MECHANISMS OF FORMATION OF SERRATED GRAIN BOUNDARIES IN NICKEL BASE SUPERALLOYS

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Abstract

The growth kinetics of particles producing serrations on grain boundaries were studied on Astroloy and an experimental low misfit alloy. The serrations developed after applying an isothermal heat treatment a few degrees below the solvus temperature of the γ' phase. In both materials, it was observed that arms which originated from dendritic particles pushed the grain boundaries on both sides and consequently produced serrations of a few microns in size (category A). In addition, in the alloy with low misfit, fans characteristic of discontinuous reaction which were approximatively a hundred microns in size were observed in regions of low particle density (category B). To identify the growth mechanisms of each category, the experimental kinetics were compared with those predicted by models of continuous and discontinuous precipitation. For the formation of large fans, it appeared that the model of discontinuous growth is in good agreement with the experimental results. However, for the second category of serrations, the continuous growth model provides a better description of the growth kinetics.

Introduction

In order to increase the resistance to crack propagation of disk alloys, it is necessary to reduce the grain boundary vulnerability at high temperatures. In this context, the development of microstructures containing grain boundary serrations shows promise for improving the mechanical properties of superalloys (1,2). The mechanisms of serration formation were therefore studied on Astroloy and on an alloy developed by Henry (3) made by P/M metallurgy and spray forming, respectively. The composition of the experimental alloy was chosen to reduce γ/γ' misfit.

Serrated grain boundaries were developed first by slowly cooling through the γ' solvus temperature and then were

more recently formed by applying an isothermal heat treatment just below the solvus temperature of the γ' phase directly after solution heat treatment. The low undercooling results in a low density of particles hence favoring the growth of arms before supersaturation is lost and coarsening begins (2, 3). Because the arms of these precipitates push the boundary on both sides, serrations of several microns are produced. If the process of formation is presently well known, the growth mechanism itself is not clearly understood. The first satisfying attempt to describe the phenomena was proposed by Henry et al. (3). They identified the γ' growth along the grain boundary with the dendritic growth. On the other hand, several authors have shown that serration formation could be related to mechanisms of discontinuous reaction (1,2). Nevertheless, none of these hypotheses, taken separately, allows the contribution of each mechanism for the growth of the intergranular particles to be taken into account.

The purpose of this study is to analyse the growth kinetics of serrations by comparing them with kinetics predicted by models of discontinuous and continuous precipitation. To simplify the analysis of the phenomena, the serrations were produced by applying aging as proposed by Henry et al. (3). This analysis is also made easier by using a low misfit alloy where the effects of coherency strain are eliminated. Then, a model was developed to simulate the growth of particles controlled by both volume and grain boundary diffusion. This version allows the role of the grain boundary as a short circuit for diffusion for the solute to be taken into account. To help solve the problem, a modification to the solution of isolated spheres originally solved by Nolfi et al. was considered (4). On the other hand, the Hillert model was used to evaluate the kinetics of a discontinuous reaction (5). This model describes the migration rate of the interface as a function of microstructural characteristics : size and distribution of the precipitates, matrix and precipitate compositions, G.B. curvature and interfacial energy.

Figure 1 : Microstructure of the Astroloy heat treated at 1130°C/30' (+ thermal etching).
P : intergranular γ' particle

Experimental Techniques and Procedures

The first alloy used in this study is Astroloy with the composition Ni-16.3Co-14.5Cr-4.35Al-3.65Ti-4.95Mo-0.018C-0.011B-0.047Zr (wt%). It was prepared by a prealloyed powder metallurgy process using the following steps : melting of the alloy in vacuum (VIM process), atomizing by a rotating electrode process (mean size of powder particle $\sim 140\mu\text{m}$) and consolidating the powder by extrusion using an 8:1 extrusion ratio. The second material is the experimental alloy developed by Henry whose composition is designed to minimize the coherency strain between the γ and γ' phases (3) : Ni-24Co-5Cr-4Al-4Ti-5Mo (wt %). It was prepared by spray forming and then was forged by General Electric. The consolidated material was homogenized by heat treatment above the γ' solvus temperature (1120°C) at 1150°C for 20h under argon.

Both superalloys were then heat treated at the temperature T_1 for 1.5h, around 20°C above the γ' solvus (T_s), before cooling down at 13°C/min until the temperature T_2 (below T_s). For generating the microstructure with serrations, the materials are maintained at T_2 during a period of time between 5 min. to a few hours before cold water quench. The temperatures T_1 used for this study were 1160°C for Astroloy and 1138°C for Henry's alloy. The temperature T_2 were selected between 1125°C and 1135°C for Astroloy and between 1090°C and 1110°C for the second. These microstructures were examined, both by optical and scanning electron microscopy on polished and etched samples. In order to made easier some observations of grain boundaries, a thermal etching (800°C/4h) is finally applied to Astroloy : this treatment allows the secondary carbides $M_{23}C_6$ to precipitate intergranularly without modifying the microstructures of the coarse γ' particles.

Figure 2 : Experimental growth kinetics of the intergranular γ' particle and serrations at 1130°C

Microstructural observations

To render easier the simulation of the γ' growth, the serrated microstructure was developed in two superalloys from an isothermal subsolvus heat treatment applied near T_s . In both materials, an optimum temperature for the treatment was selected in order to reduce the effects of chemical heterogeneities ($T_2 = 1130^\circ\text{C}$ in Astroloy and 1105°C in the alloy provided by Henry).

After a few hours of the heat treatment described above, the corresponding intragranular microstructures are characterized by a pattern of dendritic particles developed at high temperature and by a population of fine spherical particles (50nm) formed during quenching (figure 1). Depending on the heat treatment, the average length of the dendrite varies from 0.6 to 5 μm . In the case of the alloy provided by Henry, the dendrites do not have any preferential growth direction as observed in Fig.3. This observation confirms the small misfit existing between the γ and γ' phases.

As previously pointed out, the distribution of serrations in Astroloy is relatively homogeneous along grain boundaries, especially along random boundaries (see figure 1)(1). Because of the effects of lattice misfit strain, the γ' precipitates in Astroloy tend to grow along preferential directions and to split partially. Thus, the arms associated with serrations are unique and coarse in Astroloy, while they are several and thin in the experimental alloy. To study the growth kinetics of the γ' associated with serrations, the microstructures have been examined after 1,5,15,30 and 60 minutes of treatment at $T_2 = 1130^\circ\text{C}$. This examination requires the evaluation of the global volume of the particle directly in contact with the grain

Figure 3 : γ' particles of category A in the Henry's alloy heat-treated at 1105°C/1h.

Figure 4 : example of fan (category B) in the Henry's alloy heat-treated at 1105°C/1h

boundary. After sixty minutes, growth is over and coarsening begins. The results of this study are plotted in figure 2 which shows that the growth rate is drastically reduced after 30 minutes of treatment. Apparently, the growth rate changes with the level of supersaturation in the matrix.

As a consequence of compositional heterogeneities in Henry's alloy, the particle density varies from one region to another. Thus, two different categories of serrations can be distinguished on random grain boundaries as a function of the particle density. When the density around the grain boundaries is high enough, precipitates push the grain boundaries from both sides and consequently produce serrations of about ten μm in size, corresponding to category A (figure 3).

On the other hand, for the low density case (category B), the same rods produce fans on the order of a hundred μm in size (figure 4). It seems that the absence of obstacles

Figure 5 : Experimental growth kinetic of fans in Henry's alloy heat treated at 1105°C.

allows the system to attain optimized growth rates ; the rod diameters hardly vary from one part to the other of a given fan (dia. = 0.4 μm).

For the category A (the equivalent of the intergranular population in Astroloy), the growth kinetics could not been determined because of the heterogeneity of the microstructure. Instead, a study of the growth kinetics was conducted for the B category at 1105°C. The resulting microstructures were observed by SEM during a period of treatment between 15 minutes and 8 hours. In order to generate reliable data, the measurements for the category B were made on well developed fans growing on the observation plane. The average amplitude of the fan versus the time t was plotted on figure 5.

Two domains can be distinguished : during the first hour, the growth rate, which is very fast, is stabilized around $v = 2.8 \times 10^{-6}$ cm/s, whereas in the second part, the growth slows down, due to the presence of other particles ahead of the growth front. In the first situation, the products of reaction and the observed growth rate seems compatible with a discontinuous reaction.

Theoretical Models

Continuous growth model

To describe the influence of the supersaturation on the growth of the intergranular γ' particles, a classical growth model for spherical particles, which takes into account soft impingement, has been adapted for the case of precipitates associated with serrations. The original Nolfi model (4) describes the solute profile around a growing or dissolving spherical precipitate as a function of the time assuming a stationary reaction interface. The growth of grain boundary serrations is more complex than the case originally treated by Nolfi et al. (4) since both volume diffusion to the grain boundary and grain boundary diffusion must be included.

Therefore, the use of Nolfi et al.'s equations does not determine the actual solute gradient at the reaction interface ; it only allows to evaluate an order of magnitude of the γ' growth rate as function of the remaining solute concentration. An effort was made in this model to simulate the effect of short circuit diffusion along the grain boundary through the introduction of the parameter δ .

Figure 6 : Scheme of serration growth, R serratation radius, P conic arm of the γ' particle, GB grain boundary

For the simulation, the serratation surface $S+$ is represented by half of a sphere. This interface is pushed by a conic precipitate occupying a fraction δ of the serratation volume $Vs/2$ (figure 6). The morphology of the precipitate is such that the γ' surface in contact with the grain boundary ($S-$) corresponds to a fraction δ of the total surface $S+$. It is worth noting that only the fraction of particle growing behind the grain boundary is described by the model ($Vp = 2\pi R^3/3\delta$).

In order to express the growth rate of the particles, a flux balance across the reacting interface was performed. In this model, the solute diffusion is supposed to be carried out first by volume diffusion and then by grain boundary diffusion. In fact, the grain boundary represents a short circuit for the solute transport. Assuming $S+ = 2\pi R^2$, the collecting surface of the solute and $S- = S+/\delta$, the interface of reaction, the expression for the growth rate becomes :

$$v = \frac{dr}{dt} = \frac{\delta D}{(C_\beta - C_i)} \left(\frac{dC}{dr} \right)_R = \frac{\delta D}{(X_\beta - X_i)} \left(\frac{dX}{dr} \right)_R \quad (I)$$

with C_β the equilibrium solute concentration of the precipitate and C_i the solute concentration at the interface.

To evaluate the gradient of solute at the interface dX/dr as a function of the time and the size of the particle, the analytical expression of Nolfi for the solute concentration in the matrix was used (4). The matrix is assumed to be formed of equal cells delimited by a sphere of radius R_s and the particle, which is also spherical (radius R), grows from the center of the cell. The initial matrix is supersaturated with the composition C_0 and the diffusion coefficient D is assumed independant of time and

composition. The only driving force for the movements of both solute and solvent elements is that due to concentration gradients. The solute concentration $C(r,t)$ behaves according to Fick's second law.

For convenience, a new variable which represents the supersaturation is defined : $C'(r,t) = C_{eq} - C(r,t)$. From the boundary conditions (equations VIII and IX in appendix A), Nolfi gives the analytical solution of the problem :

$$C'(r,t) = \sum_{n=0}^{\infty} \frac{A_n \exp(-t/\tau_n) C_n \sin(\lambda_n r - \delta_n)}{r} \quad (II)$$

where A_n , C_n are constants $\tau_n = (\lambda_n^2 D)^{-1}$ and λ_n , δ_n are the eigenvalues of the function (see expressions appendix A).

Then, to determine the concentration profile, a mass balance between the particle and the initial matrix has been carried out. The amount of solute in the initial matrix and the amount of solute in the particle are as follows (with R_0 the initial radius of particle) :

$$\begin{aligned} \Delta M_i &= (C_0 - C_{eq}) 2\pi (R_s^3 - R_0^3)/3 ; \\ \Delta M_p &= (C_\beta - C_0) 2\pi (R^3 - R_0^3)/3 \end{aligned} \quad (III)$$

By calculating the remaining solute in the matrix ($\Delta M_i - \Delta M_p$), it becomes possible to determine the general profile of solute between R and R_s .

$$\Delta M_i - \Delta M_p = \int_R^{R_s} C'(r,t^*) 2\pi r^2 dr \quad (IV)$$

In this context, the parameter t^* allows adjustment of the concentration profile as a function of the quantity of solute available.

It is assumed that the growth of the conic arms starts from a threshold value ($R_0 = 200$ nm in Astroloy). For each step of time Δt , the composition at the interface X_i is evaluated from the Gibbs Thompson expression (6). Then, the eigenvalues and constants of the function $C'(r,t)$ are calculated (4). The concentration profile is determined by extracting the root t^* of expression IV. Finally, the concentration gradient at the interface $dC'(R,t^*)/dr$ and the migration rate V can be deduced from expression XII in Appendix A).

For the numerical applications, the size of the cells R_s was determined from the experimental surface density of particle N_v in the material : $R_s = (S/\pi)^{1/2}$ and $S = 1/N_v$. In Astroloy during the first hour at 1130°C , R_s was approximated to $4 \mu\text{m}$. The diffusion coefficient was approximated by using the expression of Swalin for aluminium in a nickel matrix (7): at 1130°C , the calculation gives $D_v = 2.0 \times 10^{-10} \text{ cm}^2/\text{s}$.

T=1130°C, Δt=10s, R_s = 4μm.

Figure 7 : Growth kinetics of serration, influence of δ

The parameter $\delta = S^+/S^-$ was chosen in this study as an adjustable coefficient which must reveal the effective area of grain boundary from which the particle draws solute. Through the theoretical curves of kinetics (figure 7), it can be shown that the parameter δ is directly linked with the maximum limit of serration growth (R_{max}). Thus, δ can be adjusted by using the experimental data R_{max} and R_s.

Discontinuous growth model

To evaluate the migration rate of the interface under conditions of discontinuous precipitation, the Hillert model was chosen as a reference (5). Schematically, this model describes the reaction $\alpha_0 \rightarrow \beta + \alpha_1$ where β and α_1 form as alternating lamellae growing edgewise into the α_0 grain. The purpose of this paragraph is to adapt this treatment describing lamellar growth to the case of rod-like growth. In our material, the β and α_1 phases could be replaced respectively by the γ' rods and the γ matrix.

The grain boundary is regarded as a thin film of boundary phase having its own molar free energy function for binary alloys (5). The free-energy losses during the movement of such an interface are evaluated from free energy diagrams. Two mechanisms of free energy dissipation are found, caused by diffusion ahead and inside the interface. For high migration rates of the interface, these retarding forces can almost disappear. The chemical deviation from local equilibrium at the interface β/α_0 , results in a force pulling the grain boundary along with the precipitating phase allowing the formation of the β/α_1 interface.

In the simplified version of the model, the concentration profile of solute in α_1 and in β along the grain boundary is considered as constant for convenience. Consequently, Hillert has avoided Cahn's treatment of the solute profile along the α_1/α_0 interface to express the migration rate V of

the grain boundary as a function of the thickness of the lamella (8). Instead, he has used the approximate treatment of the eutectoid reaction given by Zener (9) and applied it to the case of grain boundary diffusion control by Turnbull (flux balance method). Applied to the case of rod growth, this treatment gives an expression of the migration rate with the form (see appendix B equation XIII) : $V = f(r_\beta, r_{tot}, X_\alpha, X_{\alpha/\beta})$ with r_β the radius of the rods, r_{tot} the cell radius, X_α the composition of the α_1 phase and $X_{\alpha/\beta}$ the composition at α/β interface along the grain boundary.

In order to express V as a function of r_β , Hillert has used the following assumptions (10) : the growth front is held back by the action of the surface tension σ in the α_1/β interface which acts perpendicular to the growth direction. The fraction L_α is carried by the edge of the α phase which must thus have a curvature which puts the α phase under an extra pressure ΔP_α . The balance of force requires that :

$$L_\alpha \sigma = \int_{r_\beta}^{r_\alpha + r_\beta} \Delta P_\alpha dr \quad \text{and} \quad L_\beta \sigma = \int_0^{r_\beta} \Delta P_\beta dr \quad (V)$$

The fraction $L_\beta (= 1 - L_\alpha)$ is carried by the edge of the β rods.

The reaction gives chemical driving forces $\Delta G_{m\alpha}$ and $\Delta G_{m\beta}$ which balance these extra pressures. But a part of this force can be lost by diffusion in the α_0 grain. Only a part of these contributions k_α and k_β can be used. We thus obtain for the case of rods (cylindrical symmetry):

$$2L_\alpha \sigma V_m = k_\alpha \int_{r_\beta}^{r_\alpha + r_\beta} \frac{2r}{r_\beta} \Delta G_\alpha^m dr \quad \text{and} \quad (VI)$$

$$2L_\beta \sigma V_m = \int_0^{r_\beta} \frac{2r}{r_\beta} (\Delta G_\beta^{m1} + k_\beta \Delta G_\beta^{m2}) dr$$

From a molar Gibbs energy diagram, Hillert obtains approximate expressions of the chemical energies (5). By introducing them into the expressions (VI) and by using a mass balance and the expression of $\partial^2 G / \partial X^2$ (appendix B equations XIV and XV), it can be shown that the expression of the migration rate becomes :

$$\frac{v}{6K\delta D_b} = \left[\frac{r_\beta}{r_{tot}(r_{tot}^2 - r_\beta^2)} \right] \left[\left(\frac{k_\alpha (r_{tot}^2 - r_\beta^2)}{2L_\alpha r_\beta \cdot r_{rev}} \right)^{1/2} - 1 - \frac{k_\alpha \cdot L_\beta}{2L_\alpha} \right] \quad (VII)$$

According to Hillert's model, the values of L_α and L_β parameters have been approximated by expecting that grain boundary energies were equivalent for the α and β

$T = 1105^{\circ}\text{C}$; $I_{\alpha} = 0.5$; $k_{\beta} = 0$; $k_{\alpha} = 0.7$; $K = 2$; $D_b = 1.0 \times 10^{-7} \text{ cm}^2/\text{s}$

Figure 8 : Migration rate of the interface versus the radius r_{β} from the Hillert's model. Influence of r_{rev} (effect of the interface energy).

phases on a random grain boundary ($L_{\alpha} = L_{\beta} = 0.5$). On the other hand, assuming a high migration rate for the interface, the coefficient k_{α} was estimated around 1. In other words, it was assumed that the migration rate is fast enough to eliminate any volume diffusion ahead of the advancing reaction front.

The reversible radius r_{rev} has been evaluated from the Hillert formula : $r_{\text{rev}} = 2 \sigma V_m [X_s (1-X_s)] / (RT(X_0 - X_{\text{eq}})^2)$ with $X_s = (X_0 - X_{\text{eq}})/2$; $V_m = 2.10^{-5} \text{ m}^3$; $X_0 = 0.061$; $X_{\text{eq}} = 0.0586$; $T = 1378^{\circ}\text{K}$; $R = 8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$. Because the misfit is low in the Henry's alloy, σ is expected to be in the range $30 < \sigma < 90 \text{ mJ/m}^2$. Consequently, r_{rev} has been estimated between $1.3 \times 10^{-5} < r_{\text{rev}} < 4.0 \times 10^{-5} \text{ cm}$. From the curves $V = f(r_{\beta})$ (figure 8), it appeared that this parameter has a strong effect on the shape of the migration rate distribution. The maximum of the migration rate for the interface varies from 2.25×10^{-5} to $6.0 \times 10^{-6} \text{ cm/s}$ ($D_b = 1.0 \times 10^{-7} \text{ cm}^2/\text{s}$) into the interval $2.0 \times 10^{-5} < r_{\text{rev}} < 4.0 \times 10^{-5} \text{ cm}$.

The uncertainties in the grain boundary diffusion coefficient D_b has brought us to make the parameter adjustable with the experimental data. Knowing the level of the volume diffusion coefficient for aluminum in a nickel base matrix ($D_v = 2.0 \times 10^{-10} \text{ cm}^2/\text{s}$ at 1135°C), the coefficient D_b was expected to be ten to one hundred times higher ($10^{-9} < D_b < 10^{-8} \text{ cm}^2/\text{s}$).

Discussions

Fan formation

As shown previously for the category B particles, the growth rate during the very fast regime was found to be around $2.8 \times 10^{-6} \text{ cm/s}$. After one hour of treatment, the average diameter of the rods associated with the fans is

$T = 1105^{\circ}\text{C}$; $I_{\alpha} = 0.5$; $k_{\beta} = 0$; $k_{\alpha} = 0.7$; $K = 2$; $D_b = 1.0 \times 10^{-7} \text{ cm}^2/\text{s}$

Figure 9 : Theoretical kinetics predicted by the Hillert model in the case of rod growth

about $0.17 \text{ }\mu\text{m}$ to $0.21 \text{ }\mu\text{m}$. In fact, these observations are probably not representative of the real diameter during the reaction in contact with the grain boundary : after the discontinuous reaction, rods inside the fan continue to grow by consuming the remaining supersaturation. This is the reason the parameter $r_{\text{tot}} = r_{\alpha} + r_{\beta}$, which stays constant within the fans, was chosen as a reference for this study. In the second sample, the average r_{tot} was estimated to be $0.85 \text{ }\mu\text{m}$.

In order to determine a migration rate profile compatible with the experimental description, the level of r_{rev} was selected so that the peak of the curve $V = f(r_{\text{tot}})$ is close to the experimental r_{tot} (r_{rev} determines the width and the amplitude of the peak on the theoretical curve). This is how r_{rev} was selected to be $4.0 \times 10^{-5} \text{ cm}$ (the maximum limit of the chosen interval) and the value for D_b as 1.0×10^{-7} which is five hundred times higher than D_v (with $k_{\alpha} = 0.7$). The corresponding calculated kinetics $V = f(r_{\text{tot}})$ are presented in figure 9 (to relate r_{tot} and r_{β} in the expression of V , the formula XVI in appendix B was used). When r_{tot} is equal to $0.85 \text{ }\mu\text{m}$, the calculated r_{β} corresponds to $0.11 \text{ }\mu\text{m}$ with $X_{\alpha} = 0.060$ and the growth rate attains $3.0 \times 10^{-6} \text{ cm/s}$. It is worth noting that the theoretical and experimental parameters (V , r_{β}) appear to be very close. But, the value of D_b , adjusted to fit the kinetics, seems to us a little bit overestimated. This simplified simulation only allows an estimation of the order of magnitude of the migration rate in steady state conditions. However, the results of this analysis tend to confirm that the experimental kinetics for the particles in category B is compatible with those of a discontinuous reaction. Despite that fans appear only in the low misfit alloy, the occurrence of the discontinuous reaction can not be connected with the absence of misfit : after similar heat treatment, such fans have already been observed in commercial alloys with a positive misfit (11).

Development of wavy grain boundaries

In Henry's alloy, when the particle density is high enough (particles of category A), the serrations formed are very similar to those in the Astroloy (several μm of amplitude). However, these similitudes do not concern the morphology of the γ' particles which depends on the misfit level of the alloy. And the size of the intergranular particles remains close to those of the intragranular γ' particles (figure 3).

Category	A	B	Bulk	Hillert
r_B (μm)	0.5	0.2	0.5-1.0	0.09
V ($\mu\text{m/s}$)	1.66×10^{-3}	2.6×10^{-2}	0.7×10^{-3}	2.6×10^{-2}

Table 1 : The different growth kinetics in Henry's alloy.

In table 1, a comparison of the average migration rate V and rod diameter have been made between the different categories of particles present in the material. Clearly, there is at least an order of magnitude (a factor 15) between the migration rates of the category A and those observed in the category B or in the simulation (Hillert data). The microstructural observations confirm that the characteristics of the category A particles are close to those of the intragranular ones (rods diameter = $0.5 \mu\text{m}$). As in the grain, the growth of the A particles is affected by the presence of the neighbouring particles (overlapping of the diffusion fields). However, in this case, the phenomena is delayed by the grain boundary diffusion.

To identify the growth mechanism of this serration, the experimental results obtained in Astroloy at 1130°C , during the first hour of isothermal treatment, were exploited. The experimental data of growth kinetics were compared with two theoretical conditions of growth, $\delta = 1$ and $\delta = 2$, calculated through the modified Nolfi's model (figure 10). The situation $\delta = 1$ represents a state where there is no short circuit of diffusion. This condition corresponds to a classical continuous precipitation. In fact, the comparison between the curve $\delta = 1$ and the experimental one (r_{exp}) reveals that the contribution of the grain boundary is important. Despite the lack of experimental data, it appears clearly that the theoretical curve $\delta = 2$ fits very well with the experimental kinetics ; the growth limits R_{max} , located around 1600 nm , are equivalent for both theoretical and experimental descriptions. Indeed, these results, obtained for a homogeneous microstructure, suggest that neither a classical continuous model nor a discontinuous one can describe the serration formation. Consequently, the assumption of a growth rate, based on volume diffusion followed by grain boundary diffusion, appears realistic.

$$T = 1130^\circ\text{C} ; \Delta t = 10 \text{ s} ; R_s = 4 \mu\text{m} ; D_v = 2.0 \times 10^{-10} \text{ cm}^2/\text{s}$$

Figure 10 : Comparison between the experimental results (r_{exp}) and the theoretical kinetics ($\delta = 1, 2$) in Astroloy

In Henry's alloy, intermediate microstructures between A and B have also been observed. These microstructures can be the consequence of variations of the particle density in the material. Thus, an enlargement of the cell size in the matrix can explain an acceleration of the γ' particle growth. However, another assumption could explain this phenomena : as a function of the particle density, the discontinuous regime could represent a more or less important step in the growth process. In the present stage of our investigation, this migration scheme is not completely rejected .

Conclusion

Growth kinetics of particles producing serrations on the grain boundary have been studied on Astroloy and Henry's alloy. The development of serrations was achieved by applying an isothermal heat treatment, a few degrees below the solvus temperature of the γ' phase. In both materials, it was observed that arms originating from dendritic particles push the grain boundary on both sides and consequently produce serrations of a few μm (category A). However, due to a certain chemical heterogeneity in the Henry's alloy, another category of serration (category B) develops simultaneously. Arm length (nm) ie former : " fans " of about $100 \mu\text{m}$ size, characteristic of discontinuous reaction, are promoted in regions of low particle density.

The experimental growth rate of the category B were compared with those predicted by the Hillert's model. Thus, the mechanism of fan formation was clearly identified as a discontinuous growth process. On the other hand, a similar analysis operated on the category A did not allow a direct classification of the reaction ; neither the classical continuous reaction nor the discontinuous reaction describe the corresponding growth phenomena. To correlate the growth rate of these particles with the

surrounding concentration profile, Nolfi's model was adapted for the case of a migrating reaction interface. It was assumed that the solute transport was controlled successively by volume and grain boundary diffusion. Indeed, the grain boundary is considered as a short circuit for the diffusion. Despite the simplicity of the present description, the results for the simulation in Astroloy are very encouraging. Overall, the comparison of the intergranular γ' particles between both materials has revealed that coherency strain influences the morphology of the particle but not the principal mechanism of serration growth itself.

The present investigation has an important implication for the control of the grain boundary geometry : it is now admitted that the presence of serrations homogeneously distributed along the grain boundary can improve the crack growth resistance in superalloys. On the other hand, the development of very large fans in the materials are considered as detrimental from the standpoint of mechanical properties. It is therefore important to understand the conditions which favor the formation of one or another type of grain boundary geometry. Indeed such reaction products have already been observed in some commercial superalloys.

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Appendix A : Nolfi's model

The boundary conditions of the Nolfi's model (4) (with $C'(r,t)=C_{eq}-C(r,t)$, C_{eq} equilibrium concentration, $C(r,t)$ solute concentration in the matrix at the position r , R interface position, D coefficient of solute diffusion, K reaction rate constant) :

$$\left(\frac{\partial C'}{\partial r}\right)_{r=R_s} = 0 \quad (\text{VIII}) ; D\left(\frac{\partial C'}{\partial r}\right)_{r=R} - KC'(R) = 0 \quad (\text{IX})$$

The eigenvalues λ_n , δ_n are deduced from the equations (X) obtained by applying the boundary conditions to the expression $C'(r,t)$ (with $\beta = R/R_s$; $\alpha_n = \lambda_n R_s$; $\beta \cdot \alpha_n = \lambda_n R$; σ a constant reflecting the rate controlling mechanism $\sigma = (1+KR/D)^{-1}$) :

$$\tan(\alpha_n(1-\beta) - n\pi) = \frac{\alpha_n(1-\sigma\beta)}{1+\sigma\beta\alpha_n^2} \quad n = 0,1,2,3 \quad (\text{X})$$

$$\delta_n = \alpha_n - \tan^{-1}(\alpha_n)$$

By using the orthogonal properties of the Fourier function and the definition of the Fourier coefficient, Nolfi gets the expression of the constant A_n , C_n :

$$A_n = \frac{4\pi R_0^2 \Delta C_0 C_n (1-\sigma) \cos(\beta\alpha_n - \delta_n)}{\beta\alpha_n} \quad (\text{XI})$$

$$C_n = \left\{ (2\pi R_0) \left[\frac{(1-\beta)\alpha_n^2 - \beta}{\beta(1+\alpha_n^2)} + \frac{\sigma}{1+(\sigma\beta\alpha_n)^2} \right] \right\}^{-1/2}$$

The expression of the gradient of solute at the interface from the Nolfi's model (with $\tau_n = (\lambda_n^2 D)^{-1}$) :

$$\left(\frac{dC'(r,t^*)}{dr}\right)_R = \sum_{n=0}^{n_{\max}} A_n C_n \exp(-\lambda_n^2 D t^*) \left[\frac{\lambda_n}{r} \cos(\lambda_n r - \delta_n) - \frac{1}{r^2} \sin(\lambda_n r - \delta_n) \right] \quad (\text{XII})$$

Appendix B : Hillert's model (5)

Expression of the migration rate of the interface for discontinuous precipitation of rods (with r_β the radius of the rods, r_{tot} the total radius, X_0 the initial matrix composition, X_α the composition of the α phase and $X_{\alpha/\beta}$ the composition at α/β interface along the grain boundary, K constant distribution coefficient, δ thickness of the grain boundary, D_b grain boundary diffusion) :

$$v = 4K\delta D_b \cdot \frac{r_\beta}{r_{tot} \cdot (r_{tot}^2 - r_\beta^2)} \cdot \frac{(X_\alpha - X_{\alpha/\beta})}{(X_0 - X_\alpha)} \quad (XIII)$$

The rods and matrix thicknesses are related by mass balance with the following lever rule (with X_β composition of the β phase) :

$$\frac{(X_0 - X_\alpha^{av})}{(X_\beta - X_0)} = \frac{r_\beta^2}{(r_{tot}^2 - r_\beta^2)} \quad (XIV)$$

Expression of the reversible radius with σ surface tension, V_m molar volume, X_{eq} equilibrium concentration, G_α^m free energy of the α phase :

$$r_{rev} = \frac{2\sigma V_m}{(\partial^2 G_\alpha^m / \partial X^2) \cdot (X_0 - X_{eq})^2} \quad (XV)$$

In the situation of rod growth, r_{tot} can be deduced from r_β by the following expression (with k_α fraction of chemical energy contributing to the creation of the α/β interface, L_α fraction of pressure carried by the α phase, X_{eq} the equilibrium concentration and r_{rev} the reversible radius (5)):

$$(r_{tot}^2 - r_\beta^2) = \frac{k_\alpha r_\beta^3 (X_\beta - X_0)^2}{2L_\alpha (X_0 - X_{eq})^2 r_{rev}} \quad (XVI)$$