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Substitutional Dynamic Strain Ageing in an Iron - 1.1 at. % Niobium Alloy

M. R. WINSTONE, REES D. RAWLINGS
Department of Metallurgy, Imperial College of Science and Technology, Prince Consort Road, London, UK

The mechanical properties of an Fe–1.1 at. % Nb alloy have been studied in compression over the temperature range 300 to 1100° K. The substitutional niobium atoms were responsible for dynamic strain ageing which resulted in a small peak in the temperature dependence of the flow stress, negative strain rate sensitivity, and serrated stress strain curves.

The serrations were preceded by a strain rate and temperature dependent critical strain. These dependencies were analysed using theories that have been successfully applied to substitutional strain ageing in fcc structures. The analysis showed that, unlike in fcc structures, the apparent activation energy for the onset of serrated flow increased at the faster strain rates; this was attributed to the vacancies produced by the plastic deformation rapidly annealing out due to the high temperatures involved at the faster strain rates.

1. Introduction

A useful improvement in the strength of metals may be achieved by the addition of certain alloying elements which segregate to the dislocations. This segregation occurs because of a strong dislocation-solute atom interaction called strain ageing [1].

Most studies of strain ageing have concentrated on either interstitial solutes in body-centred cubic (bcc) metals [2–4] or substitutional solutes in face-centred cubic (fcc) metals [5–7]. However, from the small amount of information available it appears that strain ageing due to substitutional atoms may also be important in bcc metals. In particular, the high temperature flow stress and the creep resistance of many steels are increased by the addition of substitutional solutes such as molybdenum, titanium, etc. [8, 9].

The purpose of the present work was to attempt a detailed study of substitutional strain ageing in bcc iron. A number of factors were involved in the choice of the alloy system to be investigated. Of paramount importance was that there should be a strong interaction between the alloying atoms and dislocations, but in addition there were constitutional considerations e.g. a convenient way of studying the concentration dependence of strain ageing was to choose a system in which the amount of solute in solution could be reduced by precipitation. Furthermore, the bcc/fcc phase transformation in iron alloys can result in various sub-structures which could affect any strain ageing process; in order to avoid any possible complications due to sub-structure a system in which the fcc transformation could be easily suppressed was required.

These conditions are obtained in the iron-niobium system. The transformation to the fcc structure is easily suppressed in alloys containing more than 1 at. % niobium by quenching from the solution treatment temperature, and the niobium in solution varied by the precipitation of the Laves phase, Fe_2Nb, in subsequent heat treatment [10]. A detailed study of the kinetics of Fe_2Nb precipitation in an iron–1.1 at. % niobium alloy [11] has shown that precipitate nucleation occurs preferentially at grain boundaries and dislocations with a time exponent of $\frac{2}{3}$. This value is the same as that proposed by Cottrell and Bilby [12] for the segregation of solute atoms to dislocations. This, together with the large size difference between niobium and iron atoms, suggests that there would be a strong niobium atom-dislocation interaction in iron-niobium alloys.

Strain ageing manifests itself in two distinct ways, namely static and dynamic strain ageing. This paper is only concerned with the latter. Dynamic strain ageing is often associated with the phenomenon of serrated, or jerky, flow. Serrated flow in substitutional systems has been attributed to the interaction of mobile dislocations with moving solute atoms which have an enhanced diffusivity due to the production of a non-equilibrium vacancy concentration during plastic deformation.

This concept has been developed for substitutional strain ageing in fcc metals [6, 13, 14] to relate the strain rate $\dot{\epsilon}$, temperature T, and the critical strain to the onset of serrated flow ϵ_c, according to the equation:

$$\dot{\epsilon} = \text{constant } \epsilon_c^{(m+\beta)} \exp\,(Q/kT) \qquad (1)$$

where k is Boltzmann's constant, Q is the activation energy for the exchange of a vacancy and a solute atom, and $(m + \beta)$ is a constant. The constants m and β are defined by the following relationships:

$$C_V = B\epsilon^m \qquad (2)$$

and

$$\rho = N\epsilon^\beta \qquad (3)$$

where C_V is the vacancy concentration produced by the deformation, ρ is the mobile dislocation density, ϵ is the strain, and B and N are constants.

2. Experimental Procedure

A 15 kg ingot of an iron–1.1 at. % niobium alloy was prepared from electrolytic iron and high-purity sponge niobium by vacuum melting and casting. The analysis figures (ppm by wt) for the various impurities were C-60, N-60, O-124, P-50, S-90, Si-50. The ingot was fabricated by hot and cold working into sheet approximately 6 mm thick. Sections of the sheet were sealed in evacuated silica tubes and solution treated for 2 h at 1653 ± 5°K. The tubes were quenched into iced water and smashed to ensure a rapid quench. Ageing treatments were carried out at 793 and 903°K in nichrome-wound tube furnaces with the specimens sealed in capsules and the temperature controlled to ± 2°K.

The carbon and nitrogen interstitial content of some of the material was reduced by annealing solution-treated specimens in a stream of wet hydrogen at 1133°K for 68 h. These specimens were resolution treated before testing.

Compression specimens with nominal dimensions of 6.3 × 2.5 × 2.5 mm were cut from the heat-treated material and tested in compression jigs [15] mounted on a 5-ton Instron Universal Testing machine. Strain rates between 2.2×10^{-5} and 2.2×10^{-4} sec^{-1} were used in the temperature range 300 to 1100°K. Strain rate cycling tests, i.e. increasing the strain rate by a factor of ten and then decreasing it to the original value, were performed in order to evaluate the strain rate sensitivity which is given by [16]:

$$\lambda = \frac{\Delta\sigma}{\Delta \ln \dot{\epsilon}} \qquad (4)$$

where $\Delta\sigma$ is the increase in flow stress associated with a strain rate increment.

3. Results

The effect of the temperature on the 0.2% proof stress (0.2% P.S.) at a strain rate of 1.1×10^{-4} sec^{-1} is shown in fig. 1. The three curves presented are for the solution treated, slightly aged (1 h at 903°K), and aged-to-peak hardness (10 h at 903°K) conditions. There was a peak in the temperature dependence of the 0.2% P.S. for the solid solution in the temperature range 900 to 1100°K. There were also indications of a smaller peak at lower temperatures (725 to 875°K), although in this case the peak height was only marginally greater than the scatter of the experimental points. Ageing at 903°K removed niobium atoms from solution and as this proceeded so the peaks changed, e.g. for the slightly aged material the low temperature peak was some 70°K higher than the corresponding peak in the solution treated condition, and no peaks were observed after ageing to the peak hardness condition.

Apart from the low temperature peak being slightly more prominent, the temperature dependence of the 2% P.S. was similar to that of the 0.2% P.S. Again there was no evidence of peaks in the curve for the material aged-to-peak hardness.

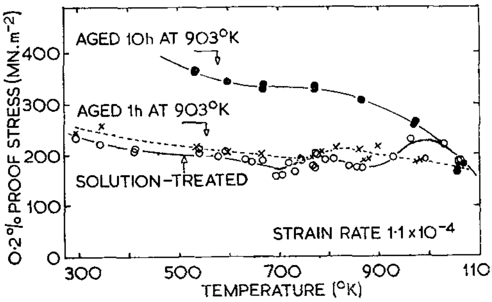

Figure 1 **Effect of temperature on the 0.2% proof stress of the Fe–1.1 Nb alloy.**

TABLE I Effect of strain rate on the temperature range of dynamic strain ageing

Strain rate (sec^{-1})	Heat treatment	Temperature range of the peak (°K)	Peak temperature (°K)	Serrated flow	
				Temperature range	T_c (°K)
2.2×10^{-5}	S.T.	550–700	595	555–695	630
4.4×10^{-5}	S.T.	630–780	700	620–765	695
1.1×10^{-4}	S.T.	725–875	790	740–885	790
2.2×10^{-4}	S.T.	740–840	800	760–840	825
1.1×10^{-4}	S.T. and aged 1 h at 903°K	765–910	860	Insufficient data to define these temperatures accurately	

S.T. = Solution treated.

The 0.2% P.S. and the 2% P.S. versus temperature plots for the other strain rates show the same features as the curves already described except that the faster the strain rate, the higher the temperature of the low temperature peak (table I).

With a basic strain rate of 1.1×10^{-4} sec^{-1}, strain rate cycling generally resulted in a positive value of the strain rate sensitivity, λ, (fig. 2a). However, in the temperature range 725 to 875°K the solution-treated alloy showed negative strain rate sensitivity, i.e. an increase in the strain rate produced a decrease in the flow stress (fig. 2b). Over the temperature range of the investigation λ varied from $+ 16$ MN/m^2 to $- 3$ MN/m^2.

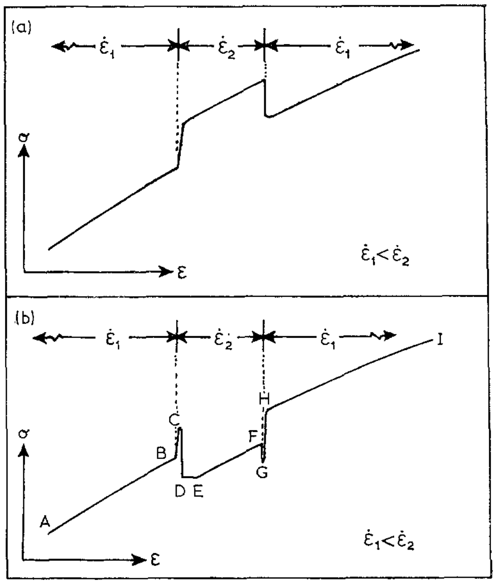

Figure 2 (a) Positive strain rate sensitivity. (b) Negative strain rate sensitivity.

The negative strain rate sensitivity occurred over the same temperature range as the low temperature peak in the flow stress versus temperature curves. The negative strain rate sensitivity was less marked in the slightly aged material and not found in the aged-to-peak hardness condition at any test temperature.

The stress-strain curves for the solution treated and slightly aged conditions of the alloy were serrated over a limited temperature range (a section of a typical serrated stress-strain curve is shown in fig. 3). The serrations became larger and more frequent as the strain increased, but the test temperature had no significant effect on the form of the serrations. Table I shows that the temperature range over which the serrations occurred corresponded to the temperature range of the lower peak in the flow stress-temperature curves.

The serrations started after a critical strain, ϵ_c, but it was very difficult to obtain an accurate value of this strain directly from the stress-strain curves, due to the gradual onset of the serrations.

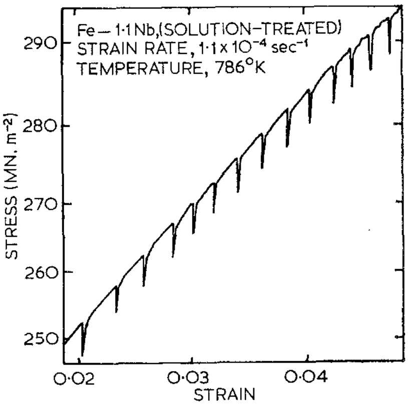

Figure 3 A section of a typical serrated stress-strain curve.

A more precise determination of the critical strain was obtained by following the procedure used by Charnock [17] of plotting the logarithm (true stress) against the logarithm (true strain). The slope of these graphs is the work hardening exponent which increases sharply at the start of serrated flow. Plots of log σ versus log ϵ always gave ϵ_c values of similar magnitude to those measured directly from the stress-strain curves but were considerably more reproducible.

The critical strain was temperature and strain rate dependent; for a given strain rate, ϵ_c decreased to a minimum at a critical temperature, T_c, and thereafter increased with temperature (fig. 4). The results are restricted to strains of less than 6 % to ensure homogeneous deformation.

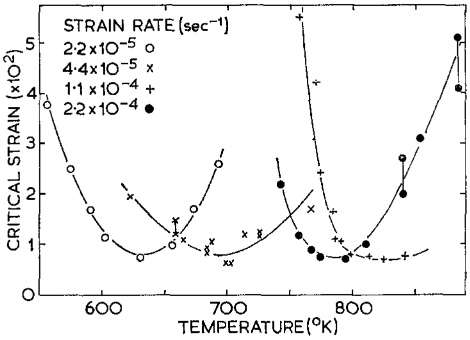

Figure 4 Effect of temperature and strain rate on the critical strain, ϵ_c.

The critical strain was not affected by:

(i) Annealing the solution treated specimens in a stream of wet hydrogen at 1133°K for 68 h and resolution treating.

(ii) Annealing the solution treated specimens at 793°K for 100 h.

4. Discussion of the Results

4.1. Evidence for Substitutional Dynamic Strain Ageing

The high temperature peak observed in the solution treated material at about 970°K, is attributed to the precipitation of Fe_2Nb during the time (approximately 45 min) required for the specimen to reach the test temperature in the compression apparatus. Precipitation occurs rapidly at these temperatures [10, 11] so that the specimens were well-aged before the commencement of the compression tests. The fact that the high temperature peak was small for the slightly aged and absent for the aged-to-peak hardness material is consistent with this explanation. The major cause of the fall-off in strength above 970°K is considered to be overageing.

In contrast to the high temperature peak, the small peak in the flow stress of the solution-treated material at 790°K was not caused by a precipitation process since annealing for 100 h at 793°K had no effect on the mechanical behaviour. However, the peak was associated with serrated flow and negative strain rate sensitivity which are characteristic of a dynamic strain ageing process.

Negative strain rate sensitivity is commonly observed when dynamic strain ageing is predominant [18, 19]. The initial rise in stress on increasing the strain rate and the initial fall in stress on decreasing the strain rate (see fig. 2b), have not been reported previously, but are consistent with the occurrence of dynamic strain ageing. When deformation is controlled by a strain ageing process the dislocations are influenced by their solute atmospheres, hence a high stress is required for plastic flow (region A-B in fig. 2b). As many of the dislocations are retarded by their atmospheres, when the strain rate is suddenly increased, the stress increases in order to move the available dislocations fast enough to accommodate the applied strain rate. At a critical stress (C) either the pinned dislocations break free, or there is the creation and multiplication of dislocations, and the deformation continues by the motion of free dislocations at a lower stress (D-E). Normal work-hardening occurs between E and F. Initially, on reducing the strain rate to its original value, the free dislocation density remains unchanged and, as a consequence, the imposed strain rate can be accommodated with a lower dislocation velocity, i.e. lower stress (F-G). However, fresh atmospheres, which impede further dislocation motion, are rapidly formed at these low dislocation velocities and result in a rise in stress (G-H). After the strain rate cycling, the stress level is such that ABHI is a smooth curve. This indicates that in this case the "yield point" at C is most likely to be caused by an unpinning mechanism since the increased dislocation density, and hence work-hardening, that would result from a creation and multiplication mechanism would have raised the flow stress at H.

The dynamic strain ageing was not due to an interstitial species as the temperatures involved were too high and reducing the interstitial content by wet hydrogen treatment had no effect.

Moreover, the serrated flow was preceded by a strain rate and temperature dependent critical strain, which is characteristic of substitutional strain ageing. The height of the flow stress peak and the magnitude of the serrations were dependent upon the amount of niobium in solution, e.g. the peak was reduced and shifted to higher temperatures by slightly ageing the alloy and disappeared completely in the aged-to-peak hardness condition. Thus, it is concluded that the substitutional niobium atoms were responsible for the strain ageing.

4.2. An Analysis of the Serrated Flow Associated with the Low Temperature Peak

At temperatures below T_c, the critical strain measurements agreed qualitatively with the theories of Cottrell [13] and Ham and Jaffrey [14] in that plots of the logarithm of the critical strain against reciprocal temperature were linear (fig. 5). However, unlike all previously reported work on substitutional strain ageing, the plots were not parallel for strain rates greater than 10^{-4} sec^{-1}. Reference to equation 1 indicates that this could be the result of a strain rate dependence of either Q, or $m + \beta$, or both.

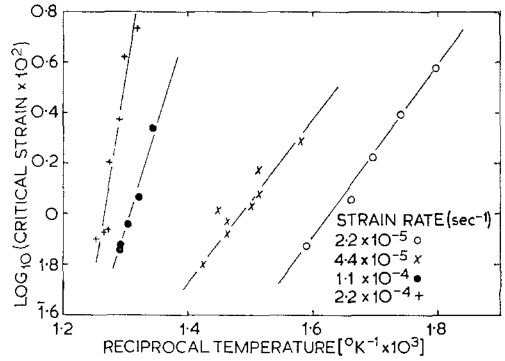

Figure 5 Logarithm of critical strain against reciprocal temperature for solution treated Fe–1.1 Nb.

The constant $(m + \beta)$ of equation (1) is normally evaluated from the strain rate dependence of the critical strain at a given temperature; $(m + \beta)$ values reported for substitutional strain ageing in fcc structures have been temperature and strain rate independent. However, since the curves in fig. 5 are not parallel for strain rates greater than 10^{-4} sec^{-1}, a unique temperature and strain rate independent $(m + \beta)$ value cannot be determined for Fe–Nb. Using the parallel curves obtained at the slower strain rates, $(m + \beta)$ was calculated to be 0.7. This is a very low value when compared with values of greater than 2 quoted for fcc alloys [6, 7]. Indeed, as resistivity measurements on bcc metals give a room temperature m value of 1.6 [20] and electron microscopy a β value in iron over a wide (77 to 673° K) temperature range of approximately 1 [21], a $(m + \beta)$ value of 2.6 might at first be expected.

The small value of $(m + \beta)$ determined in this work is believed to be the result of the high temperatures involved. The excess vacancy concentration created during the deformation of bcc iron is generally considered to be small due to the high energy of formation (about 2 eV), and the low activation energy for migration (about 0.75 eV) which enables the vacancies to move rapidly to sinks and anneal out. It is suggested that during deformation at the elevated temperature involved in the present investigation, the annealing out of the vacancies is so rapid that the vacancy concentration only increases very slowly with strain. Consequently, m should approach zero and the value of $(m + \beta)$ determined from strain ageing data should tend to the value of β. Bearing in mind that the β value of 1 determined by electron microscopy is likely to be an overestimate as it is obtained from measurements of the total dislocation density and not from the mobile dislocation density, the value of $(m + \beta)$ of 0.7 is entirely satisfactory.

The activation energy Q for the onset of serrations may be determined from the slopes of the curves in fig. 5 once a value for $(m + \beta)$ has been established (see equation 1). Although the value of 0.7 was deduced from the low strain rate data it has also been applied to the higher strain rate results, i.e. it is assumed that the variation in slope of the curves in fig. 5 is due to changes in Q not in $(m + \beta)$. This is reasonable as the strain dependence of the dislocation density is not a strong function of strain rate and temperature, and as the excess vacancy concentration term, m, is already assumed to be small, any variation will be small compared with a combined $(m + \beta)$ value of 0.7. The resulting activation energies are plotted as a function of strain rate in fig. 6.

The activation energy at the two slowest strain rates is 0.6 eV (58 kJ/mole) which is consistent with a vacancy-enhanced diffusion

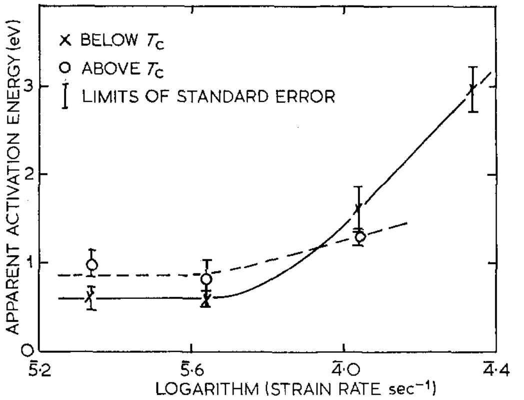

Figure 6 Effect of strain rate on the apparent activation energy for serrated flow.

mechanism. Although the excess vacancy concentration created during the deformation has been assumed to be small (i.e. m small but not zero), it is still considered large enough to swamp the small concentration of thermal vacancies so leading to an activation energy for the onset of serrations equal to the energy of motion of the vacancies.

The increase in the measured activation energy at the faster strain rates is a result of the higher temperatures required for the strain ageing. As the temperature is increased the excess vacancy concentration becomes less until at high enough temperatures m is effectively zero. When m is zero there are no excess vacancies available to enhance the diffusion rate, hence the activation energy for serrated flow should approach the value for the diffusion of niobium in iron. The experimental value at the fastest strain rate (highest temperature) of 3 eV (289 kJ/mole) is in good agreement with the activation energy for the diffusion of substitutional atoms in bcc iron.

The increase in ϵ_c at temperatures greater than T_c (fig. 4) has been observed in a few fcc alloys [22, 23], but theories for this phenomenon are not well established. Charnock [24] has attempted to explain this observation on the basis that dislocations move only in conjunction with a solute atmosphere. Using this concept he developed equations which permit the activation energy for the strain ageing process to be determined. According to the physical basis of the model, the activation energy should be equal to the activation energy for diffusion of the substitutional atoms. However, although the present data was in qualitative agreement with Charnock's equations, the activation energy obtained (fig. 6) was approximately 1 eV (96 kJ/mole). This is only about one third of the activation energy for diffusion of niobium atoms in α-iron and suggests that the qualitative agreement with Charnock's proposals may be fortuitous.

5. Summary

1. It has been established that substitutional strain ageing occurs in bcc iron. In the particular system investigated, iron-niobium, the strain ageing resulted in a small peak in the temperature dependence of the flow stress, negative strain rate sensitivity, and serrated stress-strain curves.
2. The temperature dependence of the critical strain to the onset of serrated flow at a given strain rate showed a minimum at a temperature T_c. Analysis of the data below T_c showed that the activation energy for the onset of serrated flow varied from 0.6 eV at a strain rate of 2.2×10^{-5} sec^{-1} to 3.0 eV at the highest strain rate of 2.2×10^{-4} sec^{-1}. This was attributed to the rapid annealing out at high temperatures of the vacancies produced during the deformation. The analysis of the results at temperatures greater than T_c was not satisfactory.

Acknowledgements

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