FORMATION AND REVERSION OF STRAIN INDUCED MARTENSITE ON Fe-Cr-Ni ALLOYS

FORMAÇÃO E REVERSÃO DA MARTENSITA EM LIGAS FERRO-CROMO-NÍQUEL

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ABSTRACT

Austenitic stainless steels representing a significant portion of the alloys used in the aeronautical, chemical, shipbuilding, food processing and biomechanical industries. They combine good mechanical properties with high corrosion resistance. When subjected to cold deformation, these steels exhibit a metastable phase called strain induced martensite (ferromagnetic), whose formation increases the mechanical strength and formability, allowing their wide range of applications. Heated from room temperature, the strain induced martensite transforms to austenite (non-magnetic). Is easy to find information in the literature about the strain induced martensite for 18Cr/8Ni austenitic steels, but there is no data for high nickel alloys like A286 (26Ni, 15Cr), Incoloy 800 (30-40 Ni, 21Cr) and Inconel (50Ni, 19Cr). Therefore, this work was done to verify the formation of strain induced martensite after cold working in Fe-18Cr base alloys with addition up to 60 %Ni. The reversion of this phase to austenite after annealing up to 600 ºC was also studied. Optical microscopy, magnetic characterization tests and x-ray diffraction were used to analyze the transformations.

Keywords: Austenitic stainless steel, nickel-based alloys, strain induced martensite, work hardening.

RESUMO

Os aços inoxidáveis austeníticos são materiais de alto valor agregado, representando uma parcela importante das ligas usadas, principalmente, nas indústrias aeronáutica, química, naval, alimentícia e biomecânica. Apresentam boas propriedades mecânicas aliadas à elevada resistência à corrosão. Quando submetido à deformação a frio, estes aços exibem uma fase metaestável denominada martensita induzida por deformação (ferromagnética), cuja formação aumenta a resistência mecânica e conformabilidade, permitindo sua ampla gama de aplicações. Aquecida acima da temperatura ambiente, a martensita induzida por deformação se transforma em austenita. Existem dados na literatura sobre a formação da martensita induzida por deformação em aços austeníticos 18Cr/8Ni, mas não há esta informação em ligas de alto teor de níquel como A286 (26Ni, 15Cr), Incoloy 800 (30-40 Ni, 21Cr) e Inconel (50Ni, 19Cr). Portanto, *este trabalho foi realizado para verificar a formação de martensita induzida por deformação, após o trabalho a frio de ligas Fe-18Cr base com adição de até 60% Ni. A reversão desta fase para austenita após recozimento até 600 ºC também foi estudada. Microscopia óptica, ensaios de caracterização magnética e difração de raios-X foram usados para analisar as transformações.*

***Palavras chave**: Aços inoxidáveis austeníticos, ligas a base de níquel, martensita induzida por deformação, endurecimento por trabalho a frio.*

1. INTRODUCTION

Austenitic stainless steels present austenite (γ) a FCC and paramagnetic phase in the annealed state. Austenitic steels are susceptible to martensitic transformation by cold working, high rate sputtering (thin films fabrication), subzero deformation etc **[Childress, 1998].** Stable steels, as AISI 310, may form ε martensite (HCP, paramagnetic) induced by plastic deformation. Metastable steels, as AISI 301, 302, 304, 304L, 316 and 316L may form ε martensite and a BCC, ferromagnetic martensite called α or α′ **[Tavares, 2000].** Manganon **[Manganon, 1970]** analyzed the martensite transformations in AISI 304 and established that the sequence of transformation is γ → ε → α′. He observed that the formation of α′ martensite was induced only by plastic deformation and subsequent to formation of ε-martensite. Nucleation of α′ occurred heterogeneously at intersections of ε bands or where ε bands touch twin or grain boundaries (which represent unilaterally compressed regions).

The HCP ε-phase is paramagnetic in contrast to the bcc α′ martensite, which is strongly ferromagnetic, and the only magnetic phase in the austenitic stainless steels. Because of the α′ phase, the cold worked austenitic stainless steels have detectable magnetic properties that can be eliminated by annealing. The α′ is often called strain induced martensite. The reverse transformation of ε-martensite to austenite occurs in the temperature range of 150–400 °C and the α′ → γ reverse transformation takes place at temperatures of 400–800 °C **[Mészáros, 2005].** Tavares **[Tavares, 2000]** found the range 430-710 °C for α′ → γ reverse transformation in AISI 304 deformed by cold rolling with thickness reduction of 40 %.

Talyan **[Talyan, 1998]** studying AISI 304L in uniaxial tensile test at room temperature observed that:

- The lowest strain necessary to start the α′ martensite formation increases when the strain rate is raised. For example, at strain rate of 10^{-3} s^{-1} the strain necessary is 0.2 and at strain rate of 10^{-1} s^{-1} the strain necessary is 0.4.
- After starting the α′ martensite formation, its volume fraction increases rapidly when the strain is raised. For example, at strain rate of 10^{-3} s^{-1}, the volume fraction of α′ martensite is 0% at strain = 0.2; 20% at strain = 0.4 and 50% at strain = 0.6.
- For tensile samples tested in the air at strain rate of 10^{-3} s^{-1} there was no change in the temperature of the sample, but at strain rate of 10^{-2} s^{-1} the temperature of sample raised up to 20 °C at highest strain applied (0.6) and at 10^{-1} s^{-1} the temperature raised up 30 °C at highest strain applied (0.5).
- When the tensile samples were tested in stirred water kept at 21 ºC at strain rate of 10^{-1} s^{-1} there was more production of martensite and an increase in the total elongation. He

concluded that the heating induced by deformation reduces the martensite formation and formability.

- The best results in terms of higher tensile and ductility (elongation) where found at slower strain rate (10^{-3} s^{-1}) where the martensite volume fraction was higher either.

Comparing AISI 301 with 304L **[Talyan, 1998]** also observed that:

- α′ martensite volume fraction is very sensitive to chemical composition. These steels have similar composition, with small difference in nickel (7.5 % in 301 and 8.7% in 304L) and carbon (0.10 % in 301 and 0.02 % in 304L). Deformed with strain = 0.4 at strain rate of 10^{-3} s^{-1}, the volume fraction of α′ martensite was 20% in 304L and 60% in 301 steel.
- Both steels presented at strain rate of 10^{-3} s^{-1}, approximately 300 MPa for yield strength, but AISI 301 reached 1.000 MPa for tensile strength, much higher than the 670 MPa presented by AISI 304L. The reason is that in the elastic region where yield strength was measured, there was no α′ martensite formed and the steels were austenitic. For the other hand, the tensile strength was obtained where the steels presented the maximum value for volume fraction of α′martensite: 30 % for 304L and 75% for 301 steel.

There is information on the literature about strain induced martensite in 18Cr/8Ni austenitic steels, but there is no information in high nickel content alloys like A286 (26Ni, 15Cr), Incoloy 800 (30-40 Ni, 21Cr) and Inconel (50Ni, 19Cr) **[Silva, 2010].** Therefore, this work was done to verify the formation of strain induced martensite after cold working in Fe-18Cr base alloys with addition up to 60 %Ni. The reversion of this phase to austenite after heating up to 600 ºC was also studied.

2. EXPERIMENTAL PROCEDURES

Seven Fe-18Cr alloys with nickel contents ranging from zero to 60 mass % (Table 1) were used. Initially the 0Ni alloy was annealed at 790 °C for 1 hour and quickly cooled with blown air. The other alloys (10-60% Ni) were annealed at 1050 ºC for 1 hour and cooled in water.

Table 1: Chemical composition (mass %).

Alloy	**C**	**Si**	**Mn**	**Cr**	**Ni**	**P**	**S**	**N**
0Ni	0.012	0.24	0.43	18.1	0	0.10	0.010	0.0036
10Ni	0.014	0.21	0.39	18.0	10.2	0.09	0.011	0.0033
20Ni	0.014	0.21	0.40	18.0	20.1	0.09	0.011	0.0031
30Ni	0.013	0.21	0.44	18.1	30.4	0.07	0.007	0.0033
40Ni	0.019	0.21	0.45	17.9	40.2	0.05	0.007	0.0025
50Ni	0.013	0.17	0.44	18.1	50.1	0.03	0.006	0.0024
60Ni	0.010	0.21	0.45	17.8	60.2	0.02	0.006	0.0017

The deformation was applied by cold rolling in samples with 20 mm thick. In each pass, the thickness of samples was reduced in 2 mm, to obtain a final thickness of 4 mm. The total reduction in thickness was (20-4) / 20 = 0.8 or 80%. After each pass, the sample was immersed in water to dissipate heat generated by rolling and avoid reversion of martensite formed.

The magnetic moment was measured by VSM (Vibrating Sample Magnetometer) using a GMW Magnetic System in the Laboratory for Magnetic and Thermal Properties of DFMC-IFGW-UNICAMP. The magnetic moment of the samples was measured after deformation. Therefore, the samples were annealed during 30 minutes at 200 ºC, cooled in the air and the magnetic moment was measured again. After this, the samples were submitted to another annealing during 30 minutes at 400 ºC, cooled in the air and the magnetic moment was measured again. This sequence continues to 600 ºC annealing.

Structural changes were analyzed by X-ray diffraction in Rigaku DMAX2200 equipment.

The microstructural analysis of alloys was studied with optical microscope Carl Zeiss Neophot 32 with image analyzer software Quantimet 500 MC Leica Imaging Systems. The etchings were made with the reagents:

- Vilella (1 g picric acid, 5 ml HCl and 100 ml ethanol). Used in the 0Ni alloy.
- Electrolytic: solution of oxalic acid (10%) in water, Used in other alloys (10-60% Ni).

3. RESULTS AND DISCUSSION

Microstructure

In annealed state, the 0Ni alloy showed a fully ferritic structure (Figure 1). All other alloys (Figure 2) showed austenitic structure. As the nickel content increased, there was a gradual rounding of grains and decreased the presence of twins: the10Ni alloy showed polygonal grains with many twins and 60Ni showed rounded grains, with no significant presence of twins. The change in the shape of the grains and the difference in the presence of crystal twinning are associated with the stacking fault energy, which increases when the nickel content rises.

The cold deformation caused the elongation of grains in all alloys in the direction of rolling, with shear-bands and slip-lines, less pronounced with the increasing of the nickel content.

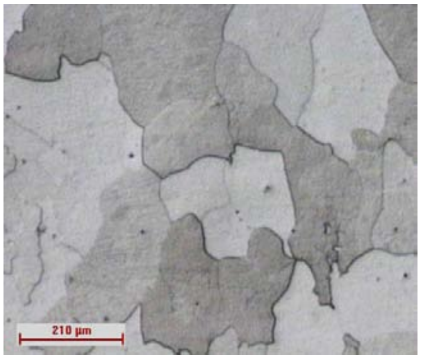
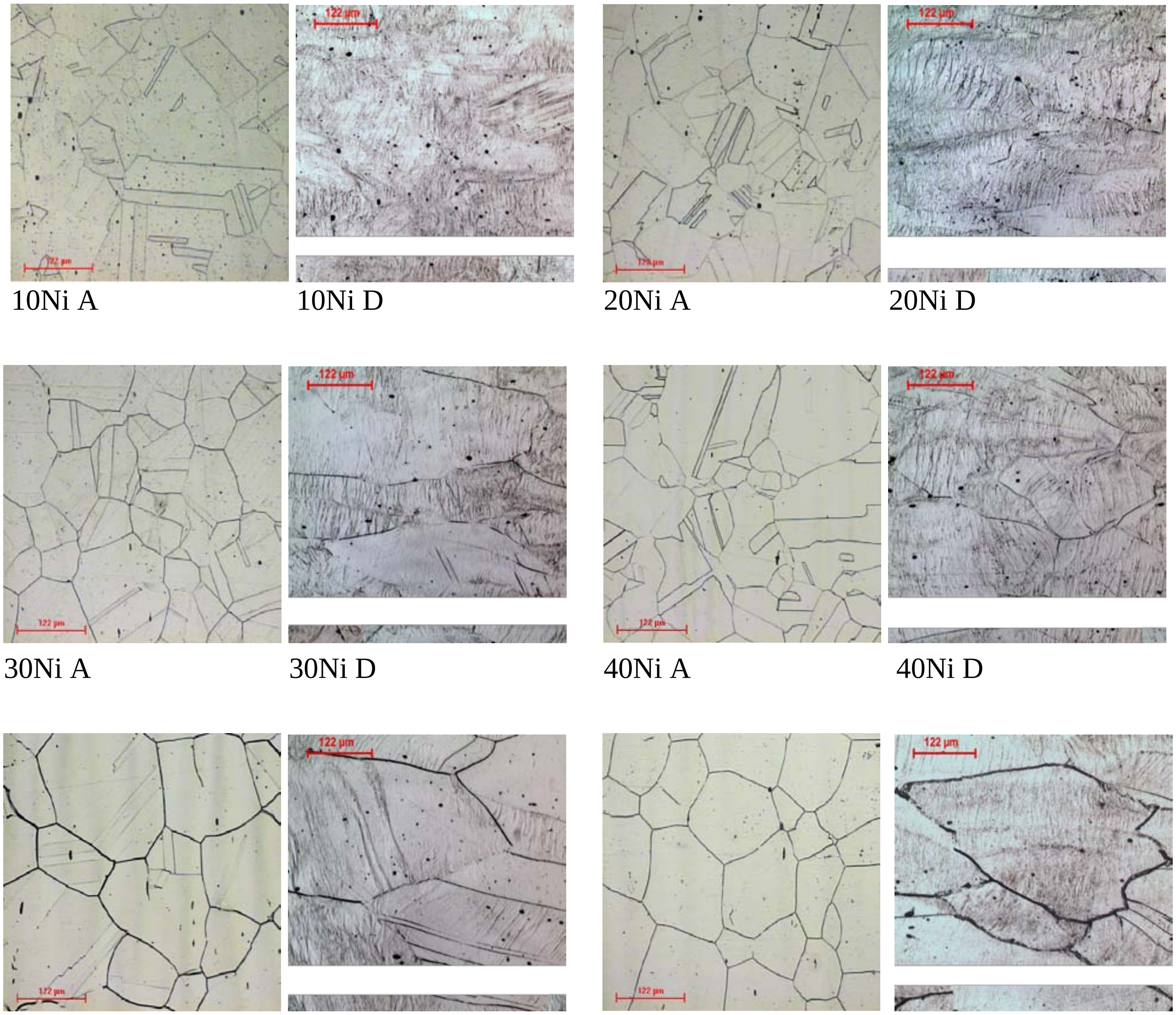


Figure 1 – Alloy 0Ni in annealed state. Etching: Vilella.



10Ni A 10Ni D 20Ni A 20Ni D

30Ni A 30Ni D 40Ni A 40Ni D

50Ni A 50Ni D 60Ni A 60Ni D

Figure 2 – Alloys with nickel addition on annealed (A) and deformed (D) state.
Etching: Electrolytic /Oxalic acid at 10% in volume.

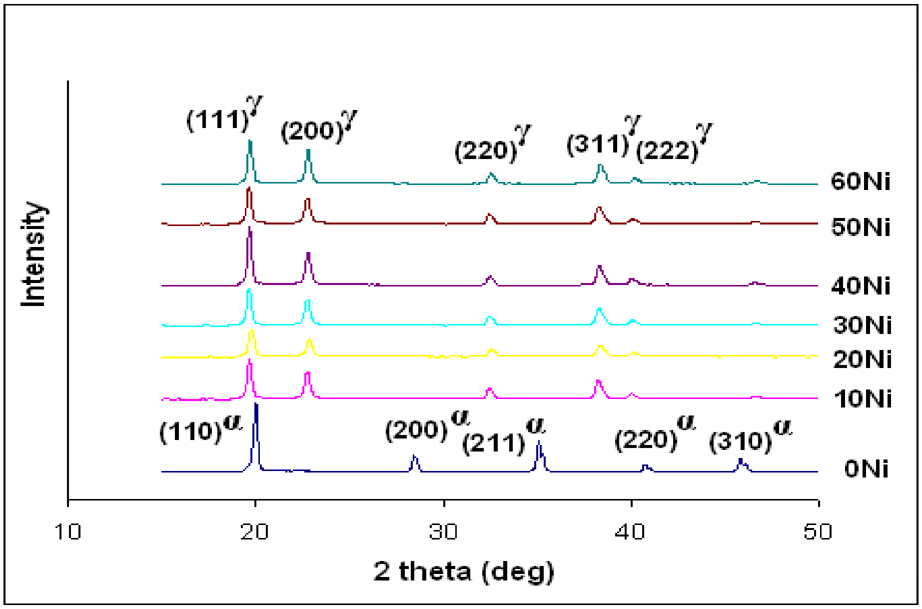
X-ray diffraction

In the annealed state, the 0Ni alloy presented only BCC phase (ferrite). The other alloys (10-60Ni) presented only FCC phase (austenite), regardless the nickel content (Figure 3).

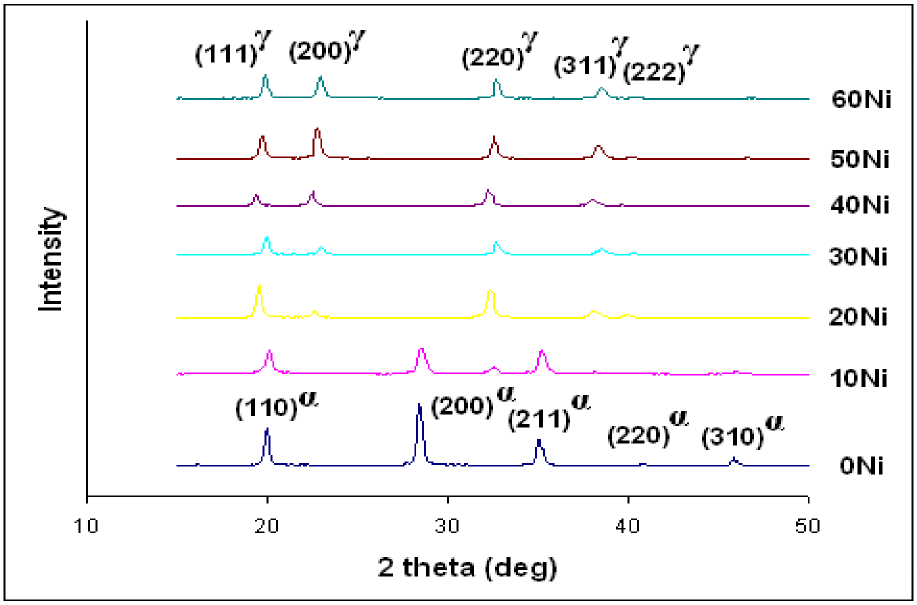
In the deformed state, except for 10Ni alloy, the other alloys showed the same structures as in the annealed state: the 0Ni alloy presented ferrite and the alloys 20Ni to 60Ni presented austenite. However, there was a change in intensity of some peaks, especially those on the planes (200) γ and (311) γ, whose intensities decreased gradually with decreasing nickel content. For 10Ni alloy, is was observed the following features:

- Disappearance of the peaks (200) γ and (311) γ;

- A significant decrease of peak intensity of the plane (220) γ compared to other alloys;
- Emergence of other peaks in the same positions of peaks (110)α, (200)α and (211)α, suggesting the formation of a phase BCC, possibly strain induced martensite type.



a) Annealed state.



b) Deformed state.

Figure 3 - X-ray diffraction of the alloys on annealed (a) and deformed (b) state.

Magnetic moment

The alloy 0Ni showed the largest magnetic moment among all the alloys (Figure 4), since its structure is the highly magnetic ferrite.

The 10Ni alloy showed high magnetization, indicating the presence of strain induced martensite, since this phase is the only ferromagnetic present in austenitic steels. For 10Ni alloy, the reversion of the martensitic phase (BCC) into austenite (FCC) did not occur until 200 °C, with high reduction of the magnetic moment after heating to 400 °C. After heating at 600 °C the residual magnetism of the 10Ni alloy was the same as the others fully austenitic alloys, indicating that there had been complete reversion of martensite. This result is in agreement with the obtained by Tavares **[Tavares, 2000]** that found the range 430-710 °C for $\alpha' \rightarrow \gamma$ reverse transformation in AISI 304 (18Cr- 8Ni) deformed by cold rolling with 40 % of thickness reduction.

Not all other Ni alloys (20 to 60 % Ni) showed increasing in the magnetic moment with deformation, indicating no significant presence of strain induced martensite.

The 50Ni alloy showed a slight higher magnetic moment among Ni fully austenitic alloys (20 to 60 % Ni). This alloy had silicon content slight lower them the other alloys (0.17 and 0.21%, respectively) and this could be the reason for this difference in magnetic behavior **[Hou, 1996].**

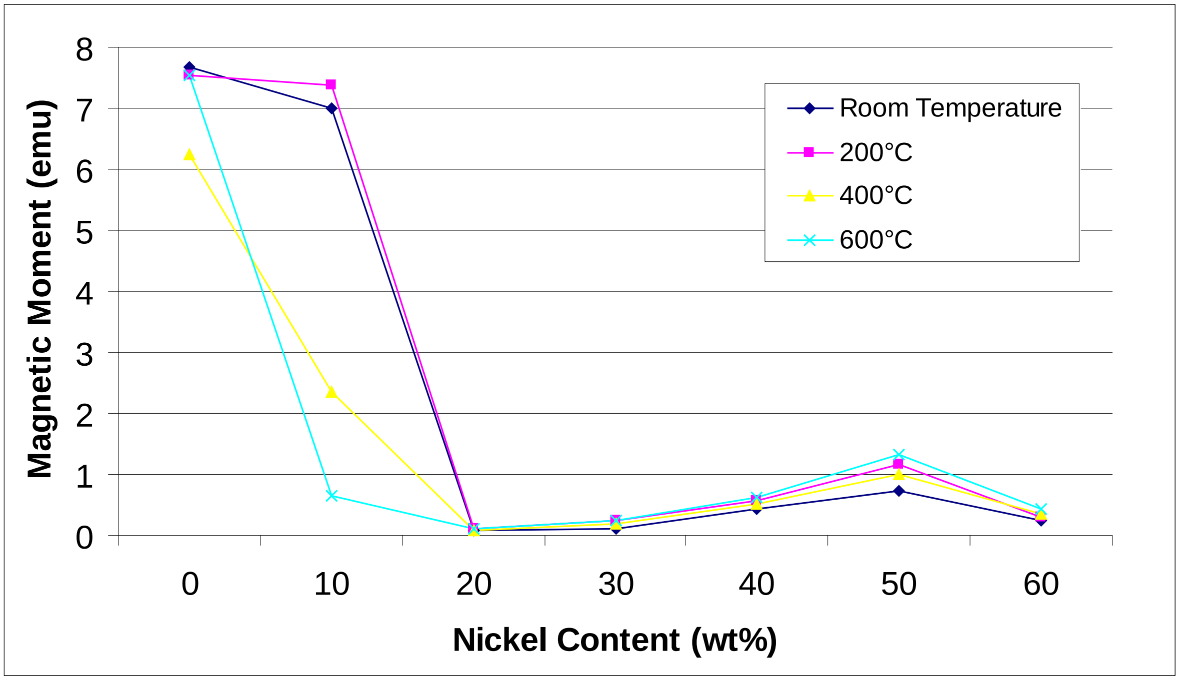


Figure 4 – Magnetic moment as function of Ni content and annealing temperature

after cold work.

4. CONCLUSIONS

The application of strain (80% reduction in thickness) in seven alloys with 18% of chromium and nickel contents ranging from zero to 60% resulted in the formation of ferromagnetic strain induced martensite (BCC) only on the 10% Ni alloy. For this alloy the reversion of strain induced martensite into austenite did not occur after annealing at 200 °C. After annealing at 400 °C the alloy showed a high reduction of the magnetic moment. After annealing at 600 °C the residual magnetism of the alloy was the same as the other fully austenitic alloys, indicating that there had been complete reversion of martensite formed by deformation.

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