ARTICLE

Stainless Shape Memory Alloys Microstructure Analysis by Optical Microscopy Using Different Etchants

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Abstract

The use of etchant to study the evolution of ε-martensite on the stainless shape memory alloys (SME) it's very important because the correct choice of etching can result not only on the identification of these phases as also in a quantitative analysis. In this work we presented some options of etchants that can be used to study the changes on the microstructure before and after the thermomechanical treatment. Using Fe-Mn-Si-Cr-Ni-Co alloys with different grains size as initial condition submitted at six-thermomechanical treatment, three etchant types are testing for analyse the γ(fcc)↔ε(hcp) martensitic transformation. The preliminary result shows that the color etching method is the more indicate to revel the stress-induced martensite, because such phase is reveled with a color. But, for such condition (chemical composition, volume fraction of phases, grain size) the composition etching will be adapted.

Keywords: Stainless shape memory alloys, ε-martensite, thermomechanical treatment, martensitic transformation.

Introduction

Some Fe-Mn-Si based alloys exhibit shape memory effects (SME) which is originated by the γ(fcc)↔ε(hcp) martensitic transformation. The Fe-Mn-Si-Cr-Ni-Co alloys present a good property of corrosion resistance and the shape memory properties of these alloys appear to depend upon the microstructure of the austenitic state[1-3]. To improve the shape memory effect a special thermomechanical treatment called training is applied. It consists in a deformation (by compression or tensile test) at room temperature to induce the mechanical ε-martensite and then anneal at temperature above A_F to revert ε(hcp)→γ(fcc)[4] to recover the shape. Repeating this cycle several times can improve SME up 50%. To follow the microstructure evolution during thermomechanical cycling is very important because it changes as the cycling proceeds.

In this work, optical microscope observations of γ phase and ε- martensite in the Fe-Mn-Si-Cr-Ni-Co based alloys are described by using different etchants. There are several papers in the literature that present many types of etchants for this kind of alloy [1,2,4-5]. Our main objective was to compare some etchants used for these type of alloy and to select the best one to follow the martensitic transformation associated with the thermomechanical treatment.

Materials and Methods

The chemical compositions (in wt.%) of alloys A and B used in this work are listed in Table 1.

Table 1. Chemical composition shape memory stainless alloys A and B (wt.%).

Elements (wt.%)	Alloy A	Alloy B
C	0.0044	0.09
Si	5.11	5.25
Mn	7.79	8.26
P	0.003	0.02
S	0.007	0.06
Co	11.85	11.84
Cr	13.02	12.81
Ni	5.74	5.81
Mo	0.01	0.01
Cr	0.31	0.16

The ingots were produced by conventional vacuum induction melting (VIM), hot rolling (1473K) and after

treated at 1323K by different times to obtain different grain sizes samples. To induce the γ(fcc)↔ε(hcp) martensitic transformation the samples was submitted to six thermomechanical cycles where such cycle correspond consisted at 4% compression (to induce the ε-martensite), heating to 873K for 30 minutes (to shape recovery) then cool to room temperature. The specimen dimensions were 20 and 9mm in length (for alloys A and B respectively) by 6mm in diameter.

For the analysis of the stress-induced martensite by optical microscopy different etchants were used where the samples were mechanically and electrolytically polished. The Table 2, present the etching using for to study the A and B alloys. Measure X-ray diffraction were use, CuKα radiation, to identify the phases formed after treatments.

Table 2. Different etchings used to prepare the samples of stress-induced martensite.

Etchants	Composition	Polishing
(1)	2mlHCl + 2mlHNO_3+ gliycerine	Mechanical
(2)	10mlH_2O+ 1,2%$K_2S_2O_5$ + 0,8%NH_4HF_2 (color etching method)	Mechanical + Electrolytically (8%$CHLO_4$+92%metanol)
(3)	100ml H_2O+15mlH Cl+15grK_2S_2 O_5 + 5grNH_4HF_2+ 10gr$Na_2S_2O_5$	Mechanical + Electrolytically (8%$CHLO_4$+92%methanol)

Results

The heat treatment resulted in samples with grain size between 35-88 and 75-129μm (alloy A and B respectively). The Table 3 shows the grain size obtained for the different heat treatment times for both alloys presented in Table 1.

Table 3. Austenite grain sizes obtained with heat treatment times.

Heat Treatment Time (minutes)	Grain Size Average	
	ASTM	μm
10	4	75
60	3.5	106
480	3.0	129

The Figures 1 and 2 shows the microstructure obtained for alloy B after six-thermomechanical cycle using etchant (1) before the shape recovery annealing and after shape recovery respectively.

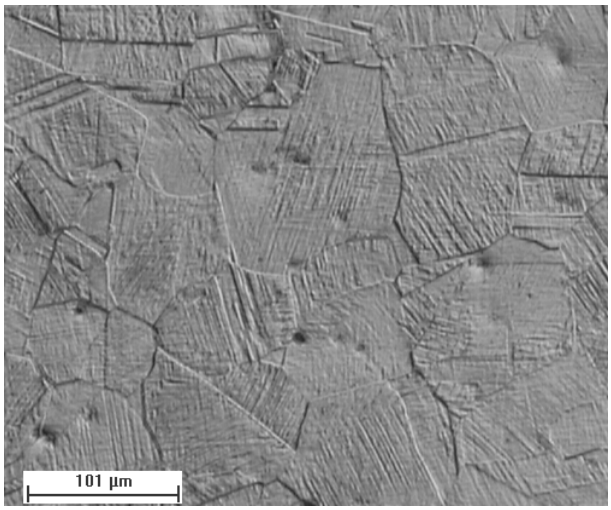

Figure 1. Optical microscopy obtained after last cycle for alloy B. Deformed state, GS = 35μm, 68% ε-martensite. Etching: type (1).

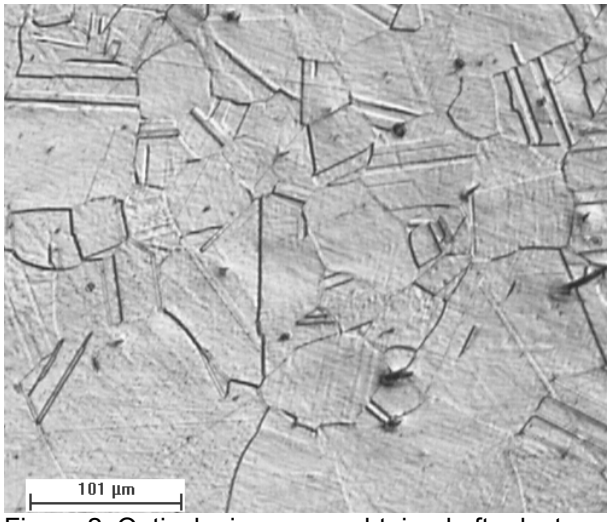

Figure 2. Optical microscopy obtained after last cycle for alloy B. Recovered state, GS = 35µm, 4% ε-martensite. Etching: type (1).

With this etchant it was possible to reveal the austenite grain size and also martensite plates. We can see the stress-induced martensite appearing as thin martensite plates randomly distributed through the material. The (1) type etchant was effective to observe the microstructure change that the material present before and after of the shape recovery annealing. In the Figures 1 and 2 also it was observed the inclusions presence that difficult the analysis by optical microscopy. When the Figures 1 and 2 are confront, we can observe that the recovered state present the microstructure clear more (volume fraction ε-martensite smaller). The (1) etchant type using in the Figures 1 and 2 is very good to analyze the morphology of theses phases and the microstructure obtained after thermomechanical treatment (grain size, inclusions, deformation bands, texture deformation), but it's not efficient to quantify the martensite hexagonal stress-induced and recovered after heating. We can only to affirm what the condition present major volume fraction, Figure 1 (deformed state) or Figure 2 (recovered state). The quantitative analyze was obtained by X-ray diffraction. That's because it was necessary to try other etchants, Figures 3 and 4.

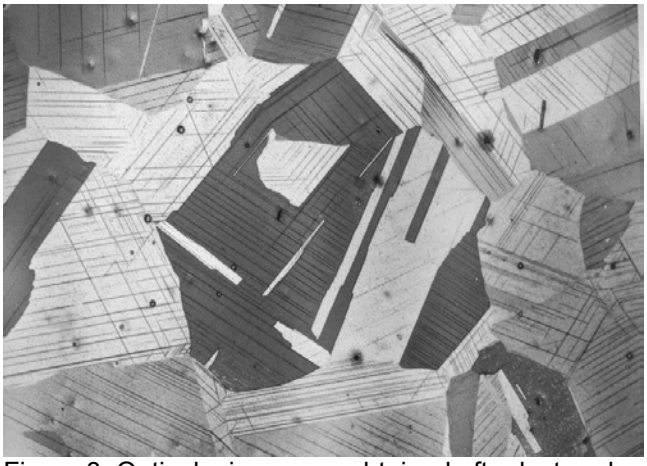
Figure 3. Optical microscopy obtained after last cycle for alloy Deformed state, GS = 35µm, 68% ε-martensite. Etching: type (3).

The etchant (3) was used to observe the martensite plates, Figure 3. With these etchant it was possible to observe different orientations of ε-martensite plates inside the austenite grain size. Whit the etchant (3), the presence of the inclusions it was more observed clearly. Other aspect observed in Figure 3, is that the difference orientation of grain size, characterized by difference of colors.

For the stainless shape memory alloys a color etching, (2) is very used [1-2,4-5], because with these type etchant, beside the austenite phase the ε and α′ martensite can also be clearly distinguished. According to Jang, W.Y. et al. The color change is due to the film thickness and to the crystallographic orientation. The etchant (2) were used on the alloy A, Figure 4, for the deformed state on the last cycle. We can see that the γ matrix appear as brown and ε- martensite appear as light brown plate. It wasn't observed the presence α′-martensite because these phases generally appear for high deformation [2,3,6]. According to authors [1,7] the α′ phase when appear is reveled by etchant (2) as a dark particle inside ε-martensite. The use of the etchant (2) it is very important, because with such phase is reveled with a different color it's possible to make a quantitative analyze and to compare with the X-ray dates.

However, when the etchant (2) is used to quantify the phases on the stainless SME alloys that present different conditions of grain size and different volume fraction of phases it's necessary to adapter the composition etchings for to such condition. It is occur because was observed that the answer time of ε-martensite is smaller when compared with the answer time of austenite using the etchant (2). In our case, samples with major volume fraction of ε-phase (that corresponded at deformed state and small grain size) have the structure reveled before when we compared with samples of smaller volume fraction of martensite. Other factor that influence negatively on the analysis by optical microscope it's the

presence of inclusions that answer before etchant (2). This effect it was more pronounced for the cases with large grain size and small volume fraction ε-martensite where the etchant time is major.

The color etching method also is very important to verify the presence of the α′-martensite, considered as detrimental to the shape recovery process [1,3,7,8], because only using X-ray diffraction this phase it is not identify when the volume fraction is very lower.

Using all the etchant types presented in this work it was observed that the morphology of stress-induced ε-martensite (plates shape inside austenite grain size), Figures 1-4, also were observed for the others conditions of grains size, Table 3. We can observe that samples with small grain size presented a major volume fraction ε-martensite on the deformed state. This affirmation was confirmed by X-ray diffraction measurement. When the samples were recovered, the volume fraction ε-phase decreased, Figure 2. Similar result were observed for the others condition of grain size in both alloys.

News adaptations of color etching method for all conditions presented in Table 3 are being studied. In other work, some sample of alloys B were submitted at high deformations to induced the α′-martensite and chemical polishing (95%CH_3OH + 5%$HclO_4$) also are testing for to remove the ε-martensite that induced during the preparation of the samples.

Conclusions

We can conclude that for theses special materials, the type of etchant is very important to analyse the evolution ε-martensite before and after the thermomechanical treatment.

The best etchant for this case is a color etching method, etchant (2) in Table 2, used to reveal the ε and α′ martensite (for high deformations). The microstructural observations depend upon the chemical composition and also the thermomechanical treatment. The etchant (2) is excellent to distinguish the γ phase from ε phase and α′ (when this phase is present). It's very important for an analysis quantitative.

The etchant (3) revealed the martensite plate's orientations and the austenite grain size.

Enchant (1) is adequate to reveal the grains boundary, consequently the grain size. The ε-martensite can also be observed.

Acknowledgments

The authors would like to thank CNPq, FAPESP, AEB and Vilares Metals SA for supporting the shape memory development Project.

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