

Effect of chemical component on shape memory effect of Fe-Mn-Si-Ni-C-RE shape memory alloy

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(Received 2003-02-20)

Abstract: Effect of chemical component on shape memory effect (SME) of Fe-Mn-Si-Ni-C-RE shape memory alloys was studied by bent measurement, thermal cycle training, SEM *etc.* Results of study indicate that the alloys with high Mn content (25%) appear better SME, especially in lower strain. SME improves evidently when Si is higher content, especially it's range from 3% up to 4%. But brittleness of Fe-Mn-Si-Ni-C-RE alloy increases by increasing the Si content. SME of the alloy is weakening gradually as carbon content increases under small strain (3%). But in the condition of large strain (above 6%), SME of the alloy whose carbon content ranges from 0.1% to 0.12% shows small decreasing range, especially of alloy with the addition of compound RE.

Key words: chemical component; Fe-Mn-Si-Ni-C-RE shape memory alloy; shape memory effect; strain

Development of Ferrous-based shape memory alloys (SMAs) needs to add a new branch in SMAs family. Thus different SMAs could be applied properly to corresponding requirement, occasion and working situation to achieve the best effect. It has been reported that FeMnSi system SMAs containing exceeding lower carbon [1] were melted in vacuum furnace using pure metal as raw materials. This study of the alloys still has been in laboratory stage, and disadvantage to popularize in commercial production because of high manufacturing cost. In the present work, ordinary low-carbon steel was used as raw material to manufacture Fe-Mn-Si-Ni-C-RE SMAs with non-vacuum induction furnace. And the effect of chemical component and compound RE on SME of the alloys was investigated, mainly effect of carbon content and some concerned academic problem was discussed, which were reported seldom.

1 Experimental

Raw materials, consisted of low-carbon iron (consisted with 0.12% and 0.25% low carbon steel), electrolytic manganese, crystallized silicon, industrial pure nickel, were melted by non-vacuum middle frequency induction furnace. After metal melting, holding 10min, and tapping at temperature about 1580°C. Compound RE was added directly into ladle, then laid aside, slagged off and poured at 1530°C. Sizes of ingots were $\phi 60$ mm \times 130 mm. The ingots were treated by annealing, which heating to 1100°C, holding for 24 h

and cooling in furnace, then cut 2 mm surface layer, and forged to 10 mm plate and $\phi 18$ mm stick. 1mm \times 10 mm \times 90 mm samples were machined from plates. Shape memory effect (SME) was measured by bent method, as shown in figure 1.

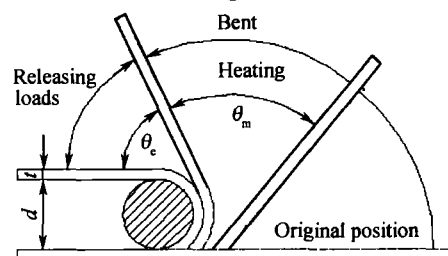


Figure 1 Schematic drawing of recovery ratio with bent measurement.

Samples were bent around cylinder mould at 180°, so pre-strain $\epsilon_p = t/d \times 100\%$, t is the thickness of samples (mm), d is the diameter of cylinder (mm). Measurement of SME in alloys could use below indexes:

Relative strain recovery ratio $\eta = \theta_m / (180 - \theta_c) \times 100\%$;

Absolute strain recovery ratio $\epsilon_a = \eta \times \epsilon_p$;

Relative super elastic strain $\epsilon_{se} = \theta_c \times \epsilon_p / 180$.

where θ_m is angular difference between after releasing loads and after annealing; θ_c is angular difference between after releasing loads and before loading.

The compositions of experimental alloys are listed in table 1. The microstructure were observed with an optical microscope of model MM6 and SEM of model

JXA-840A. The grain size was measured with the secant method. Each sample was measured for ten times. Sizes of the samples were $\phi 15 \text{ mm} \times 1 \text{ mm}$. The component of phases were measured with XRD (X-

ray Diffraction) of model D-5000. The samples for tensile test were standard, effective sizes were $\phi 10 \text{ mm} \times 50 \text{ mm}$. Temperature for quenching was 1000°C .

Table 1 The chemical composition of alloys (mass fraction) and transition temperature

Alloy number	Chemical composition / %						M_s / K	A_s / K
	Mn	Si	Ni	C	RE	Fe		
1#	24.12	3.61	4.81	0.089	Trace	Balance	362	463
2#	24.36	3.60	4.84	0.090	—	Balance	350	448
6#	15.30	4.70	4.75	0.119	—	Balance	305	402
7#	15.43	4.73	4.84	0.175	—	Balance	301	397
21#	24.15	3.62	4.88	0.090	—	Balance	349	451
23#	15.38	4.60	4.88	0.091	Trace	Balance	328	419
24#	15.40	4.62	4.85	0.090	—	Balance	318	412
8#	15.39	2.75	4.85	0.090	—	Balance	342	449
9#	15.36	3.70	4.82	0.090	—	Balance	325	324
10#	15.35	4.67	4.80	0	—	Balance	313	411

2 Results and analysis

2.1 Effect of carbon on SME

Table 2 lists some experimental data of low manganese system alloys. It is seen that SME of alloys decrease gradually along with increasing of carbon content under small strain (below 3%). But, to large strain (>6%, it's the industrial applied range generally), SME of alloys with 0.10%-0.12% C has quite small decreasing range, 10# alloys without carbon content take the second place, and alloys with 0.175% carbon content perform biggest decreasing range. So it is obvious that carbon content exists critical point in Fe-Mn-Si-Ni-C alloys, and the critical point is 0.1%-0.12% carbon content in this paper. When carbon content is greater than the value of the critical point SME would decrease accordingly. While strain greater than 6%, recovery ratio of 23# alloys which added trace amount compound RE stands out, and exceed others evidently.

SME is decided by difficult degree of stress inducing martensite and quantity of inductive plastic de-

formation [2]. At the moment of small strain, inductive plastic deformation is less, and shape memory recovery ratio is mainly decided by quantity of stress-induced martensite. Moreover, addition of carbon element would decrease martensitic transition point M_s , so quantity of stress-induced martensite in low-carbon alloys is large and SME is better in this condition. Conversely, less stress-induced martensite and poor SME are appeared in high carbon content alloys. Depending on increasing strain, plastic deformation also adds accordingly, and it is advantage to restrain plastic deformation to strengthen austenitic matrix right now. Interstitial carbon atom can solve in austenite and form solid solution to strengthen matrix. It was reported [3,4] that adding 0.3% carbon could raise strength of austenitic matrix at ambient temperature for 45 MPa, but only the matching between alloy strength and M_s point achieved the optimal value, the best SME would perform. 0.08%-0.12% carbon content is suitable value for best SME.

Table 2 Chemical composition and recovery ratio

Serial number	$\eta / \%$			
	$\varepsilon_p = 3\%$	$\varepsilon_p = 6\%$	$\varepsilon_p = 9\%$	$\varepsilon_p = 12\%$
9#	56	38	31	24
10#	59	40	30	23
6#	52	36	32	25
7#	44	33.4	26	19
23# (RE)	56	40	36	29

2.2 Effect of compound RE on alloys

(1) Effect of compound RE on microstructure and SME of alloys.

The grains of alloys become finer evidently with

addition of compound RE. The grain sizes decrease from 0.3-0.4 mm to 0.1-0.15 mm, so mechanical properties of the alloys are improved obviously. Yield strength and tensile strength of alloys without com-

pound RE were $\sigma_{0.2}=328.7$ MPa, $\sigma_b=654.5$ MPa, and with addition of compound RE were $\sigma_{0.2}=375.4$ MPa, $\sigma_b=745.2$ MPa. The added compound RE, as dispersive second phase, decreases the driver force of growth of γ phase and restrains its growth and the grain boundaries are hindered by interfacial tensile of second phase [5].

Few works about effect of compound RE on Ferrous-based SMAs were reported. Only authors [6,7] considered added trace amount RE elements could improve SME. Figure 2 shows comparison between alloys with additional compound RE (1# and 23#) and alloys without compound RE (21# and 24#). Whatever relative strain recovery ratio of the first cycle or of stability situation after training, recovery ratio with added compound RE improves evidently in figure 2, especially for small strain from 3% to 6%. In this paper, when $\epsilon_p=3\%-5\%$, η improves to 8%~15% respectively. Effect of compound RE on SME is not evident under bigger pre-strain ($\epsilon_p>10\%$). It is also indicated that both first η and stable η are not obvious between alloys with additional compound RE (1# and 23#) and without compound RE (21# and 24#) under 12% ϵ_p . Because deformative stress increases by increasing strain ϵ_p , effect of compound RE reinforced base on improvement of SME is limited.

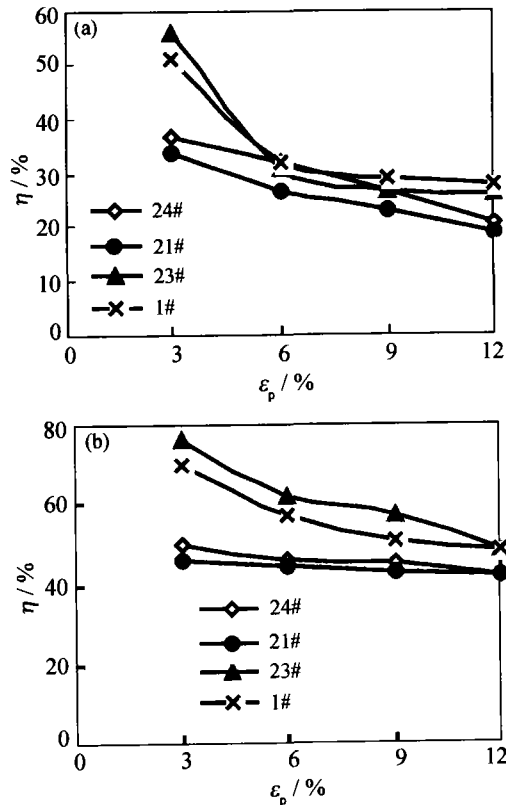


Figure 2 Comparison between alloys with added compound RE and alloys without compound RE, (a) comparison of prime recovery ratio; (b) comparison of stable recovery ratio after training.

(2) Relationships between compound RE and two-way SME.

The phenomenon in 1#, 23# alloys with compound RE that the alloys appeared little two-way SME after one training is observed. From figure 3, it is seen that two-way SME of 23# alloys with 6% pre-strain reaches almost 6%, and two-way recovery ratios of alloys with 9% and 12% pre-strain are approximate. This is not in accord with phase transition mechanism of Ferrous-based SMAs. Ferrous-based SMAs do not appear characteristics of thermal elasticity martensite, and have no two-way SME. Namely, γ phase, transitioned from stress induced ϵ martensite during heating, could not change into ϵ martensite reverse during cooling.

These is pre-existent ϵ martensite of water-quenching samples with additional compound RE, which could increase M_s point under the same other component. Effects of pre-existent ϵ martensite on SME contain two respects. In one respect, pre-existent ϵ martensite, which could strengthen matrix, become nuclear center during the transformation of stress induced martensite. The other, too much pre-existent ϵ martensite lead to intercross between martensitic variants. This causes consistence of orientation in stress-induced martensite poor and weakens its SME. So appropriate quantitative pre-existent ϵ martensite could improve SME, and a superabundance of pre-existent ϵ martensite is not benefit for SME. It is seen from figure 4 that these exists a little pre-existent ϵ martensite and they do not intercross in 23# alloys, whose SME are best mentioned above (figure 2).

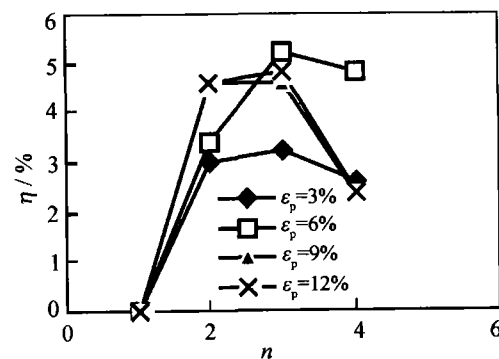


Figure 3 Two-way recovery ratio with different pre-strain in 23# alloy.

Temperature changed in range from A_{es} to M_{es} during annealing treatment when temperature is down to M_s . Thermal induced martensite formed and most of these modulated selective orientation during training cycles. So parts of thermal induced martensite replace the role of stress induced martensite and lead to bigger θ_m angle. Reservedly, when temperature increase from M_{es} to A_{es} , the parts of thermal induced martensite transform into γ matrix phase and angle θ_m decrease

accordingly. This phenomenon could be explained by Shockley partial dislocation going forward or backing off. Stacking fault energy (SFE) of alloys reduces markedly after adding compound RE, and make movement of dislocation easier. But 21# and 24# alloys without compound RE do not perform this characteristic, because the alloys have higher stacking fault energy and lower M_s point and no pre-existent ϵ martensite existed in ambient temperature microstructure after quenching and thermal induced martensite also do not exist in water quenching samples. This analysis could not explain the problem perfectly of course and it need more thorough study to give the detail mechanism.

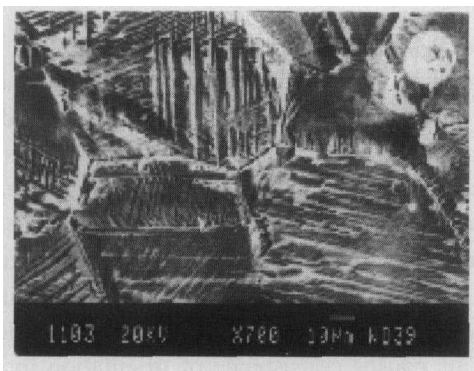


Figure 4 Microstructure after quenching in water of 23# alloy.

2.3 Effect of manganese element

(1) Effect of manganese content on SME.

Figure 5 shows relationships between shape recovery ratio and different strain in 2# alloys containing 24.36%Mn and 24# alloys containing 15.40%Mn. 2# alloys and 24# alloys contained the same component beside of manganese content. It is seen that SME of high manganese alloys (24.36%) is better, especially under situation of small strain, and towards above 5% compared with low manganese alloys.

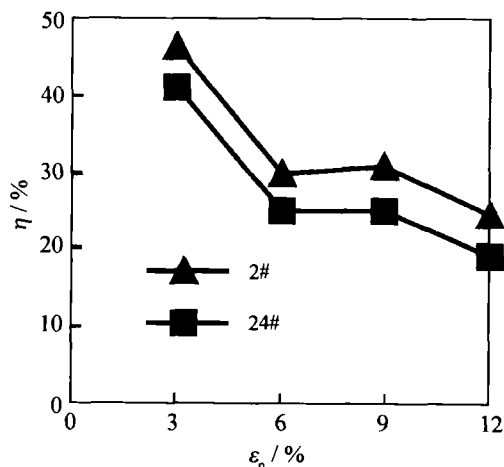


Figure 5 Effect of manganese content on SME.

(2) Result analysis.

It has been reported [8] that alloy microstructure is

consisted of γ -Fe and ϵ -martensite while manganese content is ranged from 10% to 15%. It was observed [9] that quantity of ϵ martensite hold fixedly with 22%-26% manganese content, and increasing manganese content lead to reduce ϵ martensite markedly while Mn content greater than 26%. Moreover no ϵ martensite is observed while Mn content above 30%, just in which best SME could be performed. Thus it could conclude that SME is not induced by thermal induced martensite, but produced by stress-induced martensite transition; thermal induced martensite is disadvantage to reversible transition of stress-induced martensite. So it is necessary to avoid existing of thermal induced martensite before distorting for achieving greatest SME.

In this experiment, these exist quite quantitative ϵ martensite in Fe-Mn-Si-Ni-C-RE alloys after quenching with low manganese content (15%-16%), which contain kinds of variant with different orientations. And the martensitic variants intercross reticularly each other, as shown in figure 6 (a). Loading certainly pre-strain produce much stress-induced martensite, but it is difficult for stress-induced martensite to grow because of martensitic intercrossing and collision between stacking faults. In reversible transition, lots of martensite could not transform into matrix γ austenite. Therefore shape recovery ratio of alloys with 15%-16% Mn is not too large. Little stacking faults and ϵ martensite, which make as center of martensitic nucleation, are observed in microstructure of containing 24%-25% manganese alloys, as shown in figure 6 (b). So only quite small stress need to produce stress-induced martensite because additional stress could make existed stacking faults and ϵ martensite grow. Furthermore, pre-existed stacking faults and ϵ martensite distribute dispersedly and seldom collid each other, and they could grow without intercrossing possibly. So that it is more complete and easier to accomplish stress-induced martensitic reversible transition and shape memory recovery ratio of alloys with added 24%-25% manganese is greater than with 15%-16% manganese.

From analysis above, the following three necessary requirements could be included for favorable SME.

1) Because SME correlates closely with stacking fault energy and forming and reversible transition of stress-induced martensite, all of dislocation in alloys must be wide expand type dislocation, in the middle of which stacking fault belt could form.

2) Little stacking faults and ϵ martensite must be pre-existed before loading strain.

3) Stacking faults and ϵ martensite distribute inde-

pendently and uniformly in each region within grains to avoid intercrossing between martensite and hindering martensitic growth.

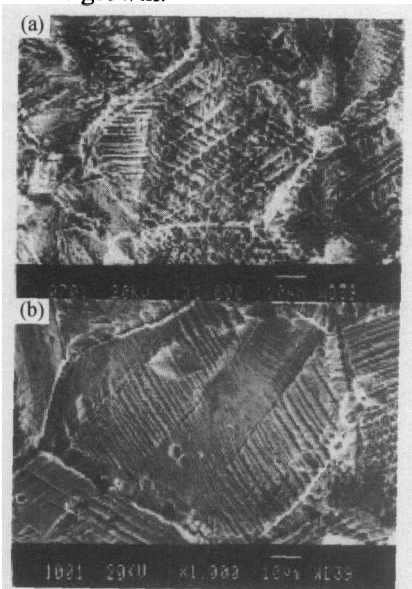


Figure 6 Effect of manganese content on microstructure, (a) 15.40% Mn; (b) 24.36% Mn.

So the change of manganese content, which could adjust quantity and morphology distribution of pre-existed martensite, affects remarkably properties of SMAs.

2.4 Effect of silicon element

(1) Effect of silicon content on SME.

Silicon content determines stacking fault energy (SFE), and makes important effect on ferrous based SMAs. Ferrous based SMAs are low SFE alloys. That stacking fault existing inside grain acted as nucleation center for stress-induced martensite transition is precondition for SME. So lower SFE, lower stress need for inducing phase change and better SME could achieve. Curves in **figure 7** show different shape memory recovery ratio with various silicon content (2.75%, 3.70%, and 4.62% respectively) in different low Mn system alloys (8#, 9#, and 24#). And higher Si content better SME could perform; especially SME is improved evidently as Si content increases from 2.75% to 3.70%. It was reported [10] that Si could improve austenitic yield strength and decreases mightily austenitic SFE after carrying out system study for effect of silicon on Fe-Mn-Si low SFE alloys and also proposed that Si content should be controlled between 4% and 6%.

(2) Effect of silicon content on brittleness of alloys.

Content of silicon affects markedly brittleness of alloys: 1) while Si content is not greater than 2.75%, Fe-Mn-Si SMAs have good plasticity and none of defect after forging. But problems would appear as soon as silicon content above the limit, and properties are

worsened obviously with increasing Si content. Two ingots of alloys with 5%-6% Si emerge crackle, which goes deep into 15 mm toward forged lamina center. When sampling with electric spark machine, external parts containing crackle should be cut off and obtained samples for training at center parts; 2) 1# and 23# alloys with additional scruple compound RE are not brought any of defects after forging. Wang [11] considered that adding scruple Mg element could improve plasticity of alloys, Fe-Mn-Si alloys containing 5% Si and scruple Mg could be rolled into steel tube. And it be also considered that adding Mg and compound RE affect as fining grains and refining grain boundaries and improve effectively thermoplasticity. It is not evident for SME to add Mg element. But in this experiment, adding compound RE improves not only handling characteristics but also SME markedly. Therefore it is a more effective technology to add compound RE.

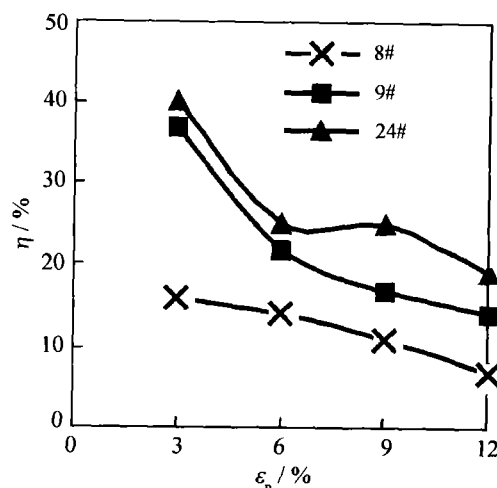


Figure 7 Effect of silicon content on memory recovery ratio.

2.5 Effect of nickel content on alloys

In this work, content of nickel element holds 5% constantly. It is considered that adding nickel is advantage to improve machinability. Effect of nickel on SME is similar to manganese, and Ni is also the element to expand γ austenitic zone and decreases M_s point. Authors [12] considered that SME is best and stress is least to induce $\gamma \rightarrow \epsilon$ phase transition when Ni content ranged from 5% to 6%.

3 Conclusions

(1) In the case of small strain, SME of Fe-Mn-Si-Ni-C-RE SMAs decreases gradually along with carbon content increasing. While in the case of big strain (above 6%), alloys containing 0.1%-0.12% carbon perform small decreasing range of SME, especially adding compound RE.

(2) Adding compound RE in Fe-Mn-Si-Ni-C-RE

alloys could fine microstructure obviously and improve SME.

(3) In Fe-Mn-Si-Ni-C-RE SMAs, higher manganese content alloys perform well SME, especially under the condition of small strain.

(4) SME is improved evidently as soon as silicon content increases from 3% to 4%, but brittleness of alloys adds while Si content too higher.

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