Thermomechanical processing effects on the structure and properties of Fe-based SMAs. I. Evolution of phase structure

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Thermomechanical processing effects on the structure and properties of Fe-based SMAs. I. Evolution of phase structure

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Abstract: The paper analyses the effects of heat treatment (HT) and mechanical alloying (MA) on the evolution of phase structure of an Fe-Mn-Si-Cr-Ni Shape Memory Alloy (SMA) obtained by powder metallurgy (PM). Using various amounts of mechanically alloyed (MA'ed) powders, namely 0 and 40 vol. %, two groups of specimens with chemical composition Fe-14Mn-6Si-9Cr-5Ni (mass.%) were produced by PM. After blending, pressing, sintering and hot-rolling, each set of samples was subjected to five different heat treatment temperatures 973, 1073, and 1373 K, respectively. Tensile pre-straining tests were performed on all samples, with increasing pre-straining degrees up to 4.5 %, in order to stress-induce ε (hcp) martensitic phase in the material. Structural analysis was implemented by means of X-ray diffraction and SEM observations. XRD and SEM investigations revealed the formation of thermally induced α'-bcc martensite, besides ε-hcp, as a particularity of this powder metallurgy, mechanically alloyed, shape memory alloy.

1. Introduction

Fe-Mn-Si-based shape memory alloys (SMAs) were used for practical applications [1] since 1991due to a number of advantages, i.e., low cost, good mechanical processability and high corrosion resistance [2]. Heating-induced reversion to γ-fcc austenite of ε-hcp stress-induced martensite, between critical temperatures A_s (for the start) and A_f (for the finish), represents the mechanism of SME occurrence [3]. At low Mn % or at high deformation degrees, besides ε-hcp, α'-bcc martensite can be additionally induced by cooling or deformation, which diminishes the crystallographic reversibility of $\gamma \rightarrow \varepsilon$ transformation [4]. The formation of stress-induced α'-bcc martensite, in a three-phase structure, has been responsible for the decrease in SME [5].

The great majority of SMAs applications used the alloys obtained through ingot metallurgy (IM, comprising melting-alloying-casting) which, especially in the case of quintenary Fe-Mn-Si-Cr-Ni SMAs, has several technological drawbacks, such as compositional segregation, difficult incorporation of Si into melt, demanganization on melting and heat treatment, time consuming chemical composition homogenization, cracking enhancement due to cooling contraction during solidification and quenching, tempering embrittlement, etc. [6].

A viable alternative for replacing IM materials could be powder metallurgy coupled with mechanical alloying. PM MA'd routine has been used for making shape memory alloys from other systems, such as Ti – Ni [7], Cu – Zn – Al [8] or Cu – Al – Ni [9]. Some of the present authors have showed that the amount of ε hcp-martensite in sintered samples could exceed 31%, if as-blended powders were used, after a final rolling pass performed at room temperature (RT) [10]. The formation of thermally induced martensite was enhanced, at PM specimens, by both MA and the increase of heat treatment (HT) temperature [11], while an optimized combination of MA'ed powder fraction and technological parameters of hot rolling (HR) and HT enabled an increase of shape recovery degree [12].

The present paper investigates the effects of heat treatment (HT) and mechanical alloying (MA) on the evolution of phase structure of an Fe-Mn-Si-Cr-Ni Shape Memory Alloy (SMA) obtained by powder metallurgy (PM).

2. Experimental details

The specimens, with nominal chemical composition 66Fe-14Mn-6Si-9Cr-5Ni (mass %), were pressed and sintered under argon atmosphere and designated as: (i) 0_MA, from as-blended elemental powders and (ii) 40_MA comprising 40 vol. % MA'ed powders, obtained after 4 hrs. high-energy ball milling under Ar atmosphere in order to inhibit the chemical reactivity of oxygen-sensitive alloying elements. In order to further increase of compactness six consecutive hot rolling passes at 1373K were performed, until samples' thickness decreased from 4 to 1 mm. Low-temperature annealing, i.e. 923 – 1073 K with 30 minutes maintaining, was also applied after hot rolling by Drucker et al. [13] but in our case the specimens were porous and the risk of chemical altering of the superficial layer was augmented. For this reason, we reduced holding time to 5 minutes that would be enough for stress relieving, after hot rolling. Before further experiments, rectangular, "dog-bone" (gauge dimensions 1×4×20 mm) were cut by spark-erosion wire cutting and carefully grinded under water flow, in order to remove the outer layers damaged by oxidizing and demanganization.

Tensile pre-straining tests were performed on an INSTRON testing machine at RT, with increasing pre-straining degrees (up to 4.5 %) during a static loading-unloading with a crosshead displacement rate of 3×10-3mm s^{-1}[14].

The gauges of "dog bone" specimens, both in initial and pre-strained conditions were cut, embedded into cold mounting resin and metallographically prepared for performing XRD patterns and SEM micrographs. The former were recorded, on 2θ = 40-100°, using a Brucker ASX D8 Advance diffractometer with Cu Kα radiation and the latter on a SEM—VEGA II LSH TESCAN microscope. Crystallographic databases were used for the identification of, α'-bcc, γ-fcc and ε-hcp phases.

3. Experimental results and discussion

Structural analysis was further focused on the specimens that were HT'ed at 1273 K (1000^0C) due to their prominent effect, as compared to the other samples. Their corresponding XRD patterns are shown in figure 1.

XRD patterns recorded on the hot rolled heat treated specimens in unstrained and pre-strained conditions, revealed the presence of the three phases, α'-bcc, γ-fcc and ε-hcp, identified by means of the non-overlapping diffraction maxima (110)α', (200)α', (101)ε, (103)ε, (200)γ and (222)γ.

It is noticeable that the increase of pre-straining degree, in the case of 0_MA samples, enhanced the formation of martensite plates due to the increase in intensity of the main diffraction maxima of the ε-martensite phase (002). Another thing to notice is that, if in initial state the 0_MA samples presented a high α' martensite intensity peak (110) with increasing the pre-straining degree its intensity decreased with almost 80%. This kind of behavior is atypical because in theory α' martensite forms at the intersections of ε-martensite and is favorited by large deformation degrees. In this case the main diffraction maxima (110) decreased with increasing deformation degree.

The behavior of 40_MA samples is as expected, α' main intensity peak increased with deformation degree while a new plane (200) can be observed at 2θ = 63°. Due to increasing pre-straining degree a

large quantity of α' martensite was induced in this types of samples which will be detrimental to shape memory effect.

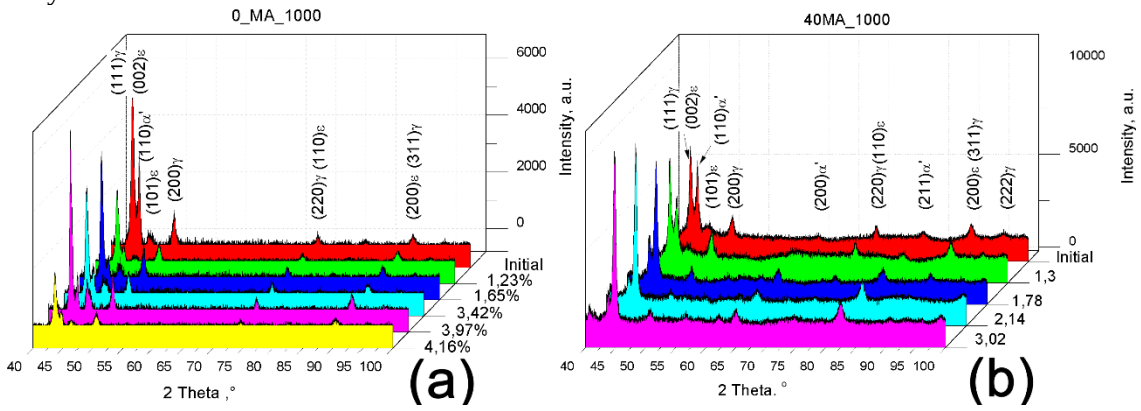

Figure 1. XRD patterns of the specimens heat treated at 1000°C, (a) 0 MA and (b) 40 MA

SEM micrographs from figure 2 reveal that ε-hcp martensite displays a typical "triangular" morphology, with narrow plates that completely cross austenite grains, from one border to the other, while α'-bcc martensite forms shorter bands with lenticular shape and deeper surface relief, which do not cross austenite grains.

At this point, one could argue that the introduction of α'-bcc martensite in an amount observable by SEM is unlikely in this kind of alloys. This observation was valid in the case of undeformed Fe-12.60 Mn-6.00 Si-9.27 Cr-4.74 % Ni-0.27 Al-0.13 Mo-0.05 C which contained 2.7 % α'(bcc) martensite [15] and in the case of Fe-14.2 Mn-5.1 Si-9.4 Cr-5.1 Ni (mass.%) that was nitrogen quenched and annealed at 923 K. Yet, in the latter alloy, increasing annealing temperature to 1223 K caused a marked rise in the amount of α'(bcc) martensite, visible on XRD pattern but not sustained by optical micrographs [16]. This tendency of α'(bcc) martensite, to increase with increasing annealing temperature, was also previously observed at the alloys under study, where the amount of this type of martensite ranged between 20-90 % [17]. It is noticeable that, with increasing MA'ed powder fraction, martensite plates became finer. This refinement should normally enhance shape recovery but a complete analysis of this effect in the pre-stressed specimens is beyond the scope of this article.

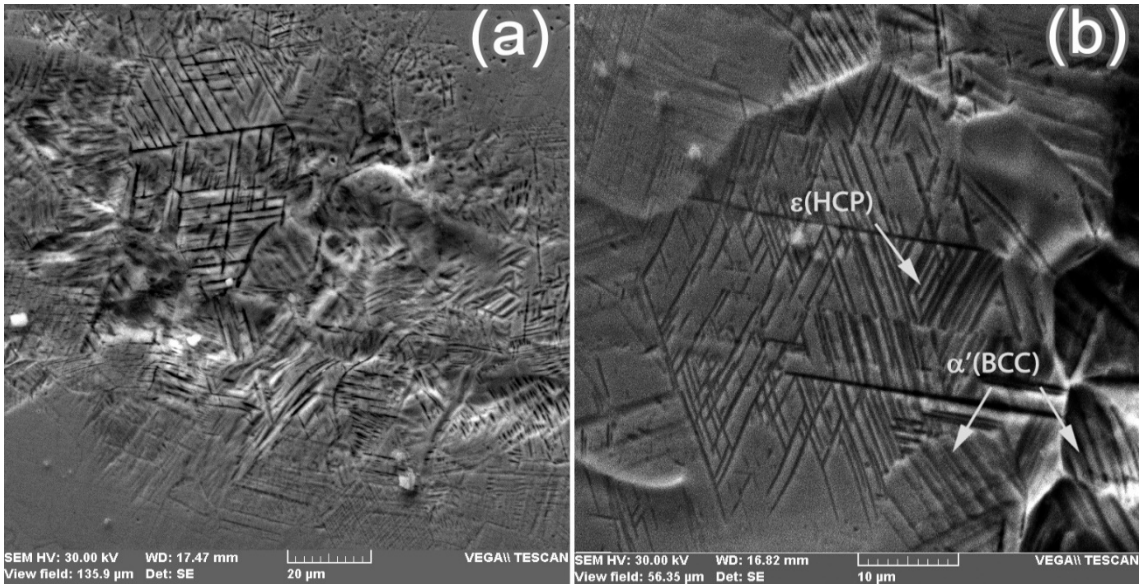

Figure 2. SEM micrographs illustrating the effects of pre-straining degree on 0 MA samples: (a) 0_MA_1000 unstrained and (b) 0_MA_1000 pre-strained at 3.97%.

Finally, the effects of MA fraction on the microstructure of PM-MA Fe-Mn-Si-Cr-Ni specimens, were presented in figure 3. Figure 3(b) shows the microstructure of specimen 40_MA_1000 which was pre-strained with 3.02 %. Although the ε-martensite quantity, which can be observed in the XRD patterns from figure 1(b), decreased the SEM micrograph showed a more complex martensite structure as compared to 0_MA.

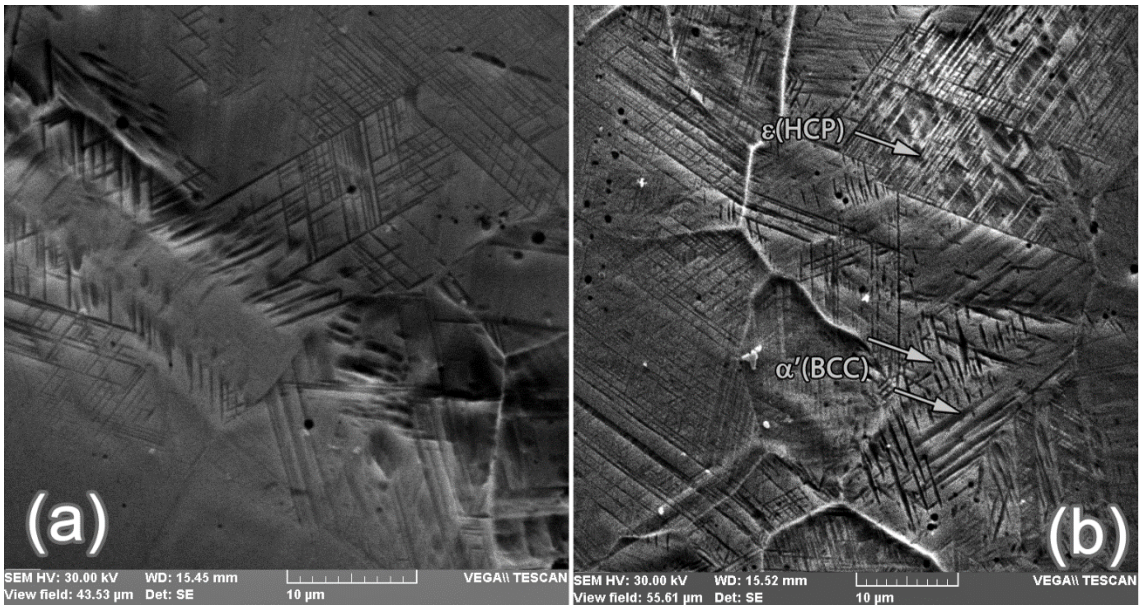

Figure 3. SEM micrographs illustrating the effects of pre-straining degree on 40 MA samples: (a) 40_MA_1000 unstrained and (b) 40_MA_1000 pre-strained at 3.02%.

4. Summary and conclusions

- XRD and SEM revealed the formation of thermally induced α'-bcc martensite, besides ε-hcp, as a particularity of these PM-MA'ed alloys.
- Martensite plate variants became more diversified with the increase of MA fraction and more complexly intersected.
- Introducing MA fraction lead to a decrease in the γ-fcc amount which transformed to α'-bcc and ε-hcp stress-induced martensites.

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