Basic creep models for a 25Cr20NiNbN austenitic stainless steels

Rolf Sandström^a, Muhammad Farooq^a, Joanna Zurek^b

^aMaterials Science and Engineering, KTH, Brinellvägen. 23, S-100 44 Stockholm, Sweden

^bForschungszentrum Juelich, Energy and Climate Research, IEK-2, D-52425 Juelich, Germany

Email: rsand@kth.se

Abstract

Basic models for solid solution and precipitation hardening during creep are presented for the austenitic stainless steels 25Cr20NiNbN (TP310HNbN, HR3C, DMV310N). The solid solution hardening is a result of the formation of Cottrell clouds of solutes around the dislocations. In addition to slowing down the creep, the solutes increase the activation energy for creep. The increase in activation energy corresponds to the maximum binding energy between the solutes and the dislocations. The formation of fine niobium nitrides during service enhances the creep strength. It is found that the nitrides have an exponential size distribution. In the modelling the critical event is the time it takes for a dislocation to climb over a particle. The creep models can accurately describe the observed time and temperature of the creep rupture strength.

Keywords: austenitic stainless, elevated temperature, precipitation, solid solution hardening.

1. Introduction

To describe experimental results from creep testing of metallic alloys empirical equations have traditionally been used. Many times it is possible to estimate the parameters in these equations but they are in general determined by fitting the equations to the observations. This makes it difficult to extrapolate the results to new conditions. To handle this situation, attempts have been made to develop fundamental creep equations without fitting parameters. For future high temperature plants such as ultrasupercritical fossil fired units and fourth generation nuclear reactors where design lives of 30 to 80 years are planned, it is of utmost importance that accurate creep models are available. The traditional approach of performing creep testing for a number of years and then apply modest time extrapolation will not work anymore.

Many austenitic stainless steels are applied at high temperatures where creep resistance is of importance. The creep strength is in general based on solid solution and particle hardening [1]. Some of the basic alloys such as 18Cr-10Ni (TP304), 17Cr-12Ni-2Mo (TP316) and 25Cr-20Ni (TP310) are only utilising a weak solid solution hardening. The most common way to increase the creep strength by particle hardening is to add microalloying elements such as Ti and Nb. To obtain a significant effect their content must be balanced with the amount of nitrogen and carbon in the steel. To raise the strength by solid solution hardening further, potent solid solution hardeners such as W can be added.

Many austenitic steels have been used for a number of years and their characteristics are well known. For example, the stress dependence of the creep rate follows the Norton equation and the creep rupture strength decreases approximately exponentially with increasing temperature. In spite of this, basic models to describe the high temperature properties have been lacking. It is the purpose of this

study to present models for solid solution and particle hardening and apply these to a 25C-20Ni NbN steel (TP310HNbN, H3RC). Steels with 25% chromium and 20% nickel are used in boilers, superheaters and chemical reactors. These steels have an excellent oxidation resistance, but only a modest creep resistance. To improve the creep resistance 0.4% niobium and 0.2% nitrogen are added. This gives both a solid solution and a particle hardening effect.

Precipitation in TP310 has been studied previously by the authors [2]. Formation of σ -phase and $M_{23}C_6$ -carbides during long term ageing was successfully modelled. The effect of coarse precipitates on mechanical properties at room temperature was also investigated [3].

2. Experimental procedure

The austenitic stainless steel 310NbN (TP310HNbN) was used in this investigation. Seamless tube material was solution treated at 1200 °C for 12 min. Its chemical composition is given in Table 1.

Table1. Chemical composition of the austenitic stainless steel 310NbN (wt. %)

Cr	Ni	C	Fe	Si	P	Nb	Mn	S	O	N
24.7	20.6	0.062	51.9	0.38	0.017	0.44	1.2	<0.001	0.016	0.182

6 specimens were investigated in the form of 20x10x2 mm plates. They were aged at 650 and 750 °C for 1000, 3000 and 10000 h in Ar with 50% H₂O air humidity. Size distributions of particles were determined with SEM and TEM. The investigations in TEM were carried out with carbon replicas. The composition of the precipitates was determined with EDS analysis.

3. Solid solution hardening

Solid solution hardening (SSH) is of great significance for the creep strength in high alloyed stainless steels. N, Mo, and W are examples of elements that are used for SSH. Basic modelling of SSH for stainless steels does not seem to have been attempted. However, SSH under creep conditions have been modelled for other types of alloys. The role of Mo and W has been analysed for 9 - 12% Cr steels [4]. Phosphorus in solid solution dramatically increases the creep strength of pure copper. This effect has successfully been explained in [5]. The basic assumption in these two papers is that atmospheres of minor elements are formed around the dislocations and follow their motion. This gives rise to a solid drag effect. From elastic stress analysis the magnitude of the interaction energy W as a function of distance and orientation can be derived. The interaction energy between a solute and an edge dislocation is given by

$$W = \frac{b}{3\pi} \frac{(1 + \nu_P)}{(1 - \nu_P)} G \nu_a \varepsilon_b \frac{y}{x^2 + y^2} \quad (1)$$

where ν_P is Poisson's number, ν_a the atomic volume, G the shear modulus and ε_b the lattice misfit between solute and matrix, and x and y are the coordinates in the glide and climb direction.

The concentration c_M of an alloying element M in solid solution that interacts with a dislocation can be expressed as [6]

$$c_M = \frac{\nu c_{M0}}{D_M} \exp\left(-\frac{W(y)}{kT} - \frac{\nu y}{D_M}\right) \int_{-\infty}^y \exp\left(\frac{W(y')}{kT} + \frac{\nu y'}{D_M}\right) dy' \quad (2)$$

where v is the dislocation speed, c_M the (average) concentration of element M (in solid solution), D_M the diffusion coefficient of element M, k Boltzmann's constant and T the absolute temperature. At low concentrations of element M, the local concentration can be quite high. The accumulation factor around the dislocations can be 100 or more. The solutes create a drag stress σ_{drag} slowing down the dislocations

$$\sigma_{\text{drag}} = \int c_M \left(-\frac{\partial W}{\partial y} \right) dy \quad (3)$$

The drag stress can be computed in different ways. For details, see [5].

The solutes are preferably located at the dislocation cores. For the dislocation to move it must break away from these solutes. An energy barrier must be overcome. The additional stress σ_{break} that must be applied can be found from the energy that is needed to move a dislocation one Burgers vector. Peach-Koehler's formula gives that the force on the dislocation segment of length $2L_M$ is $F = \sigma_{\text{break}} 2L_M b$. The consumed energy is $F b/2$. The energy balance gives

$$\sigma_{\text{break}} = \frac{W(b)}{b^3} \int c_M dy \quad (4)$$

where c_M can be found from eq. (2). The average distance L_M between the solutes that pin the dislocation is the Burgers vector divided by the local concentrations of solutes.

The total solid solution hardening is obtained by adding the contributions from the drag and the break stress in eqs. (3) and (4).

Experimental values for the lattice misfit parameter ε_b are typically not available for stainless steels. In the present study the change of lattice parameter with concentration has been determined with the help of ab initio calculations.

Fig. 1. Solid solution hardening of Nb due to solute drag and break stress (barrier), eqs. (3) and (4)

The contribution of Nb to solid solution hardening is illustrated in Fig. 1. The drag stress is quite small, which makes it even difficult to distinguish it from the total contribution. The break away stress is less than 2 MPa and almost negligible. However, the presence of Nb increases the activation energy for creep deformation due to the interaction of solutes to the dislocation cores. This increases the activation energy by 83 kJ/mol, giving a significant reduction of the creep rate. This will be discussed below.

4. Precipitation hardening

Precipitation hardening (PH) is in general the most efficient way to raise the creep strength of high temperature alloys. Estimates of the increase in strength due to PH are often based on looping of dislocations around the particles according to the Orowan mechanism. A number of expressions exist for the Orowan contribution. These are essentially temperature independent and only take the temperature dependence of the shear modulus into account. This should be contrasted to the creep strength that typically decreases exponentially with increasing temperature. Thus, an estimate of PH based on the Orowan mechanism can at best give a rough value in the low temperature range of creep.

In the past it was believed that the climb across particles was controlled by an energy barrier. However, the computed size of the energy barrier decreased with time until it became so small that it is technical insignificant [7]. Instead, it is now assumed that it is the time it takes for a dislocation to climb across a particle that is the limiting factor.

In aged specimens of 310NbN, fine niobium carbonitrides (Nb(C,N)) are present. Fig. 2 shows Nb(C,N) partially with plate like morphology. Particle sizes from about 20 to 250 nm are observed.

Fig. 2. TEM image of specimen aged for 3000 h at 750 °C (carbon replica)

Fig. 3. TEM image of specimen aged for 1000h at 750 °C (carbon replica)

A TEM micrograph of the particles at higher magnification is illustrated in Fig. 3. Unfortunately the TEM images at high magnification had poor contrast. The four analysed particles are Nb(C,N), and most likely most of the other particles as well.

In the derivation of precipitation hardening, the particle size distribution plays an important role. This has previously been demonstrated for 9 to 12% Cr steels [8]. For the 310NbN alloy in the present study, exponential size distributions have been obtained, Fig. 4.

Fig. 4. Size distributions for Nb(C,N) particles after ageing at 650 and 750 °C

The cumulative size distribution, i.e. the area fraction of particles $f(r)$ that is larger than a given particle size r can be expressed as

$$f(r) = F \exp(-\beta(r - r_0)) \quad (5)$$

F is the total area fraction of a given particle type, r_0 the smallest accurately recorded particle size, and β a constant.

There is time for a dislocation to climb across a particle if it is small enough. A limiting radius r_{lim} is considered. This is the maximum particle size that can be climbed. The limiting situation is when the times for dislocations to glide between particles and climb across particles are the same. This gives the following condition [9]

$$\eta_{\text{lim}} = 2LM_{\text{cl}}b^2\sigma_{\text{eff}}\frac{\rho}{\dot{\epsilon}m} \quad (6)$$

where σ_{eff} is the effective stress, b Burgers vector, and M_{cl} the dislocation climb mobility, L the inter-particle spacing, ρ the dislocation density, and m the Taylor factor. The creep rate $\dot{\epsilon}$ on the right-hand side of eq. (6) is a function of the amount of climb, which controls the value of r_{lim} . As a consequence no simple analytic solution exists. The main assumption when computing the particle hardening (σ_{PH}) at climb conditions is that particles that are larger than r_{lim} must be passed by the Orowan mechanism, and smaller ones can be freely climbed.

Fig. 5. Creep stress versus rupture time at 600, 650, 700, and 750 °C. The strength contributions from particles, dislocations, and solid solution hardening are shown together with the effective stress. The total applied stress is compared to experiments from [10]

Thus, the strength contribution is obtained from the Orowan equation only taking particles larger than the critical size into account.

$$\sigma_{PH} = \frac{2T_L m}{bL_{lim}} \quad (7)$$

T_L is the dislocation line tension, and L_{lim} the inter-particle spacing from particle larger than the limiting size. The effective stress can then be expressed as

$$\sigma_{eff} = \sigma_{appl} - \sigma_{disl} - \sigma_{PH} - \sigma_{sol} \quad (8)$$

where σ_{disl} , σ_{PH} , and σ_{sol} are strengthening contributions from dislocations, particles, and solid solution respectively.

The hardening contributions are illustrated in Fig. 5. The dislocations give the largest contribution to the strength. The model for the dislocation hardening can be found in [11]. The particle hardening from Nb(C,N) gives a small but significant contribution to the strength. The largest part of the effective stress is due to the activation energy for the Nb atoms to break away from the dislocations. The sum of the contributions from particles, dislocations and effective stress gives the total applied stress. The

applied stress is compared to experimental stress rupture data in [10]. A good agreement with the experimental results has been obtained

Applying (8) in a Norton equation yields a creep rate that approximately decreases exponentially with temperature in accordance with observations. This has also been demonstrated previously for a 15Cr15Ni0.1C0.4Ti steel [9] and 9-12% Cr-steels [8].

Conclusions

- Long term aging at 650 and 750 °C of the austenitic stainless steel 25Cr20NiNbN was performed. Fine precipitates of NbN with exponential size distributions were observed. The number and size of the particles increased with aging times from 1000 to 10000 h.
- The solid solution hardening part of the creep strength of 25Cr20NiNbN was computed using a model previously applied to 9 and 12% Cr steels as well as copper. The solute atmospheres around the dislocations are strongly bound. They give rise to a raised creep strength and to an increase in the activation energy for creep.
- According to the model for precipitation hardening, only larger particles contribute to the creep strength since they have to be bypassed by the Orowan mechanism. For smaller there is sufficient time for the dislocations to freely climb across the particles.
- Taking the different hardening mechanisms into account the time and temperature dependence of the creep rupture strength can accurately be predicted without the use of adjustable parameters.

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References

- [1] K. H. Mayer, F. Masuyama: The development of creep resistant steels, in: Creep-resistant steels, ed. F. Abe, T.-K. Kern, R. Viswanathan, Woodhead Publ., Cambridge, 2008, p. 15–71.
- [2] M. Farooq, R. Sandström and M. Lundberg, Precipitation during long time ageing in the austenitic stainless steel 310, High Temp. Mtrls 29, No 1, 2012, pp. 8-16.
- [3] R. Sandström, M. Farooq and B. Ivarsson, Influence of particle formation during long time ageing on mechanical properties in the austenitic stainless steel 310, High Temp. Mtrls. 29, No 1, 2012, pp. 1-7
- [4] H. Magnusson, R. Sandström, Modelling of the influence of laves phase on the creep properties in 9 % Cr steels, ASME Pressure Vessels and Piping Conference - 8th International Conference on Creep and Fatigue at Elevated Temperatures - CREEP8 , pp. 519-526, 2008
- [5] R. Sandström, H. C. M. Andersson, The effect of phosphorus on creep in copper, 2008, Journal of Nuclear Materials 372 (1), pp. 66-75, 2008
- [6] J. P. Hirth, J. Lothe, Theory of dislocations, 2nd ed., Wiley, New-York, NY, USA, 1982
- [7] W. Blum and B. Reppich, Creep Behaviour of Crystalline Solids, Pineridge Press, Swansea, United Kingdom, 1985, pp. 83–135.
- [8] H. Magnusson, R. Sandström, The role of dislocation climb across particles at creep conditions in 9 to 12 pct Cr steels., Metall. Mater. Trans. A, vol. 38, pp. 2428-2434, 2007

- [9] J. Eliasson, Å. Gustafson, R. Sandström, Kinetic modelling of the influence of particles on creep strength, *Key Eng. Mat.*, vol. 171-174, pp. 277-284, 2000
- [10] Landolt-Börnstein, Creep properties of heat resistant steels and superalloys, Group VIII, Vol. 2, Subvolume B, Springer 2004
- [11] H. Magnusson, R. Sandström: Creep strain modelling of 9 to 12 pct Cr steels based on microstructure evolution, *Metall. Mater. Trans. A* 38 (2007) pp. 2033-2039