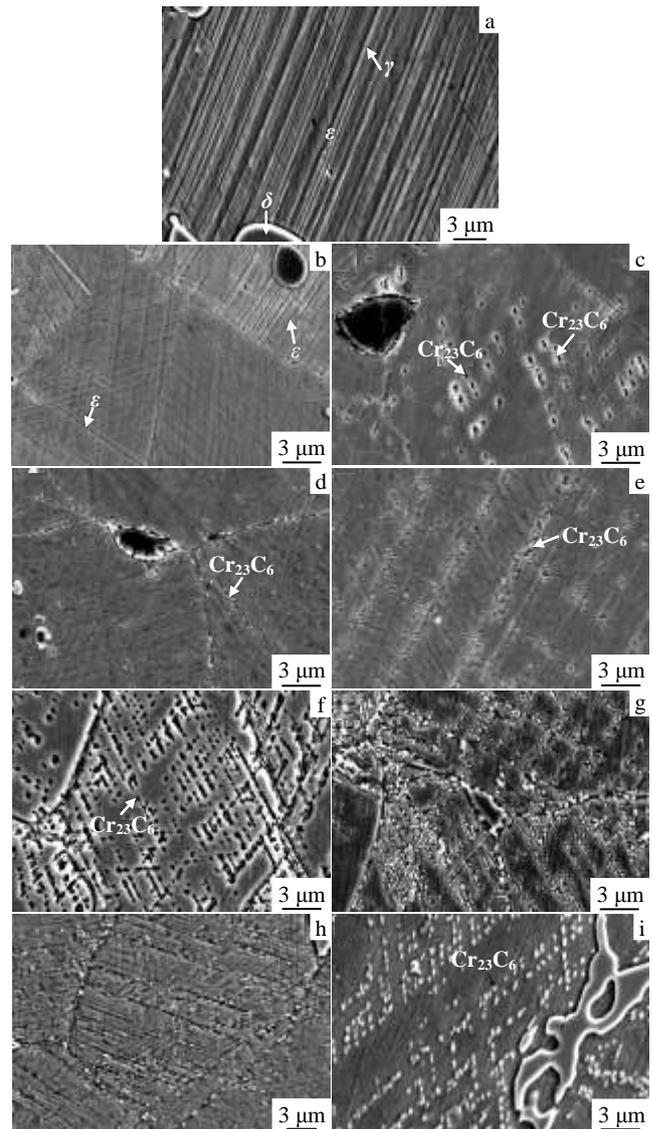

Fig.3　SEM images of specimens subjected to different treatments: (a) 10% tensile deformation; (b, c, d, e) electric pulse treatment for 3 s, 30 s, 60 s and 300 s, respectively, after (a); (f, g) aged for 60 min, 300 min, respectively, at 973 K after (a); (h, i) aged for 60 min, 300 min, respectively, at 1073 K after (a)

In Fig.4b and 4c, $Cr_{23}C_6$ carbides have nucleated, but particles are too small and $Cr_{23}C_6/\gamma$ interfaces are very vague so that these carbides can not be clearly distinguished. This indicates that ageing temperature for 973 K is a little low and it can not help carbide nuclei to grow quickly. For alloys aged at 1073 K, carbide particles grow largely enough (about 300 nm) when aged for 60 min. $Cr_{23}C_6/\gamma$ interfaces become very clear, as seen in Fig.4d. And it can be seen clearly that aligned carbides divide the ε martensite bands which belongs to the different domains. So setting 1073 K as ageing temperature for a pre-deformation alloy is reasonable. Fig.4e shows key image
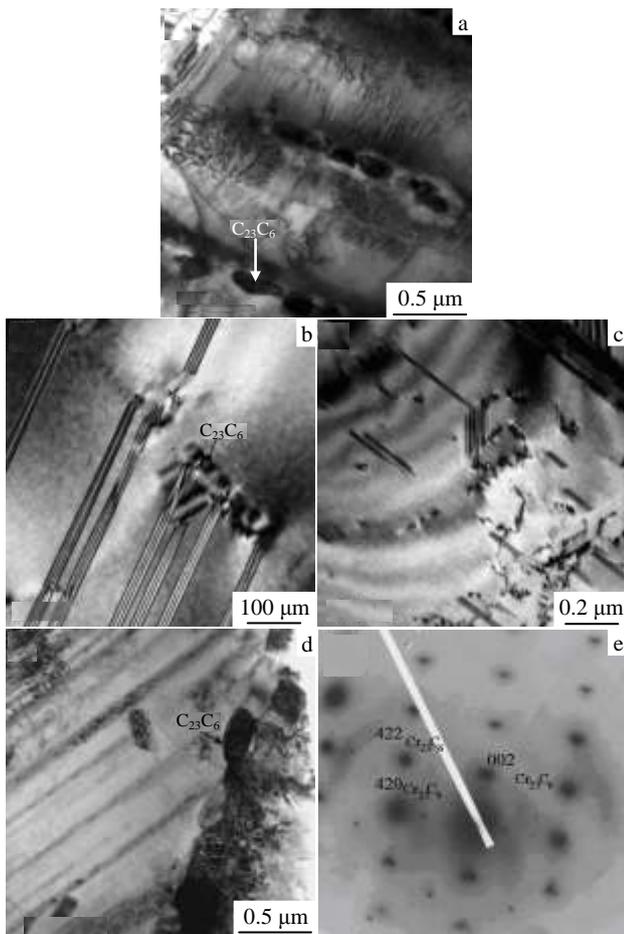
Fig.4   TEM images of specimens subjected to 5% tensile deforma-
tion after different treatments followed by 10% tensile strain:
(a) electric pulse treatment by 300 V, 1100 μF, 1 Hz for 60 s;
(b, c) aged at 973 K for 60 min; (d) aged at 1073 K for 60
min; (e) key image of selected area diffraction pattern from
$Cr_{23}C_6$ precipitate in (d)

of selected diffraction pattern from $Cr_{23}C_6$ precipitate in
Fig.4d. From Fig.4a to Fig.4d, it can be seen clearly that
electric pulse promotes carbide particles to nucleate and grow
in a very short time and brings the increase of nucleation ratio
for carbide particles.

In Fe-Mn-Si-Cr-Ni alloys, to obtain a good SME, a shape
change must be accomplished by the stress induced ε
martensite transformation, not by permanent slip. And its
reverse transformation requires great back stress filed.
Strengthening of austenite and decreasing of the critical stress
of stress induced ε martensite transformation can suppress the
occurrence of permanent slip. The collision between
martensite plates will lead to a plastic deformation of
martensite at intersections. The plastic deformation will bring
the relaxation of the back stress and decrease the reversibility
of stress induced ε martensite. Directional $Cr_{23}C_6$ particles can
subdivide austenite grains into many smaller domains so that

differently oriented martensite bands formed in these smaller
domains can avoid intercrossing or collision between
martensite plates, as shown in Fig.4. And $Cr_{23}C_6$ particles or
gathering of Cr and C atoms around particles can bring greater
back stress for reverse transformation of stress induced ε
martensite[10-12]. However, the precipitation of aligned $Cr_{23}C_6$
particles will traditionally spend a long time because it is
difficult for Cr atoms to migrate below 1073 K.

Electric pulse treatment as a new potential approach for
material processing and preparation can accelerate the
migration of atoms and the precipitation of carbides at low
temperatures[13]. Usually, the diffusion coefficient D of atoms
can be calculated by the following Eq. (1)[16]:

$$D=D_0\exp(-\Delta G/kT) \tag{1}$$

where, D_0 is the diffusion constant, ΔG is the diffusion
activation energy, k is Boltzmann constant, and T is the
temperature. When electric pulse is applied to ageing
treatment, the diffusion coefficient D will change. The
diffusion coefficient D_1 with electric pulse treatment can be
attained by Eq.(2):

$$D_1=D_0\exp(-(\Delta G+\Delta E)/kT) \tag{2}$$

where, ΔE is the variable quantity of the diffusion activation
energy resulting from the electric pulse. For $\Delta E < 0$, the
diffusion activation energy required becomes less and the
diffusion coefficient D_1 increases. When $Cr_{23}C_6$ particles in
Fig.3e are compared with ones in Fig.3f and Fig.3h, we can
see the effect of electric pulse treatment on migration of Cr
atoms.

Except that electric pulse can accelerate the migration of
atoms and the precipitation of the second phase, it can also
induce the nucleation of carbide. The basic reason is that it can
improve the nucleation ratio for carbide particles. The
precipitation of $Cr_{23}C_6$ is controlled by the mechanism of
nucleation on interface, so the equation of nucleation ratio on
grain boundary is suitable for the calculation of nucleation
ratio for $Cr_{23}C_6$ particle. And nucleation ratio I [17] on grain
boundary, when as-solid transformation happens, can be
attained by Eq.(3):

$$I = N_v A^* v(\delta/D)^{3-i} e^{-\Delta G_m/kT} e^{-B_i\Delta G^*/kT} \tag{3}$$

where, N_v is the amount of atom position where a new phase
core can be formed in unit volume of parent phase, A^* is the
amount of atom position accepted on surface of critical
nucleus, v is atomic vibration frequency, B_i is coefficient of
nucleation energy, D is average diameter of grain in parent
phase, δ is grain boundary thickness in parent phase, i is code
for nucleation site, and $\triangle G_m$ is activation energy for atomic
migration, and $\triangle G^*$ is nucleation energy for critical nucleus.
According to Eq. (3), nucleation ratio I will be improved when
electric pulse makes $\triangle G^*$ and $\triangle G_m$ fall down. So the
amount of crystal nuclei increases. The conclusion has been
confirmed in contrast to SEM images about $Cr_{23}C_6$ particles in
Fig.3e, Fig.3g and Fig.3i. Similarly, when $Cr_{23}C_6$ particles in
Fig.4a are compared with ones in Fig.4d, we can also obtain

the same result as follows: the electric pulse treatment can lower ageing temperature, shorten ageing time and induce nucleation of $Cr_{23}C_6$ carbide. Thus the shape recovery ratio is improved to 87.2% from 32% of a water-quenching alloy within 300 s by 300 V, 1100 μF, 1 Hz pulse treatment after 10% tensile pre-deformation.

3 Conclusions

1) Electric pulse treatment can accelerate the migration of Cr and C atoms and the precipitation of $Cr_{23}C_6$ carbides, lower ageing temperature, shorten ageing time and induce the nucleation of $Cr_{23}C_6$ carbides.

2) The shape recovery ratio is improved to 87.2% from 32% of a water-quenching alloy within 300 s in a Fe13Mn6Si13Cr4Ni0.1C alloy by 300 V, 1100 μF, 1 Hz electric pulse treatment after 10% tensile pre-deformation compared to the alloys aged at 973 and 1073 K.

3) $Cr_{23}C_6$ particles of an alloy by electric pulse treatment for 300 s are more and smaller.

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电脉冲处理对预变形 Fe13Mn6Si13Cr4Ni0.1C 合金形状记忆效应及显微组织的影响

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摘　要：研究了电脉冲处理对预变形 Fe13Mn6Si13Cr4Ni0.1C 合金形状记忆效应及其显微组织的影响。结果表明：电脉冲处理能加速 Cr 和 C 原子的迁移及 $Cr_{23}C_6$ 碳化物的析出，降低时效温度，缩短时效时间，并能诱发 $Cr_{23}C_6$ 碳化物的形核。因此，与 10%拉伸预变形后再经 973，1073 K 时效的合金相比，10%拉伸预变形后经 300 V，1100 μF，1 Hz 电脉冲处理的 Fe13Mn6Si13Cr4Ni0.1C 合金，其形状回复率能在 300 s 时间内从固溶态合金的 32%提高到 87.2%。

关键词：形状记忆效应；预变形；电脉冲处理；时效；$Cr_{23}C_6$ 碳化物；形核率