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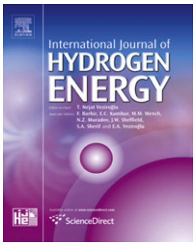

Influence of machining-induced martensite on hydrogen-assisted fracture of AISI type 304 austenitic stainless steel

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ABSTRACT

Hydrogen-assisted fracture of AISI type 304 steel has been evaluated with a special focus on the strain-induced martensite that is produced below the specimen surface during standard turning operation. Two different surface conditions were investigated: one containing martensite, resulting from the machining process, and a martensite-free state which is obtained after a proper heat treatment. Additionally, chemical composition and thickness of oxide layers, occurring in both studied cases, were analyzed by secondary ion mass spectrometry. These two different conditions were tested at room temperature in air (ambient pressure) and in hydrogen gas (40 MPa) atmosphere, respectively. Experimental results reveal a detrimental effect of machining-induced martensite on AISI type 304 steel performance in hydrogen, leading to major differences in relative reduction of area (RRA) between the as-machined and the heat-treated state for the same material. In this context, an operating mechanism based on hydrogen diffusion is discussed.

1. Introduction

Hydrogen gas storage and hydrogen use in mobile applications are related to hydrogen environment embrittlement (HEE), a phenomenon characterized by a deterioration of mechanical properties caused by the presence of external hydrogen gas. Austenitic stainless steels are frequently used for hydrogen applications due to their high ductility at low temperatures, low thermal conductivity and lower HEE compared to ferritic steels. AISI type 304 steel is the most commonly used austenitic stainless steel in general. It is often tested in the context of HEE: On the one hand for comparison with existing materials or new alloys and on the other hand due to its relatively low cost. The requirement of low costs has generated an interest in HEE of austenitic stainless steels with moderate nickel content in the range of 8–10 wt.%. In this group of steels, the resistance against HEE decreases with decreasing nickel content [1]. In order to provide a cost-effective solution, AISI type 304 steel parts are usually produced by standard cutting and turning processes which can be accompanied by the formation of strain-induced martensite at the machined surface. The intention of the present work is to elucidate the influence of present phases and microstructure at the surface on hydrogen-assisted fracture. To evaluate the influence of machining-induced martensite it is helpful to survey the possible interactions of hydrogen and austenitic stainless steels first.

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1.1. Austenite stability

For HEE of austenitic stainless steels a relation of embrittlement and austenite stability is found in literatures [2,3]. Austenite stability describes the resistance of austenitic stainless steel to transform its fcc structure to either α- or ϵ-martensite, the latter being found preferentially in Cr–Mn austenitic stainless steels due to cooling and/or deformation [4]. While ϵ-martensite is supposed to play a minor role for HEE [5,6], the formation of α-martensite with tetragonally distorted bcc structure supports the embrittlement effect significantly [7]. The latter effect arises from the diffusivity of hydrogen in the bcc lattice, being orders of magnitude higher compared to fcc iron [8]. It can thus be assumed, that HEE of conventional Cr–Ni austenitic stainless steels is proportional to their austenite stability. Han et al. investigated AISI type 304, 316 and 310S austenitic stainless steels in solution-annealed, sensitized and desensitized condition in the temperature range from 295 to 80 K. The sensitized heat treatment condition is related to a loss in wet corrosion resistance due to the precipitation of chromium rich carbides along grain boundaries. Results in hydrogen at a gas pressure of 100 kPa are compared to those obtained in helium at the same pressure [9]. First of all, no HEE was found for 310S in the different heat treatment states and all temperatures as a result of its high austenite stability. Severe HEE was found at about 220 K for 304 and 316, for the latter in the sensitized condition. The authors relate the influence of sensitization to a reduction of austenite stability due to the precipitation of carbides along grain boundaries, as only carbon in solid solution is able to stabilize the fcc structure. In case of a sufficient austenite stability due to the chemical composition, like for 310S, a reduction by carbide precipitation does not play a role for HEE. However, along carbon depleted zones the formation of strain-induced martensite is enhanced, leading to a brittle failure in the presence of hydrogen. Perng and Altstetter investigated hydrogen embrittlement of AISI 300 series at 108 kPa compared to high-manganese austenitic steels [10]. They found least HEE for an Fe–C–Al–Mn alloy and related this result to a high austenite stability. At first view, their results obtained for the Fe–C–Al–Mn alloy are in contrast to findings of Michler et al., who investigated HEE of stable high-Mn austenitic stainless steels arising from the system Fe–Cr–Mn–N [11]. The latter authors discovered severe HEE during tensile testing of these high-Mn austenitic stainless steels at 220 K. However, the only common feature of both materials, Fe–C–Al–Mn and Fe–Cr–Mn–N, is the high content of manganese and the fully stable austenitic structure, while the alloy system is completely different. According to Zhang et al., the brittle failure of high-Mn austenitic stainless steels can be attributed to their low stacking fault energy (SFE) as it induces slip planarity [12]. In general, the work of the latter authors supports the assumption of austenite stability to play a major role for HEE. They investigated eleven different austenitic stainless steels based on AISI 316 in the temperature range of 80 K–300 K and changed the nickel equivalent keeping the contents of other alloying elements constant. At the most critical temperature of 200 K a threshold value of nickel equivalent of about 10 wt.% was found. Above this value, as a result of the higher stability of the fcc phase to transform to α-martensite, no HEE was found during tensile testing in 100 kPa hydrogen gas with a strain rate of $4.2 \cdot 10^{-5}\ s^{-1}$.

1.2. Microstructural mechanisms

It is worth mentioning, that a joint movement of dislocations and hydrogen clouds is assumed by several authors as a prerequisite for hydrogen embrittlement [13,14]. This could serve as an explanation for the strong influence of strain rate on HEE, that is not found in high strain rate experiments [13,15]. The interaction of hydrogen with dislocations also explains the minimum in relative reduction of area (RRA) as a function of testing temperature. For temperatures below a critical value, hydrogen diffusivity is too low to allow it to follow dislocations [16]. At higher temperatures no α-martensite is formed. This can be attributed to the M_d temperature and a higher SFE. Additionally, the contribution of entropy hinders hydrogen to accumulate in the stress field of dislocations at elevated temperature [16].

1.3. Surface condition

In ambient atmosphere austenitic stainless steels are passivated immediately by the formation of chromium oxide and iron oxide layers. For type 304 stainless steel, semiconducting behavior of these oxide layers was found [17]. Surface oxide layers usually serve as a barrier for hydrogen dissociation and dissolution in gaseous hydrogen environments [18]. The protective function of the oxide layer against hydrogen uptake is restricted to molecular hydrogen, that needs to dissociate to enter the crystal lattice. To allow gaseous hydrogen to enter the material three prerequisites are necessary: the adsorption of molecular hydrogen, its dissociation at the surface and finally the dissolution to interstitial sites [19,20]. Due to the existence of the passivation layer, at least the second step is kinetically hindered. The situation is changed once the passivation layer is damaged. During tensile testing in high purity hydrogen at low oxygen partial pressure, the passivation layer is destroyed and fresh metal surface formed providing local areas for hydrogen to be absorbed. On the contrary, when testing in hydrogen of lower purity and higher oxygen partial pressures, less hydrogen environment embrittlement is encountered [21]. This finding can be related to the re-passivation of the surface that acts as an effective barrier for hydrogen dissociation. Fracture of oxide by tensile testing also occurs in artificial oxide layers that can be obtained by wet corrosion, high temperature treatment or oxidation in plasma. The latter approach was used by Michler et al. who investigated the influence of different coatings on HEE of 304 austenitic steels [22]. For the artificially oxidized samples no improvement of HEE was found and related to the formation of small cracks and delamination of the oxide layer.

1.4. Outline

Based on these informations one might assume a minor role of the surface microstructure on the overall mechanical