CATHODIC HYDROGENATION OF AUSTENITIC ALLOYS IN MOLTEN SALTS BATH, AT 200° OR 300°C : STUDY OF HYDROGEN INDUCED EMBRITTLEMENT

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ABSTRACT

In this work, we introduced hydrogen in austenitic stainless steel 304 L at 200° and 300°C by the means of molten salts bath electrolysis technique with various polarization potentials. The quantities of desorbed hydrogen after the metal has been cathodically electrolysed at 200° and 300°C are respectively 50 and 60 cm^3 H_2/100g. The hydrogenated metal is tensile tested after the following conditions : at 300°C hydrogenation temperature, two factors are examined to influence the mechanical properties of 304 L austenitic stainless steel: the electrolysis conditions, i.e. potential and time of cathodic electrolysis, and plastic deformation rate. The maximum embrittlement is observed for two hours electrolysis at -2 volts/Ag. This potential corresponds to the cathodic current density peak measured by potentiostatic method. The maximum stress for 304 L austenitic steel decreases while plastic deformation rate $\dot{\varepsilon}$ increases, while for 304 L hydrogenated austenitic steel, σ_m increases with $\dot{\varepsilon}$. Maximum embrittlement is also obtained at low $\dot{\varepsilon}$ value. X-rays measurements show that α' transformation is restrained when the austenitic is hydrogenated and then tensile tested to rupture, ε' is improved and α' restrained when austenite is hydrogenated, quenched at -196°C and then tensile tested to rupture. Hydrogen induced embrittlement in the austenitic structure of 304 L steel is higher when electrolysis is achieved at 200° than at 300°C. Kinetics of outgassing prove that embrittlement markedly increases when interation energy of trapping is low. Morever, there is complete recovery of mechanical properties when the hydrogenated austenite is outgassed during the same time and temperature that for cathodic polarization.

KEYWORDS

Metastable austenite; cathodic potential; hydrogen embrittlement; electrolysis temperature; tensile test; outgassing.

INTRODUCTION

Many studies were performed on metastable austenitic stainless steel under strong conditions of hydrogenation (Hasegawa, 1976; Vennett, 1967; Inoue, 1979); it means at high pressure or at high temperature. Also, works were achieved to explain the

embrittlement process of various stainless steels (Theus, 1973; Andriamiharisoa, 1979; Petit, 1973) due to hydrogen such as crack corrosion cracking, fatigue crack propagation or delayed failures. All these studies had been developped in the aim to explain hydrogen induced transformation $\gamma \rightarrow \varepsilon$ or $\gamma \rightarrow \alpha'$ on the surface of thin specimens, during cathodic electrolysis, in relation with the evolution in the mechanical properties. No attempt had been performed to measure these properties at room temperature when bulk austenitic specimens are heavily hydrogenated at high temperature.

Introducing hydrogen at high temperature in metastable austenitic stainless steel is interesting in different points of view :

1) Influence of absorbed homogeneous high concentration hydrogen within specimen thickness, on the mechanical properties of these steels.

2) Mechanisms of hydrogen trapping at high temperature.

3) Avoiding use of poison, when hydrogenated austenitic stainless steel at room temperature, in which case, one can produce a thin film of surface martensite. This martensite is due to high surface hydrogen concentration, and consequently, high deformation level in the lattice surface. The diffusion coefficient of hydrogen in annealed 304 L austenite at room temperature is in the range of 10^{-12} - 10^{-10} cm^2/s (Louthan, 1974) and at 300°C is about 10^{-8} cm^2/s (Eschbach, 1963). Fick's law shows that when the specimen thickness equals to 7.62 10^{-3} cm (0.003"), hydrogen content at specimen core would be ≃ 99 % of the surface concentration after 20 hours of hydrogenation at room temperature (Burke, 1972). Similarly, at 300°C and at the same "core/surface" hydrogen concentration as the former case, we have to introduce hydrogen during 21 minutes when the specimen is 0.1 cm thick.

In the other hand, hydrogen evolution rate is rapidly increased when the applied stress reaches the flowing stress of an hydrogenated metal (Broudeur, 1972). At higher stress, the evolution rate decreases and then stabilized, independently of the stress value.

EXPERIMENTAL

Common austenitic 304 L stainless steel are used in this work, and their chemical composition are given in table 1. The shape and dimensions of the specimen are shown in Fig. 1. The specimens are austenized at 1050°C, during one hour in dry argon and then quenched in water to obtain the austenitic structure. Hydrogen is introduced in the polished specimen at 200° or 300°C by mean of molten salts bath electrolysis technic (Elkholy, 1977). Plastic deformation rate used in this study is equal to 2.5 10^{-4} s^{-1}, unless mentionned in special cases.

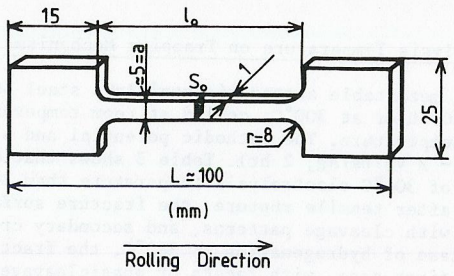

Fig. 1. Shape and size of the specimens for tensile test.

Kinetics of outgassing and tensile tests at room temperature are performed not more than 200 s after cathodic electrolysis. The kinetics of outgassing are carried out by measuring, under vacuum (10^{-3} Pa), the quantity of desorbed hydrogen out of the specimen, in function of the temperature (20° to 700°C) with constant temperature rate about 350°C/hr.

TABLE 1 Chemical composition of 304 L stainless steel

C	Si	Mn	Ni	Cr	Mo	Ti	Fe
0,023	0,38	1,79	9,66	17,65	0,10	non	balance

EXPERIMENTAL RESULTS AND DISCUSSION

Cathodic Polarization Curve

Before tensile test of hydrogenated metal, we have studied the cathodic potential evolution versus current density in function of the electrolysis temperature. Figure 2 shows three potentiostatic polarization curves for 20°, 200° and 300°C. At given potential, the current density increases with the electrolysis temperature, excepting at - 3 volts/Ag; at 20° and 200°C current densities are equal. Also the both current densities increase monotonously with cathodic potential. When cathodic electrolysis is achieved at 300°C, the current density increases rapidly to a maximum value at - 2 volts/Ag, decreases at - 3 volts/Ag, then increases again. The value of the maximum current density $(I_c)_{max}$ at - 2 volts/Ag for 300°C electrolysis temperature, is about one order of magnitude higher than for the case of 200°C electrolysis condition. We think that the decreasing current density is due to the formation of instable hydride film on the specimen surface (Galland, 1979).

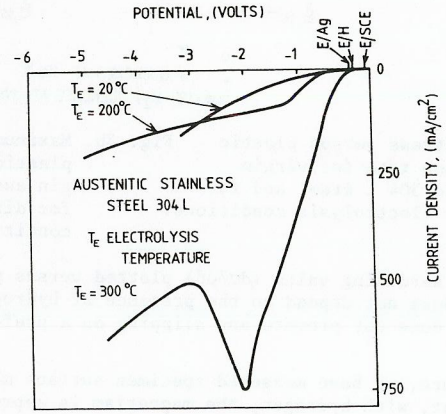

Fig. 2. Potential versus current density curves of austenitic 304 L steel, for different electrolysis temperatures, 20°, 200° and 300°C.

Cathodic Potential Polarization and Plastic Deformation Rate

To study the influence of cathodic potential polarization on the mechanical properties at room temperature of stainless steel hydrogenated at 300°C, we have choosen two values of cathodic potential conjugated with two times of cathodic electrolysis:

(-2 volts/Ag, 2 hr), (-4 volts/Ag, 2 hr) and (-4 volts/Ag, 4 hr). The minimum time choosen here is about one order of magnitude higher than the theoritical time to obtain 99 % between core and surface concentration. Figures 3a and 3b show that without hydrogen, the maximum stress σ_m of stainless steel, whether quenched at -196°C or not, is very sensitive to plastic deformation rate $\dot{\varepsilon}$. σ_{max} decreases when $\dot{\varepsilon}$ increases, showing that, at high deformation rate, the specimen temperature increases approaching the M_d temperature at which α' transformation is lower (Guillaume, 1978). On the other hand, σ_m increases with $\dot{\varepsilon}$, Fig. 3a., i.e. when dislocations motion velocity in the metal is near that of hydrogen induced by diffusion process. The maximum plastic deformation δ_m is not sensitive to plastic deformation rate. In any way, σ_m and δ_m decrease when the metal is hydrogenated at 300°C. This decrease depends on $\dot{\varepsilon}$, time and polarization potential. The maximum embrittlement is obtained when the stainless steel is polarized at -2 Volts/Ag during 2 hours, i.e. at the maximum current density (Fig. 2). Decreasing embrittlement after critical electrolysis time is probably due to retrodiffusion phenomena (Galland, 1967).

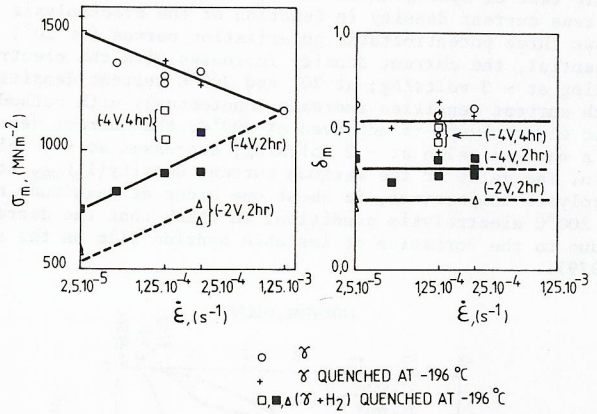

Fig. 3a. Maximum stress versus plastic deformation rate for virgin austenitic 304 L steel and for different electrolysis conditions.

Fig. 3b. Maximum plastic strain versus plastic deformation rate for virgin austenitic 304 L steel and for different electrolysis conditions.

The dependence of hardening value ($d\sigma/d\delta$) plotted versus plastic deformation shows that, fig. 4, it does not depend on the presence of hydrogen in the metal. At least, internal hydrogen does not promote any slipping on a preferential crystallographic plane.

After tensile rupture, we have measured specimen surface magnetization percentage. Figure 5 shows that, with hydrogen, the magnetism is approximately constant with $\dot{\varepsilon}$, still lower than that of stainless steel without hydrogen, in which, magnetism decreases with plastic deformation rate. Such results indicate that α' martensite transformation is restrained in the presence of hydrogen (Inoue, 1979).

The X-rays intensities peaks $\varepsilon'(100)$, $\gamma(111)$ and $\alpha'(110)$ are measured on specimen surfaces after tensile rupture with $\dot{\varepsilon} \simeq 2.5\ 10^{-5}\ s^{-1}$. Table 2 shows that, at -196°C quenching austenitic 304 L alloy, promotes $\varepsilon'(100)$ formation and reduces the percentage of $\alpha'(110)$. This evolution is more important when austenitic structure is hydrogenated before quenching. Without quenching the hydrogenated austenite, there is no $\varepsilon'(100)$ formation and $\alpha'(110)$ is markedly increased but still lower than in

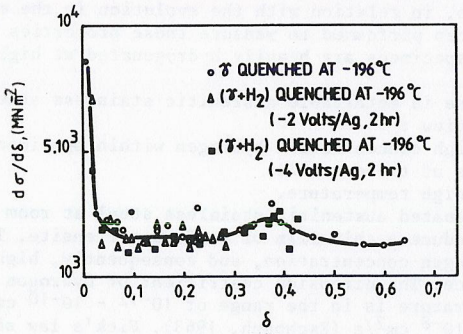

Fig. 4. Consolidation curves for different hydrogenation conditions.

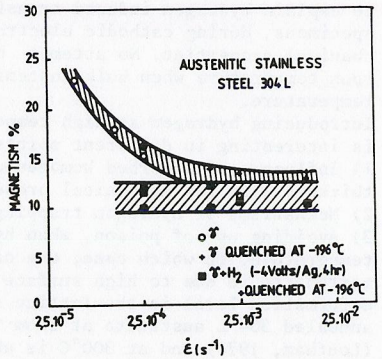

Fig. 5. Magnetism versus plastic deformation rate for the austenitic 304 L steel tensiled to rupture at 20°C. Action of internal hydrogen.

the case of γ structure without hydrogen. These results corroborate with the former ones, i.e. hydrogen decreases $\alpha'(110)$ formation and promotes $\varepsilon'(100)$ when hydrogenated austenite is quenched at -196°C.

TABLE 2 % intensity evolution of $\varepsilon'(100)$, $\gamma(111)$ and $\alpha'(110)$ after tensile rupture at room temperature. Austenitic structure hydrogenated at 300°C, with and without quenching at -196°C.

structure	% intensity		
	$\varepsilon'(100)$	$\gamma(111)$	$\alpha'(110)$
γ	0	18	82
$\gamma + H_2$	0	26	74
γ quenched at - 196°C	41	10	49
$\gamma + H_2$ + quenched at - 196°C	100	0	0

Effect of Electrolysis Temperature on Trapping Mechanisms

In this study the metastable austenitic stainless steel 304 L is cathodically electrolysed at 200°C or at 300°C, cooled at room temperature and then tensile tested to rupture at this temperature. The cathodic potential and electrolysis time are kept constant (- 2 Volts/Ag, 2 hr). Table 3 shows that σ_m and δ_m are more important in the case of 300°C electrolysis temperature than 200°C one. S.E.M. fractographs show that after tensile rupture, the fracture surface for 200°C electrolysis is brittle with cleavage patterns, and secondary cracks at grain boundaries, Fig. 6a. In the case of hydrogenation at 300°C, the fracture surface is more ductile than in the first case, with facets of quasicleavage. The fracture surface contains many coalescence microvoids, Fig. 6b. In the absence of hydrogen, the fracture surface is ductile with equiaxed dimples, Fig. 6c.

Table II : MECHANICAL PROPERTIES OF AUSTENITIC STAINLESS (*) IN FUNCTION OF TEMPERATURE OF
. HYDROGENATION
. HYDROGENATION AND OUTGASSING

Electrolysis and outgassing conditions / Mesured Parameters	γ Tensile tested at 20°	$\gamma+H_2$ at 200°C Tensile tested at 20°	$\gamma+H_2$ at 300°C Tensile tested at 20°	$\gamma+H_2$ at 200°C +outgassed at 200°C Tensile tested at 20°	$\gamma+H_2$ at 300°C +outgassed at 300°C Tensile tested at 20°
σ_m (MNm^{-2})	1040 *	568	797	995	979
$\left(\frac{\Delta\sigma_m}{\sigma_m^*}\right)$%	—	-39	-23	-4.5	-6.0
δ_m	0.46 *	0.20	0.30	0.44	0.46
$\left(\frac{\Delta\delta_m}{\delta_m^*}\right)$%	—	-56	-35	≈0.0	≈0.0

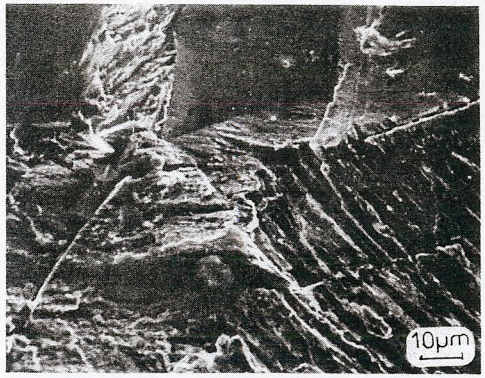

Fig. 6a. Fracture surface of cathodically electrolysed 304L austenitic steel at 200°C. Tensiled to rupture at 20°C.

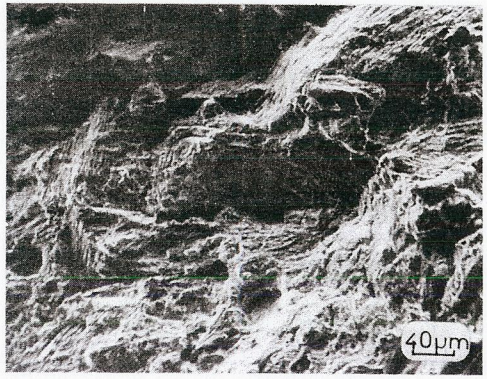

Fig. 6b. Fracture surface of cathodically electrolysed 304 L austenitic steel at 300°C. Tensiled to rupture at 20°C.

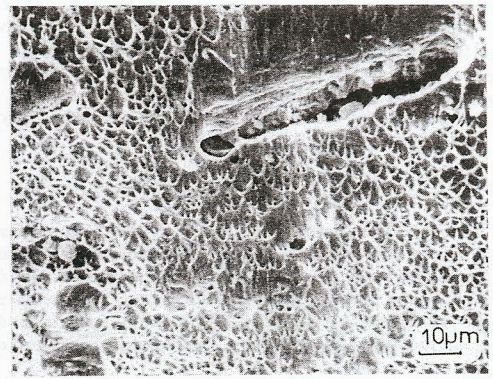

Fig. 6c. Fracture surface of 304 L austenitic steel,(tensile tested) to rupture at 20°C.

Kinetics of outgassing under vacuum (10^{-3} Pa),Fig. 7a., show that specimen cathodic electrolysed at 200°C begins to outgas at about 150°C, while the 300°C electrolysed only at about 230°C. This result indicates that in the second case, hydrogen is energetically more trapped than in the first one. Probably, interstitial to trapped hydrogen atoms ratio is very high in the 200°C electrolysis condition with respect to the 300°C one. The maximum rates of hydrogen desorption, when electrolysis is achieved at 200°C,are obtained at about 300° and 500°C. When hydrogenation is carried out at 300°C, the curve desorption rate versus temperature displays only one peak near 500°C, Fig. 7b. These results prove the existence of more than one

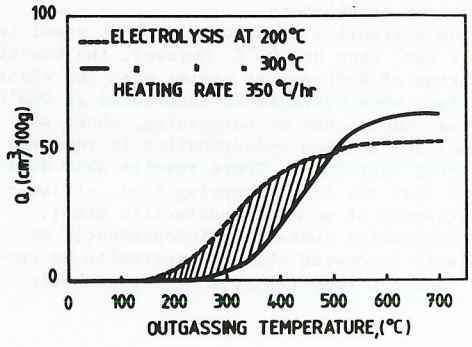

Fig. 7a. Desorbed hydrogen quantity versus outgassing temperature for austenitic 304 L steel, cathodically electrolysed at -2 Volts/Ag, 2 hr, 200° or 300°C.

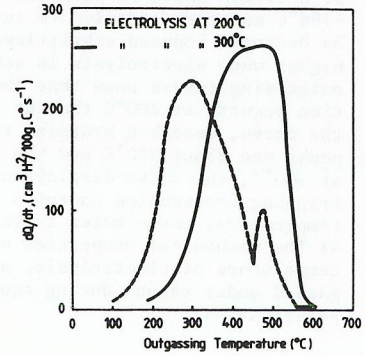

Fig. 7b. Desorbed hydrogen rate versus outgassing temperature for austenitic 304 L steel, cathodically electrolysed at -2 Volts/Ag, 2 hr, 200° or 300°C.

kind of traps. The first one (at lower temperature) contributes to the embrittlement of metastable austenitic steel.

The charged austenitic stainless steel is reheated at its electrolysis temperature during the same time that for hydrogenation and then tensile tested to rupture at room temperature. In these conditions, we have found that the mechanical properties are recovered, table 3, proving that hydrogen does not give rise to any permanent damage in the metal before tensile test, in spite of high interaction energies of trapping. The rupture surfaces show that, after outgassing, the 304 L austenitic steel is ductile with dimples or with quasicleavage and tear ridges.

CONCLUSIONS

The behaviour of austenitic structures, especially stainless steel 304 L have been studied in the presence of hydrogen. The influence of internal hydrogen previously introduced into the metal by electrolysis process of water injected in molten salts bath at 200° or 300°C, on the behaviour of mechanical properties (σ_m, δ_m) has been investigated. Kinetics of outgassing under vacuum has been done in the aim to follow the evolution of hydrogen desorption in function of outgassing or electrolysis temperatures.

The whole results suggest following conclusions :
1) The electrolysis process of water injected in molten salts bath allowed hydrogen absorption in stainless steel type 304 L, with suitable conditions of cathodic polarization, time of electrolysis (2 hours) and temperature (200° or 300°C). We have introduced in this steel an amount of about 50 ppm hydrogen
2) For a given temperature of hydrogenation, the mechanical properties (σ_m, δ_m) of the austenite at room temperature, depends on the conditions of hydrogenation, i.e. polarization potential and electrolysis time. The dependence of hardening value ($d\sigma/d\delta$) plotted versus plastic deformation shows that it does not depend on the presence of hydrogen in the metal. At least, internal hydrogen does not promote or hinder any slip on a preferential crystallographic plane in these cases.
On the other hand, hydrogen induced embrittlement at 300°C in the austenite is promoted when plastic deformation rate decreases, i.e. when the rate of dislocations motion in the metal is near from that of hydrogen atoms induced by diffusion process. In this condition α' martensite transformation is restrained in the presence of hydrogen and $\varepsilon'$is promoted when hydrogenated austenitic steel is quenched at -196°C and then tensiled to rupture at room temperature.
3) Hydrogen induced embrittlement in the austenitic structure of 304 L steel is higher when electrolysis is achieved at 200° than at 300°C. Morever, the kinetic outgassing curves show that the desorption of hydrogen is easier when the absorption occurs at 200°C than at 300°C. Also, when hydrogen is introduced at 200°C, the curve, desorbed hydrogen rate versus temperature of outgassing, shows two peaks one about 300°C and the other near 500°C. When hydrogenation is achieved at 300°C, the curve displays only one peak near 500°C. These results show different trapping interaction energies and prove that the first trapping kind, at lower temperature, contributes to the embrittlement of metastable austenitic steel.
4) The mechanical properties of the hydrogenated austenite, independently of the temperature of electrolysis, are completly recovered when the austenite is outgassed under vacuum during equivalent time and temperature that for cathodic polarization.

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