Materials Characterization 109 (2015) 128–137

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Characterization of phases in an Fe–Mn–Si–Cr–Ni shape memory alloy processed by different thermomechanical methods

V. Fuster [a,b], A.V. Druker [a,b,*], A. Baruj [c,d], J. Malarría [a,b], R. Bolmaro [a,b]

[a] Instituto de Física Rosario (CONICET-UNR), Bv. 27 de Febrero 210 bis, 2000 Rosario, Argentina
[b] Facultad de Cs. Ex., Ingeniería y Agrimensura (UNR), Av. Pellegrini 250, 2000 Rosario, Argentina
[c] Centro Atómico Bariloche, Comisión Nacional de Energía Atómica (CNEA), Av. Ezequiel Bustillo 9500, 8400 S. C. de Bariloche, Argentina
[d] Instituto Balseiro (UNCuyo), Av. Ezequiel Bustillo 9500, 8400 S. C. de Bariloche, Argentina

ARTICLE INFO

Article history:
Received 2 September 2015
Received in revised form 21 September 2015
Accepted 22 September 2015
Available online xxxx

Keywords:
Ferrous shape memory alloys
Microstructure
Phase analysis
$Fe_5Ni_3Si_2$ type intermetallic
X-ray diffraction
Rietveld refinement/Maud.

ABSTRACT

The presence of second phases in FeMnSi-based systems has been widely discussed in the literature, and also in our previous works. In this manuscript, various specimens of an Fe–15Mn–5Si–9Cr–5Ni wt.% (nominal composition) shape memory alloy were processed by different thermomechanical treatments in order to identify the phases present in each condition. TEM-EDS results indicate that the chemical composition of the second phase we found in all cases is close to 19Mn–xSi–12Cr–5Ni at. %, with x varying between 5 and 11, and Fe balance. This is compatible with a $Fe_5Ni_3Si_2$ type intermetallic phase. It forms in a temperature range between 600 and 900 °C, independently of the thermomechanical processing and the coexisting phases. Rietveld refinement of X-ray patterns was done using Maud software, and the phase was found to be isostructural to the pi-phase $Cr_3Ni_5Si_2$ with space group $P2_13$ and lattice parameter equal to 0.6227(7) nm. Phase quantification, crystallite size and accumulated microstrain were also computed as a convenient set of variables, necessary for improving refinement quality. Relevant microstructural information, i.e. stacking fault and twinning probabilities, along with dislocation density, were calculated for austenite, the matrix phase, contributing to the reliability of the determination of the crystallographic characteristics of the second phase.

1. Introduction

Fe–Mn–Si-based shape memory alloys (SMAs) have been extensively investigated during the last three decades [1,2]. Their shape memory effect (SME) is due to a stress-induced γ (austenite, FCC) ↔ ε (martensite, HCP) martensitic transformation that reverses when the material is heated above the A_f temperature. For the best recovery of the original shape the plastic deformation accompanying martensitic transformation must be negligible, and the ε → γ reverse transformation has to occur along the same crystallographic path followed during the direct transformation. The alloy's stacking fault energy (SFE), the microstructure and texture of the austenitic phase are the main parameters that affect the SME. Previous works have demonstrated that a favourable defect structure, i.e. a high density of stacking faults and an appropriate balance of dislocations, may be controlled by applying thermomechanical treatments to a material with the appropriate chemical composition [3–6].

Sade et al. [7] summarized literature indicating that Fe–Mn–Si-based SMAs usually contain between 15 and 30 wt.% Mn in order to stabilize the FCC → HCP transformation. A lower Mn content decreases the ε-martensite stability while that of the α′-martensite (BCC) increases. In fact, if the amount of Mn is lowered, the increase in Ms. temperature needs to be compensated by the addition of 4–5 wt.% Ni. Another component is Si, usually up to 6 wt.% to control the SFE and the austenite antiferromagnetic ordering temperature (Néel temperature, T_N). The addition of Cr, generally between 5 and 9 wt.%, improves the material's corrosion resistance. But when the Cr quantities are above 7 wt.%, the brittle Fe–Cr sigma phase (σ_{Fe-Cr}) can form [8]. In such cases, Ni is added to prevent σ-phase formation, in a similar way as for stainless steels [9].

The Fe–Mn–Si–Cr–Ni SMAs system provides a way for producing a training free Fe–Mn–Si-based alloy with high recovery strain. In addition, it can be expected that an even higher recovery strain can be developed in the cast condition through optimization of alloy compositions, casting parameters and heat-treatment techniques [10,11].

These SMA alloys contain elements that competitively stabilize the FCC and BCC phases and have a tendency to form different solid solutions and compounds. Many authors have reported the presence of phases that affect properties or reduce the amount of austenite available to transform to ε-martensite. We will briefly summarize their results in what follows.

Lin et al. [12] investigated the formation of a grain-boundary phase in the Fe–30Mn–6Si–5Cr SMA during annealing at temperatures ranging from 600 °C to 750 °C, which forms in a large amount at 700 °C. This phase exhibited an ordered BCC structure with a lattice parameter

* Corresponding author at: Instituto de Física Rosario (CONICET-UNR), Bv. 27 de Febrero 210 bis, 2000 Rosario, Argentina.
E-mail address: druker@ifir-conicet.gov.ar (A.V. Druker).

http://dx.doi.org/10.1016/j.matchar.2015.09.026
1044-5803/

of about 0.8798 nm, and had a similar chemical composition to that of the matrix. The SME and tensile properties of the alloy continuously degraded with increasing amounts of grain-boundary phase.

Maji et al. [13] studied the microstructure and phase stability of an Fe–15Mn–7Si–9Cr–5Ni stainless SMA in the temperature range of 600 °C to 1200 °C. They found an austenite single-phase field in the temperature range of 1000 °C to 1100 °C and a three-phase field, consisting of austenite, δ-ferrite, and the $(Fe, Mn)_3Si$ intermetallic phase, above 1100 °C. Within the temperature range of 700 °C to 1000 °C, a two-phase field consisting of austenite and a $Fe_5Ni_3Si_2$ type intermetallic phase exists, and below 700 °C, a single austenite phase field exists. Apart from these equilibrium phases, the austenite grains show the presence of athermal ε-martensite. The athermal α′-martensite has also been observed for the first time in this kind of alloys and is produced through the $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ transformation sequence.

Stanford et al. [14] investigated the stability of austenite in a number of Fe–Mn–Si-based SMAs. They found that grain-boundary BCC structure precipitates formed over a wide range of alloy compositions and heat-treatment temperatures. This grain-boundary precipitates have been identified as the chi (χ) phase. Although up to 3 vol.% of the grain-boundary precipitates were generated by isothermal ageing in the range of 500–800 °C, it was found not to markedly affect the mechanical properties or the shape memory behaviour. Afterwards, Stanford et al. [15] examined the interplay of composition, stacking fault probability (SFP) and T_N on the SME for a range of Fe–Mn–Si-based SMAs. The SFP (inversely proportional to stacking fault energy) showed little correlation to the SME for the range of examined alloy compositions. Furthermore, the T_N was not found to have a significant effect on the SME. However, the addition of interstitial elements was found to markedly decrease the SME. TEM showed that there were no carbides formed in an alloy with 0.3 wt.% C because a high Si content probably inhibits carbide formation during thermomechanical processing.

Kirindi et al. [16,17] analysed some physical and mechanical properties of martensitic transformation in an Fe–12.5Mn–5.5Si–9Cr–3.5Ni (wt.%) SMA. Compressive deformation at room temperature, when applied to the ε (HCP) phase within the austenite phase, caused the formation of α′ (BCC) martensite crystals at the intersection of prior ε-martensite plates. Newly formed ε-martensite plates were also observed.

Wen et al. [18] focused on the microstructures and shape recovery of a cast Fe–18Mn–5.5Si–9.5Cr–4Ni alloy. They attained lathy ferrite which subdivide the austenitic grains and resulted in the formation of stress-induced martensite bands in a domain-specific manner, which generated a high degree of shape recovery. In other words, in one domain only one group or one dominant group of ε-martensite bands is induced. Some σ-phase precipitated inside the ferrite. This was explained by the high Si content, which can shift the σ-phase region to that of low Cr content and accelerate the precipitation of this phase. When the Si content reaches 2.5 wt.%, the σ-phase region expands to Cr contents as low as 10 wt.% [19]. Wen et al. also found results indicating that ferrite with lathy morphology could improve the SME of Fe–Mn–Si alloys, while ferrite with island morphology could not. The reason for this effect may be that the latter cannot subdivide austenitic grains as efficiently as lathy ferrite.

To improve wear resistance, Bu et al. [20] studied the effects of ageing at 850 °C — with and without pre-deformation at room temperature — on the precipitation of second-phase particles in an Fe–14.51Mn–6.02Si–9.10Cr–5.06Ni–1.49Ti–0.16C SMA. They found that after solution treatment at 1100 °C there were massive amounts of ferrite in the austenitic grain boundaries. A subsequent ageing at 850 °C promoted the precipitation of some σ particles inside the ferrite phase and few particles within the austenite grains. In addition to the precipitates in the massive ferrite phase, numerous $Cr_{23}C_6$ precipitates were found inside the austenite grains after a solution treatment at 1100 °C for 40 min, followed by 10% tensile deformation at room temperature, and subsequent ageing at 850 °C for 30 min. EDS analysis revealed that some particles were TiC and other rod-like particles were rich in Cr, Mn and Si.

Lin et al. [21] added a little amount of rhenium (0.05–0.3 wt.%) to Fe–30Mn–6Si–5Cr alloys to improve the SME. They analysed the martensitic transformation, crystal structure, and ageing precipitates. They state that optimization of shape-memory performance can be achieved through combining pre-straining, ageing, and shape-memory training. The ageing precipitates could be observed in both the grain boundaries and within the grains. The alloys with and without Re, were aged at 700 °C for 2 h. From selected area diffraction patterns (SADP), the ageing precipitates were identified as χ-phase, with BCC structure and a lattice constant close to 0.89 nm. According to Yang et al. [22], the structure of the χ-phase is an A12 (α-Mn) type with 58 atoms in the unit cell. The composition of χ-phase is close to the matrix, but apparently with less Fe atoms and more of the other alloying elements.

Peng et al. [11] investigated the microstructure and solidification modes of cast Fe–(13–27)Mn–5.5Si–8.5Cr–5Ni SMAs, to clarify if Mn was an austenite former during solidification. Some second-phase particles appeared in the 15–27Mn alloys. In the case of 15–21Mn alloys, EDS measurements showed that their chemical compositions were compatible with the σ-phase composition. However, the character of those particles was not clear in the 23Mn–27Mn alloys. Another island-like phase was also found in 23–27Mn alloys. The EDS results on 25Mn and 27Mn alloys indicated that its Mn and Ni contents were markedly higher than those of austenite. By SADP they determined that it was the χ-phase, which is in agreement with the results of Stanford et al. [14]. In the cast Fe–Mn–Si–Cr–Ni alloys, the χ-phase precipitated during the solidification process between the ferrite dendrites by a process which is still unclear.

In a previous paper [23], we showed results on Fe–15Mn–5Si–9Cr–5Ni ribbons produced by the melt-spinning technique, and analysed the ribbon's microstructure and phase stability, evaluating their shape memory properties. The compositional Cr_{eq}/Ni_{eq} ratio, approximately 1.7, predicts that the solidification sequence should be $\text{Liquidus} \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \gamma + \delta$ [10]. Thus, the cooling rate determines whether ferrite, ferrite + austenite, or only austenite is present at room temperature, as demonstrated in different melt-spun ribbons. Other than these phases, X-ray diffraction showed less intense peaks indicating the existence of precipitated phases in certain manufacturing conditions. The analysis of the diffractograms suggested that the precipitates corresponded to a $Fe_5Ni_3Si_2$ type compound, in agreement with Maji et al. [13]. Microscopic analysis showed that the precipitates were distributed within the grains and in the boundaries. More recently, we presented a manufacturing process for shaft and pipe couplings of Fe–Mn–Si–Ni–Cr SMAs [24]. We addressed the formability and weldability of sheets rolled at 800 °C followed by annealing at 650 °C, and investigated how welding affects the mechanical and shape memory properties. X-ray patterns of the base alloy showed the predominant presence of austenite and low-intensity peaks corresponding to a second phase in the welded section. Both phases were clearly recognizable in high-magnification OM images. According to XRD analysis, we believe these peaks to be characteristic of a $Fe_5Ni_3Si_2$ precipitate. However, given the doubts other authors refer in the literature, we left the door open for further analysis.

Due to the wide interest in this issue, this article is devoted to analyse the different phases found in an Fe–15Mn–5Si–9Cr–5Ni SMA. For this purpose we subjected specimens to various thermomechanical treatments, which generated appreciable amounts of a secondary phase, hereinafter referred to as *precipitated particle phase* (PP-phase).

2. Materials and Methods

The Fe–15Mn–5Si–9Cr–5Ni wt.% (nominal composition) alloy was prepared in an induction furnace operating at 10 KHz and 30 KW.