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# Ultra-grain refinement effect on tensile and phase transformation behaviour in a metastable austenitic steel charged in hydrogen gas

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## Abstract

To ensure the safety of hydrogen systems, materials must be selected according to strength levels and susceptibility to hydrogen. Austenitic steels are notoriously resistant to hydrogen embrittlement, but usually suffer from relatively low strength levels. In this study, the material used is Fe-16Cr-10Ni, a metastable stainless steel. A slab was cold-rolled to 1.5 mm thickness and annealed to produce two different austenite grain sizes (1  $\mu\text{m}$ , ultra-fine grain, and 50  $\mu\text{m}$ , coarse grain). The plate material was charged in hydrogen gas (10 MPa, 270°C, 72 hours) and the mechanical properties were evaluated by tensile testing in air. Thermal desorption spectrometry was used to confirm that there is no significant difference in hydrogen content between the two materials and that therefore grain boundaries do not play a significant role in trapping hydrogen. Tensile testing showed that the strength was increased by grain refining but that the increase in strength did not enhance the material's susceptibility to hydrogen embrittlement. Ductility, evaluated by elongation and reduction of area, decreased in both ultra-fine-grained material and coarse-grained material. Cold-rolling coupled with saturated magnetization measurements of BCC phase content showed little difference in phase transformation for hydrogen-charged and uncharged material.

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## 1. Introduction

Hydrogen-assisted cracking, and more generally the effects of hydrogen on metals are still being actively investigated. It is necessary to ensure the tools to design materials and structures to be used in the hydrogen systems and infrastructures required for hydrogen-based transportation. In the case of austenitic stainless steels, while the formation of martensite is not a prerequisite for the so-called hydrogen embrittlement (SanMarchi et al., 2010), deformation-induced martensitic transformation does play a critical role in the hydrogen-assisted cracking (Kanezaki et al., 2008).

As the construction of a hydrogen-based infrastructure nears, the need for cost reduction without compromising the properties of the materials becomes more pressing. Here, the use of an austenitic alloy is proposed, due to austenitic stainless steels inherent resistance to hydrogen, partly due to the low hydrogen diffusivity inside FCC metals. Using a combination of cold-rolling and annealing, the strength of the alloy will be raised through grain refinement. The thermal stability of the alloy used here, Fe-16Cr-10Ni, is known to be greatly increased through ultra-grain refinement (Tomimura et al., 1993); the effect on the mechanical stability will therefore be shown here. Furthermore, the effect of solute hydrogen, charged into the material, on the mechanical stability will be also investigated.

### Nomenclature

$d$	average grain size ( $\mu\text{m}$ )
$r$	percentage of reduction by cold rolling (%)
$\sigma$	stress (MPa)
$\varepsilon$	strain (-)
$\sigma_Y$	yield stress (MPa)
$\sigma_{UTS}$	tensile strength (MPa)
$\delta$	elongation (%)
$RA$	reduction of area (%)
$C_H$	average hydrogen content (weight ppm, wppm)
$M_{d30}$	Temperature at which 50% of the material is transformed into martensite under 30% strain (K)

## 2. Experimental procedures

In this study, the material was a laboratory-developed metastable austenitic stainless steel, Fe-16Cr-10Ni. The composition is 0.002 C, 16.4 Cr, 10.1 Ni, 0.011 Si, 0.08 Mn, 0.003 P, 0.002 S, and 0.032 N (in mass %) and the balance is Fe. This composition allows more than 90% of the material to transform into deformation-induced martensite upon 90% cold-rolling. The sheet thus obtained is then annealed to different temperatures, which reverses the martensite back to austenite, with a grain size slightly smaller than the martensite block (Tomimura et al., 1993). A 15-mm thick ingot is cold-rolled to reduce its thickness by 90% to about 1.5 mm. To obtain coarse grains, the sheet is then annealed at 1173 K for 1.8 ks, and to obtain ultra-fine grains, the annealing treatment is conducted at 923 K for 0.6 ks. The resulting average grain sizes are  $d = 1 \mu\text{m}$  for ultra-fine grains and  $d = 20 \mu\text{m}$  for coarse grains. EBSD micrographs are shown in Figure 1.

After the final heat treatment, tensile specimens were cut out by Electrical Discharge Machining and polished with emery, followed by buff. The specimens were given a final electro-chemical polishing treatment in a chromic-phosphoric acid solution, which helped remove any martensite that may have formed on the specimen surface during processing.

Hydrogen charging was conducted with commercial purity hydrogen gas (99.99999% purity) at 10 MPa, 543K for 259.2 ks (72 hours). At the same time, polished chips of alloy (5×5×1.5 mm) were introduced into the hydrogen charging chamber to measure the hydrogen content. The concentration of hydrogen in the chips was measured by Thermal Desorption Spectroscopy (TDS), with a maximum temperature of 1073K and a heating rate of 0.33K/s. Tensile testing was conducted in laboratory air less than one hour after charging. The material was stored at low temperature to prevent outgassing when testing could not be conducted directly after charging. The crosshead speed was 0.2 mm/min. To investigate the transformation of the austenite into deformation-induced martensite, cold-rolling was used with 0.2 mm reduction per pass; the alloy sheet was cooled in water after each pass. The volume of martensitic phase was measured by saturation magnetization measurement, with samples 4×1.5×30 mm in size.

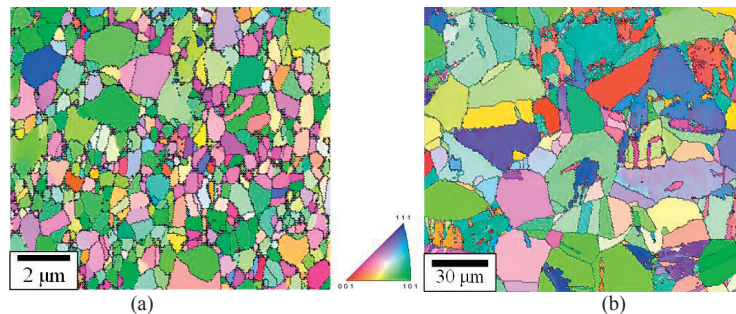


Fig. 1: Fe-16Cr-10Ni microstructure (a) ultra-fine-grained, (b) coarse-grained

### 3. Results and discussion

TDS measurements after gaseous hydrogen charging indicated that the average hydrogen content was  $C_H = 23.6$  wppm for ultra-fine-grained Fe-16Cr-10Ni and  $C_H = 22.1$  wppm for coarse-grained Fe-16Cr-10Ni. There was no significant difference in content, and therefore the effect of grain boundaries on hydrogen trapping is deemed negligible.

The results of the tensile tests are shown in Figure 2. Hydrogen did not affect the yield stress and tensile strength dramatically, however it clearly affected the ductility, particularly in the case of the coarse-grained material. Table 2 gives the average mechanical properties for hydrogen-charged and uncharged material for both ultra-fine-grained and coarse-grained steels. Most importantly, the yield stress increased more than two times and hydrogen did not affect negatively the strength gain in ultra-fine grains. Rather, the negative effect of hydrogen on ductility was lessened in ultra-fine grains. Fine grains improving the resistance of an austenitic steel to hydrogen had already been reported, to different scales (Rozenak and Eliezer, 1983; Brass and Chene, 2006). The improvement of tensile properties, along with the increased resistance to hydrogen are related to the decreased slip distance in the ultra-fine grains. In the case of the Brass and Chene study (2006), smaller grains showed a higher fraction of ductile fracture than larger grains.

Table 1. Mechanical properties

Grain size ( $\mu\text{m}$ )	Condition	$\sigma_Y$ (MPa)	$\sigma_{UTS}$ (MPa)	$\delta$ (%)	$RA$ (%)
1	Uncharged	585	793	50	76.1
	10 MPa H <sub>2</sub> charged	596	812	51	60
20	Uncharged	156	629	66.2	84
	10 MPa H <sub>2</sub> charged	153	691	51	43.7

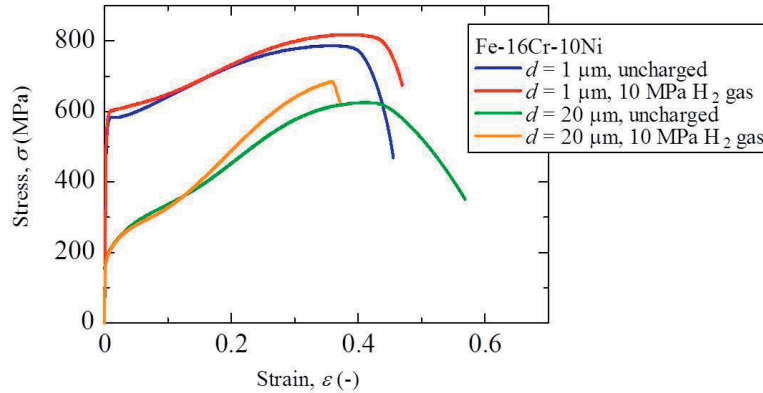


Fig. 2: Tensile properties for both materials in uncharged and charged conditions

It has been shown that the thermal stability of the alloy used in this study is greatly dependent on the grain size (Tomimura et al., 1993; Takaki et al., 2004). However the effect of grain size on the mechanical stability of the alloy, and more importantly the combined effects of grain size and hydrogen on mechanical stability are not quite clear yet. To investigate this, sheets of Fe-16Cr-10Ni were cold-rolled, with reductions of  $r = 10, 20$  and  $30\%$ . EBSD micrographs showing the amount of transformation for each grain size, condition and reduction ratio are shown in Figure 3. Table 2 shows the volume of deformation-induced martensite,  $\alpha'$ , after cold-rolling at different levels of reduction, in both ultra-fine-grained and coarse-grained materials, hydrogen-charged and uncharged. It is to be noted that EBSD micrographs in Figure 3 show only the transformation on the surface of the specimens, while Table 2 gives results obtained for volumes of material, thereby explaining discrepancies between the volume fraction of martensite and the surface fraction of martensite.

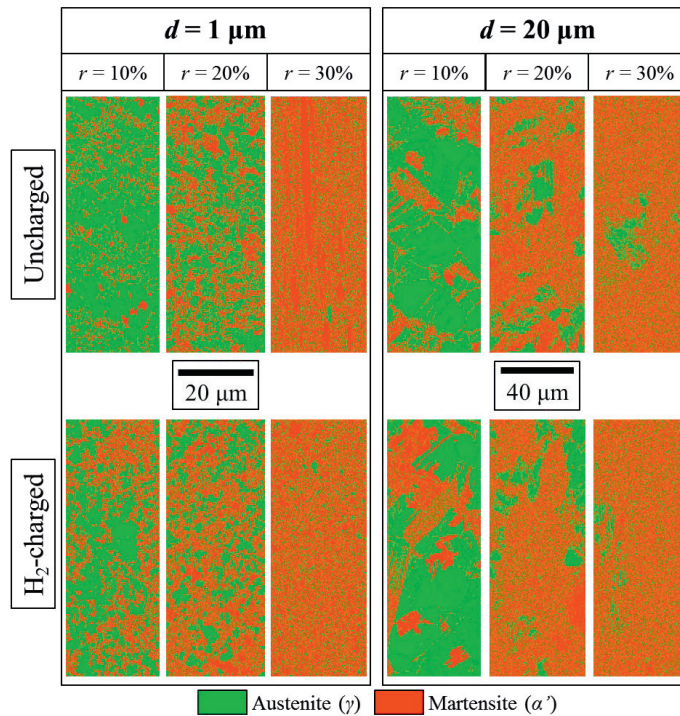


Fig. 3: EBSD micrographs of deformation-induced martensitic transformation

Table 2. Amount of deformation-induced martensite after different levels of reduction

	$d = 1 \mu\text{m}$			$d = 20 \mu\text{m}$		
	Reduction $r$ (%)	True strain $\varepsilon$ (-)	Martensite $\alpha'$ (vol. %)	Reduction $r$ (%)	True strain $\varepsilon$ (-)	Martensite $\alpha'$ (vol. %)
Uncharged	10.0	0.12	5.1	8.2	0.10	15.3
	19.7	0.25	23.2	19.7	0.25	59.9
	29.2	0.40	44.9	29.6	0.41	69.0
H <sub>2</sub> -charged	10.0	0.12	6.5	8.4	0.10	12.0
	20.3	0.26	23.4	20.0	0.26	37.6
	29.8	0.41	47.4	30.3	0.42	82.8

Using the equation (1) by Nohara et al. (1977) for the  $M_{d30}$  temperature, temperature at which 50% of the material has transformed into martensite under a strain of 30%, the calculated  $M_{d30}$  temperatures are 277.3 K (4.3°C) for ultra-fine-grained material and 286.3 K (13.3°C) for coarse-grained material. This shows that the theoretical mechanical stability of ultra-fine grains is slightly better than coarse grains in the material used here.

$$M_{d30} = 551 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29.0(Ni + Cu) - 18.5Mo - 6.8Nb - 1.42(ASM\ grain\ size - 8.0) \quad (1)$$

In the case of the ultra-fine-grained material, the amount of deformation-induced martensite was the same for each reduction ratio, whether the material was charged with hydrogen or not. On the other hand, in the coarse-grained material, the mechanical stability of the alloy was improved by hydrogen for lower strains, i.e. for  $r = 10$  and 20 %, the amount of martensite formed during cold-rolling was lower in hydrogen-charged material than uncharged material. This seems to be in agreement with reports that hydrogen localizes deformation and martensite formation (Kanezaki et al., 2008). However Hardie and Butler (1990) studied the effect of hydrogen on 304L stainless steel and found that although the mechanical stability had an effect on the intensity of hydrogen embrittlement, i.e. the amount of deformation-induced martensite affected the extent of the embrittlement, the presence of hydrogen did not influence the martensitic transformation. Singh and Altstetter (1982) reported also, using cathodic hydrogen charging, that after tensile straining there was no significant difference in martensitic transformation for hydrogen-charged and uncharged stainless steel. Results obtained after cathodic and gas charging by Narita et al. (1982) showed that hydrogen promoted transformation of austenite into  $\varepsilon$ -martensite. Mine and Kimoto (2011) reported that the ductility sensitivity of their austenitic stainless steels to hydrogen was dependent on the austenite stability. Those results show that the influence of hydrogen on austenite stability is not clear.

In the case of Fe-16Cr-10Ni, the increased thermal stability of ultra-fine grains is caused by the inability of such small grains for multi-variant martensitic transformation (Takaki et al., 2004). Inside coarser grains (above 5  $\mu\text{m}$ ), at ambient temperature, the austenite of Fe-16Cr-10Ni will transform into the most energetically favorable martensitic variant, thus having a lower thermal stability than ultra-fine grains. Figure 3 shows that the ultra-fine grains are either fully martensitic or fully austenitic, with and without hydrogen. Coarse grains, especially at  $r = 10\%$  ( $\varepsilon = 0.10$ ), are transformed only partially into martensite, evidenced by the straight red stripes inside otherwise green grains (Fig. 3), with or without hydrogen. In the case of mechanical stability, here investigated by cold-rolling, i.e. strain-controlled deformation (as opposed to tensile straining, which is stress-controlled deformation, and can be less homogeneous), there is no “choice” for the austenite to transform into an energetically favorable martensitic variant: the transformation is determined by the controlled straining. The deformation being imposed, in the ultra-fine grains, the localization of plasticity induced by hydrogen does not seem to affect the martensitic transformation behavior, as the grains can only transform into a single martensite variant. Therefore, in ultra-fine grains, the transformation behavior under straining is the same for hydrogen-charged and uncharged conditions. In the coarse-grained material,

hydrogen-enhanced localized plasticity may occur. Contrary to ultra-fine grains, under imposed strain, coarse-grained material seems to still transform into specific martensite variants, as seen in Figure 3 (with coarse-grained material at  $r = 10\%$ ). Contrary to ultra-fine grains, hydrogen seems to localize the transformation, considering that the volume fraction of martensite is less than in uncharged material, for  $r = 10$  and  $20\%$ . However for increased reduction levels, and therefore increased strain levels, the volume fraction of martensite for both charged and uncharged material reach similar values. Preliminary tests at strain levels higher than 0.4 showed that there is no effect of hydrogen on the amount of strain-induced martensitic transformation. Therefore it appears that overall there is no significant hydrogen effect on the material mechanical stability. Any stabilizing effect of hydrogen on coarse grains appears to be limited in range.

#### 4. Conclusions

Using a Fe-16Cr-10Ni metastable austenitic steel, the combined effect of grain refinement and hydrogen were investigated. Particularly, the mechanical stability of the material was analyzed. It was found that:

- Ultra-fine grains increased the tensile properties greatly, and the strength increase did not affect negatively the material response to hydrogen. Conversely, the coarse-grained material showed a very high reduction in ductility due to the presence of solute hydrogen.
- Straining the material by cold-rolling showed that the ultra-fine-grained material had an identical transformation behavior with and without hydrogen: the mechanical stability of the material remained unchanged.
- For coarse grains, hydrogen charging led to apparently less martensitic transformation for strains below 0.25. It is estimated that the hydrogen may have locally increased the plasticity. It appears there is a threshold for this phenomenon, as for increased strains, the amount of transformed martensite reaches similar values in both hydrogen-charged and uncharged material.
- Lastly, the effect of hydrogen on mechanical stability for either ultra-fine grains or coarse grains appears to be weak, or very limited in range. Therefore any hydrogen effect on this alloy may not be due to modified martensitic transformation behavior induced by hydrogen.

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#### References

- San Marchi, C., Michler, T., Nibur, K.A., Somerday, B.P.. 2010. On the Physical Differences between Tensile Testing of Type 304 and 316 Austenitic Stainless Steels with Internal Hydrogen and External Hydrogen. *International Journal of Hydrogen Energy* 35, 9736-9745.
- Kanezaki, T., Narazaki, C., Mine, Y., Matsuoka, S., Murakami, Y.. 2008. Effects of Hydrogen on Fatigue Crack Growth Behavior of Austenitic Stainless Steels. *International Journal of Fatigue* 33, 2604-2619.
- Tomimura, K., Takaki, S., Tanimoto, S., Tokunaga, Y.. 1991. Optimal Chemical Composition in Fe-Cr-Ni Alloys for Ultra Grain Refining by Reversion from Deformation Induced Martensite. *ISIJ International* 31, 721-727.
- Rozenak, P., Eliezer, D.. 1983. Effects of Metallurgical Variables on Hydrogen Embrittlement in AISI Type 316, 321 and 347 Stainless Steels. *Materials Science and Engineering* 61, 31-41.
- Brass, A.-M., Chene, J.. 2006. Hydrogen Uptake in 316L Stainless Steel: Consequences on the Tensile Properties. *Corrosion Science* 48, 3222-3242.
- Takaki, S., Fukunaga, K., Syarif, J., Tsuchiyama, T.. 2004. Effect of Grain Refinement on Thermal Stability of Metastable Austenitic Steel. *Materials Transactions* 45, 2245-2251.
- Nohara, K., Ono, Y., Ohashi, N.. 1977. Composition and grain size dependencies of strain-induced martensitic transformation in metastable austenitic stainless steels. *Journal of ISIJ* 63, 212-222.
- Hardie, D., Butler, J.J.F.. 1990. Effect of Hydrogen Charging on Fracture Behaviour of 304L Stainless Steel. *Materials Science and Technology* 6, 441-446.
- Singh, S., Altstetter, C.. 1982. Effects of Hydrogen Concentration on Slow Crack Growth in Stainless Steels. *Metallurgical Transactions A* 13, 1789-1808.



- Narita, N., Altstetter, C.J., Birnbaum, H.K.. 1982. Hydrogen-Related Phase Transformations in Austenitic Stainless Steels. Metallurgical Transactions A 13, 1355-1365.
- Mine, Y., Kimoto, T.. 2011. Hydrogen Uptake in Austenitic Stainless Steels by Exposure to Gaseous Hydrogen and its Effect on Tensile Deformation. Corrosion Science 53, 2619-2629.