# THE INFLUENCE OF PROCESSING VARIABLES ON THE MICROSTRUCTURE

# AND PROPERTIES OF PM 625 ALLOY

# James H. Davidson

TECPHY, Centre de Recherches d'IMPHY S.A. 58160 Imphy, France

## Abstract

The mechanical properties, corrosion resistance and microstructure have been studied in PM 625 alloy compacts as a function of the consolidation temperature and subsequent heat treatment conditions.

Superalloys 718, 625 and Various Derivatives Edited by Edward A. Loria The Minerals, Metals & Materials Society, 1991

### Introduction

Alloy 625 is now firmly established as an attractive candidate material for critical corrosion-limited marine engineering applications. For certain difficult-to-make components, particularly when produced in relatively small series, a HIPed-to-shape production route can be both cost-effective and technically advantageous [1].

However, compared to conventional cast or cast-and-wrought products, powder metallurgy leads to certain specific features, particularly as regards carbon, oxygen and nitrogen levels and microstructure.

The aim of the present work was to study the influence of the consolidation and subsequent solution treatment temperatures, in order to obtain an optimum combination of properties.

### Materials and experimental techniques

The experimental materials were produced from an industrial heat of nitrogen-atomized powder, sieved to  $\leq$  150  $\mu m$ . Table I gives the chemical analysis obtained from a densified compact.

Ni	Cr	Мо	Nb	С	0	N	Si	Mn	S
Bal	20.39	8.61	3.41	0.0130	0.0410	0.0300	0.183	0.015	0.0012
Р	Ti	A1	Zr	Fe	Cu	W	V	Co	
0.0070	0.010	<0.005	0.0065	0.204	<0.005	0.092	0.044	0.014	

Table I : Chemical analysis (wt. %)

Five 10 kg, ~ 80 mm diameter billets were produced by hot isostatic pressing (HIP) at 100 MPa for 3 hours at 950, 1000, 1050, 1100 and 1150°C. The average cooling rate in the autoclave down to about 600°C is ~  $5^{\circ}$ C mn<sup>-1</sup>. Test-piece blanks and micrographic specimens cut from these billets were solution annealed for 1 hour at the same five temperatures, followed by water quenching, or were left in the as-HIPed condition.

Standard tensile tests and Charpy V-notch impact tests were performed at room temperature. Intergranular corrosion resistance was assessed using the ASTM G28A test (120 hours exposure in boiling ferric sulfate-50 % sulfuric acid). In all cases, the results presented correspond to mean values for two tests.

Microstructures were studied using optical micrography and scanning electron microscopy, together with transmission electron microscopy and EDS, WDS and EELS analyses on extraction replicas.

### Results

### Tensile tests

The tensile test results are illustrated in figures 1a and 1b, as a function respectively of the HIP and solution annealing temperatures. There is a general tendency for the proof stress and ultimate tensile strength to decrease with a rise in either of these two temperatures when the other is kept constant. When one of the temperatures is high, the effect of the other is attenuated. For a given consolidation temperature, the rupture elongation increases with solution annealing temperature, whereas when the latter is held constant, the ductility reaches a maximum for a HIP temperature of 1100°C.



Figure 1 : Effect of HIP and annealing temperatures on the 20°C tensile properties.

### Impact tests

Figures 2a and 2b show that the Charpy V-notch impact strength varies in a similar manner to the tensile elongation, the effects tending to be somewhat more marked. Thus, the toughness increases continuously with solution treatment temperature and is doubled when a billet densified at 950°C is subsequently annealed at 1150°C. A maximum is again observed for a HIP temperature of 1100°C.



Figure 2 : Effect of HIP and annealing temperatures on the 20°C Charpy V-notch impact strength.

# Intergranular corrosion tests

The weight losses measured in the G28A tests, converted to uniform corrosion rates  $(mm.yr^{-1})$ , are reproduced in figures 3a and 3b. All values fall in the range from 0.5 to 1 mm.yr^{-1}, which represents a satisfactory level for 625 alloy. While there is considerable scatter, an overall trend is observed towards lower values and more uniform behaviour at higher HIP and solution treatment temperatures.



Figure 3: Effect of HIP and annealing temperatures on the G28A corrosion resistance.

### Microstructure

The powder particle solidification structure remains clearly visible after consolidation at low temperatures, figure 4a. When densification or solution treatment is carried out at higher temperatures, recrystallization, grain growth and precipitate dissolution lead to more homogeneous structures (figure 4b).



Figure 4 : General microstructure. Optical micrographs. Electrolytic etch in 50 % HCl, 50 % CH<sub>9</sub>COOH. (a) 950°C HIP (b) 1150°C HIP + 1150°C anneal.

The influence of consolidation and solution temperatures on grain size is shown in figure 5. In the as-HIPed condition, a slight grain size refinement is observed when the densification temperature is increased from 950 to 1000°C, followed by gradual coarsening at higher temperatures. This minimum subsists after solution treatment and suggests that recrystallization is less complete at the end of the 950°C HIP cycle.



Figure 5 : Effect of HIP and annealing temperatures on the ASTM grain size.

Even at 1150°C, many prior powder particle boundaries are still decorated by precipitates. This is illustrated in figure 6, which shows the relative abundance of precipitate phases for different treatments. Thus, when the final cycle temperature is 1150°C, the amount of precipitates is considerably less than in the material as-HIPed at

950°C (compare figures 6a, b and d). The precipitate density in the 1150°C consolidated material is increased by solution treatment for 1 hour at 950°C, but apparently remains less than that obtained after HIPing for 3 hours at 950°C (compare figures 6a and c). Attempts to obtain a more quantitative evaluation of precipitate densities by selective dissolution of the matrix were unsuccessful due to its high chemical resistance.



<u>Figure 6</u>: Abundance and distribution of precipitate phases. Optical micrographs. Electrolytic etch in 2 % aqueous HF solution. (a) 950°C HIP (b) 950°C HIP + 1150°C anneal (c) 1150°C HIP + 950°C anneal (d) 1150°C HIP

The nature of the phases present was studied on carbon extraction replicas for a representative selection of thermomechanical treatments. EDS analysis performed in a transmission electron microscope enabled 4 major phases to be distinguished, designated for convenience A, B, C and D. Table II reproduces the principal characteristics of these phases, while table III gives a semi-quantitative representation of their relative abundance. In the latter case, it should be noted that, because of the subjective nature of these evaluations, the differences in the abundance ratings are more significant within a given sample than from one treatment to another. The identifications indicated in table II are based on a combination of the electron diffraction patterns and the chemical compositions. This is particulary true in the case of phases A and D, identified respectively as "M<sub>6</sub>C" and "M<sub>23</sub>C<sub>6</sub>", since these two structures are quite difficult to differentiate by simple electron (or X-ray) diffraction. Phase C was identified as MC carbide, while the B phase appears to be a tetragonal MN-type nitride.

Although the majority of these compounds are designated as "carbides", the relative amounts of carbon, oxygen and nitrogen in the overall alloy composition suggested that the latter two elements should also be present. Only the  ${}^{m}M_{23}C_{6}$ " particles were small enough to be studied by EELS analysis, which indeed revealed the presence of oxygen. This was confirmed by WDS analysis of the replicas in an electron microprobe, which also indicated the presence of nitrogen, although in this case measurement was made difficult

by their small size. The other phases were also found to contain nitrogen, apparently decreasing in the order B, C, A, D. In the case of phase A, oxygen was also detected. The presence of carbon is assumed, but only for phase A was the carbon signal markedly higher than for the surrounding replica (and only in one particular replica). These results will be discussed further in the following section.

ſ			Number of	Composition range in at. % and (mean)							other	Identifi-
Phase	Size (µm)	particles analyzed	Ni	Cr	Мо	NĐ	Si	A1	Ti	ocher	cution	
	A	1-2	18	25-32 (28)	15-23 (18)	24-31 (27)	16-22 (17)	4-7 (5)			C,N,O	™ <sub>6</sub> C
	B	1-5	15		25-32 (27)	16-21 (20)	49-54 (51)				N.(C)	MN
	С	1-5	15			1-7 (4)	85-97 (93)				N,(C)	MC
	D	0.1-0.5	22		80-92 (85)				1-4 (2)	2-12 (8)	N,O,(C)	M <sub>23</sub> C <sub>6</sub>

<u>Table II</u> : Characteristics of precipitate phases

<u>Table III</u>	:	Relative	abundance	of	precipitate	phases
------------------	---	----------	-----------	----	-------------	--------

Phase	Heat treatment cycle										
	HIP 950°C	HIP 950°C + ST 950°C	HIP 950°C + ST 1150°C	HIP 1050°C + ST 1050°C	HIP 1150°C	HIP 1150°C + ST 950°C	HIP 1150°C+ ST 1150°C				
A	4	4				1					
В	1		2	3	3	3	3				
с			3	2	3	3	3				
D	3	3	3	3	3	3	3				

key : 4 = abundant, 3 = fairly abundant, 2 = rare, 1 = very rare

### Discussion

### Microstructure

Gas-atomized powders have solidification structures which can vary greatly from one particle to another, being generally equiaxed/cellular or dendritic in nature [2,3]. Segregation can be marked, but is on a very fine scale, and can therefore usually be greatly attenuated by subsequent heat treatment.

In the present case, while the 3 hour HIP cycle at 950°C is sufficient to produce 100 % densification, relatively little homogenization has occurred, and the decrease in grain size when the consolidation temperature is raised to 1000°C suggests more extensive recrystallization than at 950°C. Grain size increases generally with HIP and/or annealing temperature, reaching ASTM 6 (~ 45  $\mu$ m) at 1150°C. While the trend appears to accelerate for HIP cycles between 1100 and 1150°C, probably due to precipitate dissolution, it cannot be assumed that it would continue to do so at even higher temperatures, since the maximum powder particle size is 150  $\mu$ m and particle boundaries tend to inhibit grain growth [3]. It can be seen in figure 9 that considerable powder surface decoration remains at 1150°C.

The " $M_{23}C_6$ " - type precipitates are apparently associated mainly with prior particle surfaces and represent the major constituent decorating these sites. In spite of their small size, they remain stable over the temperature range studied, contrary to their behaviour in cast and wrought 625 alloy [4]. This stability may be due to the presence of oxygen and nitrogen. However, significant concentrations of titanium and aluminium were also detected (table II), and the possibility of separate oxide and/or nitride nuclei cannot be excluded.

When the HIP or annealing temperature does not exceed 950°C, abundant precipitation of an " $M_6C$ " - type phase is observed, containing Ni, Mo, Cr, Nb and Si, together with significant amounts of nitrogen and oxygen. The composition of this phase, at least as regards the metallic elements, is quite similar to that found in conventional 625 alloy [4].

At 1050°C and above, the " $M_6$ C" is replaced by Nb, Mo carbides or carbonitrides M(C,N), together with a nitrogen-rich Nb, Cr, Mo-containing phase. Electron diffraction studies suggest that the latter has a tetragonal structure (a = 0.434 nm, c = 0.789 nm) similar to that of (Nb, Cr) N [5].

### Tensile properties

Three different origins can be envisaged for the decrease in strength with increasing treatment temperature : recrystallization and recovery of the as-HIPed structure, grain growth and precipitate solutioning. However, the small effect of low temperature annealing after high temperature consolidation suggests that precipitation hardening plays only a minor role.

The rise in ductility with temperature is a natural consequence of the decrease in strength, in spite of grain coarsering. Acceleration of the latter between 1100 and 1150°C probably explains the maximum ductility observed for a HIP temperature of 1100°C.

#### Impact strength

The impact strength varies with heat treatment in a similar manner to the tensile ductility. Examination of the fracture surfaces reveals a certain number of decohesions at prior powder particle surfaces, becoming slightly rougher and less numerous as the maximum cycle temperature increases, figure 7a to d. At high magnification, the powder particle surfaces are seen to be covered with a network of fine dimples, about 0.5 - 1  $\mu$ m in size, formed around particles with dimensions in the range from 0.1 to 0.5  $\mu$ m, figure 7e and f. This is true for all treatments. For higher temperature cycles, such areas are interspersed with rougher, more ductile zones. Even in areas where interparticle decohesion is not clear, the overall contours of the powder grains can be discerned, figure 8g, and regions of dimples containing 0.1 - 0.5  $\mu$ m precipitates are still observed, figure 8h. Only the "M<sub>23</sub>C<sub>6</sub>" phase at prior powder surfaces corresponds to this size range. Larger particles at dimple centres were only observed occasionally. The extent of powder surface decoration is thus seen to have a dominant influence on impact fracture.

### Corrosion resistance

Micrographic examination of the G28A test specimens reveals that, for low maximum cycle temperatures, corrosion follows zones of chemical segregation, and certain powder particles are attacked preferentially, figures 8a and 8b. When the structure is more homogeneous, after high temperature treatment, corrosion occurs by pitting at grain boundaries, and overall metal loss is lower, the machining grooves remaining clearly visible, figures 8c to f. Comparison of figure 8c with figures 8d and e indicates that a 1 hour anneal at 1150°C, followed by rapid cooling, leads to less attack than a 3 hour HIP treatment at the same temperature, with slow cooling in the autoclave.



<u>Figure 7</u>: Scanning electron micrographs of impact specimen fracture surfaces. (a) 950°C HIP (b) 1150°C HIP + 1150°C anneal (c) 950°C HIP (d) 950°C HIP + 1150°C anneal (e) 950°C HIP, smooth interparticular fracture (f) 1150°C HIP + 1150°C anneal, smooth area of interparticular fracture (g) 1150°C HIP + 1150°C anneal (h) 950°C HIP + 1150°C anneal, area away from regions of clear interparticular fracture.



Figure 8 : Scanning electron micrographs of G28A specimen surfaces. (a) and (b) 950°C HIP (c) 1150°C HIP (d) 950°C HIP + 1150°C anneal (e) and (f) 1150°C HIP + 1150°C anneal.

## Conclusions

The microstructure and characteristics of PM 625 alloy are strongly influenced by the choice of consolidation and annealing temperatures, and by suitable adjustment of these parameters, ASTM grade 1 properties can be ensured in HIPed-to-shape parts.

Compared to conventional 625 grade, the air-melted and nitrogen-atomized PM version differs in its carbon, oxygen and nitrogen contents. The precipitate phases tend to include nitrogen and/or oxygen in addition to carbon.  $M_{23}C_6$ " "carbides" at prior powder particle surfaces remain stable up to at least 1150°C. As in the cast-and-wrought equivalent, "M<sub>6</sub>C" and "MC" phases are also found. "M<sub>6</sub>C" is stable at 950°C, but at and above 1050°C, it is replaced by "MC", together with a nitrogen-rich Nb-Cr-Mo phase, identified as a tetragonal MN-type "nitride".

#### References

- 1. M. Abouaf, J.L. Chenot, T. Bauduin, G. Raisson, Mém. Sci. Rev. Mét., 83 (1986) 325-334.
- 2. J.H. Davidson, C. Aubin, <u>High Temperature Alloys for Gas Turbines 1982</u>, R. Brunetaud et al. Ed., Reidel, Dordrecht, Oct. (1982), pp. 853-886.
- 3. T.C. Lu, O. Faral, J.H. Davidson, Y. Bienvenu, <u>The Materials Revolution through the 90's</u> BNF Metals Technology Centre 7th International Conf. Oxford, July (1989), paper 13.
- 4. R. Cozar, M. Rouby, B. Mayonobe, C. Morizot, Paper presented at the present conference.
- 5. P. Ettmayer et al., Monastsh. Chem., 102 (1971) 858.