HEAT RESISTANCE AND MICROSTRUCTURE EVOLUTION IN AISI 316LN + 0.1 %Nb STEEL AT 600 AND 625 °C

ŘEHOŘEK Jakub[1, 2], VODÁREK Vlastimil[1], HERNAS Adam[3]

[1]*VSB - Technical University of Ostrava, Czech Republic, EU, vlastimil.vodarek@vsb.cz*
[2]*Research Centre of Rez, Pilsen, Czech Republic, EU, jakub.rehorek@cvrez.cz*
[3]*Institute of Materials Science, Silesian University of Technology, Katowice, Poland, EU, adam.hernas@polsl.pl*

Abstract

Creep resistance of austenitic steels can be improved by small additions of strong carbide and nitride forming elements. Additions of such elements to steels have to be followed by detailed investigations on microstructural stability and surveys of creep failure mechanisms.

This paper deals with creep behaviour and microstructure evolution in the AISI 316LN + 0.1 wt. % Nb steel during long-term creep exposure at 600 and 625 °C. Creep tests with a constant tensile load were carried out in air up to times to rupture of 200 000 hours. Microstructure evolution during long-term creep exposure was studied using light microscopy, scanning and transmission electron microscopy. A small addition of niobium resulted in a reduction of the minimum creep rate and shortening of the tertiary creep stage. Investigations on microstructure evolution in creep ruptured specimens revealed the following minor phases: Z-phase (NbCrN), $M_{23}C_6$, M_6X (Cr_3Ni_2SiX type), η-Laves and σ-phase. M_6X gradually replaced $M_{23}C_6$ carbides. Primary Z-phase particles were present in the matrix after solution annealing, while secondary Z-phase particles formed during creep. Precipitation of Z-phase was more intensive at 625 °C. The dimensional stability of Z-phase particles was excellent and these particles had a positive effect on the minimum creep rate. However, niobium also accelerated the formation and coarsening of σ-phase, η-Laves and M_6X. Coarse particles, especially of σ-phase, facilitated the development of creep damage, which resulted in poor long-term creep ductility.

Keywords: Heat resistance, AISI 36LN + 0.1 % Nb, precipitation reactions, stability of minor phases

1. INTRODUCTION

Promoting of steam parameters in fossil fuel fired power plants to USC parameters presents a challenge for development of advanced materials exhibiting improved creep strength and steam oxidation resistance. Creep properties of austenitic steels can be improved by small additions of strong carbide and nitride forming elements [1]. Additions of such elements to steels have to be followed by detailed investigations on microstructural stability. Precipitation reactions in AISI 300 austenitic grades have been studied for a long time and many minor phases are now well documented [2, 3]. However, it is not true in the case of some interstitial phases in the nitrogen-bearing stabilized austenitic steels, such as NF709, 347LN, Sanicro 25, CF8C-PLUS, etc. [1]. A limited amount of information is available about such nitrogen rich minor phases as Z-phase and M_6X. Conditions of their formation are not very clear and even less understood is their relative stability [4]. The effect of the above minor phases on long-term creep properties of austenitic stainless steels is the subject of permanent interest. Z-phase is a complex NbCrN precipitate which forms in niobium stabilized austenitic steels containing a sufficient amount of nitrogen [2]. The metal-atom arrangement in a complex tetragonal unit cell is characterized by double layers of similar atoms alternating along the c axis to give an NbNbCrCrNbNb… sequence [5]. Z-phase is seldom reported, even in alloys liable to form it [2]. This could be due to the fact that its composition and its general features of formation are similar to MX (NbX) phase, where X is carbon and/or nitrogen. Very few studies have dealt with additions of niobium, carbon and nitrogen in a way that could determine whether NbX or Z-phase is the more stable minor phase. Often niobium is in excess and both NbX and Z-phase can form. Uno et. al. [6] found that only Z-phase formed in a 18Cr12NiNb steel, the niobium content being lower than that required to combine either all carbon or all nitrogen. This would indicate that Z-phase is fast enough to form first when competition between NbX and NbCrN is likely to occur. Investigations on a NF709 steel indicated that NbX phase was gradually replaced by Z-phase during long-term aging at 750 and 800 °C [7]. On the other hand, Raghavan et al. [8] deduced a greater stability of NbX phase in a 347AP steel (18Cr12Ni0.3Nb0.09N, wt. %), since Z-phase was found to precipitate from the solid solution but NbX formed residual particles. The conclusions of such a comparison have to be examined carefully as the compositions of steels were different. It is not clear whether Z-phase in austenitic steels forms from NbX precipitates as suggested by the results of Knowles [9] or directly from the solid solution [10]. It is agreed that thermodynamic stability of Z-phase in austenitic steels is very high [2, 11]. Z-phase particles in austenitic heat resistant steels are very fine even after long-term creep exposure and that is why a positive effect of this minor phase on creep resistance of austenitic steels can be expected [1]. Another important and not well understood minor phase in nitrogen-bearing austenitic stainless steels is M_6X [2]. This phase has a diamond cubic structure (η-carbide, space group Fd3m) with a wide composition range from M_3M_3X to M3M2SiX, where M and M' indicate substitutional elements, while X specifies an interstitial element, such as N and/or C [12]. It has been proved that nitrogen stabilizes this minor phase and its composition in nitrogen-bearing austenitic stainless steels is usually referred as Cr_3Ni_2SiN, although its actual composition can include substantial amounts of molybdenum and iron [2]. Dimensional stability of M_6X particles in austenitic steels is generally poor and that is why the positive effect of this phase on long-term creep properties is not to be expected [2]. The lack of the thermodynamic data on the Cr_3Ni_2SiN phase prevents to take it into account in computer simulations of microstructural evolution in heat resistant steels.

This paper deals with the effect of a small niobium addition to a wrought AISI 316LN steel on creep properties and microstructural evolution during long-term creep exposure at 600 and 625 °C.

2. EXPERIMENTAL PROCEDURES

The evaluation of creep properties was carried out on wrought AISI 316LN steel with an addition of 0.1 wt. % Nb, see **Table 1**.

Table 1 Chemical composition of the AISI 316LN + 0.1 wt. % Nb steel, wt. %

C	N	Mn	Si	P	S	Cr	Ni	Mo	Nb	B
0.023	0.16	1.34	0.48	0.014	0.013	18.1	12.5	2.82	0.106	0.0012

Table 2 Temperature of solution annealing, grain size and yield points at +20 and +300 °C

T [°C]	Grain size [μm]	$R_p0.2_{20°C}$ [MPa]	$R_p0.2_{300°C}$ [MPa]
1050	20 ± 8	392	245

Temperature of solution annealing, austenitic grain size and yield points at +20 °C and +300 °C after solution annealing, are summarised in **Table 2**. Long-term creep rupture tests with a constant tensile load were carried out in air at temperatures of 600 and 625 °C. The stress dependences of the time to rupture were described by the Seifert parametric equation [13]:

$$\log(\sigma) = A_1 + A_2P + A_3P^2;\ P = T(\log t_r + A_4) \qquad (1)$$

where σ is the initial applied stress, T is the test temperature, t_r is the time to rupture and A_1 to A_4 are constants. The equation (1) was applied for the calculation of the $R_{m/600°C/10^4h}$ and $R_{m/600°C/10^5h}$ values. The creep properties of the steel investigated were compared with the creep characteristics of the niobium free AISI 316LN steel as a reference material [15]. Microstructural investigations were conducted on the material after solution annealing and on creep ruptured test-pieces of the cast investigated in order to understand the factors and processes responsible for creep behaviour. Parameters of creep ruptured specimens are specified in **Table 3**. Investigations were carried out by means of scanning (SEM) and transmission (TEM) electron microscopy. Specimens were taken from heads of creep ruptured specimens. Thin foils for TEM investigations on a JEM 2100 microscope were prepared by twin-jet polishing (a Tenupol unit) in an electrolyte consisting of 95 % CH_3COOH and 5 % $HClO_4$ at room temperature and the voltage of 80V. Selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) techniques were used for identification of minor phases on carbon extraction replicas. The size of precipitates was characterised by equivalent diameters.

Table 3 Creep parameters of the specimens investigated

Specimen	**Temperature [°C]**	**Time to Rupture [h]**	**RA [%]**
B1	600	19 508	46.4
B2	600	55 320	17.6
B3	600	223 603	11.4
B4	625	102 602	10.6

3. RESULTS

A small niobium addition to the AISI 316LN steel resulted in fine austenitic grain sizes in the as-received state after solution annealing. It was demonstrated that grain growth during annealing at 1050 °C was inhibited by Z-phase particles. The typical size of these primary Z-phase particles was about 100 nm, **Figure 2**a. These particles precipitated during either thermomechanical pretreatments or solution annealing. The solvus temperature of the NbCrN phase in austenitic stainless steels was reported to be between 1250 and 1350 °C, depending on the steel composition [2]. Z-phase particles formed short rods elongated in the $[001]_Z$ direction. This is in accordance with the minimum directional mismatch, but some particles exhibited roughly comparable growth in the $[001]_Z$ direction and in the $<100>_Z$ directions lying in the base plane [14]. This is thought to be attributable to the complicated double layer structure of Z-phase. Electron diffraction studies on Z-phase revealed the tetragonal unit cell, with parameters consistent with those reported by Jack and Jack, [5].

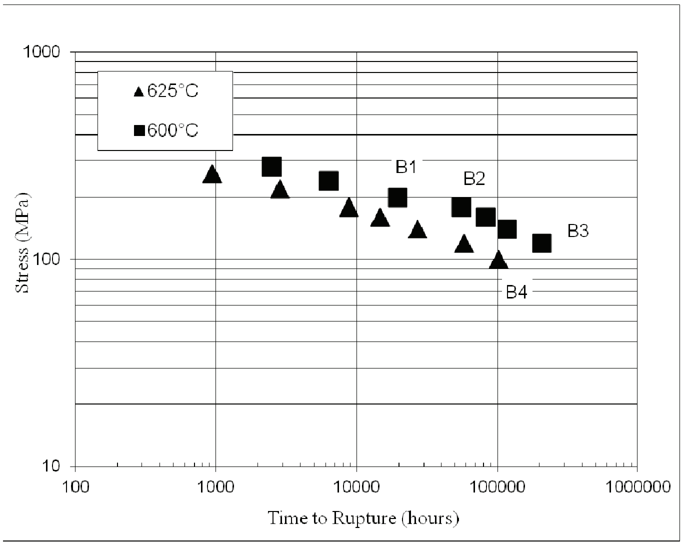


Figure 1 Dependence of stress on the time to rupture at 600 and 625 °C

Results of long-term creep rupture tests at 600 and 625 °C are shown in **Figure 1.** Specimens for microstructural characterisation are marked B1, B2, B3 and B4. A small addition of niobium to the AISI 316LN steel resulted in a reduction of the minimum creep rate and shortening of the tertiary creep stage [11]. The results of creep strength calculations for 600 °C are shown in **Table 4**. At time to rupture of 10^4 hours a small addition of niobium to the AISI 316LN steel seemed to enhance the creep strength but at longer times to rupture niobium actually appeared to impair the creep strength. The standardized creep strength values of niobium free AISI 316LN steel at 600 °C for 10^4 and 10^5 hours are 221 and 151 MPa, respectively [15].

Table 4 Calculated long-term creep strength values at 600 °C

$R_{m / 600\,°C / 10^4\,h}$ [MPa]	$R_{m / 600\,°C / 10^5\,h}$ [MPa]
226	144

Creep rupture ductility (R.A.) values showed a pronounced decrease with prolonging time to rupture at both temperatures investigated, **Table 3**. Results of studies on minor phase evolution in the specimens B1 to B4 are summarised in **Table 5.** The following precipitation sequence was determined: fine secondary Z-phase particles, chromium rich $M_{23}C_6$ carbides, which were gradually replaced by M_6X (Cr_3Ni_2SiX type), η-Laves and σ-phase. No NbX particles were found to precipitate during creep exposure. Secondary Z-phase particles formed from the solid solution.

Table 5 Summary of minor phases identified after creep exposure at 600 and 625 °C

Specimen	Minor Phases
B1	prim. Z-phase, σ-phase, sec. Z-phase, η-Laves, $M_{23}C_6$, M_6X
B2	σ-phase, M_6X, η-Laves, prim. Z-phase, $M_{23}C_6$, sec. Z-phase
B3	σ-phase, M_6X, η-Laves, prim. Z-phase, sec. Z-phase
B4	σ-phase, M_6X, η-Laves, prim. Z-phase, sec. Z-phase

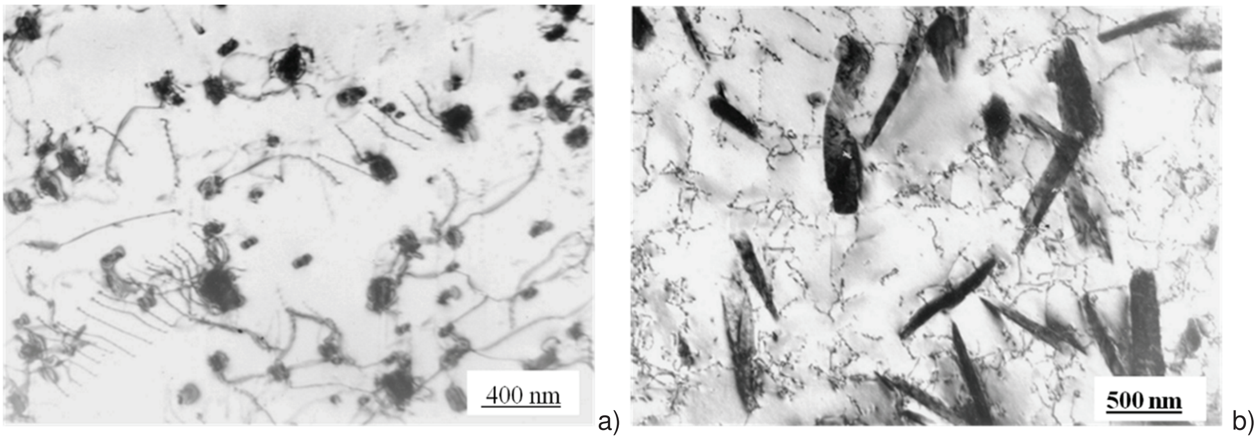
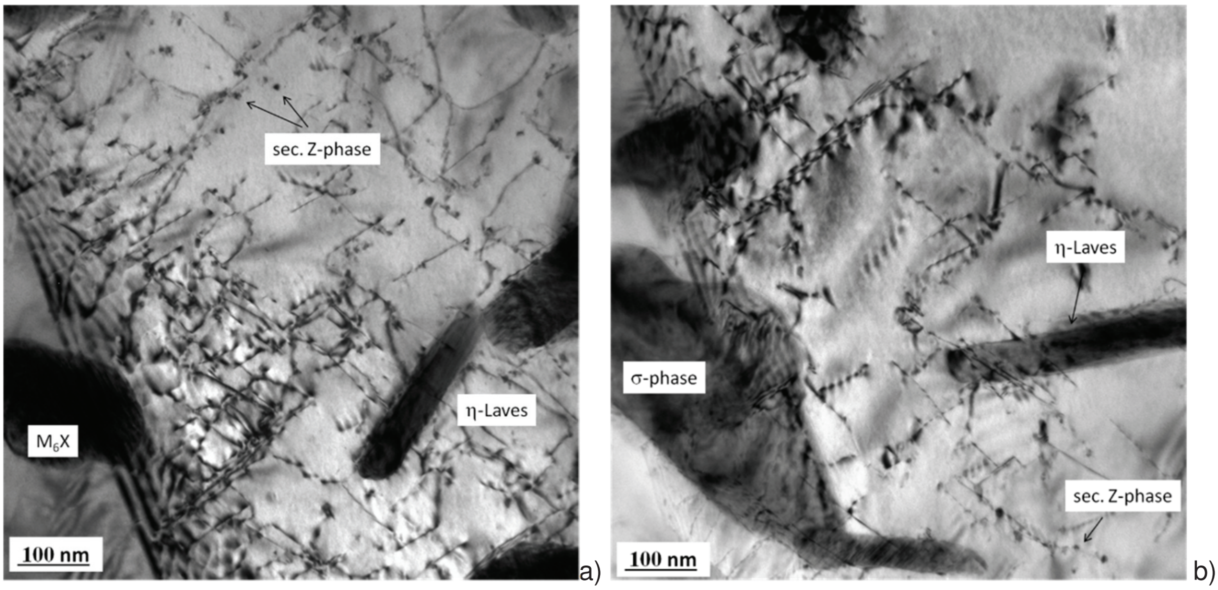


Figure 2 a) Primary Z-phase particles, solution annealed material, b) Needles of η-Laves in the specimen B3

Prolonging of creep exposure at 600°C was accompanied by gradual replacement of $M_{23}C_6$ by M_6X and additional precipitation of all other minor phases. After the longest exposure at 600 °C austenite grain boundaries were decorated by coarse σ-phase, middle size M_6X and primary Z-phase particles. Intragranular needles were mostly formed by η-Laves, **Figure 2b**. Furthermore, a small number density of very fine secondary Z-phase particles was present in the matrix, **Figures 3a, b**. Precipitation of secondary Z-phase was more intensive at 625 °C. **Figure 3b** shows pinning of dislocations in the specimen B3 by fine secondary Z-phase particles. Dimensional stability of Z-phase particles during long-term creep exposure at 600 and 625 °C was very high. The average size of secondary Z-phase particles in the specimen B3 was determined as d = 6 ± 2 nm and in the specimen B4 as d = 11 ± 4 nm.



a) b)

Figure 3 a) Precipitation in the specimen B2, b) Precipitation in the specimen B3

4. DISCUSSION

It was proved that the precipitation sequence during creep exposure at 600 and 625 °C was identical: fine secondary Z-phase particles, chromium rich $M_{23}C_6$, which were gradually replaced by M_6X, η-Laves and σ-phase. The Nb/(C + 6/7N) ratio in the cast investigated is low (0.7) and therefore the competition for niobium between NbX and Z-phase (NbCrN) can be expected. Microstructural investigations confirmed that Z-phase was fast enough to form first. There were no NbX particles found even after the longest creep exposure at 600 °C. This proves that in the steel investigated Z-phase is more stable than NbX. The dimensional stability of Z-phase was found to be excellent. A number density of $M_{23}C_6$ particles decreased with increasing time of creep exposure. Particles of this phase were gradually replaced by M_6X (Cr_3Ni_2SiX) at longer exposures [2].

Formation of σ-phase particles is promoted by elements like chromium, niobium, titanium and molybdenum [15]. Silicon also promotes and accelerates its formation [2, 16]. Coarse particles of this phase facilitated the formation and interlinking of creep cavities. Coarse σ-phase particles contributed significantly to relatively poor creep ductility of the cast investigated after long-term creep exposure. Niobium addition also accelerated the formation of η-Laves (Fe_2Mo type). Needles of this phase started to precipitate at grain boundaries and at longer times of exposure were intensively formed inside of austenite grains. η-Laves and σ-phase particles contained only low amounts of niobium. Based on the typical size, precipitates observed in the steel investigated after long-term creep exposure at 600 °C can be classified as follows: coarse σ-phase particles reached size from 1 to 10 μm, η-Laves, M_6X and primary Z-phase particles were usually in the range from 0.1 to 1 μm and the secondary Z-phase particles reached only several nanometres.

5. CONCLUSION

A small addition of niobium to the AISI 316LN steel resulted in a reduction of the minimum creep rate and shortening of the tertiary creep stage. The minimum creep rate reduction can be related to precipitation of fine particles of Z-phase. The positive effect of niobium on the creep resistance in the first and second stages of creep was gradually surpassed by its effect on acceleration of the σ-phase, M_6X and η-Laves formation. Coarse σ-phase particles at austenite grain boundaries promoted the formation of creep defects. The results demonstrate that fine intragranular Z-phase particles can have a positive effect on the minimum creep rate, but the final effect of niobium on long-term creep properties will also depend on its influence on the stability of other minor phases in the matrix.

ACKNOWLEDGEMENTS

The presented work was financially supported by the Ministry of Education, Youth and Sport Czech Republic Project LQ1603 (Research for SUSEN). This work has been realised within the SUSEN Project realized in the framework of the European Regional Development Fund (ERDF) in project CZ.1.05/2.1.00/03.0108. The authors wish to acknowledge the financial support from the projects No. LE 13011 "Creation of a PROGRES 3 Consortium Office to Support Cross-Border Co-operation", No.LO1203 "Regional Materials and Technology Centre - Feasibility Programme", SP 2016/111 and SP2016/103.

REFERENCES

[1] CHI, C., YU, H., XIE, X. Alloy steel properties and use. Precipitation in Creep-Resistant Austenitic Stainless Steels, 2011, pp. 171-201.

[2] SOURMAIL, T. Advanced austenitic stainless steel for ultra-supercritical (USC) fossil power plants. Materials Science and Technology, 2000, vol. 17, no. 1, pp. 1-14.

[3] WEISS, B., STICKLER, R. Phase instabilities during high temperature exposure of 316 austenitic stainless steel. Metallurgical and Materials Transactions, 1972, vol. 3, no. 4, pp. 851.

[4] VODÁREK, V. Stability of Z-phase and M6X in creep-resistant steels. Scripta Materialia, 2012, vol. 66, no. 9, pp. 678-681.

[5] JACK, D. H., JACK, K. H. Structure of Z-phase, NbCrN. Journal of Iron and Steel Research, International, 1972, vol. 210, no. OCT, pp. 790.

[6] UNO, H., KIMURA, A., MISAWA, T. Effect of Nb on Intergranular Precipitation Behavior of Cr Carbides in N-Bearing Austenitic Stainless-Steels. Corrosion, 1992, vol. 48, no. 6, pp. 467-474.

[7] SOURMAIL, T., BHADESHIA, H. K. D. H. Microstructural evolution in two variants of NF709 at 1023 and 1073 K. Metallurgical and Materials Transactions, 2005, vol. 36A, no. 1, pp. 23-34.

[8] RAGHAVAN, A., KLEIN, C. F., MARZINSKY, C. N. Instabilities in stabilized austenitic stainless steels. Metallurgical and Materials Transactions, 1992, vol. 23A, no. 9, pp. 2455-2467.

[9] KNOWLES, G. The creep strength of a 20%Cr-25%Ni-Nb steel containing controlled particle dispersions. Metal Science, 1977, vol. 11, no. 4, pp. 117-122.

[10] ROBINSON, P. W., JACK D. H. Precipitation of Z-phase in a high-nitrogen stainless steel. Journal of Heat Treating, 1985, vol. 4, no. 1, pp. 69-74.

[11] VODÁREK, V. Creep behavior and microstructural evolution in AISI 316LN + Nb steels at 650 °C. Materials Science and Engineering, 2011, vol. 528, no. 12, pp. 4232-4238.

[12] STADELMAIER, H. H. Developments in the Structural Chemistry of Alloy Phases. Metal-Rich Metal-Metalloid Phases, 1969, pp. 141-180.

[13] SEIFERT, W. Kammer der Technik. Warmfeste Metallische Werkstoffe, Zittau, 1977.

[14] VODÁREK, V. Morphology and orientation relationship of Z-phase in austenite. Scripta Metallurgica et Materialia, 1991, vol. 25, no. 3, pp. 549-552.

[15] European Creep Collaborative Committee Data Sheets. ECCC Data Sheets, 2014. pp. 75-76.

[16] MINAMI, Y., KIMURA, H., IHARA, Z. Microstructural changes in austenitic stainless steels during long-term aging. Materials Science and Technology, 1986, vol. 2, no. 8, pp. 795-806.