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研究課題名（英文） Ultra-grain refinement as prevention against hydrogen-assisted crack propagation

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研究成果の概要（和文）：結晶粒径の微細化によって降伏応力がはるかに増加した。水素ガス暴露（10、40、100MPa）によって、すべての材料の延性が低下したが、最大水素量でも超微細粒材（粒径1μm）の伸びは30%もあった。すべての粒径で、固溶水素による固溶強化が起きた。粒径が小さくなると、水素脆化に必要な水素量が高くなる。
水素の有無にかかわらず、粒径がひずみ誘起マルテンサイト変態に影響せず、マルテンサイト変態が水素に減少されることが分かった。高水素量と低ひずみでマルテンサイト変態が起きない。固溶水素によって、粒径5μm以下の場合、延性過負荷で破壊するが、それ以上の粒径の場合、水素誘起き裂進展で破壊することが分かった。

研究成果の概要（英文）：Grain size refinement led to a large increase of yield stress. Hydrogen charging at different hydrogen pressures (10, 40 and 100 MPa) led to a hydrogen-induced decrease of ductility in the alloy. The ultra-fine grain material (1 micron grains) still retained an elongation of 30% under the highest hydrogen content. There is a solid solution strengthening effect of hydrogen. Hydrogen embrittlement requires larger hydrogen contents in smaller grained material. There was no evidence of cracking of martensite-austenite boundaries, i.e. martensite transformation did not appear as a factor for susceptibility to hydrogen. Large solute hydrogen contents delay the formation of strain-induced martensite and completely cancel it at low strains. There was no effect of grain size on strain-induced martensite, with or without hydrogen. Finally, cracking in small grains seems to be dominated by ductile tensile overload while cracking in large grains is dominated by hydrogen-induced crack propagation.

研究分野： 機械工学

キーワード： hydrogen embrittlement　austenite　grain refinement　steel

１．研究開始当初の背景

(1) Hydrogen as an energy carrier is most attractive, due to the possibility of long term storage, efficient electricity production and relative easiness of transportation (through gas tanks or pipelines). Hydrogen does cause embrittlement and an overall reduction of mechanical properties of metals.

(2) Grain size refinement is well-known to increase the yield stress of metals, with the Hall-Petch relationship. Extreme high strains have recently been used to obtain nano-sized grains, but those methods (ECAP, HPT, etc.) are not suitable for large scale material production.

(3) At the same time, austenitic alloys are recommended for hydrogen-related equipment, due to their relative resistance to hydrogen embrittlement. Austenitic alloys do suffer of a relative high cost combined with a lower strength (due to the nickel content).

(4) To summarize, to use hydrogen safely and at low cost, suitable metals are required. Strengthening an austenitic alloy through grain refinement will allow a higher strength while retaining a modicum of hydrogen resistance, without increasing cost. However, modern grain refinement methods are not suitable for the industry.

２．研究の目的

This research focuses on the use of ultra-fine grained austenitic stainless steel, processed through conventional cold-rolling and annealing, and how resistant such steel is to hydrogen-induced cracking.

３．研究の方法

(1) A metastable austenitic stainless, with 16% chrome and 10% nickel (Fe-16Cr-10Ni) is solution-treated and cold-rolled to a final thickness reduction of 90% (usual final thickness of 1.5mm) [1]. At this point, the material is more than 90% fine martensite. Next, annealing above 600 °C reverses the martensite back to austenite (reversion treatment). By controlling the time and temperature, the grain size of the reversed austenite is controlled: 650°C for 10 min. gives 1μm grains (ultra-fine grains or UFG), at 750°C for 10 min. the grain size is about 5μm, and at 900°C for 30 min. the grain size is about 20μm. Once the steel is heat-treated, tensile test specimens (gauge dimensions: 18×3×1.5 mm) are cut out and polished to a mirror finish (buff and electro-chemical polishing).

(2) Before testing, some specimens are hydrogen-charged in high-pressure hydrogen gas (10, 40 and 100 MPa) at 270°C for 72 hours.

(3) Tensile tests were conducted in room temperature (RT) with crosshead speed of 0.2 mm/min.

(4) Cold-rolling at RT to form strain-induced martensite was also conducted, with a thickness reduction ratio of 0.2 mm/pass.

(5) Notched tensile specimens were tensile-tested within a scanning electron microscope (SEM) chamber to observe the initiation and propagation of a crack in hydrogen-charged specimens. The crosshead speed was 5 μm/s.

(6) The fracture surface of the tensile specimens was analyzed with an SEM.

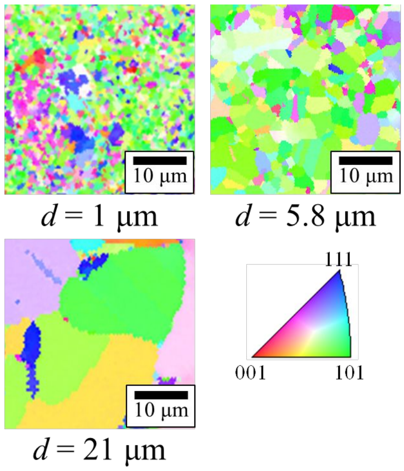
(7) The microstructure before and after testing was analyzed with electron-backscattered diffraction (EBSD).

(8) The hydrogen content was confirmed by thermal desorption spectroscopy (TDS), with a heating rate of 0.33°C/s up to a maximum temperature of 800°C.

(9) Finally, the amount of martensite in the cold-rolled specimens was measured with magnetization saturation measurements.

４．研究成果

(1) Figure 1 shows EBSD maps of the three grain sizes investigated. In all cases, the material is fully austenitic. Table 1 shows the precise chemical composition of the alloy.



d = 1 μm　*d* = 5.8 μm

d = 21 μm

Fig. 1: EBSD maps for each grain size

Table 1: Chemical composition of Fe-16Cr-10Ni alloy (mass %)

C	Si	Mn	P	S	Ni	Cr	N	Fe
0.002	0.011	0.08	0.003	0.002	10.1	16.4	0.032	Bal.

(2) The hydrogen content did not vary greatly between grain sizes, and therefore the average hydrogen content for each hydrogen charging condition was taken as the following shown in Table 2.

Table 2: Average hydrogen content

p_{H2} (MPa)	Average C_H (wppm)
uncharged	0.3
10	24.5
40	39.4
100	71.1

(3) Figure 2 shows the tensile tests results for all grain sizes and all hydrogen charging pressures. Grain size refinement increased the yield stress dramatically from less than 200 MPa to about 590 MPa. Hydrogen charging led to a slight increase of the yield stress, showing an actual solid solution strengthening effect of hydrogen. It is also obvious that the ductility was reduced by hydrogen in all cases, most dramatically for the 21 μm grains. However, the 1 μm grains retained an elongation of 30%.

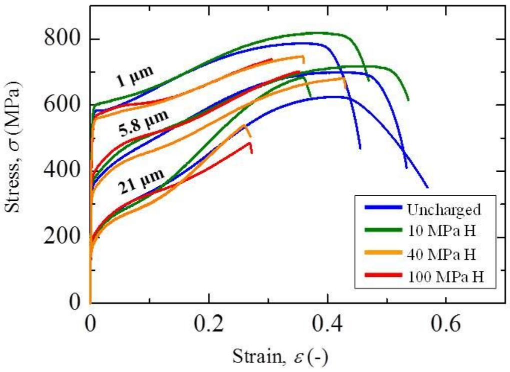


Fig. 2: Tensile test results for all grain sizes and hydrogen charging pressures

The effect of hydrogen on ductility is also shown on the reduction of area graph in Figure 3. It can be seen that a reduction of grain size (below 6 μm) is an efficient way to retain ductility in the presence of low hydrogen content (10 MPa hydrogen charging). At larger hydrogen contents, the ductility is uniformly decreased. Furthermore, the ductility after charging in 40 MPa hydrogen gas and after charging in 100 MPa hydrogen gas is almost the same, indicating that there is a saturation of the hydrogen effect and larger solute hydrogen contents may not further decrease the material ductility.

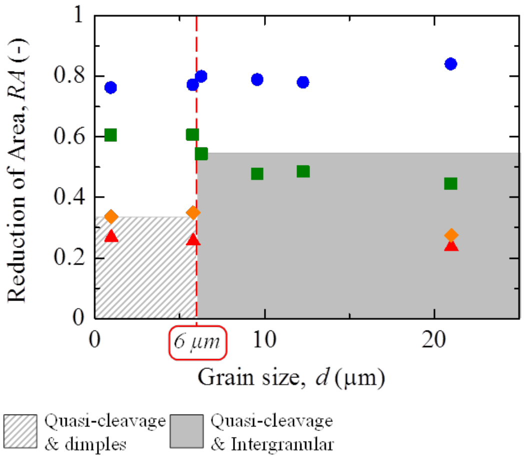


Fig. 3: Evolution of the reduction of area with hydrogen content (grayed areas show how the fracture surface evolve with hydrogen content and grain size)

(4) Representative micrographs of the fracture surfaces are shown in Figure 4, where it is clear that increasing hydrogen content led to a more brittle fracture surface with a reduction in dimple size, transgranular and intergranular cracking as well as cracking along annealing twin boundaries.

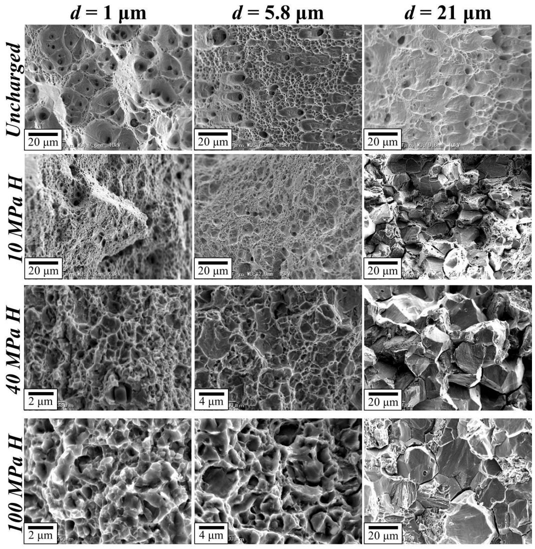


Fig. 4: Examples of the fracture surfaces for the three grain sizes and all conditions

(5) The volume fraction of martensite after cold-rolling for all grain sizes and all hydrogen content is shown in Figure 5. As there was no effect of grain size on the

volume fraction of martensite at a specific strain, all grain sizes are represented together for each hydrogen charging condition. There is clear that larger solute hydrogen contents reduce the amount of strain-induced martensite in the Fe-16Cr-10Ni alloy. A high hydrogen content (100 MPa hydrogen-charged) also prevents martensitic transformation at low strains (ε < 0.20). For a better understanding, EBSD phase maps are shown in Figure 6.

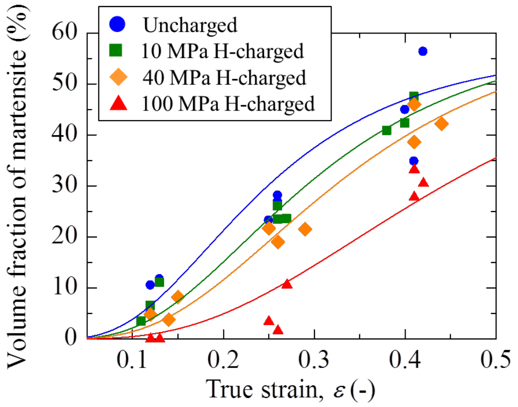


Fig. 5: Evolution of martensite content with strain for all hydrogen contents

An analysis of the data with the model by Olson and Cohen [2] shows that the α parameter decreases and the β parameter increases with increasing solute hydrogen content. This may mean that the stacking fault energy slightly increases and that it is easier to generate martensitic embryos.

It appears that hydrogen strongly reduces the number of slip system intersections, thereby strongly decreasing the number of possible martensite embryos, even though there is a slight increase in the austenite-to-martensite transformation rate. The overall result is a hydrogen-induced increase in austenite stability.

(6) The results of notched tensile tests are shown in Figure 7. In that case a load drop was experienced for the 1 μm grains, due to an issue with the micro-tensile testing device. However for the 1 μm and 5.8 μm grains, it can be seen that the specimens failed due to ductile tensile overload, with a drop in tensile stress before failure. In the large 21 μm grains, the failure was sudden without much plasticity or drop in stress. The micrograph in Figure 8 shows how a crack originated at the notch root, which then propagated until failure, i.e. hydrogen-induced cracking.

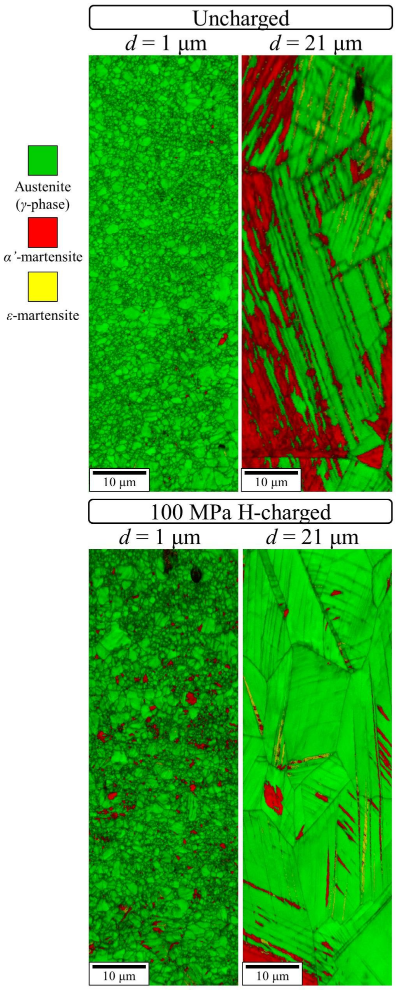


Fig. 6: Phase maps of 100 MPa-hydrogen-charged and uncharged material after 10% cold-rolling

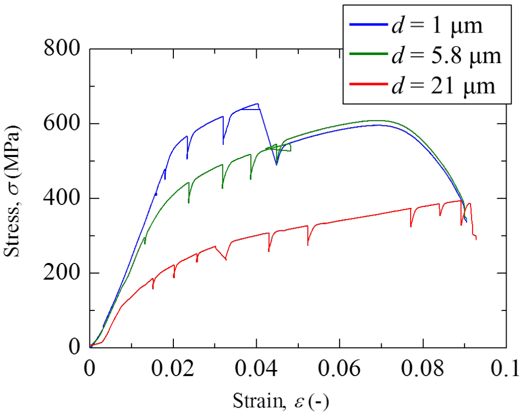
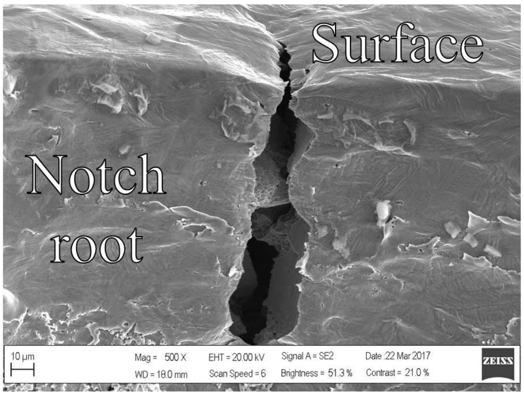


Fig. 7: Tensile test data for notched specimens inside an SEM chamber. Note the different behavior at the fracture strain

(9) Concluding remarks:

Hydrogen can cause a large decrease in ductility in metastable austenite, but grain refinement helps retain ductility at low hydrogen content. Furthermore, failure in small grains is not caused by hydrogen-induced cracking, but by ductile tensile overload, i.e. ductile failure. In the larger grains, the failure is irrevocably brittle, evidence by cracking along grain and twin boundaries.

Fig. 8: SEM micrograph showing a hydrogen-induced crack propagating from the notch root onto the specimen surface in 21μm material (100 MPa hydrogen charging)



In this case, martensite formation is independent of grain size, but large solute hydrogen contents can lead to an increase in austenite stability.
In conclusion, grain refinement is a good means of reducing hydrogen effect in austenite, but it can be improved.

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５．主な発表論文等
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〔図書〕（計　0件）

〔産業財産権〕

○出願状況（計　0件）

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〔その他〕
日本材料学会学術奨励賞，2017 年 「超組織微細化したオーステナイト系ステンレス鋼における水素の影響に関する研究」

６．研究組織

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