Proceedings of ASME Turbo Expo 2004
Power for Land, Sea, and Air
June 14-17, 2004, Vienna, Austria

GT2004-54214

THE COARSENING KINETIC OF γ' PARTICLES IN NICKEL-BASED SUPERALLOYS DURING AGING AT HIGH TEMPERATURES

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ABSTRACT

Nickel-based superalloys are widely used in applications requiring strength at high temperature, and in particular in manufacturing of several important components of both aeronautics and land based gas turbines. The main property of these materials is due to their particular microstructure consisting of a fcc lattice nickel matrix (γ phase), strengthened by precipitation of a second phase $Ni_3(Ti,Al)$ (γ' phase), having fcc lattice. During aging at high temperatures, γ' precipitates increase their size, following a kinetic law described by the classical LSW theory.

In this work the growth kinetic of γ' precipitates for the superalloy GTD 111 has been investigated by SEM. Samples of the alloy have been aged in the typical range of service temperatures for times up to 8000 hours.

For each sample a large number of images has been acquired and the size and distribution of γ' particles have been evaluated. Plotting the average size values, corresponding to the different times and temperatures analyzed, it was possible to obtain the growth kinetic of these particles, finding that the above mentioned theory gives a good description of the observed behaviour.

The data obtained for GTD 111 have been also compared with other data referring to INCONEL 738, obtained from samples aged in the same conditions and analyzed in the same way. GTD 111, when compared to IN738, resulted to have a much slower growth kinetic, resulting in a much higher creep resistance.

From the collected data it was possible to calculate also the activation energy for the diffusion process for both alloys, finding out values in agreement with those obtained by other authors and very close to the activation energies of Ti and Al in Ni matrix.

INTRODUCTION

Nickel-based superalloys are widely used materials in manufacturing of both industrial and aeronautical gas turbines, due to their superior mechanical properties, especially resistance to high temperatures and creep.

Creep resistance is particularly interesting in all those cases in which mechanical components are both mechanically and thermally loaded, like in the case of gas turbines rotor blades.

The reason for the high creep strength in nickel base superalloys is mainly due to their particular microstructure [1], consisting of an fcc lattice nickel matrix (γ phase), strengthened by precipitation of a second phase γ', consisting of $Ni_3(Al,Ti)$ particles, coherent with γ matrix, that act like obstacles for the motion of dislocations.

γ' precipitates are chemically active and during aging at high temperatures they increase their size, following a kinetic law described by classical Lifschitz-Slyozov-Wagner theory (LSW) [2]. This theory, starting from considerations related to the equilibrium dimension of the precipitate at a certain temperature T and neglecting the degree of supersaturation of a solid solution, prescribes a coarsening kinetic of γ' phase precipitates as proportional to the cubic root of aging time, according to equation:

$$\overline{R}^3(t) - \overline{R}^3(0) = \frac{8}{9}\frac{D\sigma V_m C_\infty}{RT}t = kt \qquad (1)$$

where C_∞ is the degree of supersaturation of the solid solution, V_m is the molar volume of solute, σ is the particle-matrix interfacial tension and D is the diffusion coefficient.

This proportionality has been confirmed for various nickel-base superalloys, and remains the most important contribution of the LSW theory, while the same theory does not provide

satisfactory predictions for the precipitate dimensions distribution.

Starting from LSW, many other theories have been developed with the same aim of describing analytically the γ' coarsening process (for example the theories MLSW (Modified Lifschitz-Slyozov-Wagner) [3], LSEM (Lifschitz-Slyozov Encounter Modified) [4] and the most recent ETK (Enumoto-Tokuyama-Kawasaki) and YEGG (Yao-Elder-Guo-Grant) [5,6]): all these theories have confirmed the proportionality with the cubic root of aging time, while they differ significantly in predicting the particle size distribution.

In this study the growth kinetic for the nickel-based superalloy GTD111 has been investigated by SEM. Aim of the work was to set up an analysis methodology for evaluating the growth kinetic and other secondary data, like the activation energy for the coarsening process, still not available, at present, for this alloy. The results obtained for GTD111 in terms of γ' coarsening kinetic and activation energy were compared with other data referring to IN738, obtained from samples aged in the same conditions and analyzed in the same way.

MATERIALS AND METHODS

GTD111 is a nickel-based superalloy developed by General Electric and widely used in manufacturing of first and second stage buckets in heavy duty gas turbines.

In table No. 1 the nominal compositions of GTD111 and of IN738LC, used in this work as comparison, are reported.

Element (wt%)	Ni	Cr	Co	Al	Ti	Mo	C	W	Ta
GTD111	60.5	14	9.5	3.0	4.9	1.5	0.1	3.8	2.8
IN738LC	62.4	16	8.5	3.5	3.5	1.7	0.1	2.6	1.7

Table 1. Principal elements in GTD111 and IN738LC alloys.

In order to evaluate the growth kinetic, samples of conventionally casted (CC) GTD111 have been aged at three temperatures in the range of 780-980°C for times up to 8000 hours. Before the test, the material was submitted to the standard heat treatment (solution and ageing) according to GTD111 specification.

At fixed times, samples have been extracted, mounted in phenolyc resin and prepared for observation with SEM. By using an image analyzer, a large number of image fields have been acquired for each sample and the size and distribution of a very large number of γ' particles have been evaluated, in order to achieve a growth kinetic based on a conspicuous statistical population.

The first task in our study was to establish the optimal number of image fields to acquire in order to have a statistically meaningful result. For this aim 300 fields were taken from the as cast sample, collecting in this way a very large number of γ' particle measurements. All this fields were then clustered in series of 10, 20, 30, 50, 60, 100 and 150 consecutive measures, calculating for each series the average value for particle diameter. In this way it was possible to evaluate the variation in the average value considering a different number of image fields.

All the results obtained are shown in Fig. 1.

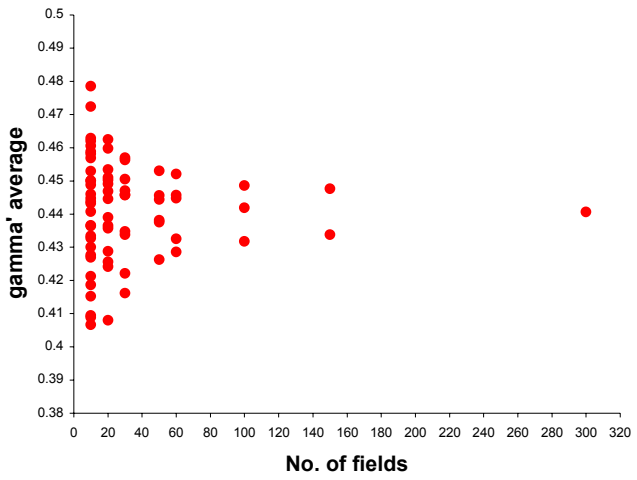

Figure 1. Average particle diameter values obtained considering a different number of image fields.

From the graph it is clear that the dispersion in the measurement of the average diameter decreases going from 20-30 to 100-150 measures.

In spite of the fact that according to this study it is possible to consider the acquisition of 50-60 fields sufficient to obtain a reasonably accurate average value, we decided to acquire 150 fields for each sample.

The reason for this choice is the considerable decrease in the number of particles in the samples aged for longest, because of the coarsening of γ' precipitates: taking into account a much larger number of measurements, it is possible to have a statistics based in all cases on a large number of measurements.

RESULTS

During aging at elevated temperatures the most relevant microstructural evolutions concern two main aspects: morphology and composition of carbides and shape and dimension of γ' precipitates.

Concerning to carbides, it is well known from literature [1], that in many superalloys carbides of type MC, that are the only initially present in the alloy, have the tendency to evolve in carbides of type $M_{23}C_6$, following the reaction:

(2) $$MC + \gamma \rightarrow M_{23}C_6 + \gamma'$$

This transformation was observed in our alloy GTD111; as it is clear from Fig. 2, carbides of type $M_{23}C_6$ tends to align along the grain boundaries and are surrounded by γ' resulting from dissolution of MC carbides. The EDS spectra corresponding to the two families of carbides show how the MC carbides are particularly rich in titanium and, during the decomposition, set this element free to form new γ' phase, that clusters at the grain boundaries around the smaller $M_{23}C_6$ carbide particles.

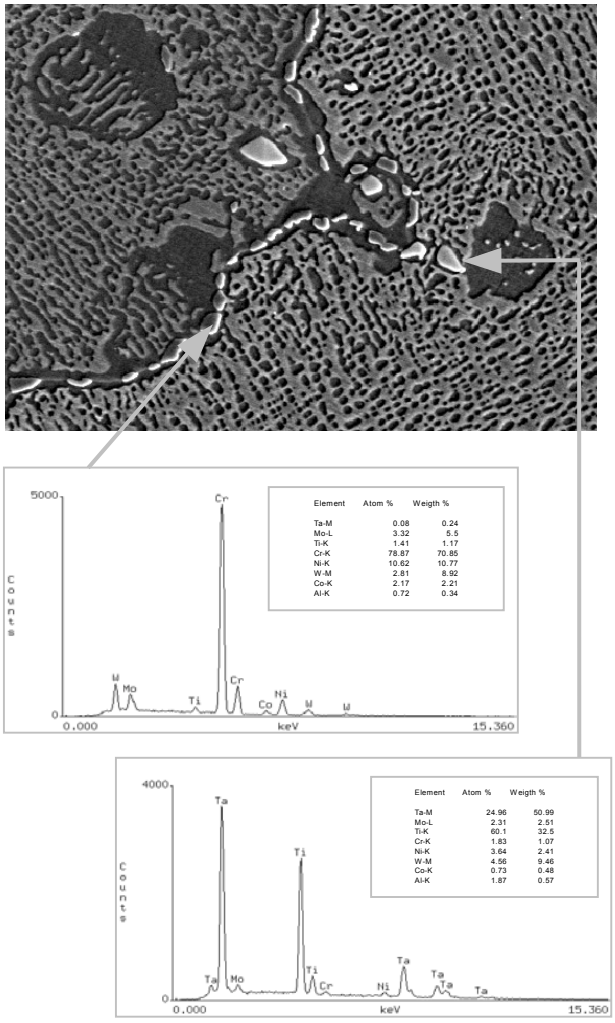

Figure 2. Carbides type MC and $M_{23}C_6$ at a grain boundary and corresponding EDS spectra. SEM 1000x.

Referring to γ' phase, Fig. 3 shows the microstructure of the material after the standard heat treatment; as it is clear two different populations of particles can be distinguished, a main population consisting of larger cubic-shaped γ' primary particles, having a mean diameter of about 0.4 μm, and a second population of much smaller round-shaped γ' secondary particles.

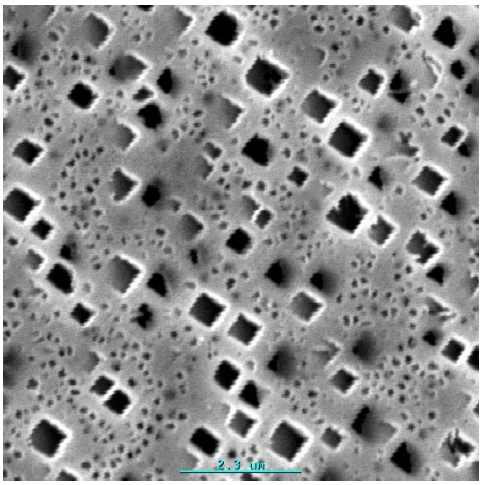

Figure 3. Microstructure of GTD111 after the standard heat treatment, SEM 10000x.

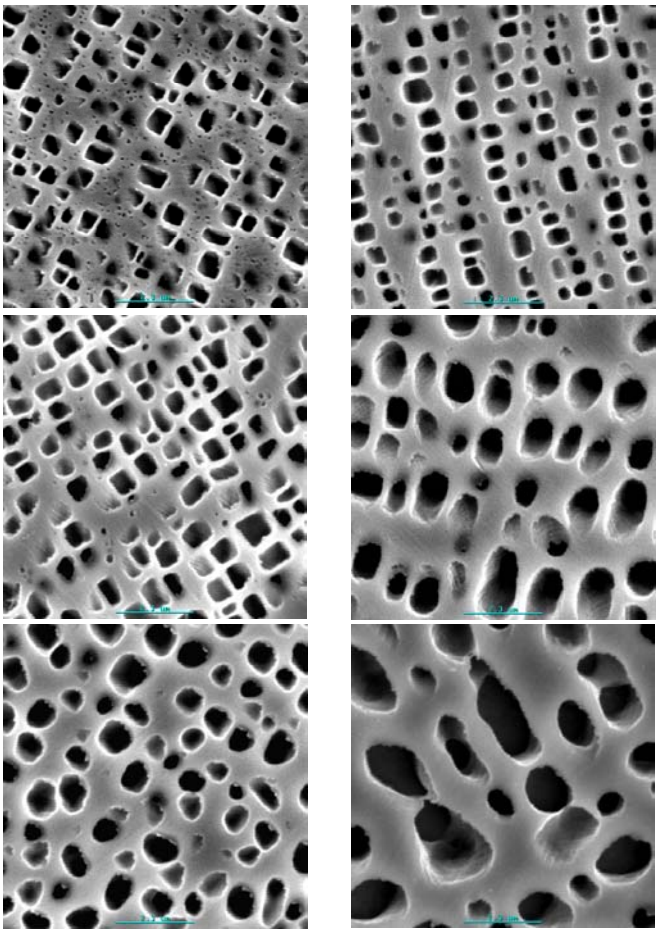

Figure 4. Typical aspect of GTD111 microstructure for temperatures below 870°C (left column) and above 950°C (right column), for 100, 1000 and 5000 hours of aging, SEM 10000x.

γ' precipitates evolution is shown in Fig. 4 for temperatures below 870 and above 950 °C at three aging times. Two main phenomena can be distinguished, the coarsening and changing in shape of the γ' primary particles, that deviate from the original cubic to a more rounded morphology, and the dissolution of small γ' secondary particles. The latter process is very fast at the two highest test temperatures and much slower below 850°C, temperature at which some particles have still not disappeared even after thousands of hours of aging.

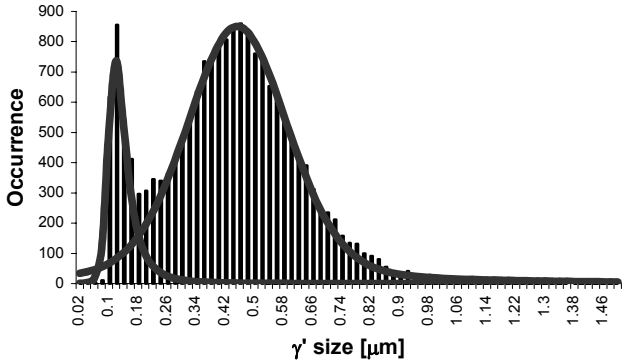

Figure5a. γ' particles size distribution in GTD111. Sample after standard heat treatment (not aged material).

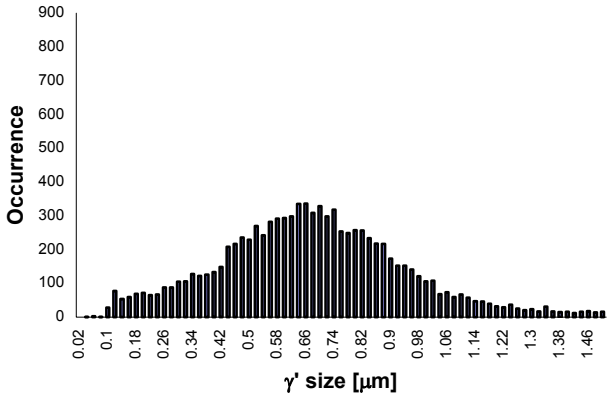

Figure5b. γ' particles size distribution in GTD111. Sample aged 3000 hours at 950°C.

In consideration of the fact that γ' secondary precipitates are totally absent in the most aged samples, and are in general not easily detectable because of their very small size, we decided to focus our attention on the growth kinetic of γ' primary particles only.

For this aim we calculate the average size of the primary population, separating with an appropriate software the two different contributions to the total distribution.

An example of the results obtained is shown in Fig. 5a, referring to the not aged sample used for comparison, where are reported the two distributions of primary and secondary populations.

The growth of γ' primary particles and dissolving of γ' secondary particles is clear comparing this particles size distribution with the second one shown in Fig. 5b, referring to a sample aged for 3000 hours at 950°C.

In the not aged alloy it is evident the presence of the two distinct populations of primary and secondary particles, in the second distribution it is clear how the peak corresponding to the secondary population has completely disappeared, and the primary particles have significantly increased their size.

In Fig. 6 we report the average values of the diameter computed from image analysis for the γ' primary particles at the three test temperatures examined ($T_3 > T_2 > T_1$). It can be seen how the results are in good agreement with the predictions of the LSW theory, because the proportionality of the γ' particles size to the cubic root of the aging time is respected in all the investigated range of temperatures.

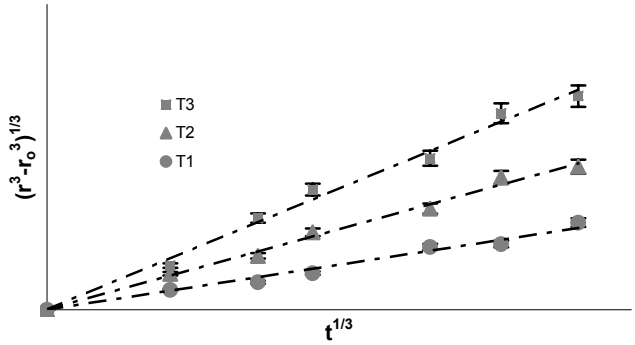

Figure 6. Growth kinetics of the γ' primary precipitates in GTD111 for three test temperatures ($T_3 > T_2 > T_1$).

From the slopes of the curves in Fig. 6 corresponding to the different temperatures investigated, is now possible to calculate the activation energy of the coarsening process.

Reconsidering equation (1) and making explicit the dependence of the diffusion coefficient D on temperature:

$$D = D_0 e^{-Q/RT} \tag{3}$$

we obtain the following new equation:

$$\ln\left[k^3 T\right] = \ln B - \frac{Q}{RT} \tag{4}$$

where k is the slope of each curve in Fig. 6 and Q is the activation energy of the coarsening process that we want to estimate.

Plotting on a graph $\ln[k^3T]$ versus 1/T it is possible to calculate the value for the activation energy Q (Fig. 7) that we found corresponding to 276 KJ/mol.

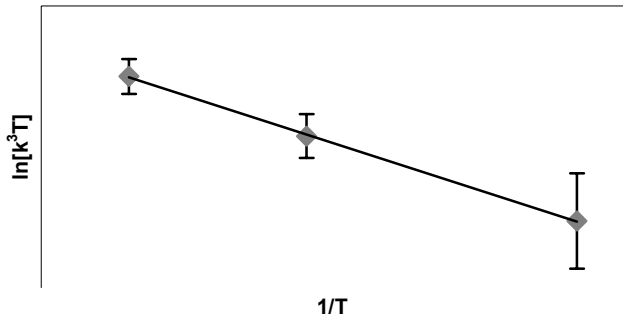

Figure 7. Calculation of the activation energy for the coarsening process in GTD111.

DISCUSSION

In this work a methodology study has been conducted in order to find first of all the most correct way to obtain dependable results regarding γ' particles dimensions and, consequently, growth kinetic, also thinking at future similar researches focused on the same matter.

Data collected show the importance of acquiring a large number of image fields in order to calculate the average particles size, because of the microstructural ununiformities typical of the investigated material, that force to have a statistics based on a very large number of particle measures.

The growth kinetic of GTD111 has been compared with the kinetic obtained with the same methodology for IN738 superalloy.

In Fig. 8 are shown as example the coarsening curves for GTD111 and IN738 obtained at a same temperature in the investigated temperature range. As it is clear, GTD111 shows a significative slower kinetic, that is in agreement with the much better creep performances shown by this alloy, according to General Electric experience and to what reported by other authors [7]. This allows the use of this material at higher service temperatures than IN738.

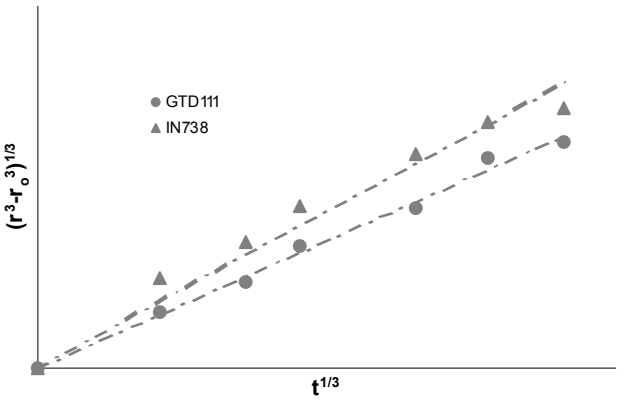

Figure 8. Comparison in the γ' coarsening rate between GTD111 and IN738 for the same test temperature.

The better behavior in terms of particles coarsening rate for GTD111 superalloy can be observed also comparing the curves regarding the activation energy for the coarsening process, shown in Fig. 9.

The slopes of the curves indicate that values of the activation energy for the two alloys are practically the same (we found a value of 274 KJ/mol for Q in IN738), but the different position in terms of $\ln[k^3T]$ is the evidence of a slower kinetic for GTD111 alloy.

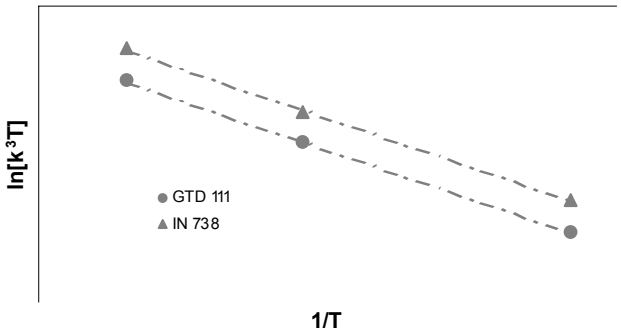

Figure 9. Comparison in the activation energies for γ' coarsening process between GTD111 and IN738.

Values for activation energy Q for GTD111 found in this study are comparable with those obtained by other authors [8,9] in similar works and in line with the corresponding values of Q for other nickel-based superalloys, as shown in Tab. 2.

Alloy	Q (KJ/mol)
GTD111	276
IN738	274
NIM80A	274
NIM90	257
NIM105	263
Inconel939	265
Udimet700	270

Table. 2. Comparison in activation energy values for various commercial nickel-base superalloys.

The value of 276 KJ/mol we found is also compatible with the corresponding activation energies for the diffusion of Al and Ti (the main constituents of γ' phase) in Ni matrix, respectively 268 and 269 KJ/mol.

The knowledge of the parameters now discussed, describing the coarsening process of γ' precipitates in GTD111, has a great importance from a practical point of view, because it can be spent in metal temperature estimations of serviced gas turbine buckets. For this aim, image analysis must be carried out on metal samples taken from the section whose temperature we want to know, and from a section assumed as not interested

by any microstructural alteration, because of the low temperature experienced, typically the shank region, to be used as comparison. The difference obtained in terms of γ' primary particles size between the samples, gives a measure of the material degradation and can therefore be used, together with the curves of γ' coarsening, for a dependable estimation of the metal temperature in the examined section.

Future developments of the present study will be focused on the coarsening kinetic of GTD111 and other commercial nickel-based superalloys for much longer times (up to 20000-24000 hours), in order to check if the law of proportionality with the cubic square of aging time, according to LSW theory, is followed for very long time even at the highest temperatures or whether there are deviations from this trend, as suggested by some authors [10].

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