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Emphasis of Embrittlement Characteristics in 304L and 316L Austenitic Stainless Steel

Rati Saluja[1*], Dr. K.M.Moeed[2]
[1]*Department of Mechanical Engineering, Integral University, Lucknow, U.P., India,*
[2]*Jr. Associate Professor, Integral University, Lucknow, U.P., India,*

Abstract: *High toughness and good oxidation resistance is achieved by using austenitic stainless steels at temperatures that range from cryogenic temperatures, to elevated temperatures. The embrittlement phenomenon in 304L and 316L austenitic stainless steel welds exposed to high temperature is accelerated by the existence of delta ferrite which further transforms to intermetallic phases. Cracks can also occur in various regions of the weld with different orientations, in the underlying weld metal or adjacent HAZ due, to low-melting liquid phases, which allow boundaries to separate under the thermal and shrinkage stresses during weld solidification and cooling. Specific alloy composition and alloying additions can also have a major effect on weldability, mechanical properties and the as microstructure of weldment. Competing factors add to the complexity of the phenomenon, but must be examined in order to learn how to limit detrimental effect. The review concentrates on effect of various embrittlement mechanisms on nuclear materials (304L & 316L austenitic stainless steel) to provide an initial source of information for materials selection by designers and operators and for failure analysis.*
Keywords: *Austenite, Embrittlement, Fatigue, Ferrite, Sigma phase, Stress corrosion cracking, Thermal Aging,*

I. Introduction

A concern, when welding the 304 L and 316L austenitic stainless steels, is the susceptibility to solidification and liquation cracking [1]. Kain affirmed major issues in shaping the design life are the selection of material and life prediction of austenitic stainless steel the issue of Stress Corrosion Cracking (SCC). He ensured that absence of sensitisation and Low Temperature Sensitisation (LTS) over the complete design life of the components will ensure freedom from early onset of intergranular stress corrosion cracking [2].

Osama M. Alyousif estimated that intergranular cracking was resulted from hydrogen embrittlement due to strain-induced formation of martensite along the grain boundaries, while transgranular cracking took place by propagating cracks nucleated at slip steps by dissolution [3]. M. G. Adamson reported the observation of rapid, severe embrittlement of 316 austenitic stainless steel by liquid tellurium–caesium mixtures in the temperature region 500–700°C [4]. Thus any observed deleterious effect of chemical environment on the alloy mechanical properties such as the ‘hot’ embrittlement of austenitic stainless steel by liquid zinc is very important [5, 6].

Old has mentioned that fission products such as caesium, cadmium and tellurium might embrittle the austenitic stainless steel cladding of fast reactor fuel pins in certain conditions [7]. Toribio has examined the embrittlement process in steels at different strain rates. He observed that the deleterious effect of hydrogen generally decreased with increasing displacement rate [8] Grargi discusses the mechanistic aspects of thermal aging embrittlement (TAE), as well as manifestations of TAE in austenitic stainless steel welds and castings [9].

Also of interest is the anticipated swelling behaviour of the steels at high exposure levels and potentially higher swelling levels associated with life extension. Thus to limit detrimental effect caused by temperature, it is of great importance to the economy to reveal details of effect of various embrittlement on austenitic stainless steel.

II. Types Of Embrittlement

2.I Low Temperature Embrittlement

Between the weld fusion line and the HAZ there is a residual strain of 15-20%. Since all the Low temperature sensitisation LTS related cracking has been in this region, it is pertinent to study the LTS behaviour of stainless steels which are in cold-worked condition. It was analysed that type 304 L and 304 stainless steels have a tendency to transform into martensite upon cold rolling [3].

The martensite phase sensitised very fast between 300^{o}C to 500^{o} C. This changed the LTS behaviour completely from that of an all-austenitic stainless steel. He stated that the sensitized 304 showed intergranular cracking, the DOS developed in the annealed materials after the LTS treatment was not sufficient to make it susceptible to inter granular stress corrosion cracking. However, type 316LN stainless steel was found to be the most resistant grade of stainless steel to LTS [2].

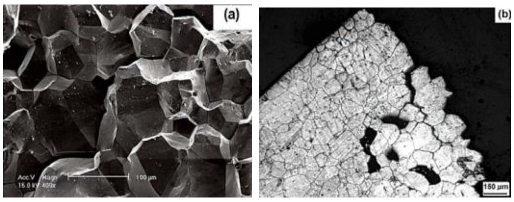

Fig. 1; Complete intergranular cracking of the sensitized type 304 stainless steel (a) intergranular facets of the fracture surface and (b) secondary intergranular branches emanating from the main intergranular crack [2].

2.2 Thermal Aging Embrittlement Phenomenology (TAE)

TAE is a time and temperature dependent degradation mechanism. It is caused by the thermally activated movement of lattice atoms over a long period of time. This degradation process can occur without application of mechanical load [9].

2.2.1 Aging behavior above 500°C temperatures

Prolonged exposure in the temperature range of 565-925°C results in chromium depletion from the grain boundaries, making them susceptible to intergranular corrosion [28]. Islands were typically found to be all ferrite or all sigma. These ferrite regions were substantially enriched in chromium, with levels nearly identical to those found in sigma phase. These observations indicate that the nucleation of sigma phase in ferrite is the rate limiting step for the transformation. They indicate that although the chromium enrichment of ferrite is a necessary step, it is not sufficient for sigma formation. Also, the fact that partially transformed ferrite areas were rarely observed indicates that once nucleation of sigma phase begins as shown in figure 2 [12].

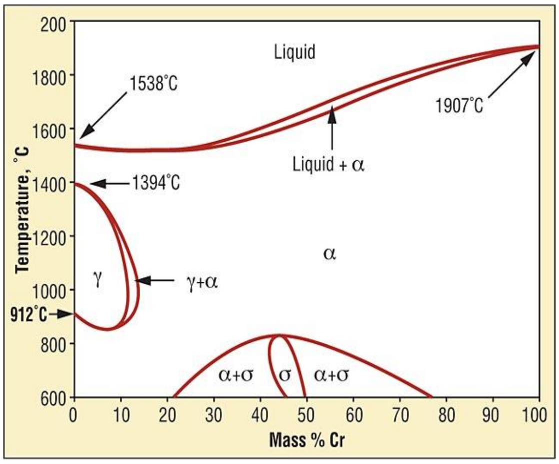

Fig. 2: The Fe-Cr phase diagram indicating sigma phase embrittlement [28]

The most rapid sigma-phase formation occurs in the range of 700-900°C [9]. Sigma phase embrittlement has been shown to cause severe loss of ductility, toughness, and corrosion resistance resulting in cracking and failure of components, especially those subjected to impact loads or excessive stress [28].

2.2.2 Aging at temperatures 475°C

The aging at temperatures less than 550°C showed no evidence of ferrite to sigma phase transformation but precipitation of $M_{23}C_6$ carbide at the austenite/ferrite interface was found to occur [13]. During the initial stages of aging, within the ferrite a fine scale spinodal decomposition of ferrite into iron rich alpha and chromium rich alpha phases was observed. Abundant precipitation of G-phase was also observed in addition to the spinodal decomposition within the ferrite. G-phase is a nickel rich silicide that has been identified in austenitic stainless steel welds and castings [10].

If austenitic steels are used in the temperature range 350-550°C, a serious decrease in toughness will be observed after shorter or longer times. The phenomenon is encountered in alloys containing from 15 to 75 % chromium and the origin of this embrittlement is the spinodal decomposition of the matrix into two phases of body-centered cubic structure, α and α′. The former is very rich in iron and the later very rich in chromium. This type of embrittlement is usually denoted as 475°C embrittlement [11].

2.3 Hydrogen Embrittlement (HEE)

Embrittlement effects are typically confined to near-ambient temperatures, maximizing near room temperature and diminishing at higher or lower temperatures [9].

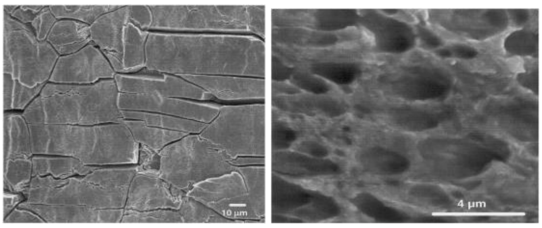

Fig. 3 a: Brittle transgranular and intergranular multiple cracking on specimen surface,
Fig. 3 b: Ductile fracture near brittle zone,
(Cathodic charging on type 316L steel during slow strain rate test, cathodic polarisation 100 mA/ cm^2, strain rate 10^{-6} s^{-1}, strain to fracture 13%.) [14]

Ductile failure on hydrogen charged samples can be explained by the presence of relatively low amounts of hydrogen. A high content of hydrogen is necessary to introduce brittle fracture in 304L and 316L austenitic steels. In relation with the hydrogen content of the material, hydrogen embrittlement can occur not only in the form of brittle cracks [13].
Hydrogen embrittlement is a very complicated process with many underlying mechanisms. To date, three main embrittlement mechanisms have been proposed:
1. Hydrogen-enhanced decohesion (HEDE),
2. Hydrogen-enhanced localized plasticity (HELP),
3. Hydride-induced embrittlement (HIE) [18].

2.3.1 Hydrogen Enhanced Decohesion (HED)

Diffusion of hydrogen is influenced both by temperature and chemical potential gradients [19]. In this case, the chemical potential gradient refers to the force imposed on the atoms due to a concentration gradient [20]. A lattice expansion caused by the hydrostatic tensile stress surrounding a crack tip locally reduces the effective hydrogen concentration and, thus, the chemical potential, resulting in a flux of hydrogen toward it [21].

2.3.2. Hydrogen-Enhanced Localized Plasticity (HELP)

Hydrogen concentration on a local scale can increase dislocation activity in the immediate vicinity [22, 24]. The increase in local dislocation activity causes local stress concentration, contributing to failure initiation at planar defects where hydrogen is not present [23]. A brittle fracture surface facilitated by the HELP mechanism will have evidence of slip, dimples, and tear ridges [22, 25].

2.3.3. Hydride-Induced Embrittlement (HIE)

The process consists of the diffusion of hydrogen, precipitation of hydrides, heat flow, and material deformation [20]. Crack propagation is assisted through the repeated formation and cleavage of hydrides in the stress zone at the crack tip [26].

A hydride nucleates in an area reaching terminal solid solubility, and creates an additional stress concentration at its tip. The stress field between the hydride and crack tips facilitates the growth of the precipitate toward the crack [27].

2.4 Internal Reversible Hydrogen Embrittlement (IRHE) and Hydrogen Gas Embrittlement (HGE)

At low temperatures IRHE occurred below a Ni content of 15% increased with decreasing temperature, reached a maximum at 200 K, and decreased with further decreasing temperature, similarly to the temperature dependence of HE in 316 stainless steel.

At room temperature, IRHE and HGE could be observed below a Ni content of 14% and decreased with increasing Ni content. Dimple ruptures caused by hydrogen segregation occurred in only IRHE at 150 K. The content of strain-induced martensite increased with decreasing temperature and Ni content. Thus, the susceptibility to IRHE and HGE depended on Ni content. Both IRHE and HGE could be controlled by the amount of strain-induced martensite above 200 K, whereas they were controlled by the hydrogen transport below 200 K.

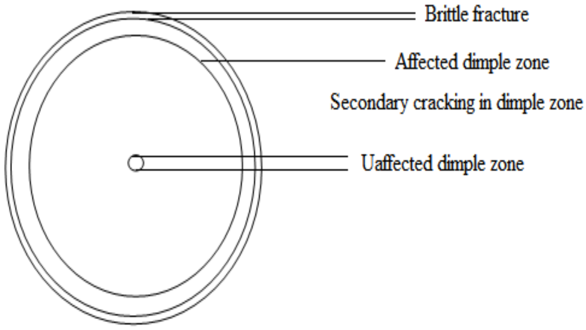

Fig.5: Schematic presentation of typical fracture surface obtained after hydrogen embrittlement test, cathodic charging on type 316 L [13].

2.5 Synergistic Tellurium–Caesium Embrittlement

Old has mentioned that fission products such as caesium, cadmium and tellurium might embrittle the austenitic stainless steel cladding of fast reactor fuel pins in certain conditions [7]. Admson reported the observation of rapid, severe embrittlement of AISI 316 stainless steel by liquid tellurium–caesium mixtures in the temperature region 500–700°C [4]. Hot shortness occurs with the most pronounced loss in ductility [30]. The influence of molten tellurium and tellurium/ cesium mixtures on the mechanical properties is that steel got embrittled at temperatures above 600^{o}C due to extensive chemical interaction and grain boundary penetration; adding even 2% cesium at 600^{o}C caused tellurium to severely embrittle the steel; similarities to zinc embrittlement exists indicating that tellurium may also degrade by a two step process, with cracks initiating because of the chemical interaction, but propagating because of surface energy reductions [31].

2.6 Swelling and Void Induced Embrittlement

Void swelling of 304L and 316 L steel falls strongly in swelling rate at temperatures below 335°C and should not reach large swelling levels even at high dpa levels [32]. Large voids associated with cracking along denuded zone adjacent to grain boundaries at 335°C and 73 dpa in an annealed stress-free tube when tested in reactor component. High dose neutron irradiation at elevated temperatures causes swelling of austenitic steels, which is a dominating effect in changing not only the volume of the metal, but also causing significant and measurable changes in both electrical resistance and elastic moduli.

Neustroeve stated that lower dpa rates decrease the duration of the transient regime of swelling and therefore increase swelling at a given exposure level. It has also been convincingly shown that lower dpa rates cause swelling to occur at lower temperatures that encompass all temperatures of relevance to PWR and VVER internals in 304L steel [39].

Voids initially harden the matrix, but as the swelling level becomes significant, the elastic moduli decrease strongly, with the consequence that the steel actually softens with increasing swelling, even as the elongation decreases as a result of void linkage during deformation, the strength again decreases as swelling increases.

Finally, zero deformation levels occur at higher swelling levels, arising most likely from a segregation of nickel to void surfaces that induces a martensitic instability and produces a zero tearing modulus [33].

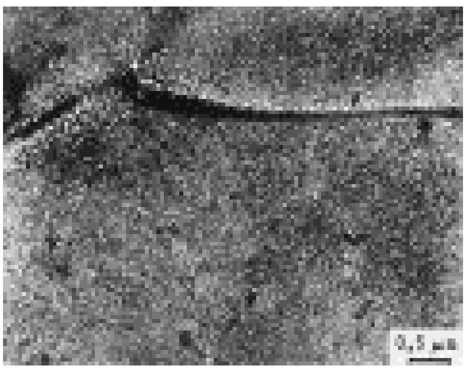

Fig. 6, Large voids associated with cracking along denuded zone adjacent to grain boundaries at 335°C and 73 dpa in an annealed stress-free tube [32].

III. Effect of Various Parameters on Embrittlement

3.1 Effect of temperature on HEE

HEE increased with decreasing temperature, reached a maximum at around 200 K and decreases rapidly with decreasing temperature down to 80 K. Sensitization enhanced HEE and decreased a temperature immune to HEE. HEE of the type 316 series stainless steels from 300 K to the maximum HEE temperature depended on the transformation of strain induced martensite and the behavior. Below the maximum HEE temperature depended on the diffusion of hydrogen [15].

Fig.4: 316 tested in 25 MPa H2 at 20^{o}C showing martensite ahead of a crack tip [5]

3.2 Effect of fatigue on HE

Fatigue crack growth rates in the presence of hydrogen are strongly frequency dependent for 304L & 316 L steels. With decreasing loading frequency down to the level of 0.0015 Hz, the non diffusible hydrogen definitely increases fatigue crack growth rates. If the non diffusible hydrogen at O-sites of the lattice is reduced to the level of 0.4 wppm by a special heat treatment, then the damaging influence of the loading frequency disappears and fatigue crack growth rates are significantly decreased [16].

3.3 Effect of nitrogen on HE

Addition of nitrogen improved resistance to hydrogen cracking regardless of the failure mode. Fracture surfaces of cathodically charged steels showed intergranular brittle zones on each side of the fracture surfaces. AlSl type 316 with nitrogen alloying stainless steel is more resistant to hydrogen embrittlement than AlSl type 321 with nitrogen alloying steel. Nitrogen alloying of stainless steel increased the mechanical properties in hydrogen environments by increasing the stability of austenite [17].

IV. Conclusion

A thorough understanding of both the stainless steel is essential to use them successfully. 316LN austenitic stainless steel is more resistant to hydrogen embrittlement than type 304LN as nitrogen alloying of stainless steel increased the mechanical properties in hydrogen environments by increasing the stability of austenite. It is also observed that HEE of types 304 and 316 stainless steels depended on the testing temperature, and the maximum HEE occurred at around 220 K independent of the type of heat treatment.

Figure 7 demonstrates the generalized regimes of austenite stability as a function of temperature and nickel content. It can be seen here that stability of the austenite phase is primarily dependent on nickel content, but enhanced with a decrease in temperature. Embrittlement will occur when the austenite phase is unstable, whether the instability is due to chemistry or temperature [18].

The Thermal aging embrittlement in 316L weld was higher compared to 304L weld for similar aging condition. The kinetics of aging embrittlement was established based on Arrhenius relationship. A constant activation energy was determined for 304L weld in the temperature range 335-400 °C, however, 316L weld showed different activation energy values in each temperature range [38].

SA Type 304 SS and is most susceptible to high swelling rates and maximum irradiation temperature has been estimated to be in the range of 380-420°C. Although further studies are needed to more accurately calculate the temperature for EOL and life-extension conditions, 380°C is believed to be a more likely upper limit [39].

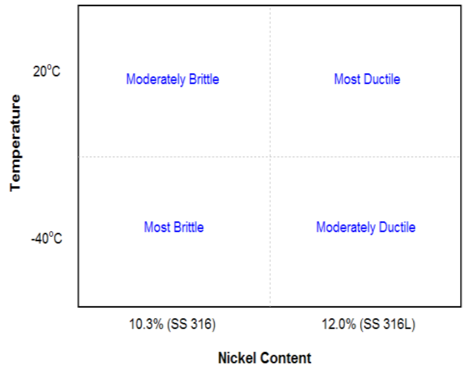

Figure 7: Austenite phase stability grid [18]

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