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Long term coarsening of γ' precipitates in a Ni-base superalloy

A. GES, O. FORNARO, H. PALACIO
IFIMAT-CICPBA, Universidad Nacional del Centro de la Provincia de Buenos Aires, Pinto 399 (7000) Tandil, Argentina

The mechanical properties of a Ni-based superalloy strongly depend on the distribution and size of the precipitate particle γ' phase: $Ni_3(Al, Ti)$. Such particles grow during the initial heat treatment and it is very important to predict the kinetic growth owing to their technological application at high temperatures. In this work, we performed analysis of particle coarsening in IN-713C during long ageing times at constant temperature, given an initial size and volume fraction distribution of the γ' precipitate phase, and the evaluation of two different heat treatments through the microstructure analysis and γ' morphology. We found that for short ageing times, $t < 2500$ h, the coarsening can be approximated by a linear volumetric growth as predicted by Lifshitz, Slyozov and Wagner (LSW) theory. For a time greater than 2500 h the growth rate of γ' precipitate shows an asymptotic behaviour in both heat treatments.

1. Introduction

It is known that the mechanical properties of a Ni-based superalloy strongly depend on the distribution and size of the precipitate γ' phase: $Ni_3(Al, Ti)$. Since such precipitate particles can grow during the initial heat treatment, it is very important to be able to predict the kinetics of growth and subsequent behaviour of this precipitate phase [1, 2]. For the same reason, some works have been done to analyse the effect of distinct heat treatments over the size and distribution of the γ' precipitate phase [3].

The precipitation of a new phase from a supersaturated solid solution involves three steps: (i) nucleation of the new phase; (ii) growth of the nuclei using the matrix elements and (iii) coarsening of the precipitates through the Ostwald ripening process. Greenwood [4], Lifshitz and Slyozov [5] and Wagner [6] have analysed the diffusion nature of Ostwald ripening process, under the assumptions of negligible volume fraction and spherical particles. The process is such that the particle's coarsening is due to the diffusion of the forming precipitate elements through the interface with the matrix. The coarsening law can be written as

$$\bar{r}^3 - \bar{r}_0^3 = kt \tag{1}$$

where $\bar{r}$ and $\bar{r}_0$ are the sizes of the particle at time t and 0, respectively and the growth parameter, k is given by

$$k = \frac{8}{9}\frac{\Gamma V_m D c_m}{RT} \tag{2}$$

with Γ being the surface energy per unit area of the matrix-particle phase boundary, V_m the molar volume, D the diffusion coefficient of the constitutive particle element in the matrix, c_m the matrix concentration of such element in equilibrium, R the gas constant and T the temperature.

This theory of diffusion-controlled particle coarsening, can be successfully applied when precipitate volume fraction is small, approaching zero [7]. This is not the case for Ni-based superalloys, where the volume fraction is often as high as 50 vol % and up to 70 vol % for the ultimate designs of last generation superalloys as CMSX2 or CMSX4 [8]. In addition to this, there exists a consensus on the fact that the elastic coherency stresses induced by the lattice parameter mismatch between the precipitate and the matrix, influences the behaviour during the coarsening, and has significant importance when changes in the precipitate morphology appear [9, 10]. The influence of neighbourhood particles over the coarsening behaviour was also analysed [11, 12].

As asymptotic behaviour for long ageing time was reported for alloys with high γ' precipitate volume fraction. In this case the coarsening does not follow a linear law [1, 2].

As Kirkaldy says, this situation is characteristic of a growth–death equation of population dynamics and can be described as

$$\frac{d(\bar{r}^3)}{dt} = \alpha(V - \bar{r}^3) \tag{3}$$

which is, in some way, Greenwood's law of particle size competition in Ostwald ripening [13]. In this context, the term $(\bar{r}^3 + V) = \text{const.}$ and might be interpreted as the molar volume which could contribute to the precipitate coarsening. By integrating this equation, we obtain

$$\bar{r}^3 = V - (V - \bar{r}_0^3)e^{-\alpha t} \tag{4}$$

where α has the meaning of volumetric growth velocity. We can see that this expression drives to an equation such as Equation 1 for short ageing time, taking the linear terms in a series expansion. Furthermore, we can find the relation between α and the growth rate estimated as LSW

$$(V - r_0^3)\alpha = k \qquad (5)$$

For long ageing time, $\bar{r}^3$ tends to V; hence, this would be the maximum value which the particle could grow, without taking into account morphological changes. This value is very difficult to obtain analytically, particularly in multicomponent alloys, such as the commercial superalloys.

In this work, we have performed a detailed study of the γ' precipitate coarsening kinetics behaviour in a IN-713C Ni-based superalloy for long ageing times. For this purpose we developed two sets of heat treatments, which provided different initial distribution of such precipitates [3], and then we carried out the samples ageing at constant temperature.

2. Experimental procedure

The superalloy used was type IN-713C, whose composition can be summarized as follows: C = 0.12, Cr = 12.5, Mo = 4.2, Nb = 2.0, Ti = 0.8, Al = 6.1, Ni = balance. The samples were prepared by cutting small pieces of 1 cm^2 section by 1 mm thickness from a as-cast ingot, and then using two different heating treatments for them: the first or "Standard" one consists of a solution treatment (2 h at 1176 °C, air cooled) and a precipitation treatment (16 h at 926 °C, air cooled), suggested by the alloy supplier. The second or "Test" consists of one solution annealing (2 h at 1176 °C, air cooled), and three precipitation heat treatments (2 h at 1180 °C, air cooled, 16 h at 950 °C, air cooled and 16 h at 760 °C, air cooled) [3]. The samples were aged at 950 °C, in such a way that γ' growth was obtained. Then the samples were removed from the oven at different time intervals up to 20 000 h and analysed by using a scanning electron microscopy (SEM). The particle size, distribution and statistical dispersion were obtained by employing an image analysis system. Since the γ' precipitates in a cubic shape we have taken the edge particle half-length as suggested by MacKay *et al.* [1]. The experimental values obtained are summarized in Table I.

3. Results and discussion

We can separate the discussion into two different fundamental aspects: (i) the analysis of the particle coarsening during the ageing at constant temperature, given an initial size and volume fraction distribution of the γ' precipitate phase; (ii) the evaluation of the different heat treatment through the microstructure analysis and γ' morphology.

In the first aspect, the discussion could be expressed in ageing time terms. In a previous work Ges *et al.* [3] confirm that the γ' coarsening follows a linear behaviour, similar to LSW law, during an ageing up to 900 h for the same alloy. Other authors report similar behaviour for different Ni-based alloys [1, 2, 14, 15]. In addition to this, they suggest that it could be possible to predict γ' growth over service lifetimes, i.e. in the

TABLE I Average size particle obtained for ageing during time *t* for the two different mentioned heat treatment: "Standard" and "Test"

t (h)	$(\bar{a}/2)^3_{Std}$ ($nm^3 \times 10^9$)	$\pm\Delta(\bar{a}/2)^3_{Std}$ ($nm^3 \times 10^9$)	$(\bar{a}/2)^3_{Test}$ ($nm^3 \times 10^9$)	$\pm\Delta(\bar{a}/2)^3_{Test}$ ($nm^3 \times 10^9$)
0	0.020 76	0	0.059 14	0
120	0.105 74	0.0538	0.081 63	0.056 07
360	0.125 69	0.041 69	0.091 86	0.048 43
624	0.136 96	0.0624	0.113 03	0.058 77
1015	0.202 95	0.060 18	0.242 51	0.06
1125	0.209 35	0.070 15	0.108 95	0.062 34
1276	0.161 06	0.026 86	0.214 92	0.05
1444	0.244 52	0.073 12	0.325 33	0.05
1708	0.2178	0.075	0.196 49	0.055
2380	0.276 61	0.08	0.214 35	0.065
3652	0.944 09	0.075	0.597 86	0.08
5139	0.784 86	0.06	0.598 61	0.080 61
7569	1.111 75	0.09	0.709 77	0.075
10377	1.645 51	0.075	0.777 84	0.065
12441	1.418 19	0.075	0.779 55	0.06
15705	1.384	0.088	0.996 79	0.06
20073	1.4652	0.158 01	1.019	0.088

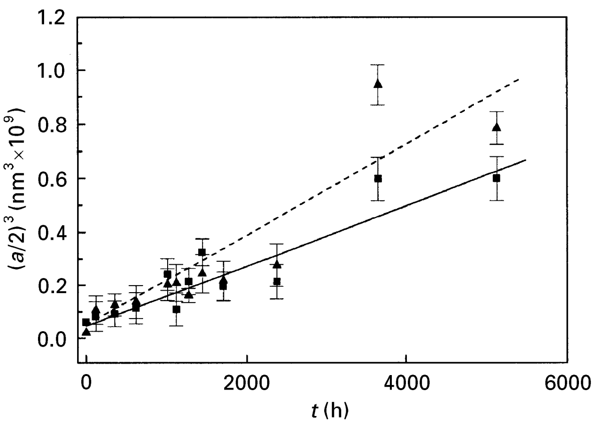

Figure 1 Estimation of growth parameter, *k*, in the first ageing stage. (▲) Standard; (■) Test.

TABLE II Growth rates for "Standard" and "Test" heat treatments

k [$nm^3\,h^{-1}$]	Ges *et al.*	This work
k_{Std}	117 129	129 996
k_{Test}	104 400	69 984

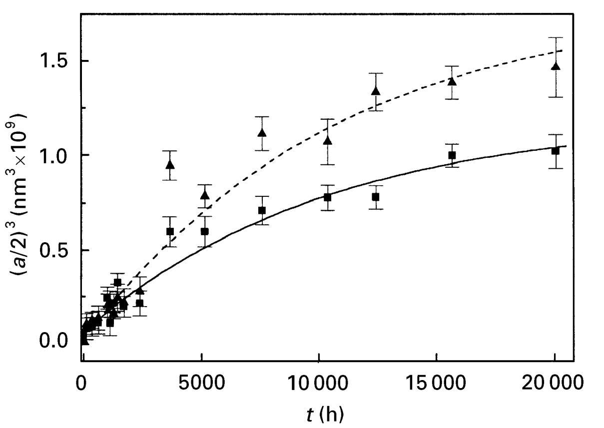

Figure 2 Experimental data and their adjustment according to Equation 4 for the total ageing time. (▲) Standard; (■) Test.

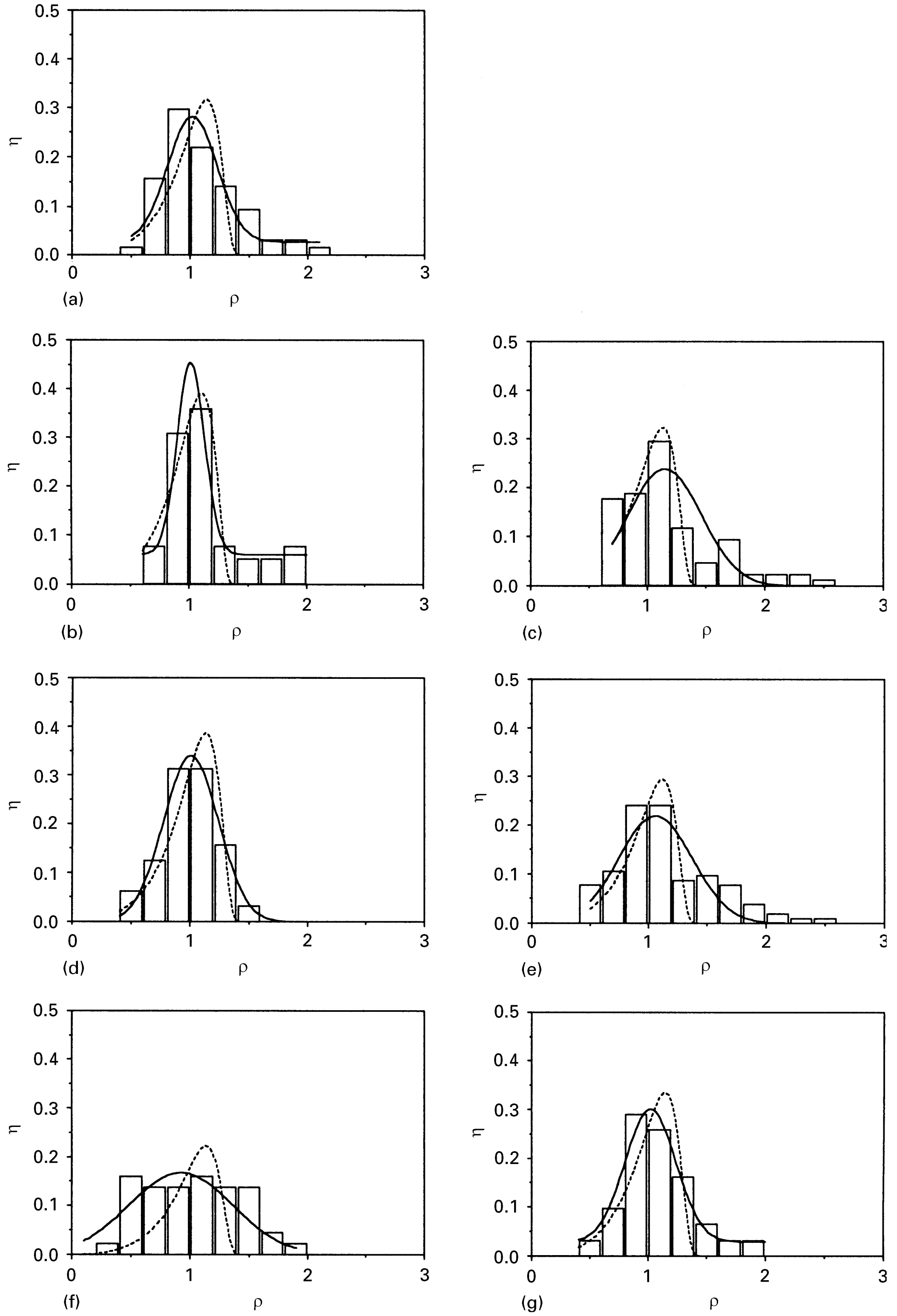

Figure 3 Experimental particle size for (a) as-cast, (b) and (c) 1125 h for Standard and Test, respectively. (d) and (e) the same for 3652 h and (f) and (g) the same for 20 073 h. Superimposed are —— Gaussian distribution and ------- LSW theory.

order of 10 000 h. In our experience, we observed that during the first ageing stage, up to 2500 h, the measured size of precipitated γ' can be approximated by a linear law, similar to Equation 1, as can be seen in Fig. 1, where we represent $(\bar{a}/2)^3$ vs. ageing time. We also observed that both sets of samples, corresponding to "Standard" and "Test" heat treatments, have different growth rates, represented by the slope, k_{Std} and k_{Test}, of the linear fit in this representation. We found out that the value of "Standard", k_{Std} is larger than the "Test" one, k_{Test}. These values are shown in Table II.

For a time greater than 2500 h it could be seen that the growth rate of γ' precipitated tended to decrease, in such a way that it shows evidence of a saturation behaviour, for both sets of heat treatments. For this reason, we can fit the experimental values using an expression such as Equation 4, which has the appropriate exponential decay form. Taking into account that we can evaluate the parameter k in the first growth stage, we use this value together with Equation 5. In the same way, the problem is reduced to finding only a variable, which is the volume V. In

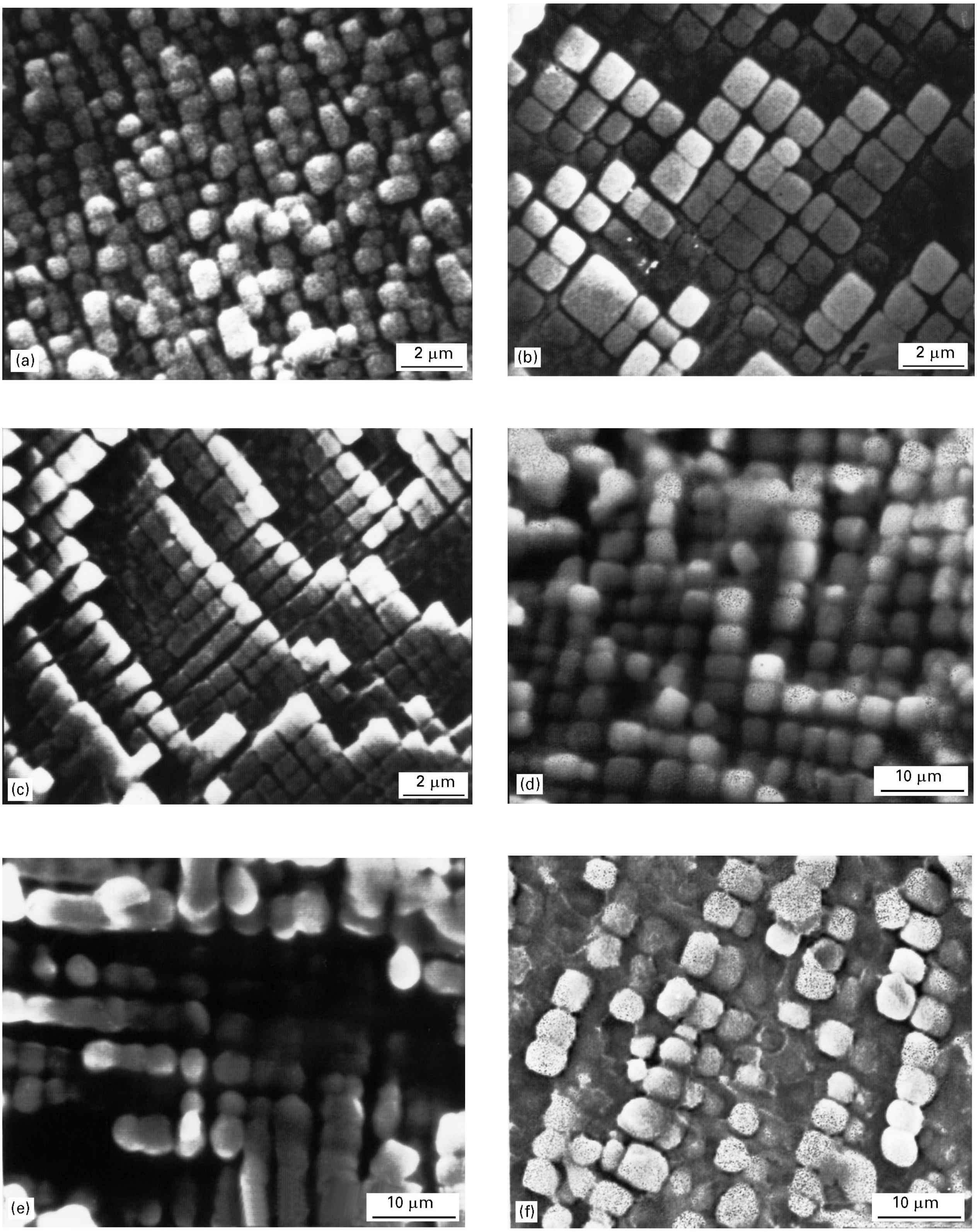

Figure 4 Typical microstructures obtained through SEM (a) γ' precipitate phase for an as-cast condition; (b) "Standard" treatment, at 1276 and (c) "Test" treatment for 1125 h. (d) and (e) "Standard" and "Test" for 10 377 and 12 441 h; (f) and (g) the same for 15 705 and 20 073 h.

Fig. 2 we show the coarsening for the total interval around 20 000 h of ageing. We show both the experimental values and the fitted curve obtained from Equation 4, for both heat treatments.

Considering the previous discussion about the kinetics of γ' precipitated during the ageing, it is possible to make some remarks with regard to the performed heat treatments. Given the importance that the γ' precipitate has in the mechanical properties of a heat-treated superalloy and in service conditions, it is desirable to know about the time evolution of such particles. It is known that the γ' kinetic growth has different speeds of volumetric growth depending on the initial distribution and size of precipitate γ' [3]. From the analysis of Fig. 2, and from the values in Table II, it can be observed that the slope of the "Test"

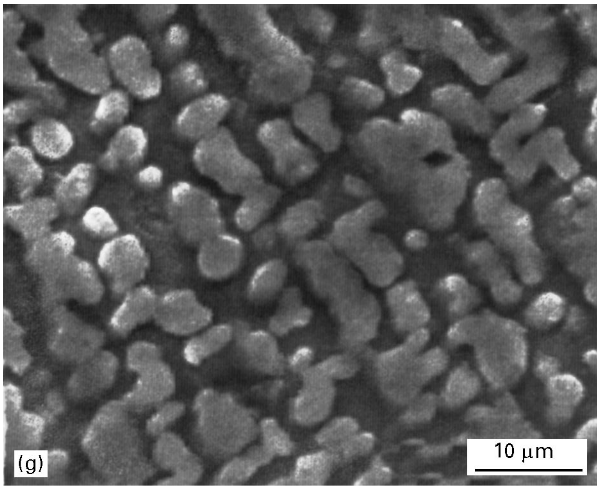

Figure 4 Continued

treatment is lower than the slope of the "Standard" one. This fact implies a lower γ' growth speed for the "Test" treatment, though in the growth start the particle size is bigger than the "Standard" treatment. For this reason, we could say that the "Test" treatment predicts a greater service lifetime.

In Fig. 3 can be seen some typical γ' size distributions obtained in our experiment. Fig. 3a shows as-cast condition, while in the remaining ones we compare the two heat treatments, (b) and (c) corresponding to the "Standard" and "Test" treatments respectively, for 1125 h; (d) and (e) the same for 3652 h, and (f) and (g) the same for 20 073 h. In the picture, η is the normalized frequency, ρ the normalized particle size, $(a/\bar{a})$. The distribution predicted by the LSW theory and Gaussian function have been superimposed for comparison.

In Fig. 4 can be observed the particle growth sequence during the ageing at constant temperature obtained by using SEM. Fig. 4a shows the γ' phase in an as-cast sample, Fig. 4b, d and f correspond to the "Standard" treatment at 1276, 10 377 and 15 705 h, respectively; Fig. 4c, e and g correspond to the "Test" treatment for 1125, 12 441 and 20 073 h, respectively. Finally, it can be noted that there is not an evident change in the γ' morphology during the full ageing for both heat treatments used. However, in Fig. 4g, there is some tendency for the particles to become slightly ragged, with a less clear cuboid form after very long heat treatment. There also appears to be some coalescence.

4. Conclusions

We have studied the behaviour of the γ' precipitated particle in IN-713C for long ageing times at constant temperature ($T = 950\,^{\circ}\mathrm{C}$) for two different heat treatments, "Standard" and "Test", which give us distinct initial size and volume fraction of cuboidal γ' precipitated.

For short ageing times, $t < 2500$ h, the coarsening can be approximated by a linear volumetric growth as predicted by LSW theory (Equation 1). We then estimated the growth parameter, k, for both cases, and found that the rate growth in "Standard" treatment is greater than the "Test" one during this first stage.

The total coarsening in both cases has an asymptotic behaviour. Such a situation is better reflected by Equation 4. This fact suggests that the LSW theory could not be securely used to predict the coarsening behaviour for long ageing times, considering that the γ' is formed by more than one element in a superalloy and the high initial volume fraction of this phase.

The initial mean size of γ' precipitated in the "Test" treatment is greater than the mean size measure in the "Standard". In spite of this fact, the final γ' size is smaller in the first treatment, since the growth velocity is lower for "Test" than for "Standard".

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References

1. R. A. MACKAY and M. V. NATHAL, *Acta Metall. Mater.* **38** (1990) 993.
2. D. McLEAN, *Met. Sci.* **18** (1984) 249.
3. A. GES, H. PALACIO and R. VERSACI, *J. Mater. Sci.* **29** (1994) 3572.
4. G. W. GREENWOOD, *Acta Metall. Mater.* **4** (1956) 243.
5. I. LIFSHITZ and V. SLYOZOV, *J. Phys. Chem. Solids* **19** (1961) 35.
6. C. WAGNER, *Z. Elect.* **65** (1961) 581.
7. A. J. ARDELL, *Acta Metall. Mater.* **20** (1972) 61.
8. K. HARRIS, G. L. ERIKSON and R. E. SCHWER, "Metals handbook", 10th Edn, Vol 1, Properties and Selection (ASM International, Materials Park, OH, 1989) p. 581.
9. M. DOI, T. MIYAZAQUI and T. WAKATSUKI, *Mater. Sci. Engng.* **67** (1984) 247.
10. T. MIYAZAQUI, K. SEKI, M. DOI and T. KOZAKAI, *ibid.* **77** (1986) 125.
11. W. C. JOHNSON, P. W. VOORHEES and D. E. ZUPON, *Met. Trans.* **20A** (1989) 1175.
12. P. W. VOORHEES, G. B. MACFADDEN and W. C. JOHNSON, *Acta Metall. Mater.* **40** (1992) 2979.
13. J. S. KIRKALDY, *Met. Trans.* **24A** (1993) 1689.
14. D. J. CHELLMAN and A. J. ARDELL, *Acta Metall.* **22** (1974) 577.
15. K. TRINCKAUF, J. PESICKA, C. SCHLESIER and E. NEMBACH, *Phys. Status Solidi* **131A** (1992) 345.

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