Effects of Heat Treatment on Prior Particle Boundary Precipitation in a Powder Metallurgy Nickel Base Superalloy

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Abstract. PPB precipitation in powdered Rene'95 is analyzed. The effects of PHT on PPB precipitation are studied. It is found that fracture along PPB is ductile in microscale. During PHT, the phase transformation on powder surface is similar to PPB interface. PHT cannot reduce the degree of contamination on powder surface. But the precipitates on surface are coarsened. The coarsening enlarges distances between precipitates. As the result, microfracture property is improved at PPB.

1. Introduction

In powder metallurgy processing of nickel base superalloys, special care has to be taken to eliminate the adverse effects of prior particle boundary (PPB) precipitation [1]. The problem is resulted from powder surface contamination. The surface contamination originates from solidification segregation and surface adsorption [2]. On the surface of argon atomized (AA) Rene'95 powder, the contents of carbide formers Nb, Ti and oxide former Zr are enriched. Abundant ZrO_2 and other oxides and M'C carbides are found on the surface [2]. Many other researchers have contributed to the studies in the area, as can be found in a comprehensive review by R. Thamburaj et al. [3]. Although several approaches from pre-consolidation treatments, consolidation parameters and post consolidation heat treatments have been put forward to tackle the defect, up to now the most effective and reliable is still large deformation processing, such as hot extrusion (HEX) or hot isothermal forging (HIF). The deformation processes are very expensive and often provide challenges to the facilities available. So other cost-effective and reliable methods are yet to be desired.

For the past few years, research on the control of PPB precipitation through powder heat treatment (PHT) has been undertaken in the Institute of Aeronautical Materials. PHT processing was first proposed by Dahlen et al. [4]. It was deduced that the treatment can stabilize carbides in form of MC or $M_{23}C_6$ in interior of powders, so that they will not reprecipitate at PPB on hipping [4, 5]. The initial trial introduce of the method to Rene'95 was very successful in our laboratory [6]. After processing ductility of directly hipped material is doubled. Furthermore, it is found that the underlining mechanism is different from that by Dahlen [4]. The details of analyses and results are reported in the paper.

2. Experimental

The alloy selected for study is Rene'95. The powders were −150 mesh commercial blends atomized in argon. Details about powder composition can be found in [2]. After degassing

and canning, the canned powder was soaked at pre-selected temperatures to undergo PHT processing. The treated powder can be either analyzed by microstructural characterization methods or consolidated by HIP.

ESCA and Auger spectroscopy were utilized to investigate segregated species and their compounds on powder surface and fracture surface of consolidated materials. TEM examination and EDS analysis of extraction replica were made to identify surface precipitates. Quantitative metallurgraphy was used to measure the size of precipitates both inside powder and on powder surface. Thin electron transparent films parallel and transverse to tensile axis were cut from room tensile fractured specimen to study the behavior of PPB precipitates under deformation.

Bulk material was ground down to 600 grit abrasive paper and electrolytically polished in an electrolyte of 80% ethyl alcohol and 20% perchloric acid at 30 volts at room temperature. The polished surface was characterized by the above methods to form a basis standing for bulk composition for further comparison.

3.   Results

3.1.   Identification of PPB precipitation in directly HIP compacted materials

The fractography of hip compacts without PHT has a spherical morphology ruptured along PPB. Auger spectra recorded from the fracture surface show that there is only slight enrichment of sulfur, other interfacial elements were not observed, Fig. 1. Depth profiling results shown in Fig. 2 reveals that particles of carbides and oxides are formed at PPB, because as etching proceeds, maximum peaks of carbon and oxygen appear at sub-surface. The decrease of carbon and oxygen intensity with etch depth is also very gradual.

TEM observation of HIP compacts shows that PPB precipitates are much finer in size than carbides inside powders. The former usually ranges from 0.05 to 0.15 μm, the latter has a size of about 0.5 μm. These PPB precipitates line up along PPB in very high density, delineating the bonding interface between adjacent powders. Figure 3 is a TEM micrograph of PPB precipitation. STEM + EDS analyses prove that the particles have very high Zr and
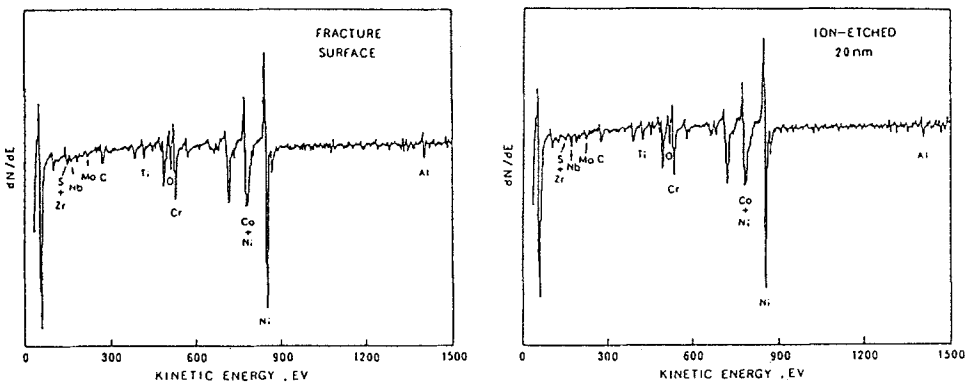

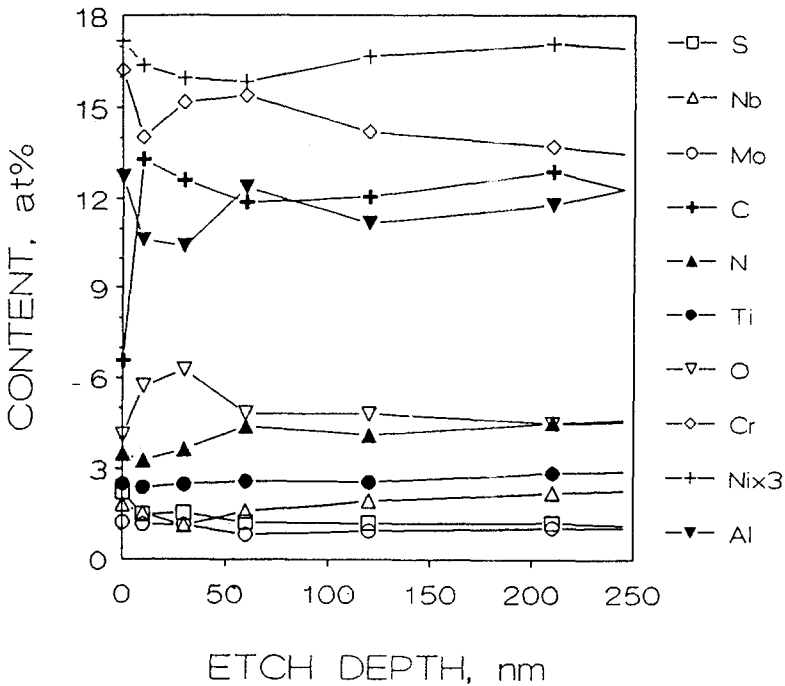*Figure 1.*   Auger spectra recorded from surface fractured along PPB.

Figure 2. Auger depth profiling of surface fractured along PPB.

Nb contents [2, 6]. Diffraction analysis shows that most of them are ZrO_2 oxides and MC carbides. $M_{23}C_6$, M_6C carbides and Cr_2O_3, Al_2O_3 oxides are also observed [7].

Figure 4 is a high magnification SEM picture of the fracture surface of HIP compact. The fracture is ductile in microscale. In the dimples there are fine particles, which are identified enriched with Zr or Nb. These are the PPB precipitates observed by TEM analysis in Fig. 3. Transmission electron micrograph of thin foils taken from tensile specimen is shown in Fig. 5. Voids are observed at PPB precipitate-matrix interface.

3.2. Surface chemistry and precipitation behavior on heat treated powder surface

ESCA spectra recorded from ion etched surface of heat treated powders are shown in Fig. 6 for strong oxide formers. Less stable Zr, Cr, Al, Ti and Nb are oxidized. More stable metallic elements Ni, Co, W, and Mo are not oxidized.

Compared to as-received powder surface [2], thermodynamically more stable oxides such as Cr_2O_3 and NbO_2 are formed on PHT surface. Figure 7 shows the compositional changes on etched surface of powders processed at different temperatures. The marked difference is that Zr contents on heat treated surface are much higher than that on AA surface and the bulk content, irrespective of processing temperatures. At intermediate PHT temperatures, Al content is lowered. W content decreases as PHT temperature increases. But generally, PHT does not decrease the quantity of oxides on the surface, which is well demonstrated in Fig. 8. The figure is obtained by splitting the contents in Fig. 7 into two separate parts in oxide state and in metallic state according to ESCA peak deconvolution. Zr, Cr and
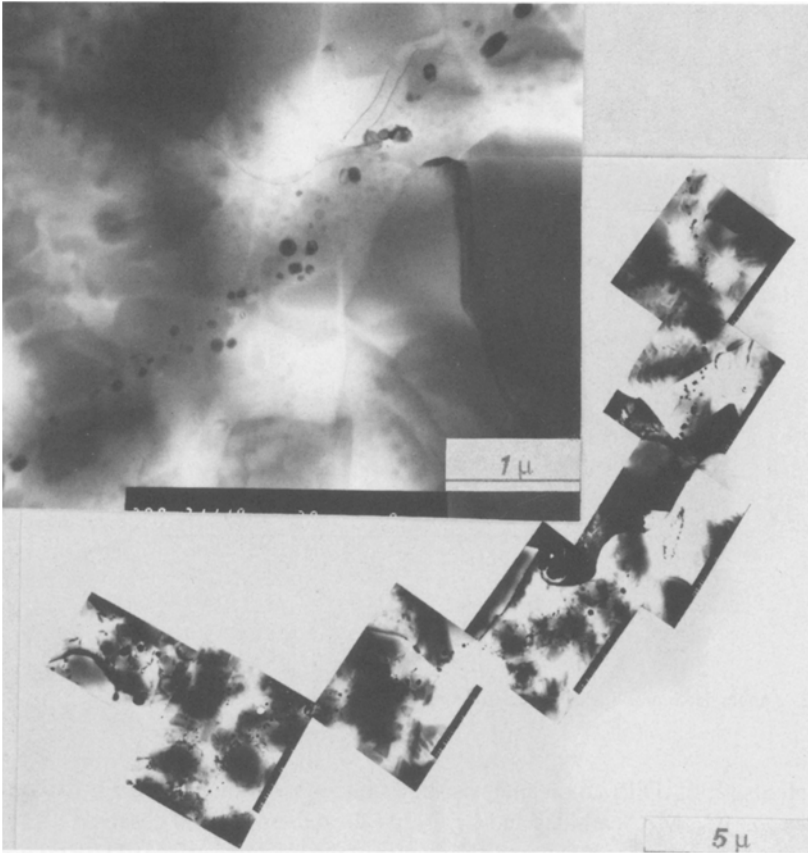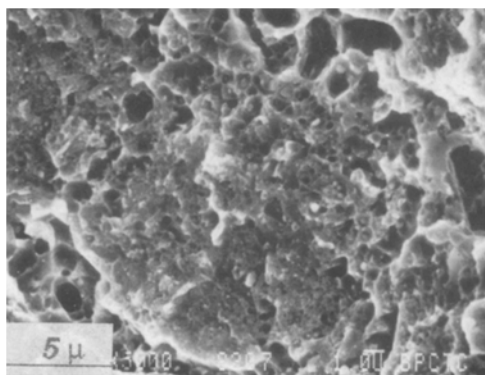
Figure 3.   TEM micrograph of PPB.

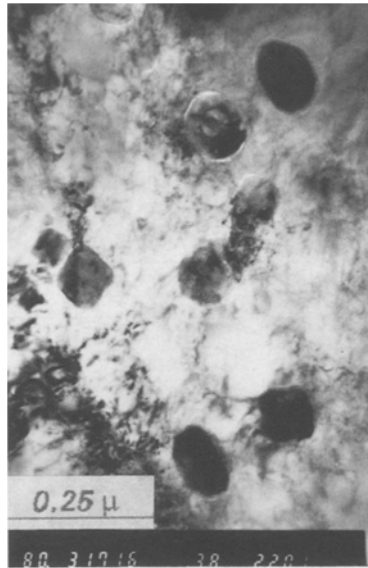*Figure 4.*   Fractography of PPB failure.

Figure 5. Voids at PPB-matrix interfaces in materials strained to 12%.
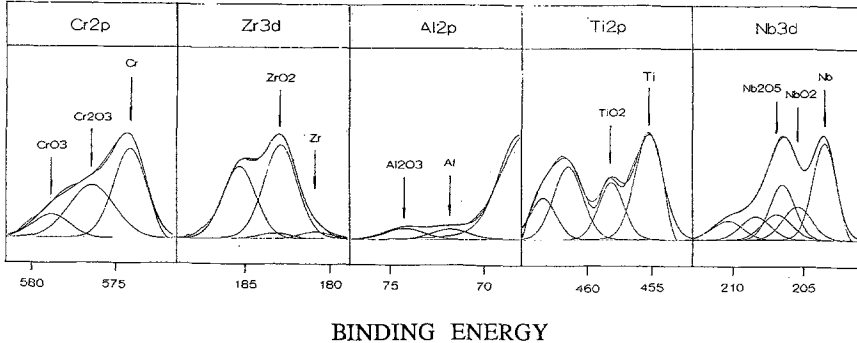

BINDING ENERGY

Figure 6. ESCA spectra recorded from PHT powder surface for oxidized elements.

Nb oxides are increased, Ti in oxide state remains about the same level as on AA surface. Therefore, oxides are more abundant on PHT surface than on AA surface and polished bulk surface. It can be concluded that after PHT the amount of oxides on powder surface is not decreased. As to carbides, the energy shifts for the metallic elements in carbides from their elemental states solutioned in matrix are very small, their contents cannot be determined by ESCA. But surface replica taken from PHT powder surface shows that primary M'C carbides located at interdendritic area on AA surface are still present on PHT surface [7]. They do not dissolve in matrix during PHT. They are transformed to MC with normal composition and lattice parameters. Besides, small secondary carbides precipitate between large primary carbides at surface oxides, as shown in Fig. 9. These newly formed carbides usually have very high contents of Zr. Table 1 lists the EDS results. As PHT time is

Table 1. Composition of surface precipitates in Rene'95 after PHT at 1064°C for different time by EDS (wt%).

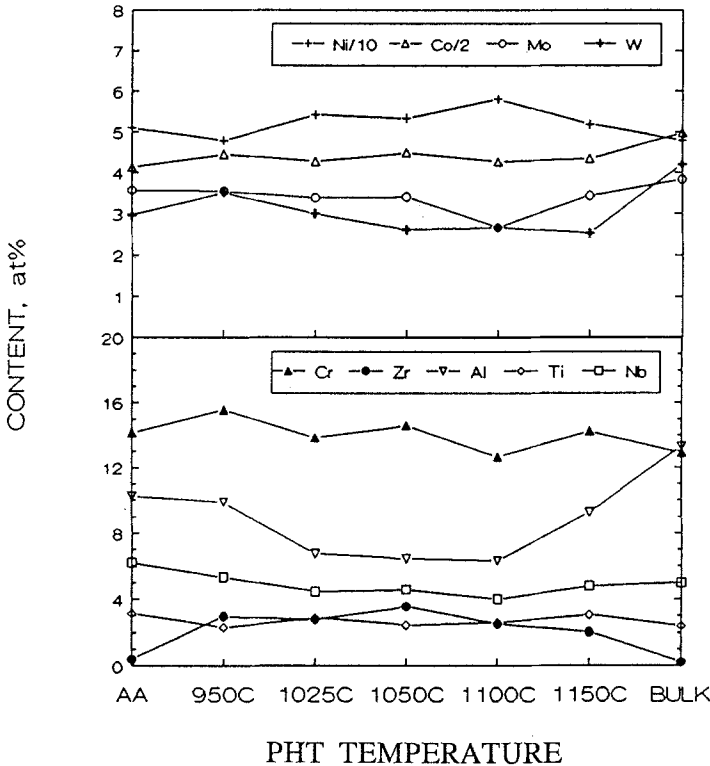| Hr	Type	Al	W	Nb	S	Ti	Cr	Zr	Mo
2	Primary	2.26	16.56	41.64	3.11	15.12	9.58	5.23	4.47
	Secondary	1.94	13.77	32.91	1.92	14.15	11.08	16.39	6.06
4	Primary	1.41	12.38	57.75	4.84	11.78	2.56	2.41	4.84
	Secondary	1.85	23.28	37.21	1.88	7.38	3.67	18.10	4.62

PHT TEMPERATURE

Figure 7. ESCA depth profiling of PHT powder surface.

prolonged, W content is decreased, Nb content is increased. EDS and diffraction analyses indicate that the surface precipitates are still MC, $M_{23}C_6$, ZrO_2 and other oxides, as in the case of PPB in HIP compacts without PHT.

The surface analysis results and phase analysis are intercorrelated. ZrO_2 oxides and Cr/Al oxides are found by both methods. The transformation of M'C to MC on the surface reduces W content in carbides. At high temperatures and longer processing time, W content is lower. The variation of Al content is complicated. In our research work, Al is found very sensitive to oxidation environment and prolonged storage. After PHT, contents of Al in metallic state are all lowered. The general trend may be related to γ' transformation. Research work is now under way to find the cause.

The size of precipitates on powder surface and carbides in the interior of powder is measured for a number of powders processed at different temperatures and times. The
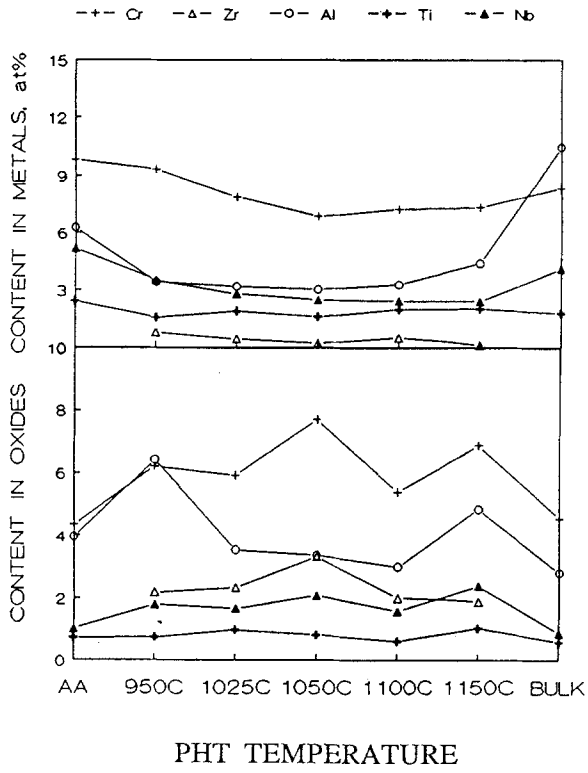
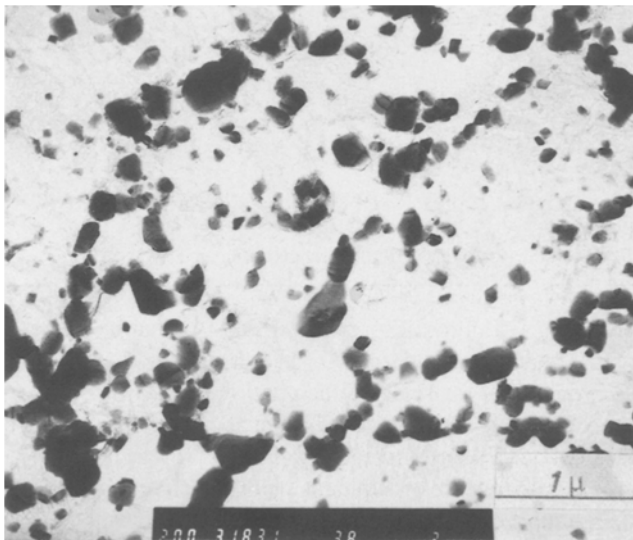*Figure 8.* Contents in oxides and in metallic states on PHT powder surface.

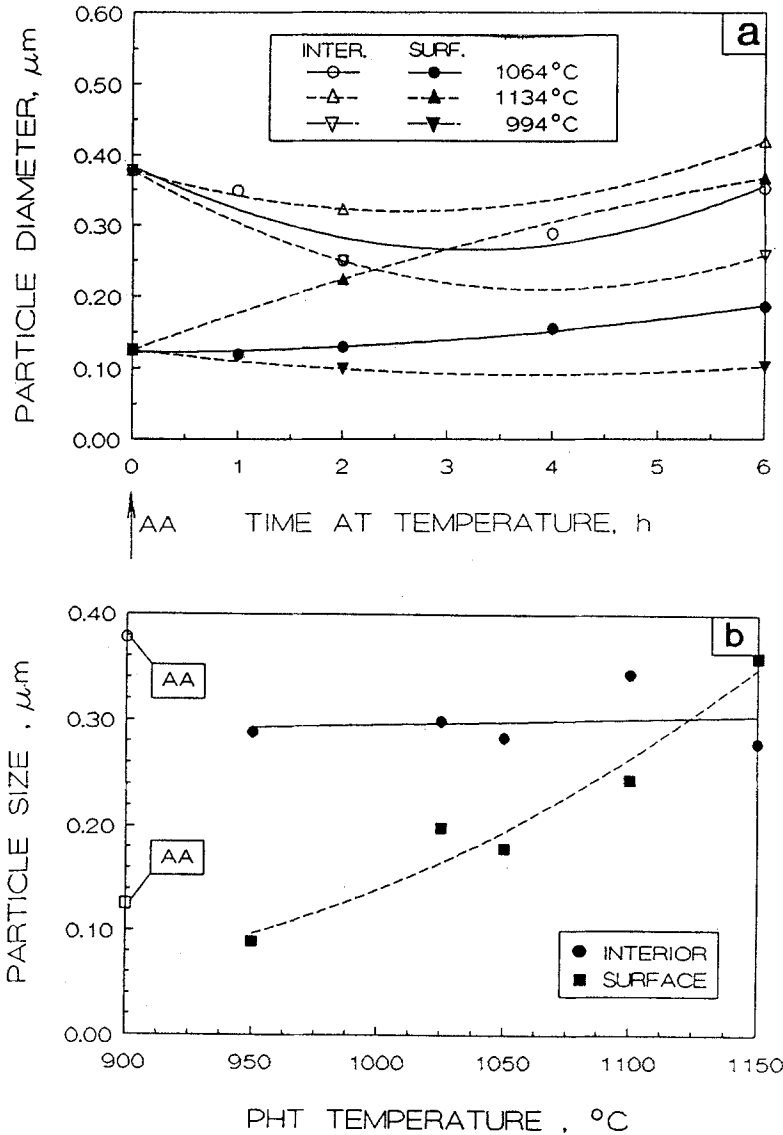*Figure 9.* TEM micrograph of replica taken from PHT powder surface.

*Figure 10.* Variation of particle sizes with PHT temperature and time.

results are shown in Fig. 10. From Fig. 10a and Fig. 9 it can be drawn that precipitates both on powder surface and in powder are formed through a complex process of $M'C \rightarrow MC$ transformation of primary carbides, precipitation and growth of secondary carbides and reduction and coarsening of oxides. So the averaged size of particles first drops down then goes up, especially at lower temperatures. Figure 10 reveals that when processed at high enough temperatures, surface precipitates will coarsen more quickly than carbides in powder. Their sizes may eventually exceed those of the carbides in the interior of powder.

PPB precipitation in PHT compacts is presented in Fig. 11. PPB particles are much coarser and sparsely populated. On impact fracture surface, little of PPB morphology can
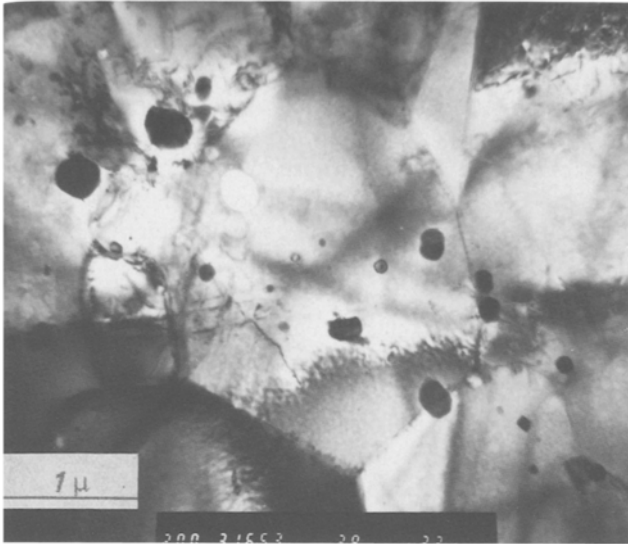
Figure 11.   TEM micrograph of PPB in a PHT processed compact.
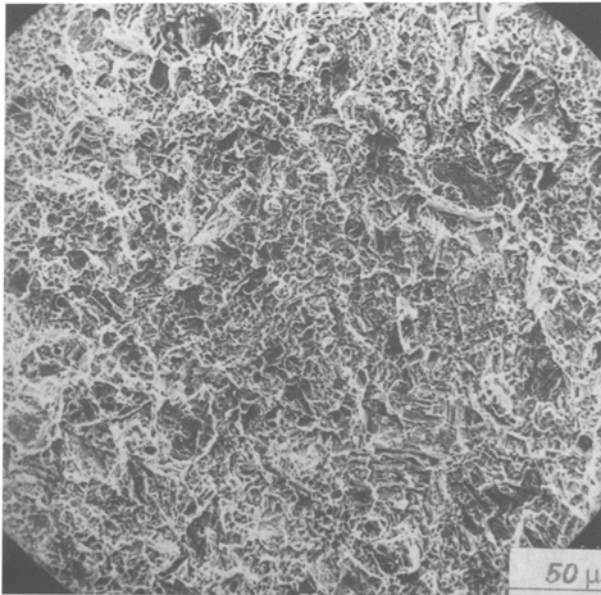
Figure 12.   Impact fracture surface of PHT compact.

be found, Fig. 12. The ductility of materials from PHT processed powder is two times that without PHT [6]. SEM observation of limited LCF specimen shows that no PPB origin was found in PHT processed compact, while for HIP compacts without PHT about 50% of the origins were PPB.

4. Discussion

On as-received powder surface carbides and oxides are present. In PHT process, the surface carbides do not dissolve and diffuse into powder interior. They are transformed to more stable ones. New carbides are added onto the surface from supersaturated matrix. Fine oxide particles on AA surface are changed to more stable larger particles. The total amount are also increased. The surface compositional changes and phase transformations on PHT surface is just like those at HIP PPB interface. Therefore, phase transformation and homogenization of solidification segregation can not explain the strong influence of PHT on PPB failure.

Microfracture analysis gives us a more deep insight into the PPB problem. Brittle fracture along PPB is ductile in micromechanism. Voids first occur at PPB precipitate-matrix interface when applied strain, and more specifically, the interfacial stress resulted from dislocations piled up at the precipitates reaches a critical limit. The growth and coalescence of these voids result in final rupture. Therefore, according to the dislocation theory developed by Ashby [8] for microdimple fracture, the distance between PPB precipitates should be increased in order to strengthen PPB interface.

Of all the possible sources of increasing interparticle distance on powder surface, the reduction of precipitation rate of secondary carbides on surface seems unlikely, though an uncontact surface can reduce the nucleation rate for secondary carbides [7]. Because on AA surface, numerous oxides are present, secondary carbides can precipitate readily by the oxide nuclei. Precipitation coarsening is the determining factor in enlarging the distance between particles. When powder is soaked at PHT temperature, uncontact free surface of powder promote the coarsening of carbides. For heavily alloyed nickel base superalloys like Rene'95, carbides are usually very stable up to 1200°C. So on PHT the total volumetric amount of precipitates on surface remains almost constant once the precipitation stage is finished. When precipitates there are coarsened, their sizes are increased, the distances between the particles will be enlarged simultaneously. The relation between distance and particle size can be obtained by mathematical reasoning as

$$\lambda/\rho \propto \sqrt{\rho} \tag{1}$$

where λ is averaged center-to-center distance between particles, ρ is averaged particle diameter. The increased interparticle distance as a result of rapid coarsening of surface precipitates will improve the microfracture property in the vicinity of PPB, and so to increase the ductility of compact.

Experiments clearly show that the rapid coarsening on surface is free surface related. The underlining mechanism is possibly short-circuit surface diffusion, but we need further research work to clarify it.

5. Conclusions

1. PPB failure of HIP compacts is ductile in nature. The rupture is not caused by any interfacial segregation species. Voids are first formed at PPB precipitate-matrix interface as a result of dislocation pile-up and stress concentration at the site.
2. PHT neither changes the surface segregation situation of AA powder, nor the type of precipitates. After processing, surface carbides and oxides are more abundant.

3. The surface of PHT powder undergoes a complex process of phase transformation, precipitation and coarsening. Surface precipitates are quickly coarsened at high temperatures. The coarsening process enlarges the distance between particles at the same time. Therefore the microfracture behavior near PPB is improved to eliminate final rupture along it.
4. PHT enhances the ductile properties of HIP consolidated P/M Rene'95.

Acknowledgment

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