Online: 1990-01-01

Materials Science Forum Vols. 56 - 58 (1990) pp. 655-660 Copyright Trans Tech Publications, Switzerland

SHAPE MEMORY EFFECT IN Fe-Mn-Si-Cr-Ni POLYCRYSTALLINE ALLOYS

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ABSTRACT

Fe-Mn-Si ternary alloys have a good shape memory effect(SME) and their recoverable strain exceeds 2% by a thermomechanical treatment. However, they have two problems, poor corrosion resistance and complicated fabrication process. We have succeeded to develop new polycrystalline shape memory alloys in the Fe-Mn-Si-Cr-Ni system. Some of these alloys have good corrosion resistance comparable to that of stainless steel(SUS 403). And their recoverable strain without the thermomecanical treatment is superior to that of Fe-Mn-Si ternary alloys with the thermomechanical treatment.

1. INTRODUCTION

Fe-Mn-Si alloys show a good SME. Sato et al. found that a single crystalline Fe-30Mn-1Si(in wt%) alloy exhibits complete SME when it is deformed in a specific direction[1,2]. We have found that polycrystalline Fe-Mn-Si alloys show almost complete SME if a suitable combination of Mn and Si content is selected[3]. We have also found that a thermomechanical treatment improves their SME remarkably[4]. The thermomechanical treatment comprise the repetition of slight deformation and annealing at 773-973K. But these alloys are easily corroded and the thermomechanical treatment complicates processing. Generally it is well known that the corrosion resistance is improved by adding Cr. However an addition of Cr caused a decrease of Ms temperature and too much addition caused ferrite formation. In order to keep Ms temperature at around room temperature Mn content must be reduced. Ni must be added to inhibit the formation of ferrite. In this study we show new Fe-Mn-Si-Cr-Ni polycrystalline alloys which have fairly good corrosion resistance and their recoverable strain without the thermomechanical treatment is superior to that of the conventional alloys with the thermomechanical treatment. And the possible reason of such improvement is also discussed.

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2. EXPERIMENTAL

Alloys with chemical compositions, Mn:13-32, Si:5-6, Cr:0-15, Ni:0-8(in wt%) were prepared by vacuum induction melting. Their compositions are shown in Table 1. Ingots were annealed at 1423K for an hour and rolled to plate 15mm in thickness. The rod specimens (4mm diameter x 23mm length) were cut from the plate and heated at 873K for ten minutes in order to eliminate the influence of machining. The magnitude of SME was determined by amount of the recovered strain when heated at 573K after tensile deformation by 3%. For obtaining critical stresses for slip deformation and for martensite transformation temperature dependence of the yield stress was measured. The transformation temperatures were determined by the change of electric resistance. Neel temperature(Tn) was determined by temperature dependence of magnetic susceptibility. Volume of ganmma and epsilon phases were determined by the integrated strength of X ray diffraction. Corrosion resistance was monitored with a neutral salt spray test. 5%NaCl was sprayed on the samples 2ml/hr and the fraction of rust was measured with time.

3.RESULTS AND DISCUSSION

Table 1 shows the compositions of alloys, transformation temperatures, recoverable strain when heated at 573K after tensile deformation by 3%, and recoverable strain after the themomechanical treatment. 32Mn6Si(S-14) and 28Mn6Si5Cr(S-15) are the conventional alloys. 20Mn5Si8Cr5Ni(S-2) and 20Mn5Si10Cr5Ni(S-10) obtain especially good SME. 16Mn5Si12Cr5Ni(S-10), 13Mn5Si10Cr6Ni(S-12) and 13Mn5Si11Cr7Ni(S-13) also show fairly good SME. The recoverable strains of these alloys after the treatment were 1.7-2.2%. At least recoverable strain of 2% is required for pipe joint application.

Table 1 Comparison of recoverable strain and transformation temperature for alloys.

	composition(wt%)				Ms	As	initial	after the
	M_{Π}	Si	Ċr	Ni				treatment
S- 1 S- 2 S- 3 S- 4 S- 5 S- 6 S- 7 S- 8 S- 9 S-10 S-11 S-12 S-13 S-14	25.5 20.4 19.9 17.5 16.9 18.3 17.9 16.5 16.4 16.0 13.7 13.3 13.0 31.5	5.7 5.0 5.0 5.1 5.0 5.1 5.0 5.1 5.0 4.9 4.7 6.0	7.9 8.0 10.1 8.5 10.0 11.7 13.9 8.4 10.3 11.6 8.0 9.6 11.4	5.0 5.0 5.0 5.5 6.3 5.5 4.9 5.0 4.4 5.8 6.8	261.2K 225.7K 254.3K 254.0K - 214.5K - 267.2K 274.5K 276.8K 243.6K 293.0K	354.5K 355.1K 370.0K 365.8K - 328.7K 342.4K 369.2K 382.3K 406.8K 385.1K 367.5K 388.2K	0.97% 2.05% 1.95% 1.11% 1.20% 0.95% broken 0.98% 1.10% 1.45% 0.91% 1.59% 1.64% 1.00%	1.15% 2.20% 2.10% 1.98% 1.76% - 1.34% 1.76% 2.07% 1.12% 2.02% 1.96% 1.85%
S-15	27.6	6.1	5.0	-	283.OK	392.2K	1.20%	1.80%

In the new alloys Ni was added according to the diagram of Hull[5] considering the balance of Cr and Ni in order to suppress the formation of ferrite phase.

Figure 1 shows the critical lines under recoverable strain and stress can be used at the same time. This figure indicates that S-2 and S-10 alloys have larger region for SME, when we consider a combination of stress and strain than S-15.

Figure 2 shows the corrosion resistance to salt water. Percentage of rust grown with time is shown. The larger the amount of Cr content, the better corrosion resistance is achieved. The corrosion resistance of the alloy whose Cr content is more than 8% in weight is comparable to that of stainless steel

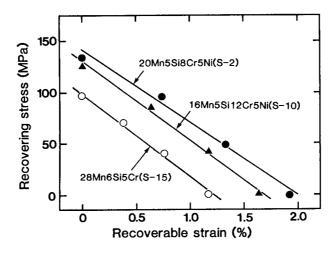


Figure 1 Comparison of recoverable strain and recovering stress between present and conventional alloys

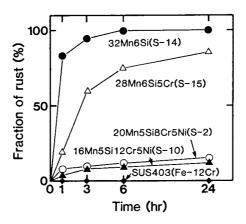


Figure 2 Results of neutral salt spray test. 5%NaC1,2m1/hr,308K

(SUS403) along with remarkably good SME in comparison with the conventional alloys.

Why do the new alloys have such good SME? The deformation just above Ms temperature is most favorable for obtaining the shape memory alloys utilizing stress-induced martensitic transformation. Suppose that we deform them at room temperature, it is desirable Ms temperature should lie just below room temperature. According to table 1,S-2,10,11,12 and conventional S-15 alloys meet this condition. Since Neel temperature(Tn) of S-14 is about 293K and free energy of gammma phase is stabilized, martensitic transformation does not take place[6]. But without magnetic transformation Ms temperature should lie near room temperature. Th temperatures of Fe-Mn-Si-Cr-Ni alloys are lower than Ms temperature owing to a large amount of Cr and Ni, and therefore they do not affect the transformation. For example Tn is 177.7K in S-2 alloy (Fe2OMn5Si8Cr5Ni) and 168.7K in S-3 alloy (Fe2OMn5Si1OCr5Ni) respectively and far below room temperature.

Table 2 Volume fraction of martensite phase at room temperature and at 77K.

	C	omposi	tion(wt%	R.T.	77K	
	Mn	Si	Cr	Ni		
S- 2	20.4	5.0	8.0	5.0	0%	34.0%
S-10		5.0	11.6	4.9	0%	29.8%
S-14	31.5	6.0	-		1.5%	14.4%
S-15	27.6	6.1	5.0		2.0%	24.3%

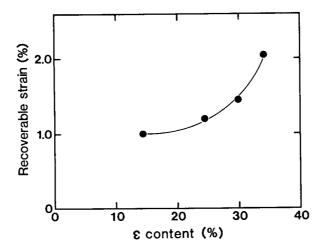


Figure 3 Relationship between the amount of epsilon phase after cooling down to liquid nitrogen temperature and the recoverable strain

In order to obtain a good SME Ms temperature should lie just below room temperature. It is also necessary that they should have a large amount of martensite phase which can be used to compensate deformation strain. We estimated the amount of martensite phase by cooling. Table 2 shows that the amount of martensite phase for four kinds of alloys before and after cooling with liquid nitrogen. The volume fraction at room temperature is measured after heating above 573K. The other phase except ganmma and epsilon cannot be observed in these alloys. In S-2 and S-10 alloys a larger amount of martensitic phase by 5-10% can be used in comparison with that of the conventional alloys as the stress-induced martensitic transformation. Figure 3 shows the relationship between the amount of epsilon phase and the recoverable strain. The larger the amount of epsilon phase after cooling down to liquid nitrogen temperature, the larger recoverable strain can be obtained.

Figure 4 shows temperature dependence of yield stress for S-2 and S-14 alloys. Critical stress for martensite formation and that for slip deformation are temperature dependent. The former is positive and the latter is negative temperature dependent. These stresses are approximated by yield stress. In order to generate martensite without introducing slip deformation, the shaded portion should be made use of in Figure 4. The critical stress for slip deformation of S-2 alloy is higher than that of S-14 conventional alloy. And the critical stress for martensite formation of S-2 alloy is a little lower than that of S-14. This means that the shaded portion is larger than that of the conventional alloy. Addition of Cr and Ni strengthens the matrix of austenite.

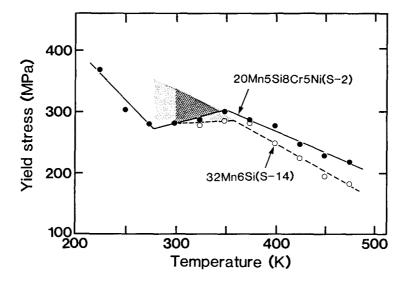


Figure 4 Temperature dependence of yield stress which coresponds to the critical stress for martensite formation and that of for slip deformation

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4.CONCLUSION

Fe-Mn-Si-Cr-Ni alloys show better SME than that of the conventional alloys and have good corrosion resistance. The following conditions are required for the improvement of SME.

- (1)Cr content should be higher than 8% in weight.
- (2)Ms temperature should lie near room temperature.
- (3)A large amount of martensite should be formed when cooled below Ms temperature.
- (4)Slip deformation should be absent.

ACKNOWLEDGMENT

The authors would like to express their appreciation to Professor Mori and Professor Sato, Tokyo Institute of Technology for their useful discussion. They are also grateful to Dr.M.Murakami of International Superconducting Technology Center for his collaboration.

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