

Ageing of austenitic iron alloys containing nitrogen

P. FERGUSON*, J. H. DRIVER†, A. HENDRY

Wolfson Research Group for High-Strength Materials, The University, Newcastle upon Tyne, UK

The Lifshitz–Wagner theory of coarsening applied to the experimental data for titanium and vanadium nitride precipitates in austenitic iron–nickel steels shows that Ostwald ripening is controlled by diffusion of the substitutional titanium or vanadium solute atoms. The influence of oxygen impurity is shown to modify both the VN coarsening behaviour and growth morphology.

1. Introduction

The relatively high thermodynamic stability of transition metal nitrides compared to the carbides means that fine stable dispersions of nitride precipitates may be used in steels designed for high temperature applications. Nitride precipitation may be obtained by conventional quench-ageing treatments [1], or by internal nitriding [2]; the latter method is more suited to the development of a fine homogeneous nitride dispersion but is restricted to thin sections. Evans [3] has shown that internal nitriding of a titanium-containing austenitic stainless steel to precipitate TiN produces significant improvements in creep strength, giving a material suitable for fuel element cladding in nuclear reactors for which the overageing characteristics of the precipitate at elevated temperatures are of great importance. The current work is a study of the coarsening behaviour of the fcc titanium and vanadium nitrides, TiN and VN, in binary austenitic Fe–35wt%Ni alloys for which the Lifshitz–Wagner theory of coarsening is shown to apply. The information of an iron–vanadium spinel and the effect of dissolved oxygen on VN growth morphology is also described.

2. Theories of particle coarsening

A dispersion of particles with limited solubility in the matrix tends to coarsen by the growth of large particles at the expense of smaller ones. The

driving force is the reduction of the interfacial energy, but the type of function which describes the coarsening depends on whether the growth is controlled by the diffusion of solute atoms in the matrix or by the transfer of solute across the particle–matrix boundary. The rate of coarsening under diffusion-controlled conditions has been expressed by Lifshitz and Slyosov [4] and by Wagner [5], and although these theories were primarily formulated for spherical particle growth in a liquid medium, their applicability to particle growth in solid matrices is well substantiated by experiments on a variety of systems [6]. In the theory of coarsening controlled by solute volume diffusion of the mean value, \bar{r} , of critical dimension $r = 2(dV/dA)$, of a particle with volume V and surface area A increases with time, t , according to the equation:

$$\bar{r}^3 - \bar{r}_0^3 = kt \quad (1)$$

where \bar{r}_0 is the mean particle size at the onset of coarsening, \bar{r} is the mean particle size after time t , and k is the rate constant given by:

$$k = \frac{2\gamma DC_e V_m^2}{\rho^2 RT} \quad (2)$$

where γ is the interfacial energy of the particle–matrix boundary, D is the coefficient of diffusion of the solute in the matrix, C_e is the concentration of solute in equilibrium with a particle of infinite

*Present address: MMRD, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA.

†Present address: Département de Métallurgie, Ecole National Supérieure des Mines de St. Etienne, 42023 St. Etienne, France.

size, V_m is the molar volume of the precipitate and ρ is the numerical constant related to the distribution of particle sizes and theoretically $\rho = 3/2$.

The alternative step in the mass-transfer mechanism that could control the growth process is the transfer of solute atoms across the particle–matrix interface for which Wagner [5] predicts a linear relationship between \bar{r}^2 and t . The Lifshitz–Wagner theory of diffusion-controlled coarsening predicts a quasi-steady state particle size distribution with a cut-off size (ρ) of 1.5. The values of ρ in the present investigation varied from 1.5 to 2.0. Values of $\phi > 1.5$ are commonly observed in solid systems and Ardell [7] has suggested that the discrepancy may be caused by large particle–matrix strains, but this cannot be attributed solely to the nature of the solid-state system since a similar deviation has been found in the coarsening of a liquid phase in a liquid [8]. Modifications to the Lifshitz–Wagner theory to take account of particle “encounters”, that is when the interparticle spacing is sufficiently small for a particle to influence the growth rate of its neighbours or to coalesce with them, have been proposed [9, 10]. The modified theories predict a strong dependence of growth rate on volume fraction of precipitate at fractions greater than ~ 0.05 . However in the present work the volume fraction is 0.0074 in which case the interparticle spacing is sufficiently large that the simple Lifshitz–Wagner theory may be applied.

3. Experimental details

Annealed 0.1 mm thick strip specimens of Fe–35 wt % Ni–0.5 wt % Ti and Fe–35 wt % Ni–0.5 wt % V were nitrided in 10NH₃:90H₂ and 2NH₃:98H₂ gas mixtures respectively at 700°C to nitrogen saturation. These treatments develop a modulated structure in the titanium alloy of mean wavelength 5.5 nm [11] and a homogeneous dispersion of vanadium–nitrogen clusters of mean radius 1.0 nm in the vanadium alloy [12]. Nitrided specimens were sealed in silica capsules evacuated to < 1.33 cPa and aged at 800 to 1000°C. Several areas of each specimen were examined at 100 kV in a Philips EM300 electron microscope using thin foils and particle-size measurements were taken directly from bright-field plates using a calibrated optical magnifier. The measurements were grouped into appropriate size intervals to provide a histogram of the distribution from which the mean particle size \bar{r} (Equation 1) was determined.

During ageing, both TiN and VN particles grow as octahedra which appear square in $\{001\}_\gamma$ projection and the typical growth dimension equivalent to a mean particle size (\bar{r}) was taken as $\bar{a}/2.45$ where \bar{a} is the average octahedron edge length. X-ray powder photographs of narrow strip (0.5 mm width) cut from nitrided and aged thin foil specimens were taken on a 9 cm Unicam camera with crystal reflected FeK α radiation from a LiF monochromator.

4. Results

The linear relationship between \bar{r}^3 and t predicted by Equation 1 is shown in Fig. 1 to be generally obeyed for TiN and VN growth in austenite. The intercept \bar{r}_0^3 reflects the time taken for coarsening to start and in both cases it is observed to be negligible for the ageing temperatures considered and is in agreement with previous studies [11, 12]. The values of the rate constant k obtained from Fig. 1 are listed in Table I. At all temperatures studied the coarsening rate of VN is greater than for TiN.

An unusual feature of the coarsening of VN at 1000°C is apparent from Fig. 1b; the initial rapid coarsening denoted by line (i) changes dramatically after 10 h to the slower rate of line (ii), approximately equal to the coarsening rate at 900°C. The X-ray powder photographs of Fig. 2 shows that this change is due to VN precipitates (fcc, $a = 0.4133$ nm) transforming to an iron–vanadium spinel with $a = 0.8410 \pm 0.0002$ nm. The spinel unit-cell dimension is intermediate between that of Fe₃O₄ ($a = 0.8396$ nm) and FeV₂O₄ ($a = 0.8485$ nm) and indicates a composition Fe_{1.2}V_{1.8}O₄. Both VN and iron–vanadium spinel [13] grow as octahedra with faces parallel to $\{111\}_\gamma$ planes and edges parallel to $\langle 110 \rangle_\gamma$ directions giving the appearance of squares in $\{001\}_\gamma$ foil planes; octahedral facets are visible on

TABLE I Particle coarsening rate constants for (a) TiN, (b) VN precipitates

Samples	Temperature (°C)	Coarsening rate constant, k (nm ³ h ⁻¹)
(a)	830	6.10×10^{-2}
	900	0.11
	1000	1.56
(b)	800	0.10
	900	1.58
	1000	59.1, line (i)*
		0.97, line (ii)*

*Of Fig. 1b.

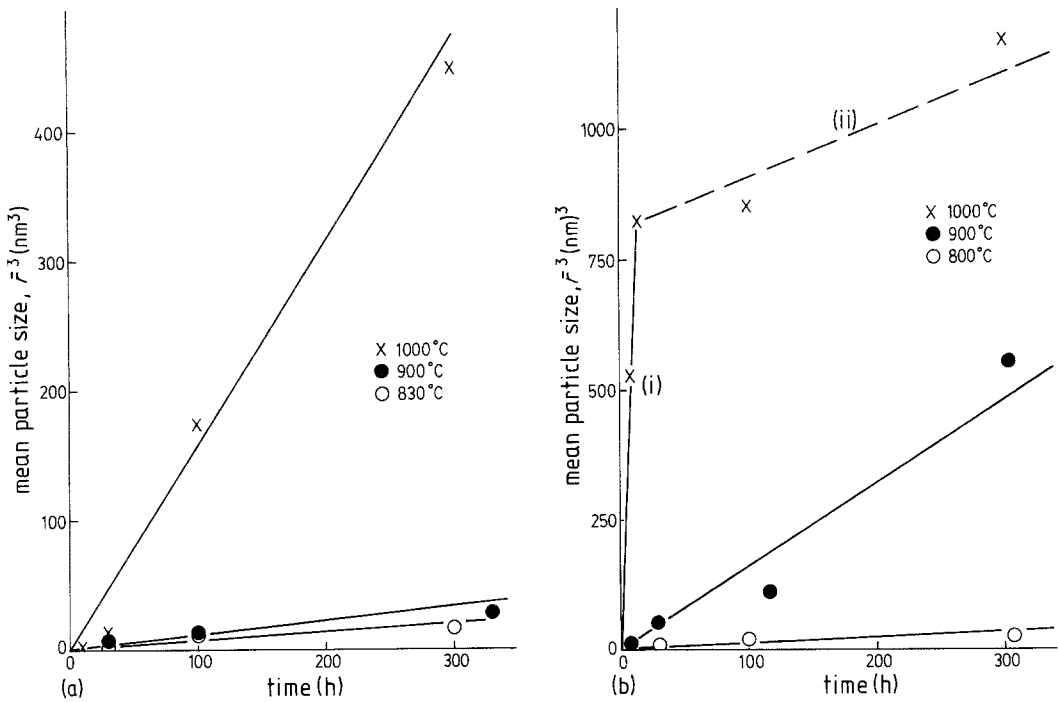
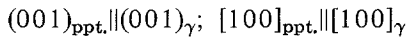


Figure 1 Variation of mean particle size with time at various temperatures for (a) TiN in Fe-35 wt% Ni-0.5 wt% Ti nitrided 6 h at 700°C in 10NH₃:90H₂, (b) VN in Fe-35 wt% Ni-0.5 wt% V nitrided 16 h at 700°C in 2NH₃:98H₂.

the arrowed spinel precipitate of Fig. 3. Electron diffraction shows the orientation relationship of both the VN and spinel precipitates with the austenite matrix is:



which suggests that VN transforms to spinel by *in situ* oxidation at 1000°C.

5. Discussion

The \bar{r}^3 against t results are in broad agreement with the Lifshitz-Wagner theory of coarsening controlled by solute volume diffusion and calculated coarsening rates for TiN in Fe-35 wt% Ni are lower than those of VN (see Table I). In the present systems both nitrogen and substitutional solute atoms must diffuse to permit Ostwald ripen-

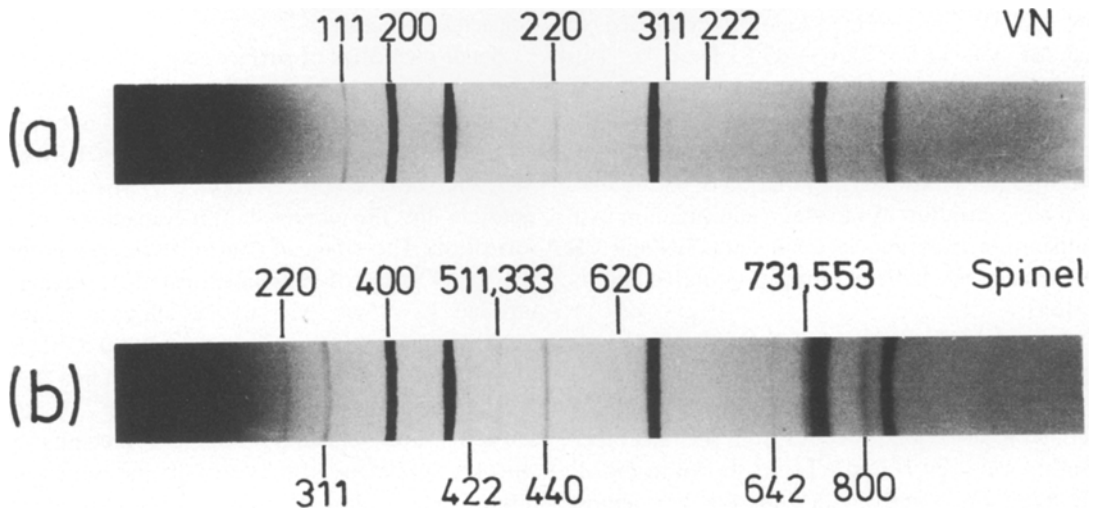


Figure 2 X-ray powder photographs of Fe-35 wt% Ni-0.5 wt% V nitrided 16 h at 700°C in 2NH₃:98H₂ and aged in vacuo showing (a) VN precipitation at 900°C for 1000 h, (b) iron-vanadium spinel precipitation at 1000°C for 300 h.

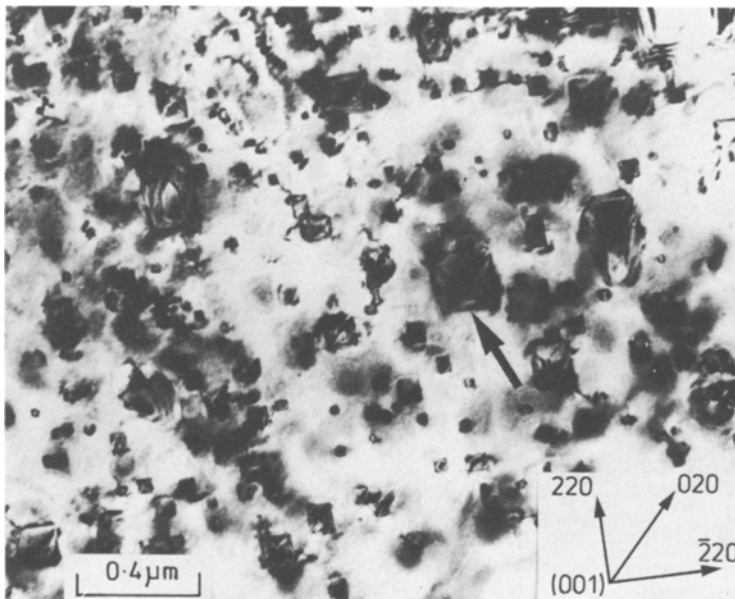


Figure 3 Electron micrograph showing iron-vanadium spinel precipitates in Fe-35 wt% Ni-0.5 wt% V nitrided at 16 h at 700°C in 2NH₃:98H₂ and aged in vacuo at 1000°C for 300 h.

ing, but as the diffusion rates for titanium and vanadium are several orders of magnitude lower than those of nitrogen, the rate controlling step must be diffusion of titanium and vanadium atoms in the austenitic matrix. TiN and VN both have rocksalt structures, the same orientation relationships with the matrix, and the same octahedral growth morphologies. Thus, the values for γ and V_m in Equation 2 must be of very similar magnitudes and as the diffusivity of titanium is only slightly lower than vanadium in austenite [14] the difference in coarsening rates may be attributed to a variation in the value of C_e due to the higher free energy of formation (i.e. chemical stability) of TiN ($\Delta G^{1273K} = -216.7 \text{ kJ mol}^{-1}$) compared to that of VN ($\Delta G^{1273K} = -67.8 \text{ kJ mol}^{-1}$). This difference results in the equilibrium concentration of titanium in the austenitic matrix being lower than that of vanadium for the same nitrogen concentration in solution. The variation of the equilibrium concentration of vanadium and titanium with temperature is extremely small since TiN and VN are virtually insoluble in nitrogen saturated austenite [15].

Arrhenius plots of $\ln k$ against $1/T$ for coarsening of TiN and VN are shown in Fig. 4. The temperature dependence of k (Equation 2) may be ascribed to diffusion processes from the linear relationship between r^3 and t [4, 5] shown in Fig. 1. The terms C_e , γ and V_m in Equation 2 are almost independent of temperature and the volume fraction of precipitate is fixed by the nitriding treat-

ment and does not change on ageing. The values of the activation energy for coarsening of TiN and VN precipitates determined from Fig. 4 as 224 and 358 kJ mol^{-1} respectively, are consistent with those for diffusion of titanium (251 kJ mol^{-1} , [16]) and vanadium (284 kJ mol^{-1} , [17]) in austenite. The value for diffusion of nitrogen in austenite is significantly lower (168 kJ mol^{-1} , [18]) and so the coarsening rate is that determined by the slower diffusing substitutional atoms. The activation energy for self-diffusion of iron in austenite (286 kJ mol^{-1} , [14]) is similar to that for substitutional solute diffusion and matrix atom diffusion must also participate in controlling the coarsening process.

Small quantities of surface-active elements may retard precipitate growth. The oxidizing potential of an evacuated vitreous silica capsule is not negligible due to the equilibrium established between SiO₂ and water vapour at 1000°C [19] and is responsible for the observed iron-vanadium spinel formation. The effect of controlled oxygen potentials on VN growth was investigated by ageing a nitrided Fe-35wt%Ni-1wt%V alloy in a non-oxidizing alumina reaction tube at 1000°C. Thin-foil examination of a specimen aged 24 h in a flowing gas mixture of 65CO:35CO₂ ($p_{O_2} \equiv 203 \text{ pPa}$) showed iron-vanadium spinel precipitation whereas specimens heat-treated in the same conditions but at lower oxygen potentials showed VN precipitation characterized by a change in growth morphology. The typical form of VN

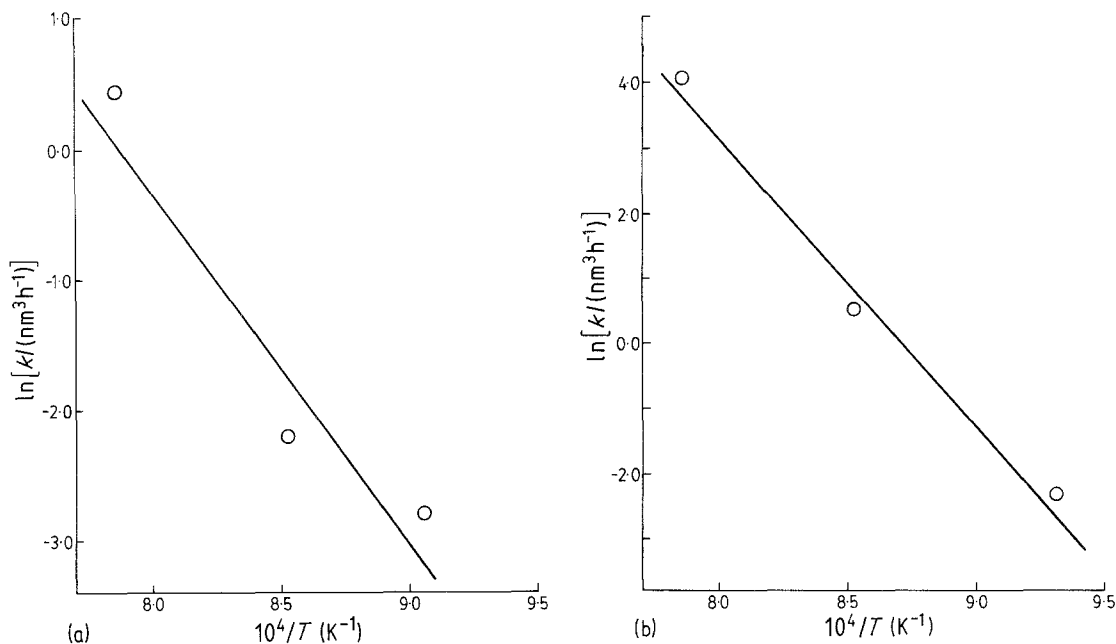


Figure 4 Arrhenius plots of $\ln k$ against $10^4/T$ from the coarsening data of Table I for (a) TiN, (b) VN precipitates.

observed in the present work and shown in Fig. 5a is modified to a needle morphology for some precipitates in nitrated Fe-35wt%Ni-1wt%V aged for 40 h at 1000°C in a controlled H₂O:H₂ gas flow equivalent to $p_{O_2} = 1.01$ fPa. The VN needles shown in Fig. 5b are presumed to be produced by selective interfacial adsorption of oxygen because they are found only in certain areas of the specimen. Particles of the normal morphology primarily occur but show a pronounced variation in size from grain to grain. Oxygen has been shown

to have a marked influence on the growth of Si₃N₄ [20] and γ' -Fe₄N [21] precipitates in α -iron and in both cases the growth mechanism changed from diffusion control to interfacial control when a critical oxygen potential was exceeded. Although the present results for TiN and VN coarsening show the process to be diffusion controlled, they also clearly illustrate how interfacial adsorption of oxygen can influence precipitate growth or in the extreme case cause particle oxidation.

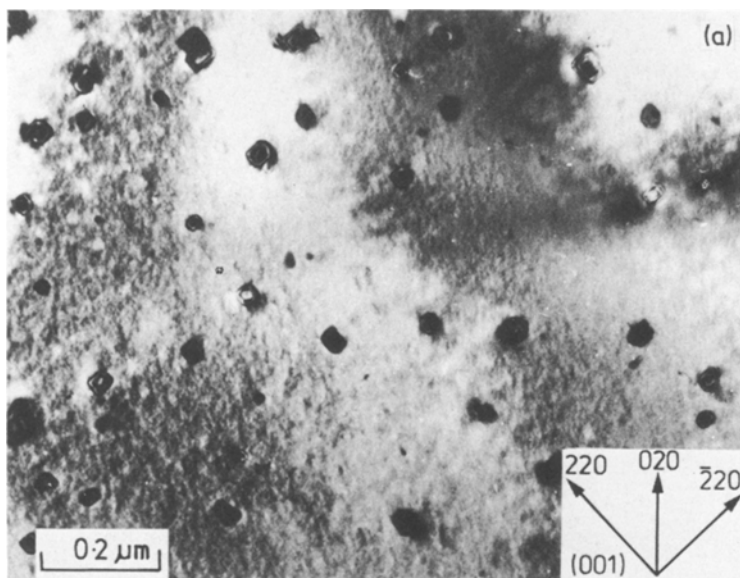
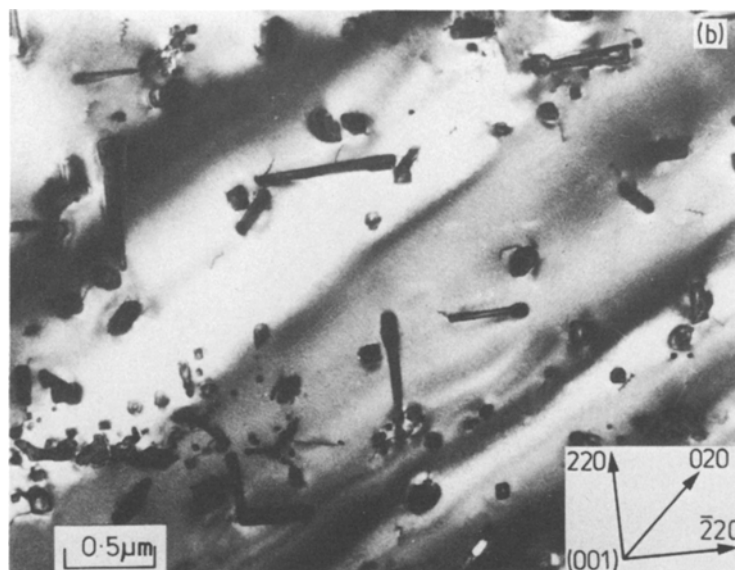


Figure 5 Electron micrographs showing (a) VN precipitates in Fe-35 wt % Ni-0.5 wt % V nitrated 16 h at 700°C in 2NH₃: 98H₂ and aged in vacuo at 900°C for 1000 h, (b) VN precipitates in Fe-35 wt % Ni-1.0 wt % V nitrated 16 h at 700°C in 2NH₃: 98H₂ and aged at 1000°C for 40 h in an oxygen potential of 1.01 fPa.



6. Conclusions

(a) The growth of TiN and VN precipitates in Fe-35wt%Ni is adequately explained by the Lifshitz-Wagner theory and is controlled by titanium and vanadium atom diffusion.

(b) The greater resistance to coarsening by TiN precipitates compared to VN precipitates is a result of the higher intrinsic chemical stability of TiN.

(c) Above a critical oxygen potential, VN transforms to an iron-vanadium spinel at 1000°C. Below this partial pressure the morphology of VN particles are modified by selective oxygen adsorption at the precipitate/matrix interface.

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