Positive and Negative Effects of Hydrogen on Tensile Behavior in Polycrystalline Fe-30Mn-(6- x)Si- x Al Austenitic Alloys

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Abstract

We investigated the tensile properties of Fe-30Mn-(6- x)Si- x Al (in wt.%, $x = 0, 2, 3, 6$) austenitic alloys precharged with hydrogen gas at 10 MPa. The Fe-30Mn-6Al alloy showed hydrogen-improved elongation through enhancement of work hardening capacity in the plastic instability condition, although the other alloys did not. This improvement in elongation is considered to be a result of a reduction in stacking fault energy because deformation twinning appeared only in the hydrogen-precharged condition.

Keywords: martensitic phase transformation; hydrogen embrittlement; tension test; twinning; austenitic steel

Hydrogen is recognized as a negative solute element that deteriorates mechanical properties of advanced high strength steels. For instance, martensitic steels [1,2], dual-phase steels [3], transformation-induced plasticity (TRIP) steels [4,5], and twinning-induced plasticity (TWIP) steels [6-8] have been reported to show hydrogen-assisted cracking and its associated embrittlement.

Although hydrogen negatively affects mechanical properties in most cases, embrittlement is caused by various factors: enhancement of dislocation motion [9], reduction in surface energy and increase in interface energy [10], promotion of vacancy formation [11], reduction in stacking fault energy, etc. [12]. When hydrogen embrittlement occurs, all of these factors are noticed only as negative effects.

However, a reduction in stacking fault energy of austenitic steels is generally known to enhance work hardening [13,14], which improves tensile elongation [13]. For instance, TWIP steels were recently designed by decreasing stacking fault energy to promote deformation twinning in austenitic steels [15,16], which have drawn attention as a new class of high strength steels with excellent workability. Therefore, the hydrogen effect decreasing the stacking fault energy is expected to enhance work hardening through promotion of deformation twinning or suppression of dislocation cross-slip. Furthermore, hydrogen would segregate to partials and stacking faults due to strain aging and Suzuki effect, enhancing the effect of hydrogen on work hardening. Accordingly, the tensile elongation is also expected to be improved by hydrogen.

Astafrova et al. [17] reported that hydrogen could promote deformation twinning in a single-crystalline Hadfield steel, and accordingly, elongation and strength were improved. However, a similar strategy for positively utilizing hydrogen in polycrystalline austenitic steels has never been reported. In this paper, we report an example of positive effect of hydrogen on tensile elongation in terms of a reduction in stacking fault energy.

Fe-30Mn-(6-x)Si-xAl ($x = 0, 2, 3, 6$) austenitic alloys were prepared using vacuum induction melting with high-purity pure metals. Chemical compositions of the Fe-30Mn-(6-x)Si-xAl ($x = 0, 2,$

3, 6) alloys are listed Table 1. The Fe-30Mn-6Si alloy is known to be a shape memory alloy with deformation-induced ϵ -martensitic transformation [18,19]. In this study, Si was substituted by Al to increase stacking fault energy [15]. The stacking fault energies of the Fe-30Mn-6Si, Fe-30Mn-4Si-2Al, Fe-30Mn-3Si-3Al, and Fe-30Mn-6Al alloys have been calculated to be 16, 33, 41, and 64 $\text{mJ}\cdot\text{m}^{-2}$ by using the most recent thermodynamic data [15]. In high-Mn austenitic alloys, with increasing stacking fault energy, deformation mode changes from ϵ -martensitic transformation to deformation twinning and slip dislocation glide [13,14]. In other words, the Fe-30Mn-4Si-2Al has a smaller amount of deformation-induced ϵ -martensite [19] (which has been developed as a damping material [20,21]), and the Fe-30Mn-3Si-3Al is a typical composition of the TWIP steel [15]. Then, the deformation mode of the Fe-30Mn-6Al alloy is simple slip dislocation glide. Therefore, we expect that the deformation modes in the respective alloys change according to the hydrogen effect decreasing stacking fault energy.

Ingots of the alloys were hot-forged and rolled at 1273 K and subsequently solution-treated at 1273 K for 1 h. Water quenching was performed to suppress uncontrolled second phase formation and segregation. Tensile specimens with gage dimensions of 5.5 mm in diameter and 20 mm in length were produced by lathe. The specimen surface was mechanically polished to a mirror finish. Tensile tests were conducted at ambient temperature and at an initial strain rate of $6.7 \times 10^{-5} \text{ s}^{-1}$. Hydrogen was precharged in a high temperature, high pressure gas atmosphere. More specifically, the specimens were exposed to a hydrogen gas atmosphere at 543 K and at 10 MPa for 200 h. Hydrogen contents of the Fe-30Mn-6Si, Fe-30Mn-4Si-2Al, Fe-30Mn-3Si-3Al, and Fe-30Mn-6Al alloys charged with hydrogen were measured to be 9.86, 11.16, 14.94, and 31.23 mass ppm, respectively. These hydrogen content were determined by thermal desorption analysis from ambient temperature to 873 K operated at a heating rate of 100 $\text{K}\cdot\text{h}^{-1}$. The Fe-30Mn-6Si and Fe-30Mn-4Si-2Al specimens were tensile-tested within 1 h after the hydrogen precharging. Because the Fe-30Mn-3Si-3Al and Fe-30Mn-6Al alloys do not show thermally induced martensitic

transformation, the specimens of these two alloys were preserved at 193 K in a freezer to suppress hydrogen desorption. Then, the tests were also conducted within 1 h after retrieving them.

Optical microscopy, electron backscatter diffraction (EBSD) measurements, and transmission electron microscopy (TEM) were performed to observe damage and its associated microstructures. The specimens for optical microscopy were mechanically polished and etched with 10% HNO_3 +90% $\text{C}_2\text{H}_5\text{OH}$. The specimen for the EBSD measurement was mechanically polished to remove any damaged layer. The EBSD measurement was performed at an accelerated voltage of 15 kV with a beam step size of 100 nm. The specimen for the TEM observation was prepared by mechanical polishing and subsequent electrochemical polishing. The TEM observation was performed at an accelerated voltage of 400 kV.

Fig. 1 shows the nominal stress–nominal strain curves for the four alloys with and without hydrogen charging, and the tensile properties are summarized in Table 2. The Fe-30Mn-6Si and Fe-30Mn-4Si-2Al alloys, in which the deformation mode is ϵ -martensitic transformation, show distinct deterioration of the elongations by hydrogen uptake due to premature fracture, although the work hardening capacity is slightly enhanced in the initial stage of deformation as shown in Figs. 2a and 2b. The elongation and work hardening behavior of the Fe-30Mn-3Si-3Al alloy are not affected by hydrogen (Fig. 2c). This is probably because, the typical composition of the Fe-30Mn-3Si-3Al has already been optimized for occurrence of deformation twinning [15]. Therefore, it is considered that a further decrease in stacking fault energy could not affect the twinning behavior significantly. In contrast to these results, and surprisingly, a positive hydrogen effect appears on the elongation of the Fe-30Mn-6Al alloy. As indicated in Fig. 2d, the hydrogen-improved elongation is attributed to the enhancement of work hardening capacity in terms of Considère’s criterion. Therefore, in the following, we present hydrogen-related microstructures to discuss the reasons why the hydrogen negatively and positively affected the elongations of Fe-30Mn-4Si-2Al-Si and Fe-30Mn-6Al alloys, respectively.

The number of damage incidents is drastically increased by the hydrogen uptake as shown in Figs. 3a and 3b. More specifically, the damage incidents arise from cracking in or along ϵ -martensite as indicated in Fig. 3c. In other words, the reason for the property deterioration associated with premature fracture is hydrogen-assisted damage formation when the deformation-induced ϵ -martensitic transformation is significant. This hydrogen-assisted ϵ -martensite cracking has been reported in conventional research [12,22].

The most notable finding of this study is the positive effect of hydrogen on the elongation in the Fe-30Mn-6Al alloy. As already clarified in Fig. 2d, the improved elongation is originated from enhanced work hardening in the plastic instability condition. The set of micrographs shown in Fig. 4 indicates that the hydrogen charging promoted deformation twinning, which enhanced the work hardening capacity. As indicated by Fig. 4b, deformation twinning occurs heterogeneously. The heterogeneous appearance of deformation twins is attributed to the tensile crystallographic orientation dependence of twinning [23,24]. The promotion of deformation twinning implies a reduction in stacking fault energy. Moreover, hydrogen reducing stacking fault energy is considered to segregate on stacking faults in terms of Suzuki effect. The hydrogen segregation due to Suzuki effect would assist to take the partials apart, decreasing the twinning stress. Also note that Mahajan and Chin have proposed [25] that the twin nucleation requires that two different partials approach each other within 10 Å for the rearrangement of the dislocation core structure. Since hydrogen reduces the repulsive force acting between dislocations in an austenitic steel [9], the effect of hydrogen may promote the rearrangement of the dislocation core structure. This paper is the first to report improvement in elongation stemming from hydrogen-assisted deformation twinning in the polycrystalline austenitic steel, although the hydrogen-assisted twinning phenomenon has been reported previously [17,26,27]. Hence, we conclude that the hydrogen-reduced stacking fault energy can be positively utilized as a new structural material design strategy in hydrogen-related fields.

In summary, we found a specific condition that can demonstrate the positive effect of hydrogen on tensile mechanical properties of high-Mn austenitic steels. More specifically, it was elucidated that hydrogen-assisted deformation twinning can be utilized effectively even in polycrystalline austenitic steels. Although deformation twins in TWIP steels [7,8,28] and ϵ -martensite in TRIP steels [22] have been reported to be the initiation sites of hydrogen-induced damage, hydrogen-assisted deformation twinning enhanced work hardening capacity and its associated uniform elongation without any damage formation in or along the deformation twins. This phenomenon is envisaged to be applied in new material design strategies in hydrogen environments.

Acknowledgments

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Figure captions

Fig. 1 Nominal stress–nominal strain curves of the Fe-30Mn-(6- x)Si- x Al alloys with and without hydrogen charging.

Fig. 2 Work hardening rates plotted against true strain in the (a) Fe-30Mn-6Si, (b) Fe-30Mn-4Si-2Al, (c) Fe-30Mn-3Si-3Al, and (d) Fe-30Mn-6Al alloys. TRIP: transformation-induced plasticity; TWIP: twinning-induced plasticity.

Fig. 3 Hydrogen-induced damage associated with ϵ -martensite in the Fe-30Mn-4Si-2Al alloy. Optical micrographs of the uniformly deformed parts of the fractured specimens (a) without and (b) with hydrogen charging. (c) Phase map showing a ϵ -martensite-related **hydrogen-assisted** crack.

Fig. 4 Optical micrographs of the fractured specimens (a) without and (b) with hydrogen in the Fe-30Mn-6Al alloy. (c) Bright-field transmission electron microscopy image of the hydrogen-charged Fe-30Mn-6Al alloy. (d) Corresponding diffraction pattern and (f) its key diagram. (f) Dark-field transmission electron microscopy image showing deformation twins. The beam axis is $\langle 110 \rangle$.

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Table 1 Chemical compositions of the alloys used (wt.%).

Alloys	Mn	Si	Al	Fe
Fe30Mn6Si 0Al	30.08	6.08	0.004	Bal.
Fe30Mn4Si 2Al	29.99	4.06	1.98	Bal.
Fe30Mn3Si 3Al	29.86	3.04	2.98	Bal.
Fe30Mn0Si 6Al	30.1	0	5.75	Bal.

Table 2 Mechanical properties of the Fe-30Mn-(6- x)Si- x Al alloys with and without hydrogen gas charging. σ_B : tensile strength, $\sigma_{0.2}$: 0.2% proof stress, δ_t : uniform elongation, δ_u : total elongation, ϕ : reduction of area.

Alloy	Hydrogen charging	σ_B (MPa)	$\sigma_{0.2}$ (MPa)	δ_t (%)	δ_u (%)	ϕ (%)
Fe30Mn6Si0Al	Non-charged	769	204	33.0	32.7	27.9
	H-charged	660	200	18.3	18.2	18.1
Fe30Mn4Si2Al	Non-charged	682	258	77.3	67.9	71.7
	H-charged	665	278	60.0	55.1	43.2
Fe30Mn3Si3Al	Non-charged	587	209	97.7	82.6	83.6
	H-charged	589	220	98.9	84.2	78.1
Fe30Mn0Si6Al	Non-charged	475	192	56.4	45.3	84.7
	H-charged	473	187	65.4	50.7	81.7

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