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PHASE TRANSFORMATION INFLUENCE ON CORROSION RESISTANCE OF AISI 316 AUSTENITIC STAINLESS STEEL

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În această lucrare se prezintă influenţa stării de tensiuni asupra transformării martensitice indusă, în cazul oţelului inoxidabil AISI 316, de deformarea plastică la rece. Această transformare este legată de instabilitatea austenitei la temperaturi apropiate sau scăzute faţă de temperatura camerei.

Pentru a stabili o legatură între starea normală de tensiuni, numită şi stare hidrostatică de tensiuni, şi transformarea martenitică rezultatele experimentale au fost urmate de simulare numerică.

This paper focus on the influence of stress states on the deformation-induced α' martensitic transformation in AISI Type 316 austenitic stainless steel. The induced martensite is related to the austenite (γ) instability at temperatures close or below room temperature. The susceptibility of structural transformation is a function of the composition of the deformed steel.

In order to establish the links between mean normal stress, named tensile hydrostatic stress, and martensitic transformation, experimental tests were followed by numerical simulation.

Keywords: cold plastic deformation, austenitic stainless steel, martensitic transformation, martensite, normal stress, numerical simulation

1. Introduction

The material flow during plastic deformation process considerably affects the product quality – its structure and properties, the process efficiency and the deformation force amplitude. The changes of basic properties (resistance and plasticity) of the deformed material present importance to ensure the final mechanical characteristics of the parts for an appropriate behavior in working condition [1-3].

Austenitic stainless steels are extensively used in different industrial applications and therefore it is very important to control their microstructure evolution, physical and mechanical properties. It is known that in the case of such materials plastic deformation can induce transformation of austenite into

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martensite. Acording to Perdahcıoglu et al. the initiation of transformation will always be from a virgin 100% austenite material [4].

In austenite stainless steels the deformation process can induce the formation of two types of martensite:

Austenite γ (FCC)→ martensite ε (HCP)→ martensite α'(BCC)

The transformation sequence above mentioned was proposed by some authors.[5, 6] However the direct transformation γ α' through dislocation reactions was found to be possible [7,8]. But it is also suspected that ε -martensite forms at lower temperatures (<-50ºC) [4].

Processing parameters, such as stress state, temperature and rate of deformation can have a strong influence on the amount of ε and α' martensite. Also of great influence is the steel composition and stacking fault energy [5, 9].

Eichelman and Hull have developed an equation which gives an approximation of α'martensite formation temperature – Ms:

$$Ms\ (\%C) = 1302 - 42(\%Cr) - 61(\%Ni) - 33(\%Mn) - 28(\%Si) - 1667\ (\%[C + N]) \quad (1)$$

The necessary energy for the martensitic transformation is supplied by the plastic deformation process. The supplied energy can increase the temperature of martensite formation to M_d which is the temperature below which martensite will form under deformation. Angel et al. [5] have studied the dependence of temperature with composition for different steels and formulated Equation 2.

$$Md(30/50)(\%C)= 413-13.7(\%Cr)-9.5(\%Ni)-8.1(\%Mn)-18.5(\%Mo)-9.2\ (\%Si)-462\ (\%[C+N]) \quad (2)$$

M_d is the temperature which limits deformation induced martensitic transformation, and no martensite can form above this temperature.

The increase of α' martensite by martensitic transformation induced by plastic deformation causes a change in physical properties of austenitic stainless steels. The martensitic transformation is expected to change by stress states.

Even though stainless steels are known having a good resistance to general corrosion because they form a thin chromium rich passive surface film [7,10], they are susceptible to localized corrosion attack such as pitting, intergranular corrosion, and stress corrosion cracking [7,10, 11].

2. Results

This paper is focused on the influence of stress states on deformation-induced α' martensitic transformation in AISI type 316 austenitic stainless steel. It is also analyzed the influence of martensite formation on the corrosion resistance of austenitic stainless steel. Corrosion analysis showed that martensitic transformation which occurs due to plastic deformation process has a substantially influence on the corrosion resistance of heat exchanger plates made of AISI type 316 austenitic stainless steel.

In order to study the influence of cold plastic deformation processes on martensitic transformation Erichsen cupping test and extrusion samples (Fig. 1) of commercial stainless steels AISI 316 were applied.

a) b) c)

Fig. 1. AISI 316stainless steel; Erichsen cupping test (a) and extruded (b) samples; c) microstructure

Samples of AISI 316 austenitic stainless steels with the following chemical composition: 0.04%C, 0.51%Si, 1.48%Mn, 0.021%P, 0.002%S, 17.05%Cr, 10.53%Ni, 2.05% Mo, 0.44%Cu, 0.05%V and 0.03%Ti were used for investigation. AISI 316 is an austenitic stainless steel from the CrNiMo type [7].

M_s and M_d (30/50) temperatures were calculated with Equations 1 and 2 and their values are -186.23ºC and 6.295ºC respectively. A M_s temperature of -186.23ºC serves to indicate that cooling to absolute zero would not induce transformation. M_d (30/50) which refers to the temperature that 50% of austenite is transformed to martensite with 30% of deformation, suggest that the formation of martensite at room temperature is very possible.

The microstructural analysis (Fig. 1b, 1c) recorded on samples electrolitically etched with 50% distilled water solution plus 50% HNO_3, highlighted an austenitic structure with twin crystals and rare carbides in the grains mass.

Mechanical properties of AISI 316 austenitic stainless steel are shown in Table 1 [2]:

Table 1.

Mechanical properties of investigated AISI316 austenitic stainless steel (SS-EN 10 002-1)

Material	Direction	$R_{p0.2}$*	R_m*	A_5	n	r
AISI316	0	258	615	48.9	0.42	0.47
	45	273	608	53.4	0.41	1.56
	90	285	648	53.3	0.42	0.96
	x_m⌒	**272**	**620**	**52.3**	**0.42**	**1.14**

⌒ x_m= mean value=$(x_0+2x_{45}+x_{90})/4$; *$R_{p0.2}$, R_m-are in MPa.

The martensitic transformation of AISI 316 austenitic stainless steel samples has been investigated by powder X-ray diffraction (XRD) with Cu-Kα radiation using a RIGAKU diffractometer with high resolution. Some results of the X-ray diffraction patterns performed on extruded samples (extrusion ratio, ε = 1.42) are presented in Fig. 2. The diffractogram shows only phases γ and α'. There is no peak indicating the presence of ε martensite. This means that ε martensite is or can be only a step of martensite transformation. In this work probably the reaction γ→ε→α' has been completed or the cold deformation generated only γ→α' reaction [5].

The martensite amount depends on processing parameters such as stress state, temperature and rate of deformation. A great influence has also the steel composition and initial austenite grain size. [9]

However, the transformation of austenite (γ) into martensite (α') can not be the single cause of the increase of hardness. It is also influenced by the ratio between the main elements of stainless steel chemical composition: Cr, Ni and Mo. [7, 10].

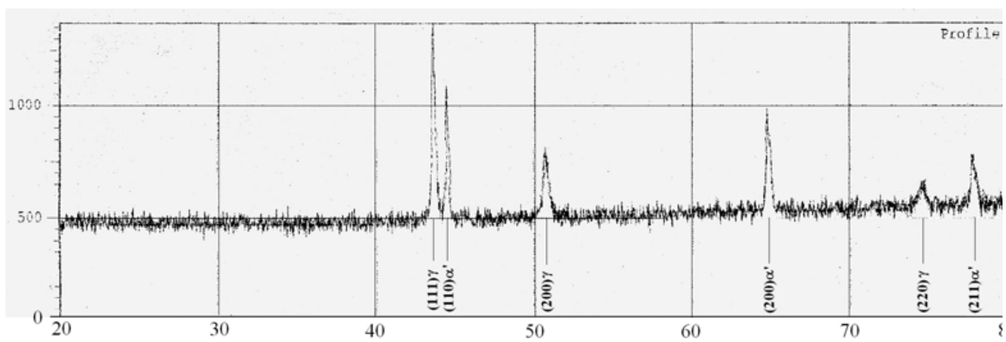


Fig. 2. X-ray diffraction pattern

Similar to the thermal stress which occurs and determines martensite transformation during heat treatment, the stress due to plastic deformation process determines sliding of reciprocal displacement of the adjacent atoms with fraction of their inter-atomic distance.

The martensite transformation involves a suddenly reorientation of C and Fe atoms from the fcc solid solution of γ-Fe to a body centered tetragonal (bct) solid solution, which is martensite. The phase transformation is accompanied by volume expansion [1, 7, 8, 12].

The measurement of Vickers microhardness was performed with 200g load. Fig. 3 shows the microhardness distribution before and after extrusion, as a function of the radial distance from center.

The average ASTM grain size of all samples was 7.4. The austenite stability decreases with increasing grain size. Thus, coarse-grained austenite will be more susceptible to martensitic transformation [9].

Cold plastic deformation increases the final flow stress of austenitic stainless steels more than for the other steels. This increase can be attributed to austenite (γ) instability which partially transforms into martensite (α') [1, 2, 7].

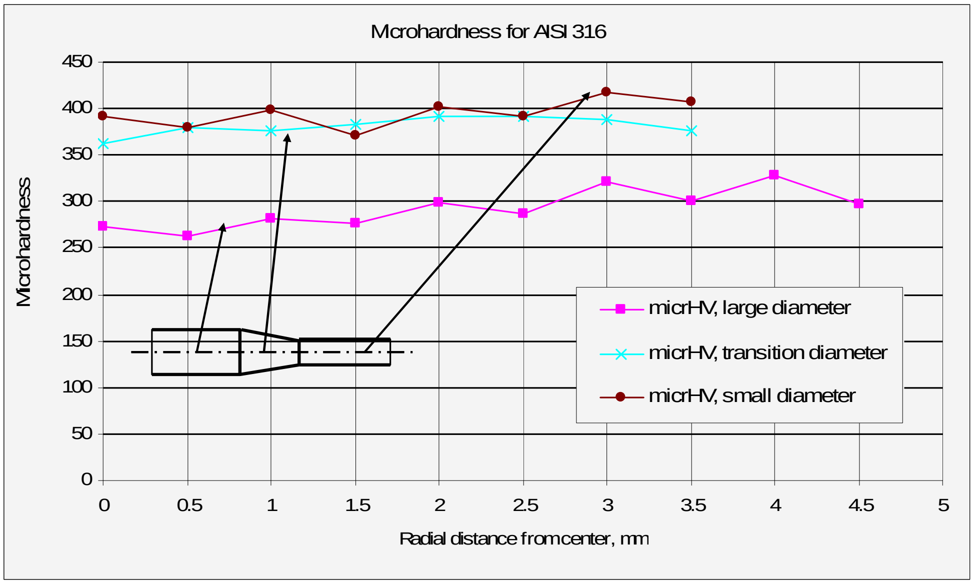


Fig. 3. Microhardness of AISI 316 as a function of the radial distance from center

The martensite presence in the steel structure contributes to a special hardness of steel [7, 13].

3. Discussion

Austenitic steels posses high plasticity characteristics and can be cold-pressed. However austenite is not a stable phase and during cold processing, which favors martensitic transformation, the hardening phenomena which occur may or may not be in favour of further processing.

Due to their superior corrosion resistance, good formability and toughness the austenitic stainless steels are used in plate heat exchanger applications. AISI 316 stainless steel is used for pressing of heat exchanger plates [2]. It has good corrosion behaviour, considering the fluid action (chlorine-treated water) in the heating circuit as well as in the secondary circuits. The working conditions of heat exchangers which were the same the testing conditions are presented in Table 2 [10]:

Table 2.

Testing conditions

Parameter	Heating agent		Measurement units
	warm	cold	
Fluid type	water	water	-
-pH	6.5-7.5		unit pH
-Chlorine-treated water	22.18-83.75		mg/l
Extreme pressure	10	10	bar
Input temperature	65	12	°C
Output temperature	40	52	°C
Safe working pressure dropping	0.2-0.3	0.2-0.3	bar
Extreme winter temperature	80/50	12/62	°C

The influence of the deformation process on the corrosion resistance of AISI 316 stainless steel was also analyzed on the heat exchanger plates supplied by SC Apaterm SA Galati. The plate heat excenger consists of a pack of corrugated metal plates and is universally used for heating, cooling and heat recovery in chemical processing, food processing, etc.

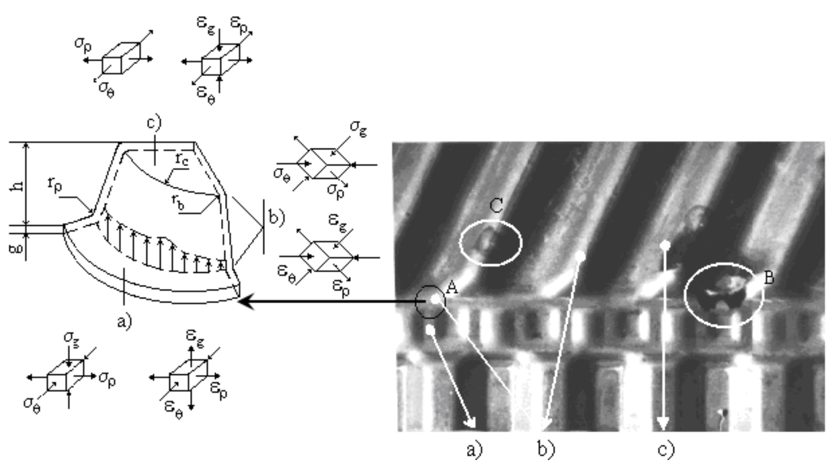


Fig.4. Heat exchanger deformed plate- short end of the channel
A - deformed zone; B – corroded zone; C-start up of pitting corrosion (pit)
a, b, c: stress and strain state in deformed plate zones

The plates of heat exchanger were produced by the deep drawing process (Fig. 4) [2, 10]. The initial sheet thickness was 0.8 mm and the mechanical properties of AISI 316 austenitic stainless steel are presented in Table 1 [2].

In Fig. 4 it can be noticed that almost all surfaces of the plate are exposed to stretching or overstretching which favours martensite transformation. Harder than austenite, during the deep drawing process martensite can determine material failure. In the case of deformed plate three types of failures could be possible, failure at apex, failure at channel or failure at short end of channel [2, 10]. The failure could be either necking or/and fracture such as in Fig. 5.

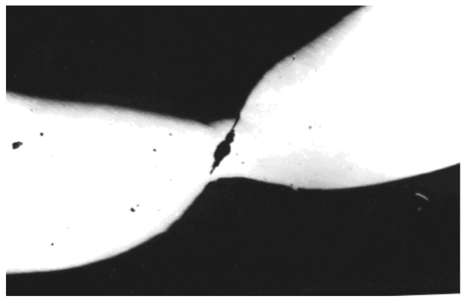


Fig. 5 Necking and fracture in deformed zone

Because martensite is not “close packed” its dimensional stability is affected, so in essence the same mass of steel will occupy a large volume as martensite than it does as austenite. That means the martensitic phases will induce volume changes compared to the parent austenite. Corrosion resistance will normally be much lower for two-phase material that it is for a single-phase material of similar chemical composition [7, 11,14].

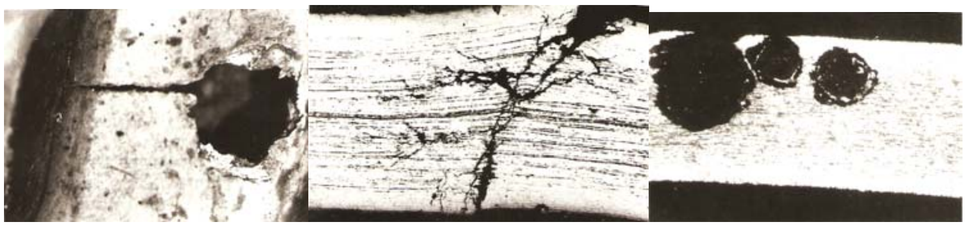
Corrosion analysis showed that martensitic transformation which occurs due to plastic deformation had a substantially influence on the corrosion resistance of heat exchanger plates made by AISI 316 austenitic stainless steel.

The number of pits increases with deformation and is associated to defects introduced by the deformation process leading the arisen of preferential sites for pits nucleation [5, 10, 13]. This is because the martensitic transformation does not take place in whole plate and therefore on the plate can appear zones with two-phase structure and with different hardness. Zones with martensitic structure are stronger and harder than austenitic ones and consequently less resistant to corrosion.

The austenitic stainless steels are susceptible to some types of corrosion, namely pitting, crevice, stress corrosion cracking and sensitization, Fig. 6. Note the deep undercutting which is typical of chloride-induced attack on stainless steel.

Stress corrosion cracking could appear in the austenitic stainless steels in corroding atmospheres like chloride solutions, at elevated temperatures in access of 60°C and during tensile stresses, Fig. 6c [10, 13].

The hardness surveys and corrosion tests displayed predictable changes, in stainless steel properties due to the martensite formation such as increased corrosion susceptibility and greater hardening.



a) b) c)

Fig. 6. Types of Corrosion
a) Crevice corrosion b) Pitting corrosion c) Stress corrosion

Corrosion means damage of a material consequent to various interactions with the environment, so as the material structure suffers damage and do no more comply with the requirements. The material in the gasket area is often submitted to corrosion crevice, since the fluid is easily kept in the small space between the gasket and the material.

Pitting is induced in the presence of crevices or impurities such as sand, dirt, etc. Corrosion crevice may vary in appearance from almost uniform attack up to pitting at the metallic surface.

Any aggressive solution (acid or neutral), including natural waters, but especially those containing chlorine anions are the ones resulting most frequently in this type of corrosion [13].

In the case of stainless steels used for heat exchanger plates the corrosion under tension determines the intergranular braking. As usually the cracks begin from the places hardened by plastic deformation.

4. Numerical simulation analysis

The deformation behavior of the cold plastic deformed stainless steels has been also analyzed using FEM code MARC/AutoForge.

The FEM simulations were carried out (Fig. 7) as an isothermal, axisymmetric problem applying quadrilateral elements. The material behaviour is governed by the incremental theory, the Von Misses yield criterion, the isotropic hardening rule [16, 17].

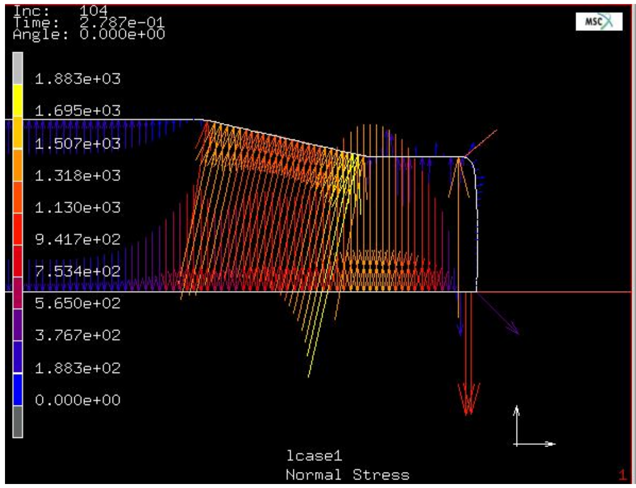


Fig.7. FEA normal stress diagram of 316 austenitic stainless steel cold extruded

Considering that the flow stress of austenitic stainless steel is described as the composition of flow stress of austenitic phase and flow stress of martensitic phase in agreement with the volume fraction of of each phase, the fornula of flow stress is defined as [15]:

$$\sigma = \sigma_A\,(1\text{-}M) + \sigma_M\,M \qquad (3)$$

where σ represent the flow stress of metastable austenitic stainless steel; σ_A is the flow stress of austenitic phase; σ_M is the flow stress of martensitic phase; M is the volume fraction of martensitic phase; and 1-M volume fraction of austenitic phase.

The flow stress diagrams obtained by numerical simulation allows us to determine the volume of deformation fractions. The α' martensitic transformation easily occurs with an increase of tensile hydrostatic stress. In other words, the transformation easily occurs with an increase of mean normal stress which assists volume expansion.

5. Conclusions

In AISI 316 austenitic stainless steel deformation - induced α' martensitic transformation occurs by plastic deformation. However this transformation does not occur in the whole part. It occurs only locally where there are favorable conditions for transformation and it causes a change in mechanical and physical properties of austenitic stainless steel. The changes in fundamental characteristics (resistance and plasticity) are to be considered for an appropriate behaviour of plates in use. In the case of deformed plate three types of failures could be possible, failure at apex, failure at channel or failure at short end of channel. The failure could be either necking or/and fracture either at the apex or along the channels of the herring – bone pattern. On the plate can appear zones with two-phase structure and with different hardness. Zones with martensitic structure are stronger and harder than austenitic ones and consequently less resistant to corrosion.

Stress corrosion cracking could appears in the austenitic stainless steels in corroding atmospheres like chloride solutions, at elevated temperatures in access of 60°C and during tensile stresses.

In the case of stainless steels the corrosion under tension determines the intergranular braking. As usually the cracks begin from the places hardened by plastic deformation process.

Corrosion crevice is likely to occur due to manufacture deficiencies such as inadequate deformation tools. It might start where the surface is damaged locally.

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