EFFECT OF HYDROGEN CONCENTRATION AND MnS INCLUSIONS ON THE EMBRITTLEMENT OF A HIGH STRENGTH STEEL

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ABSTRACT
Premature failure or degradation of mechanical properties of high strength steels due to the influence of hydrogen (H) causes significant problems in industries. Among many factors, MnS inclusions play an important role during forming of steels in the stage of rolling, whose presence affect mechanical properties of final products. Additionally, they act as active centers in the capture of molecular hydrogen, thus increasing the embrittlement of the steel. The aim of this paper is to contribute to the understanding of inclusions - hydrogen interaction in a high strength steel. Severe hydrogen loading of steel was performed by cathodic electrolytic charging with the addition of poisons that inhibit the recombination reaction of hydrogen and weaken the atomic bonds of the metal. Subsequently fractographic and structural aspects were analyzed using microscopy and energy dispersive spectrometry. The type, morphology and distribution of cracks was related to the amount of hydrogen added. Sulphide inclusions were found to play an important role stimulating the nucleation of cracks.

Keywords: hydrogen embrittlement, high strength steel, cracks, inclusions, fractography.

EFECTO DE LA CONCENTRACIÓN DE HIDRÓGENO Y LAS INCLUSIONES DE MnS EN LA FRAGILIZACIÓN DE UN ACERO DE ALTA RESISTENCIA

RESUMEN
Un problema significativo a nivel industrial es la influencia del hidrógeno (H) en el deterioro de las propiedades mecánicas de los aceros. Resulta muy importante poder evaluar el comportamiento que presentan las inclusiones de sulfuro de manganeso (MnS) durante el conformado del acero en la etapa de laminación, debido a que la presencia de las mismas afecta a las propiedades mecánicas del producto. Adicionalmente, éstas actúan como centros activos en la captura de hidrógeno molecular, aumentando de esta manera la fragilidad del acero. Para lograr situaciones severas de ingreso de hidrógeno se realizaron ensayos de carga electrolítica con el agregado de venenos que inhiben la reacción de recombinación de hidrógeno y debilitan los enlaces atómicos del metal. Posteriormente se analizaron los aspectos fractográficos y estructurales mediante microscopía óptica, electrónica de barrido y análisis dispersivo en energía con la finalidad de caracterizar el efecto fragilizante del hidrógeno. El tipo y distribución de las fisuras halladas presentó diferencias en relación al porcentaje de H incorporado. Los sulfuros presentes constituyeron, en la mayoría de los casos, los núcleos para el crecimiento de fisuras.

Palabras clave: Fragilización por hidrógeno, HSS, grietas, inclusiones de MnS, fractografía.

INTRODUCTION

Even at room temperature, hydrogen is one of the interstitial elements that more easily diffuses into steel. Hydrogen can be located in solid solution or it can be trapped at different sites of the microstructure. At room temperature, the diffusion depends on trapping energies, where hydrogen diffuses mainly to crystalline defects (interstitial sites, dislocations and vacancies), while at higher temperatures, the same interaction can occur with precipitates and also with inclusions. Hydrogen interactions with structural traps, such as crystalline defects (interstitial sites, dislocations and vacancies), and impurity traps, were discussed by Vlasov and Fedik [1]. Although the incorporation of hydrogen is undesirable because it deteriorates their mechanical properties, in later stages of processing (galvanizing, electroplating, etc.) its absorption is unavoidable. In such situations, the presence of certain species present in the environment acting as promoters, increase the hydrogen absorption capacity of the steel. Sulfur in steels improves machinability through sulfide inclusions like manganese sulfide (MnS), because they become elongated in the rolling direction, causing anisotropy in the mechanical properties. In addition, Clusters of inclusions reduce the toughness and ductility considerably [2]. Nowadays attention is also focusing on the role that MnS inclusions play in the embrittlement of steels. According to the classical work by Sims and Dahle [3], the morphology of MnS can be classified into three types: Type I (randomly scattered globular sulfides), Type II (thin cylindrical sulphides), and Type III (angular sulphides). Based on a previous work [4], it was verified that the generation of cracks in rolled product responds to the presence of Type II inclusions, which form highdensity chains of inclusions, also resulting in a large anisotropy in the rolled material, mainly due to deformation and elongation of MnS inclusions. These localized sulfides area favor the propagation of cracks due to the strong reduction in the ductility and toughness that they generate on the material. When hydrogen was involved in fatigue fracture, generally, embrittling effects are focused on structural imperfections developed by deformation as hydrogen trapping sites [5-6]. The purpose of this paper is to show an analysis of the influence of hydrogen trapped at MnS inclusions on fatigue mode of fracture in high strength steel.

MATERIALS AND METHODS

Forged bars of structural resulphurized high strength steel were used for this study. Cylindrical fatigue samples were machined with the longitudinal axis parallel to the bar rolling direction to minimize the effect of manganese sulphide stringers present in the material that could affect crack propagation. The chemical composition is presented in Table 1.

Table 1. Chemical composition in wt.-%

%C	%Mn	%Si	%V	%W	%Cu
0.41	1.82	0.15	0.01	<0.045	0.17
%P	%Ti	%Cr	%N	%S	%Mo
0.02	0.17	0.16	0.06	>0.088	0.058

Cathodic hydrogen chargings prior to mechanical testing were performed at room temperature using a constant voltage of 2.1 V during 6.5 hours in 1N a solution of H_2SO_4 with graphite anodic electrode, sometimes the addition of 0.25 g / L of $NaAsO_2$ acting as H-promoting agent. After precharging, and to obtain a smooth surface for the fatigue tests, all the specimens were initially ground and polished. In order to avoid temperature effects on hydrogen diffusion during grinding, liquid cooling system was used. Cyclic tension-compression deformation tests were carried out in air at 20ºC in an INSTRON 1362 testing machine under total strain control with total strain range of 1,5%. A fully reversed triangular form signal of 10 s period was selected. For comparison, charged and uncharged samples were tested. From a metallurgical point of view, the material exhibited pearlitic grains and ferrite at grain boundaries (78% pearlite - 22% ferrite). The measured grain size was about 30µm, determined with an Olympus GX51 microscope attached with a Leco IA 32 image analyzer system. A special microprint technique developed from Schober and Dieker [7] was employed to reveal hydrogen presence and distribution applying an Ag solution salt. Because of hydrogen interaction with the salt, metallic Ag particles are reduced. When metallographic samples were observed with scanning electronic microscopy (SEM) those bright irregular particles of Ag revealed were hydrogen was occluded. Finally, in order to evaluate the crack propagation mechanisms, fracture surfaces were investigateds by SEM. Ductile and brittle areas were calculated for all uncharged and charged samples, using an image analyzer software according to the methodology proposed by Michalska et al. [8].

RESULTS AND DISCUSSION

The fracture surfaces of charged and uncharged samples show marked differences. Increased roughness is observed in charged samples, as reported by Sozanska et al. [9], and also small surface cracks, particularly when poison was added. Evident increment of brittle areas in relation with the amount of hydrogen incorporated to the sample as shown in Figure 1, in contrast with the ductile fracture surface observed in uncharged specimens.

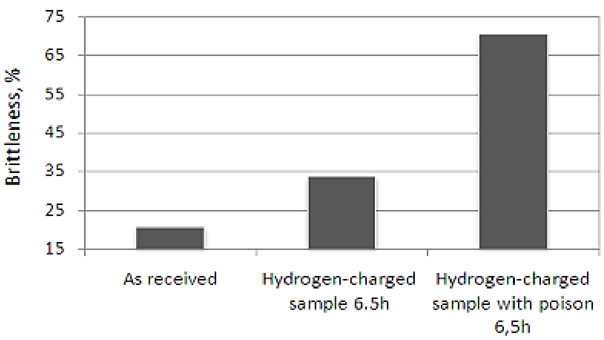

Fig.1. Evolution of brittleness.

This observation is illustrated in Figure 2, which shows the fracture surfaces of uncharged and charged samples. Whereas the presence of numerous dimples with a broad range of sizes is observed for an uncharged sample (Figure 2a), the fracture surface changes drastically to a mixed fracture type mainly characterized by quasicleavage zones with a scarce amount of striations (Figure 2b) due to the addition of hydrogen promoters.

High densities of elongated cylindrical sulfides, several of which form high-density colonies of sulphides, were identified as type II MnS, according to the criterion established by Sims and Dahle [3]. Besides, numerous sub-surface cracks were detected, possibly due to the generation of a critical stress state by hydrogen trapped at inclusions.

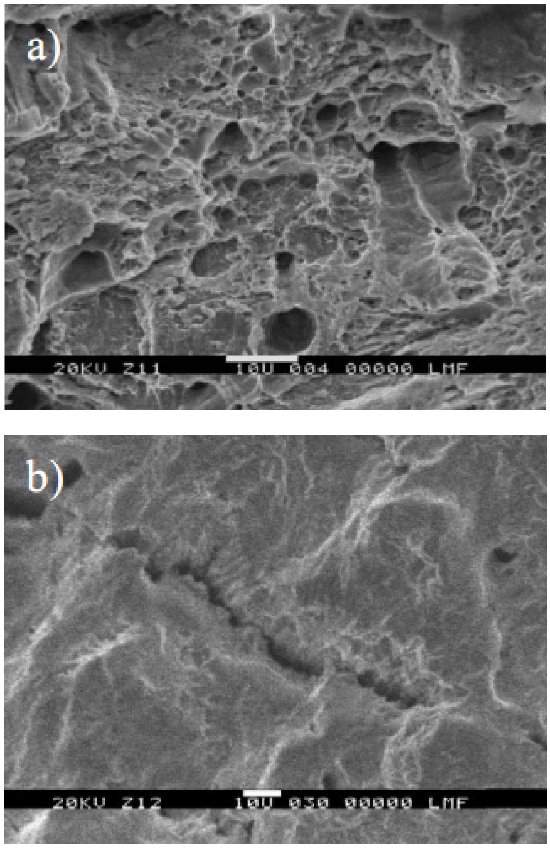

Fig.2. SEM images: a) Uncharged b) charged with poison added.

This presumption could explain the fracture of inclusions, as well as their decohesion from the matrix or lead to crack interconnection. Special attention was paid to identify crack morphologies and their relation to the presence of MnS inclusions along the fracture surface. In this sense, it was found that the amount of transgranular cracks initiated at the surface increased from 65% of the

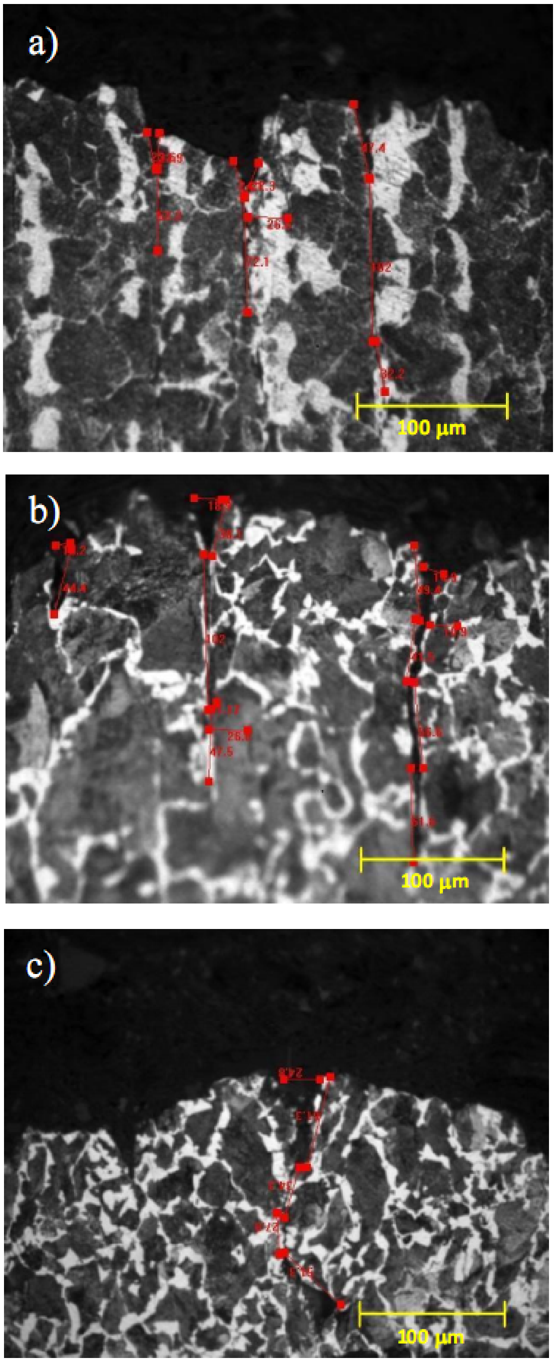

Fig.3. Cracks with linear development, [M] 500X: a) uncharged, b) H charged c) H charged with poison.

total cracks in uncharged samples to 90% when poison was added. Crack nucleation was found to occur preferentially in ductile ferrite. Figure 3 shows images of fracture surfaces with cracks of different morphologies. The predominant type found in uncharged samples was "mixed in V" which were several microns deep, crossing pearlitic grains. As hydrogen content increased, geometries described as "irregular", "zig-zag", "curved" and "linear" were observed in addition to that previously mentioned. The "mixed in V" crack type originated at the fracture surface and developed linearly up to 200 µm. However, the other types of cracks were located preferentially in the subsurface regions.

It can also be noted in Figure 3 that in the charged samples with poison added, crack growth was more developed. Figure 4 shows that the fraction of cracks associated with MnS inclusions increases with hydrogen charging and reaches a maximum value of 74% of total cracks. Perhaps this result is related with a higher affinity of hydrogen with the sulphide inclusions than with others lattice imperfections, as suggested by Tsuchida *et al*. [10]. It is suggested that hydrogen interstitial atoms situated at an inclusion/matrix interface promote voids nucleation resulting in cracks of several microns length between different sulphides as those observed in poison charged samples.

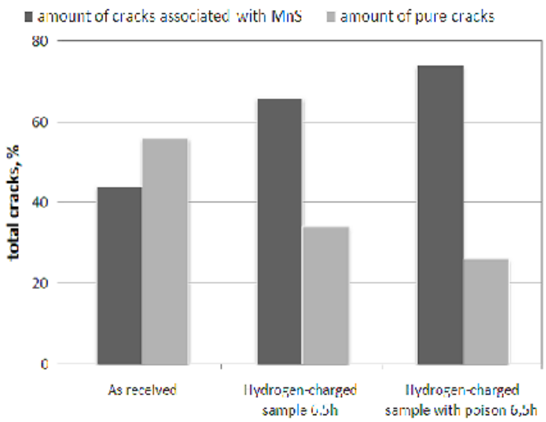

Fig.4. Fraction of cracks associated with MnS inclusions.

Figure 5a shows a SEM image of a crack, in which Ag crystal decoration technique developed by Schober and Dieker [7] was used to reveal distribution of hydrogen. The bright spots are Ag crystals that highlight the presence of hydrogen atoms. Figure 5b shows X-ray

Energy Dispersive Analysis (EDS) of specific points along the crack where MnS inclusions were detected. Crack propagation is attributed to hydrogen trapped at inclusions.

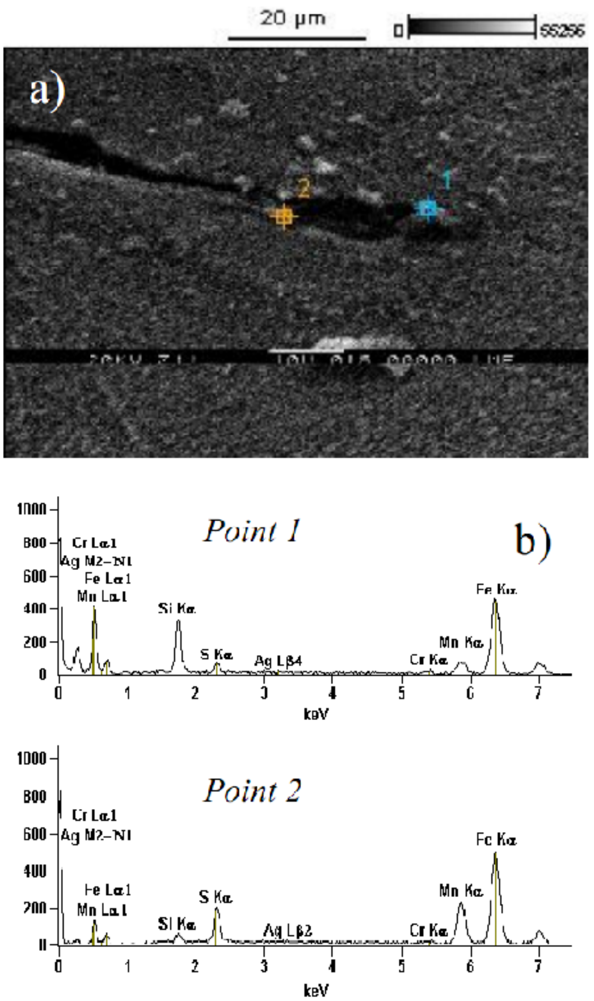

Fig. 5 a) Identification of H associated with MnS inclusion and crack, and b) EDS analysis of points 1 and 2 of Figure a).

CONCLUSIONS

The results reported in this paper indicate that manganese sulphide inclusions are the main cause for hydrogen embrittlement in high strength steels. The effect of inclusions was attributed to hydrogen trapping, that generated a high stress causing their decohesion from the matrix. This effect appears more pronounced when promoting species were added to the electrolytic solution during charging.

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