1. Introduction

Ni-base alloys are highly resistant to corrosion, and as such, used for piping and structural members for chemical plants and other facilities that work in severely corrosive environments.\(^1\)\(^-\)\(^3\) Even high-grade Ni-base alloys, however, sometimes undergo stress corrosion cracking or embrittlement through degradation over time; this was considered to result from hydrogen in the material. The hydrogen embrittlement of Ni-base alloys is, characteristically, more strongly influenced by plastic deformation than that of iron and steel, and because of their lower stacking fault energy than that of steel, many studies have associated the hydrogen embrittlement of Ni-base alloys with stacking fault energy.\(^4\)\(^-\)\(^7\)

Various mechanisms have been proposed as the cause of embrittlement cracking due to interstitial hydrogen, for example, the hydrogen-induced decohesion model and the hydrogen-enhanced dislocation plasticity model. The former suggests that hydrogen condensates locally at stress concentration portions such as crack ends, which weakens the lattice binding energy.\(^5\)\(^-\)\(^10\) In this case, the failure due to hydrogen embrittlement occurs in the form of cleavage fracture, often occurring especially along crystallographic planes of low indices with low surface energy. With an fcc phase, for example, cleavage fracture occurs along \{111\}_C or \{100\}_C, and facets composed of the cleavage planes are formed near grain boundaries.

According to the latter model, solute hydrogen accelerates the occurrence of dislocations even at low stress, which decreases plastic flow stress locally.\(^11\)\(^-\)\(^14\) H. K. Burnbaum and his group installed a special cell in a high-voltage electron microscope, observed the dislocation behavior of different materials in situ in a hydrogen atmosphere, and reported that hydrogen enhanced the mobility of dislocations.\(^15\)\(^,\)\(^16\) This model can account for phenomena such as the formation of shear bands at crack ends under hydrogen influence.

Nagumo et al. proposed the theory of hydrogen-enhanced, strain-induced vacancy.\(^17\) The theory explains the reduction in the ductility of metals due to a significant increase in the vacancy concentration resulting from plastic deformation in a hydrogen environ-
ment. Takai et al. reported the plastic-deformation-induced vacancies affect the hydrogen embrittlement in Inconel625. In addition, hydrogen accelerated the formation of vacancies and the vacancies once formed were stabilized by hydrogen. The study also proved that embrittlement occurred in the specimen, which was deformed under cathodic hydrogen charging and heat treated afterward to remove hydrogen. Then, it is concluded that hydrogen itself was not essential for the embrittlement, but the existence of vacancies induced by it was.

Some commercially used Ni-based alloys include ordered phases and phases of intermetallic compounds. High-grade oil well tubes of Ni-Cr-Mo, Ni-Cr-Mo-W and similar alloys are often used in corrosive environments at high temperatures (150 to 300°C). Because metastable ordered phases form in these alloys through long aging treatment at 550°C or lower, various material problems have been discussed in relation to the transformation into such ordered phase. In fact, it has been clarified that the mode of fracture due to hydrogen embrittlement changes from grain boundary fracture to twin boundary fracture as a result of the ordering transformation, which agrees well with the general change in the plastic deformation behavior of these alloys due to ordering transformation.

The present paper outlines the governing factors of the hydrogen embrittlement of Ni-base alloys from the viewpoint of plastic deformation; more specifically, it relates to the relationship between sensitivity to hydrogen embrittlement and stacking fault energy, the effects of hydrogen on the behavior of dislocations and those on the same of ordered alloys. I hope this is of some assistance for the material design of commercially used Ni-base alloys.

2. Relationship between Stacking Fault Energy and Sensitivity to Hydrogen Embrittlement of Ni-base Alloys

Figure 1 shows the tensile properties (TS and YS) of Ni-Cr-Fe ternary alloys under hydrogen charging. The contents of C, P and S of the specimens are 0.001% or lower. The alloys were prepared by vacuum melting, ingots were hot-forged and then hot-rolled into prescribed sizes, their average grain size was controlled to 80 μm through solution treatment at the prescribed temperature, the test pieces underwent a tensile test while hydrogen was charged to them by cathode electrolysis, and were evaluated in terms of elongation and tensile strength. The cathode electrolyte was prepared by adding 1.4 kg of thiourea per cubic meter of a 1N-H₂SO₄ solution. The hydrogen charging was conducted at a potential controlled to 900 mV/ S.C.E. and a current density of 10 to 300 A/m², and the tensile strain velocity was 3×10⁻⁴/s.

Without the influence of hydrogen, the work hardening coefficient and tensile strength increased monotonously as the Ni content increased. The mode of fracture of the specimens in this case was ductile fracture. Under hydrogen influence, intergranular fracture occurred, and elongation and tensile strength lowered. The decrease in elongation and strength due to hydrogen became apparent when the Ni content exceeded 50%. When Cr content increased, on the other hand, the work hardening ratio and strength increased, and the effects of hydrogen charging were mitigated.

To clarify the relationship between hydrogen embrittlement sensitivity and stacking fault energy, I measured the stacking fault energy of Ni-Cr-Fe ternary alloys in the following manner: 2% tensile strain was applied to the test pieces under hydrogen charging, and then, after determining the Burgers vectors of the slip dislocations, the widths of extended dislocations were measured by the weak-beam method.

Stacking fault energy (γ) is given as the inverse of the extended dislocation width (w₀) as follows:

\[ \gamma = \frac{\mu_{III} b^2}{8 w_0 \left( 1 - \nu_{III} \right)} \]

Here, the modulus of rigidity (μ_{III}) and the Poisson ratio (ν_{III}) of a \( b=1/2<110> \) slip on \( \{111\} \) were obtained according to the theory of anisotropic elasticity, using the values of elastic compliance (\( C_{11}, C_{12}, C_{44} \)) measured by the pulse echo method.

\[ \mu_{III} = \left( C_{44} / C_{44}' \right)^{1/2} \]

Fig. 1  Effects of hydrogen charging and alloy chemistry on tensile properties of Ni-Cr-Fe alloys
\[
\frac{\mu_{\text{II}}}{1-V_{\text{II}}} = \frac{1}{3} \left( 2 + \frac{C_{11}^p}{C_{33}^p} \right) \left( C_{11}^p + C_{12}^p \right) \left[ C_{11}' \left( C_{11}^p + C_{12}^p + 2C_{55} \right) \right]^{-1/2} \tag{3}
\]

\[
C_{11}^p = C_{11} \quad C_{22}^p = \frac{1}{2} \left( C_{11} + C_{12} \right) + C_{44}
\]

\[
C_{12}^p = C_{12} \quad C_{23}^p = \frac{1}{2} \left( C_{11} + C_{12} \right) - C_{44}
\]

\[
C_{44}^p = C_{44} \quad C_{55}^p \left( C_{11}^p + C_{12}^p \right) = \left[ \frac{1}{2} \left( C_{11} + C_{12} \right) + 2C_{44} \right] C_{11} \right]^{1/2} \tag{4}
\]

Figure 2 shows example views of dislocation configurations. With a high Ni content, dislocations on certain slip planes tend to be planar, leading to rises in dislocation concentration near grain boundaries.

Figure 3 shows the result of the measurement of stacking fault energy. When the Cr content is constant, it has a maximum near 50% Ni content, and decreases with the increase in the Ni content; this trend is obvious in the photomicrographs of Fig. 2. When the Fe content is constant, in contrast, stacking fault energy decreases with the increase in Cr content.

It seems that there are singularities near the chemical composition of 50% Ni in both the stacking fault energy and the tensile properties with hydrogen charging. This chemical composition range is substantially the same as that of magnetic transformation, which indicates that the characteristics of the plastic deformation of Ni-Cr-Fe alloys and those of its hydrogen embrittlement are influenced considerably by magnetism. As a theory on the relation between plastic deformation and hydrogen, the hydrogen-enhanced strain-induced vacancy mechanism has been proposed. In addition, regarding the study on hydrogen and lattice vacancies in Ni-base alloys, there are several reports on hydrogen supersaturated vacancies and magnetic properties. For example, Fukai et al. consider that, when hydrogen is forced to solve in a Fe-Ni system, the crystal structure changes and lattice vacancies arise in vast quantities, and when interstitial hydrogen atoms are trapped in vacancies, their energy is lowered leading to a change in the magnetic properties.

It is necessary to take magnetism into consideration to clarify the effect of chemical composition on hydrogen embrittlement and deformation behavior.

On the other hand, it has become clear for the first time through the present study that sensitivity to hydrogen embrittlement and stacking fault energy are not mutually correlated: with respect to the content of Ni (or that of Fe), stacking fault energy decreases and hydrogen embrittlement sensitivity increases with the increase in Ni (Fe) content, but these two have a negative correlation with the Cr content. This leads to the conclusion, therefore, that the conventional model maintaining that hydrogen embrittlement is accelerated by the decrease in stacking fault energy is not always applicable to Ni-base alloys.

3. Effects of Hydrogen on Plastic Deformation of Single-crystal Ni-Cr Alloy

To clarify the behavior of dislocations from the plastic deform-
tion mechanisms that affect the plastic deformation and hydrogen embrittlement of Ni-base alloys, I prepared single-crystal specimens of Ni-Cr alloys and examined plastic deformation inside crystal grains. Figure 4\(^1\)\(^9\),\(^22\) shows stress-strain curves of single-crystal specimens of 80%Ni-20%Cr, 70%Ni-30%Cr and 60%Ni-40%Cr alloys (in mass %) at a tensile test under hydrogen charging with the tension applied in the <001> direction. After hydrogen charging, deforming resistance increased with all the specimens, but the effects of hydrogen decreased as the Cr content increased. The hydrogen concentration after the test was roughly 3 ppm in all the specimens.

Figure 5\(^1\)\(^9\),\(^22\) shows images of the dislocation configurations of the specimens after 10% deformation in the normal atmosphere through a transmission electron microscope (TEM). Substantially the same dislocation configurations were observed in all the specimens. Planar dislocations, which are groups with the same Burgers vector formed on specific slip planes, are responsible for plastic deformation, and the components of these planar dislocations have been confirmed to be close to pure edge. When identical specimens were subjected to the same 10% strain under hydrogen charging, however, curved dislocations (hereinafter called hydrogen-induced dislocations) increased (see Fig. 6\(^1\)\(^9\),\(^22\)). These hydrogen-induced dislocations included screw components in a high proportion; sometimes they were seen to form dislocation loops or dipoles, or to cross-slip to another slip plane. Increase in Ni content accelerates the formation of hydrogen-induced dislocations, but increase in Cr content suppresses it. Because hydrogen adsorption barely changes depending on the Cr content, it is considered that Cr decreases interactions between dislocations and hydrogen, and as a consequence, suppresses hydrogen embrittlement.

Mechanisms of the shape change of dislocations due to hydrogen include (1) local concentration of hydrogen in high-energy edge dislocations leading to their change into low-energy screw components, and (2) change in the dislocation core structure caused by hydrogen, but the details are still unclear. More direct microstructural observations and mathematical operations are expected to fundamentally clarify the mechanism.

As mentioned above, many Ni-base alloys undergo order-disorder transition. A Ni\(_2\)Cr-type ordered phase forms in Ni-Cr-Fe alloys through long aging treatment at low temperature, provided that the chemical composition is close to the stoichiometry of Ni\(_2\)Cr, and in this relation, the influence of long- or short-range order on hydrogen embrittlement has been discussed. In view of this, the influence of structural ordering on hydrogen-induced dislocations will be discussed in Section 4 below.

4. Effects of Hydrogen on Plastic Deformation of Ordered Ni\(_2\)Cr Alloy

Through aging treatment at 500°C for 1 000 h, a 70Ni-30Cr alloy transforms into a Ni\(_2\)Cr-type ordered phase, and domains of ordered phases with less than 10 nanometers in size are formed (see Fig. 7\(^1\)\(^9\),\(^22\)). Aged single-crystal specimens of the above alloy were
subjected to the tensile test in normal atmosphere and under hydrogen charging. Figure 8 shows the stress-strain curves of the two cases; the tension direction is $<001>_{\text{C}}$ of fcc. The formation of superlattices increases yield strength and the work hardening coefficient, but under hydrogen charging, yield strength falls markedly and the material hardens and softens alternately and repeatedly in the plastic deformation region.

Figure 9 shows dislocations in a 70Ni-30Cr specimen after 10% tensile deformation in the $<001>_{\text{C}}$ direction in normal atmosphere. Without hydrogen, superlattice dislocation triplets are responsible for plastic deformation of an ordered Ni$_2$Cr alloy, and the components of the superlattice dislocations are close to pure edge. When a 10% strain was applied in the $<001>_{\text{C}}$ direction under hydrogen charging, slip traces appeared at specimen surfaces. Note that the superlattice dislocation triplets were rarely seen in the deformation structure and ordinary dislocations occurred in preference (see Fig. 10). The Burgers vector of the hydrogen-induced dislocations was $b=1/2[110]_{\text{C}}$ (in terms of cubic crystal), and they included a considerable amount of screw components. There were also dislocation dipoles and planar dislocation groups.

When the strain was increased to 15%, traces of slip along $\{111\}_{\text{C}}$ appeared at the specimen surfaces in addition to cracks (see Fig. 11). Deformation structures corresponding to the slip traces were analyzed, and the dislocation density was increased on specific slip planes by dislocation pairs derived from dislocation dipoles. Also found through Burgers vector analysis was the occurrence of twinning dislocations having a Burgers vector of $b=1/6[211]_{\text{C}}$. Through cross check of the analysis result of the slip traces in the SEM image against the direction of the twinning dislocations, it was concluded that the specimen surface traces along $\{111\}_{\text{C}}$ corresponded to deformation twins.
Fig. 10 SEM surface image and corresponding TEM bright-field images of deformation structure in single-crystal, ordered 70Ni-30Cr specimen after aging at 500°C for 1000 h and 10% tensile deformation under hydrogen charging.  

Fig. 11 SEM surface image and corresponding TEM bright-field images of deformation structure in single-crystal, ordered 70Ni-30Cr specimen after aging at 500°C for 1000 h and 15% tensile deformation under hydrogen charging.
The mechanism that gives rise to hydrogen-induced dislocations in an ordered phase is as follows: to maintain the symmetry of a Ni₃Cr-type ordered phase, superlattice dislocation triplets have to be composed of edge components; however, because the said triplets are huge dislocation structures of edge components, penetrating hydrogen concentrates locally at superlattice dislocations to minimize the energy of the entire system; and by turning into low-energy screw dislocations, they become ordinary dislocations. This interpretation is supported by the fall of yield stress at the tensile test under hydrogen charging. In addition, whereas twin deformation did not occur without hydrogen as long as the strain was 50% or less, with hydrogen it occurred from low-strain ranges. This is presumably because planar dislocations and hydrogen-induced dislocations led to the formation of barriers that may serve as the nuclei of twins within crystal grains.

The relationship between the degree of order and susceptibility to hydrogen embrittlement is explained below; the samples used here are polycrystalline specimens of a 70Ni-30Cr alloy, and a Ni-Cr-Mo-Fe alloy prepared from the former by partially replacing Cr and Ni respectively with Mo and Fe. The contents of C, P and S were 0.001% or less, the average crystal grain size was controlled to approximately 80 μm, and aging treatment was conducted at 500°C for 10000 h at the longest. The degree of order was measured by X-ray diffraction.

Figure 12 shows the advance in lattice order of the two alloys depending on the chemical composition of the alloy. Also for the Ni-base alloys, single and poly-crystal specimens of Ni-Cr-Fe and Ni-Cr model alloys were subjected to a tensile test under hydrogen charging, and dislocation behavior was observed. As a result, with high-Ni alloys of low stacking fault energy, edge dislocations tended to align in a planar manner on specific slip planes, but during the tensile test under hydrogen charging, edge dislocations turned into screw dislocations. It was also clarified that the higher the Ni content, the more hydrogen-induced screw dislocations formed, and the higher the Cr content the less hydrogen-induced screw dislocations formed, which agreed well with the trend of hydrogen embrittlement sensitivity.

In contrast, the stacking fault energy of the alloys did not always show correlation to hydrogen embrittlement sensitivity.

To clarify the influence of lattice order on the formation of hydrogen-induced screw dislocations, 70Ni-30Cr alloy specimens were aged at 500°C for long periods, and a Ni₃Cr-type ordered phase was obtained. In the ordered phase, superlattice dislocations consisting of edge dislocations governed the material’s deformation when there was no hydrogen, but when there was hydrogen, edge dislocations became ordinary dislocations having screw components. These ordinary dislocations with screw components, namely hydrogen-induced dislocations, interact with each other to cause twinning deformation. In addition, these findings clarified that crystal plasticity is changed greatly by interstitial hydrogen, and that the effects of hydrogen on crystal plasticity may change significantly depending on the chemical composition of the alloy. Also for the practical use of alloys prone to becoming an ordered phase, it is necessary to control the degree of order and the rate of ordering transition, which is presumably possible by adding a third alloy element.

Further studies are required on the following issues. To clarify the mechanisms of different types of fracture, three-dimensional analysis of grain boundaries and interfaces between twins and those between them and the base metal is indispensable in addition to that of material behavior during plastic deformation. Luckily, such analysis has been made practicable by comparatively simple methods. In clarifying the mechanisms of the embrittlement and corrosion due to hydrogen, an important point is how to separate environmental factors from material factors. Theoretical and quantitative prediction of material deterioration and damage and the method for their control need to be established through reproductive experiments and

5. Conclusion

To clarify the effects of hydrogen on the plastic deformation and dislocations of Ni-base alloys, single and poly-crystal specimens of Ni-Cr-Fe and Ni-Cr model alloys were subjected to a tensile test under hydrogen charging, and dislocation behavior was observed. As a result, with high-Ni alloys of low stacking fault energy, edge dislocations tended to align in a planar manner on specific slip planes, but during the tensile test under hydrogen charging, edge dislocations turned into screw dislocations. It was also clarified that the higher the Ni content, the more hydrogen-induced screw dislocations formed, and the higher the Cr content the less hydrogen-induced screw dislocations formed, which agreed well with the trend of hydrogen embrittlement sensitivity.

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theoretical verification of the phenomena in an adequately controlled environment.

References

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