JOURNAL OF MATERIALS SCIENCE **40** (2005) 6207–6215

Precipitate growth activation energy requirements in the duplex size γ' distribution in the superalloy IN738LC

I. ROY
Materials Group, Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA, USA

E. BALIKCI
Department of Aerospace Engineering, University of Colorado, Boulder, CO, USA

S. IBEKWE
Mechanical Engineering Department, Southern University, Baton Rouge, LA, USA

A. RAMAN[*]
Materials Group, Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA, USA
E-mail: meraman@lsu.edu

The precipitate growth features in the duplex size (fine and coarse) precipitate distribution, obtained by quenching the alloy from the holding temperature of 1140°C, was studied by treating the alloy for various times in vacuum at selected temperatures in the range 800–1100°C. It was found that both the fine and the coarse precipitate particles grow with time, apparently aided by the particle movement in the matrix and coalescence, by the so-designated Precipitate Agglomeration Mechanism (PAM). At 1100°C the fine particles grew to the size of the coarse particles in about 100 hours and a near single coarse size of about 840 nm was obtained in the matrix. The activation energies for the growth of both the fine and coarse particles were calculated using particle sizes at different temperatures after 25 h of aging and at 1040 and 1100°C for different aging times. These were found to decrease continuously with an increase in size of the particles, meaning that the coarse particles grow more easily than the fine particles, requiring less activation energies. This behavior could be attributed to the greater attractive force with which the coarser particles would attract the finer particles.

1. Introduction

IN738LC is a modern, cast nickel-based superalloy utilized at high temperatures in gas turbine engine environments. Durability of this superalloy at high temperatures is dependent on the strengthening by the γ' $Ni_3Al(Ti,Nb)$ precipitates. The volume fraction of the precipitate phase in this alloy is about 40 to 43%.

The alloy is generally used at high temperatures in the duplex size distributed condition of γ'. The alloy's microstructure control and stabilization are necessary for its effective utilization at high temperatures. Developing suitable processes to reduce the grain size of the parent phase and preventing the growth of parent grains and precipitate particles are of fundamental importance in high temperature applications. The current study focuses on the stability of the duplex size γ' precipitate microstructure in the alloy IN738LC at high temperatures.

A standard heat treatment that is generally applied in the industry to IN738LC is a solution treatment at 1120°C—2 h/water quench (WQ) and a subsequent aging treatment at 850°C—24 h/furnace cooling (FC). This treatment gives the duplex size distribution for the γ' precipitates in the matrix. A microstructure with fine γ' precipitates develops if solutionizing is carried out at 1200°C—2 h/accelerated argon cooling (AAC) [1, 2]. Annealing at lower temperatures after this solution treatment leads to precipitate growth. Aging at 1120°C—24 h/WQ produces coarse size γ' precipitates of about 700 nm size. A further treatment of 1140°C-6 h/WQ produces a duplex size precipitate microstructure [3]. Furnace cooling from 1200°C showed the

---

[*] Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-005-3154-6

joining of fine particles to form coarser particles. Also, annealing specimens containing fine precipitates at high temperatures led to their growth and eventually to alignment of particles at some stage, causing the slow evolution of raft-like patterns. Two different γ' precipitate growth processes were observed in general—merging of smaller precipitate particles with adjacent smaller or larger precipitate particles by migration in the matrix (precipitate agglomeration by the Precipitate Agglomeration Mechanism-PAM) [2], and growth through solute absorption from the matrix (by the Ostwald Ripening Mechanism-ORM) [2–4].

The mechanism and growth characteristics of the γ' precipitate in the duplex size (fine and medium) distribution has been documented earlier by Footner and Richards [5] who treated the duplex precipitate size specimens at 750°C for 15000 h. (625 days). Their results demonstrated that a single coarse size is achievable after about 10,000 h (417 days) at 750°C. Moshtaghin and Asgari [6] who took up the study of coarsening of particles in the duplex size distribution in the alloy IN738LC found the area fraction of the primary (coarse) particles increasing with time, while that of the secondary (fine) particles decreased, when annealed for 3000 h (125 days) at 850°C. They also found that the growth of the secondary (fine) γ' particles (d^3 vs. t plot) deviated from the linear trend predicted by the LSW theory [7] for a given temperature, and, instead, showed a curvilinear trend, indicative of increased difficulty in their growth with increase in size. They suggested that this deviation of the coarsening kinetics from the linear behavior may be related to the elastic interaction of the particles in a coherent system.

The current research takes up this issue and critically analyzes the simultaneous growth features of both the fine and the medium size precipitate particles in the duplex size microstructure when the alloy samples with the duplex size γ' precipitate particles are heated for different lengths of time at temperatures in the range of 800–1100°C. Through determination of particle sizes after various holding times at different temperatures, the activation energies for the growth of both the fine and coarse γ' particles are determined using the LSW model and analyzed.

2. Experimental procedure

Small pieces of the alloy IN738LC, about 4 mm thick and 6 mm edge length, were wrapped in stainless steel foils, sealed in silica tubes in vacuum, and solution treated at 1200°C for 4 h. The tubes, each containing four to six samples, were quenched in cold water and then reheated at 1120°C for 24 h resulting in a coarse precipitate microstructure. The temperature was then raised to 1140°C and the coarse precipitates were allowed to dissolve partially into the matrix. Water quenching the capsules after 6 h at 1140°C yielded the starting γ' precipitate duplex size distribution [3].

The capsules were later broken and each sample was then wrapped in stainless steel foil and individually sealed under vacuum in silica capsules. They were heat treated at 800, 850, 900, 980, 1040 and 1100°C for periods of 1, 3, 7, 13, 25, 50, and 100 h. Six to eight capsules, each carrying one sample, were put in the furnace at one of the chosen temperatures. Only selected times among those given above were adopted at the different temperatures and these are given in Table I along with the heat treatment schedule followed. The samples were individually removed after the specified time periods at the given temperatures and quenched in cold water. Cold water quenching was to retain the

TABLE I Heat treatment schedule and Sizes of precipitate particles for IN738LC after different treatments

Annealing Temp.°C ↓	Annealing Time (h) →	Precipitate Sizes (μ m)						
		1	**3**	**7**	**13**	**25**	**50**	**100**
800	Microstructure	X				X	X	
	Fine	0.06				0.12		
	Coarse	0.31				0.38		
850	Microstructure					X		
	Fine					0.21		
	Coarse					0.48		
900	Microstructure		X		X	X	X	
	Fine					0.28		
	Coarse					0.55		
980	Microstructure	X	X	X	X	X	X	X
	Fine					0.37		
	Coarse					0.64		
1040	Microstructure	X	X	X	X	X	X	
	Fine	0.21	0.25	0.3	0.35	0.44	0.55	
	Coarse	0.48	0.525	0.58	0.64	0.69	0.73	
1100	Microstructure	X	X	X	X	X	X	X
	Fine	0.3	0.355	0.390	0.440	0.520	0.625	0.84
	Coarse	0.56	0.6	0.650	0.70	0.736	0.775	0.84

1. *Treatment undergone by the as-received material*: Cast from the melt + hipping at 1185°C – 2 h/argon cooling to room temperature (RT) + solution treating at ~1120°C – 2 h/ argon cooling to RT + aging at 843°C – 24 h/argon cooling to RT. The as-received material showed a duplex size distribution for the precipitates with sizes around 500 and 150 nm, respectively [2].

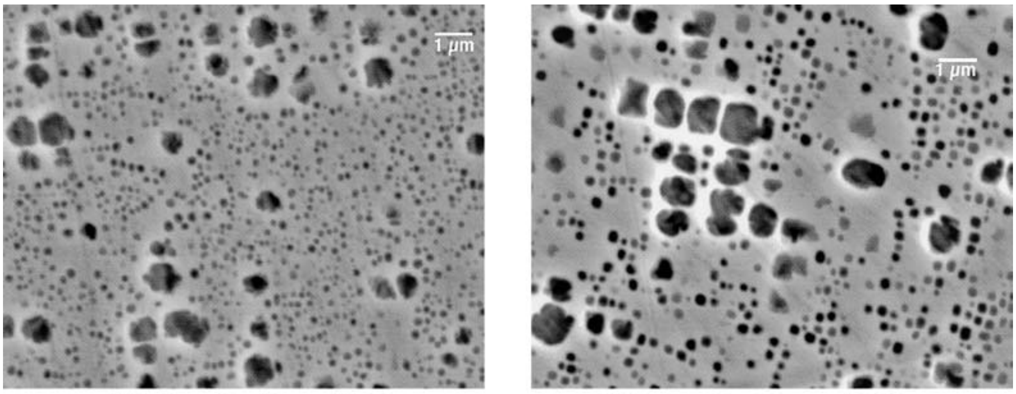
2. *Initial treatment in vacuum to produce duplex size precipitate microstructure* 1200°C – 4 hr/water quench to RT + 1120°C – 24 h + 1140°C – 6 h/water quench to RT. This produces fine cooling precipitates in the matrix along with partially dissolved medium size precipitates.

3. Precipitate coarsening treatments in vacuum for the duplex-treated samples (subsequent quenching in water to RT after treatment) and precipitate particle sizes (X in the rows of microstructure refers to specimen that has been analyzed using an SEM).

precipitate sizes in the microstructure after the given reheating.

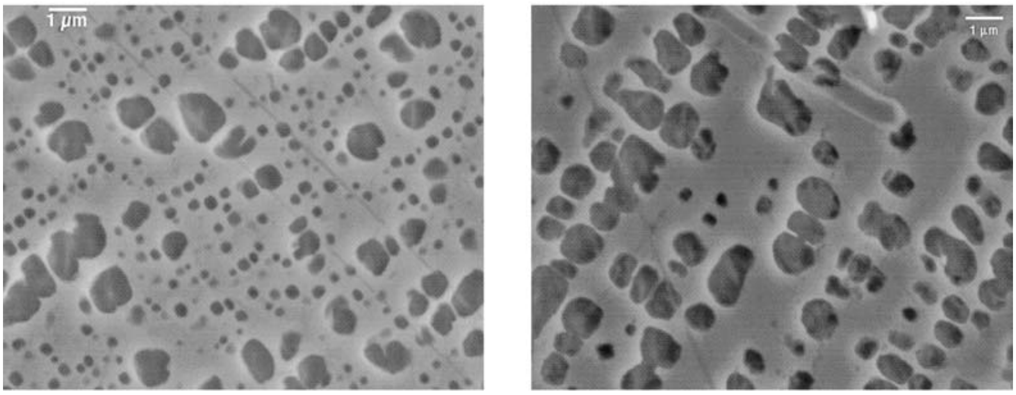
For precipitate microstructure studies, the samples were ground using grinding papers with coarse 120 to fine 600 grit size abrasives and polished on rotating wheels with fine alumina powder of size down to 0.05 micron. After cleaning, they were etched with a solution of composition 33% HNO_3 + 33% acetic acid + 33% H_2O + 1% HF (vol.%) [3]. A JEOL 840A Scanning Electron Microscope (SEM), equipped with an ultra-thin window Energy Dispersion Spectrometer (EDS), was used to characterize the size, morphology and composition of the precipitate particles.

Microstructures were digitally recorded using a Macintosh Quadra data acquisition and control system and analyzed for precipitate grain size later. Sizes of about 100 small precipitate particles and as many medium size coarse precipitates as available in the pictures were determined manually by measuring the lengths along several diagonals and averaging those for each case. The sizes for both the coarse and fine particles measured this way were found to lie in a small range for each, with particles near a single size for each being dominant. The average sizes of particles were then obtained for both the fine and coarse precipitates from the dominant size data collected. These average precipitate sizes for both the fine and the coarse particles are also incorporated in Table I. Precipitates in selected microstructures were also analyzed for composition using the EDS attached to the SEM. Photomicrographs were generally recorded at 2500, 8000 and 16000×. Some of these micrographs are reproduced in Figs 1–3. In these figures the magnification is maintained at 8000×



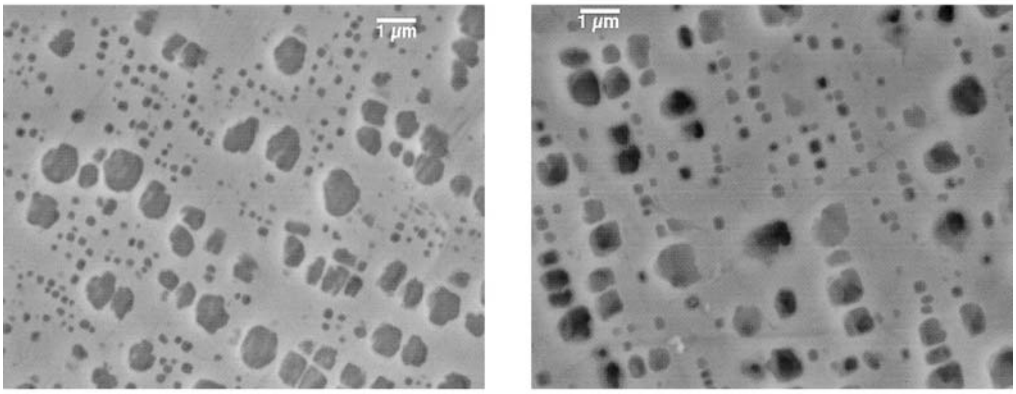
1040 Deg C - 1 hour / WQ

1040 Deg C - 7 hours / WQ



1040 Deg C - 13 hours / WQ

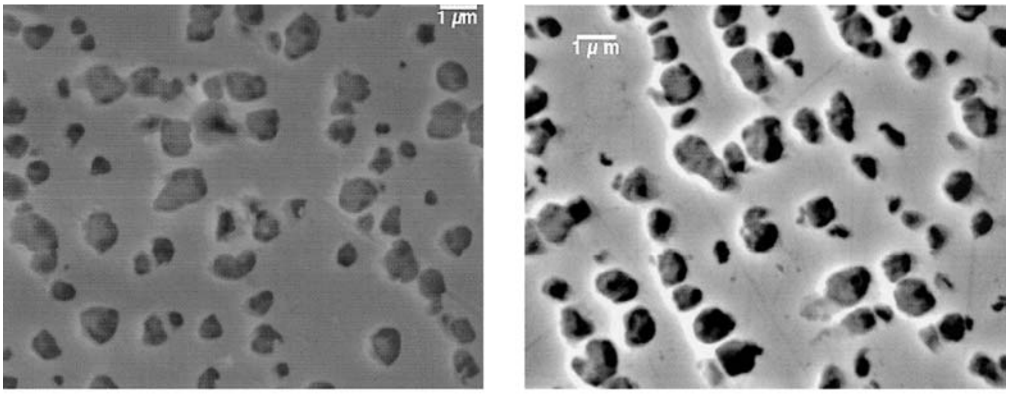
1040 Deg C - 50 hours / WQ



1100 Deg C - 1 hour / WQ

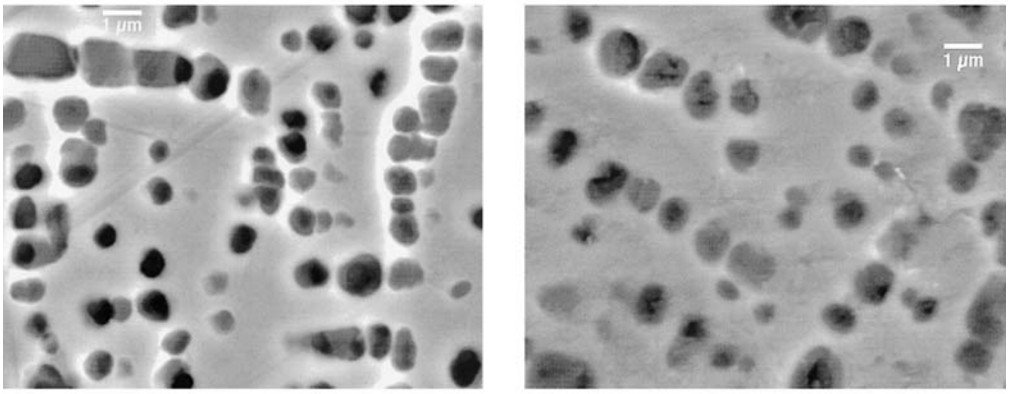
1100 Deg C - 3 hours / WQ

Figure 1 Microstructures obtained after annealing for various times at 1040 and 1100°C. (*Continued.*)



1100 Deg C - 7 hours / WQ

1100 Deg C - 13 hours / WQ



1100 Deg C - 50 hours / WQ

1100 Deg C - 100 hours / WQ

Figure 1 (*Continued*).

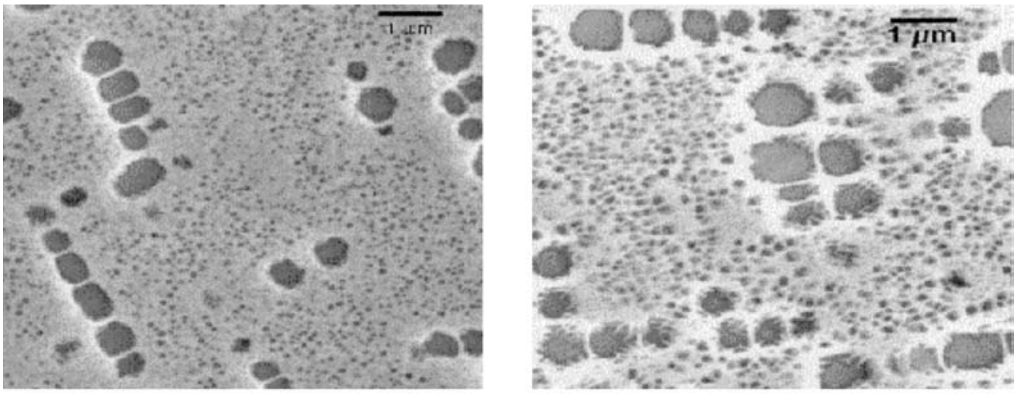
to facilitate direct comparison between the different microstructures.

3. Results and discussion

Both the fine and medium size γ' precipitates grew with time at a given temperature (e.g., 1040°C). Fig. 1 shows the microstructures obtained after annealing for various times at 1040 and 1100°C, respectively. Precipitate shapes and sizes obtained after 25 h heat treatments at the different temperatures used are shown in Fig. 2. It is seen that the growth is slow at lower temperatures, whereas the growth rate is noticeably high at 1040 and 1100°C, as expected. The fine precipitates are found not only to join with each other and coarsen, they also merge with the adjacent medium size precipitates, coarsening them further (see Fig. 3). The fine precipitates gradually coarsen to the size of the growing medium size coarse precipitates and after a certain time interval a single unimodal coarse size is realized throughout, in line with the observations of Footner and Richards [5]. Thus, nearly single size coarse precipitates were found after only 100 h of treatment at 1100°C (compare with 10,000 h at 750°C [5]). It is thus established that the duplex sized precipitates would grow faster at higher temperatures and ultimately become single sized coarse particles. The particles also line up and form rafts. Further heat treatments are underway using longer holding times at 1100°C in order to determine the maximum size attainable for the coarse precipitates.

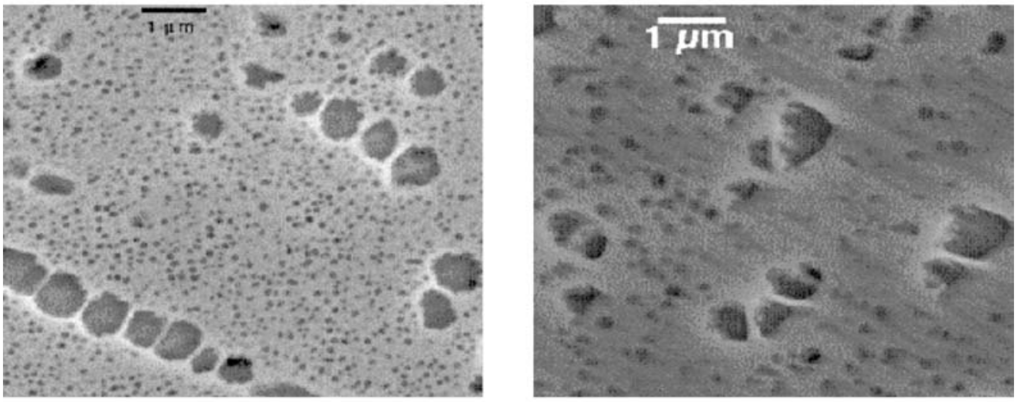
Treating the fine-precipitate-containing alloy at 1120°C for longer times showed earlier that the precipitates would grow to a certain maximum size beyond 700 nm and then begin to dissolve partially even at 1120°C [3]. (1130–1150°C is judged to be the normal range for precipitate's partial dissolution and duplex precipitate size evolution upon quenching). Similar dissolution could occur at 1100°C after a much longer time. This possibility is also under further study.

Agglomeration of fine particles with each other and also with the coarse ones, contributing to coarsening by the Precipitate Agglomeration Mechanism (PAM) [1], was found in the microstructures of a few heat treated samples at the initial stages, such as the one in Fig. 3. PAM postulates the prevalence of an attractive force of sufficient magnitude between adjacent precipitate particles when there is considerable strain energy present in the matrix due to misfit between the matrix and the precipitate. The strain energy is elastic in nature and evolves due to the volume misfit, as well as the interfacial structural misfit between the two. In addition, the precipitate, being much stiffer than the matrix, exerts a force on the softer matrix proportional to its mass. The total strain energy can be reduced considerably by merging adjacent particles, which translates into an attractive force between the particles, one that becomes significant when the particles are close to each other and their strain fields overlap. The strain energy would increase also with increasing size of the particles. Hence coarser particles would exert a larger force on smaller



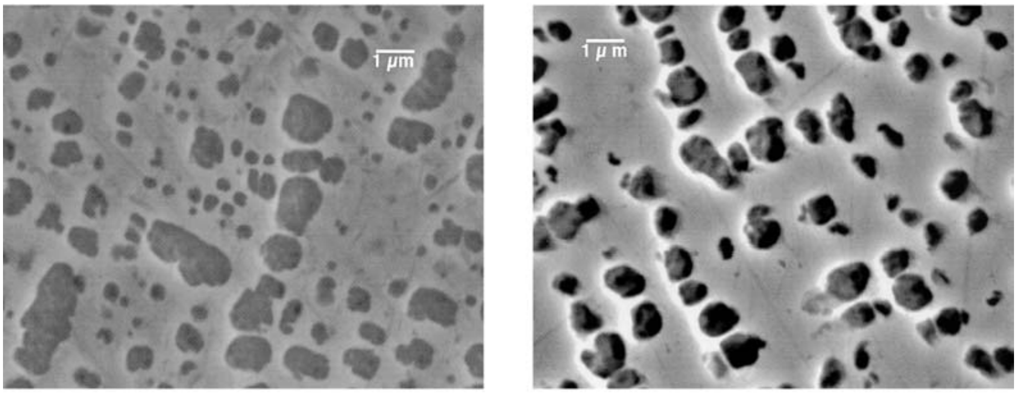
800 Deg C / 25 hours / WQ

850 Deg C / 25 hours / WQ



900 Deg C / 25 hours / WQ

980 Deg C / 25 hours / WQ



1040 Deg C / 25 hours / WQ

1100 Deg C / 25 hours / WQ

Figure 2 Precipitate microstructures obtained after 25 h heat treatments at the different temperatures given.

particles and the agglomeration of the finer ones with the coarser would be lot easier than the agglomeration of the fine ones with the adjacent fine ones. It can also be noted here that because of agglomeration there will be a precipitate denuded zone around such consolidated coarser particles as well.

It is apparent from microstructure analysis that the particles in the duplex precipitate size microstructure attract the nearby ones through elastic interactions and join with them, leading to their coarsening by the agglomeration process, simultaneously denuding the zone around them from the fine ones. Note that the fine particles join with each other too forming coarser particles (and the fine ones near the coarser ones merge with the latter), an observation that Moshtagin and Asgari seem to have overlooked.

From the sizes of precipitates obtained from different microstructures and the temperatures and times involved, the molar activation energy for the growth process for both the fine and the coarse precipitates were calculated using the LSW formula:

$$d_t^n - d_0^n = Kt, \text{ where } K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

wherein d_0 is the initial size of the particle to start with at $t = 0$, d_t is the size after a heating time of 't' at the temperature T, n is the growth exponent (generally assumed to be 3 for volume diffusion control), and Q is the molar activation energy for the growth process [4]. It is not certain, however, whether this equation, originally given by Lifshitz and Slyazov [7] and Wagner

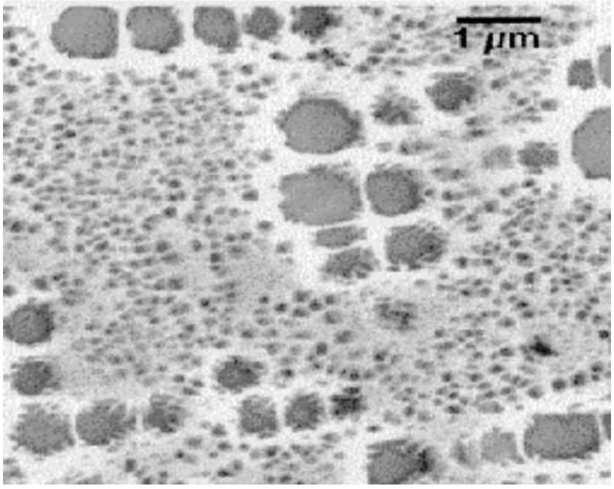


Figure 3 Agglomeration of fine particles with each other and with the coarse ones contributing to coarsening by the Precipitate Agglomeration Mechanism (PAM).

[8], would still be valid for the precipitate growth by the Precipitate Agglomeration Mechanism, although the latter could still involve some volumetric diffusion of atoms in the agglomeration process.

Size data obtained are plotted in Fig. 4 for the 25 h treatment at different temperatures and in Fig. 5a and b for different times at 1040 and 1100°C, respectively. The data in Fig. 4 are replotted as ln d vs. $1/T$ plots in Fig. 6. The plots in Fig. 6 were found to have three nearly linear segments in the temperature ranges 800–850, 850–900, and 900–1100°C. From the slopes of these linear segments, the corresponding Q values were obtained. Each Q value was then taken to prevail in the corresponding temperature range and was plotted in a separate figure against the mean temperature, as Q vs. mean T plots (Fig. 7). These data points appear as small markers in the figure. Data points for 850, 900 and 980°C were obtained from the corresponding d values by interpolation and their values are shown by larger markers in the plot. Values for the first two temperatures are close to the averages obtainable from the Q values of the two straight line segments going through these two points. Corresponding to temperatures of all of these data points in the plot the d values were known (or could be obtained from the equations of straight lines given) and using this data Q vs. d data was plotted in Fig. 9 (plots for 25 h treatment at different temperatures).

From the data of precipitate sizes at the two temperatures 1040 °C and 1100°C (given in Fig. 5), activation energy Q for the precipitate growth process could be calculated from the two values of the size data for each of the coarse or fine precipitates corresponding to the two temperatures for a specific time. These Q values, the lower for the coarse and the higher for the fine, were taken to prevail in the temperature range 1040–1100°C and were taken corresponding to the mean temperature 1070°C for the specific holding time. Fig. 8 gives the plots of Q for coarse and fine particle growth vs. holding time 't' for the mean temperature 1070°C. From the average of the logarithms of the precipitate sizes at the two temperatures for a given holding time the size of the precipitate at the mean temperature for the corresponding holding time could be obtained and the above Q vs. 't' plots could be converted to corresponding Q vs. d plots. These plots are also included in Fig. 9 (plots for mean temperature 1070°C for different times). The data for the plots given in Fig. 9 are given in Table II.

The results obtained show that the activation energies for the growth of coarse precipitate particles are smaller than the analogous values for the growth of fine ones. There is a continuous decrease in the activation energy for the growth of the coarse or fine particles with an increase in temperature (25 h data at different temperatures). The activation energy for the growth also is found to decrease with increasing size of the precipitate particle by increasing the holding time at a given temperature (data from 1040 and 1100°C, represented for the mean temperature 1070°C), for both the fine and coarse precipitates. The data for the coarse particles from both of the above sets fall nearly on a continuously falling curve toward the tail end of the plots. Slight offset is seen, however, between the two sets of data for the fine precipitates and this can be attributed to scatter in the size data of fine precipitate particles

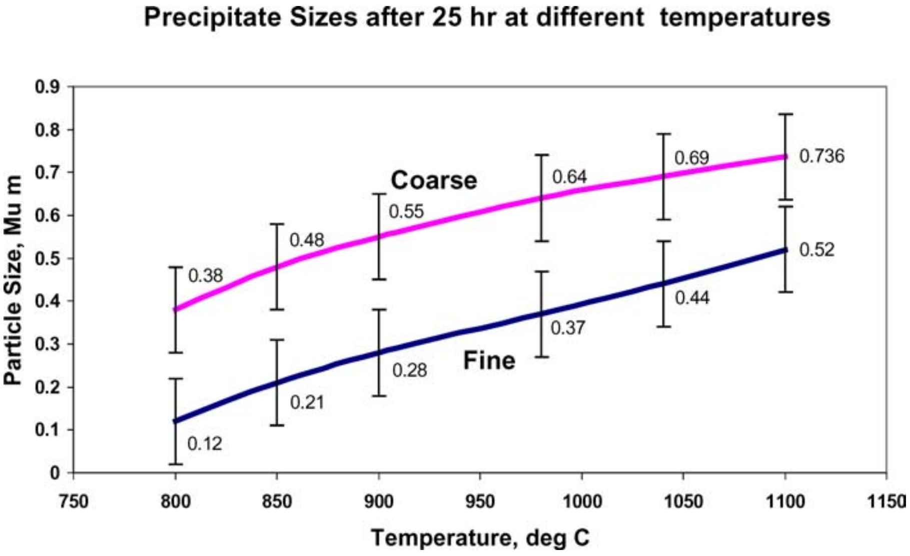


Figure 4 Plot of precipitate size data obtained for the 25 h treatment at different temperatures.

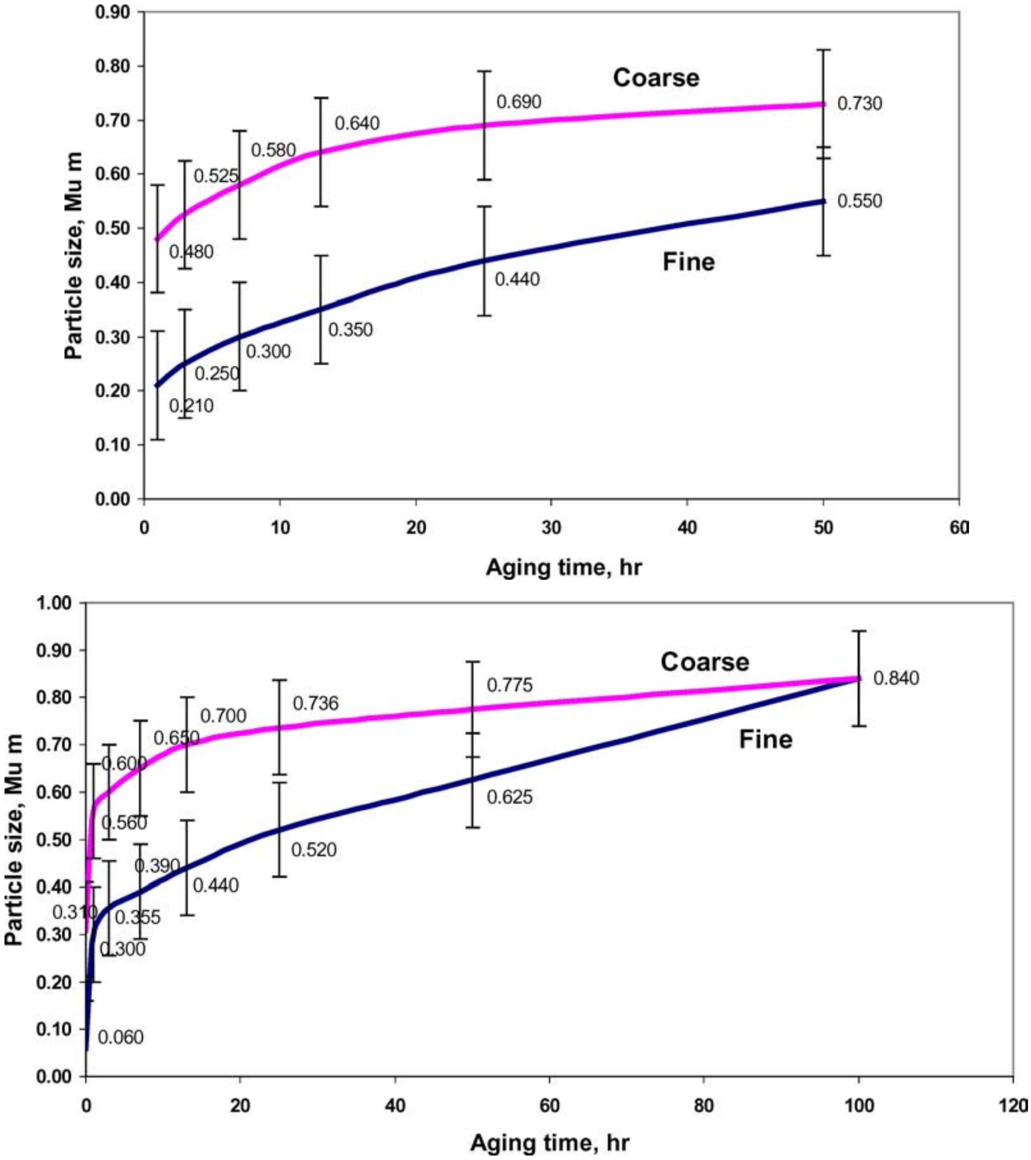


Figure 5 (a and b) Plots of precipitate size data obtained for different times at 1040 and 1100°C, respectively.

in the various microstructures at different temperatures leading to possible inaccuracies in the estimation of the average sizes.

Fig. 9 also shows the best fit mean curve (dotted) for the variation of Q with d. This curve is represented by the polynomial: $y = 6E - 10x^4 - 3E - 06x^3 + 0.0035x^2 - 2.1934x + 612.52$, where $y = Q$ and $x = d$. Further work is needed to correlate variation of Q with other parameters such as d^2 (proportional to precipitate surface area) and d^3 (proportional to precipitate volume).

The above results clearly indicate that the activation energy for the growth of precipitate particles in the duplex size range is not a constant, but depends on the size of the particles. It decreases with increasing size of the particles in the duplex structure, which implies that the coarser particles grow more easily in the duplex structure, needing less activation energy, than the finer particles. This can be attributed to the elastic interaction, as Moshtaghin and Asgari [6] point out, and to larger attractive force (enunciated in the PAM model [1]) the coarser particles would exert on the finer particles, while the corresponding agglomerating force would be weaker for the finer ones. The larger attractive force from the coarser particles would make it easier for the fine particles to move in the matrix and this

TABLE II Data for Fig. 9 giving Q vs. d (d in nm and Q in kJ/mol)

$d_{1070-\mathrm{f}}$	$Q_{1070-\mathrm{f}}$	$d_{1070-\mathrm{c}}$	$Q_{1070-\mathrm{c}}$	$d_{25\mathrm{h}-\mathrm{f}}$	$Q_{25\mathrm{h}-\mathrm{f}}$	$d_{25\mathrm{h}-\mathrm{c}}$	$Q_{25\mathrm{h}-\mathrm{c}}$
252.58	267.3	513.8	102.02	122.24	336.64	374.23	140.52
291.4	233.39	559.195	92.96	211.45	250	468.4	110
336.3	196.62	609.26	78.97	285.07	189.17	545.75	89.51
390.19	171.48	659.69	67.1	364.6	150	636.69	68.3
458.26	133.77	714.84	52.38	420.77	120	686.01	51.46
583.95	95.75	754.85	44.82	504.9	101.52	726.69	42.23

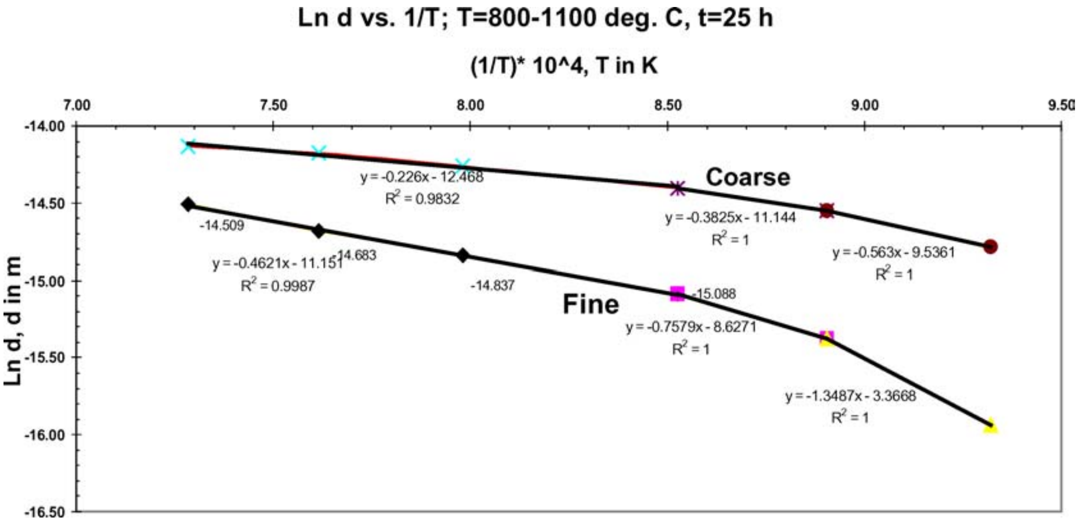


Figure 6 The precipitate size data in Fig. 4 shown as ln *d* vs. 1/*T* plot.

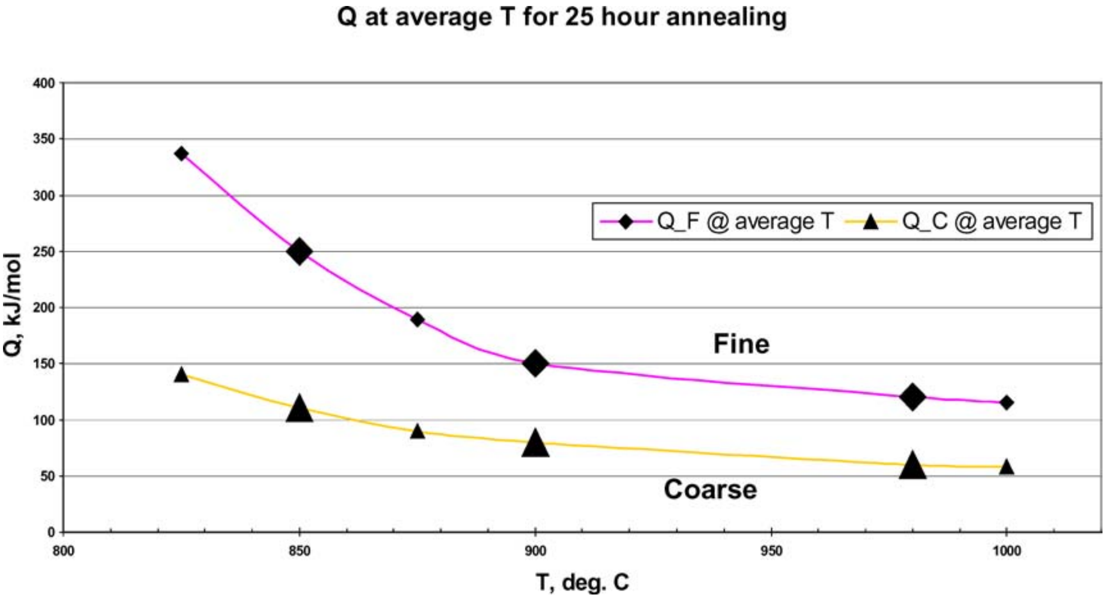


Figure 7 *Q* vs. *T* plots for 25 h annealing. (825, 875 and 1000°C are mean temperatures, while 850, 900 and 980°C are actual temperatures used).

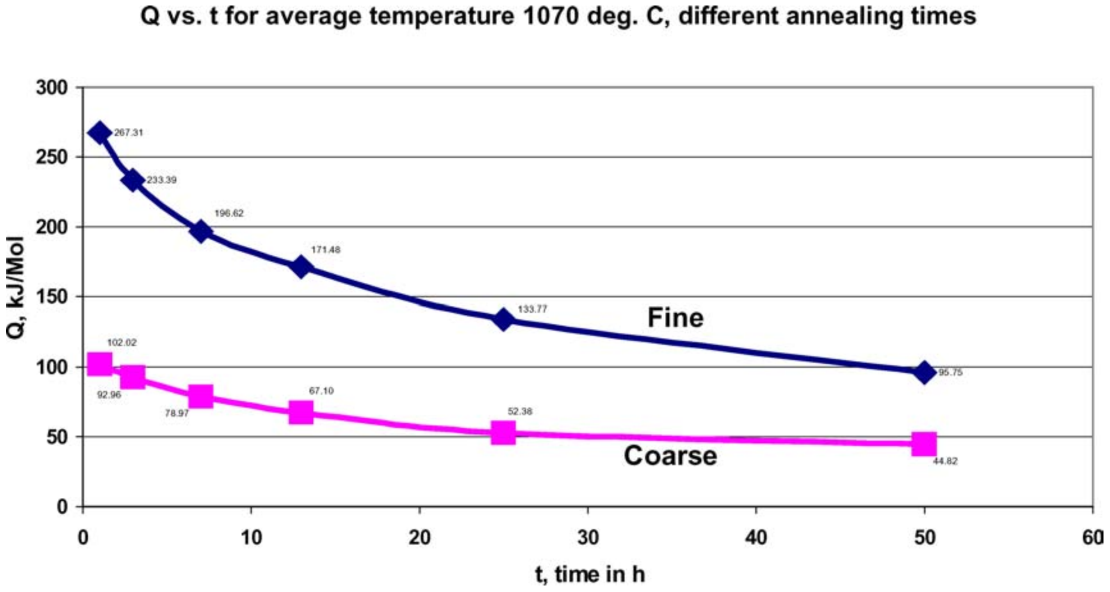


Figure 8 *Q* vs. holding time ‘*t*’ for the mean temperature 1070°C.

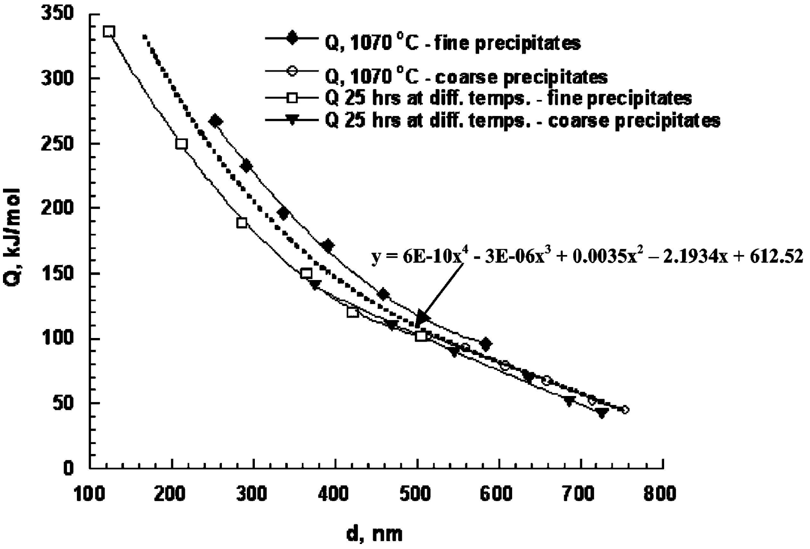


Figure 9 Q vs. 'd' plots for the average precipitate sizes at the mean temperature 1070°C corresponding to various times, and for different temperatures for 25 h annealing time.

apparently leads to a reduction in the activation energy needed for particle agglomeration and the resultant size increase. Since the attractive force will increase with the increase in size of particles, progressively, there is also less activation energy needed to consolidate the adjacent particles and contribute to the size increase of the particles. Thus, the results obtained in this study reinforce the Precipitate Agglomeration Mechanism-PAM, enunciated earlier for the growth of particles in the duplex size precipitate microstructure [1].

Acknowledgments

Support from NASA through a DGAP Grant, No. NASA(2000-01)-DGAP-08 and a NASA/LEQSF(01-05)-LASPACE project, sponsored through the LA Board of Regents and LaSPACE consortium, is sincerely appreciated.

References

1. ERCAN BALIKCI, PhD Dissertation (LSU, Baton Rouge, LA, May 1998) p. 51.
2. ERCAN BALIKCI, A. RAMAN, and R. MIRSHAMS, *Met. and Mat. Trans. A* **28A** (10/1997) 1993.
3. ERCAN BALIKCI, A. RAMAN, and R. MIRSHAMS, *Zeitschrift für Metallkunde* **90** (2/1999) 132.
4. D. A. PORTER and K. E. EASTERLING, "Phase Transformations in Metals and Alloys", 2nd edn. (Chapman & Hall, New York, 1993) p. 44, 116, 314.
5. P. K. FOOTNER and B. P. RICHARDS, *J. Mater. Sci.* **17** (1982) 2141.
6. R. S. MOSHTAGHIN and S. ASGARI, *Mater. and Desi.* **24** (2003) 325.
7. I. M. LIFSHITZ and V. V. SLYOZOV, *J. Phys. Chem. Solids* **19** (1961) 35.
8. C. WAGNER, *Z. Elektrochemie* **65** (1961) 581.

Received 12 March 2004
and accepted 6 May 2005