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The Effect of cryogenic heat treatments on the mechanical behavior of hydrogen filled steels.

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Abstract:

The noble interest of this article is the study, the effect of heat treatments at low temperatures at -196°C and structure on the mechanical behaviour of steels cathodically charged with hydrogen. The standardized tensile test specimens undergo characterization techniques by mechanical test, hardness, tensile. Underwent austenization heat treatments for 35minutes at 1050°C following a rapid water quench, following by a tempering for 30 minutes at 680°C, after having a cryogenic quenching for 30minutes by the liquid nitrogen (N_2) gaz at -196°C in immersion succession ranging from 20cycles time. A cathodic loading was in a pyrex cell to be filled with an aqueous solution of sulfuric acid H_2SO_4 at 0.05M for different loading times from 1hour to 8hours with a step of 1hour. The application of these methods and technicals aims to improve the mechanical properties of these respect to the embrittlement mechanism. The results of the different mechanical properties given in the form of experimental curves to be noted after the mechanical fracture test by tensile at ±20°C temperature using an instrumented tensile machining reference : Frank GMBH, with industrial conditions, the maximum load is constant at 400KN and nominal speed deplacement at (έ=23.0mm/min).

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

Keywords : Steels, Heat treatments, Cryogenic treatments, Hydrogen, Metallographics, Mechanical properties.

1. Introduction

Austenitic stainless steel of DINX2CrNi19.11/1.4306 grade is AISI304L steel they are widely in various chemical sectors, petrochimecals as well as oil transport. On the one hand uses and works much more in envionmentals medium and the different temperature cycles in order to undergo mechanical cycles which are related to compression and tensile. On the other hand, these materials are caused by a fragility inside the crystal lattice causing the penetration of the hydrogen molecule (H_2) (J. Chêne., 2009 ; S. Lunch., 2012). In order to expose a total degradation of these mechanical properties which leads to hydrogen embrittlement H.E (A. Marie Brass et al., 2000; A. Cécile Bach., 2018). At the same time, experimental work (B. Grimault et al., 2012, F. Lacoviello et al., 1997 ; C. Hamissi et al., 2016 ; A. Cécile Bach., 2018), highlighted the study of the phenomenon of hydrogen embrittlement. The essential aim of this experimental work is to carry out a comparative study of the two types of steels families, the first is standard stainless steel : X2CrNi19.11/1.4306 and the second is the low alloy industrial steel of the standard grade : E335/1.0060. To better understand and analyze the effect of the heat treatments at low temperature on the mechanical behaviour of the latter in relation to the retardation of the mechanism of hydrogen embrittlement (H.E) to the two noble alloys.

1 Experimental work

1.1Materials

The materials of this study is a high alloy stainless steel of the grade : X2CrNi19.11 their chemical composition is cited in Table 1.

The second material used is a low alloy steel of grade : E335 used for the manufacture of screws and mechanical parts in the ORSIM

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

production unit located in Oued Rhiou. Their chemical composition is shown in Table 2.

Table 1. Chemical composition by mass (%) of AISI304L stainless steel.

Fe%	**C%**	**Cr%**	**Ni%**	**Si%**	**Mn%**
69,45	0,0638	17,97	9,65	0,0115	1,66
P%	**S%**	**Nb%**	**Mo%**	**Al%**	**Co%**
< 0,00030	0,0284	0,0490	0,368	0,0078	0,0985
B%	**V%**	**Ti%**	**Cu%**	**W%**	**Pb%**
0,0152	0,0888	0,0052	0,717	0,0319	0,0047

Table 2. Chemical composition by mass (%) of steel E335.

Fe%	**C%**	**Cr%**	**Ni%**	**Si%**	**Mn%**
98,10	0,322	0,171	0,125	0,233	0,723
P%	**S%**	**Nb%**	**Mo%**	**Al%**	**Co%**
0,0321	< 0,00020	0,0022	0,511	0,0466	0,007
B%	**V%**	**Ti%**	**Cu%**	**W%**	**Pb%**
0,0026	0,002	0,0198	0,105	0,205	~ 0,0304

The initial mechanical properties above all and without heat treatments of the two types of materials used are presented in Table 3.

Table 3. Mechanical properties of the two types materials study AISI304L and E335.

Materials	$\sigma_é$ (MPa)	σ_m (MPa)	σ_r (MPa)	**Z** (%)	**A** (%)	**HV(30)** (N/mm^2)	**E** (MPa)	υ
AISI304L	520	600	339	70%	93%	175.0	200.000	0.27
Steel E335	384	518	362	51%	40%	213/230	210.000	0.28

The experimental part consists of using standardized tensile specimens of cylindrical shape with the dimensions which are represented in (Figure 1), are obtained by machining according to the standard DIN50125 using a semi-automatic lathe of reference Trens, a, s Suvozi, type 91132 Trencen – Slovakia.

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

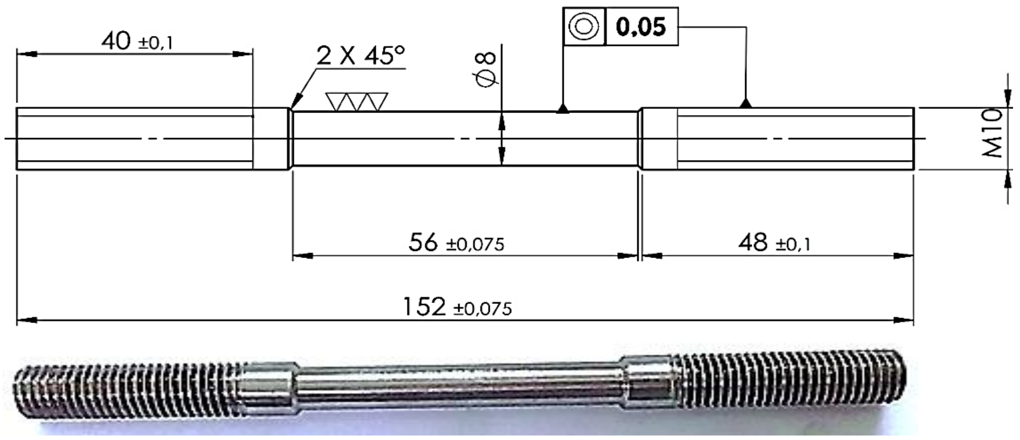


Figure 1 : Shape and dimensions of the type tensile test specimen used according to the standard DIN50125 [6].

1.2 Heat treatment (quenching, tempering)

After the manufacture of specimens of two types of steel. Have undergone an austenization heat treatment, consisting of heating for 30 minutes at 1050°C, followed by water quenching.

The next step consists of applying a temper at 680°C for 35 minutes then cooling in the open air (temperature room ±20°C) (see Figure 2), in order to obtain a very homogeneous internal structure with stable austenite. For which we have better softening for machining and good ductility as well as excellent resistance to corrosive attacks.

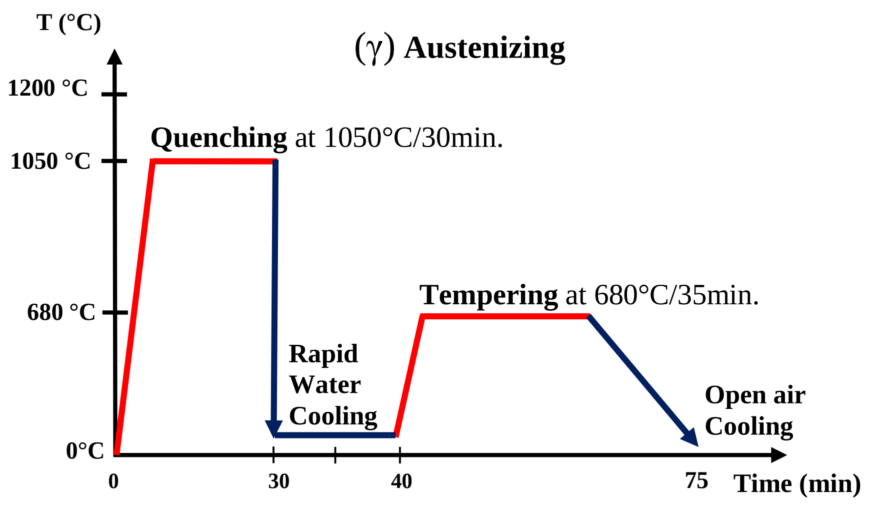


Figure 2 : Diagram of heat treatments (austenization) applied [7].

Print ISSN: 2785-9533 - Online ISSN: 2785-9541

VOLUME 6, ISSUE 2, 2023, 92 – 108

1.3 Cryogenic heat treatment at -196°C

Another technique of cyclic heat treatment by cold quenching (cryogenic treatment) in order to use nitrogen (N_2) gaz in liquid form, its use temperature is -196°C.

The diagram of treatment cycle with shown in (Figure 3). The operation followed by a succession of immersion of the test specimens with a number of 1cycle up to 20 cycles and maintenance of 30 minutes with a warm-up of 45 minutes Figure 4 (a), (b).

After the cyclic cryogenic heat treatments, stripping was applied to clean all the surroundings and surfaces of the specimens of the two types materials.

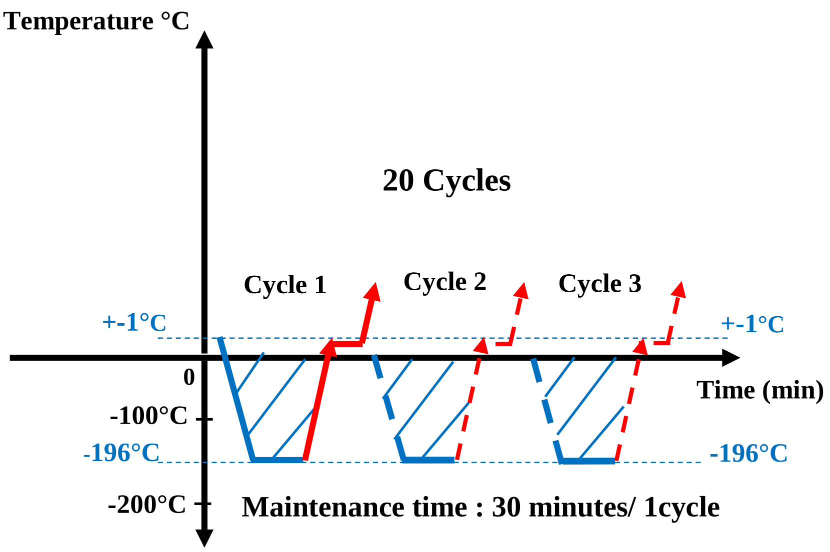
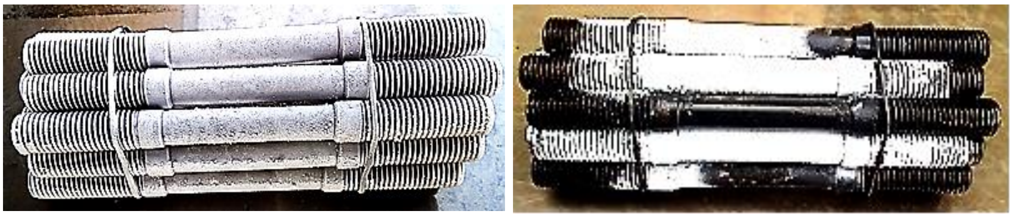


Figure 3. Diagram of the cryogenic quenching treatment used [7].

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

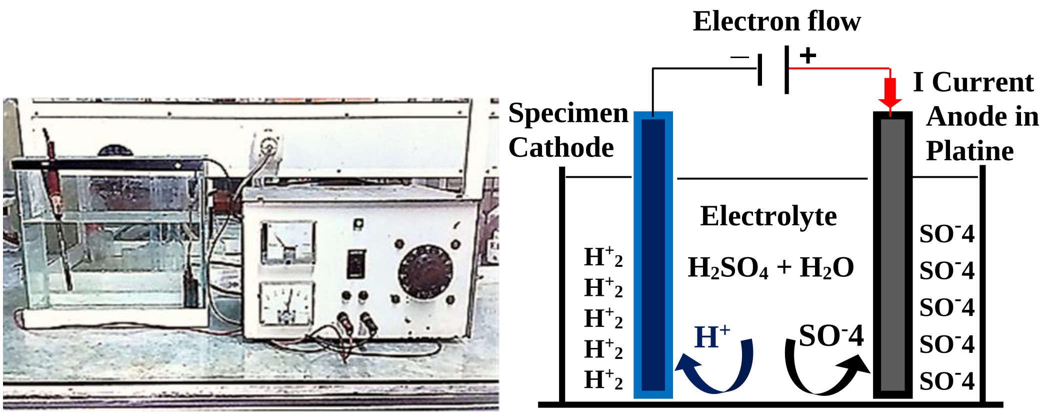


(a) (b)

Figure 4 : Representation of the applied deep cryogenic treatments used.
(a) : cryogenic quenching at 30 minutes, (b) : heated in the open air at 45 minutes.

1.4 Hydrogenated conditions at 20°C

The two types of materials, was loaded by the cathodic method in a solution cell of purely sulfuric acid 97-98% (H_2SO_4) at 0.05M. The electrolytic charging was carried out in industrial conditions adopted with a power supply of 1,5A, and a current density of 100mA/cm^2 and for the different charging durations time : 1h00 until 8h00 with a step of 1hour according to the operating principle represent in Figure 5 (a) and (b).



(a) (b)

Figure 5 : (a) : The cathodic loading cell, (b) : Diagram of loading operation used.

1.5 Mechanical fracture tensile

Just after loading by the hydrogeneted method, a mechanical tensile tests were used on the Frank GMBH reference instrumented machine of type : 83431 with slow nominal speeds of (έ =23.0mm/min) in

INTERNATIONAL JOURNAL OF
ADVANCED SCIENTIFIC RESEARCH AND INNOVATION

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

order to deduce the experimental curves recorded and highlight the mechanical properties during the test tensile fracture specimens test Figure 6 (a), (b).

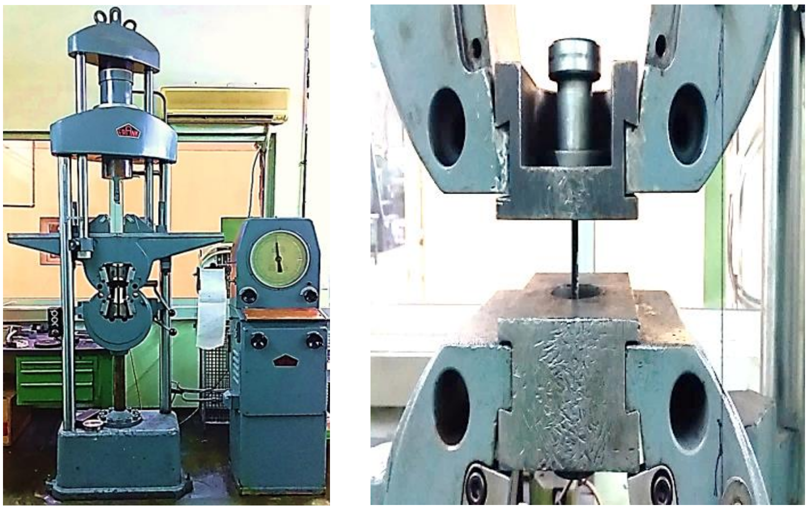


Figure 6 : Frank GMBH tensile, (a) : Tensile machine, (b) : Specimen used.

1.6 Microstructural Evolutions

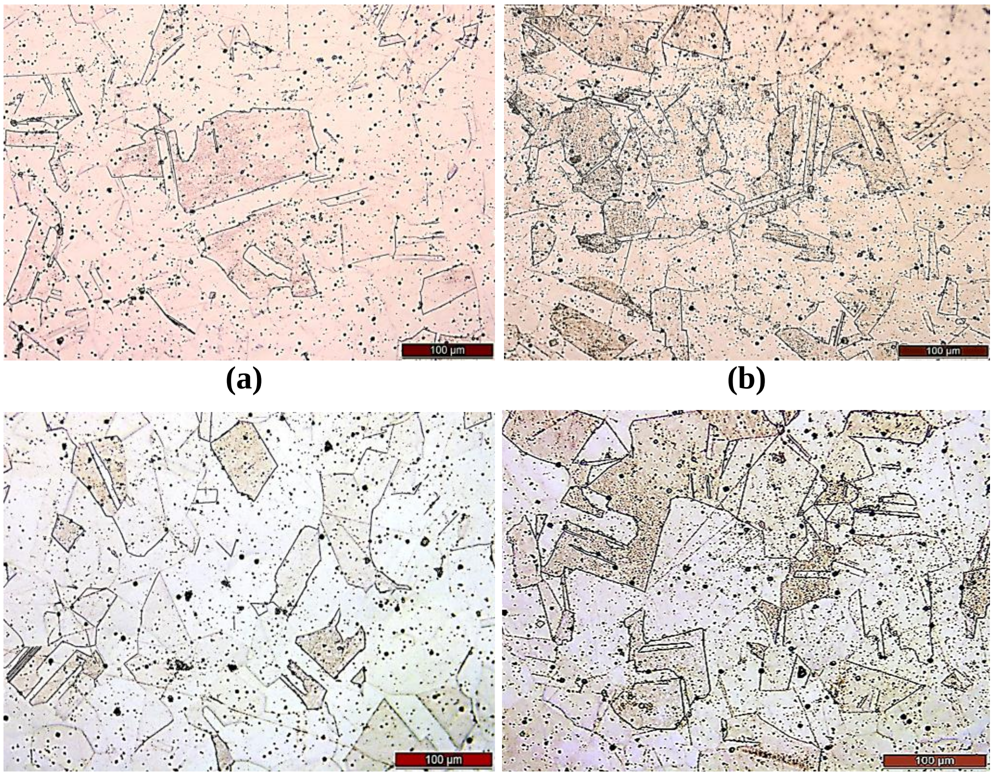
The next step is to carry out a metallographic examination of AISI304L steel at the temperature room ±20°C. we use an electrolytic attack (6V, 10 to 45 seconds) : of 10grams oxalic acid in 100milliliters of water to prepare and obtain aqueous solution of the oxalic acid ($C_2H_2O_4$) for the purpose of highlighting see the microstructural evolutions Figure 7 (a), (b), (c), (d).

At the same time, we prepared anthor chemical attack for the E335 steel. Whose compostion of 3% of Nitric acid (NHO_3) and 97% of absolute ethanol alcool (C_2H_5OH), so we can observe and take different states of the metalographics using a Leica DM4-GMBH reference optical microscopic (O.M), see Figure 8 (a), (b), (c), (d).

The microstructural analysis of the states a stainless steel of grade X2CrNi19.11/AISI304L is shown in Figure 7, in the raw state without heat treatments Figure 7 (a), we see that the austenitic ast structure is composed of several austenitic paltes associated with fine black spots. In quenched state Figure 7 (b), the microstructure sample is composed of several black-colored slatted martensitic plates and other gray plates is austenite with the presence of

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

precipitation in the joints of grains. The Figure 7 (c), the aspect of this microstructure is still composed of martensite with dispersed platelets which change to spheroïdal form when the tempering temperature reaches at 680°C. In Figure 7 (d), consists of platelets in martensite and others in austenite with the presence of carbides (black dots in very dark) resulting from the refinement of the initial grain G. Prieto et al. [13], which reduces the surface porosity and prevents the diffusion of hydrogen by giving a lightness improvement of their mechanical properties of this type of steel.



(a) **(b)**

(c) **(d)**

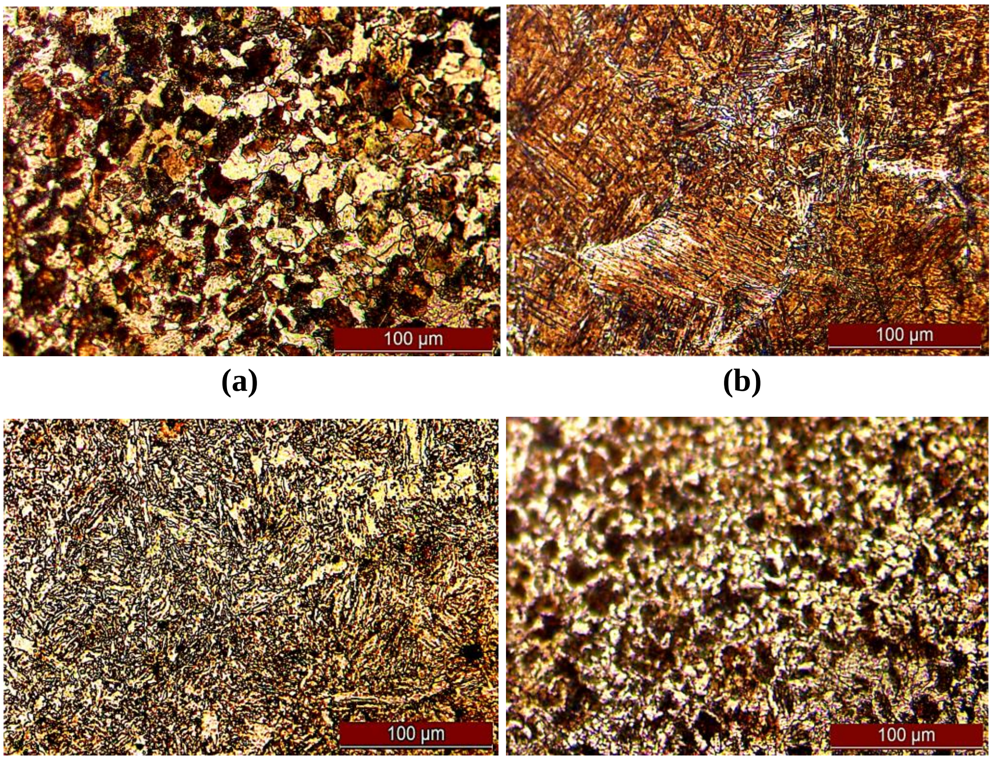
Figure 7 : (a), (b), (c), (d) : (OM) observation of the states micrographics of AISI304L stainless steel (x100µm) before and after heat treatments.

Figure 7. (a) : Raw state without heat treatments ; Figure 7. (b) : Quenching at 1050°C, rapid water cooling. Figure 7. (c) : Quenched and tempered at 680°C, open air cooling ; Figure 7. (d) : Cryogenic treatments and hydrogeneted at 8hours in acid sulfuric (H_2SO_4) at 0.05M.

INTERNATIONAL JOURNAL OF
ADVANCED SCIENTIFIC RESEARCH AND INNOVATION

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 **VOLUME 6, ISSUE 2, 2023, 92 – 108**

Concerning the microstructural analysis of E335 steel which is show in Figure 8, in the raw state Figure 8. (a), is composed of ferrite and perlite platelets. The microstructural appearance in the quenched state Figure 8. (b), composed of several slatted martensite plates aligned in parallel inside the plates (LI. Hongying and al.; 2013; I. ABAIDI et al.; 2017). After the tempering treatment at 680°C Figure 8. (c), we see that the microstructure changes its shape to martensite in slats and ferrite in the presence of carbides in the form of rods. Figure 8. (d), the microstructure consists of ferrite and carbides which change form rod shape to a spheroïdal shape (the tempering treatment enhanced the grain refinement G. Prieto et al. [13], and spheroïdization of the cementite inclusions) when the tempering temperature reached at 700°C, according (LI. Hongying and al.; 2013; I. ABAIDI et al.; 2017).



(a) **(b)**

(c) **(d)**

Figure 8 : (a), (b), (c), (d) : (OM) observation of the states micrographics of E335 steel (x100µm) before and after heat treatments.

Figure 8. (a) : Raw state without heat treatments ; Figure 8. (b) : Quenching at 1050°C, rapid water cooling. Figure 8. (c) : Quenched and tempered at 680°C, open air cooling ; Figure 8. (d) : Cryogenic treatments and hydrogenated at 8hours in acid sulfuric (H_2SO_4) at 0.05M.

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

2. Results and discussions

2.1. Mechanical properties

The numerical results of the mechanical properties of the studied stainless steel AISI304L, are obtained after the mechanical test of fracture by tensile at a slow nominal speed (23.0mm/min) which is represented in the Table 4. While the numerical data results of steel E335 is mentioned in the Table 5.

Table 4. Mechanical data results of the stainless steel type AISI304L after fracture tensile.

Specimens	**Loading hydrogen in (hours)**	**σm** (MPa)	**σé** (MPa)	**σr** (MPa)	**A** (%)	**Z** (%)
Reference	Loading 0h	600,141	520,424	339,702	93.330	70.840
Quench + temper	Loading 0h	634,111	543,524	362,349	106,660	70,840
1	Loading 1h	566,171	475,583	339,702	77,330	68,650
2	Loading 2h	588,818	475,583	362,349	80,000	67,900
3	Loading 3h	577,494	475,583	362,349	73,330	68,650
4	Loading 4h	611,464	475,583	362,349	81,330	69,390
5	Loading 5h	588,818	475,583	351,026	88,000	70,120
6	Loading 6h	566,171	498,230	351,026	74,660	69,390
7	Loading 7h	544,847	475,583	339,702	80,000	70,120
8	Loading 8h	520,877	475,583	339,702	80,000	70,840

Table 5. Mechanical data results of the stainless steel type E335 after fracture tensile.

Specimens	**Loading hydrogen in (hours)**	**σm** (MPa)	**σé** (MPa)	**σr** (MPa)	**A** (%)	**Z** (%)
Reference	Loading 0h	518,612	384,996	362,349	40,000	51,930
Quench + temper	Loading 0h	475,583	339,702	317,055	46,660	64,000
1	Loading 1h	486,907	339,702	339,702	45,330	53,770
2	Loading 2h	428,025	339,702	294,409	38,660	64,800
3	Loading 3h	452,937	339,702	317,055	38,660	55,560
4	Loading 4h	430,290	339,702	317,055	45,330	55,560
5	Loading 5h	452,937	339,702	226,468	38,660	54,670
6	Loading 6h	464,260	317,055	317,055	40,000	55,560
7	Loading 7h	473,319	339,702	317,055	46,660	55,560
8	Loading 8h	471,054	339,702	328,379	42,660	54,670

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

The analysis of the results obtained and which are represented in the figures below, (Figures 9 to 12). Allowed us to deduce the following remarks : Firstly, we see that the yileds strength (σm, σr) decreases slightly with the number time of loading hours for AISI304L stainless steel. But decreases significantly in the case of E335 steel (see Figures 9 and 10).

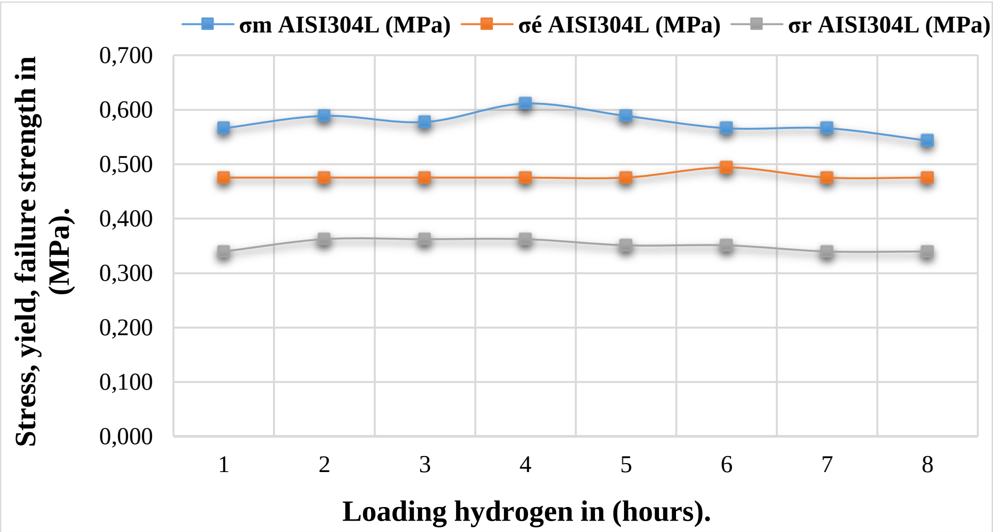


Figure 9 : The effect of heat treatments **versus** time hydrogen pre-loading in (hours) on the mechanical strength of AISI304L stainless steel.

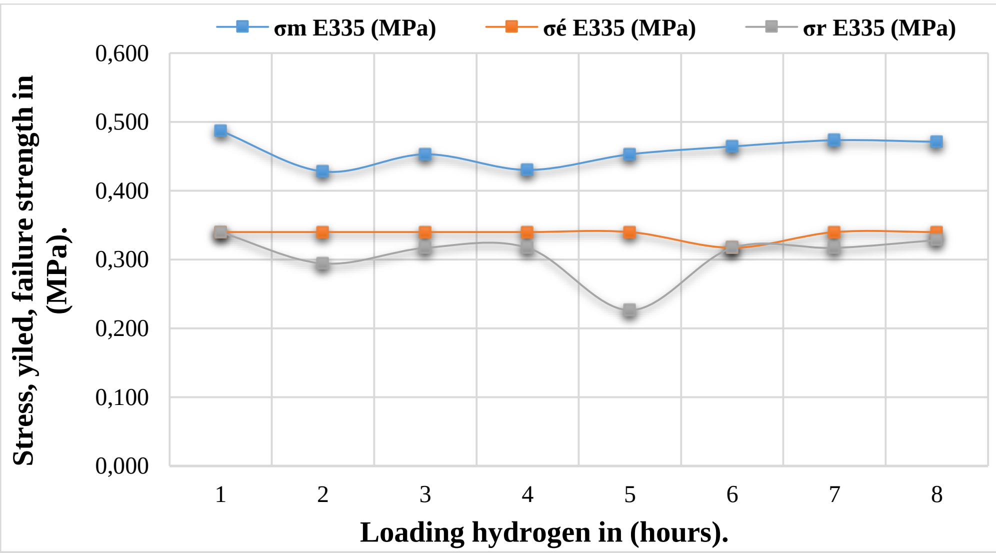


Figure 10 : The effect of heat treatments **versus** time hydrogen pre-loading in (hours) on the mechanical strength of E335 steel.

Secondly, the plasticity of AISI304L stainless steel remains almost constant with the increase in the number of loading times in hours.

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

While for E335 steel increases significantly and improves and becomes constant during the increase in the number of heat treatments cycles (see Figures 11 and 12).

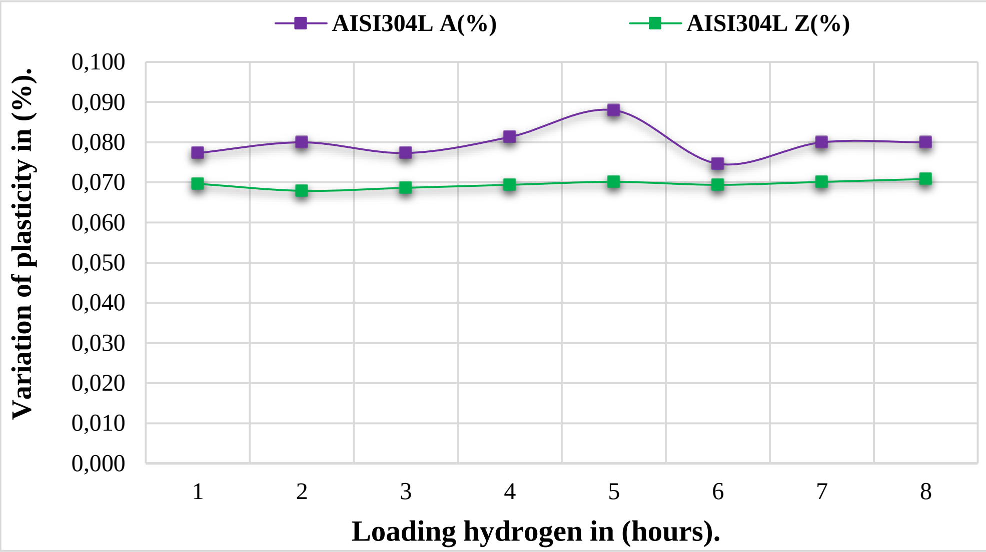


Figure 11 : The effect of heat treatments **versus** time hydrogen pre-loading in (hours) on the plasticity and ductility of AISI304L stainless steel.

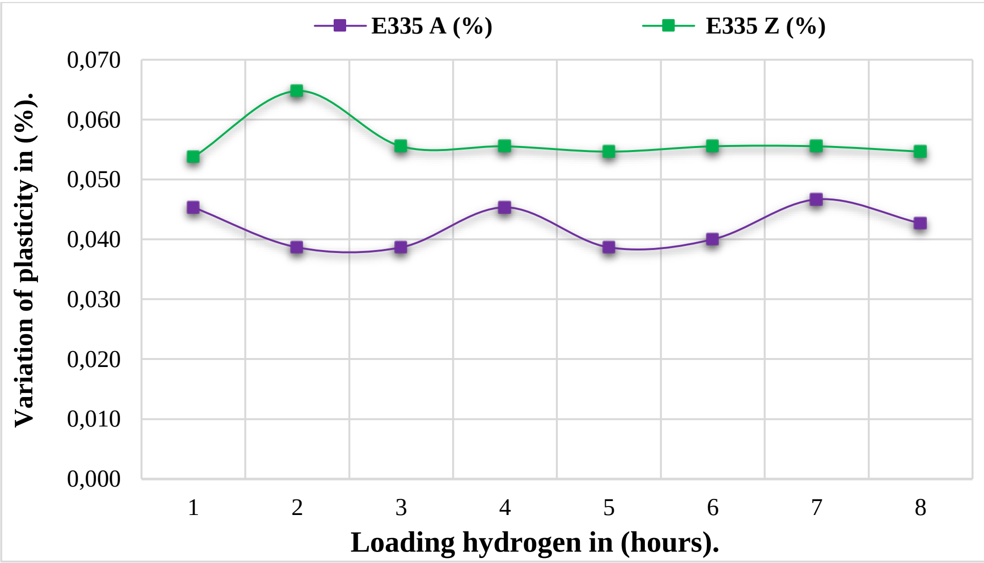


Figure 12 : The effect of heat treatments **versus** time hydrogen pre-loading in (hours) on the plasticity and ductility of E335 steel.

A behaviour expected by an yield strength (σé), which decreases slight and becoms almost constant by an average value of approximately 475.583 (MPa) depending on the number of loading times in hours for AISI304L stainless steel. While for the case of E335 steel it decreases significantly to almost as constant by a value

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

on average of around 339.702 (MPa) (see two Figures 9 and 10).

Comparison of these data results of mechanical properties before and after the hydrogenated process shows that hydrogen slightly improves the yield strength (C. Hamissi, et al., 2016), see Figure 13.

Of these types of steels studies AISI304L and E335 in relation to the application of a seccession of heat treatments at low temperatures at -196°C, so these results lead to significantly delaying the phenomenon of hydrogen embrittlement (HE) which can be explained by modifications to the yield strength (σé) as well as the ductility, and plasticity of the two types steel (R. Laugevin, et al. ; 2015).

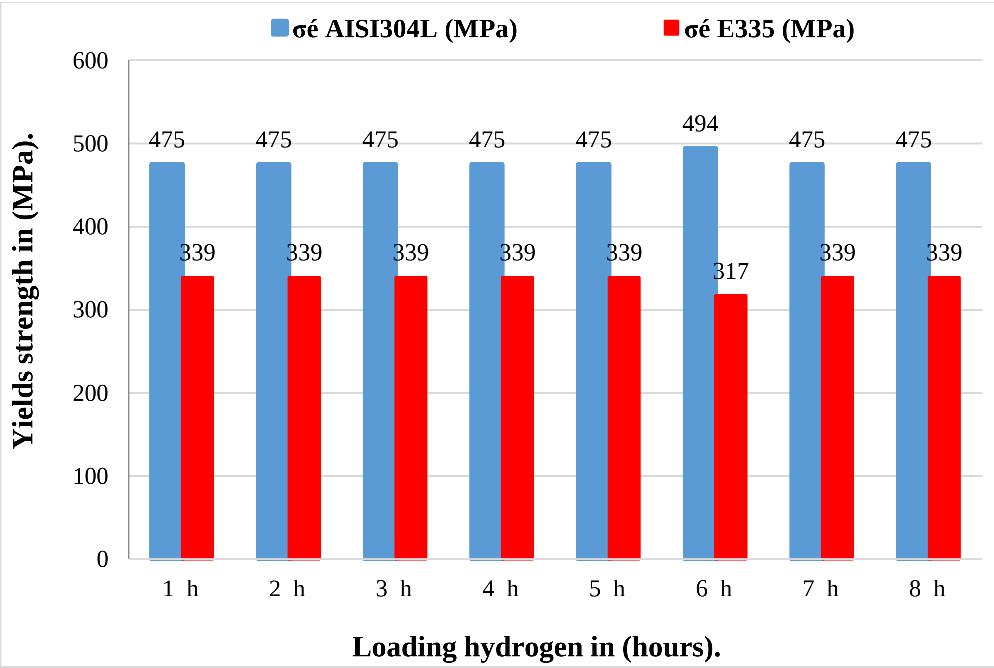


Figure 13 : Comparison of the variation the yield strength (σé) of the two types of steel grades after heat treatment, cryogenic treatment in cycles times AISI304L and E335.

The influence of increasing the temperature of the tempering treatment at 700°C, can lead to a reduction in mechanical variation such as the yield strength (σé) and the failure strength (σr) with an increase in ductility and significantly improved plasticity (M.K. Khani Sanij, et al., 2012 ; LI Hongying, et al.; 2013 ; I. ABAIDI, et al.; 2017).

Print ISSN: 2785-9533 - Online ISSN: 2785-9541 VOLUME 6, ISSUE 2, 2023, 92 – 108

3. Conclusion

Hydrogen embrittlement of steels is characterized by a decrease in the ductility of the material and sometimes by total embrittlement. Under the effect of heat treatment in cyclic seccession by cryogenic quenching at -196°C, there is a delay in the phenomenon of hydrogen embrittlement (H.E), this can be explained by these treatments significantly improving and correcting the mechanical properties of steels such as ductility and plasticity. Therefore, the effect of these heat treatments in this case is due to the refinement of the initial grain which reduces the surface porosity and prevents the diffusion of hydrogen giving a lightness improving the mechanical properties of the stainless steel of the grade AISI304L. Concerning the industrial steel of mechanical construction E335, the effect of heat treatment in cryogenic cycles are very effective in order to the grain and the spheroïdization of the inclusions of the cementite which makes it possible to obtain better and good ductility of this type steel. Cryogenic heat treatments with liquid nitrogen (N_2) depending on the number and immersion time can be 20times cycles. Consists of saturated a part is absorbed by the test specimens with the aim of protecting the surface of the middle part is given a hardening which increases these surface hardnesses which become higher and can significantly resist the hydrogenation medium which is aggressive.

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