# Publication I

Mykola Ivanchenko, Ulla Ehrnstén, Vitaliy Nevdacha, Yuriy Yagodzinskyy, and Hannu Hänninen. 2004. Dynamic strain aging of nitrogen-alloyed AISI 316L stainless steel. In: Nuri Akdut, Bruno C. De Cooman, and Jaques Foct (editors). Proceedings of the 7th International Conference on High Nitrogen Steels 2004. Ostend, Belgium. 19-22 September 2004. GRIPS' Sparkling World of Steel, volume 1: Proceedings, number 4, pages 641-649. ISBN 3-937057-09-9.

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Mykola Ivanchenko, Ulla Ehrnstén, Vitaliy Nevdacha, Yuriy Yagodzinskyy and Hannu Hänninen:

# Dynamic strain aging of nitrogen-alloyed AISI 316 L stainless steel

Dynamic strain aging (DSA) of nitrogen-alloyed AISI 316L stainless steels with three different contents of nitrogen and a commercial AISI 316NG stainles steel designed for nuclear industry applications was investigated by means of slow strain rate tensile tests. The nitrogen contents of the materials varied in the range of 0.028 - 0.176 wt. %. Tensile tests were performed at three different strain rates,  $10^{-4}$ ,  $10^{-5}$  and  $5 \times 10^{-6}$  s<sup>-1</sup> in the range of temperatures of 200 to 400 °C. DSA occurs in studied stainless steels at temperatures below 300 °C when the strain rate is less than  $10^{-4}$  s<sup>-1</sup>. It was also observed that nitrogen alloying suppresses the DSA development in the studied materials and shifts its occurrence to higher temperatures. Mainly A type of jerky flow was observed at temperatures and strain rates used in the study. Fourier analysis of the stress serations was performed and an average time between the stress pulses was estimated to be 2.7 ks. The activation enthalpy of DSA appearance in AISI 316NG stainless steel obtained from the strain rate – temperature map of DSA was found to be 1.24 eV, which is close to 1.45 eV, which is the enthalpy of nitrogen diffusion in AISI 316NG stainless steel. The presence of free nitrogen in the steel lattice and its diffusion parameters were studied by using low-frequency internal friction method.

Dynamic strain aging (DSA) occurs in alloys containing solute atoms, which can rapidly and strongly segregate to dislocations during straining. DSA phenomenon leads to an inhomogeneous plastic flow or 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 manifest DSA behaviour in a wide range of temperatures which depends on the actual strain rate. The DSA range can continue from about 200 °C up to 800 °C and can be separated into two sub-ranges at slower strain rates [1]. Mainly two types of serrated yielding or jerky flow have been observed in DSA of austenitic stainless steels. The A type, which corresponds to a sequence of separate pulses of the flow stress, is caused by the repeating Lüders band propagation along the gauge length of the specimen. The second, the B type, appears as short-term oscillations of the stress-strain curve and relates to localised shear band formation [1].

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]. An activation analysis carried out for AISI 303 and AISI 304 stainless steels showed that the enthalpy of the onset point for serrated flow can be approximately related to the enthalpy of carbon and nitrogen diffusion in the austenite lattice [2].

A specific effect of nitrogen on DSA in model Cr-Ni and Cr-Mn austenitic stainless steels was investigated in [3]. It was shown that nitrogen extends the DSA range from room temperature up to 800 °C. The austenitic stainless steels studied in [3] had a tendency to deformation-induced marten-

M.Sc. (Tech) Mykola Ivanchenko, PhD Student, Laboratory of Engineering Materials, Helsinki University of Technology, Espoo, Finland; M.Sc. (Tech) Ulla Ehrnstén, Senior Research Scientist, Materials in Nuclear Environment, VTT Industrial Systems, Espoo, Finland; Dr. Vitaliy Nevdacha, Research Scientist; Dr. Yuriy Yagodzinskyy, Research Scientist; Dr. Hannu Hänninen, Professor, Laboratory of Engineering Materials, Helsinki University of Technology, Espoo, Finland

site phase formation and twinning and these processes may have markedly affected and masked the initial stages of DSA phenomenon.

DSA phenomenon in stable austenitic AISI 316L stainless steel with different nitrogen contents was studied in [4]. It was clearly shown that nitrogen alloying shifts the onset temperature of DSA to higher values. At the slowest strain rate  $(2 \times 10^{-4} \text{ s}^{-1})$  applied, and with a nitrogen content of about 0.1 wt.%, the onset temperature of serrations was found in the vicinity of 400 °C.

Nitrogen-alloyed austenitic AISI 316L (AISI 316NG) stainless steels are widely used in nuclear power plant applications. It is expected that the use of nitrogen alloying instead of carbon in AISI 316 type stainless steel ensures its necessary strength properties and reduces its sensitivity to IGSCC in boiling water reactor (BWR) environments. Studies of nitrogen effects on DSA of AISI 316LN stainless steels at temperatures around the reactor operating temperatures close to 300 °C are, thus, of great interest.

The aim of the present investigation was to study the effects of nitrogen alloying on DSA phenomenon in austenitic AISI 316L stainless steels in the vicinity of 300 °C. A special attention was paid to DSA behaviour in the austenitic AISI 316NG stainless steel.

#### Experimental

Three model austenitic AISI 316L type stainless steels with different nitrogen contents and a commercial nuclear grade AISI 316NG stainless steel were used in the study. The chemical compositions of the materials are shown in **Table 1**.

The model stainless steels with different nitrogen contents were prepared as 50 kg ingots by using a laboratory induction vacuum furnace. The ingots were reduced in thickness to 6 mm by hot rolling. The hot-rolled plates were annealed at 1120 °C and pickled in  $HNO_3 + HF$  solution with subsequent reduction of the 6 mm plates to 2 mm by cold rolling. The final 2 mm thick plates were annealed at 1120 °C and pickled in  $HNO_3 + HF$  solution with subsequent reduction of the 6 mm plates to 2 mm by cold rolling. The final 2 mm thick plates were annealed at 1120 °C and pickled in  $HNO_3 + HF$  solution. All tensile test specimens were cut from the plates in transverse to their rolling direction.

Specimens of 2 mm in thickness were cut from AISI 316NG stainless steel pipe in its longitudinal direction.

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. Strain rates of  $10^{-4}$ ,  $10^{-5}$  and  $5 \times 10^{-6}$  s<sup>-1</sup> were applied in the tensile tests at three different temperatures, i.e. 200, 288 and 400 <sup>0</sup>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. Temperature dependencies of internal friction  $Q^{-1}$  and square of the pendulum natural frequency which is proportional to the shear modulus of the studied materials were measured by inverted torsion pendulum in the temperature range of -170 to 525 °C. The amplitude of the specimen torsion deformation in the

Tab	le	1:	Chemical	compositions	of	the	studied	stainless	steels	in	weight	%	
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Туре	c	Si	Mn	Р	S	Cr	Ni	Мо	Cu	AI	<b>O</b> <sub>2</sub>	<b>N</b> <sub>2</sub>
AISI 316	0,022	0,51	1,5	0,026	0,002	16,8	11	2,1	0,2	0,02	0,004	0,028
AISI 316	0,022	0,52	1,5	0,027	0,002	16,8	11	2	0,19	0,02	0,004	0,085
AISI 316	0,022	0,53	1,5	0,027	0,002	17	11	2,1	0,18	0,02	0,005	0,176
AISI 316NG	0,022	0,38	1,66	0,027	0,002	17	12,5	2,28	0,11	0,01	0,007	0,093

pendulum did not exceed  $10^{-5}$  and the natural frequency of the pendulum was changing in the range of 0.5 - 3.0 Hz. Heating rate of the specimens during IF measurements was kept at 2 K/min.

The IF specimens with typical sizes of about  $0.3 \times 2 \times 35$  mm were cut from the studied stainless steel plates by an abrasive disc-saw in the same directions as the tensile test specimens. IF specimens were polished with 1200 grit emery paper.

## **Evaluation of the results**

General view of DSA in studied stainless steels. DSA can be observed in all studied nitrogen-alloyed AISI 316L stainless steels at testing temperatures above 200 °C and strain rates slower than 10<sup>-4</sup> s<sup>-1</sup>. Typical engineering stress-strain curves obtained at the strain rate of 10<sup>-5</sup> s<sup>-1</sup> are shown in Figs. 1 a, b and c for model AISI 316L stainless steels with 0.028 and 0.176 wt.% nitrogen, and for AISI 316NG stainless steel with 0.093 wt.% nitrogen, respectively. 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 materials with the lowest nitrogen content of 0.028 wt.% as some weak pulses on the stress-strain curve just before the specimen fracture (Fig. 1 a). A comparison of the obtained stress-strain curves allows to conclude that nitrogen alloying suppresses the DSA development in AISI 316L type stainless steels. Actually, 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. The similar effect of nitrogen on DSA in AISI 316LN stainless steels was obtained in [4] for higher strain rates of testing.

Mainly A type serrations were observed in the present tests. Irregular pulses of the flow stress observed at lower testing temperatures and nitrogen content become more regular in the tests with higher nitrogen alloying of the material and higher testing temperature. Only for the specimen with the lowest nitrogen content of 0.028 wt.% tested at 400 °C, a transition from A type to B type serrations was observed at the final stage of the test (Fig. 1 a). It can also be seen that the amplitude of the DSA serrations decreases with the increase of the nitrogen content.



Fig. 1: Engineering stress-strain curves obtained at the strain rate of  $10^{-5}$  s<sup>-1</sup> 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.

**Tensile properties**. Temperature dependencies of yield stress, ultimate tensile stress and elongation to fracture obtained for the studied stainless steels at strain rate of  $10^{-5}$  s<sup>-1</sup>, are shown in Figs. 2 a, b and c, respectively. Nitrogen alloying increases the strength properties of the AISI 316L stainless steels in the testing temperature range, while the elongation to fracture decreases markedly with increased nitrogen content except in the case of the commercial AISI 316NG stainless steel, which



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

demonstrates highest elongation to fracture in the whole range of testing temperatures.

Yield stress decreases markedly with testing temperature while ultimate tensile stress is almost constant in the studied temperature range. The last result corresponds to the plateau on the temperature dependencies of the ultimate tensile stress observed in [4] for AISI 316LN stainless steels in the DSA temperature range.

The elongation to fracture varies with the testing temperature and nitrogen content only slightly. A more explicit analysis needs additional tensile tests in a wider temperature range.

Effect of prestraining on DSA in AISI 316NG stainless steel. Commercial AISI 316NG stainless steel was tensile tested after prior tensile deformation of 5 and 20 % at room temperature. Engineering tensile stress-strain curves obtained for the prestrained steel at strain rate of  $10^{-5}$  s<sup>-1</sup> and testing temperature of 288 °C are compared to the stress-strain curve of the as-supplied AISI 316NG stainless steel in Fig. 3.

It can be seen that 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. It seems that cold working facilitates the DSA development in AISI 316NG stainless steel. Actually, DSA serrations become visible on the stress-strain curve obtained at testing temperature of 200 °C after 5 % prestraining, as can be seen in Fig. 4, while much less serrations appear in the assupplied AISI 316NG stainless steel (Fig. 1 c).

DSA serrations and their evolution with temperature. The A type serrations observed in the studied stainless steels correspond to quasi-regular separate pulses of flow stress and the average time between the pulses can be obtained by using Fourier transformation of the oscillating flow stress in time. Fourier spectra of DSA serrations observed in the

stress-strain curves of AISI 316NG stainless steel, carried out at the strain rate of 10<sup>-5</sup> s<sup>-1</sup> at the studied temperatures, are shown in Fig. 5. At a testing temperature of 200 °C, when no serrations were observed, the Fourier spectrum of the flow stress signal represents only a random noise of the dynamometer and is a monotonic decreasing function of frequency. In the presence of quasi-regular serrations on the stress-strain curve, as it can be seen at 288 and 400 °C in Fig. 5, some maxima arise in the Fourier spectra. The maxima shown by arrows correspond to separate pulses which reflect the repeated advancement of the Lüders band throughout the specimen. The average time between pulses at 400 °C can be estimated to be 2.7 ks.

The effect of the nitrogen content in the AISI 316L stainless steel on the Fourier spectra of DSA serrations is shown in Fig. 6. The materials were tensile tested at the temperature of 288 °C and the strain rate of 10<sup>-5</sup> s<sup>-1</sup>. It can be seen that nitrogen alloving suppresses markedly the amplitude of DSA serrations in the whole range of frequency. High amplitude irregular pulses of the flow stress observed in the stainless steel with 0.028 wt.% of nitrogen become smaller and quasi-regular with the average time between pulses being about 2.3 ks, when nitrogen content increases to 0.176 wt.%.



## ENGINEERING STRAIN





**Fig. 4:** Engineering stress-strain curves obtained at a strain rate of 10<sup>-5</sup> s<sup>-1</sup> at different testing temperatures for AISI 316NG stainless steel with 5 % prestraining at room temperature.

**Internal friction measurements.** 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. Typical temperature dependencies of IF obtained for AISI 316NG stainless steel in as-supplied state and after deformation at room temperature are shown in **Fig. 7**. Two IF peaks situated at about -50 °C and 100 °C, which markedly increase with the amount of cold deformation, represent presumably an anelastic response of dislocations interacting with point defects produced in the austenite crystalline lattice by cold deformation [5]. It is well established [6] 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.



Because the amplitude of the Snoek-like peak is proportional to the free nitrogen concentration in the stainless steel crystalline lattice [6], one can see in Fig. 7 that nitrogen atoms are present in the solid solution of AISI 316NG steel at temperatures around 288 °C. Moreover, the concentration of the free nitrogen atoms in the lattice increases markedly with the amount of prestraining. The last result corresponds to the above-mentioned effect of the prestraining on DSA development in AISI 316NG stainless steel (Fig. 4) and an assumption that free nitrogen atoms in the solid solution play a key role in DSA of austenitic stainless steels.

The observed increase of the nitrogen Snoek-like peak amplitude in the prestrained stainless steel is reduced with aging time at elevated temperatures due to escape of free nitrogen from the solid solution to dislocations. A dependency of the Snoek-like peak of nitrogen on the aging time at temperature of 340 °C is shown in **Fig. 8**.

The peak reduction process can be described as a sum of three exponential decay functions (shown by dotted lines in Fig. 8) 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 one can be related to long-range diffusion escape of nitrogen from solid solution to dislocations and, probably, to grain boundaries.

The increase of the shear modulus with time during aging which is also shown in

**Fig. 5:** Fourier transformation spectra of the flow stress signal in the tensile tests of AISI 316NG stainless steel at a strain rate of 10<sup>-5</sup> s<sup>-1</sup> and different temperatures. Arrows correspond to quasi-regular separate pulses.

**Fig. 6:** Fourier transformation spectra of the flow stress signal in the tensile tests of AISI 316L stainless steels with different nitrogen content at a strain rate of 10<sup>-5</sup> s<sup>-1</sup> and 288 °C.

Fig. 8, evidences pinning of dislocations by nitrogen atoms. Actually, the dislocation pinning process which results in a reduction of the average dislocation segment length, leads to a decrease of the anelastic part of the effective shear modulus [7].

## **Discussion of results**

The results obtained in the present investigation are in good accordance with previous study [4] of nitrogen effects on DSA in AISI 316 stainless steels. A map of DSA shown in **Fig. 9** summarises the serrated flow appearance in AISI 316NG stainless steel at different strain rates and testing temperatures. In the case of filled circles DSA takes place while open circles represent the tests in which no serrations were observed.



**Fig. 7:** Temperature dependencies of internal friction for AISI 316NG stainless steel in as-supplied state and after prestraining by tension 5 % and 20 %.

Open and filled grey circles above a horizontal dashed line are part of data obtained by Kim *et al.* in [4] at strain rate of  $2 \times 10^{-4}$  s<sup>-1</sup>. Finally, the dotted line in Fig. 9, which was obtained in [4] for strain rates higher than  $10^{-4}$  s<sup>-1</sup> and which forms a boundary for testing parameters where DSA occurs, extends also to lower strain rates applied in the present investigation.

It can be seen from Fig. 9 that all filled circles obtained for AISI 316NG stainless steel containing 0.093 wt. % of nitrogen belong to the DSA-area predicted in [4] in the tests of AISI 316L stainless steel with 0.103 wt. % of nitrogen.

Actually, the dotted line in the DSA-map represents a critical strain rate for the DSA occurrence as a function of testing temperature. Obviously, such a dependency can be expressed as

$$\dot{\varepsilon}_c = \dot{\varepsilon}_c^0 \exp \frac{-H}{k_B T}$$

where  $\dot{\varepsilon}_c^0$  is a pre-exponential factor,  $k_B T$  is temperature in energy units and H represents an apparent enthalpy of the DSA occurrence. The enthalpy calculated from the dotted line in Fig. 9 is about 1.24 eV and its value approaches the enthalpy of nitrogen diffusion in the austenite lattice. In fact, the enthalpy of nitrogen diffusion in the studied AISI 316L type stainless steels may be estimated from the maximum temperature of the nitrogen Snoek-like IF peak shown in Fig. 6. Using a simple condition for relaxation time  $\tau$  at the peak temperature

$$\omega\tau(T) = \omega\tau_0 \exp\frac{H_d}{k_B T} \approx 1$$

and the so-called Wert's approximation [7]  $\omega \tau_0 \approx 10^{-12}$  for elemental diffusion jumps of interstitial nitrogen atoms in the austenite lattice, one can obtain for the nitrogen diffusion enthalpy,  $H_d \approx 1.45$  eV at peak temperature of 350 °C.



**Fig. 8:** Amplitude of the Snoek-like peak of nitrogen and normalised shear modulus of AISI 316NG stainless steel as a function of aging time at 340 °C. Dotted lines represent the three components of the peak amplitude decay.



**Fig. 9:** DSA-map of AISI 316NG stainless steel. Filled circles correspond to strain rate and temperature values at which DSA was observed on stress-strain curves. Data points shown by grey circles above dashed line were obtained in [4]. The dotted line is the boundary for the DSA appearance.

parent enthalpy of DSA occurrence and the enthalpy of the nitrogen elemental diffusion jump allows to assume that diffusion redistribution of nitrogen occurs in the crystalline lattice of the stainless steels during their plastic deformation. Another fact supporting such a suggestion comes from a comparison of the average time between separate pulses of the flow stress in DSA (Fig. 5) and the characteristic time of the nitrogen Snoek-like internal friction peak reduction with aging time (Fig. 8). Actually, the average time between flow stress pulses of 2.7 ks corresponds well to 2.6 ks obtained in the present investigation for the nitrogen atom escape from solid solution to dislocations in AISI 316NG stainless steel. It seems that nitrogen atom accumulation on dislocations or some dislocation configurations precedes the Lüders band propagation as an elemental DSA event.

An agreement between the ap-

A suppression of the DSA development in the studied stainless steels caused by nitrogen alloying looks contradictory in terms of the abovementioned model for the possible role of the nitrogen diffusion redistribution in DSA mechanism. The suppression effect of nitrogen in DSA may be caused by an increase of the flow stress with nitrogen alloying of the steel. The increase of the actual stress can change conditions of the DSA occurrence to higher onset deformations. However, a detailed mechanism of the DSA occurrence in the stainless steels needs a further investigation.

## Conclusions

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

Nitrogen suppresses the DSA development in AISI 316L type stainless steels. The onset defor-

mation 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.

#### Acknowledgements

This presentation is prepared within the project Structural operability and plant life management (RKK and XVD), 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), p. 137/150.
- [2] L.H. de Almeida, P.R.O. Emygdio: Scr. Met. et Mater., 31 (1994), p. 505/510.
- [3] R. Ilola, M. Kemppainen, H. Hänninen: Dynamic Strain Aging 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), p. 407/412.
- [4] D.W. Kim, W.-S. Ryu, J.H. Hong: J. Mater. Sci., 33 (1998), p. 675/679.
- [5] C.F. Burdett, I.J. Queen: Met. Rev., 43 (1970), p. 47/65.
- [6] 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), p. 47/52.
- [7] A.S. Nowick, B.S. Berry: Anelastic Relaxation in Crystalline Solids, Academic Press, N.Y., London, 1972, 677 p.