INFLUENCE OF HYDROGEN AND TEMPERATURE ON THE MECHANICAL BEHAVIOUR IN AN AUSTENITIC STAINLESS STEEL

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Abstract: The mechanical behaviour of an austenitic stainless steel has been studied in this work, by means of two techniques: disk pressure embrittlement test (French standard NF E 29-723) and special biaxial tensile test. Specimens for both techniques are embedded disks, loaded by a continuously increasing gas pressure until rupture. Tests have been performed at various temperatures, between 18°C and 655 °C, with loading speeds from 0.06 to 7 MPa/min. Their main results have been recorded as relationships between gas pressure and specimen deflection until its burst or cracking. Other observations (fracture, microstructure, etc.) are performed to assess the structural evolution with the temperature.

The influence of hydrogen is evaluated by the comparison of the rupture parameters of specimens tested similarly under helium and hydrogen. The embrittlement index, E.I is determined as the ratio of the rupture pressures under helium and hydrogen taking into account also the effects of the loading speed and the gas purity.

It has been noticed that the mechanical behaviour of the steel is strongly influenced by the apparition of a second phase in the austenitic structure: the deformation induced martensite, α', which presence is identified by microscopic observations and X-ray diffraction. At room temperature, the steel presents a relatively high sensitivity to the hydrogen embrittlement ($2.20 \leq$ E.I ≤ 2.40), while, with the temperature increasing, together with the reduction of the martensitic transformation, it was observed a rapid diminution of this sensitivity.

Obtained results allow to define the performance of this steel for thin walls applications, as it is the case of expansions bellows in the chemical industry.

1. INTRODUCTION

Usually hydrogen gas embrittlement problems are considered to be not so crucial in austenitic structures as in ferritic or martensitic materials [1, 2]. However, some unstable austenitic stainless steels can present unexpected variations of their behaviour in function of the loading mode, working environment and temperature. The characterisation of such behaviour by standard tensile testing appears often as not representative of what really happen in service conditions, especially in the case of pressure vessels. For this reason it is became necessary to apply a specific testing system, which could enable the evaluation of the material properties in conditions better related to its utilisation ones [3-6]. By means of such system, in this work it is intended to characterize the behaviour of an austenitic stainless steel, in relation with its possible use for expansion bellows and hydrogen vessels in the chemical industry.

2. EXPERIMENTAL TECHNIQUES AND INVESTIGATED MATERIAL

The hydrogen embrittlement is evaluated by the disk pressure testing, according to the French standard NF E29-732. The specimen is an embedded disk (Ø 58 mm), loaded by continuously increasing pressure of gas until rupture or cracking. The embrittlement index (E.I.) is defined by the ratio of rupture pressure under helium, pHe and under hydrogen, pH_2 (E.I. = pHe/pH_2).

The evolution of the mechanical behaviour with the temperature and the simultaneous effect of hydrogen are studied by biaxial tensile tests. These tests are performed following the same principle of disk testing, but with an increased radius (r = 4 mm) in the embedding zone, intending to localise the maximum loading at the disk pole and to obtain biaxial stresses in the cupola (Figure 1).

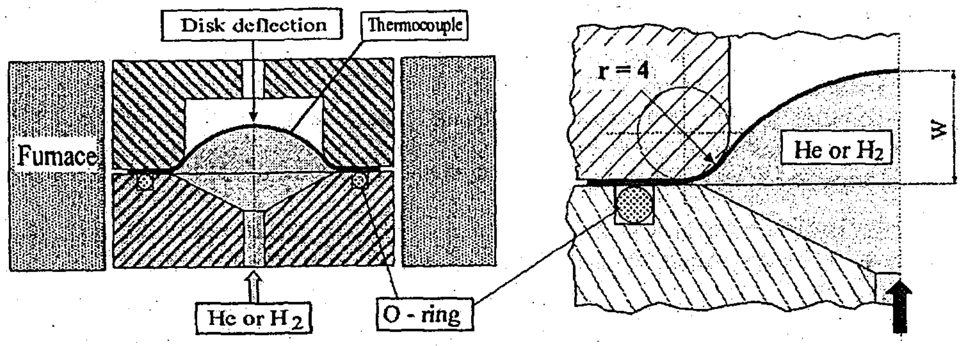

Figure 1: Disk pressure cell for biaxial tensile testing.

Tested disks are been subject to macroscopic examinations, while the characterisation of the structure and metallurgical parameters is realised by optical microscopy, SEM and X-Ray diffraction.

The investigated material is an AISI 321 Stainless Steel, which composition (Table 1), corresponds to the grade X6CrNiTi 18 -10 and to the index 1.4541 of the European standard EN 10088.

Table 1: Chemical composition of the investigated AISI 321 stainless steel

C	S	Mn	Ni	Cr	Mo	Ti	N
0.038	0.52	1.47	8.98	17.65	0.31	0.4	0.014

3. HYDROGEN EMBRITTLEMENT AT 20 °C

3.1 RESULTS OF STANDARD TESTS

There are performed three disk tests under helium and three others under hydrogen, with loading speeds (pressure increase rates) from 0.06 MPa/min to 6 MPa/min. Rupture pressures and embrittlement indexes as functions of loading speeds are shown on Figure 2. In order to evaluate the effect of hydrogen purity on the embrittlement of the steel, there are performed other tests, substituting the tightening metallic O-ring with an elastomer O-ring. Their results are shown on Figure 3

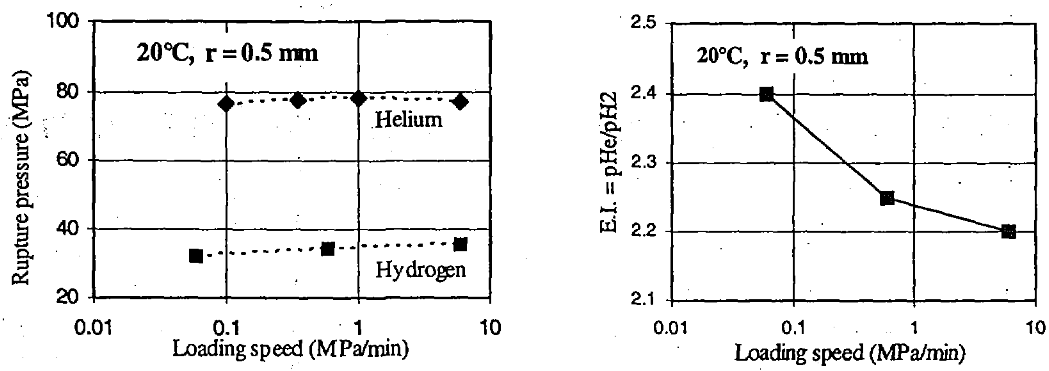

Figure 2: Effect of loading speed on the rupture pressures and embrittlement index E.I.

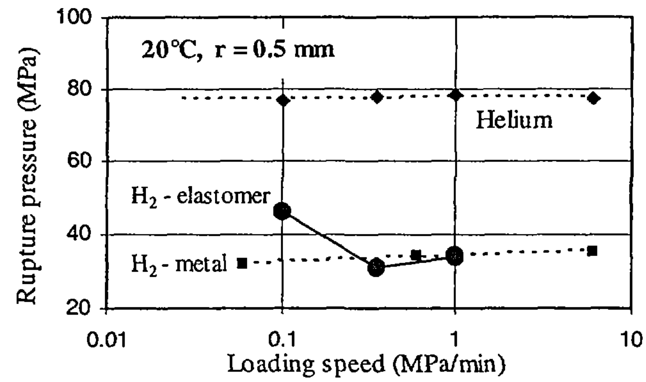

Figure 3: Effect of hydrogen purity on the rupture pressures: pure hydrogen in the case of tests realised with a metallic O-ring; polluted hydrogen in the case of test realised with an elastomer O-ring.

3.2. OBSERVATIONS AND ANALYSES

Fracture surfaces of disks tested with helium and hydrogen are examined by SEM fractography. It was observed that with helium the fracture of the steel is ductile with typical dimples of deformation. On the contrary, with hydrogen, the fracture is a brittle one, of type transgranular with secondary cracks. Microscopic observations have demonstrated that in deformed zones of disks tested under helium as well under hydrogen, it appears a second phase, with needle-shaped grains.

Through X-Ray diffraction analysis it is found that this phase has a BCC unit cell with lattice parameter a = 2.8749 Å. On the base of these data it was ascertained that the observed second phase is α'-martensite.

An indirect confirmation of the nature of this phase was also the appearance of magnetic behaviour of the steel after its plastic deformation.

3.3. DISCUSSION

- Obtained results clearly show that hydrogen has an embrittlement effect on the investigated steel, which index, E.I., is higher than 2 for all the range of loading speeds.

- The pronounced sensitivity to hydrogen of this steel, explains the relatively low influence of the loading speed on the embrittlement index. Anyhow, the direction of this influence responds to that ascertained by other studies as well [4].

- The sensitivity to hydrogen of the steel is conditioned by its stability, which index, Δ, can be calculated according to a "modified Post and Eberly formula" [1]:

$$\Delta = Ni + 0.5\,Mn + 35\,C - 0.0833\,(Cr + 1.5\,Mo - 20)^2 - 12$$

For the investigated steel, it follows that the stability index is Δ = - 1.25. Such value characterises it as disposed to the martensitic transformation, even at temperatures sensibly higher than M_s. Consequently, it can be affirmed that this steel, during the test, is subject to a strain-induced martensitic transformation, which parameter, $M_{d\,(30/50)}$, can be calculated by the Angel's formula [7]:

$M_{d\,(30/50)} = 413 - 9.5\,Ni - 13.7\,Cr - 8.1\,Mn - 9.2\,Si - 18.5\,Mo - 462\,(C+N)$, where $M_{d\,(30/50)}$ is the temperature at which 50% α'-martensite is formed after a true tensile strain (ε), of 30%.

For the chemical composition of the investigated steel, it follows that $M_{d\,(30/50)}$ = 39°C. Taking into account the fact that the disks deflection preceding the rupture, is equivalent to a true tensile strain, of about 52% [8], it can be deduced not only that during disk pressure tests at room temperature (i.e., below M_d) it is formed an amount of α'-martensite, but also that this amount must be greater than 50%.

The embrittlement effect, stimulated by the martensitic transformation, is also considerably influenced by the hydrogen purity. Figure 3 indicates that for low loading speeds, the rupture pressure under hydrogen is higher when tests are performed with an elastomer O-ring; that means that the steal can be easily passivated. This passivation leads to the E.I. decrease of about 30%: from E.I. = 2.3, for pure hydrogen (tests with a metallic O-ring), to E.I. = 1.56, for polluted hydrogen (tests with an elastomer O-ring).

Together with the increase in loading speed, the passivation effect decreases, as result of its backwardness towards the creating of new deformation surfaces.

4. BEHAVIOUR IN BIAXIAL TENSILE TESTING

4.1. TEST RESULTS

There are performed 17 tests with helium at various temperatures, between 18°C and 650°C. Disks are heated inside the test cell with heating speed of 3 °C/min and than they are pressured with loading speed of 6 MPa/min (Figure 4). Other tests are performed to study the influences of the loading speed and hydrogen at three temperature levels: 20 °C, 300 °C and 600 °C (Figure 5).

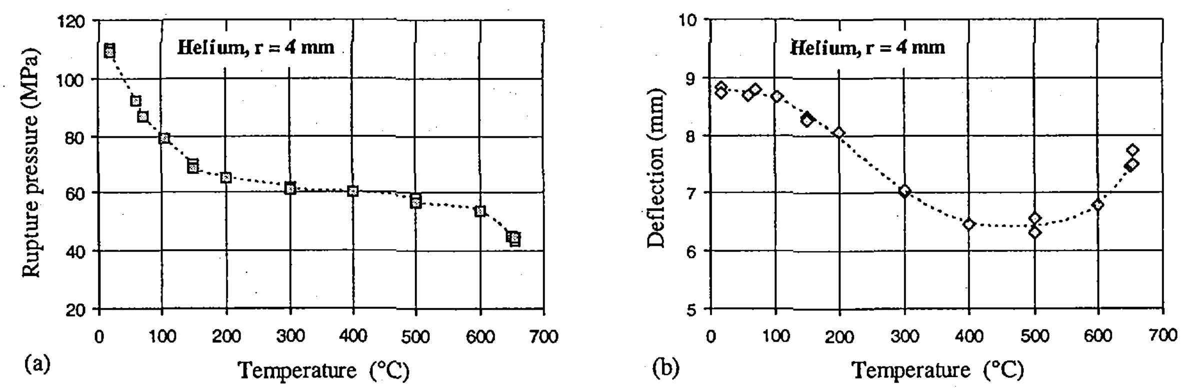

Figure 4: Influence of temperature on the rupture pressure (a) and deflection (b) in biaxial tensile testing.

4.2. MACRO AND MICROSCOPIC EXAMINATIONS

The disks tested at 300°C and 600°C present the common microstructure of a deformed austenite, where it is not observed the presence of the α'-martensite. While macrographs of the disks ruptured at 600°C, with a low loading speed (0.15 MPa/min), show a network of fine cracks on the disk cupola and in its embedding zone; micrographs of these zones evidence the presence of precipitations on the grain boundaries and intergranular cracks.

4.3. *DISCUSSION*

4.3.1 THE EVOLUTION OF THE MECHANICAL BEHAVIOUR WITH THE TEMPERATURE

The rapid decrease of the rupture pressure, pHe, on the first section of the pHe – T curve (up to about 150°C), accompanied by an insignificant diminution of the rupture deflection, must be related to the decrease of α'-martensite amount [9]. In fact, taking into consideration the value of $M_{d\ (30/50)}$, calculated for the investigated steel (39°C) and the average temperature extent of the martensitic transformation [10], it can be deduced that the upper limit of the martensite formation is between 130 and 160°C; such limit responds to the moment when the pHe – T curve changes its course (at about 150°C).

The simultaneous decrease of the rupture pressure and deflection (more marked for the deflection) on the second section of this curve (200 °C – 450 °C), when martensite is no more created, responds to the normal decrease of the mechanical properties as effect of temperature increasing.

On the third section of the pHe – T curve, above 500°C, the rupture pressure decreases and the rupture deflection increases because the material becomes subject to annealing processes [10].

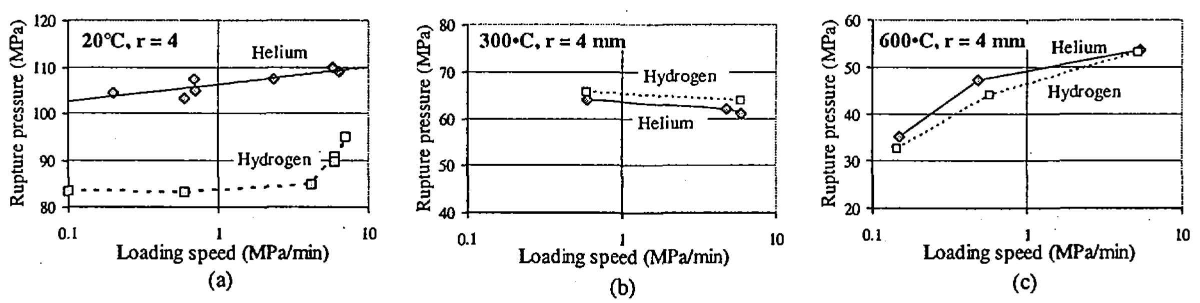

Figure 5: Influence of loading speed and hydrogen on the rupture pressures at three temperature levels: (a) 20°C, (b) 300°C, (c) 600°C.

4.3.2 THE INFLUENCE OF THE LOADING SPEED AND HYDROGEN

This influence depends on the temperature and we can specify it for three levels, 20°C, 300°C and 600°C.

Temperature 20°C: With helium the influence of the loading speed is small, like it was for the standard test. On the contrary, with hydrogen it appears that the rupture pressures increase significatively when the loading speed is increased from 4 to 7 MPa /min.

The higher stress concentration that is realised during the standard test, due to the small radius in the embedding zone (r = 0.5 mm), leads to the formation of a higher density of dislocations, which are "vehicles" of the hydrogen diffusion in the material [4]. That is the reason why during the standard test, even for low loading speeds, the quantity of the hydrogen that enters in the steel is sufficient to cause its embrittlement. While, for the biaxial tensile testing (r = 4 mm), as the density of dislocations is lower, the necessary time to introduce the same quantity of hydrogen will be longer; that explains the displacement of the loading speed influence threshold toward lower values.

This reasoning can be applied also to explain the differences of embrittlement indexes found by two kind of testing: E.I. = 2.40 for the standard test and E.I. = 1.29 for the biaxial tensile one. So, the standard testing, imposing the deformation of the steel in more severe conditions brings better into evidence the embrittlement effect of the hydrogen.

Temperature 300 °C: The absence of the embrittlement effect and the inconsequential influence of the loading speed must be explained by the martensite absence. It is evident that the austenite structure in itself is not sensitive to hydrogen.

Temperature 600 °C: The decrease of rupture pressures together with the disk deflection, for small loading speeds (< 1 MPa/min) give evidence of an embrittlement phenomenon. But on its base it can't be the hydrogen effect, not only because values of pHe and pH_2 are quite similar, but also for the fact that at 600 °C, as well as at 300 °C, there is not created any amount of martensite. The reasons of this embrittlement must be found in the beginning of precipitation processes, as it is revealed also by microscopic examinations.

5. CONCLUSIONS

The disk pressure tests evidence the fact that the AISI 321 stainless steel is sensitive to hydrogen embrittlement (E.I. > 2), but this sensitivity is not so pronounced to exclude flatly it from any application in which the working environment contains hydrogen. It is advisable to avoid the use of this steel in direct contact with pure hydrogen, while, under mixed atmospheres (containing hydrogen), as a result of passivation, the steel behaviour may be compatible with defined safety norms.

The sensibility to hydrogen is due to the steel propensity to martensitic transformation induced by the plastic deformation. After the passing of the martensitic transformation zone (above 150°C), the influence of hydrogen becomes negligible.

The range of heating temperatures up to about 600°C, within which there is a normal decrease of the steel strength (not depending on the time), can be considered as permissible for its use. While, above this limit, because of the rapid decrease of the rupture pressures, related to precipitation phenomena and accentuated with the time prolongation, the use of this steel may be not safe.

The disk pressure testing, used also as biaxial tensile testing is a sensitive and reliable method; it allows to study different phenomena and parameters in order to qualify materials for specific applications, which working conditions (pressure, hydrogen presence, temperature...) are better simulated by it than by other testing systems.

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