Dynamic Strain Ageing of Deformed Nitrogen-alloyed AISI 316 Stainless Steels

U. Ehrnstén[1], M. Ivanchenko[2], V. Nevdacha[2], Y. Yagozinskyy[2], A. Toivonen[1]
and H. Hänninen[2]

[1]Materials and Structural Integrity, VTT Technical Research Centre of Finland, Kemistintie 3,
P.O. Box 1704, FIN-02044 VTT, Finland, email: ulla.ehrnsten@vtt.fi
[2]Department of Mechanical Engineering, Helsinki University of Technology
Puumiehenkuja 3, P.O. Box 4200, FIN-02015 HUT, Finland

1 Abstract

Intergranular stress corrosion cracking has occurred in BWR environment in non-sensitised, deformed austenitic stainless steel materials. The affecting parameters are so far not fully known, but deformation mechanisms may be decisive. The effect of deformation and nitrogen content on the behaviour of austenitic stainless steels was investigated. The materials were austenitic stainless steels of AISI 316L type with different amounts of nitrogen (0.03…0.18%) and they were mechanically deformed 0, 5 and 20%. The investigations are focused on the dynamic strain ageing (DSA) behaviour. A few crack growth rate measurements are performed on nuclear grade AISI 316NG material with different degrees of deformation (0, 5 and 20%). The effects of DSA on mechanical properties of these materials are evaluated based on peaks in ultimate tensile strength and strain hardening coefficient and minimum in ductility in the DSA temperature range. Additionally, internal friction measurements have been performed in the temperature range of -100…600 °C for determining nitrogen interactions with other alloying elements and dislocations (cold-worked samples). The results show an effect of nitrogen on the stainless steel behaviour, e.g. clear indications of dynamic strain ageing and changes in the internal friction peaks as a function of nitrogen content and amount of deformation.

Keywords: Dynamic strain ageing, Stainless steels, Environmentally assisted cracking

2 Introduction

In the early 70´s, numerous cases of intergranular stress corrosion cracking occurred in boiling water reactors (BWR) in AISI 304 type austenitic stainless steels. The root cause for this cracking is a combination of tensile stresses, an oxidising environment and a sensitised material. The remedial actions taken have involved all three major parameters, e.g. application of narrow-gap welding technique to reduce residual stresses, increase of the overall purity of the primary water, application of hydrogen or noble metal water chemistry as well as reducing the amount of carbon in the stainless steels to avoid sensitisation. Nitrogen is added to maintain the strength level of austenitic stainless steels with reduced carbon levels. In the early 90´s cases of intergranular cracking in non-sensitised, low carbon stainless steel materials of types AISI 316NG and AISI 304L were observed. Several cases have so far been reported and cracking has been observed both in the HAZ of the welds as well as in the base metals far away from any weld. Although all affecting parameters are so far not known, deformation seems to be a common parameter. Several open questions are still connected to this type of cracking, such as a possible difference in the behaviour between different types of austenitic stainless steels, the effect of chemical composition, the effect of cold work (amount and temperature), the influence of constraint during welding, etc.

The affecting mechanisms may include dynamic strain ageing (DSA) and environmentally enhanced creep. Dynamic strain ageing occurs in alloys containing solute atoms, which can rapidly and strongly segregate to dislocations and lock them during straining. The maximum

Back

effect of DSA corresponds to such conditions, where the solute atoms can follow by diffusion the changes of the dislocation structure. DSA phenomenon leads to an inhomogeneous plastic flow and serrated yielding during straining at elevated temperatures and results often in a remarkable degradation of mechanical properties for a number of engineering alloys.

Austenitic stainless steels show DSA behaviour in a wide range of temperatures (~200 – 800 °C), which depends on the actual strain rate. Interstitial carbon and nitrogen atoms dissolved in the crystal lattice play a determining role in DSA of austenitic stainless steels in the temperature range between 200 °C and about 600 °C [1,2,3]. Literature results have, however, also shown that nitrogen alloying shifts the onset temperature of DSA to higher values [4].

The aim of the present investigation was to study the effects of nitrogen alloying and deformation on DSA phenomenon in austenitic AISI 316L stainless steel at ~ 300 °C. The effect of deformation of AISI 316NG steel on the cracking behaviour in BWR water was additionally investigated using rising and constant displacement.

3 Experimental

Three model austenitic AISI 316L type stainless steel materials with different nitrogen contents and a commercial nuclear grade AISI 316NG stainless steel were used in the study. A sensitised AISI 304 steel was additionally used in the crack growth rate tests. The chemical compositions of the materials are shown in Table 1. Details concerning the manufacturing of the model materials can be found in [5]. The effect of deformation was investigated by prestraining the materials at room temperature in tension before preparation of test specimens.

Table1: Chemical compositions of the studied stainless steels in weight %.

Type	Code	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	O_2	N_2
AISI 316L	1042	0.022	0.51	1.47	0.026	0.002	16.8	11.0	2.1	0.20	0.02	0.004	0.028
AISI 316L	1043	0.022	0.52	1.50	0.027	0.002	16.8	11.1	2.0	0.19	0.02	0.004	0.085
AISI 316L	1045	0.022	0.53	1.53	0.027	0.002	17.0	11.2	2.1	0.18	0.02	0.005	0.176
AISI 316NG	BB44	0.022	0.38	1.66	0.027	0.002	17.0	12.5	2.28	0.11	0.01	0.007	0.093
AISI 304	165	0.042	0.47	0.88	0.026	0.018	18.2	10.2					

All blanks for the tensile test specimens were cut from the plates, transverse to their rolling direction, and in the longitudinal direction from the AISI 316NG stainless steel pipe. The microstructure and hardness (HV 10) were determined. Tensile tests for observing DSA were carried out using a 25 kN MTS 858 test machine equipped with a MTS High-Temperature Furnace 653.02, at strain rates of 10^{-4}, 10^{-5}, 5×10^{-6} and 10^{-6} s^{-1}, and temperatures of 200, 288 and 400 °C. All tensile test specimens were prepared according to ASTM standard E 8M (sheet-type sub-size specimens). Tensile tests were performed according to the standards SFS-EN 1002-1 and ASTM E21 (Standard Test Method for Elevated Temperature Tension Tests of Metallic Materials).

Internal friction method was used in the study for evaluation of the free nitrogen content and its diffusion redistribution in the crystalline lattice of the studied stainless steels. Details of the test parameters are given in [5].

Crack growth rate tests in simulated BWR NWC environment (DO_{out} 500 ppb, κ_{in} < 0.1 µS/cm, T 290 °C, p 92 bar) were performed using rising and constant displacement tests and 10 x 10 x 55 mm^3 SEN(B) specimens. Six specimens, five made of AISI 316NG and one of

Back

sensitised AISI 304 (1050 °C/20 min + 680 °C/1 h + 500 °C/24 h) material were tested in the same autoclave equipped with bellow loading devices. The AISI 316NG steel was tested in non-deformed (one specimen), and deformed conditions (two specimens with 5% and two with 20% deformation). The sensitised AISI 304 steel, used as a reference specimen to enable comparison of the test results with literature data, was tested in non-deformed condition. The tests were started with a displacement rate of 5.5 x 10^{-8} mm/s, which was reduced to 5.5 x 10^{-9} mm/s when stable crack growth was detected and further with constant displacement tests after about 600 h testing time. The total testing time was 1198 h. The crack growth was continuously monitored using the DC-PD technique. After the tests, the cracks were opened by fatigue, the final crack lengths were measured and the cracking morphology was determined using SEM.

4 Results

The microstructure of all materials was austenitic. The grain size of the model alloys was smaller than that of the commercial AISI 316NG steel, Table 1. The slope of the increase in hardness was similar for all alloys, Figure 1.

Table 1. Grain sizes and hardness of the investigated materials.

Material and code	Grain size ASTM No / µm	Hardness [HV10]		
		0% def.	5% def.	20% def.
AISI 316L, 1042	7 / 36	136	172	229
AISI 316L, 1043	6.5 / 43	159	191	255
AISI 316L, 1045	8 / 25	179	215	284
AISI 316NG, BB44	5 / 71.8	147	174	227
AISI 304, 165	4 / 101	nd	nd	nd

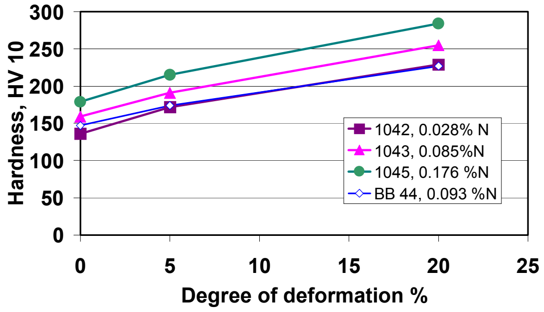


Figure 1. Hardness versus degree of deformation for AISI 316L materials.

Nitrogen alloying increases the strength properties of AISI 316L stainless steels in the testing temperature range and the elongation to fracture decreases with increasing nitrogen content except in the case of the commercial AISI 316NG stainless steel, which demonstrates highest elongation to fracture in the whole range of testing temperatures, Figure 2. Yield stress decreases with testing temperature, while ultimate tensile stress is almost constant in the studied temperature range. As a function of temperature, the elongation to fracture varies with the nitrogen content only slightly. The strain hardening coefficient increases with increasing testing temperature and decreasing nitrogen content, Figure 2d.

Serrated yielding was observed in all AISI 316L stainless steels at testing temperatures above 200 °C and strain rates slower than 10^{-4} s^{-1}, Figure 3. DSA serrations on the stress-strain curves are well-defined at testing temperatures of 288 and 400 °C, while at 200 °C they appear only for the material with the lowest nitrogen content of 0.028 wt %. The obtained stress-strain curves indicate that nitrogen alloying suppresses the DSA development in AISI 316L type stainless steels. Further, the amplitude of the stress pulses decreases markedly with the increase of nitrogen content and only a few pulses are present on the stress-strain curves of the stainless steels with 0.093 and 0.176 wt. % of nitrogen at testing temperature of 288 °C. A similar effect of nitrogen on DSA in AISI 316LN stainless steels was obtained in [4] for higher strain rates of testing. Prestraining at room temperature leads not only to an increase of yield and ultimate tensile stresses, but it reduces also the onset deformation of DSA, Figure 4a. It seems that cold working facilitates the DSA development in nitrogen-alloyed stainless steels. DSA serrations become visible on the stress-strain curve for AISI 316NG steel

Back

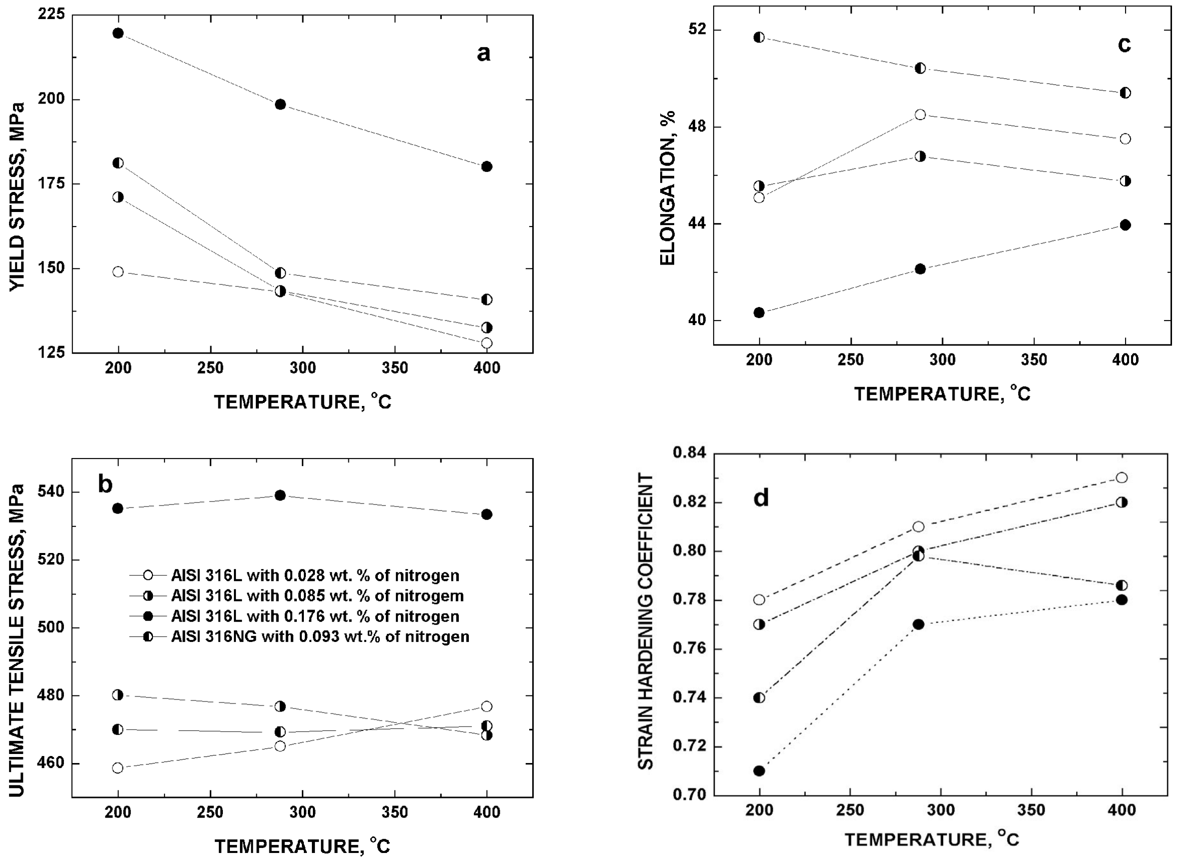


Figure 2. Temperature dependencies of yield stress (a), ultimate tensile stress (b), elongation to fracture (c) and strain hardening coefficient (d) for the studied stainless steels. Symbols defined in (b) apply for all pictures.

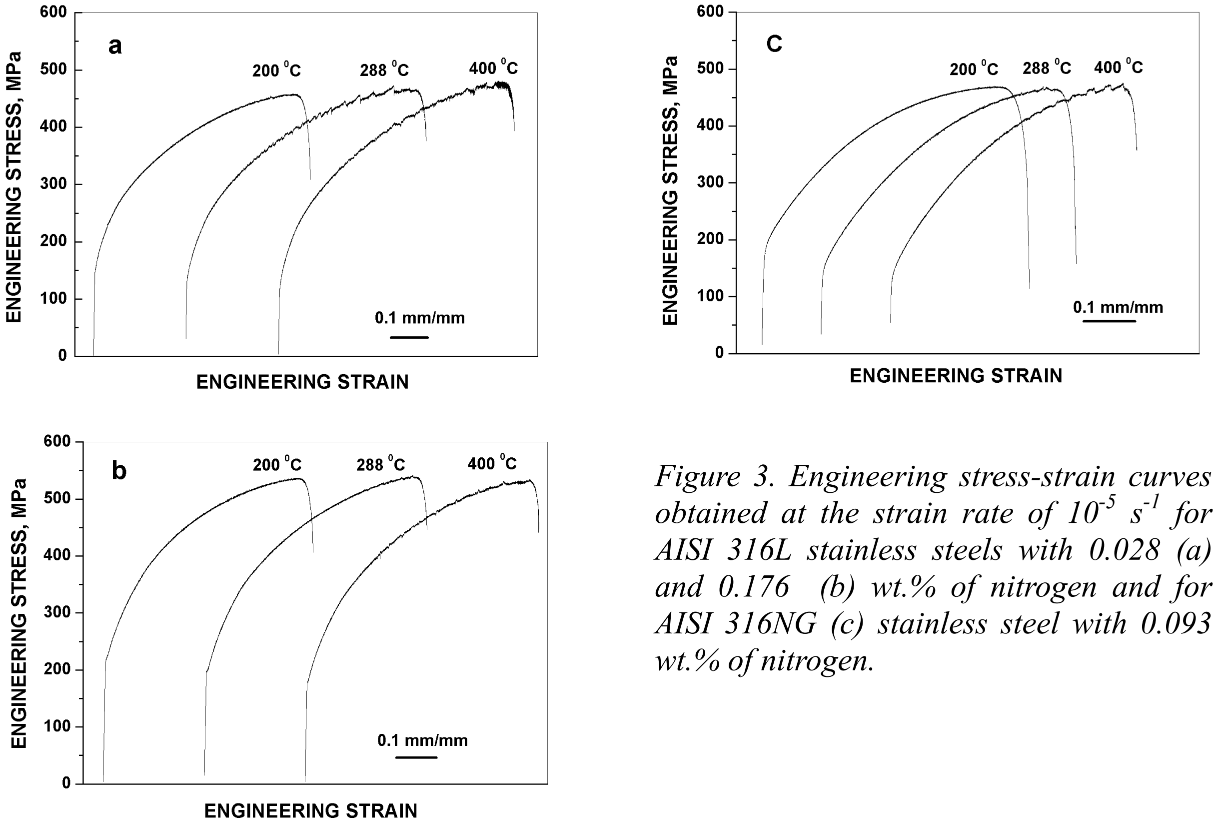
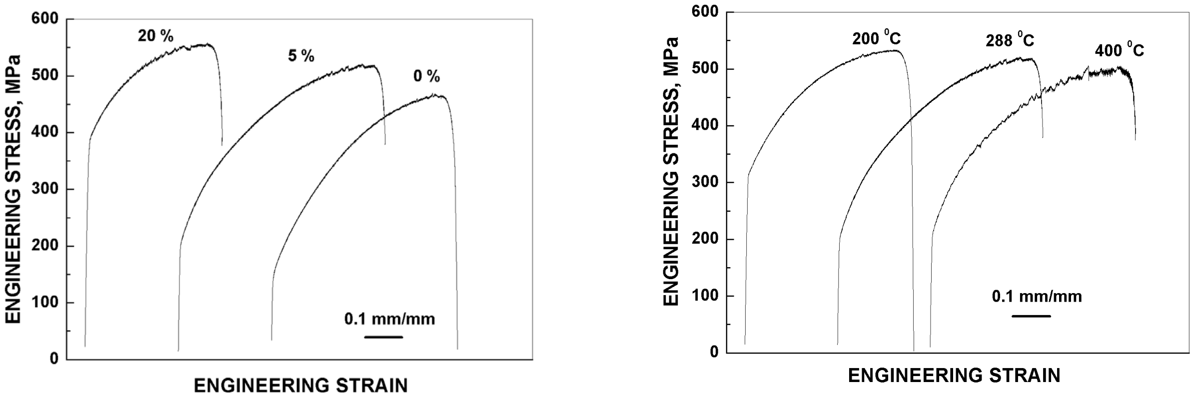


Figure 3. Engineering stress-strain curves obtained at the strain rate of 10^{-5} s^{-1} for AISI 316L stainless steels with 0.028 (a) and 0.176 (b) wt.% of nitrogen and for AISI 316NG (c) stainless steel with 0.093 wt.% of nitrogen.

Back



(a) (b)

Figure 4. Engineering stress-strain curves obtained at 288 °C and strain rate of 10^{-5} s^{-1} *for prestrained AISI 316NG stainless steel (a) and for AISI 316NG stainless steel with 5 % prestraining at different temperatures (b).*

obtained at testing temperature of 200 °C after 5 % prestraining, Figure 4b, while much less serrations appear in the as-supplied material, Figure 3c.

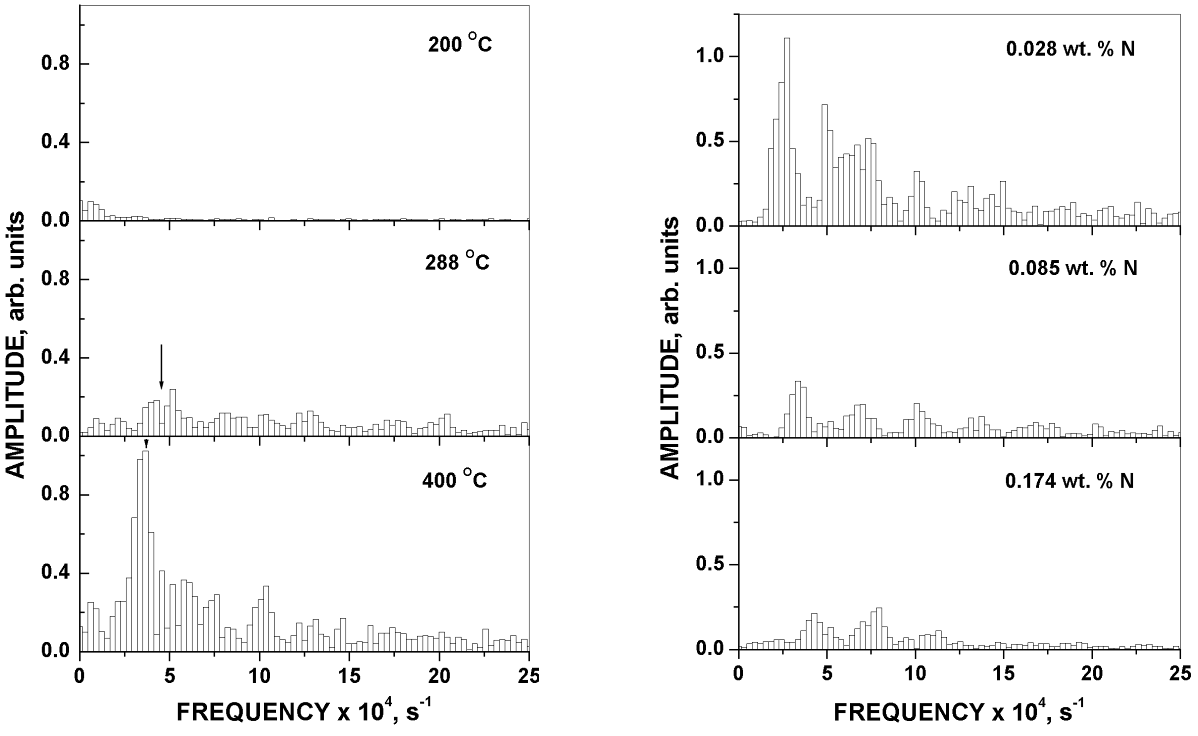
The A type serrations [1] observed correspond to quasi-regular separate pulses of flow stress. For evaluation of the average time between the pulses the obtained stress-strain curves were transformed to the frequency dependency using Fourier analysis. Fourier spectra are shown in Figure 5. In the presence of quasi-regular serrations on the stress-strain curve, as it can be seen for testing temperatures of 288 and 400 °C in Figure 5a, some maxima arise in the Fourier spectra, while no distinct maxima are present in the spectrum at 200 °C, when serrations are missing. The maxima shown by arrows in Figure 5, correspond to the flow stress pulses, which reflect the repeated advancement of the Lüders band throughout the specimen. The average time between pulses, which is reciprocal to the frequency of maximum in the Fourier spectrum, can be estimated to be 2.7 ks for the testing temperature of 400 °C.

Nitrogen alloying suppresses the amplitude of DSA serrations as it is seen in Figure 5b. High amplitude quasi-regular pulses of the flow stress observed in the stainless steel with 0.028 wt.% of nitrogen become smaller when nitrogen content increases to 0.176 wt.%, and the average time between pulses is then about 2.3 ks.

Internal friction (IF) in the studied stainless steels was mainly measured to check the presence of interstitial nitrogen atoms in the crystalline lattice of the studied austenitic stainless steels. Two IF peaks were observed, Figure 6, situated at about −50 °C and 100 °C, which increase with the amount of cold deformation. They represent presumably an anelastic response of dislocations interacting with point defects produced in the austenite crystalline lattice by cold deformation [6]. It is well established [7] that IF peak in the vicinity of 350 °C is caused by a Snoek-like relaxation process due to elemental diffusion jumps of interstitial nitrogen atoms in FCC crystalline lattice of austenite.

The amplitude of the Snoek peak is proportional to the free nitrogen concentration. Thus, Figure 6 reveals that free nitrogen atoms are present in the AISI 316NG steel at 288 °C. The concentration of the free nitrogen atoms in the lattice increases with the amount of prestraining, in line with the tensile test results showing an earlier onset of DSA in deformed materials. The observed increase of the nitrogen Snoek-like peak amplitude in the prestrained stainless steel is reduced with ageing time at elevated temperatures, Figure 7, due to escape of free nitrogen from the solid solution. The peak reduction process can be described as a sum of

Back



(a) *(b)*

Figure 5. Fourier transformation spectra of the flow stress signal in the tensile tests of AISI 316NG stainless steel at a strain rate of 10^{-5} s^{-1} and different temperatures (a), and of AISI 316L alloys at a strain rate of 10^{-5} s^{-1} and 288 °C (b). Arrows in (a) correspond to quasi-regular separate pulses.

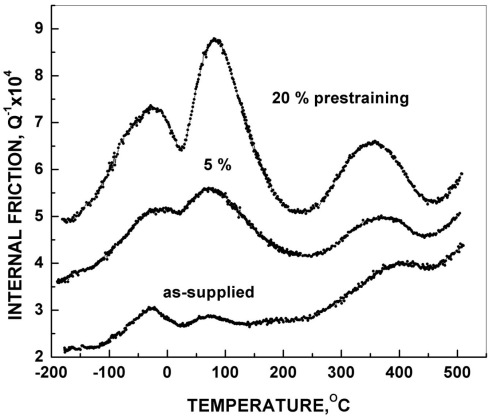


Figure 6. Temperature dependencies of internal friction for AISI 316NG stainless steel in as-supplied state and after 5 % and 20 % prestraining.

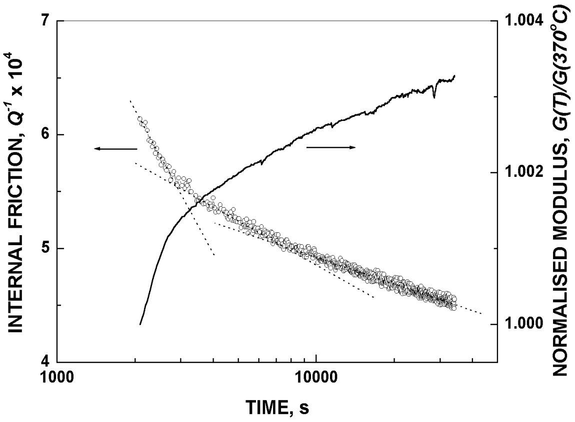


Figure 7. Amplitude of the Snoek-like peak of nitrogen and normalised shear modulus of AISI 316NG stainless steel as a function of ageing time at 340 °C. Dotted lines represent the three components of the peak amplitude decay.

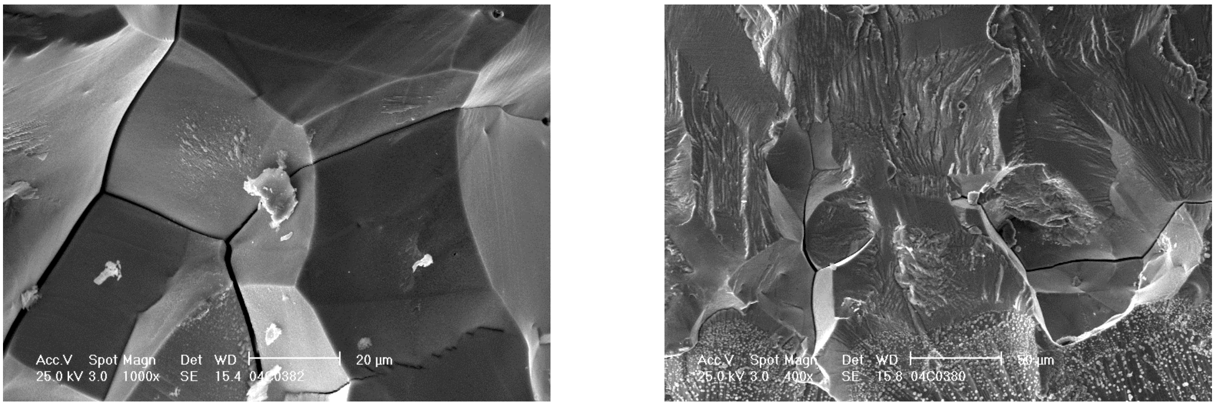
three exponential decay functions (shown by dotted lines in Figure 7) with characteristic decay times of 0.6, 2.6 and 14.2 ks. The origin of the fastest component of the process is still unclear, while the second and third ones can be related to long-range diffusion escape of nitrogen from solid solution to dislocations and, probably, to grain boundaries. Ageing also results in an increase of the normalised shear modulus, indicating pinning of dislocations by nitrogen atoms due to ageing [5,7].

Back

The characteristic decay time of 2.6 ks, which represents the long-range diffusion of nitrogen to dislocations, is close to the value of the average time between serration pulses obtained above from stress-strain curve by Fourier analysis (2.7 ks). It seems that the repeated pinning of dislocations by diffusion of mobile nitrogen atoms, which is related to the advancement of Lüders bands, is a key element of DSA in AISI 316L steels at testing temperatures used in this study.

In the crack growth rate tests fully intergranular cracking was obtained in the sensitised AISI 304 stainless steel specimen and in one of the two 20% prestrained AISI 316NG steel specimens. Some IG fracture was also observed in one of the two 5% prestrained AISI 316NG steel specimens, Figure 8. All other specimens revealed transgranular cracking. The crack growth rates obtained for the sensitised AISI 304 material are in the order of 10^{-7} mm/s and are similar to those obtained using 10 x 10 x 55 mm^3 SEN(B) and 25 mm C(T) specimens in reference [9]. The crack growth rates of sensitised AISI 304 steel specimens depend on the loading mode: the crack growth rates are lower by a factor of 2 to 10 under constant displacement than under rising displacement conditions. All of the crack growth rates are also plotted as a function of loading rate, in terms of J-integral increase rate dJ/dt, in Figure 9b. dJ/dt is a measure of loading rate independent of the specimen size and loading geometry. The interconnections between crack growth rate, fracture morphology and loading rate/type are discussed in more detail in reference [9].

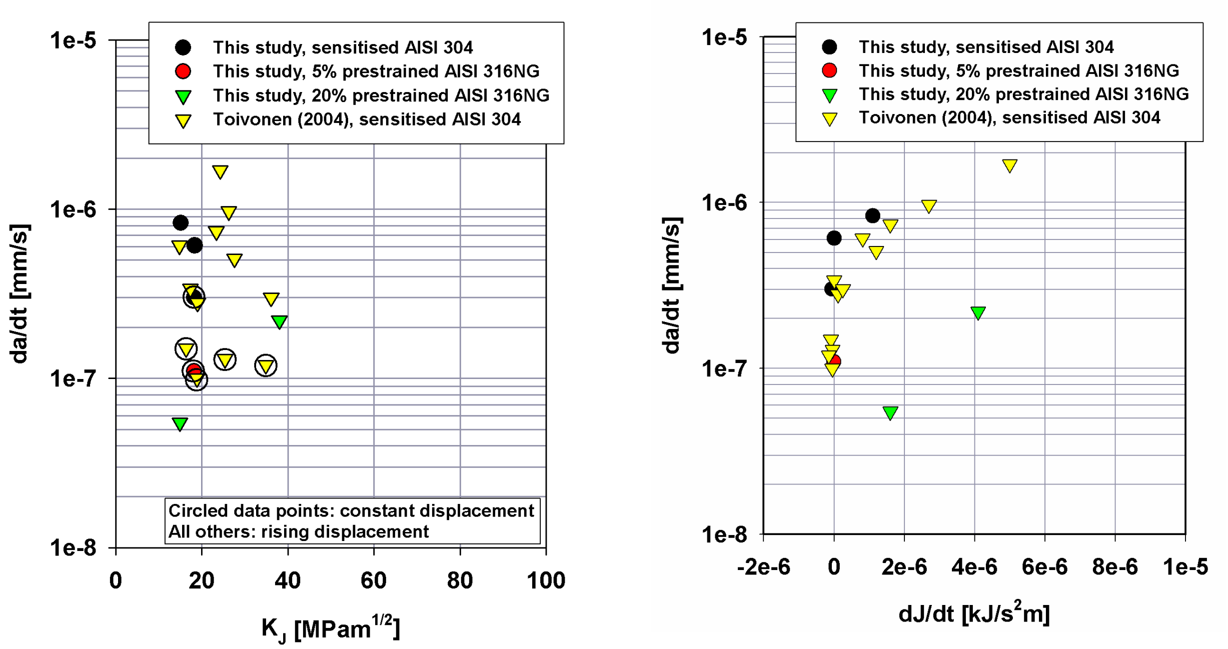
The results revealed a higher tendency for the 20% deformed AISI 316NG steel to intergranular environmentally assisted cracking (EAC) in BWR NWC environment compared to non-deformed, non-sensitised material. However, the susceptibility to EAC is much lower than that in sensitised stainless steels, in accordance with expectations. The crack growth rate at a similar loading rate (i.e., dJ/dt) is one order of magnitude higher in the sensitised AISI 304 steel compared to that in 20% deformed AISI 316NG. The crack growth rate in 5% deformed AISI 316NG steel showing mixed transgranular and intergranular cracking was in the same order as in the sensitised AISI 304 steel. However, there was a ripple loading fatigue component of R ~0.9 and f ~1 Hz present during that test, which can be expected to result in partially transgranular fracture morphology and also in enhanced crack growth rate. More tests are, however, needed in order to determine the EAC crack growth rates of non-sensitised stainless steels as a function of degree of deformation and chemical composition.



(a) (b)

Figure 8. Fractographs showing fully intergranular cracking in the 20% prestrained AISI 316NG specimen (a) and mixed trans- and intergranular cracking in the 5% prestrained AISI 316NG specimen (b) after constant displacement testing in BWR NWC environment.

Back



(a) (b)

Figure 9. Crack growth rate as a function of K_J for the crack growth rate tests with observed intergranular cracking (a) and as a function of the loading rate in terms of dJ/dt (b). A fatigue component of R ~0.9 and f ~1 Hz was present during the constant displacement phase of the 5% prestrained AISI 316NG specimen.

5 Discussion of results

The results obtained in the present investigation are in good accordance with literature data on nitrogen effects on DSA in AISI 316L stainless steels. A map of DSA, shown in Figure 10, summarises the serrated flow appearance in AISI 316NG stainless steel at different strain rates and testing temperatures. The dashed line in Figure 10 forming a boundary for testing parameters, where DSA occurs, extends to lower strain rates applied in the present investigation as compared to those in [4].

The enthalpy calculated using the dashed line in Figure 10 is about 1.24 eV and its value approaches the enthalpy of nitrogen diffusion in the austenite lattice. This value is very close to the enthalpy of nitrogen diffusion calculated from the Snoek-like IF peak, 1.45 eV at 350 °C [5].

The obtained strain hardening coefficient values are high, especially for the elevated testing temperatures, where DSA serrations are remarkable. In fact, in these conditions, the stress-strain curves do not follow the Holomon law in the whole plastic strain range. The strain hardening coefficient is highest for the stainless steel with the lowest nitrogen content, in which the DSA serrations are most pronounced.

Back

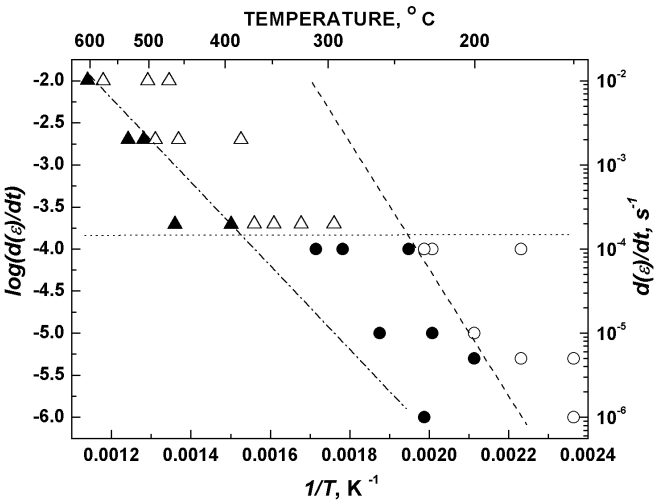


Figure 10. DSA-map of AISI 316NG stainless steel. Filled symbols correspond to strain rate and temperature values at which DSA (serrated yielding) was observed on stress-strain curves. Data points shown by triangles above the dotted line were obtained in [4]. The dashed lines are the boundaries for the DSA appearance in this study and in [4].

The DSA-results showing that nitrogen alloying suppresses the onset strain and temperature range of DSA indicate that nitrogen alloying may also lower the EAC susceptibility, if DSA is considered to be a part of the decisive mechanism. The crack growth rate test results obtained in this study are in line with literature and field experience showing increased susceptibility and increased crack growth rates in non-sensitised stainless steels due to deformation [10]. However, the crack growth rates in deformed, non-sensitised stainless steel are lower than those in sensitised stainless steel in BWR NWC environment. Crack growth rate tests on stainless steels have revealed a correlation between susceptibility to intergranular cracking, CGR and yield strength [10]. The yield strength increases as a function of deformation, but also as a function of nitrogen content. As these materials are non-sensitised, corrosion must be less decisive and localisation of deformation to the grain boundaries more important than in the case of sensitised stainless steels.

A suppression of the DSA development in the studied stainless steels caused by nitrogen alloying looks contradictory as DSA, e.g. in low alloy steels, is enhanced by free interstitials. The suppressive effect of nitrogen on DSA may be caused by the increase of the flow stress with nitrogen alloying of the steel causing an increase of the actual stress and consequent possible changes in the deformation response. DSA is expected to result in localisation of plastic deformation to grain boundary regions. This is also the case in deformed materials, where DSA was observed at all studied nitrogen levels. A detailed mechanism of the role of DSA in EAC and the role of deformation as well as stainless steel composition needs further investigations to reveal the main parameters affecting EAC in deformed, non-sensitised stainless steels in high temperature water such as BWR NWC.

6 Conclusions

- DSA in nitrogen-alloyed AISI 316L type stainless steels can occur at temperatures below 300 °C, when strain rates are slower than 10^{-4} s^{-1}.

- Nitrogen suppresses the DSA development in AISI 316L type stainless steels. The onset deformation of DSA serrations shifts to higher values of strain and the amplitude of the flow stress pulses decreases with increase of nitrogen content.

- Prestraining at room temperature reduces the onset deformation of DSA in AISI 316NG stainless steel.

- An apparent activation enthalpy of DSA in AISI 316NG stainless steel is about 1.24 eV at temperatures around 300 °C. The value of enthalpy of DSA corresponds well to the enthalpy of nitrogen diffusion in AISI 316NG steel obtained by the internal friction method being about 1.45 eV.

- Prestraining increases the susceptibility of non-sensitised AISI 316NG stainless steel to intergranular stress corrosion cracking in BWR NWC environment. The crack growth rate is, however, lower than that for sensitised stainless steel.

Acknowledgements

This presentation is prepared within the project Structural operability and plant life management (RKK and XVO), which is coordinated by Teollisuuden Voima Oy. The work has been funded by the National Technology Agency (Tekes), Teollisuuden Voima Oy (TVO), Fortum Power and Heat Oy, Fortum Nuclear Services Ltd., FEMdata Oy, Neste Engineering Oy, Fortum Oil and Gas Ltd. and VTT. The Swedish Nuclear Power Inspectorate, SKI, participated also in this work. Their funding is gratefully acknowledged.

References

[1] L. H. de Almeida, I. LeMay, P. R. O. Emygdio: Mater. Characterization, 40 (1998), pp. 137 - 150.

[2] L.H. de Almeida, P.R.O. Emygdio: Scr. Met. *et* Mater., 31 (1994), pp. 505 - 510.

[3] R. Ilola, M. Kemppainen, H. Hänninen: Dynamic Strain Ageing of Austenitic High Nitrogen Cr-Ni and Cr-Mn Steels, Proc. of 5th Int. Conf. "High Nitrogen Steels´98", Mat. Sci. Forum, 318-320 (1999), pp. 407 - 412.

[4] D. W. Kim, W. Ryu, J. Hwa Hong, S. Choi: Journal of Nuclear Materials, 254 (1998), pp. 226-233.

[5] M. Ivanchenko, U. Ehrnstén, V. Nevadacha, Y. Yagodzinskyy, H. Hänninen. ‘Dynamic Strain Ageing of Nitrogen-alloyed AISI 316L Stainless Steel. To be published.

[6] C.F. Burdett, I.J. Queen: Met. Rev., 43 (1970), pp. 47 - 65.

[7] Yu. Jagodzinski, S. Smouk, A. Tarasenko, H. Hänninen: Distribution of Interstitial Impurities and their Diffusion Parameters in High-Nitrogen Steels Studied by Means of Internal Friction, Proc. of 5th Int. Conf. "High Nitrogen Steels´98", Mat. Sci. Forum, 318-320 (1999), pp. 47 - 52.

[8] A.S. Nowick, B.S. Berry: Anelastic Relaxation in Crystalline Solids, Academic Press, N.Y., London, 1972, 677 p.

[9] A. Toivonen: Stress Corrosion Crack Growth Rate Measurement in High Temperature Water using Small Precracked Bend Specimens. VTT Publications 531, 2004, 206 p. + App.

[10] P. Andresen, P. Emigh, M. Morra, R. Horn: Effects of Yield Strength, Corrosion Potential, Stress Intensity Factor, Silicon and Grain Boundary Character on the SCC of Stainless Steels. 11th Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Stenvenson, WA, Aug. 10-14, 2003, pp. 816-833.