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The Influence of Oxide and Sulphide Inclusions in Microalloyed Structural Steels on the Mechanism of Hydrogen Induced Cracking

Vpliv oksidnih in sulfidnih vključkov v mikrolegiranih konstrukcijskih jeklih na mehanizem z vodikom induciranega pokanja

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The effect of different microstructures and oxide or sulphide inclusions on the corrosion and hydrogen uptaken of two fine-grained microalloyed steel grades has been investigated. In the practice, fine-grained structural steels appear to be more or less susceptible to hydrogen induced cracking, probably because of various strong interactions between the absorbed hydrogen and the various alloying elements or inclusions, acting as traps. Such effect was examined by cathodic polarization, and by SEM examination of the fracture surface.

Key words: microalloyed steels, oxide, sulphide traps, hydrogen embrittlement

Preiskovan je bil vpliv mikrostrukture oz. oksidnih in sulfidnih vključkov na korozijo ter navzemanje dveh mikrolegiranih jekel za vodik. V praksi se je pokazalo, da so finozrnata konstrukcijska jekla več ali manj občutljiva na z vodikom inducirano pokanje, verjetno zaradi močne interakcije med absorbirnim vodikom in različnimi legirnimi elementi ali vključki, ki delujejo kot pasti. Takšen vpliv je bil preiskovan s katodno polarizacijo in z SEM analizo prelomnih površin.

Ključne besede: mikrolegirana jekla, oksidne, sulfidne pasti, vodikova krhkost

1. Experimental, results and discussion

1.1 Cathodic polarization experiments

The aim of the work was to investigate the resistance of two microalloyed steel grades with ferrite + bainite (F + B), and ferrite + pearlite (F + P) microstructure to hydrogen embrittlement (HE) due to the action of trapped internal atomic hydrogen. This hydrogen was produced by cathodic charging at room temperature in deaerated 1N H_2SO_4, containing 10 mg/l of As_2O_3 as poison.

The chemical composition and microstructure of the investigated steel grades are listed in **Table 1**.

The selection between different steel grades and the study of mechanisms were performed electrochemically by cathodic polarization in the above-mentioned solution at a current density of 3,7 mA/cm^2. Smooth tension specimens with a diameter of 10mm were stressed at a constant load equal to 60 % of their yield strength. After cathodic charging for different periods of time, all the specimens were taken out of the corrosion cell and finally tested by means of a tensile test, with the intention of determining the reduction of area and of fractographic analysis.

Table 1: Chemical composition and type of microstructure

Type of microstructure	Composition (wt. %)										
	C	Mn	Si	P	S	Cr	Mo	Ni	V	Nb	Cu
Fine-grained ferrite+bainite	0,08	0,36	0,34	0,011	0,004	0,56	0,27	0,17	-	0,03	0,35
Fine-grained ferrite+perlite	0,17	1,48	0,41	0,012	0,016	-	-	-	0,08	-	0,21

Tests of the microalloyed low-carbon steel grade with F + B microstructure, alloyed with small amounts of chromium, molybdenum, copper and niobium, showed that the fine-grained ferrite-bainite microstructure has a high resistance to HE, despite the moderate quantity of oxide particles. It is obvious that, from the HE point of view, these oxides do not play an important part.

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It can be considered that almost all these traps were occupied by hydrogen after 2^h of cathodic charging, since the reduction of area (from 79 to 70 %) at this time is the same as after 3 hours of charging.

The fine-grained microalloyed steel with F + P microstructure showed a high degree of susceptibility to HE, due to the action of various oxide and sulphide particles in the ferrite-pearlite microstructure. In addition, vanadium carbides (this kind of steel is alloyed with manganese and vanadium) probably represent very attractive traps, because of the strong interaction between the traps and the absorbed hydrogen. Reduction of area was drastically reduced, from 76 % to values between 18 to 23 %, after 3 hours of charging. Moreover, the results show that the steady-state stage had not yet been achieved, and a further lowering of reduction of area might still be expected.

1.2 Fractographic examination

The findings of fractographic analysis of the fracture surfaces of specimens which were, after several hours of cathodic charging, tested to failure in the tensile testing machine agree well with the results of reduction of area. In the case of the (F + B) microalloyed steel, with its high resistance to hydrogen embrittlement, the fracture surface has a predominantly ductile appearance. However, in a few places characteristic spots **(Fig. 1)** can be observed, which, in the case of the less resistant (F + P) steel, are considerably more pronounced and more numerous **(Fig. 2)**.

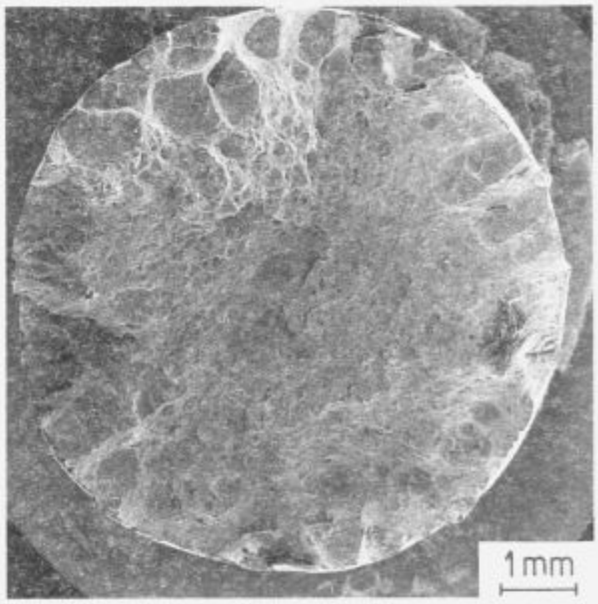

Figure 2: The fracture surface of the (F+P) steel, with larger and more numerous spots after 3^h of cathodic charging
Slika 2: Prelomna površina (F+P) jekla z večjimi in številnejšimi pegami po 3 urah katodne polarizacije

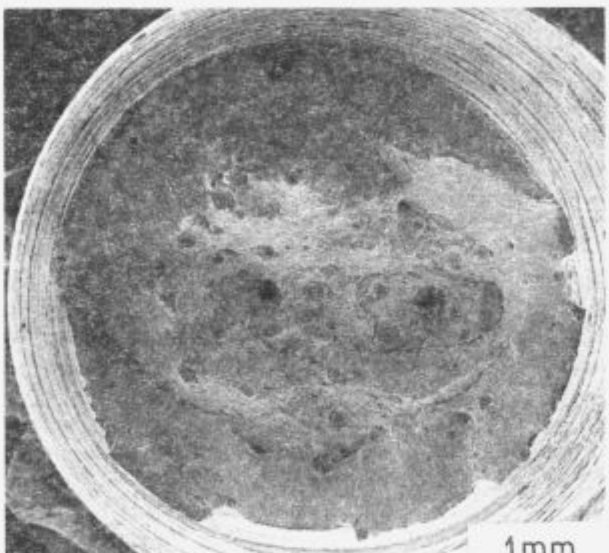

Figure 1: The fracture surface of the (F+B) steel, with the spots occurring after 3^h of cathodic charging
Slika 1: Prelomna površina (F+B) jekla s pegami, ki se pojavljajo po 3 urah katodne polarizacije

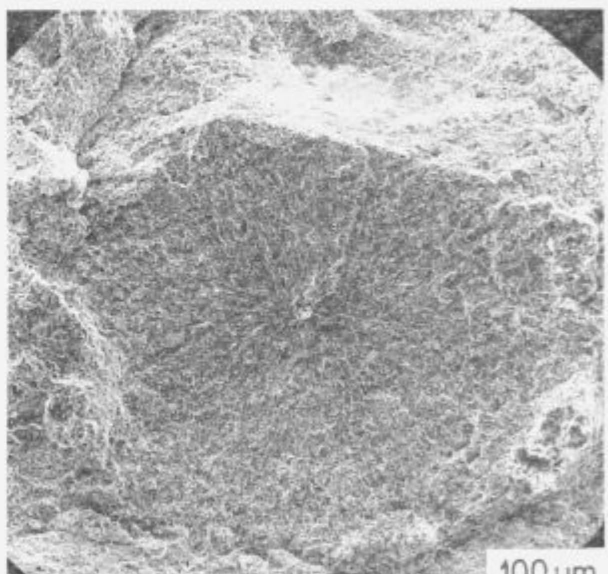

Figure 3: (F+P) steel, after charging, with a characteristic spot and inclusion in the middle
Slika 3: (F+P) jeklo po polarizaciji s karakteristično pego in vključkom v njeni sredini

In nearly all cases, in the middle of the spot an oxide inclusion occurs **(Fig. 3)**, which obviously operates as an effective trap for hydrogen. In the vicinity of such inclusions the fracture surface has a transgranular appearance **(Fig. 4 and 5)**. In the case of the (F + B) steel these places only occur rarely, which has an important effect on the measured reduction of area, which remains very high, even after 3 hours of charging.

The mechanism of forming the pots, which have such fateful consequences for the toughness of steel and its resistance to hydrogen embrittlement, could be the following. The spots may occur in those cases when there is a high enough local concentration of absorbed hydrogen in the vicinity of (e.g.) an oxide inclusion, which acts as a trap. Such a condition can be quickly established in the case of cathodic polarization, where the fugacity of hydrogen is great, or else possibly, over longer intervals, in the case of corrosion processes. In the case of cathodic polarization, the spots always occur in a plane which is at right-angles to the axis of loading of the specimen (**Fig. 6a**); for this reason, it is necessary that for their formation there is a stress in the material (the zig-zag cracks observed in stepwise cracking occur without the presence of these stresses by means of a re-combination of atomic hydrogen into molecular hydrogen according to Zappfe's pressure theory). Due to the sufficiently effective trap, with a high interaction energy with hydrogen, a critical concentration of hydrogen builds up at the interface between the trap and the lattice. As a result, at a certain distance within the vicinity of the spheroidal inclusion, a sub-microscopic initial crack (**Fig. 6b**) occurs in the lattice, growing in a direction at right-angles to the direction of loading of the material. Due to the presence of a constant stress in the material, a tri-axial state-of-stress occurs at the end of the initial crack, resulting in numerous dislocations,

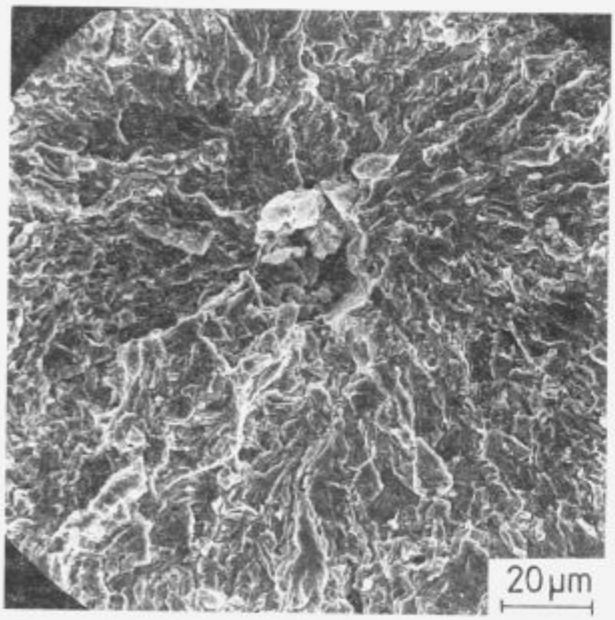

Figure 4: Magnification of **Fig. 3**. The transgranular mode of fractures can be seen in the vicinity of the inclusion

Slika 4: Sl. 3 pri večji povečavi. V bližini vključka se pojavlja transkristalna oblika preloma

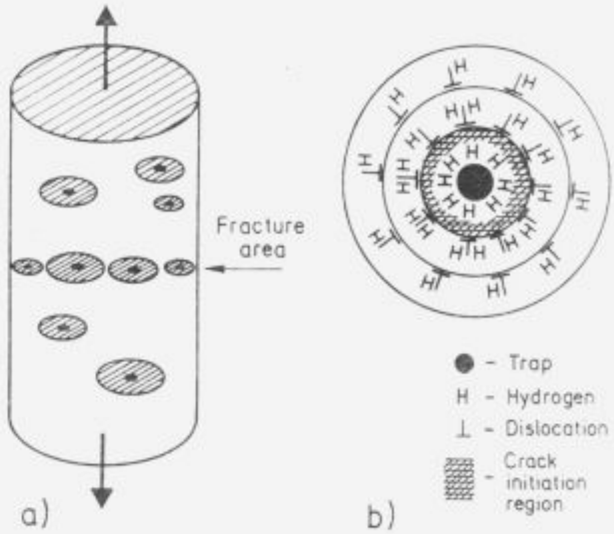

Figure 6: A schematic presentation of the mechanism which makes possible the concentric growth of cracks around a central trap (inclusion)

Slika 6: Shematičen prikaz mehanizma, ki omogoča koncentrično rast razpok okoli centralne pasti (vključka)

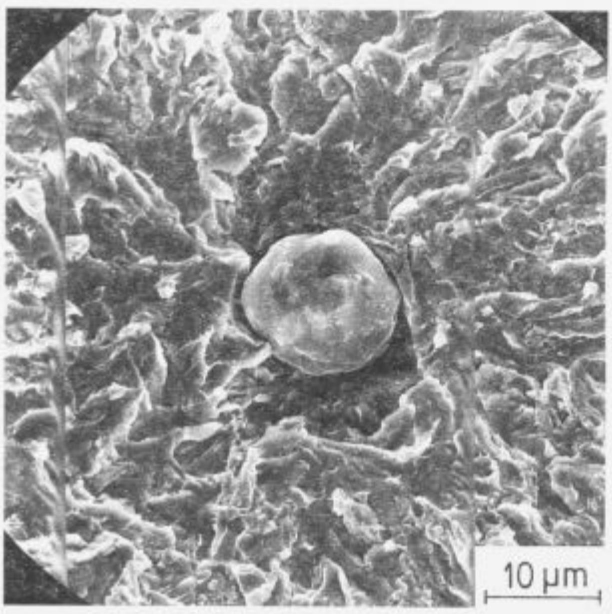

Figure 5: The transgranular nature of the fracture surface of a spot in the (F + B) steel, with a characteristic oxide inclusion in the middle of the spot

Slika 5: Transkristalna narava prelomne površine pege v (F+B) jeklu s karakterističnim oksidnim vključkom v njeni sredini

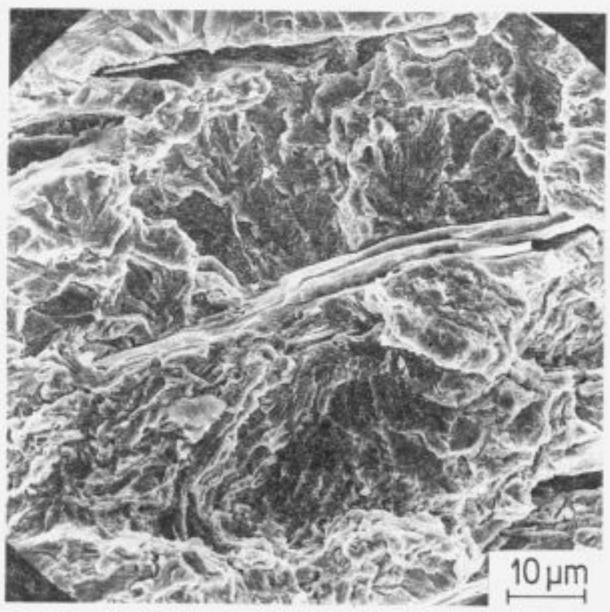

Figure 7: (F+P) steel after cathodic polarization with a fragmented sulphide inclusion and a cleavage fracture surface in its vicinity

Slika 7: (F+P) jeklo po katodni polarizaciji s fragmentiranim sulfidnim vključkom in cepilno naravo prelomne površine v njegovi bližini which, as is well-known, can act as sufficiently effective traps for hydrogen. Thus, at the head of the initial crack a new critical quantity of atomic hydrogen builds up, which can act according to the pressure theory, or, even more probably, according to the Troiano-Oriani decohesional mechanism. According to the latter, atomic hydrogen reduces the binding force between atoms of iron, causing the further growth of the crack, whose progress is made possible through the constant diffusion of hydrogen at the crack tip, where only dislocations are present. It is the latter which, after the establishment of the initial crack, are the main driving force in the further development of the crack. Thus the cycles of hydrogen accumulation and trans-crystallic splitting keep repeating themselves, which makes possible a roughly concentric growth of the crack around the inclusion, giving the cleavage nature of fracture surface. During the tensile testing of

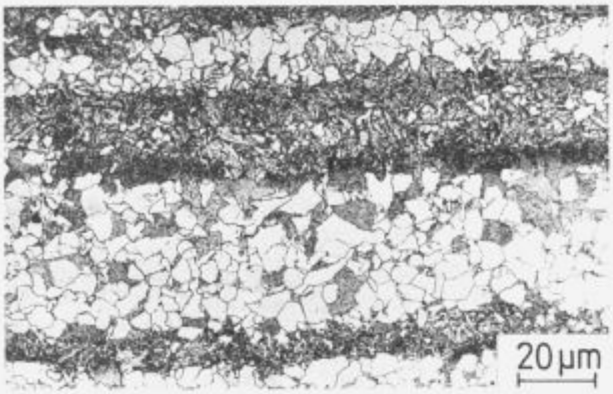

Figure 8: The microstructure of (F+P) steel, with characteristic strips
Slika 8: Mikrostruktura (F+P) jekla s karakterističnimi trakovi

such damaged material, the final fracture occurs along the plane where the greatest decohesion is present due to the presence of the greatest number of spots **(Fig. 6a)**.

In the case of (F + P) steel, apart from concentric growth of spots due to the presence of oxide inclusions, growth in the shape of an ellipse was also observed **(Fig. 2)**. The same mechanism can be applied for this mode of spot. The deviation from a more or less perfectly circular shape can be ascribed to the presence of sulphide inclusions (MnS), which are spread out along the direction of rolling (sulphide inclusions represent very effective irreversible traps - **Fig. 7**, with an energy of interaction between them and hydrogen of approximately 0,98 eV[4]. The deviation could also, even more likely, be ascribed to the striplike microstructure **(Fig. 8)**, which is typical for steels alloyed with manganese (F + P steel contain 1,48 % of Mn). The ellipsoidal shape of the spots could also occur along strips with an increased quantity of segregated manganese, which tends to catalyse the formation of bainitic or even martensitic nests. It is probable that such nests in the ferrite-pearlite microstructure may represent traps, around which, taking into account the same hypothesis, otherwise round spots are formed, but with their coalescence just one oblong elliptical shape occurs **(Fig. 9)**.

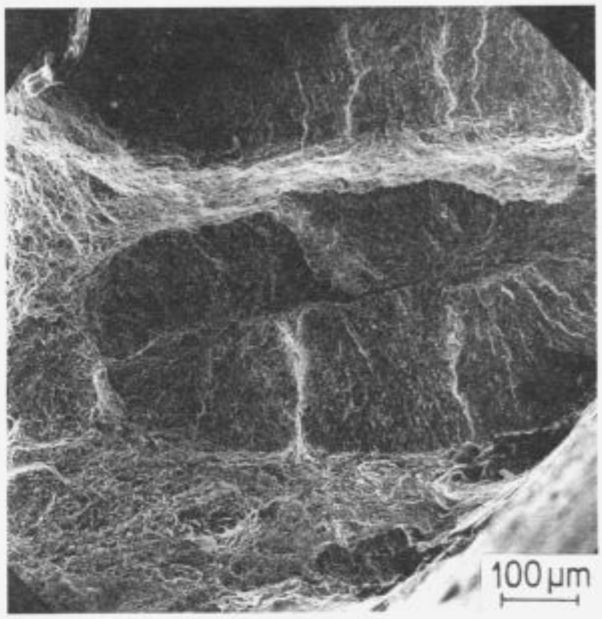

Figure 9: Spots in the shape of an ellipse in (F+P) steel
Slika 9: Pege v obliki elipse v (F+P) jeklu

2. Conclusions

The investigations clearly show the strong influence of different oxide or sulphide inclusions on hydrogen uptaken in microalloyed structural steels with ferrite-bainite or ferrite-pearlite microstructure. Tests performed electrochemically by cathodic polarization have shown that ferrite-bainite microstructure has a high resistance to hydrogen embrittlement, despite of moderate quantity of oxide particles. On the contrary ferrite-pearlite microstructure showed a high degree of susceptibility. This lowering of susceptibility could be attributed to various oxide, sulphide and vanadium carbide particles, liable to occur quasi cleavage fractures.

In the vicinity of oxide or sulphide inclusions acting as traps for hydrogen, characteristic brittle spots took place, which in the case of the less resistant ferrite-pearlite steel, are considerably more pronounced and more numerious. The final fracture of the prestressed steel occurs along the plane where the greatest decohezion is present due to the presence of the greatest number of spots.

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