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Effect of nitrogen on the dynamic strain ageing behaviour of type 316L stainless steel

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The dynamic strain ageing (DSA) behaviours of type 316L stainless steels containing different nitrogen contents (0.01–0.15 wt% N) were studied in tension under varying strain rates (1×10^{-2}–$2 \times 10^{-4}\,s^{-1}$) and the test temperatures (R.T.–1023 K). The temperature range for DSA was moved to higher temperature for increasing nitrogen contents. The critical strain, ε_c for the onset of serration increased with nitrogen content at 773 K and then became almost constant at 873 K. Type A and B serrations were observed at 873 K with the value of the strain required to effect the transition from type A to type B serration increasing for nitrogen contents upto 0.1 wt% and then becoming saturated. The activation energy for DSA was 23.4–26.2 kcal mol^{-1} (97.8–109.5 kJ mol^{-1}) at the onset and 65.0–76.6 kcal mol^{-1} (271–320.2 kJ mol^{-1}) at the end of serration. The lower activation energy was related to vacancy diffusion and the higher activation energy was attributed to the diffusion of chromium to dislocations. The activation energy for DSA was slightly increased with nitrogen addition. DSA was retarded by an increase in the nitrogen content since nitrogen reduced the chromium diffusion to dislocations due to a strong interaction between the nitrogen and chromium. © *1998 Chapman & Hall*

1. Introduction

Austenitic stainless steel (type 316) is a prospective structural material for use in liquid metal cooled nuclear reactors due to its resistance to neutron irradiation and corrosion, allied to good mechanical properties such as high temperature strength, ductility, and toughness. The precipitation of carbides in type 316 stainless steel results in a reduction in the corrosion resistance and creep rupture ductility. Nitrogen alloyed type 316L stainless steel has recently been studied for use as a structural material in reactors because since nitrogen is the most effective solid solution hardening element it retards the precipitation of carbides, and is therefore beneficial for the corrosion and creep resistance properties. It has been reported that the yield strength and tensile strength increase with nitrogen addition without reducing elongation [1, 2].

The operating temperature of a liquid metal cooled nuclear reactor is ~873 K at which temperature dynamic strain ageing occurs in type 316 stainless steel. Fracture resistance is decreased by dynamic strain ageing because the strength is increased and in addition the elongation is also decreased. Thus, dynamic strain ageing needs to be understood for the safe operation of nuclear power plants operating at high temperatures. According to Cottrell [3] and McCormick [4], the factors that affect dynamic strain ageing are temperature, strain rate, dislocation density, vacancy concentration, and concentration and diffusivity of solute atoms. The dynamic strain ageing of austenitic stainless steel is based on the interaction between solute atoms and dislocations at temperatures where the solute mobility is sufficient to lock mobile dislocations. It is known that the solutes responsible for dynamic strain ageing in austenitic stainless steel are interstitial atoms or vacancies at low temperatures and chromium ions at high temperatures [5].

The effect of interstitial solute concentration on dynamic strain ageing has been studied [5, 6]. Carbon and nitrogen, that are the most common interstitial solutes, have a similar size and diffusivity and are therefore treated in random and have not yet been treated as separate species that influence dynamic strain ageing in austenitic stainless steel. However the interaction strength between chromium and nitrogen is stronger than that between chromium and carbon, and short range order is formed if nitrogen is added to the austenitic stainless steel. Therefore, the effect of nitrogen on the dynamic strain ageing behaviour in austenitic stainless steel may be different from that of carbon at high temperatures. However this point has not been systematically studied. The objective of this study is to investigate the effect of nitrogen concentration on the dynamic strain ageing behaviour of type 316L stainless steel.

2. Experimental procedures

Four 120 mm thick laboratory ingots, weighing 30 kg each, containing different nitrogen contents were prepared by vacuum induction melting (VIM). The chemical compositions of these ingots are listed in Table I. The ingots were milled to a thickness of 100 mm and then hot rolled to a 15 mm thickness. The hot rolled materials were then annealed at 1373 K for 1 h and water quenched. The tensile test specimens were taken in the rolling direction and machined to a cylindrical shape with a 25 mm gauge length and a 4 mm diameter.

The tensile tests were performed in air using an Instron model 4505 tester in the displacement control operation mode. All the specimens were held at the test temperature for 1 h before the tests were started. The temperature was maintained to within ± 2 K during the period of the test. Of the four different specimens, the N01 and N10 specimens were tested at strain rates of $1\times10^{-2}\,s^{-1}$, 2×10^{-3} s, and $2\times10^{-4}\,s^{-1}$ and the other two specimens were only tested at $2\times10^{-3}\,s^{-1}$.

3. Results and discussion

3.1. Tensile properties

The variations in the yield stress, ultimate tensile stress (UTS), and elongation are plotted as a function of the test temperature in Fig. 1. The yield stress was observed to decrease gradually with increasing temperature whilst the UTS showed three regions with temperature in which (1) the UTS decreased gradually with increasing temperature (below 573 K); (2) a plateau was seen in the temperature range of 573–773 K, during which serrations occurred; and (3) the UTS decreased markedly above 773 K, during which recovery occurred by the rearrangement and annihilation of dislocations due to the cross slip and climb of dislocations. The extent of the elongation decreased with increasing temperature, with a minimum at about 673 K, and increasing values with increasing temperature after this point. The minimum elongation seemed to be determined by a dynamic balance between dynamic strain ageing and recovery. When nitrogen was added the yield stress and UTS increased but no loss of elongation occurred.

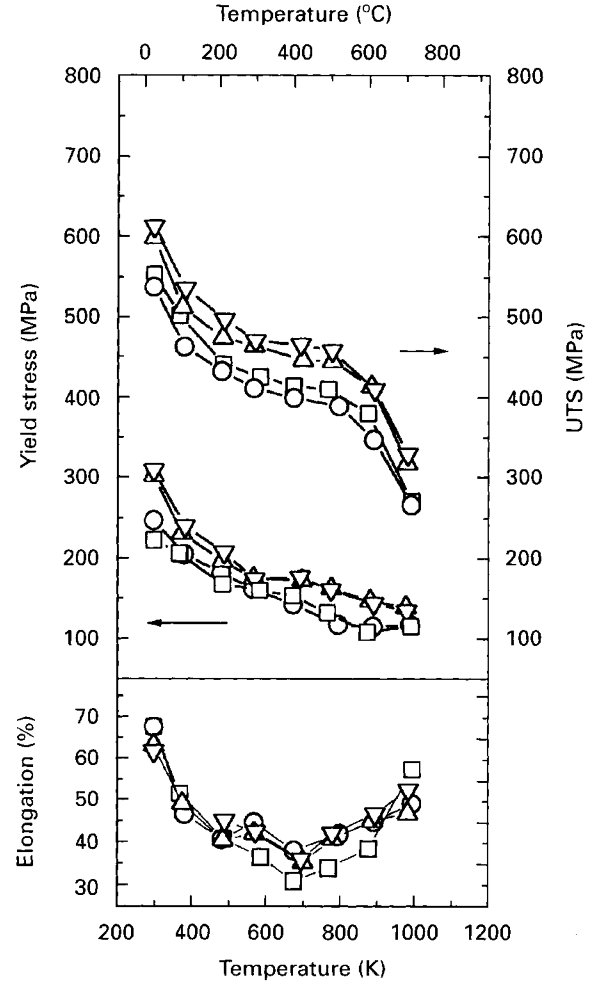

Figure 1 Variation of tensile properties with temperature for a strain rate of $2\times10^{-3}\,s^{-1}$ of samples: (□) N01, (○) N04, (△) N10 and (▽) N15.

Typical stress-elongation curves with temperature for N01 were shown in Fig. 2. Serrations occurred after critical strain in a certain temperature range. Similar curves for the specimens containing different nitrogen content were obtained with temperature but the temperature range and critical strain for serration were different.

3.2. Temperature range for dynamic strain ageing

Several models [3, 4, 7] have been proposed to explain serration (dynamic strain ageing) phenomena observed in flow curves. Cottrell [3] has proposed a solute-dragging model whereby an instability in the flow stress develops when the dislocation velocity is increased beyond the drift velocity of the solute atoms in

TABLE I Chemical compositions of the four experimental melts

Specimen ID	C (wt %)	Si (wt %)	Mn (wt %)	Ni (wt %)	Cr (wt %)	Mo (wt %)	N (wt %)	Fe (wt %)
N01	0.020	0.58	1.06	12.08	18.16	2.19	0.011	Balance
N04	0.018	0.67	0.95	12.21	17.78	2.36	0.042	Balance
N10	0.019	0.70	0.97	12.46	17.23	2.38	0.103	Balance
N15	0.020	0.67	0.96	12.19	17.88	2.41	0.151	Balance

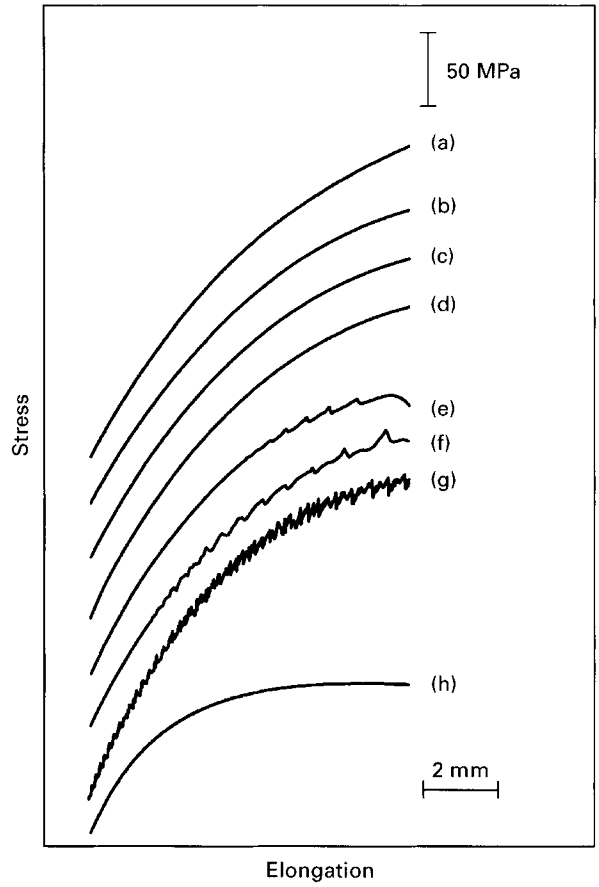

Figure 2 Typical flow curves of the N01 sample tested at a strain rate of $2 \times 10^{-3}\,\text{s}^{-1}$ and temperatures of (a) R.T., (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K, (g) 883 K and (h) 973 K.

the stress field of the dislocations. Cottrell postulated that this mechanism can operate even at temperatures that are too low for bulk solute diffusion, provided that the alloy acquires an excess of vacancies as the result of previous plastic deformation. Applying this model to strain ageing, serration due to solute locking will initiate when:

$$\dot{\varepsilon} = \frac{4b\rho C_v D_0 \exp(-Q_m/kT)}{l} \qquad (1)$$

where $\dot{\varepsilon}$ is the strain rate, C_v is the vacancy concentration, D_0 is the diffusion frequency factor, l is the effective radius of the atmosphere, b is a Burgers vector, ρ is the dislocation density, Q_m is the effective activation energy for solute migration, T is the temperature (K), and k is the Boltzmann constant.

This model has been applied to substitutional alloys but it cannot be applied to interstitial containing alloys because it is based on the diffusion of vacancies. The temperature and strain rate dependence of dynamic strain ageing can be explained by this model but any effect due to the solute atom concentration could not be explained. McCormick [4] has developed an arrest model based on the jerky nature of the thermally activated motion of dislocations. During deformation a mobile dislocation spends most of its time trying to pass obstacles. Once the obstacle is passed, the dislocation segment jumps at a high velocity to the next obstacle. The interaction between mobile dislocations and diffusing solute atoms mainly occurs during the time that a dislocation is waiting in front of an obstacle. If the diffusion coefficient is high enough to saturate the dislocation with an impurity cloud during the waiting time, serration will start. McCormick proposed a relation between the strain rate and temperature for dynamic strain ageing of:

$$\dot{\varepsilon} = \left(\frac{\alpha C_0}{C_l}\right)^{3/2} \frac{3L\rho C_v U_m D_0 \exp(-Q_m/kT)}{kTb} \qquad (2)$$

where C_l is the solute concentration at the dislocation line which is required to lock it, C_0 is the solute concentration in the alloy, $\alpha \approx 3$, and U_m is the solute-dislocation binding energy.

As is shown in Fig. 3, the test results showed that the temperature range in which dynamic strain ageing occurred was shifted to higher temperatures when the strain rate increased, which agrees with both of the above models. However according to the model of McCormick, the temperature for the onset of serrations must decrease with increasing solute concentration in the alloy assuming that the solute concentration required to lock the dislocations is constant. The nitrogen addition, however, increased the temperature range in which dynamic strain ageing occurred. In other words the dynamic strain ageing was not enhanced but was in fact retarded with increasing nitrogen concentration in type 316L stainless steel, which contradicts the model of McCormick.

3.3. Critical strain for dynamic strain ageing

The dislocation density, ρ, and vacancy concentration, C_v, are dependent on the strain and are generally represented by $C_v = K\varepsilon^m$, $\rho = N\varepsilon^\beta$ respectively. Substituting these equations into Equation 2 gives the

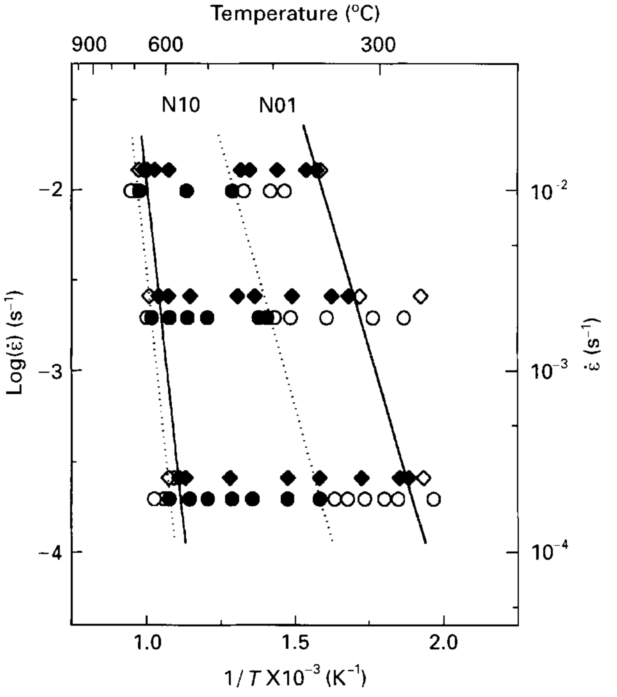

Figure 3 Test conditions where serrations occurred during tensile tests of (◇) N01 and (○) N10. Open symbols: no serration, solid symbols: serration.

critical strain for serration as:

$$\varepsilon_c^{m+\beta} = \left(\frac{C_1}{\alpha C_0}\right)^{3/2} \frac{\dot{\varepsilon} kTb \exp(Q_m/kT)}{3LNKU_m D_0} \qquad (3)$$

where m is a vacancy related constant, β is a constant related to the dislocation density, and K and N are empirical constants.

Nakada and Keh [6] have studied the effect of carbon concentration on the critical strain for a Ni–C alloy. Their results indicate that the critical strain decreased with an increase in the carbon concentration at a constant temperature and strain rate. Almeida and Emygido [5] have reported that the critical strain in 303 stainless steel decreased with an increase in the temperature and a decrease in the strain rate. These results agreed with the proposed model.

In this study, as is shown in Fig. 4, the critical strain, ε_c, for serration decreased with an increase in the temperature and a decrease in the strain rate, which is consistent with the proposed model. However, the critical strain increased linearly with nitrogen content at 773 K and was almost constant at 873 K, which contradicts the proposed model and the results of Nakada and Keh [5]. From these results, the effect of nitrogen on dynamic strain ageing in austenitic stainless steel is different from that of carbon, although both nitrogen and carbon are present as interstitial atoms.

3.4. Serration type

Three main distinct forms are observed to exist for f.c.c. substitutional alloys namely the A, B, and C types of the Brindley and Worthington classification [8]. Type A serrations develop each time a deformation front is emitted from one end of the specimen gauge, and are therefore separated by a longer time interval. Type B serrations occur concurrently with the successive development of highly localized narrow deformation bands when the deformation spreads discontinuously across the gauge length. They follow each other, separated only by short time intervals. Type B serrations occur at a higher temperature than do type A serrations. Type C serrations are yield drops that occur below the general level of the flow curve and are therefore considered to be due to dislocation unlocking. Type C serrations occur at higher temperatures and lower strain rates than in the case of type A and B serrations.

In this study, only type A serration occurred below 873 K. At 873 K, type A serration was observed to occur at small strains followed by type B serration at higher strains. The strain required to promote the transition between serration types was affected by the nitrogen content as is shown in Fig. 5. The transition strain was observed to increase upto nitrogen contents of 0.1 wt % at which point it became saturated. At 973 K the serration was not observed at nitrogen contents of 0.04 wt % with type A serration being observed at nitrogen contents of 0.1 wt % and both A and B type serrations occurred at nitrogen contents of 0.15 wt %. These results are in agreement with the previous observation that nitrogen increased the temperature for the onset of dynamic strain ageing.

3.5. Activation energy

The activation energy for dynamic strain ageing was determined from Equation 2 from a plot between

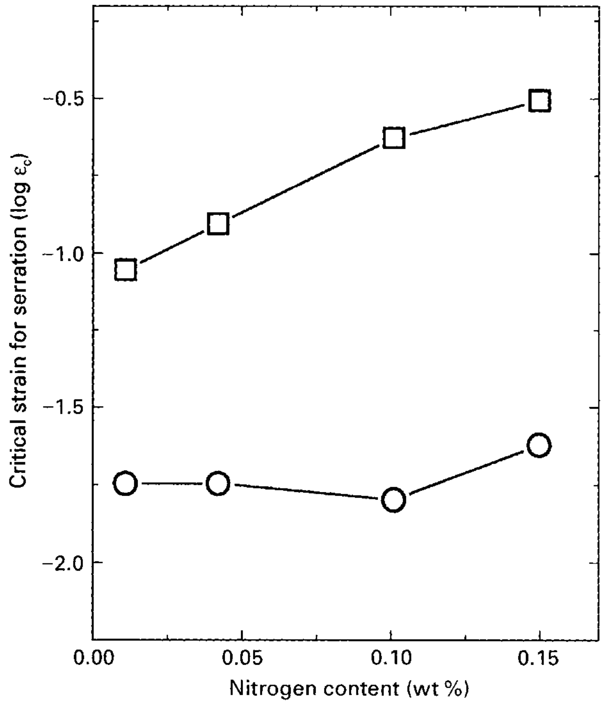

Figure 4 Variation of the critical strain, ε_c, for serration as a function of nitrogen content tested at a strain rate of 2×10^{-3} s at temperatures of: (□) 773 K and (○) 873 K.

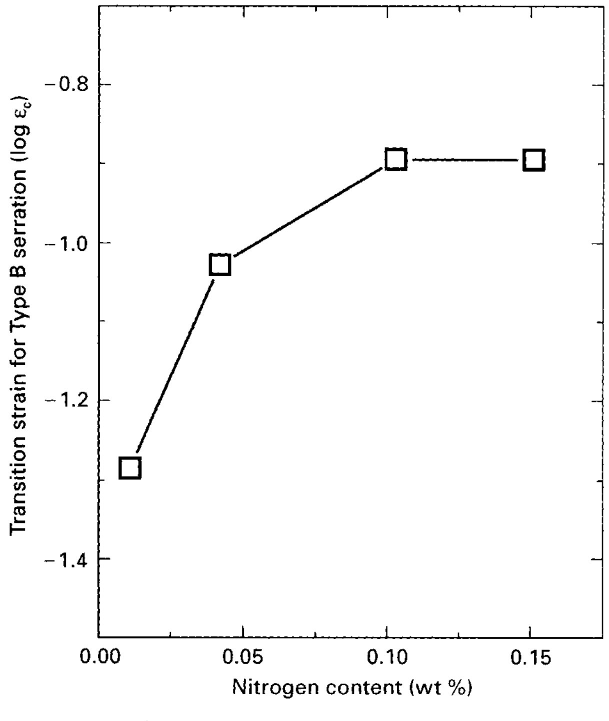

Figure 5 Variation of the strain for transition from type A to type B serration as a function of nitrogen content tested at a temperature of 873 K and a strain rate of 2×10^{-3} s^{-1}.

TABLE II Activation energies for dynamic strain ageing

Serration	Activation energy kcal mol^{-1} (kJ mol^{-1})	
	N01	N10
Onset	23.4 (97.8)	26.2 (109.5)
End	65.0 (271.7)	76.6 (320.2)

strain rate and temperature and the derived values are listed in Table II for the N01 and N10, samples.

Several reports exist in the literature [9–17] that concern the activation energy for dynamic strain ageing in austenitic stainless steel. The reported activation energies are: 32–34 kcal mol^{-1} (134–142 kJ mol^{-1}) for carbon, 20–22 kcal mol^{-1} (84–92 kJ mol^{-1}) for a vacancy, 67 kcal mol^{-1} (280 kJ mol^{-1}) for chromium, and 33 kcal mol^{-1} (138 kJ mol^{-1}) for carbon-vacancy pair. A comparison of the activation energy values obtained in this work with those previously reported in the literature leads to the suggestion that the onset of serration is associated with vacancies and the end of the serration with chromium species. In addition the activation energy for dynamic strain ageing was observed to increase with nitrogen addition. Thus it can be concluded that nitrogen influences dynamic strain ageing at high temperatures due to a strong interaction between nitrogen and chromium.

When the nitrogen concentration was increased, the temperature range in which dynamic strain ageing occurred shifted to higher temperatures, and the activation energy for dynamic strain ageing and the critical strain for serration both increased. These results cannot be explained using the model of McCormick but can be understood on the basis that nitrogen did not directly interact with the dislocation but instead reduced the diffusivity of chromium due to a strong interaction between nitrogen and chromium. Therefore, nitrogen retarded dynamic strain ageing.

4. Conclusions

In order to investigate the effect of nitrogen concentration (0.01–0.15 wt % N) on the dynamic strain ageing of type 316L stainless steel, tensile tests were performed over a range of test temperatures and strain rates. The results obtained can be summarized as follows:

(1) The temperature range for dynamic strain ageing was shifted to higher temperatures with increasing nitrogen content.

(2) The critical strain for serration increased with increasing nitrogen content upto 773 K. At 873 K, the critical strain was almost constant and we observed a change in the serration type from type A to B as defined by Brindley and Worthington [8]. The transition strain between serration types increased up to nitrogen contents of 0.1 wt % and then saturated.

(3) The activation energy for dynamic strain ageing indicated that vacancies and chromium species were responsible for the low and high temperature serration behaviour respectively. Nitrogen increased the activation energy for dynamic strain ageing.

(4) Dynamic strain ageing was retarded by the nitrogen addition because nitrogen strongly interacted with the chromium to decrease the diffusion of chromium to the dislocations.

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