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Hydrogen Embrittlement of Advanced High-strength Steel S960MC Used in Transport and Vehicle Industry and the Influence of Potassium Thiocyanate during Hydrogenation

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Abstract

Advanced high-strength steels (AHSS) are currently facing a serious challenge from hydrogen embrittlement, which significantly affects their mechanical properties. Problems arise when hydrogen diffuses into the material and accumulates at grain boundaries, inclusions, or microcracks, degrading the material's characteristics. The main objective of the study is to investigate the effects of adding potassium thiocyanate (KSCN) to the sulfuric acid base solution during electrolytic hydrogenation using microalloyed martensitic AHSS grade S960MC. An increase in hydrogen diffusion into the examined material across its full surface is produced by adding thiocyanate ions to the electrolyte. This is the rationale behind the decision to add KSCN to the sulfuric acid base solution. The addition of KSCN to the base environment induced a considerable reduction in fracture strain, and the degradation was attributed to hydrogen buildup at grain boundaries, impurities and microcracks. These steels have an extensive list of applications in the automotive industry and are frequently used in the form of sheets for welding. Therefore, it is important to understand how their mechanical characteristics and behaviour vary in various circumstances, including hydrogen-rich environments.

Keywords

hydrogen embrittlement, advanced high-strength steel, electrolytic hydrogenation, potassium thiocyanate, transport

1 Introduction

Due to its advantageous qualities and affordable price when compared to other materials, steel is used across many industry sectors including automotive industry. It is a widely used and important component of the global economy. Currently, a lot of emphasis is being paid on lightening steel structures, reducing CO_2 emissions, increasing energy efficiency and the efficiency of the use of energy sources. In this way, transportation also becomes greener (David, 2022). The above criteria can be achieved by the creation of advanced high-strength steels (AHSS) with particular mechanical qualities, metallurgical traits, and innovative processing methods. This allows the automotive industry to achieve significantly reduced costs while achieving improved efficiency, safety standards, and manufacturability. For example, in the construction of modern buildings, steel structures, vehicles, cranes and handling equipment, steels with an increased yield strength of 690–1,100 MPa are increasingly used. In recent years, steels with a yield strength above 1,300 MPa have been developed (Aiello et al., 2023; Depover et al., 2018; Lovicu et al., 2012; Mičian et al., 2020; Perka et al., 2022; Schaupp et al., 2020; Schaupp et al., 2021; Váňová et al., 2018b; Zhao and Jiang, 2018). However, with increasing yield strength, the susceptibility to degradation of mechanical properties in the presence of hydrogen is higher. Metals interact with hydrogen in a way that reduces their fracture strain, toughness, and even strength (Aiello et al., 2023; Fangnon et al., 2021; Schaupp et al., 2018). Various factors, including the steel's chemical composition, microstructure, mechanical properties, and environmental conditions, can

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impact its susceptibility to hydrogen embrittlement (Ennis et al., 2016; Ma et al., 2021; Sojka, 2007). For example, potassium thiocyanate (KSCN) is added as a stimulator of hydrogenation. In the presence of potassium thiocyanate, hydrogen absorption increases continuously throughout the studied potential range (Tsygankova and Kos'yanenko, 2007).

The main goal of this work was to determine if the potassium thiocyanate influences hydrogen embrittlement of advanced high strength steels. Samples with three different surface treatments were subjected to electrolytic hydrogenation. This was intended to simulate the penetration of hydrogen into the material in an aggressive environment. Samples were hydrogen charged at two different environments. The first electrolyte was a sulfuric acid solution with added potassium thiocyanate, while the second was a sulfuric acid solution without potassium thiocyanate. Since potassium thiocyanate helps easier diffusion of hydrogen into the steel (Váňová et al., 2018a), changes in the mechanical properties of the samples were monitored in the initial state, after hydrogenation in a solution of sulfuric acid plus potassium thiocyanate, and after hydrogenation in a solution of sulfuric acid without the addition of potassium thiocyanate.

2 Experimental material

The material used for this research was thermomechanically rolled advanced high-strength steel S960MC in the form of sheet with a thickness of 3 mm. Tables 1 and 2 provide information on the alloying elements and mechanical properties of the experimental material. This material, characterized by low carbon content and heightened chromium content, underwent grain refinement through thermomechanical treatment, yielding tensile strength values of up to 1,150 MPa. Consequently, a fine martensitic microstructure was formed.

Table 1 Alloying elements of advanced high-strength steel S960MC in as received state [wt. %]

C	Si	Mn	P	S	Al	Nb
0.085	0.200	1.150	0.014	0.011	0.026	0.004
V	Ti	Mo	Cu	Cr	Ni	N
0.014	0.018	0.116	0.019	1.110	0.049	0.012

Table 2 Mechanical properties of advanced high-strength steel S960MC

Yield strength [MPa]	Tensile strength [MPa]	Fracture strain [%]
1014	1162	4

3 Hydrogen charging

The specimens (Fig. 1) of the experimental material underwent electrolytic hydrogen charging in three states: as received (AR) with the oxide layer, after grinding the oxide layer (G), and with a blasted surface (B). The sample served as the cathode, and a platinum-plated tungsten mesh acted as the anode. Hydrogenation occurred in two distinct environments. The first electrolyte consisted of a 0.05 M sulfuric acid (H_2SO_4) solution with the addition of 1 g of potassium thiocyanate (KSCN) per liter. The second electrolyte was a 0.05 M sulfuric acid solution without potassium thiocyanate. The hydrogenation process took place over 4 hours at a current density of 1 mA/cm^2 and a temperature of 20 ± 2 °C. After hydrogenation, the samples were dried, and tensile tests were made within 5 minutes. The tensile tests were performed using a multifunctional LFV 100 kN servohydraulic test machine. Tensile test specimens were loaded at a rate of v = 0.5 mm·min^{-1}, which corresponds to a deformation rate of approximately 10^{-4} s^{-1}.

4 Results and discussion

Table 3 displays the mechanical properties of the samples in both the initial state and after undergoing hydrogen charging. The diffusion and recombination of hydrogen atoms within the experimental steel led to a reduction in

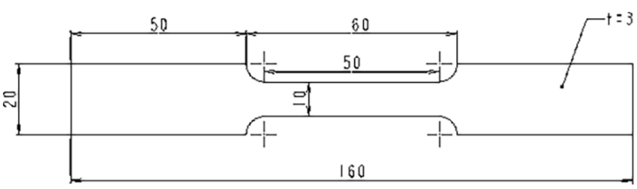

Fig. 1 The shape and sizes of the used tensile specimens

Table 3 Results of mechanical properties of samples with every surface condition with different test conditions

	Test conditions	Yield strength [MPa]	Tensile strength [MPa]	Fracture strain [%]
AR	Initial state	988.05	1157.32	4.11
	H_2SO_4	1037.67	1149.13	4.19
	H_2SO_4 + KSCN	936.11	928.97	0.19
G	Initial state	1043.16	1156.29	5.42
	H_2SO_4	1065.39	1190.08	4.40
	H_2SO_4 + KSCN	1038.71	1056.39	0.92
B	Initial state	976.72	1056.84	9.31
	H_2SO_4	798.46	1053.39	9.64
	H_2SO_4 + KSCN	975.85	985.18	1.89

fracture strain and tensile strength. The impact of hydrogen on yield strength varied depending on the surface condition and the environment. Samples with a ground surface (G) exhibited the most substantial decrease in yield strength, whereas samples with a blasted surface (B) showed the least reduction. However, changes in mechanical properties are clearly illustrated in the tensile diagrams (Figs. 2–4).

It can be clearly seen from the tensile diagrams that the addition of potassium thiocyanate to the sulfuric acid solution caused a significant decrease in the mechanical properties of the samples in every surface condition. During the tensile test, samples that were hydrogen-charged in the solution of H_2SO_4 plus KSCN broke at lower stress and strain comparatively with the samples that were hydrogen-charged in H_2SO_4 only. Those samples were less affected by the hydrogen, thus, failure occurred

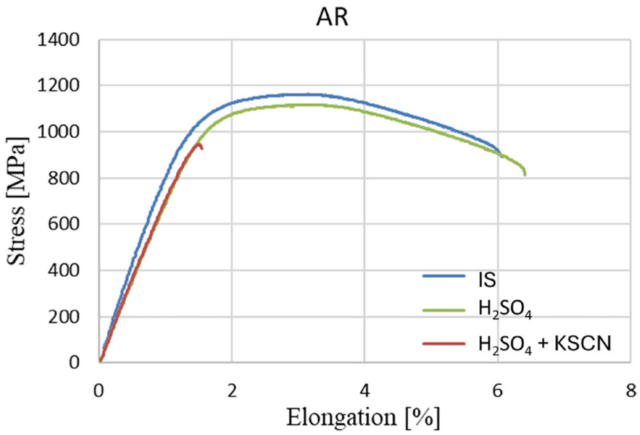

Fig. 2 Tensile diagrams of samples in their as received state (AR), in initial state (IS) and after hydrogen charging in solution of H_2SO_4 and in solution of H_2SO_4 plus KSCN

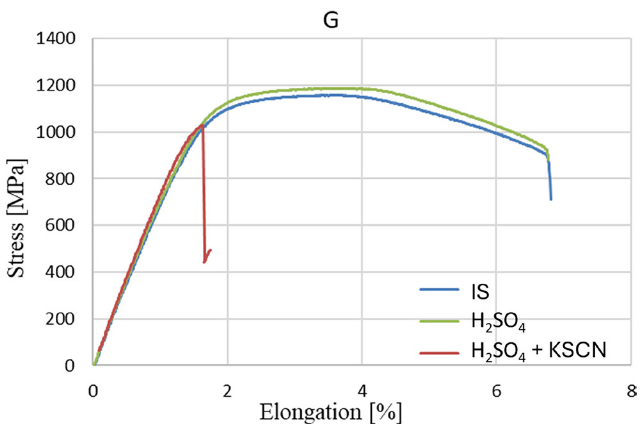

Fig. 3 Tensile diagrams of samples after grinding the oxide layer (G), in initial state (IS) and after hydrogen charging in solution of H_2SO_4 and in solution of H_2SO_4 plus KSCN

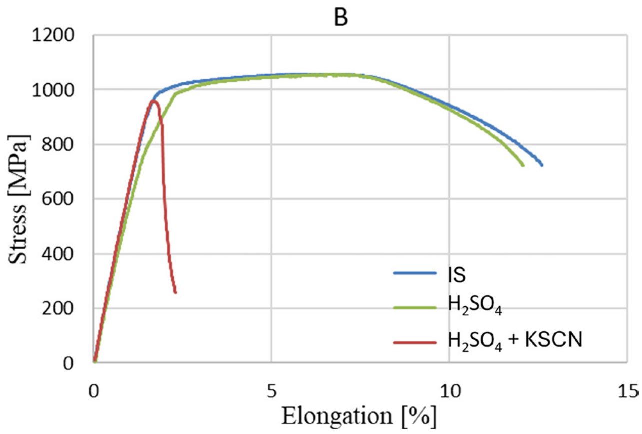

Fig. 4 Tensile diagrams of samples with a blasted surface (B), in initial state (IS) and after hydrogen charging in solution of H_2SO_4 and in solution of H_2SO_4 plus KSCN

at higher stress and strain values. Váňová et al. (2018a) in their research, hydrogenated the samples in the same way as was done in this study, i.e., in a solution of sulfuric acid with the addition of potassium thiocyanate. They found that for samples that were hydrogenated in solution without KSCN with a current density of 5 mA/cm^2, it was confirmed that KSCN helps the easier diffusion of hydrogen into steel. In comparison to the initial state, samples displayed slightly reduced yield strength, then a decrease in tensile strength only by 91 MPa occurred, and ductility lowered by 22%, where these samples showed a lower index of hydrogen embrittlement F, and that was 80%. Another type of thiocyanate was used in research made by Takagi and Toji (2012). More precisely, it was ammonium thiocyanate, which is also known as a catalyst in the electrolytic hydrogen charging methods. They investigated the effect of the NH_4SCN concentration of the solution on the diffusible hydrogen content and hydrogen embrittlement resistance. They found out that as the NH_4SCN concentration increased, the diffusible hydrogen content also increased. They performed two different methods of hydration - the immersion method of hydration and the cathodic hydration method. Cathodic hydrogen charging was performed with an aqueous solution of 3% NaCl + 0.3% NH_4SCN at a current density of 0.1 mA/m^2 for 48 hours. It is assumed that hydrogen was trapped at the same type of trap site, regardless of the hydrogen charging method, because the shapes and peak temperatures of the hydrogen evolution curves were basically identical.

On a JEOL 6490LV scanning electron microscope operating in secondary electron mode, a fractographic analysis of the fractures obtained after the tensile test was carried out. The fracture surfaces of the samples in their as received state, after removing the oxide layer by grinding and with the blasted surface obtained after tensile tests did not differ significantly from each other. Therefore, it can be stated that the samples' surface treatment had little to no impact on the fracture character. The changes in the fracture character were affected by the different environments during the hydrogenation of the samples.

The character of fracture of samples that were mechanically tested in the initial state, and thus without hydrogenation (Fig. 5), had the character of a ductile fracture (Fig. 5 (b)), including the fracture character around the segregation belt (Fig. 5 (a)). The fracture surface of the sample had the character of a ductile fracture even in the region of crack branching at the segregation belts (Fig. 5 (c)). Overall, the fracture surface was made up of ductile fracture with dimple morphology (Fig. 5 (d)).

Samples that were hydrogenated only in a sulfuric acid environment did not show any signs of hydrogen embrittlement (Fig. 6 (a), (b)). The fracture surfaces had the character of ductile fracture with dimple morphology (Fig. 6 (d)). Even in the region of crack branching at the segregation belts (Fig. 6 (c)), the fracture surface had the character of a ductile fracture.

So it can be said that it does not differ from samples that were not exposed to hydrogen at all. The fracture surfaces of the samples therefore show a similar fracture character.

Samples that were hydrogen-charged in a sulfuric acid solution with the addition of potassium thiocyanate showed a transgranular quasi-cleavage fracture (Fig. 7 (a), (b)), which is a manifestation of hydrogen embrittlement. The fracture surface was also formed by shallow pits (Fig. 7 (c)) with the appearance of fish-eyes, which are also a manifestation of hydrogen embrittlement.

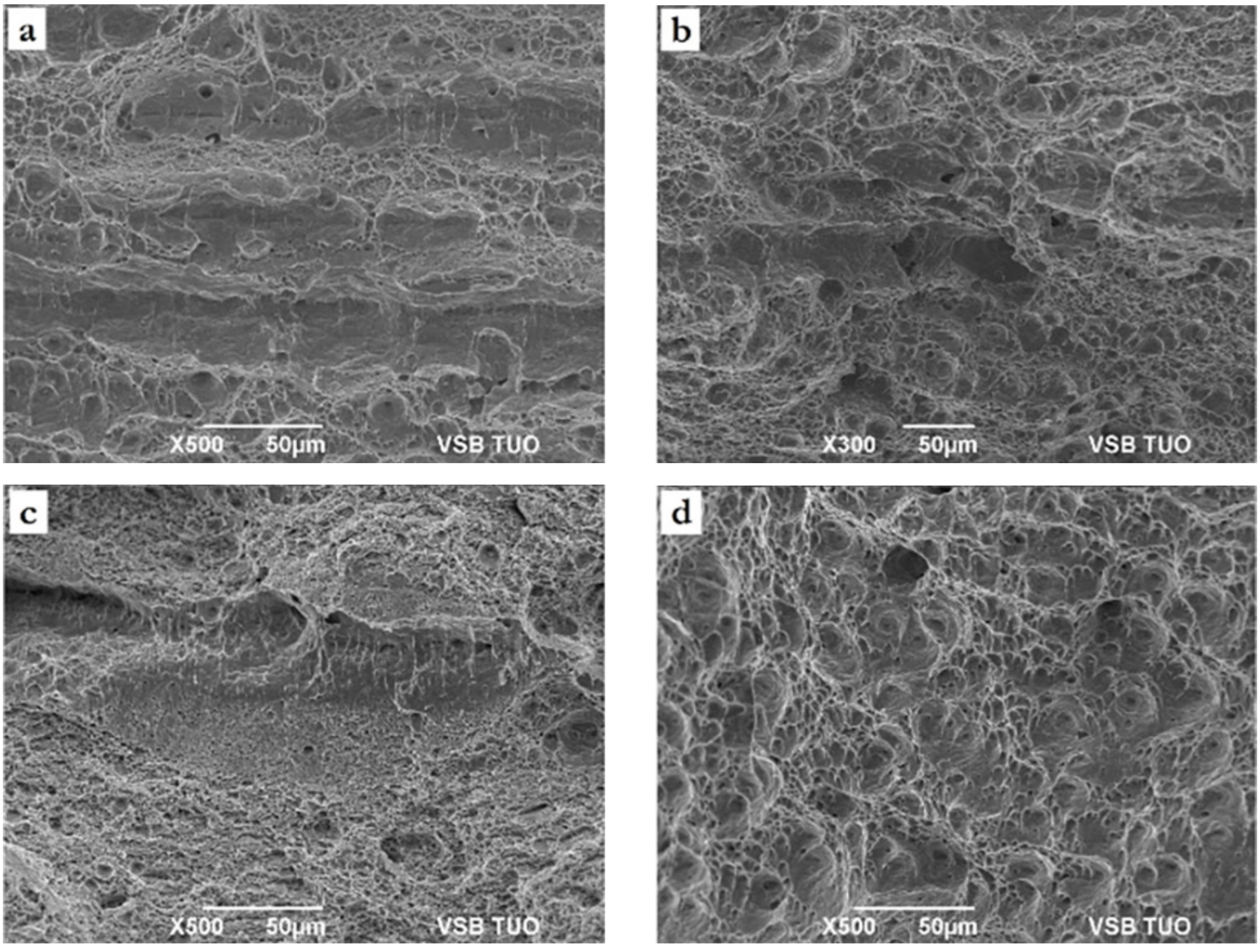

Fig. 5 Fractographic analysis of the fracture surface without hydrogen charging (a) ductile fracture even around segregation belts, (b) ductile fracture with shallow pits, (c) an opening crack with ductile fracture, (d) ductile fracture with dimple morphology

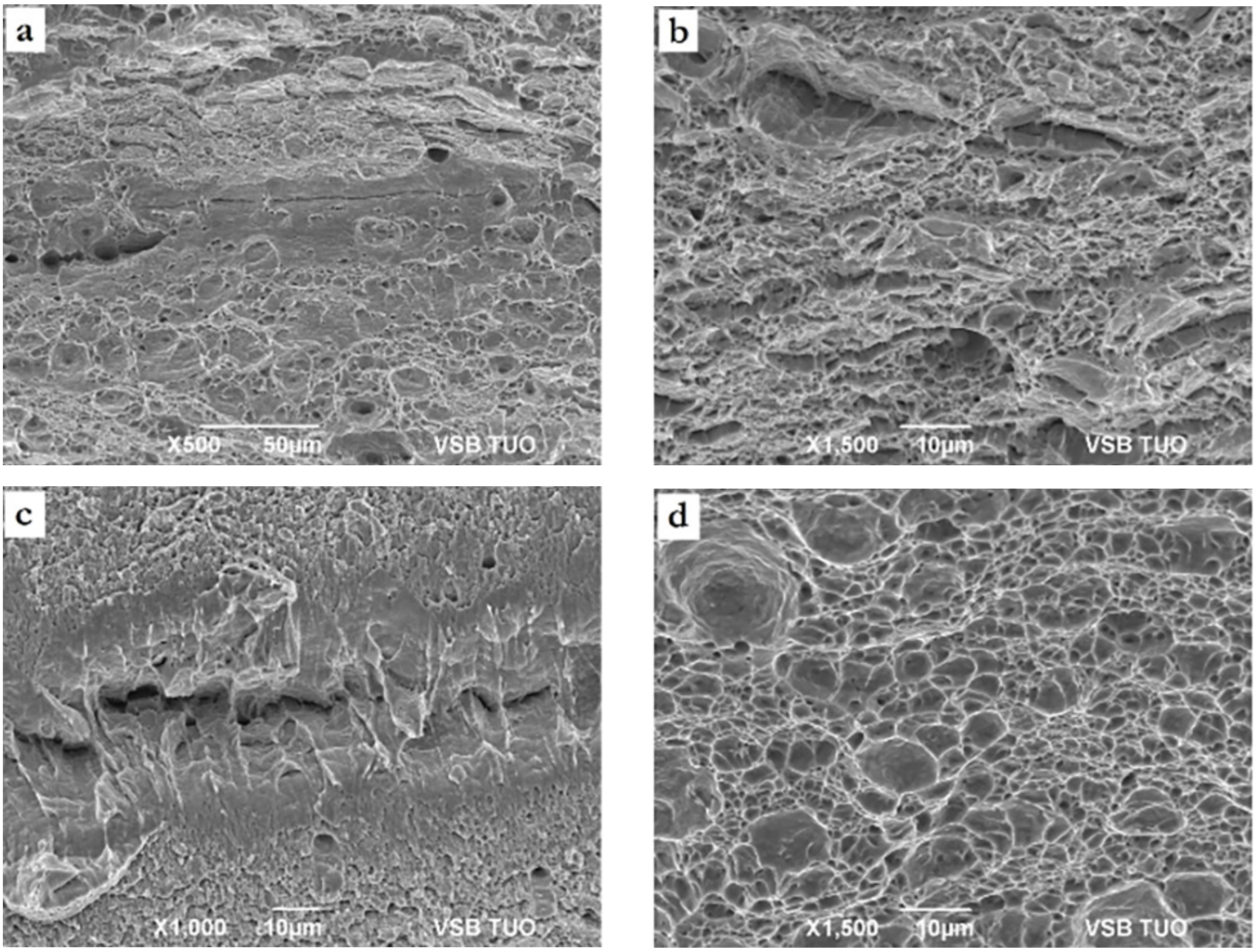

Fig. 6 Fractographic analysis of the fracture surface after hydrogen charging in an environment of H_2SO_4 (a) no indication of hydrogen embrittlement, ductile fracture even around the crack, (b) ductile fracture with shallow pits, (c) an opening crack with ductile fracture, (d) ductile fracture with dimple morphology

Larger inclusions are the main source of fish-eye formation, which extends into transgranular ductile fracture from quasi-cleavage fracture (Fig. 7 (d)).

In the research done by Váňová et al. (2018a) similar fracture surface character was obtained. In their case, the fracture surface of the sample, which was tested in the initial state without hydrogenation, was formed by two types of fractures: transcrystalline ductile fracture with dimple morphology at the edges of the fracture surface and transcrystalline quasi-cleavage fracture in the center of the fracture surface. While in the sample that was exposed to hydrogen, the character of the fracture was different. The fracture surface of this sample had the random mixture character of a transcrystalline ductile fracture with dimple morphology and a transcrystalline quasi-cleavage fracture with local occurrence of small of fish-eyes. Those fish-eyes are typical for hydrogen embrittlement and were formed around non-metallic inclusions and in the area of segregation bands.

5 Conclusion

The aim of the paper was to point out the influence of hydrogen on the mechanical properties of S960MC steel. Basically, it can be said that hydrogen embrittlement is manifested mainly by a decrease in the tensile strength of the tested steel and a significant decrease in fracture strain. Potassium thiocyanate has been shown to have a large effect on the hydrogen embrittlement of S960MC steel during hydrogenation. From the results, potassium thiocyanate helps easier diffusion of hydrogen into the steel, which was reflected in the decrease in mechanical properties. On the other hand, samples that were hydrogenated in a sulfuric acid solution without the addition of potassium thiocyanate showed only a negligible difference in mechanical properties. The highest influence of hydrogen embrittlement was recorded in samples with grinded surface.

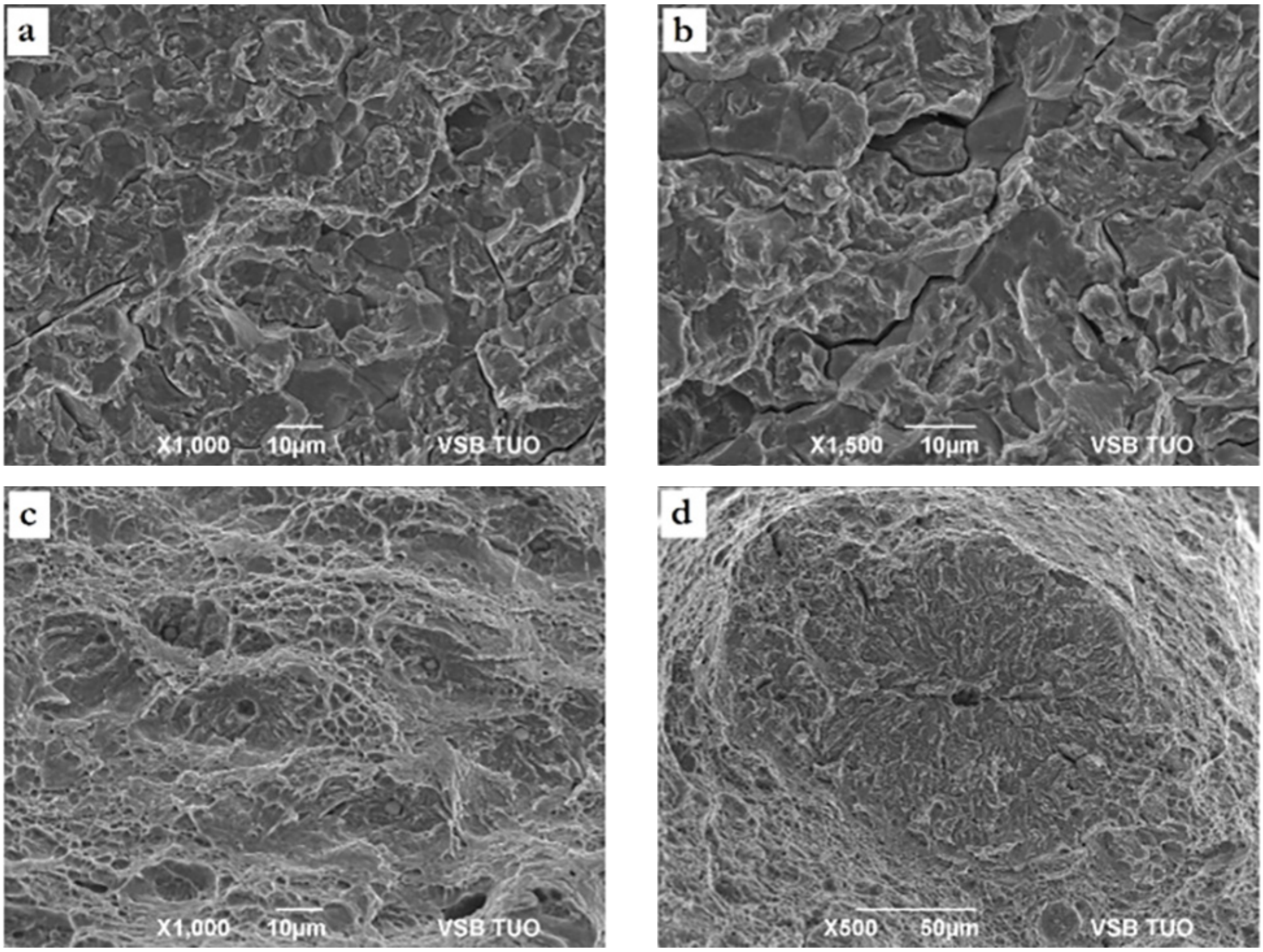

Fig. 7 Fractographic analysis of the fracture surface after hydrogen charging in solution of H_2SO_4 plus KSCN (a) partly transgranular quasi-cleavage fracture, (b) transgranular quasi-cleavage fracture, (c) fish-eyes around MnS inclusions, shallow pits, (d) fish-eye with quasi-cleavage fracture

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