THE ROLE OF OXIDATION ON THE CREEP BEHAVIOUR OF A COMMERCIAL PURITY NICKEL

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ABSTRACT

The role of oxide scale on the creep behaviour of nickel of commercial purity has been investigated. Creep specimens of the metal were exposed to air at 1050°C for 11 h and creep tested at 700°C. Exposure of the specimens to air led to the formation of oxide scale and manganese oxide in the matrix and along the grain boundary of the near surface region. The presence of oxide scale led to creep strengthening resulting into reduced creep rate whereas manganese oxide particles along the grain boundary caused early cavity nucleation leading to enhanced creep rate. Growth and interlinkage of cavity nuclei in the internally oxidized region led to the formation of grain boundary cracks which became easy path for oxygen diffusion from the air-environment and this also assisted the growth of these cracks. One of these cracks acted as notch resulting into poor creep strain-to-fracture.

KEY WORDS

Nickel, creep, oxidation, environment, crack

INTRODUCTION

When nickel is heated or tested in air at elevated temperatures, oxide scale forms. The scale may either spall off or adhere to the base metal depending upon factors such as the oxide scale thickness and the bond strength at the oxide-material interface. In the case of spallation, the effective load bearing cross-sectional area of the base metal is reduced, as a result of which degradation of the mechanical properties occurs. On the other hand, if the oxide scale is adherent with the base material, its mechanical behaviour may be improved. A clear understanding of the effect of oxide scale on high temperature mechanical behaviour is important since materials subjected to stresses at elevated temperatures in air undergo concurrent oxidation and creep deformation. To understand the role of oxidation on the creep behaviour of materials during creep is somewhat complex since thickness of the oxide scale varies with the creep exposure time. However, this problem can be simplified to some extent using creep specimen with known oxide scale thickness. Limited data are available wherein the role of oxide scale on creep behaviour has been studied. One example is that of 20Cr-25Ni-Nb stainless steel wherein the presence of oxide scale led to creep strengthening [Francis,1970]. Similarly, in the case of aluminium, oxide scale produced by the process of anodizing led to improved creep life [Singh et al,1976].

A commercial grade nickel was selected to study the effect of oxide scale on its creep behaviour. Nickel was particularly chosen for this purpose since considerable body of data is available both on its oxidation and creep behaviour [Bricknell and Woodford, 1981,1982, Douglass, 1959, Shahinian, 1957, Shahinian and Achter, 1959].

EXPERIMENTAL PROCEDURE

The chemical composition of nickel selected for creep study, in wt. per cent, is as follows : 0.022C-0.171Mn-0.042Si-0.06Fe-0.013Cu-balance nickel. The metal was supplied in the hot-rolled condition in the form of 8mm diameter rod. 16 test bars of 70mm length were cut from the rods. Out of these, 12 test bars were machined to specimen dimensions of 3mm gauge diameter and 25mm gauge length. Three test bars were encapsulated in evacuated quartz tubes. Vacuum in the quartz tube was maintained better than 10^{-4} torr. The 12 specimens, the 3 encapsulated test bars and the remaining one test bar were heated in air at 1050°C for 11 h. The encapsulated test bars were then machined to the specimen dimensions (hereafter referred as vacuum-exposed specimen). Creep tests were performed at 700°C ± 1C in air at three stresses, 40, 60 and 90 MPa at constant load. Creep strain of the specimens was measured using two Linear Variable Differential Transducers (LVDTs) attached to the specimen ridge. The tested specimen as well as a small sample from the air-exposed test bar were mid-sectioned, polished and etched. Etching was done using a solution of 7.5 ml HF, 2.5 ml HNO_3 and 200 ml methanol. Polished and etched specimens and the sample were examined by optical and scanning electron microscopy and Electron Probe Micro Analyzer(EPMA).

RESULTS

Initial Microstructures After Oxidation

Figure 1 shows optical micrograph of the sample taken from the 8mm diameter rod exposed to air at 1050°C. Two regions can be seen in the air-exposed metal: (1) oxide scale of about 50 μm thickness at the surface (2) particles in the matrix as well as along the grain boundary upto a depth of about 0.4 mm from the surface. The scale was not completely compact but contained substantial amount of voids. The particles were analyzed and found to be manganese oxide [Pandey, 1996].

Creep Testing Data

Figures 2 (a), (b) and (c) show creep curves at 40, 60 and 90 MPa respectively of specimens exposed to air (curves 1 and 2) and

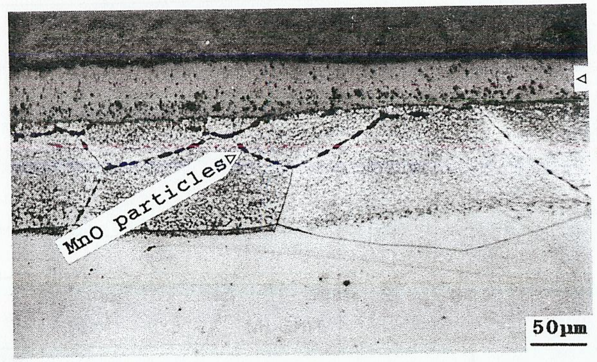

Fig.1 **Micrograph showing oxide scale and particles along the grain boundary and within the grains of the metal after exposure to air at 1050°C for 11h.**

vacuum (curve 3). Curve 2 represents the creep behaviour of the air-exposed specimen after removal of the oxide scale. Creep tests were also performed at the three stresses on the air-exposed specimens after machining the internally oxidized region upto a depth of 0.4 mm. The creep behaviours of these specimens were found about the same as that of the vacuum exposed one and, therefore, are not shown in the Figures. Figure 3 demonstrates that the air-exposed specimen with the oxide scale is stronger leading to creep strengthening at all stresses. However, this effect is more pronounced at lower stresses (Fig.3a). It can also be noticed that after removal of the oxide scale, there is considerable reduction in creep strength and this effect is more notable at 60 MPa. Another important point to be noticed is creep ductility embrittlement in the air-exposed specimen, both in the as-exposed and after removal of the oxide scale (Fig.3b). However, creep ductility of the air-exposed specimen after removal of the oxide scale increased but it was much lower than that of the vacuum exposed specimen.

Microstructures After Creep Testing

Metallography revealed that nearly all the grain boundaries in the near surface region of the air-exposed specimens were associated with cracks (Fig. 4a), whereas such cracks were found absent in the vacuum-exposed specimens. In fact, dynamic recrystallization occurred during creep of both vacuum-exposed specimen and air-exposed specimen machined to remove internally oxidized region (Fig. 4b).

DISCUSSION

Creep testing results showed that oxidation of nickel led to strengthening as the steady state creep rates of the as air-exposed specimens were considerably lower than that of the

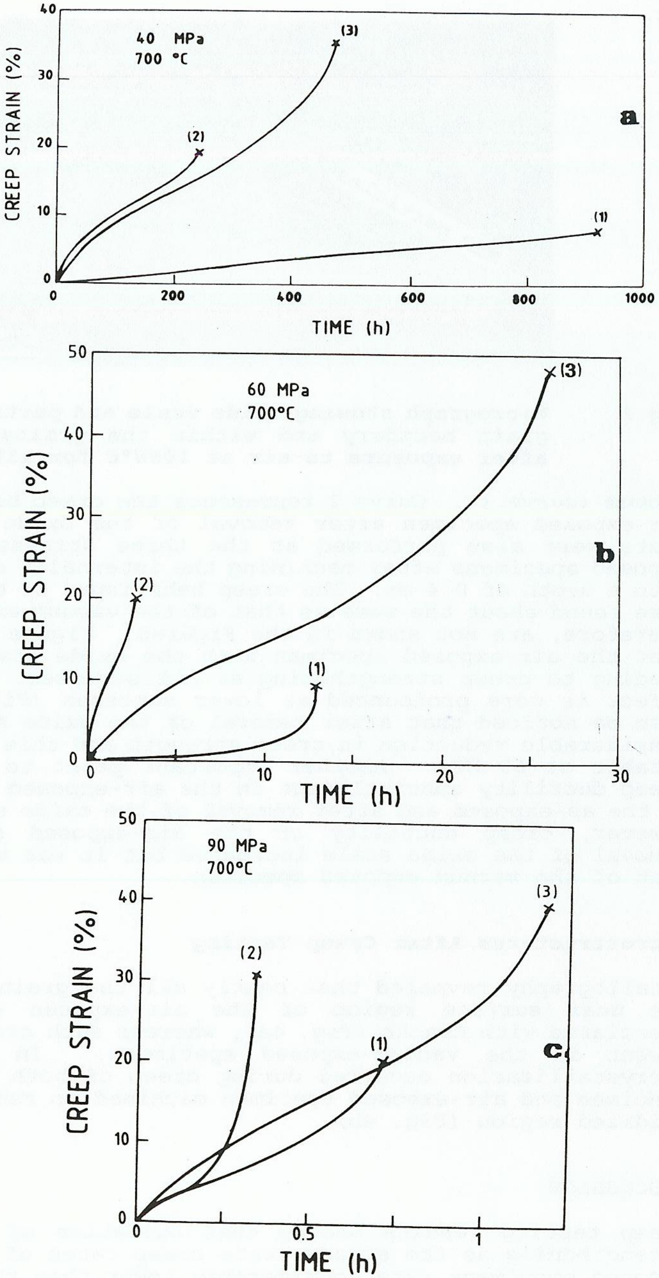

Fig.2 Creep curves at 700°C of testpieces after testing at (a) 40 MPa (b) 60 MPa and (c) 90 MPa (1) pre-exposed to air (2) pre-exposed to air and after removal of the oxide scale and (3) pre-exposed to vacuum.

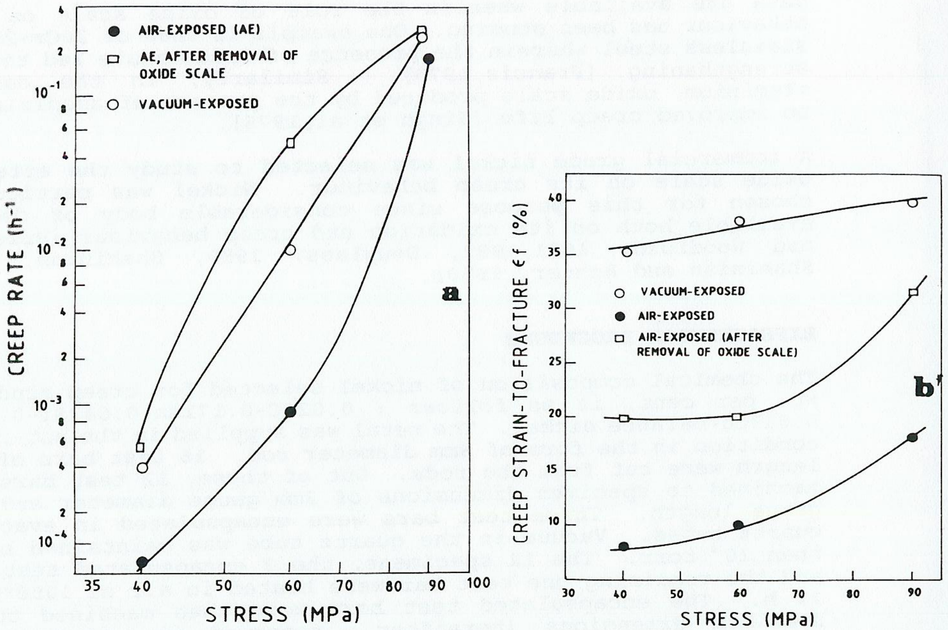

Fig.3 Creep data of the specimen exposed to vacuum and to air (with and without oxide scale) plotted between applied stress and (a) creep rate, ϵ_s, and (b) creep strain-to-fracture, ϵ_f.

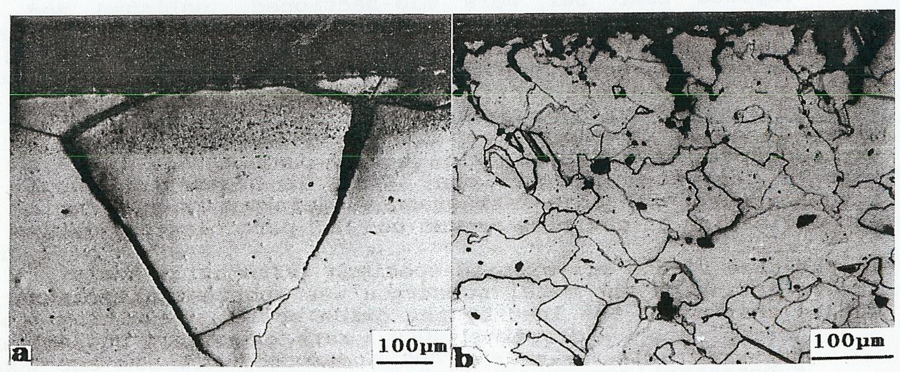

Fig.4 Showing (a) grain boundary cracks in the air-exposed specimen after testing at 60 MPa and (b) Dynamically recrystallized grains in the air exposed specimen after testing at 60 MPa after removal of the internally oxidized region.

vacuum exposed specimens (Fig.3a). Considerable enhancement in the steady state creep rate of the air-exposed specimen after removal of the oxide scale provides further strong support about the role of oxide scale on the creep behaviour of the metal. Two aspects of air-exposed specimen that need to be addressed are: (i) higher creep rate of the air-exposed specimen after removal of the oxide scale (Fig. 3a) and (ii) creep ductility embrittlement (Fig. 3b). The two issues can be explained after comparing the microstructure of the air and vacuum exposed specimens. The basic difference between the microstructure of the air-exposed specimen (after removal of the oxide scale) and vacuum exposed specimen is that MnO particles were present both in the matrix and along the grain boundary of the former. When stress was applied, cavities nucleated around MnO particles present along the grain boundary either upon creep loading or during creep depending on the applied stress. Nucleation of cavities reduced the load bearing cross-sectional area of the specimen resulting into faster creep rate. Growth and interlinkage of cavities led to the formation of crack which became easy path for oxygen diffusion. Oxygen available at the crack tip reacted with nickel and formed its oxide which is brittle and thereby assisted crack growth. The crack acted as notch resulting in creep ductility embrittlement. Maximum degradation of creep properties occurred in the air-exposed specimen without oxide scale due to faster creep rate coupled with poor creep ductility. A comparison of the creep rate between air-exposed specimen without oxide scale and vacuum-exposed specimen (Fig.3a) provides some interesting information about the rate of cavity nucleation.In the case of vacuum exposed specimen, the process of cavity nucleation was delayed due to the absence of MnO particles and extensive recrystallization during creep (Fig. 4b). Higher creep rate obtained at 60 MPa in the air-exposed specimen without oxide scale provides evidence that cavities around MnO particles nucleated instantly upon creep loading due to higher applied stress. Whereas when the applied stress was 40 MPa, the rate of cavity nucleation was slower due to stress relaxation occurring around MnO particles. As the deformation progressed, cavities got nucleated due to stress buildup at the particle-matrix interface. Growth and interlinkage of cavities led to poor creep strain-to-fracture and reduced creep life. At 90 MPa, creep strain-to-fracture in the air-exposed specimen (without oxide scale) is slightly lower than that of the vacuum exposed one. This is because the applied stress was so high that intragranular deformation was dominant and nucleation of cavities around the MnO particles got delayed.

In the case of the air-exposed specimen (with oxide scale), the stress acting on the metal substrate was substantially reduced due to sharing of the load by the oxide scale, resulting into lower creep rate. Accordingly, the rate of cavity nucleation around the particles in the grain boundary reduced. However, as the deformation progressed, sufficient stress built up around the MnO particles, causing its decohesion. Nucleation growth and interlinkage of cavities led to the formation of cracks and reduced creep strain-to-fracture. It is noted that whereas the creep rate and creep-strain-to-fracture of the specimen exposed to air followed a systematic trend, the same is not the case with the fracture lifetimes (Fig. 5). This is because lifetimes

depended on both creep rate and strain-to-fracture.

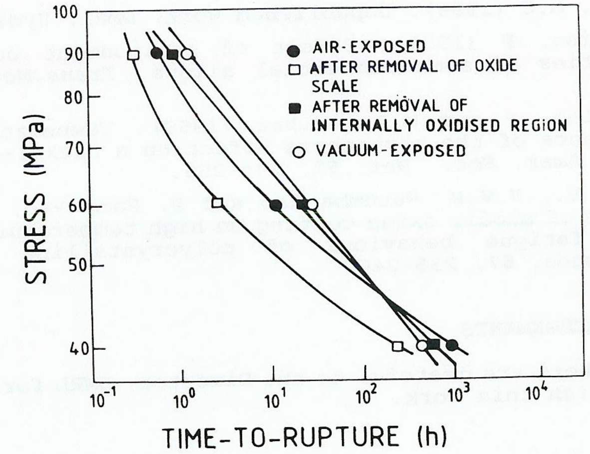

Fig.5 **Plots between stress and time-to-rupture of air-exposed and vacuum-exposed specimens: * air-exposed; □ air-exposed, after removal of the oxide scale; ■ air-exposed, after removal of the internally oxidized region; ○ vacuum exposed.**

CONCLUSIONS

1. The presence of oxide scale in nickel led to creep strengthening.

2. Diffusion of oxygen in the metal during oxidation led to the formation of manganese oxide, both in the matrix and along the grain boundary. On creep loading, cavities nucleated around these oxide particles in the grain boundary, leading to creep weakening and reduction in creep ductility.

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