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Creep deformation and fracture behaviour of a nitrogen-bearing type 316 stainless steel weld metal

G. Sasikala *, M.D. Mathew, K. Bhanu Sankara Rao, S.L. Mannan

Materials Development Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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Abstract

Creep properties of a nuclear grade type 316 stainless steel (SS) weld metal containing ~0.08 wt% of nitrogen were studied at 873 and 923 K. These properties were compared with those of a type 316 SS weld metal without nitrogen. In general, the nitrogen-bearing weld metal exhibited better creep and rupture properties. The rupture strengths of the nitrogen-containing weld metal was ~40% higher than that for the type 316 SS weld metal at both the temperatures. The steady-state (minimum) creep rates were up to two orders of magnitude lower for the nitrogen-containing weld metal compared to 316 SS weld metal. Rupture ductility of nitrogen-containing weld metal was lower at all the test conditions; the long-term ductility at 923 K was below 5%. The differences in creep behaviour of the two weld metals are discussed with respect to the influence of nitrogen on microstructural evolution in the two weld metals. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Austenitic stainless steel (SS) of AISI type 316 is being widely used as a major structural material for fast breeder reactor components in view of its good high temperature mechanical properties, compatibility with the coolant liquid sodium and adequate weldability. However, in general, austenitic stainless steels have relatively poor resistance to intergranular stress corrosion cracking (IGSCC) in chloride and caustic environments. Type 316 SS welds exposed to marine environments have been reported to fail by IGSCC in the heat affected zone (HAZ) due to sensitization and presence of residual stresses introduced during welding. A nitrogen-alloyed low carbon (0.03 wt% max) version of this steel, designated 316L(N) SS has been chosen for the high temperature structural components of the prototype fast breeder reactor presently in an advanced stage of design at Kalpakkam. Minor variations in chemical composition, microstructure and its stability and thermo-mechanical history have been found to lead to wider variations in high temperature behaviour of base and weld metals [1]. The ASME code case N-47 specifies the allowable stress for a welded component as the lower value between (i) the allowable stress limit for the base metal (which in turn is the lowest among 66% of the stress to cause rupture, 80% of the stress to cause the onset of tertiary creep, and 100% of the stress to cause 1% creep strain in the design life), and (ii) 0.8 $R^{*}\sigma_{\min}$ where R is the ratio of rupture strength of the weld metal to that of the base metal, and $\sigma_{\min}$ is the expected minimum stress to rupture for the base metal [2]. To take into account, the lower ductility of the weld metal, the permitted deformation at a weld is restricted to half that for the base metal.

Austenitic stainless steels are susceptible to hot cracking during welding. In order to reduce the tendency for hot cracking, the chemical composition of the welding consumable is adjusted such that the primary mode of solidification is ferrite. The resultant weld deposit contains about 3–10% delta ferrite. The duplex microstructure consisting of austenite and ferrite phases is highly unstable at high temperatures and δ-ferrite transforms to carbides and brittle intermetallic phases such as sigma. Consequently, the creep properties of the weld metal would be significantly influenced by the

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[*] Corresponding author. Tel.: +91 4114 40202; fax: +91 4114 40396; e-mail: gsasi@igcar.ernet.in

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kinetics as well as the nature of the products of this transformation which in turn strongly depend on the chemical composition of the deposit [1,3,4]. This investigation is aimed at understanding the creep behaviour of the 316 and 316L(N) weld metals. Special emphasis is laid on the transformation behaviour of δ-ferrite during creep at elevated temperatures and its influence on the creep properties.

2. Experimental

Constant-load creep rupture tests have been carried out at 873 and 923 K in a wide range of stress levels varying between 100 and 335 MPa. All-weld specimens were taken along the welding direction, from weld pads prepared by manual metal arc welding. Details of the welding procedure are reported elsewhere [1]. The gage length of the samples was 50 mm and gage diameter was 8 mm for the 316 and 10 mm for the 316L(N) weld metals. The temperature over the gage length was controlled to within ±2 K. The chemical compositions of the two weld metals are given in Table 1. Both the weld metals were tested in the as welded condition; they had a duplex microstructure containing δ-ferrite (~4.5% in 316 and ~7% in 316L(N)) with vermicular morphology distributed in an austenite matrix (Fig. 1).

Light optical metallography was carried out on tested samples to study the nature of creep damage. Scanning electron microscopic investigations were carried out on the fracture surface as well as on the polished transverse sections of tested samples to identify the mode of fracture and thus to identify the mechanisms of fracture. Also, these techniques aided in qualitatively assessing the transformation behaviour of δ-ferrite under creep. For a semi-quantitative assessment of the transformation behaviour, magnetic (using a Magne-gage calibrated with reference pads as per AWS standards) method was used to determine the residual δ-ferrite content in the creep tested samples.

3. Results and discussion

3.1. Creep properties

The variation of rupture life with applied stress for both the weld metals at 873 and 923 K are shown in Fig. 2(a) and (b), respectively. The rupture strength of 316 SS weld metal is ~40% lower compared to that of the 316L(N) SS weld metal at both the temperatures. The dashed lines in these figures represent the expected minimum stress to rupture specified by ASME N-47 for 316 SS weld metal, i.e., $R^{*}\sigma_{\min}$. It may be noted that except for the 316 SS weld metal at very short rupture times, the rupture strengths of both the weld metals are higher than the values given by the ASME code. In terms of rupture life, 316L(N) SS weld metal is better by a factor of ~10 compared to 316 SS weld metal.

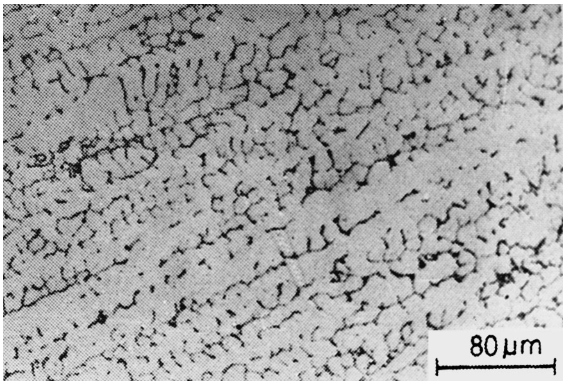

Fig. 1. Initial microstructure of the 316 and 316L(N) weld metals showing the vermicular morphology of δ-ferrite in the austenite matrix.

Variation of minimum creep rate ($\dot{\varepsilon}_s$) with applied stress (σ) at 873 and 923 K are given in Fig. 3(a) and (b), respectively. A power law relationship between $\dot{\varepsilon}_s$ and σ is found to be obeyed by both the weld metals. The stress exponent n is found to be ~12 for the 316 SS weld metal at both 873 and 923 K. However, for 316L(N) weld metal, n is ~18.8 at 873 K and 10.6 at 923 K. These values for the stress exponent suggest that for both the weld metals, dislocation creep is the rate controlling mechanism. Creep rates for 316 SS weld metal are generally higher by a factor of about 50 compared to 316L(N) SS weld metal. Plots of variation of rupture elongation with rupture life for the two weld metals at 873 and 923 K are given in Fig. 4(a) and (b), respectively. At both the temperatures, 316L(N) SS weld metal exhibits lower ductility than 316 SS weld metal. For both the weld metals, there is a deterioration in ductility at longer rupture lives. At 873 K, in the case of 316 SS weld metal, upto about 4000 h, there is no significant variation in ductility; however, beyond that a clear decrease is observed. In 316L(N) SS weld metal at 873 K,

Table 1
Chemical compositions (in wt%) of the two weld metals of 316 and 316L(N) SS

Element	C	Ni	Cr	Mo	Mn	Si	S	P	Cu	B	N
316	0.060	11.9	18.8	2.06	1.42	0.58	0.010	0.010	0.05	0.0005	–
316L(N)	0.052	11.5	18.6	2.20	1.74	0.64	0.007	0.022	0.04	0.0009	0.067

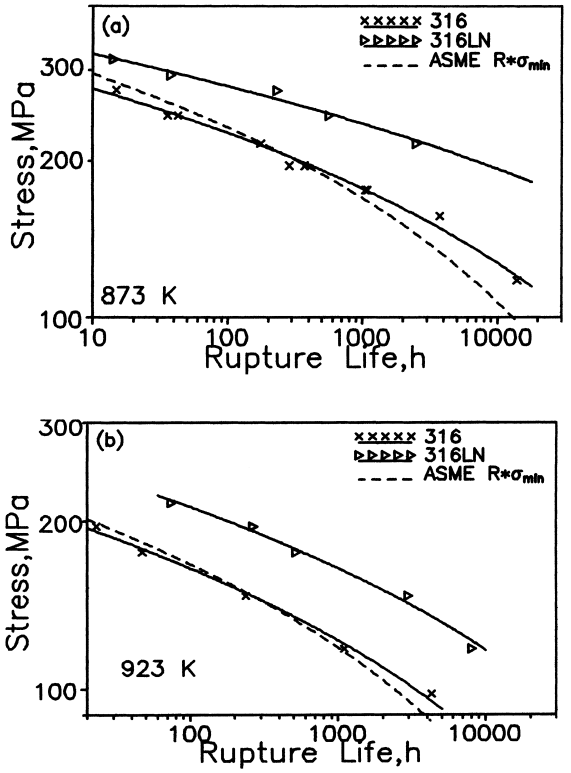

Fig. 2. Variation of rupture life with applied stress at (a) 873 K and (b) 923 K for weld metals of types 316 and 316L(N) SS. The dashed lines represent the ASME curves for expected minimum stress to rupture for the 316 weld metal.

the ductility is in the range 15–20% except at a rupture life of ~40 h when it is ~30%. However, there is a clear, though marginal variation in ductility with increasing rupture lives. At 923 K, on the other hand, both the weld metals exhibit clear decrease in ductility with increasing rupture lives. These observations can be rationalised based on the differences in the amount of δ-ferrite present in the two weld metals and its transformation behaviour at the above temperatures.

The presence of δ-ferrite can influence the creep deformation behaviour in a complex manner; in the short-term creep tests, the network of δ-ferrite, the crystal structure being a more open bcc, offers an easier path for diffusion compared to fcc austenite. The δ–γ interfaces can also act as effective diffusion paths. During long-term creep tests, the δ-ferrite network breaks down and transformation to various phases occurs. The nature, morphology and distribution of the transformation products can significantly influence the creep deformation and fracture behaviour of the weld metal. Thus, the effect of δ-ferrite on the creep behaviour depends on the conditions of testing. In the case of weld metals containing δ-ferrite, addition of nitrogen, a strong austenite stabiliser, is expected to reduce the ferrite content. However, in the case of 316L(N) weld metal investigated here, the contents of other alloying elements in the welding electrode are adjusted such that the resultant deposit contains a specified amount of δ-ferrite for avoiding hot cracking. The important differences between the two weld metals considered here are (i) the difference in the chemical composition, mainly with respect to the interstitial alloying element N and (ii) the δ-ferrite content. In addition, the alloy content of 316L(N) weld metal is high with respect to molybdenum and manganese. Also, the phosphorous and boron contents in this weld metal are twice that in 316 SS weld metal. The effect of these elements in modifying the properties of the austenite phase in the weld deposit becomes important in deciding the behaviour of the weld metal. Another important effect that cannot be discounted is that of nitrogen on the transformation behaviour of δ-ferrite, particularly on the kinetics as well as the nature, morphology and distribution of the products.

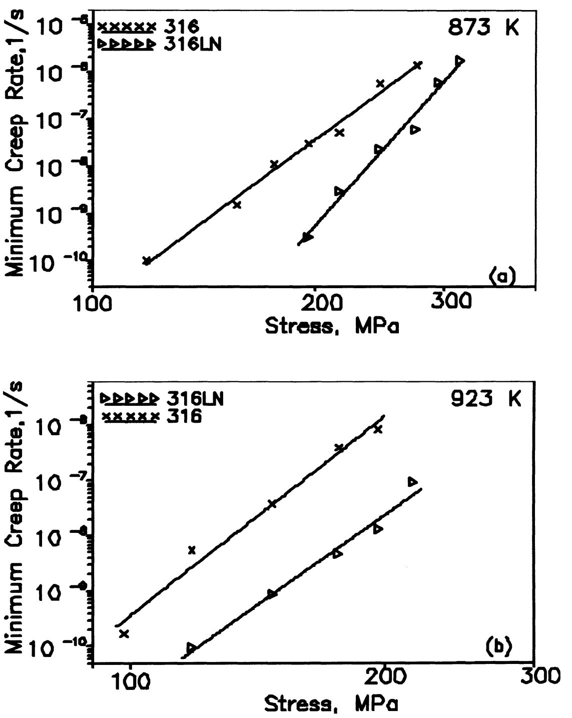

Fig. 3. Variation of minimum creep rate with applied stress at (a) 873 K and (b) 923 K for the weld metals of types 316 and 316L(N) SS.

Creep deformation behaviour of type 316 SS base metal has been widely studied [5–7]. It is well established that nitrogen is a potent solid solution strengthener compared to carbon in austenitic SS [8]. Nitrogen introduces strong elastic distortions into the crystal lattice and also increases the internal friction, thus making the movement of dislocations through the lattice more

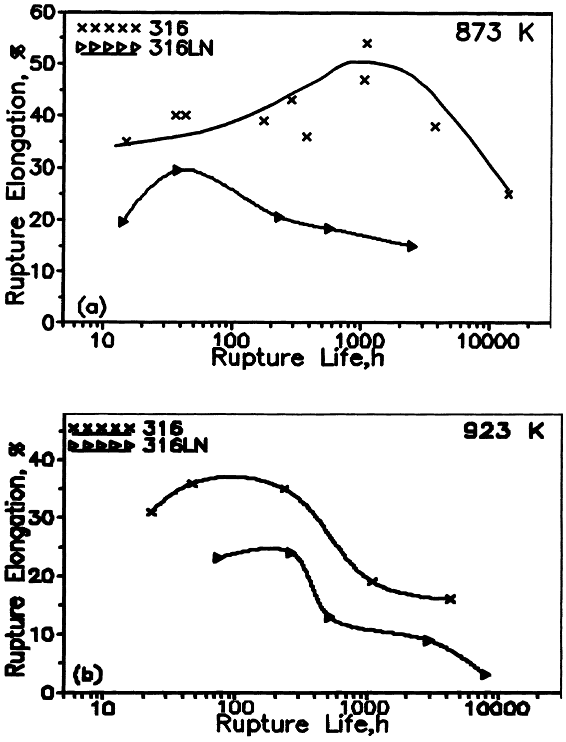

Fig. 4. Variation of rupture elongation with applied stress at (a) 873 K and (b) 923 K for the weld metals of types 316 and 316L(N) SS.

difficult. Also, it is well understood that, in austenitic stainless steels, nitrogen delays the onset of precipitation of any phase that has lower solubility for it, till all the nitrogen is otherwise removed as precipitates [9]. However, since austenite has a good solubility for nitrogen, it requires more than 0.15 wt% of nitrogen for the occurrence of nitrides [10]. Further, the presence of nitrogen is known to retard the coarsening of $M_{23}C_6$ precipitates in type 316 SS base metal, by reducing the diffusivity of substitutional elements such as chromium [11]. Thus, the long-term elevated temperature properties of nitrogen-containing base metals are found to be superior to those of the nitrogen-free varieties [12]. The higher amounts of Mo and Mn also could contribute to the strengthening of this weld metal compared to 316 SS weld metal. In addition, presence of higher amounts of boron and phosphorous could significantly enhance the creep life. It is well known that, in type 316 base metals, boron segregates to the grain boundaries and incorporates itself into the carbides reducing the lattice mismatch between the matrix and the precipitate and thus preventing coarsening of the precipitates [5]. Hence, the extent of grain boundary sliding is reduced leading to lower creep rates as well as delayed cracking, thus extending the time to onset of tertiary creep. It is reported that presence of higher amounts of phosphorous can reduce the creep rates by a factor of 1000 times possibly due to enhanced grain boundary strengthening by fine precipitation of carbides and improves the creep strength substantially [13]. However, the presence of phosphorus is known to be deleterious from the ductility point of view.

It may be noted that the initial δ-ferrite contents in the two weld metals are different; $\sim$4.5 FN in 316 weld metal and $\sim$7 FN in 316L(N) weld metal. The effects of this difference can be qualitatively explained in the following manner. At 923 K, when the δ-ferrite network breaks down very rapidly, typically within the first few hours, the initial δ-ferrite content is not expected to influence the deformation behaviour to any significant extent. The observed differences in the creep rates of the two weld metals at this temperature can be attributed solely to the different extents of solid solution strengthening of the austenite phase in the two weld metals. However, at 873 K, the kinetics of δ-ferrite transformation is slow, i.e., the breaking down of the network is delayed. Thus, at higher stresses, when the time to onset of secondary (where the minimum creep rates are determined) is considerably short, one can expect the δ-ferrite network to provide easier diffusion paths resulting in higher creep rates than would be expected in the absence of such paths. At lower stresses, however, the time to onset of secondary is long enough for the δ-ferrite network to break down resulting in lower creep rates. Also, a contribution to strengthening from fine precipitates is expected. These factors manifest themselves as a higher stress-dependence of creep rate at 873 K.

The difference in the rupture ductilities of the two weld metals can also be understood from a consideration of the initial δ-ferrite contents. The 316L(N) SS weld metal, which contains a higher amount of δ-ferrite, is expected to contain a larger amount of the brittle intermetallic phase σ giving rise to lower ductility. The fact that the decrease in ductility at longer durations is more rapid at 923 K (i.e., close to the minimum time in the time-temperature-transformation diagram for σ-phase in this class of weld metals) than at 873 K is in agreement with this argument. Thomas [15,16], from a study of effect of δ-ferrite from 0 to 10 FN on the creep rupture ductility of type 316 SS welds reported an optimum ductility at a δ-ferrite content of $\sim$5 FN.

3.2. *Transformation of δ-ferrite during creep*

The high temperature properties of δ-ferrite containing weld metals are generally controlled by the kinetics as well as the nature of products of transformation of δ-ferrite. A detailed characterisation of the transformation of δ-ferrite during creep in the two weld metals is carried out. Both qualitative (optical microscopic) and quantitative (magnetic) methods were used in this investigation. Fig. 5(a) and (b) show the

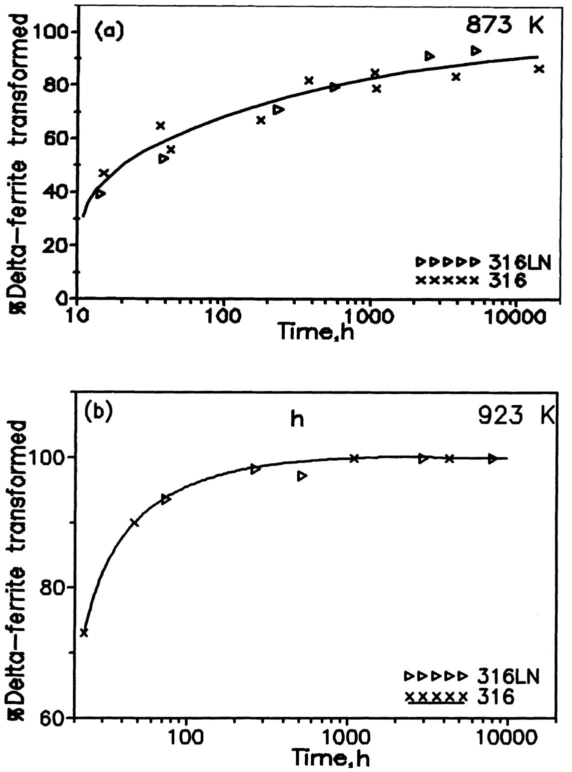

Fig. 5. Variation of the extent of δ-ferrite transformation with exposure time for the two weld metals at (a) 873 K and (b) 923 K. The applied stresses corresponding to the same exposure time were about 40% lower for 316 weld metal compared to that for 316L(N) weld metal.

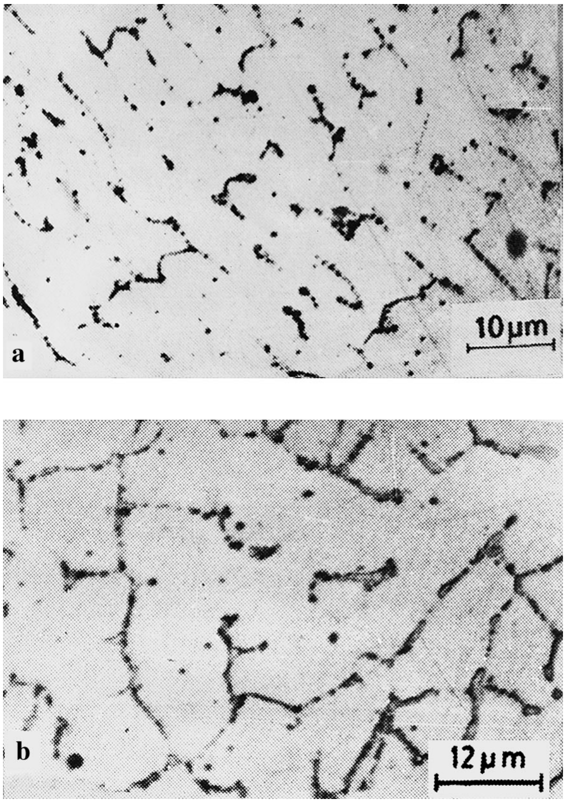

Fig. 6. Micrographs showing the breaking down of δ-ferrite network into carbides in less than 100 h at 923 K in the weld metals of (a) 316 and (b) 316L(N).

variation of percentage transformation of δ-ferrite with creep time at both the temperatures as determined from the residual δ ferrite content of the crept samples. It may be observed that the presence of nitrogen does not seem to significantly affect the extent of δ-ferrite transformation at both the temperatures. At 873 K, even after 5000 h of exposure, the extent of transformation is only about 85% (Fig. 5(a)). In both the weld metals, the extent of transformation is higher at 923 K, and is almost complete within about 100 h (Fig. 5(b)).

The microstructures of the two weld metals after exposure to creep at 923 K are shown in Figs. 6 and 7. It may be seen that the δ-ferrite transforms to carbides in less than 100 h and continued exposure results in the formation of an intermetallic phase σ. The transformation takes place in the following sequence: (i) in less than 50 h, the δ-ferrite network breaks down forming carbides, (ii) continued exposure results in the formation of an intermetallic phase σ and (iii) on further exposure, the σ-phase particles coarsen to form large islands of σ-phase. From short duration test samples, influence of nitrogen on the extent of decomposition of δ-ferrite could not be detected (Fig. 6). However, prolonged exposure leads to coarsening of σ-phase particles which is more rapid in 316 SS weld metal compared to that in 316L(N) SS weld metal (Fig. 7).

At 923 K, the incubation period for carbide precipitation for a nitrogen-free deposit of 316 SS weld metal is reported to be ~0.1 h compared to ~1–2 h required in the presence of ~0.15% nitrogen [9]. The effect of nitrogen on the onset of precipitation cannot be assessed by examining the samples tested to failure, since the exposure times are much longer than these. Nevertheless, the effects of nitrogen in modifying the kinetics of precipitation can significantly influence the creep properties in general and more importantly, the minimum creep rate. The effect of N on coarsening of σ-phase particles is very clear from the micrographs of samples failed after long durations.

At 923 K, in the case of 316 SS weld metal, failure except at very high stress levels resulted from the nucleation, growth and linkage of cavities at the coarse and brittle σ-phase particles. However, in 316L(N) weld metal, extensive cracking associated with σ-phase was observed only at the lowest stress level investigated. In this weld metal at other stress levels, failure generally

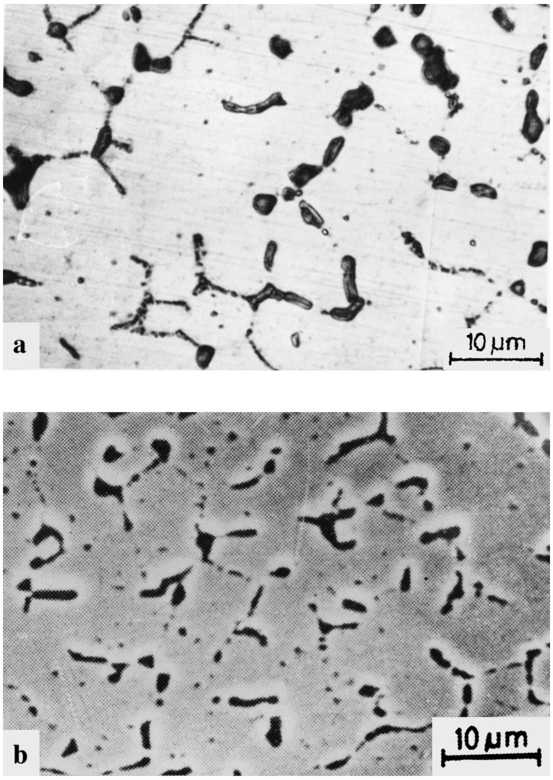

Fig. 7. Micrographs showing the coarsening of σ-phase particles after long duration exposure at 923 K in the weld metals of (a) 316 after 4300 h and (b) 316L(N) after 8000 h.

At 873 K, failure of 316 SS weld samples at all the stress levels was ductile transgranular with rupture elongation of the order of ~40%, and the fracture surfaces had a characteristic dimpled appearance (Fig. 8(a) and (b)). A decreasing trend in rupture elongation was noticed only at the lowest stress level corresponding to a rupture life of ~15,000 h. In this case too, the fracture surface morphology was the same. The 316L(N) weld metal on the other hand, showed progressive increase in the incidence of cavities with decreasing stress level, i.e., increasing rupture times (Fig. 9(a)–(c)). This correlates well with gradual decrease in rupture elongation with decreasing stress level. (At 923 K also, similar cavities were observed at an intermediate stress level of 145 MPa.) It may be noticed that the morphology and distribution of these cavities are uniform. It is known that Laves and η phases form in the base metal of type 316L(N) SS at this temperature [14]. However, no such particles were detected at these cavities on the fracture surface. It is possible that they are lost in the process of ultrasonic cleaning of fracture surface before examination. At 923 K, after long exposure, i.e., at the lowest stress levels employed in the study, the fracture surface resulted from transgranular ductile rupture. The absence of creep cavities except at the lowest stress level in 316L(N) weld metal at this temperature can be qualitatively understood as follows. In this weld metal, as discussed earlier, the presence of nitrogen delays the formation of σ-phase till all the nitrogen is removed as precipitates. Nitrogen can precipitate only by local enrichment of nitrogen to a level beyond its solubility in the matrix, i.e., >0.14 wt% by diffusion. After this happens, the σ-phase particles do precipitate locally, i.e., in those regions where the nitrogen has been removed from solution by precipitation. However, the coarsening of these σ-phase particles is very slow since Cr from remote areas has to diffuse for the coarsening and the diffusivity of Cr is known to be reduced by the presence of nitrogen. Also, the strength mismatch between the γ region and σ-phase can be expected to be smaller compared to that in 316 weld metal since the strength of the γ region in 316L(N) weld metal is tremendously improved by the presence of nitrogen. The presence of brittle precipitates that do not act as cavity nucleation sites can lead to further strengthening and consequent reduction in ductility. However, very long exposure (i.e., under low stresses) at higher temperature leads to the coarsening of σ-phase such that they can act as cavity nucleation sites.

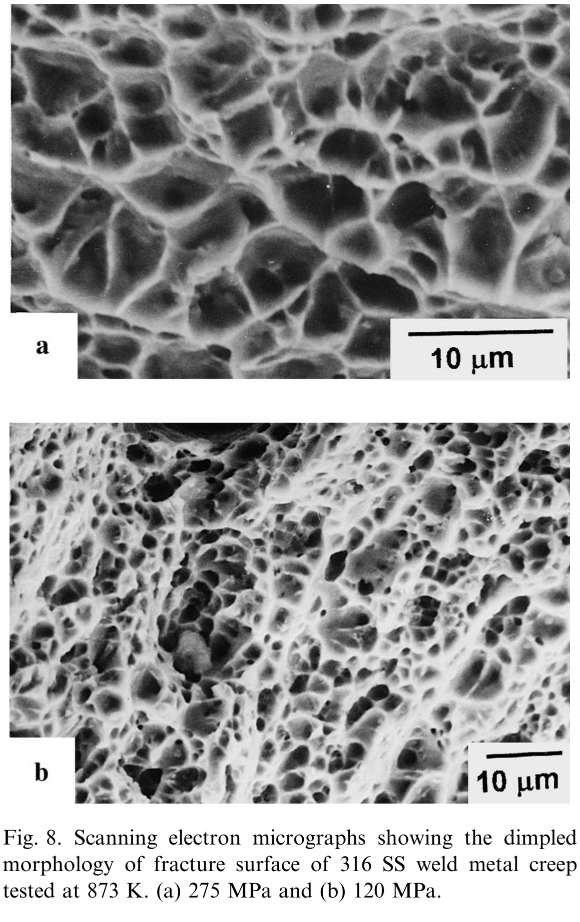

Fig. 8. Scanning electron micrographs showing the dimpled morphology of fracture surface of 316 SS weld metal creep tested at 873 K. (a) 275 MPa and (b) 120 MPa.

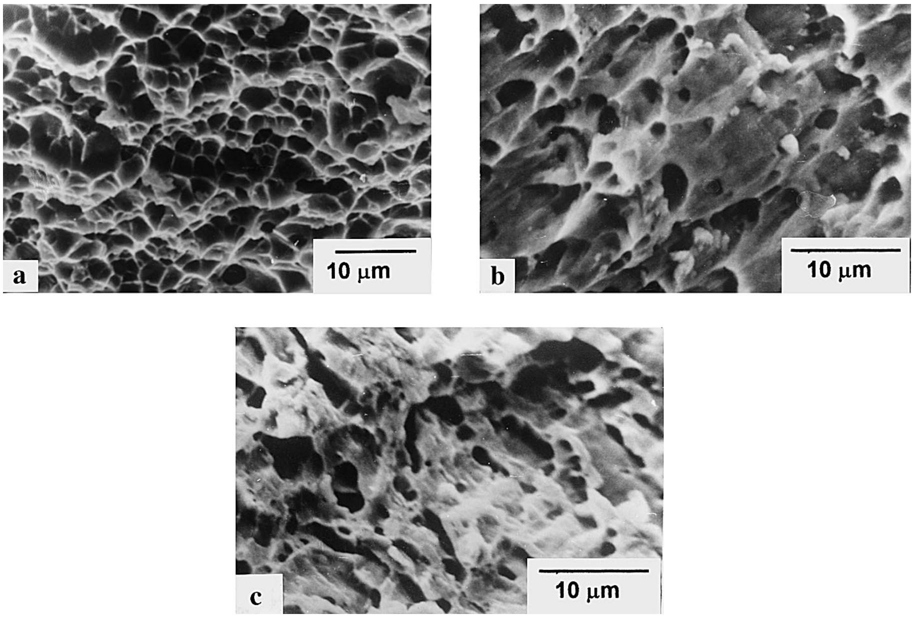

Fig. 9. Scanning electron micrographs showing the increasing incidence of cavitation on the fracture surface of 316L(N) weld metal creep tested at 873 K. (a) 300 MPa, (b) 245 MPa and (c) 215 MPa.

of both the weld metals appeared 'fibrous' which is characteristic of inter-dendritic failure (Fig. 10(a) and (b)). This indicates that nucleation, growth and linkage of cavities at second phase particles that form along the δ–γ interface causes failure in both the weld metals. Presence of nitrogen delays the nucleation and growth of carbides and σ-phase with which creep damage is associated thus delaying the onset of tertiary creep damage. As a consequence, the nitrogen-bearing weld metal exhibits an improvement in rupture life.

4. Summary

A comparative study of the creep rupture properties of the weld metals of two nuclear grade steels with and without N at 873 and 923 K was carried out. The rupture strength of the nitrogen-bearing weld metal was found to be ~40% higher than that of the nitrogen-free weld metal. The steady-state (minimum) creep rates were up to two orders of magnitude lower for the nitrogen-bearing weld metal compared to that for the nitrogen-free weld metal. Rupture ductility of nitrogen- bearing weld metal was lower at all the test conditions; the long-term ductility at 923 K was less than 5%. Apparently, the presence of nitrogen does not significantly influence the extent of δ-ferrite transformation as determined from Magne-gage measurements on the creep samples tested to failure. However, the size, distribution and morphology of the δ-ferrite transformation products which dictate the high temperature deformation and

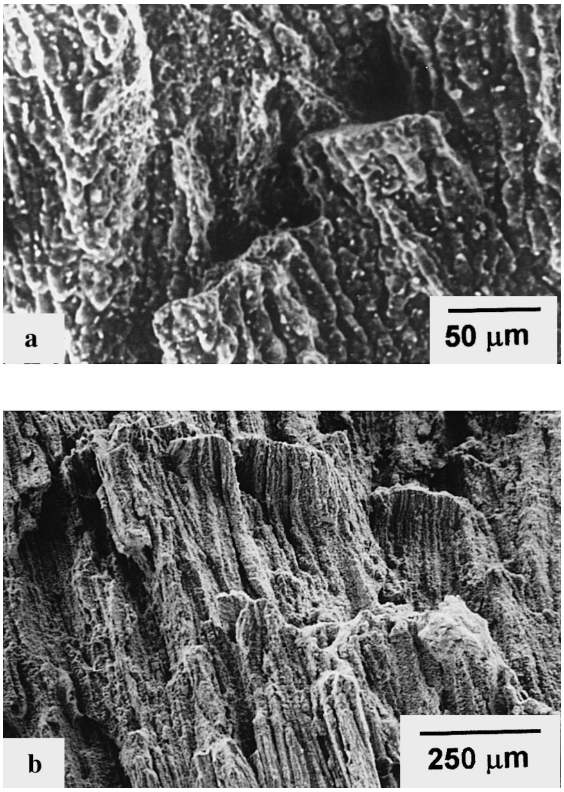

Fig. 10. Scanning electron micrographs showing the fracture surface of the two weld metals creep tested at 923 K under 120 MPa. (a) 316L(N) SS weld metal (b) 316 SS weld metal.

fracture behaviour of δ-ferrite containing weld metals are significantly influenced by the presence of nitrogen.

Thus, the following conclusions may be drawn from this study:

1. Presence of nitrogen increases the creep rupture strength of the 316 SS weld metal by solid solution strengthening and by retaining the fine nature of the precipitates.
2. Nitrogen increases the creep rupture life by delaying the precipitation and coarsening of deleterious particles, like σ-phase.
3. The lower ductility of the nitrogen-bearing weld metal is due to its higher δ-ferrite content.

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References

[1] M.D. Mathew, G. Sasikala, S.L. Mannan, P. Rodriguez, Trans. ASME, J. Eng. Mater. Technol. 115 (1993) 163.
[2] ASME Boiler and Pressure Vessel Code, American Society of Mechanical Engineers, Code Case N-47, 1992.
[3] J.J. Smith, R.A. Farrar, Int. Mater. Rev. 38 (1993) 25.
[4] S.R. Keown, R.G. Thomas, Met. Sci. 15 (1981) 386.
[5] D.G. Morris, D.R. Harries, Met. Sci. 12 (1978) 525.
[6] S.L. Mannan, P. Rodriguez, Met. Sci. 17 (1983) 63.
[7] M.D. Mathew, S. Latha, G. Sasikala, S.L. Mannan, P. Rodriguez, Nucl. Technol. 81 (1988) 114.
[8] J. Foct, A. Hendry (Eds.), Proceedings of the International Conference High Nitrogen Steels, Lille, Institute of Metals, London, May 18–20, 1988.
[9] E. Folkhard, in: Welding Metallurgy of Stainless Steels, Springer, New York, 1986, p. 103.
[10] C.J. Nojak, in: D. Peckner, I.M. Bernstein (Eds.), Handbook of Stainless Steels, McGraw Hill, New York, 1977.
[11] J.K.L. Lai, Mater. Sci. Eng. 61 (1983) 101.
[12] M.D. Mathew, G. Sasikala, K.B.S. Rao, S.L. Mannan, Mater. Sci. Eng. A148 (1991) 253.
[13] C.M. Shepherd, A.W. James, in: B. Wilshire, D.R.J. Owen (Eds.), Creep and Fracture of Engineering Materials and Structures, The Institute of Metals, Swansea, UK, 1987, p. 413.
[14] K. Taguchi, Sixth Int. Conf. Creep and Fatigue: Design And Life Assessment at High Temperatures, 16–17 April 1996, Institution of Mechanical Engineers, London, Paper No. C494/045/96, pp. 221–230.
[15] R.G. Thomas, Weld. J. 57 (1978) 81.
[16] R.G. Thomas, in: Proceedings of the Specialists Meeting on Mechanical Properties of Structural Materials Including Environment, Chester, UK, IWGFR-49 1, 1983, p. 297.