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The influence of heat treatment atmosphere and maintaining period on the homogeneity degree of a Fe-Mn-Si-Cr-Ni shape memory alloy obtained through powder metallurgy

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An Fe-14Mn-6Si-9Cr-5Ni (mass. %) shape memory alloy obtained through powder metallurgy, containing a mixture of 50% commercial powders and 50% mechanical alloyed powders, was subjected to different heat treatments in order to increase chemical homogeneity degree. The heat treatments consisted of using three types of treatment atmospheres (air, nitrogen and argon) and three isothermal maintaining times (6×10^2 s, 24×10^2 s and 48×10^2 s). The obtained microstructures were then analysed by optical and scanning electron microscopy.

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1. Introduction

Shape memory effect of in Fe-based shape memory alloys (SMAs) is caused by the thermally induced reversion to austenite (fcc) of a stress-induced martensite (hcp), on heating. Fe–Mn alloy system is often considered as a new class of SMAs of great technical importance, but in this system a poor shape recovery was observed and one of the solutions to solve this problem was alloying with several elements such as Si, Cr, Co, Ni and C [1].

Obtaining Fe-Mn-Si-Cr-Ni SMAs through classical metallurgy must overcome a series of difficulties related to compositional segregation [2], difficult incorporation of Si into melt [3], Mn loss on melting and heat treatment, which currently occurs in stainless steels [4], time consuming chemical composition homogenization [5] and quenching [6].

One alternative technology, meant to overcome most of the inconveniences encountered in classical metallurgy processing, is powder metallurgy (PM). Furthermore, most of the drawbacks in preparing grain-refined microstructures of Fe-Mn-Si-Cr-Ni SMAs with homogenous structure can be eliminated by mechanical alloying (MA) [7].

Considering that shape memory capacity, can be affected by various factors, such as pre-strain amount, deformation temperature, annealing temperature and thermo-mechanical training [8-10], the present paper aims to analyse the effects of heat treatment atmosphere and maintaining period on the homogeneity degree PM-MA'ed Fe–Mn–Si–Cr–Ni SMA.

2. Experimental details

Powder mixtures with nominal composition Fe-14Mn-6Si-9Cr-4Ni (mass. %) were prepared as a mixture of equal volumes of as received and ball milled powders. The powder mixtures were pressed and sintered at 1390 K, under cracked ammonia and repeatedly hot rolled, at 1373 K, with 15% thickness reduction per pass, until reaching a 0.7 mm-thickness [11].

After machining, hot rolled specimens were heat treated to 1473 K and held for periods of time ranging between 6 and 48×10^2 s, under three different protective atmospheres: (i) vacuum, (ii) nitrogen and (iii) argon. Thus, nine different specimens were obtained which were further prepared by grinding and polishing.

The specimens were etched with a solution of 1.2% $K_2S_2O_5$ + 1% NH_4HF_2 in 100 ml distilled water, before being analyzed by optical (OM) and scanning electron (SEM) microscopy. OM micrographs were recorded on a MEIJI THENO CH microscope equipped with Evolution VF video camera operated with QCapture software. SEM observations were performed by means of a FEI Quanta SEM-FIB 200 3D dual beam microscope, under protective atmosphere.

3. Results and discussion

The alloy under study was subjected to three different heat treatment atmospheres: air, nitrogen and argon and also to three different maintaining periods: 6×10^2 s, 24×10^2 s and 48×10^2 s. The nine resulting specimens have been designated as summarized in Table 1.

Table 1. Summary of the designation of different samples obtained using different treatment atmospheres and maintaining periods.

Treatment atmosphere	**Maintaining periods**		
	6 × 10^2 [s]	**24× 10^2 [s]**	**48× 10^2 [s]**
Air	S1	S4	S7
Nitrogen	S2	S5	S8
Argon	S3	S6	S9

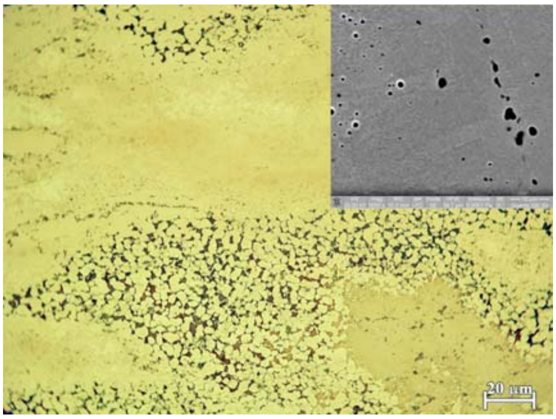

Fig. 1. Optical and scanning electron microscopy of S1.

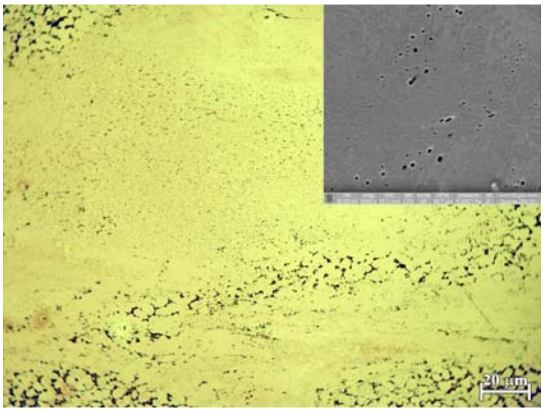

Fig. 2. Optical and scanning electron microscopy of S2.

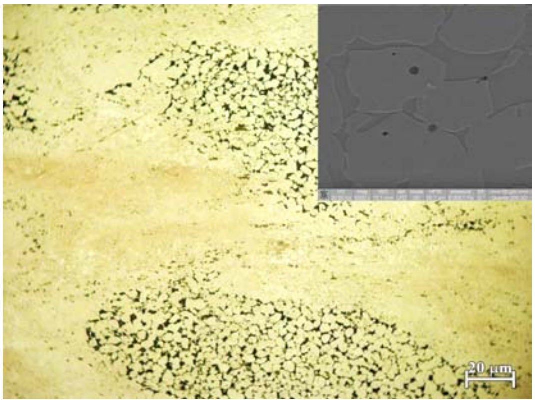

Fig. 3. Optical and scanning electron microscopy of S3.

After microscopic observation of samples S1-S3, according to Figs. 1-3, respectively, it was noticed that the structural homogeneity degree of the samples annealed for 6 × 10^2 s was low. All three samples contained oxidized areas, representing the black dots from the SEM insets, as well as large areas of chemical segregation, presented in the inset of Fig. 3. The oxidized areas were rich in Mn and Si and the observed ferrite-segregated zones, resulting from the preferential alloying of Fe grains by Cr, were formed due to low dissolving rate of Cr grains in as-received powders. As a result of the presence of Cr-rich ferrite zones, surrounded by austenitic matrix, a typical aspect of duplex steel was recognized on OM micrographs [12, 13].

Although structural homogeneity of S1-S3 samples was low, considering the treatment atmosphere, the highest homogeneity degree was obtained by the sample S1, heat treated in air. The other two samples, S2-S3, presented almost the same size of segregation areas, regardless of treatment atmosphere.

Even though the sintering process was carried out in a protective atmosphere and some of the heat treatments were made in protective atmospheres, argon and nitrogen, all of the three samples presented oxidized areas, which can be noticed from the SEM insets.

With increasing the maintaining period to 24 × 10^2 sec, an increase of homogeneity degree in the sample S4, heat treated in air, was observed, while the sample heat treated in argon underwent a decrease in homogeneity and thus the segregation areas increased in size, as observed in Figs. 4-6.

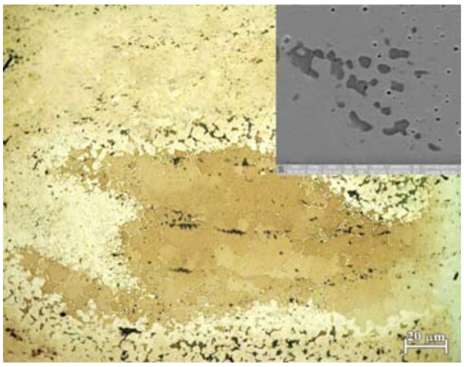

Fig. 4. Optical and scanning electron microscopy of S4.

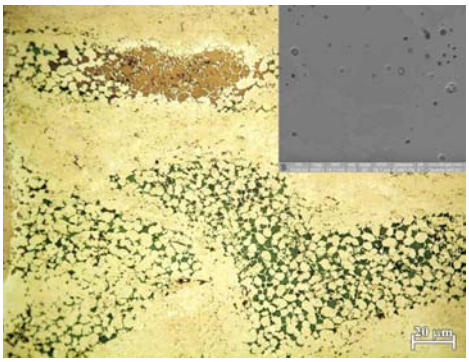

Fig. 5. Optical and scanning electron microscopy of S5.

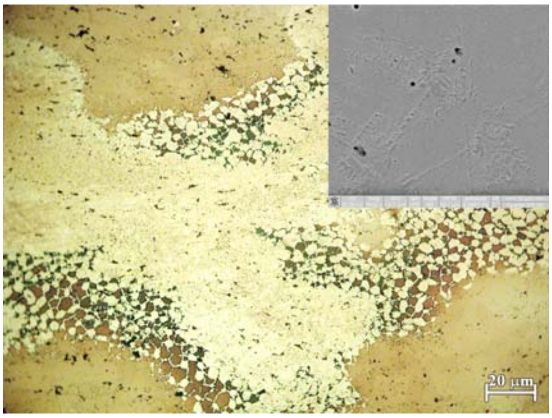

Fig. 6. Optical and scanning electron microscopy of S6.

Another observed aspect was the occurrence of an additional type of segregation areas, which can be seen in the middle of ferrite-segregated zones, areas that were rich in Mn, Si and oxygen, such as the black spots on the SEM inset of specimen S4 in Fig. 4. In other words, increasing annealing time, from 6×10^2 s to 24×10^2 s led to the obtainment of a less homogeneous microstructure. The effect was mainly caused to the formation of a second type of segregation area.

When annealing time was increased to 48×10^2 s, the highest degree of homogeneity was achieved in the case of sample S7, although the sample was heat treated in oxidizing atmospheres which lead to an increase in oxidation. Moreover, the two types of segregation zones previously observed were no longer present in the microstructure of sample S7, shown in Fig. 7.

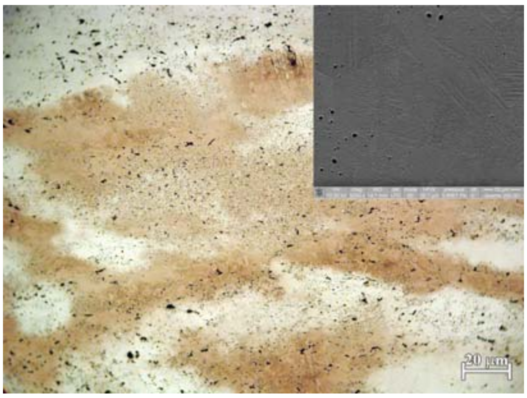

Fig. 7. Optical and scanning electron microscopy of S7.

The homogeneity degree for the sample S8 presented only a slight decrease, since both segregation areas are still present in the microstructure, as illustrated in Fig. 8.

The use of argon atmosphere, in the case of 48×10^2 s holding, led to a slight improvement in homogeneity degree for the sample S9, as compared to sample S8. This situation is illustrated in Fig. 9, which reveals the effects of 48×10^2 s holding in Argon atmosphere.

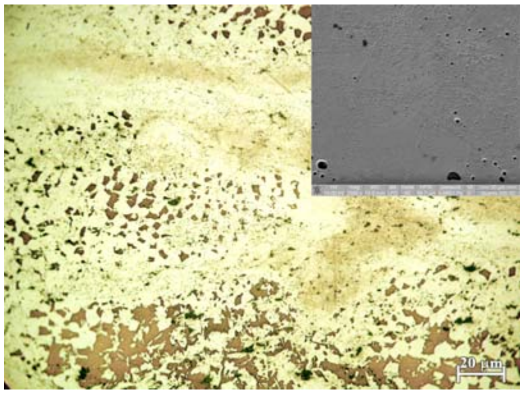

Fig. 8. Optical and scanning electron microscopy of S8

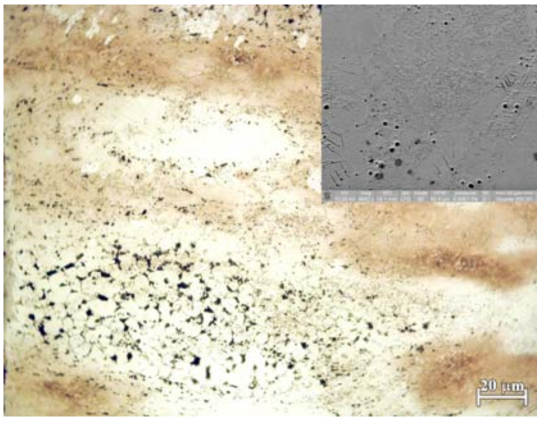

Fig. 9. Optical and scanning electron microscopy of S9.

At S9, Fig.9 shows that, although the ferrite-segregated zones were still present, the areas covered by this type of segregation were much smaller.

Another aspect, noticed while analyzing both optical and scanning electron micrographs of the samples, was the presence of martensite plates, which are illustrated in the representative details shown in Fig. 10, in the case of S7.

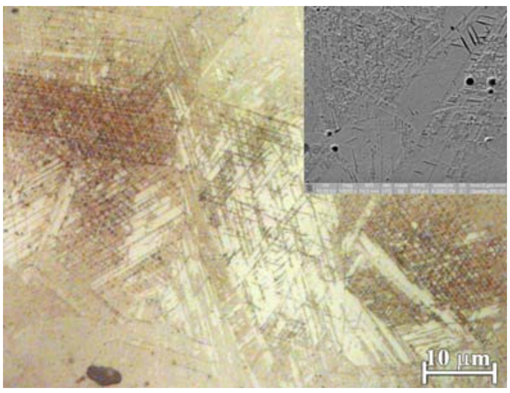

Fig. 10. Optical and scanning electron microscopy of S7.

It was observed that the presence of martensite plates became more and more frequent with increasing the maintaining periods and reached the maximum complexity, from the point of view of average plates number, in sample S7. The optical and scanning electron microscopy revealed the presence of ε hexagonal close packed and α' body centre cubic martensites for this sample [14, 15].

The use of colour etching enable to clearly distinguish the two types of martensite plates, considering that ε martensite plates appear as light brown colour while α' martensite, formed at the intersection of ε plates, occur as black lines [16].

4. Conclusions

The influence of heat treatment atmosphere and maintaining period on the structural homogeneity degree of a Fe-Mn-Si-Cr-Ni shape memory alloy, obtained through powder metallurgy from equal powder volumes in as-received and mechanically alloyed states, analyzed in the present study, can be summarized as follows.

- Varying the maintaining period, from 6×10^2 s to 24×10^2 s and further to 48×10^2 s, and treatment atmosphere (air, nitrogen and argon), two types of segregations were observed, ferrite-segregated zones and Mn, Si and oxygen-rich zones.
- Although two protective atmospheres were used, argon and nitrogen, the highest structural homogeneity degree was achieved maintaining for after 48×10^2 s maintaining at 1473 K in air.
- The increase of structural homogeneity degree was accompanied by the occurrence of two types of martensite, ε hexagonal close packed and α' body centre cubic, which were also best revealed at the sample annealed for 48×10^2 s in air.

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