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# Comparative study: sensitization development in hot-isostatic-pressed cast and wrought structures type 316L(N)-IG stainless steel under isothermal heat treatment

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**Abstract**

This work focuses on the relative sensitization resistance of type 316L(N)-IG stainless steel (SS). Cast and wrought structures SS after solid hot-isostatic pressing (solid-HIP) operation are investigated under isothermal heat treatment. Wrought SS/SS solid-HIP joint sensitization is taken also into consideration. These experiments employed the quantitative double-loop electrochemical potentiokinetic reactivation (DL-EPR) and oxalic acid etch screening tests. A copper–copper sulfate-16% sulfuric acid test applied for strongly sensitized cast SS to reinforce the results were received by the methods mentioned above. Results from all employed methods correlate well. Sensitization was detected neither in cast nor in wrought SS in as-HIPed condition excluding wrought SS/SS solid-HIP joints. Significant difference between sensitization development rates was determined in cast and wrought SS structures when annealing at 675 °C for a duration up to 50 h.


## 1. Introduction

Austenitic stainless steels (SSs) are widely used as structural materials for the water-cooled nuclear power plants equipment due to their high resistance to general corrosion [1]. However, SSs are susceptible to local corrosion damage under certain environmental conditions. The primary forms of this localized corrosion attack are intergranular corrosion (IGC), stress corrosion cracking (SCC), and pitting formation. Particularly, the sensitization phenomenon is often responsible for intergranular stress corrosion cracking (IGSCC) failures happened to BWR primary water recirculation pipelines and in-vessel components [2,3].

Sensitization refers to the loss of corrosion resistance after heat treatment (or slow cooling) in the particular temperature range where chromium carbide precipitations are thermodynamically stable (<800 °C) and chromium diffusion is sufficiently rapid (>500 °C) so that SS can become sensitized in a relatively short time. The primary composition changes when SS sensitizing is the preferential grain boundary precipitation of chromium-rich carbides and an associated depletion of chromium in the adjacent region occurs [4]. The sensitization resistance is directly related with the SS' features: bulk chemical composition, local alloy element distribution inhomogeneity, previous thermal and mechanical history, steel structure, average grain size and grain size variation [5,6].

Type 316L(N)-IG SS sensitization behavior is of practical interest as the solid-HIPed steel and SS/SS joints are proposed for ITER in-vessel material and units. HIP thermal cycle comprises the stage of relatively slow cooling through the sensitizing temperature range. The subsequent sensitization resistance of solid-HIPed type 316L(N)-IG SS is one of the main material features from the equipment service reliability standpoint.

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## 2. Experimental

### 2.1. Materials

Two solid-HIPed 316L(N)-IG type SS heats are used having the bulk chemical compositions as listed in Table 1. The Previous thermal history is as follows:

*'as-received' cast structure SS*

- solution annealed at 1083 °C for 4 h and quenched,
- solid-HIP (1121 °C, 4 h, 105 MPa),
- reannealed at 1083 °C for 4 h and quenched;

*'as-received' wrought structure SS*

- solid-HIP (1100 °C, 4 h, 100 MPa).

*Isothermal sensitizing heat treatment* performed for specimens of cast SS and wrought SS/SS solid-HIP joint in furnace at 675 °C for 15 and 50 h. There were three standard methods used to evaluate the degree of sensitization (DOS). Quantitative DL-EPR test [7] using the principle of preferential surface passivity breakdown over the chromium-depleted zones when reverse potentiokinetic scanning. The sequence of polarization is as follows. The tested surface was exposed to the acid solution 0.5 M $H_2SO_4$ + 0.01 M KSCN at 25 °C for 2 min. Solution de-aeration was not applied. The tested surface potential is first scanned anodically starting from the corrosion potential to the potential +300 mV (vs. SCE). As soon as this potential is reached, the scanning direction is reversed and the potential is decreased at the same rate to the corrosion potential. The voltage scan rate was 100 mV/min. The reactivation ratio was used to express DOS of the tested SS, i.e. the ratio of the maximum reactivation current to the maximum activation current.

As reported [8] AISI 321 SS becomes susceptible to IGSCC in high-temperature water when the DL-EPR ratio reaches the levels starting from 1.0–1.5%. If the DL-EPR ratio should arise up to 10% SS becomes susceptible to IGC.

The oxalic acid etch screening test was also used to obtain the qualitative comprehension of sensitization spread. The 1 μm polished SS surface was etched in an oxalic acid water solution at room temperature with a current density of 1.0 A/cm$^2$ for 1.5 min. The etched surface is examined using a metallurgical microscope at 250× magnification. In this method an intermediate SS DOS subdivision (from unsensitized to severely sensitized conditions) may be done qualitatively referring to a range of intergranular dissolution extents. The Classification of the obtained etch structures is given in this study as described in [9]. Being classified as 'Interdendritic Ditches'

Table 1
Bulk chemical composition of 316L(N)-IG SS material investigated (wt%)

| Heat | C | Cr | Ni | Mo | Mn | Si | N | Cu | Ti | Co | P | Nb | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cast | 0.03 | 17.7 | 12.1 | 2.4 | 1.85 | 0.92 | 0.08 | 0.17 | <0.1 | 0.05 | 0.024 | 0.02 | 0.004 |
| Wrought | 0.02 | 17.5 | 12.2 | 2.4 | 1.73 | 0.41 | 0.06 | 0.23 | <0.01 | 0.07 | 0.025 | <0.01 | 0.001 |

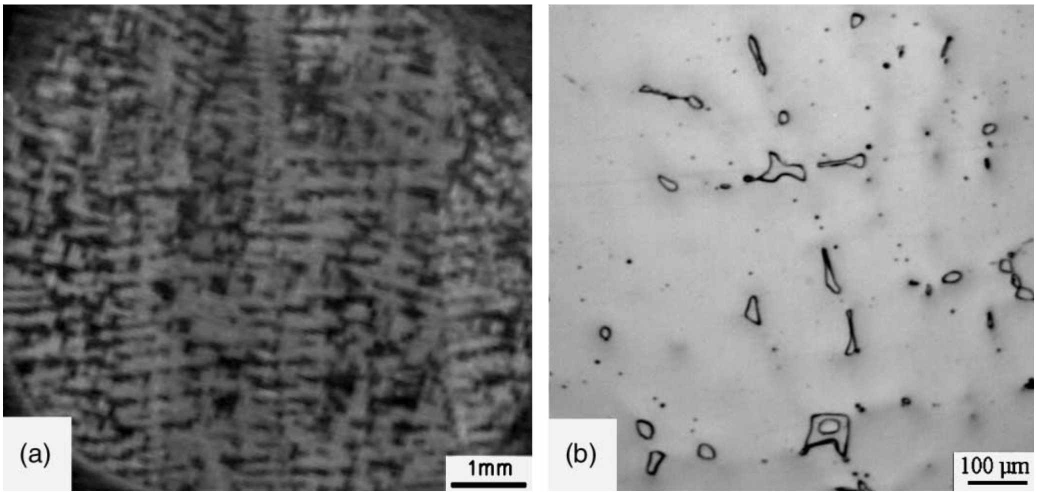


Fig. 1. 'As-received' cast SS macrostructure revealed by DL-EPR test etching (a) and typical distribution and appearance of the α-phase in cast SS revealed by oxalic acid etch test (b).

in cast SS or 'Ditch Structure' in wrought SS etch structure means that SS is strongly sensitized (failed as susceptible to IGC).

Copper–copper sulfate-16% sulfuric acid test [10] was applied in this work when sensitization degree of cast SS reached the level of susceptibility to IGC. Specimens boiled for 24 h were bent through a 180° bend for further visual inspection of fissures appearance.

## 3. Results

*'As-received' condition:* Cast SS macro- and microstructures before sensitizing heat treatment are illustrated in Fig. 1(a and b). It has a typical columnar dendrite structure with large grains – 2 mm and larger. Dendrites are orientated at regular intervals in the cast SS. Fig. 1(b) shows a typical micrograph of α-phase inclusions in cast metal.

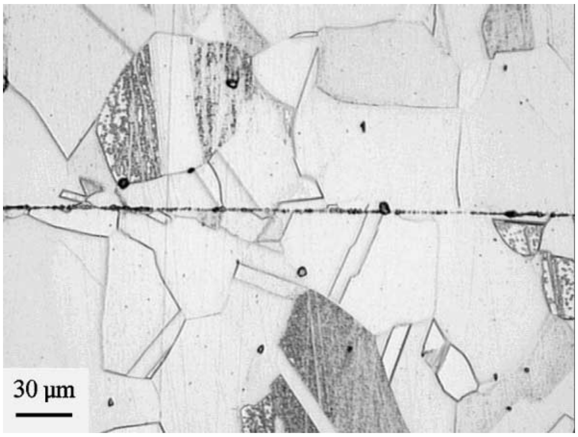


Fig. 2. Oxalic acid etch microstructure for 'as-received' solid-HIP joint (in the figure middle) of wrought SS.

The wrought SS microstructure and solid-HIP joint are illustrated in Fig. 2. The α-phase presence was not detected in wrought SS. Both cast and wrought SS structures were perfectly unsensitized in 'as-received' conditions. Discrete inclusions are visible along the solid-HIP line after oxalic acid etching. DL-EPR ratios are also determined for wrought SS in the range about of 0–0.04% that is normal for unsensitized SS. Oxalic acid etch structures can be classified as 'Isolated Ferrite Pools' and 'Step Structure' for cast and wrought SS types which are characterized as unsensitized.

*Isothermal sensitization behavior at 675 °C:* The curves plotted in Fig. 3(a) quantitatively illustrate the difference in sensitization resistance of SS depending on its structure. After sensitizing for 50 h, cast SS was failed as susceptible to IGC by DL-EPR, oxalic acid etching, and copper–copper sulfate tests. DL-EPR polarization curves (Fig. 3(b)) which characterize the high DOS developed in the cast structure. Sensitization development in cast SS is illustrated in Fig. 4. The 'Interdendritic Ditches' oxalic acid etch microstructure (Fig. 4(b)) illustrates the high DOS developed within 50 h. DL-EPR ratios are determined in the ranges 1.2% and 9.8% for 15 and 50 h, respectively. Annealed for 50 h, cast SS also failed by copper–copper sulfate test within 90° bending because of fissures formation. The sensitization mode in the cast structure is observed in accordance with a mean orientation of the dendrites, Fig. 5.

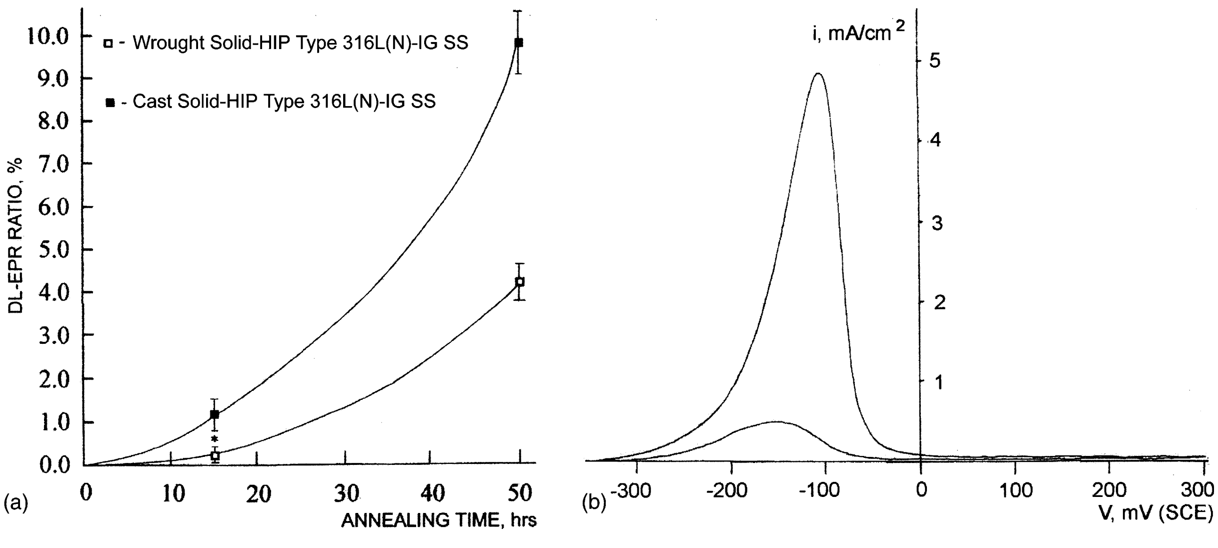


Fig. 3. Sensitization development curves (obtained by DL-EPR test) for solid-HIP type 316L(N)-IG SS as a function of isothermal annealing time at 675 °C (a) and DL-EPR polarization curves for 50 h annealed solid-HIP cast SS for DOS being 9.8% (b).

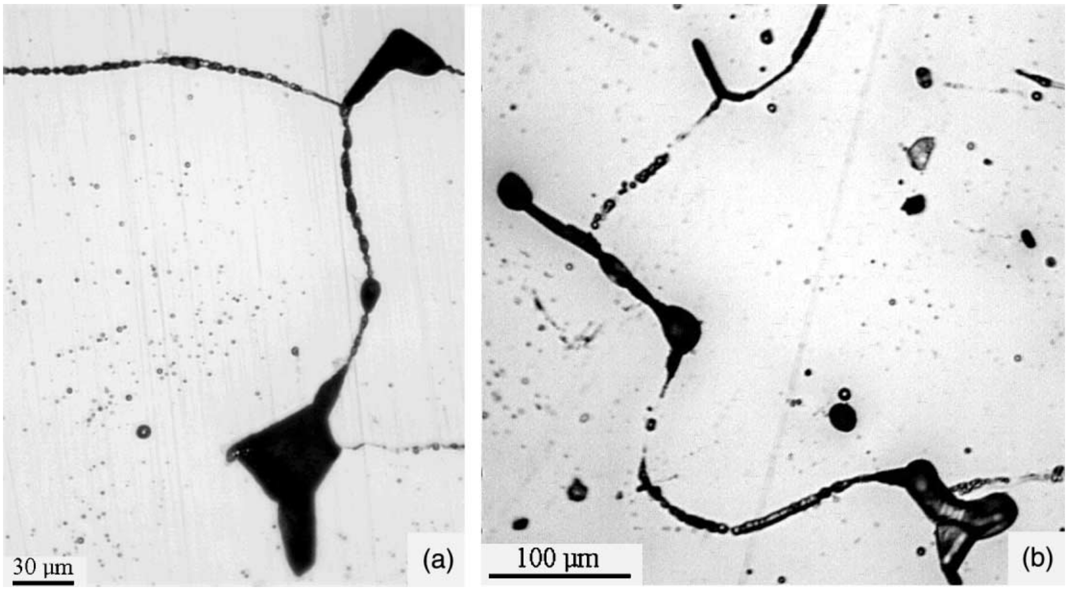


Fig. 4. Oxalic acid etch microstructures for solid-HIP cast SS annealed at 675 °C for 15 h (a) and 50 h (b).

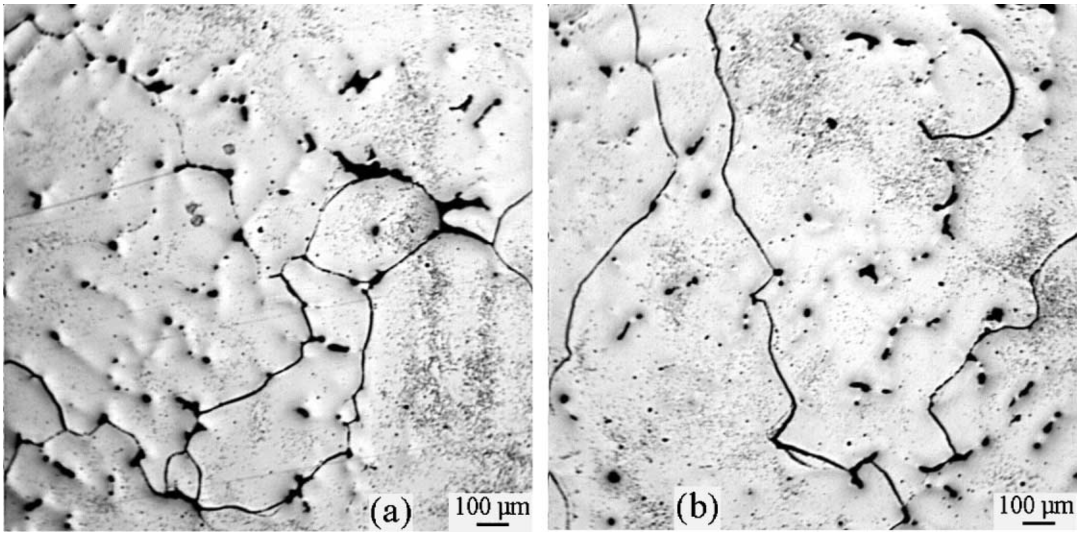


Fig. 5. Sensitization modes revealed by oxalic acid etch test in solid-HIP cast SS annealed at 675 °C for 50 h. Cross (a) and longitudinal (b) sections relatively to leading axis of dendrites orientation in cast SS.

Wrought SS sensitization is retarded and developed slower than cast structure SS. Wrought SS DOS did not reach the level of susceptibility to IGSCC after 15-h sensitizing annealing. Growth of earlier nucleated precipitations was detected in the solid-HIP line as well the nucleation of new precipitations, Fig. 6(a). The DL-EPR ratio value had slightly increased up to 0.2% for wrought SS after 675 °C, 15 h heat treatment characterizing SS as slightly sensitized from the IGSCC standpoint.

The 50-h heat treatment approached wrought SS DOS above the level of susceptibility to IGSCC. The etch structure (Fig. 6(b)) can be classified as 'Dual Structure'; these results are in good agreement with DL-EPR test results for wrought SS. The DL-EPR ratio is determined as 4.2%. The, solid-HIP joint became perfectly sensitized as it is qualitatively revealed by oxalic acid etching. Energy dispersion X-ray microanalysis (EDX, 15 kV, 1 nA) performed to compare the Cr

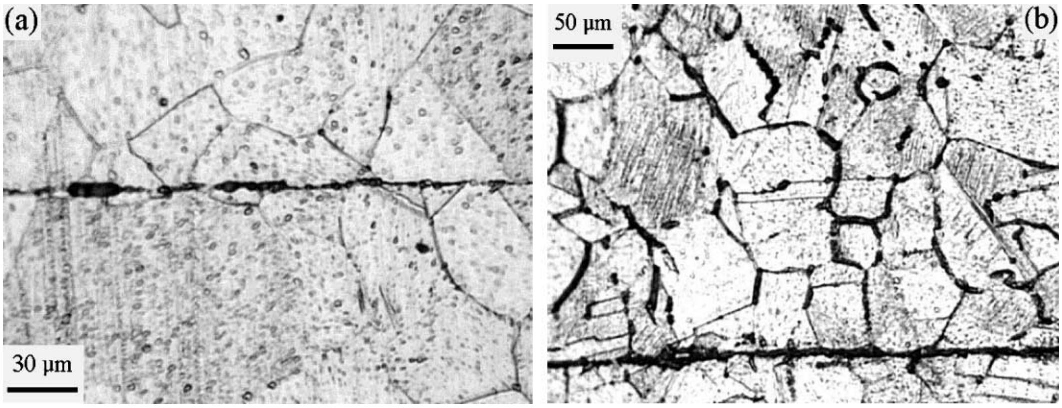


Fig. 6. Oxalic acid etch microstructures for solid-HIP joint of wrought SS annealed at 675 °C for 15 h (a) and 50 h (b).

content revealed that the chromium content (element %) both along the sensitized grain boundary and in solid-HIP line exceeds the average level in wrought SS by 1.0% and 1.2%, respectively. This result may be directly related with the chromium-rich secondary phase formation.

## 4. Conclusion

The isothermal sensitization behavior of solid-HIP type 316L(N)-IG SS has been estimated. Cast and wrought steel structures are taken into consideration comparatively.

Wrought structure is revealed as more resistant to attack by sensitization compared with cast steel structure. Sensitization is delayed and develops slower in wrought structure. However, attention should be paid to type 316L(N)-IG SS solid-HIP joint when cooling through the sensitizing temperature range or under isothermal heat treatment. Solution-annealing heat treatment should be performed finally to avoid sensitization (and further susceptibility to IGSCC) in the solid-HIP line.

Cast structure steel can hardly be considered as resistant to sensitization at 675 °C within the relatively short-time heat treatment (for 15 h) from the subsequent susceptibility to IGSCC standpoint. Disposal of sensitization developed in the cast structure is related with the dendrites three-dimensional orientation.

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## References

[1] Yu. Balandin et al., NPPs Structural Materials, Energoatomizdat, Moscow, 1984.
[2] S. Buch, Piping Failures in United States Nuclear Power Plants: 1961–1995, Swedish Nuclear Power Inspectorate Report 96:20 (1996).
[3] O. Wachter, Nucl. Eng. Des. 168 (1997) 35.
[4] E. Bain, R. Aborn, J. Rutherford, Trans. Amer. Soc. Steel Treat. 18 (1930) 837.
[5] R. Paskali, A. Benvenuti, D. Wenger, Corrosion 40 (1984) 21.
[6] S. Bruemmer, Corrosion 42 (1986) 27.
[7] JIS G 0580-1986, Method of Electrochemical Potentiokinetic Reactivation Ratio Measurement for Stainless Steels.
[8] O. Wachter et al., VRG Kraftwerkstechnik 76 (1996) 777.
[9] ASTM A 262-93a, Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels, Practice A – Oxalic Acid Etch Test for Classification of Etch Structures of Austenitic Stainless Steels.
[10] ASTM A 262-93a, Practice E – Copper–Copper Sulfate-16% Sulfuric Acid.