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Abnormal effect of nitrogen on hydrogen gas embrittlement of austenitic stainless steels at low temperatures

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ABSTRACT

Hydrogen gas embrittlement (HGE) of nitrogen alloyed 316 series austenitic stainless steels was investigated in the temperature range from 80 K to 300 K. Nitrogen and nickel have the same stabilizing ability for austenite, while they show different effect on HGE. Above 200 K, both nitrogen and nickel weaken HGE with decreasing strain induced α' martensite, but HGE of nitrogen alloyed steels is severer than that of nickel alloyed steels in the case of the same α' martensite content. At 150 K, almost no HGE is found in nickel alloyed 316 steels, while nitrogen causes an abnormal increase of HGE at 150 K. There are two factors influencing HGE in nitrogen alloyed 316 steels at low temperatures: one is planar slip caused by nitrogen; the other is hydrogen transport by dislocations in the localized shear slip band. It is evident that nitrogen-induced planar slip plays an important role in HGE of nitrogen alloyed 316 steels at low temperatures.

Introduction

Hydrogen energy, particularly in conjunction with fuel cells, is expected to be the next generation energy that will greatly reduce CO_2 emission and be renewable comparing with fossil fuels [1–6]. However, there are many issues that must be overcome before commercializing hydrogen energy. Hydrogen storage is the key technology for the fuel cell development. Till now, the present hydrogen storage systems include gaseous hydrogen, liquid hydrogen and hydride storage systems [7–14]. Metallic materials used for the components of these hydrogen storage systems are always exposed to hydrogen, whereas hydrogen embrittlement (HE) in hydrogen atmosphere (hydrogen gas embrittlement: HGE) is critical for the safe use of fuel cells, particularly liquid

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hydrogen storage at low temperatures. Austenitic stainless steels are good candidate structural materials for the components used in hydrogen storage systems, but they suffer from HGE [15–20]; thus their HGE resistance needs to be improved.

Nitrogen as an alloying element in austenitic stainless steels is a strong austenite stabilizer and an effective strengthener for solid-solution of austenite [21,22]; thus, it is favorable for high nitrogen austenitic stainless steels to obtain higher strength without losing ductility and to substitute expensive nickel by nitrogen in austenitic stainless steels [22–24]. The strengthening of austenite by nitrogen has been studied extensively, particularly that at low temperatures. In metastable austenitic stainless steels, such as AISI316LN (17Cr–12Ni–1Mn–2.5Mo–0.5Si- (0–0.3)N) [25–28] and AISI304LN (18Cr–10Ni–1Mn–0.5Si- (0–0.3)N) [26,28], the yield strength (YS) increased greatly with increasing nitrogen content and with decreasing temperature, however, nitrogen had little effect on the ultimate tensile stress (UTS) since strain-induced α' martensite besides nitrogen also contributed to UTS at low temperatures. The ductile fracture with dimples was found at 77 K by the Charpy impact test in the type of 316LN steel with 0.14 and 0.25 wt.% nitrogen [29,30]. However, with nitrogen content increasing to 0.56 wt.%, the 316LN steel showed the ductile to brittle transition (DBT) behavior, and some flat facets were found in dimples on its fracture surface at 77 K [31].

In stable austenitic stainless steels, such as 17Cr–10Mn–5Ni–1N, 26Cr–31Ni–2Mn–3Mo- 0.35N [22], 18Cr–16Ni–10Mn-0.4N [32], 18Cr–18Mn-0.5N and 19Cr–19Mn- 0.8N [33], the strengthening effect by nitrogen became more effective with decreasing temperature than that in metastable austenitic stainless steels [22,32–34]. Owen and Grujicic [35] interpreted the abnormal nitrogen effect on the increase in the yield strength of austenitic steels at low temperatures in terms of the nitrogen-caused bcc-like splitting of the dislocation core. However, the temperature behavior of the yield stress is obviously consistent with Seeger's theory [36]. The nature of the nitrogen effect on the yield strength at low temperatures was explained by Gavriljuk et al. based on the nitrogen-induced splitting of dislocations at low temperatures [32]. Metals and alloys with a FCC structure are generally ductile even at low temperatures. However, the DBT behavior and the cleavage-like fracture were observed at low temperatures in high-N and high-Mn stable austenitic steels, such as 18Cr–18Mn- (0.5–0.7)N [32,34,37], 19Cr–19Mn-(0.8–0.9)N [30,31,33] 18Cr–16Mn–2Mo-0.66N [29], 17Cr–13Ni–1Mn–2Mo-0.5Si-0.56N [31,33]. Tomota et al. [31] suggested that the slipping-off of active slip planes resulted in the brittle fracture in high-N austenitic steels, whereas Liu et al. [38] proposed that the brittle fracture attributed to the annealing twin boundary cracking.

Nitrogen improves the HE resistance of metastable austenitic steels under cathodic and thermal hydrogen charging at room temperature. In metastable austenitic stainless steels, such as AISI304 (18Cr–10Ni–1Mn–0.5Si) [39], AISI316 (17Cr–13Ni–2Mn–2Mo–0.4Si), AISI321 (17Cr–11Ni–2Mn–0.4Si–0.5Ti) [40], nitrogen alloying decreased the hydrogen-induced degradation of mechanical properties because nitrogen can stabilize austenite to suppress the strain-induced α' martensitic transformation and α' martensite with bcc structure is inherently more susceptible to hydrogen induced cracking than austenite with fcc structure [41].

In stable austenitic stainless steels, such as 21Cr–6Ni–9Mn [42], 18Cr–19Mn [43], HE was strongly dependent upon nitrogen content. Above 0.31 wt.% nitrogen, a change from ductile rupture to intergranular fracture appeared in the H-charged 21Cr–6Ni–9Mn steel [42]. The hydrogen-charged 18Cr–19Mn steel also showed the change from ductile rupture to intergranular fracture below 1.0 wt.% nitrogen, and the fracture mode changed from intergranular to transgranular above 1.0 wt.% nitrogen [43]. A hypothesis was proposed that the short-range order (SRO) caused by nitrogen might trigger planar-slip [44–47]. Both nitrogen and hydrogen assist the coplanar dislocation motion which greatly enhances hydrogen induced cracking in austenitic stainless steels [48–50]. Although it was reported that HE is dependent on temperature and HE at low temperatures is more severe and reaches a maximum at around 200 K [16,41,51,52], the effect of nitrogen on HGE of austenitic stainless steels at low temperatures has not been investigated yet.

In this study, the effect of nitrogen on HGE of Fe–11-Ni–17Cr–2Mo alloys, based on the type 316 stainless steel, was investigated in the temperature range from 80 to 300 K. The role of nitrogen in HGE of nitrogen alloyed 316 steels at low temperatures was discussed in comparison with nickel alloyed 316 steels.

Experimental

Type 316 stainless steels of Fe–11Ni–17Cr–2Mo alloy, whose chemical composition of metallic element is comparable to type 316LN ASTM A276, were melted in at given pressures of nitrogen to change the nitrogen content up to 0.244 wt.% to study the effect of nitrogen on HGE of the materials. The materials are called as nitrogen-alloyed materials in this paper. The stability of austenite can be evaluated by nickel equivalent Ni_{eq}:

$$Ni_{eq} = Ni + 0.65Cr + 0.98Mo + 1.05Mn + 0.35Si + 12.6(C + N) \quad (1)$$

where all elements are in weight fraction [53]. The chemical compositions of these nitrogen-alloyed steels, their Ni_{eq} are listed in Table 1. In addition, type 316 stainless steels of Fe(10–15)Ni17Cr2Mo alloys were vacuum-melted with the nickel content from 10wt.% to 15wt.% to compare with HGE of the nitrogen-alloyed materials. The materials are also called as nickel-alloyed materials in this paper. Nickel contents are 9.88, 10.97, 12.11, 12.90, 13.90 and 14.88 wt.%, and their corresponding nickel equivalents are 24.20%, 25.24%, 26.45%, 27.17%, 28.29% and 29.18%, respectively. The HGE of the nickel-alloyed materials at 200 K is referred to compare that of nitrogen-alloyed materials. The details of the HGE of the nickel-alloyed materials are described elsewhere [54].

These alloys were solution annealed at 1373 K for 5 min after forging into round bars, and then machined into cylindrical tensile specimens with a gauge length of 20 mm and