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論文内容要旨

Abstract

The changes in corrosion properties caused by displacement damage of type 304 stainless steel were investigated by means of energetic particle irradiation technique. Solution-annealed specimens were irradiated using 1 MeV-H^+ ion beam up to 0.1, 0.5 and 1.0 dpa at about 300℃, 400℃ or 500℃. Electrochemical potentiokinetic reactivation (EPR) testing was carried out before and after the ion irradiation to clarify the effects of irradiation on corrosion behavior. In case of samples irradiated at 300℃ or 400℃, the results of EPR testing on the irradiated surfaces showed no etching trenches at grain boundaries. On the other hand, in case of the specimens irradiated at 500℃, passive film at and around grain boundaries was etched. The radiation induced segregation(RIS) at grain boundaries was evaluated by a transmission electron microscope(TEM). The correlation between corrosion behavior and the development of microstructure and segregation was discussed.

1. Introduction

Austenitic stainless steel is used extensively in the core components of light water reactors (LWRs), and is going to be used in the structural component of the fusion experimental reactor. Irradiation assisted stress corrosion cracking (IASCC) is one of the major concerns of stainless steel in LWR environment. Radiation induced segregation (RIS), that represents chromium depletion and nickel enrichment, caused by neutron irradiation is regarded as one of controlling factors of IASCC. To estimate the effect of chromium depletion at grain boundaries on corrosion behavior, the electrochemical potentiokinetic reactivation (EPR) test is very useful.

In order to study the neutron irradiation effect of neutron, energetic particle beam irradiation using accelerators have been performed as simulation experiments. Damage distribution by neutron is almost uniform along the depth of specimen, but that produced by ions are not uniform along incident direction and have clear depth distribution. Light-ion irradiation allows samples to be damaged to the depths of 5~6 μm within a comparatively short time (< 12 h). Since the corrosion behavior evaluated by EPR test is affected by chemical properties from the surface to 2-3μm depth of the austenitic stainless steel, the light ion irradiation can introduce enough damage level and damage area to evaluate the corrosion behavior of irradiated surface including grain boundaries.

The purposes of this study are to establish the testing method using miniature size specimens for ion-irradiation experiments and to clarify the change in corrosion behavior of irradiated stainless steel caused by displacement damage under controlled irradiation conditions such as temperature and fluence.

2. Methods

The material used in this study was type 304 stainless steel. Disks of 3 mm in diameter and about 250 μm thick were punched out from 75% cold-worked stainless steel. The disks were solution annealed at 960℃ for 60 sec in an evacuated quartz tube and water quenched after the heat treatment. The grain size of the heat-treated sample was about 20 μm. The specimen surface was mechanically polished by buffing to make a clean and flat surface. The specimen thickness after polishing was about 200 μm.

The ion-irradiation experiment was carried out using a Dynamitron accelerator at Tohoku University. Irradiation was conducted using 1MeV H^+ ions. The displacement damage was almost uniformly induced from the irradiation surface to a depth of about 5 μm. The examined displacement damage levels in this work were 0.1, 0.5 and 1 dpa. The typical damage rate was 3.4×10^{-5} dpa/sec, and temperature of each specimen during irradiation was 300℃, 400℃, and 500℃ within an error of ±10℃, which was measured by an infrared pyrometer. These irradiation experiments were conducted in a vacuum of less than 5.0×10^{-6} Torr.

The EPR test was carried out for the ion-irradiated specimens and unirradiated sensitized specimens. In order to estimate the corrosion behavior, double-loop EPR (DL-EPR) testing was conducted in this work. The DL-EPR testing was carried out in a test solution of 0.5 mol/l H_2SO_4 and 0.01 mol/l KSCN at about 30±1℃, and a saturated calomel electrode (SCE) was used as a reference one. The potential sweep rate was 100 mV/min. The degree of sensitization was evaluated by the reactivation ratio (*Ir*/*Ia*), where *Ia* is the maximum anodic current and *Ir* is the maximum reactivation current. After EPR testing, a surface observation was performed using a JOEL JSM-5310LV scanning electron microscope (SEM).

Microstructure analysis and evaluation of grain-boundary segregation were carried out using a TEM (HITACH HF-2000) with an EDX analysis system. The analysis beam size was about 3nm.

3. Results and Discussion

(1) EPR testing on specimens irradiated at 300℃ or 400℃

The surface after the EPR tests of the unirradiated solution annealed specimen was nearly flat. This result indicates stable passive film formation. The thermally sensitized specimens showed significant etching at and around grain boundaries. The width of the etched groove was about 5~6 μm on average. This preferential corrosion may have been caused by chromium depletion in the vicinity of the grain boundaries. Specimen size effects on corrosion behavior were small in the case of sensitized condition.

The surfaces after EPR tests of the specimens irradiated at 300℃ up to 0.1 and 1 dpa showed pitting, which could not be observed in the solution annealed specimens. Surface pitting in the transgranular part might be attributed to the irradiation, because this phenomenon was observed only in irradiated specimens and the number of pits increased with irradiation dose. No etching trenches along grain boundaries clearly observed in irradiated specimens by 0.1 dpa and 0.5 dpa. On the other hand, in the specimen irradiated to 1 dpa showed the etching trenches along grain boundaries were observed, but it was difficult to distinguish whether they were the sequence of pits or the dissolution caused by RIS.

The corrosion behavior of specimens irradiated at 400℃ up to 0.1 and 1 dpa was similar to that of specimens irradiated at 300℃: a large number of pitting at surface and no etching trenches along grain boundaries. Chromium concentration at grain boundaries of 304SS was changed from 18.5 wt% to 13.5 wt% after hydrogen ion irradiation at 300℃ up to 1dpa. Although RIS was occurred in ion irradiated specimens, the stability of passive film at and around grain boundaries seemed to be still maintained.

(2) EPR testing on specimens irradiated at 500℃

Specimens irradiated at 500℃ showed different corrosion behavior in this EPR testing condition from those of specimens irradiated at 300℃ or 400℃. Surface conditions after the EPR testing of specimens irradiated at 500℃ up to 0.1 and 1 dpa showed the dissolution of passive film at and around the grain boundaries, and the dissolution width increased with the irradiation dose. Narrow etching trenches were clearly observed at grain boundaries. Reactivation ratio of those specimens also increased with dose. Therefore, these results indicatd the correlation between the dissolution volume and the reactivation ratio. On the other hand, the surface pitting after EPR testing which was observed in the specimens irradiated at 300℃ and 400℃ was not observed in specimens irradiated at 500℃. To clarify whether there was the effect of thermal sensitization or not, EPR testing on the unirradiated specimen annealed at 500℃ for 8 hours was conducted. As a result, the reactivation ratio was 0.5 %, and this indicated that the effect of thermal sensitization was little. So it was revealed that the reactivation ratio obtained in EPR testing on specimens irradiated at 500℃ corresponded to the degree of activation at and around grain boundaries induced by the hydrogen ion irradiation. One of the causes of that activation change might be RIS: more chromium depletion or wider chromium depleted area by higher temperature irradiation. To clarify the conditions in which etching trenches along grain boundaries can be observed in EPR testing, further investigation on RIS of specimens irradiated at 500℃ is needed.

(3) Microstructural observation

Microstructures of specimens irradiated at 400℃ and 500℃up to 0.1 dpa were investigated. Irradiation defects such as the faulted loops or black dots were observed, and the defect density tended to decrease with the irradiation temperature; about 4×10^{21} /m^2 in the specimens irradiated at 400℃, 2×10^{20} /m^2 in those irradiated at 500℃. Cavities were not observed in this work. On the other hand, large precipitations induced by the irradiation were not observed either.

The chromium depletion at grain boundaries in the specimens irradiated at 400℃ to 0.1dpa was measured and it was revealed that chromium depletion at grain boundaries occurred and the minimum chromium concentration at grain boundaries was 13 wt% and the width of depleted area was about 35 nm. This might be attributed to RIS. In EPR testing, these specimens did not show the etching along grain boundaries. In the case of the specimens irradiated at 500℃ to 0.1 dpa, the chromium depletion at grain boundaries was also occurred. The minimum chromium concentration at grain boundaries was 12 wt%, and the width of chromium depleted area was about 70 nm. Specimens irradiated in this condition showed the etching along grain boundaries after EPR testing. These results suggest that enough chromium depletion at grain boundaries is necessary to occur the dissolution of passive film near grain boundaries in EPR testing.

4. Conclusion

The corrosion behavior of type 304 austenitic stainless steel irradiated with hydrogen ion was investigated using EPR testing combined with TEM observation after irradiation at 300℃, 400℃ and 500℃ up to 0.1, 0.5 and 1 dpa. The results are summarized as follows;

(1) It was confirmed that 3 mm disk specimens could be used to estimate corrosion behavior of austenitic stainless steel using EPR test.
(2) In the specimens irradiated at 300℃ and 400℃, the surface pitting was observed within grains after EPR testing. The number density of pits and the reactivation ratio increased with irradiation dose. No etching trenches at and around grain boundaries were observed, nevertheless RIS was occurred in the specimens irradiated at 400℃ to 0.1dpa. So it was suggested that the corrosion resistance at grain boundaries after ion irradiation was still maintained.
(3) In the specimens irradiated at 500℃, etching trenches at and around grain boundaries were observed, and surface pits were absent. The width of etching trenches and the reactivation ratio increased with irradiation dose. It was suggested that high-temperature irradiation enhanced RIS and also the recovery of damage defects and therefore it suppressed the chemical activation within grains.
(4) The correlation between the changes in corrosion properties and the development of RIS and microstructures was discussed.

論文審査結果の要旨

軽水型原子炉の炉内構造材料として使用され、さらに核融合実験炉の構造材料としても使用が検討されているオーステナイトステンレス鋼には、中性子照射環境下で高温水あるいは水蒸気中で使用されるために照射誘起応力腐食割れという課題があり、その機構には多くの因子が関与すると考えられている。本研究では関連する因子の内で、特に照射により生成される原子はじき出し損傷による材料の腐食特性変化に着目し、その挙動を基礎的立場から実験的に明らかにしたものである。軽イオンとして代表的な水素イオンを用いて、種々の温度やフルエンス条件で照射したSUS304ステンレス鋼について、電気化学的再活性化（EPR）法を適用し、照射による腐食特性変化挙動を詳細に調べ、イオン照射とEPR法を組合わせる腐食特性評価法について検討するとともに、腐食特性変化に及ぼす照射条件の影響を明らかにしている。本論文はこの成果をまとめたもので、全8章よりなる。

第1章は緒言であり、本研究の背景および目的を述べている。

第2章は実験方法についてまとめており、実験試料、軽イオン照射実験、EPR法による腐食試験、および電子顕微鏡による微細組織観察と粒界偏析測定について述べている。

第3章では、EPR法による鋭敏化評価に及ぼす試験片寸法と結晶粒径の影響について調べ、微小試験片としての3 mm直径の透過電子顕微鏡用ディスク試料を用いる有効性を明らかにしている。

第4章では、水素イオン照射材の腐食特性評価において、照射まま表面では孔食により再活性化率が大きく評価されるに対して、照射表面属を除去した場合には腐食挙動が異なることを示している。さらにヘリウムイオン照射の制約について付言している。

第5章では、オーステナイトステンレス鋼の腐食特性変化に及ぼす照射温度、照射フルエンスおよび照射速度の影響について系統的に調べ、特に照射温度の役割が大きく500℃照射において明瞭な粒界腐食が生ずることを明らかにしている。

第6章では、水素イオン照射したステンレス鋼における微細組織と粒界偏析について電子顕微鏡を用いて実験し、イオン照射条件と粒界クロム量の減少挙動の関係を調べている。

第7章は考察であり、EPR法を水素イオン照射材に適用する場合の問題点、ステンレス鋼の腐食特性変化に及ぼす照射条件と微細組織および粒界偏析との関係について検討し、軽イオン照射と中性子照射による腐食特性変化機構の差異について検討している。

第8章は総括である。

以上要するに本論文は原子炉炉内構造用ステンレス鋼の原子はじき出し損傷による腐食特性変化について、水素イオン照射材にEPR法を適用して腐食特性評価を行う際の有効性と注意点を調べるとともに、原子はじき出しによる再活性化率の照射温度、照射フルエンス、照射速度依存性を系統的に明らかにし、特に照射温度の役割が重要であることを実験的に明瞭に示して腐食特性変化の機構に対して重要な知見を得ており、量子エネルギー工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。