Production and Characterization of Stainless Steel Based Fe-Cr-Ni-Mn-Si(-Co) Shape Memory Alloys

J. Otubo, P.R. Mei and S. Koshimizu*

FEM/DEMA, State University of Campinas, CP 6122, CEP 13081-970, Campinas, SP, Brazil
* CNEN/IPEN, CP 11049, CEP 05422-970, Sao Paulo, SP, Brazil

Abstract. It is well known that the Fe based alloys can exhibit shape memory effect due to the γ to ε martensitic transformation. The effect may not be as striking as observed in the NiTi alloy but it might become attractive from the practical point of view. In this work, two compositions of Fe-Cr-Ni-Mn-Si(-Co) stainless steel based shape memory alloy, prepared by the VIM technique, will be presented. The results are good with shape recovery of 95% for a pre-strain of 4% after some training cycles. In terms of workability the alloys produced are worse than the usual AISI304. However, adjusting the thermo-mechanical processing, it is perfectly possible to produce wire as thin as 1,20mm in dia. or down.

1. INTRODUCTION

As pointed out by Miyazaki and Otsuka [1] in a review article, the most famous shape memory alloy is the NiTi developed in the early sixties with shape recovery up to 7%. More recently iron based shape memory alloys have been developed such as Fe-Pt, Fe-Pd, Fe-Co-Ni-Ti, Fe-Mn-Si, etc.[1,2] . Among the iron based alloys, the most studied is Fe-Mn-Si [3-12] which present non-thermoelastic martensitic transformation, γ(fcc) to ε(hcp). This martensite could also be induced mechanically and its reversion to austenite by heating promotes shape recovery. According to Murakami et al., [12] for this alloy, the best composition in terms of shape memory, is Mn from 28% to 33% and Si from 4% to 6%. Unfortunately, the shape recovery for this alloy is not so high with its maximum around 2%, which is not enough for most practical applications. Another problem is its poor corrosion resistance.

To improve the corrosion resistance and also the shape memory effect, a great number of research in stainless steel based shape memory alloys have been carried out [13-17].

For this work, two compositions, aiming mainly at workability test, by rolling and drawing, and also to check the influence of composition, microstructure and training cycles on shape recovery were produced.

2. EXPERIMENTAL PROCEDURES

2.1 Ingot preparation: melting and forging

The ingots were melted in a Vacuum Induction Melting (VIM) furnace. Two alloys were produced, their composition being: 1) Fe-9,08Cr-4,77Ni-13,61Mn-5,27Si-0,037C named CrNi and Fe-13,02Cr-5,74Ni-7,81Mn-5,16Si-11,85Co-0,044C named CrNiCo (the percentage are in weight %).The ingots final dimensions were $70 \times 70 mm^2$ on the top and $60 \times 60 mm^2$ at the bottom.

The ingots were heated to 1453K/7200s and hot forged to $40 \times 40 mm^2$ bars. These bars were longitudinally sectioned into smaller $20 \times 20 mm^2$ bars. Part of these bars were machined for tensile test samples and part left for workability testing.

2.2 Workability testing

The workability testing was done by hot rolling and cold drawing. For hot rolling the bars were heated to 1373K/3600s and hot rolled to 5,60x5,15 mm^2 (CrNi) and 6,75x6,75mm^2 (CrNiCo) wire rods with rounded corners.

After rolling, the wire rods were solution treated at 1323K/2400s and then water quenched.

Initially, these wire rods were calibrated by drawing to 5,0 mm in dia. (CrNi) and 5,6 mm in dia. (CrNiCo) using a bull block drawing machine, secondly a new heat treatment was carried out at 1323K/2400s, thirdly they were then pickled in a solution of HNO_3 + HF + water and then finally rinsed with jet of water.

After pickling the wire rods were drawn down to 1,20mm in dia. using the same bull block with dry soap as a lubricant. During drawing operation the wires were annealed at 1323K in a continuous annealing furnace using 60%N_2 + 40%H_2 as a protective atmosphere.

2.3 Tensile testing

The samples for tensile testing were machined from solution treated (1323K/3600s) 20x20mm^2 bars. The dimensions were 6,20mm in dia. by 25 mm in gauge length. The tensile tests were carried out on a MTS 810 tensile test machine coupled with an electric furnace. The strain rate used was $1,4x10^{-4}s^{-1}$. The length variation and the temperature control during the tensile recovery annealing cycle were measured by a strain gauge and thermocouple respectively attached to the sample.

The cycle used to check the shape memory effect was: tensile deformation up to pre-strain of 4% at room temperature, unloading to zero stress, heating to 723 K or 873 K in air, holding for 600s at the top temperature and then cooling down to room temperature. The heating and cooling rate were not controlled. The above cycle was repeated up to 7 times in some samples. From the above test the following parameters could be recorded: tensile stress at 4% strain; yield stress at 0,2% strain; elastic shape recovery (shape recovery after unloading) termed R_E; shape recovery due to heating and cooling termed R_{SM} and finally, total shape recovery R_T (=R_E + R_{SM}). Usually the data shown in literature are R_T. Yang [16] called the R_E a superelastic recovery.

2.4 Dilation measurements

The transition temperatures, M_s (martensitic starting temperature), A_s (reverse martensitic transformation temperature) and A_f (end of austenitic transformation temperature) measurement were carried out by dilation testing. The heating and cooling rate was $16,6x10^{-2}$ K s^{-1}.

3. RESULTS AND DISCUSSION

3.1 Workability

During rolling no other major problem could be seen provided that the rolling temperature was kept above 1173K.

Now, during cold drawing, the maximum total area reduction possible was 50%. Higher area reduction could cause wire breakage. Therefore the annealing had to be done every 45 to 50% of area reduction. Pointing the wire for drawing, using rolling pointer, was another difficulty. The wire nose used to work harden very fast and started to break. The problem was solved by welding ductile stainless steel wire such as AISI 304 and using it as a nose. In comparison to AISI 304 stainless steel, these two alloys presented worse workability.

3.2 Tensile test and shape recovery

Figure 1 presents the results of shape recovery for the CrNi alloy, cycled between tensile deformation at room temperature and heating to 723K, AM1.5 sample or, 873K, AM1.6 sample. As presented before, three parameters were analyzed: R_E (elastic recovery upon unloading), R_{SM} (shape memory recovery) and R_T (total shape recovery).

In terms of elastic shape recovery, the AM1.5 sample heated to 723K/600s presented increasing values from 12,4% in the first cycle to 16,2% in the fifth cycle while the AM1.6 sample heated to 873K/600s showed constant values around 13.9% elastic shape recovery.

Related to memory shape recovery upon heating the difference between these two samples were significant. The AM1.6 sample heat treated at higher temperature showed better performance with 64.4% recovery in the first cycle and ending up with 80% in the sixth cycle. For the AM1.5 sample the shape recoveries were 58,1% and 70,4% in the first and the fifth cycle respectively. Both samples stabilized in the third cycle.

Taking into account the elastic shape recovery and the memory shape recovery, that is, R_T, the values were 78% and 70% at the first cycle and 95% and 86.6% after the third cycle for AM1.6 and AM1.5 respectively. These results show the better performance for the sample annealed at 873K. 95% shape recovery of 4% pre-strain means 3,8% shape recovery in absolute values comparable to the best results published in literature [15, 16, 19, 20].

The influence of the heat treatment temperature could also be noted on tensile stress as a function of the number of cycles as can be seen in Figure 2. For the AM1.5 sample the 0,2% yield stress decreased and the stress at 4% strain increased as the number of cycles increased, while for the AM1.6 sample, the values of 0,2% yield stress and the stress at 4% strain were constant along the number of cycles. The above results show that the heating to 723K and the keeping of the samples per 600s was not enough to completely eliminate the mechanically induced martensite for the CrNi alloy.

Figure 3 compares the results of shape recovery as a function of number of cycles for AM1.6 sample (CrNi) and AM2.4 sample (CrNiCo) for the same high temperature heat treatment (873K), showing the better performance of the former. In terms of total shape recovery, the AM2.4 sample (CrNiCo) showed small, but increasing values, even at the seventh cycle with almost 90% shape recovery while the AM1.6 sample (CrNi) stabilized at the third cycle with 95% shape recovery as stated above.

Figure 4 presents comparative results of tensile tests, for these two alloys, also for high temperature heat treatment (873K). The tensile stress at 4% strain of the AM2.4 sample kept growing as the number of cycles increased while the 0,2% yield stress kept almost constant for all the cycles with its values slightly higher than that of AM1.6 sample. These results could be indicating that the heat treatment temperature for the CrNiCo alloy should be higher than 873 K in order to get a high reverse transformation of the stress induced martensite or a better shape recovery.

In comparing these two alloys, some other differences could be seen.

As presented in references [17,18], for the same heat treatment, the CrNiCo alloy always showed a larger grain size. For example, the grain size of the 5,0 mm in dia. wire CrNi alloy heat treated at 1323K/2400s was around 65μm, while for the CrNiCo alloy under the same conditions, was 180μm. Tan Shiming et al., [21] working with Fe-Mn-Si polycrystalline alloy, showed that the larger the grain size the lower the shape memory recovery, ranging from 75% shape recovery at 10μm grain size to 20% at 60μm. They attributed this shape memory decrease to the increase of perfect dislocation due to grain size increase.

Another visible difference was in relation to the volume fraction of thermally induced martensite. When the two alloys were solution treated and then quenched in liquid nitrogen, the thermally induced martensite were around 50% and 25% for CrNi and CrNiCo alloys respectively. Otsuka et al. [14] produced a series of Fe-Mn-Si-Cr-Ni alloys and they demonstrated that the higher the volume fraction of thermally induced martensite the better the shape memory recovery.

For the other hand, the amount of thermally induced martensite, at deformation temperature, could have diverse effects on shape recovery. As shown by Federzoni [22], the shape recovery increased up to a maximum of 10% of the thermally induced martensite. Above this value, the shape recovery started to
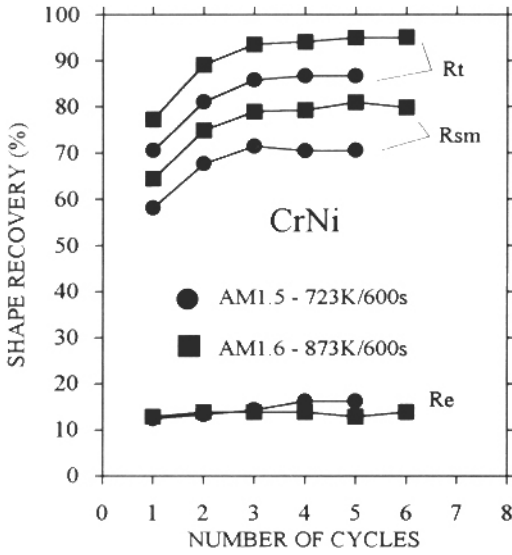
Figure 1. Shape recovery as a function of training cycle for CrNi alloy annealed at 723K and 873K respectively.
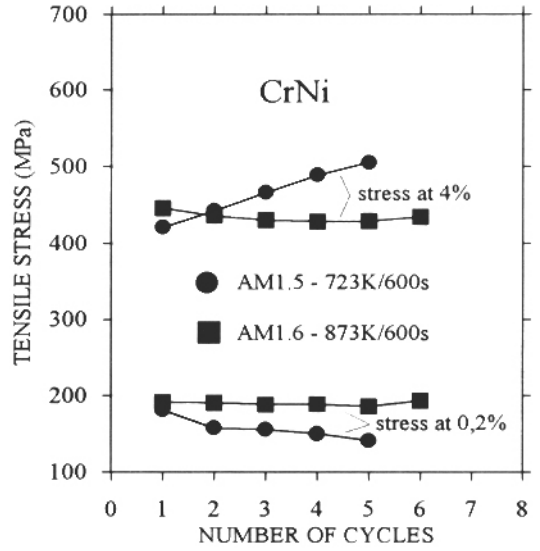

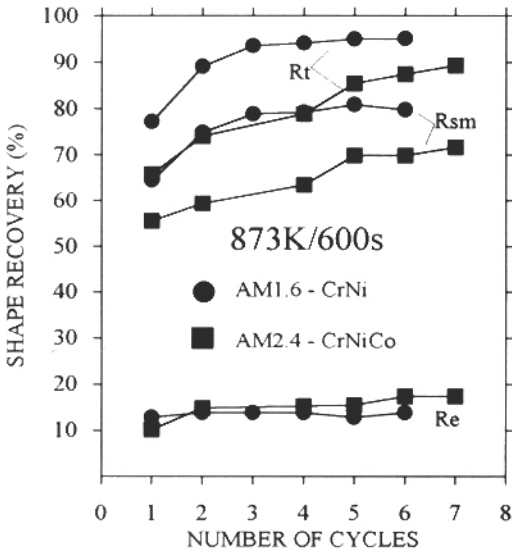**Figure 2.** Tensile stress at 0,2% strain and 4% strain for CrNi alloy annealed at 723K and 873K respectively.

Figure 3. Shape recovery as a function of training cycle for CrNi alloy and CrNiCo alloy annealed at 873K.
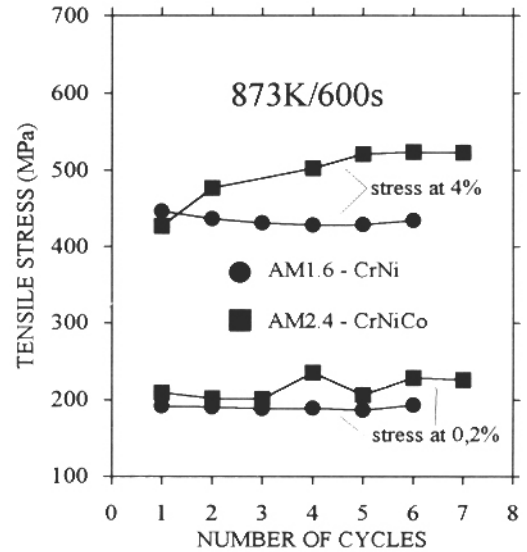

Figure 4. Tensile stress at 0,2% strain and 4% strain as a function of training cycle for CrNi alloy and for CrNiCo alloy annealed at 873K.

decrease very slowly and at 60% of the thermally induced martensite, the shape recovery was the same as that of 0% of thermally induced martensite.

The reason for better shape recovery of CrNi alloy compared to CrNiCo alloy could be due to smaller grain size and capacity of inducing larger amount of thermal martensite of the former.

3.3 Transformation temperatures

Table 1 presents the results of the transition temperatures M_s, A_s and A_f obtained from dilation measurements. Three different independent thermo-mechanical treatments were used for each alloy composition: 1) Solution treated at 1323K/2400s and then water quenched wire rod presenting a small amount of thermal martensite; 2) Solution treated at 1323K/1800s and then quenched in liquid nitrogen 3,60 mm in dia. drawn wire presenting a large amount of thermal martensite and 3) 4% pre-strained tensile tested sample without recovery heating with stress induced martensite.

The martensitic starting temperatures, M_s, were 308K and 312K respectively for CrNi and CrNiCo.

For both alloys, the reverse transformation temperature, A_s, was not affected either by the increase of the volume fraction of the thermally induced martensite, (condition 2), or by the increase of stress induced martensite, (condition 3), with its value around the 368K. For the A_f the difference in volume fraction of thermally induced martensite had also no effect on the CrNi alloy (473K), and only a small effect on the CrNiCo alloy (468 to 478K). However it presented a great effect when the increase in martensite volume fraction was mechanically induced. The A_f found were 593K and 623K for the CrNi and CrNiCo alloys respectively. That is, the A_f increase was more pronounced in CrNiCo alloy.

Federzoni et al. [23] and Ohtsuka et al. [24] obtained the similar results of A_f temperature increase when the martensite was stress induced. The necessity of higher reversion temperatures were attributed to the introduction of defects during deformation which makes the reversion of some ε martensite plates difficult

The above result of higher A_f, that is, higher stability of stress induced martensite for CrNiCo alloy, could be indicating the necessity of higher temperature annealing during the tensile-heating cycle for shape recovery.

Table 1. Transformation parameters as a function of thermo-mechanical processing.

ALLOY	CONDITIONS	$M_s(K)$	$A_s(K)$	$A_f(K)$
CrNi	1) wire rod/1323K/2400s/water	308	368	473
	2) 3,6mm wire/1323K/1800s/water + liquid nitrogen	-	368	473
	3) 4% pre-strain	-	368	593
CrNiCo	1) wire rod/ 1323K/2400s/water	312	368	468
	2) 3,6mm wire/1323K/water + liquid nitrogen	-	368	478
	3) 4% pre-strain	-	368	623

4. CONCLUSIONS

For these two alloys no other major problem could be seen during hot rolling as long as the rolling temperature was kept above 1173K. The maximum total area reduction for cold drawing was 50%. Higher area reduction caused wire breakage.

In terms of shape recovery, annealing at 873K showed better results than annealing at 723K for both CrNi and CrNiCo alloys with 95% and 90% shape recovery respectively after some training cycle for a pre-strain of 4% comparable to the best results known up to now. While the shape recovery for the CrNi alloy stabilized at the third cycle, the CrNiCo alloy showed an increasing tendency of shape recovery even at the seventh cycle.

For both alloys, the tensile stress at 4% strain increased and, the yield stress at 0,2% strain decreased, as the number of cycles increased, when the annealing temperature was 723K. For 873K only the CrNiCo alloy showed the same behavior while the CrNi alloy presented constant stress values.

For the same thermo-mechanical treatment, the CrNi alloy presented small grain size when compared to the CrNiCo alloy and this could be one of the reasons for the better performance of the former.

The volume fraction of thermally induced martensite of the CrNi alloy was twice that of the CrNiCo alloy. Thermally induced martensite did not affect A_s or A_f but the stress induced martensite did affect the A_f, pushing it to a higher temperature being more pronounced in the CrNiCo alloy.

Acknowledgments

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