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Improving Hydrogen Embrittlement Resistance of Precipitation Hardened Nickel-Alloys

Luca Foroni

Foroni SpA – Stainless Steels and Super Alloys
Via Ambrogio Colombo, n. 285
Gorla Minore (VA), 21055
Italy

Carlo Malara

Foroni SpA – Stainless Steels and Super Alloys
Via Ambrogio Colombo, n. 285
Gorla Minore (VA), 21055
Italy

ABSTRACT

Hydrogen embrittlement susceptibility of precipitation hardened Ni- alloys is a complex function of several factors such as chemical composition, deformation mode, grain size and grain boundary precipitation of carbides and intermetallic phases. Understanding the role of these factors is fundamental in identifying metallurgical conditions that can enhance resistance of precipitation hardened Ni-alloys to hydrogen embrittlement.

Analysis of hydrogen embrittlement data and a new test program have been carried out to further investigate the role of such factors and determine metallurgical conditions capable of improving hydrogen embrittlement resistance of UNS N09955 and UNS N07716 alloys. Results of the study are presented and discussed in this paper.

Key words: UNS N09955, alloy 955, UNS N07716, alloy 716, precipitation hardened nickel-alloys, hydrogen embrittlement

INTRODUCTION

Precipitation hardened (PH) Ni-alloys are widely used in the oil and gas industry since they provide an excellent combination of corrosion resistance and mechanical strength. Their use in the manufacture of API¹ 6A pressure-containing and pressure-controlling components is subject to the stringent requirements of specification API Standard 6ACRA.^(1,2) However, matching the requirements of API Standard 6ACRA does not preclude susceptibility of some PH Ni-alloys to hydrogen embrittlement (HE)

¹American Petroleum Institute (API), 1220 L St., N.W., Washington, D.C. 20005-4070

and this in some cases has led to premature and unexpected failures of components made from such materials.⁽³⁻⁵⁾

Much effort has been devoted to understanding HE. Several mathematical models have been proposed to describe the complex interaction between hydrogen and material microstructure in terms of several factors, i.e. deformation mode, chemical composition, grain size and grain boundary precipitation of carbides and intermetallic phases.⁽⁶⁻¹¹⁾ Understanding the role of these factors is fundamental in identifying metallurgical conditions that can enhance HE resistance of PH Ni-alloys.

In this paper, analysis of HE data and a new test program have been carried out to further investigate the role of such factors and determine metallurgical conditions that are helpful in improving HE resistance of UNS N09955 and UNS N07716 alloys. Results of the study are presented and discussed in this paper. For brevity, in the following text alloy UNS N09955 is identified as alloy 955 and alloy UNS N07716 is identified as alloy 716.

Main Factors Affecting HE Susceptibility

Main factors affecting HE of PH Ni-alloys are: deformation mode, chemical composition, grain size and precipitation of carbides and intermetallic phases at grain boundaries. They are briefly reviewed in the following.

Deformation Mode

In general, plastic deformation mode can be either planar or by cross-slip. The planar deformation mode consists of dislocation motion along certain preferred combinations of crystallographic planes (slip planes) and directions. A consequence of this deformation mode is the pile-up of dislocations at an obstacle, such as a grain boundary, resulting in the build-up of stress concentrations. When deformation occurs by cross-slip, dislocations can circumvent obstacles in a given slip plane by moving onto another slip plane which intersects the original slip plane, providing a site for relief of the stress concentration. It turns out that materials are more susceptible to HE if they deform by planar slip.^(12,13) In PH Ni-alloys, the presence of γ' and γ'' coherent precipitates resulting from the precipitation hardening heat treatment promotes slip planarity.⁽¹⁴⁻¹⁶⁾ Coherent precipitates have crystal plane spacing matching that of the parent structure. Once deformation initiates on a plane, the precipitate is cut and surfaces with orientations that may not match up with that of the parent crystal planes are created. This process requires energy consumption and, accordingly, continued deformation on the same plane rather than new planes is favored.

Therefore, PH Ni-alloys are inherently prone to HE because of the presence of coherent precipitates that forces deformation to be planar. The coarser the coherent phases, the greater planarity of deformation.

Chemical Composition

PH Ni-alloys contain transition metals such as Cr, Ni, Fe and Mo. In a transition metal, repulsive forces arise from overlapping of electron d-bands and determine the metal interatomic distance. Electrons of hydrogen atoms enter the electronic d-bands of a transition metal. This increases the electron concentration of these bands and the repulsive forces, thereby decreasing the cohesive strength of the lattice (decohesion theory). Ni has higher concentration of electrons in the 3d band compared to Fe. Therefore, Ni-alloys containing more Fe are less susceptible to HE.^(17,18)

Grain Size

Grain size provides the space for dislocation movement. As grains get smaller in a material, dislocations have less space to move before they hit a grain boundary. When dislocations cannot move very far before fracture, the plastic deformation decreases and the material's fracture becomes more brittle.⁽¹³⁾ Moreover, smaller grain size results in more grain boundaries, providing more path for hydrogen diffusion and trapped concentration.⁽¹⁹⁾ In other words, the HE susceptibility increases as the grain size becomes finer.

Grain Boundary Precipitates

As a result of the thermomechanical processing and heat treatment, intermetallic phases (such as δ phase, η phase, σ phase, ...) and carbides (M_6C , $M_{23}C_6$, ...) can be present at grain boundaries of PH Ni-

alloys. They constitute trapping sites for hydrogen that favor hydrogen diffusion along grain boundaries and this is further enhanced by larger grain boundary precipitates.

Analysis of HE Data

HE data of PH Ni-alloys have been obtained by comparing results of Slow Strain Rate Tensile (SSRT) tests performed under cathodic polarization with results of SSRT tests performed in an inert environment (air) under the same other conditions.^(20,21) Details of the test procedure are given elsewhere.⁽²²⁾ Results of these tests are summarized in Figure 1 which reports the elongation to failure ratio (EFR) for each tested grade, where EFR is the ratio between elongation to failure under cathodic polarization and elongation to failure in inert environment for that grade. Tested grades are in compliance with API Standard 6ACRA and designated accordingly by reporting the last 3 digits of the UNS² number of the alloy followed by a number indicating the minimum yield strength expressed in ksi units.

Based on the actual chemical composition, the tested grades cover the following ranges of transition elements:

- Cr: from 17 to 22 %;
- Ni: from 27 to 62 %;
- Mo: from 3 to 8 %;
- Fe: from 4 to 35 %.

The grain size of the tested grades as determined according to ASTM⁽³⁾ E112 ranges from No. 5 (65 μm) to No. 3 (130 μm).⁽²³⁾ Partial coverage of grain boundaries with similar precipitates was observed on all tested grades except 718 grades that showed very low coverage with delta phase traces.

It can be seen that the biggest difference among the studied grades is their iron content which spans from 4 % in alloy 716 grades to 35 % in alloy 935, i.e. about nine times the iron content of alloy 716.

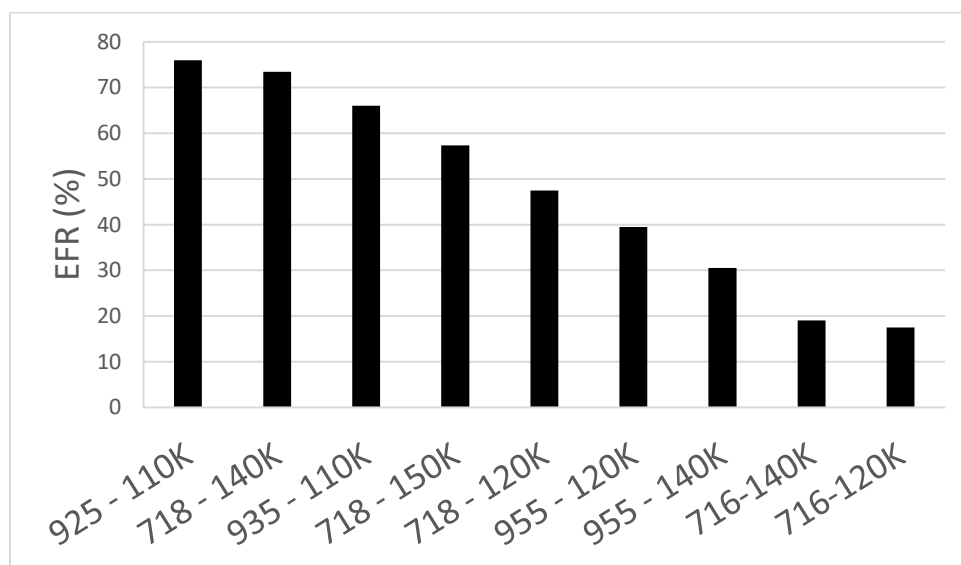


Figure 1 –Elongation to Failure Ratio (EFR) for each tested grade. EFR is the ratio between elongation to failure under cathodic polarization and elongation to failure in inert environment for that grade. Tested grades are in compliance with API Standard 6ACRA and designated accordingly by reporting the last 3 digits of the UNS number of the alloy followed by a number indicating the minimum yield strength expressed in ksi units.

² Unified Numbering System for Metals and Alloys (UNS), Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International.

³ American Society for Testing and Materials (ASTM) International, 100 Barr Harbor drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA.

These data are well correlated as a function of the Fe content of the tested grade (Figure 2) and the correlation improves when the mean EFR (EFR_m) of a given alloy, calculated as the arithmetic mean of EFR values of various tested grades of that alloy, is used (Figure 3).

The strong correlation of HE susceptibility, as measured by EFR, with Fe content of the tested grades indicates that Fe content is a factor of major importance in determining HE susceptibility of PH Ni-alloys. HE susceptibility of PH Ni-alloys increases as their Fe content decreases indicating that decohesion theory is a valid tool to understand HE of these materials.

The difference in HE susceptibility of different grades of the same alloy can be explained as a function of amount and size of hardening coherent precipitates, and of grain boundary precipitates resulting from different processing. In alloy 718, γ' and γ'' phases are the finest in the 140K grade, the coarsest in the 120K grade and of intermediate sizes in the 150K grade. In the same alloy, the density of γ' and γ'' phases in the 150K grade is higher as compared to the 140K grade, while the density of such phases in the 120K grade is intermediate between the density of the 140K grade and that of the 150K grade.⁽²⁴⁾ These microstructural features are consistent with the increase of HE susceptibility as more and coarser hardening coherent phases precipitate. In all three grades of alloy 718, delta phase is present as small precipitates over just a few grain boundaries and cannot therefore account for the difference in HE susceptibility exhibited by the three tested grades of alloy 718.

A similar situation is observed with the tested grades of alloy 955. In this alloy, the 120K grade has only fine γ'' phase while the 140K grade has γ'' phase similar to the 120K grade and fine γ' phase for a total volume fraction of precipitates about twice that of the 120K grade. Again, this is consistent with greater HE susceptibility when more and coarser hardening coherent phases precipitate. Both tested grades of alloy 955 have some carbides present over a few grain boundaries but they cannot account for the difference in HE susceptibility between the 120K grade and the 140K grade of alloy 955.

The aforementioned comments indicate that, besides the chemical composition which determines the inherent HE susceptibility, the heat treatment, which determines amount and morphology of the precipitation hardening phases, can greatly affect the HE susceptibility of PH Ni-alloys. This aspect has been further investigated in order to optimize mechanical strength and HE susceptibility and, ultimately, to reduce HE susceptibility of alloys 955 and 716. While providing very good corrosion resistance even in very severe environments where other PH Ni-alloys would not, these two alloys show low (alloy 716) or moderate (alloy 955) resistance to HE as a consequence of their relatively low Fe content. Increasing their resistance to HE is therefore of the greatest importance in order to extend the range of their applications.

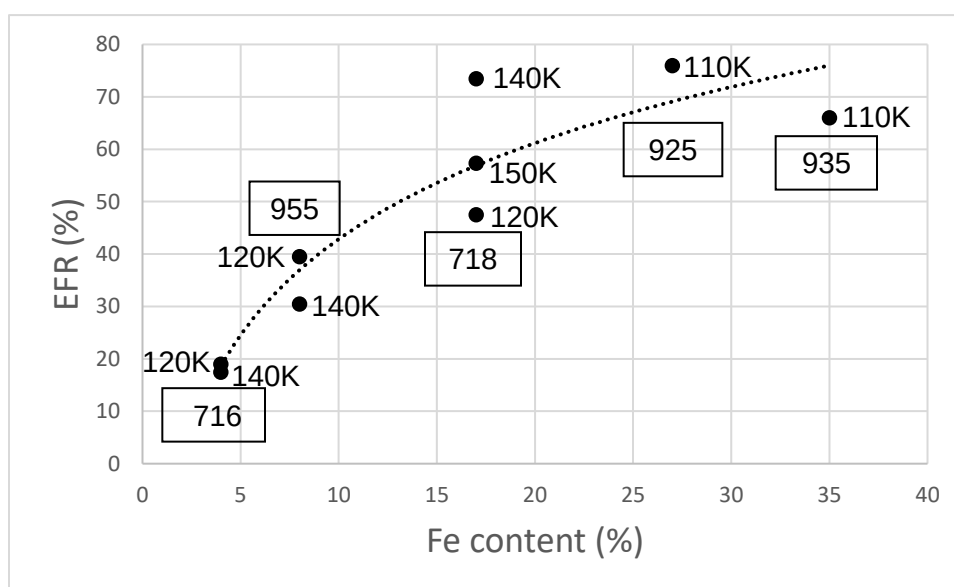


Figure 2 – Elongation to failure ratio (EFR) as a function of the Fe content of each tested grade. Each alloy is designated by the last 3 digits of its UNS number.

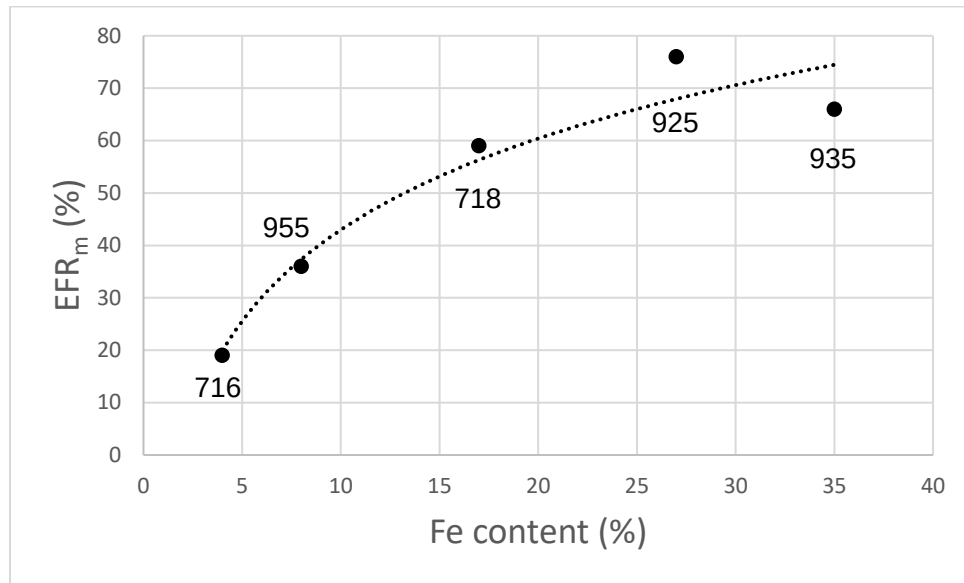


Figure 3 - Mean Elongation to Failure Ratio (EFR_m) as a function of the Fe content of each tested alloy. EFR_m is the arithmetic mean of EFR values of each tested grade of that alloy. Each alloy is designated by the last 3 digits of its UNS number.

EXPERIMENTAL PROCEDURE

Alloy Manufacturing Process

Alloy 955 bars of 127 mm in diameter have been produced as per API 6ACRA – 120K grade of the same alloy except precipitation hardened at 718 °C for 7 hours followed by air cooling.

Alloy 716 bars of 120.65 mm in diameter have been produced as per API 6ACRA – 120K grade of the same alloy except precipitation hardened at 718 °C for 4 hours followed by air cooling.

For both alloys, the melting practice consisted of raw material melting in EAF (Electric Arc Furnace) followed by AOD (Argon Oxygen Decarburization) refining followed by bottom pouring into round ingots. Each ingot is re-melted by consumable-electrode Vacuum Arc Re-melting (VAR) process and converted into round bars through the following main manufacturing steps:

- VAR ingot homogenization consisting of a controlled temperature process to remove primary segregation;
- Primary conversion of the VAR ingot to a square bloom followed by bloom forging to a round bar by computer-controlled state-of-the-art forging equipment to obtain uniform reduction from center to surface through a reproducible process;
- Heat treatment under conditions of tight temperature control using furnaces calibrated and surveyed to aerospace requirements of AMS⁴ 2750E.⁽²⁵⁾

Alloy Characterization

The aforementioned bars have been characterized in terms of mechanical properties, microstructure and HE susceptibility.

Mechanical Properties

Mechanical properties have been evaluated in the longitudinal direction at mid radius of bar prolongations by ASTM E8 tensile tests on standard 4D specimens, ASTM E23 impact tests on Charpy-V-Notch specimens and ASTM E18 hardness tests.⁽²⁶⁻²⁸⁾

⁴ Aerospace Material Specification, Warrendale, PA: SAE International