THE INFLUENCE OF POWDER PARTICLE SURFACE COMPOSITION ON THE PROPERTIES OF A NICKEL-BASED SUPERALLOY PRODUCED BY HOT ISOSTATIC PRESSING

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The present work was carried out on PM Astroloy with varying C, O and S contents, produced either by argon atomisation (mean particle diameter 60 µm) or by the notating electrode process (mean particle diameter 450 µm). The first aim was to examine the microstructure and the composition of the particle surfaces and to determine the nature and the quantity of the gases desorbed during heating under vacuum. The experimental techniques employed were transmission electron microscopy, Auger electron spectroscopy and mass spectrometry. For the different types of powder, significant variations were observed in the amounts of amorphous and combined carbon as well as in the quantity of the adsorbed species. The second goal was to study the relation between surface analysis and the mechanical properties after densification. Significant effects of carbon and oxygen levels were observed on tensile, impact and creep properties, whereas, within the limited range of concentrations investigated, the influence of sulphur content could not be cleanly established.

INTRODUCTION

While numerous investigations have emphasised the importance of powder particle surfaces in determining the properties of PM products, few experimental studies have been devoted to the subject. In the case of superalloy powders, the deleterious effects of carbides segregated at prior particle boundaries has been known for a number of years (1), and has led to the development of special low carbon grades (2). However, it is possible that other elements, such as sulphur or oxygen, segregated or adsorbed at prowder surfaces, may also play a part in the weakening of interparticle boundaries (3,4,5). Furthermore, it is known that the conditions of powder production, together with the conditioning treatments applied before canning, play a decisive role in determining the quality of the densified product (6,7). The purpose of the present research was to evaluate the effects on mechanical properties of carbon, sulphur and oxygen at powder particle surfaces and to distinguish between segregation related to the solidification process and adsorption due to atmospheric contamination.

MATERIALS

Astroloy powders were produced by both argon atomisation (AA) and by the CLET rotating electrode process (RE). In the case of AA powders, particles of diameter greater than 160 μm were eliminated, whereas for the RE powders the upper limit was 630 μm . The mean particle sizes obtained in this way (50 % by weight above and below) were \sim 60 μm and \sim 450 μm for AA and RE powders respectively. One batch of RE powder was also screened to exclude particles greater than 250 μm , giving a mean diameter of \sim 200 μm . No particular precautions were taken to prevent containation, all handling being carried out in air. The powders were canned in bild-steel containers, sealed by electron beam welding after degassing in vacuum at room temperature, and then densified to billets of approximately 2,5 κM . Hot isostatic pressing (HIP) was carried out in argon at 100 NPa; at 1140°C for the gas-atomised and fine RE powder and at 1170°C for the coarse RE powder. Table 1 gives details of processing and chemical compositions.

		mean							p.p.m.							
Billet N°	HIP"	particle size (um)	Со	Cr	Мо	Ti	Al	Fe	P	Si	Mrt	В	С	s	0	ĸ
AA 1	1	60	16.9	14.8	5.1	3.45	3.87	0.40	30	200	-	221	150	40	80	32
AA 2	1	60	16.8	14.6	5.2	3.54	4,10	0.25	n.d.	200	-	n.d.	350	30	70	22
AA 3	1	60	17.0	14.7	5.4	3.57	4.15	0.22	n.d.	400	500	n.d.	360	42	120	31
RE 1	2	450	17.0	;4 8	5.4	3.25	4.18	0.01	40	100	600	230	180	14	50	7
RE 2	2	450	16.9	14.8	5.4	3.25	4.18	10.0	50	100	500	223	480	16	50	≤ 5
RE 3	2	450	17.3	15.0	5.0	3.50	4.00	n.d.	30	200	-	n.d.	440	40	40	16
RE 4	2	450	16.9	15.2	5.2	3.45	4.24	0.01	20	100	300	230	420	60	50	< 5
RE 5	1	200	16.9	15.2	5.2	3.45	4.24	10.01	20	100	300	230	420	60	40	

TABLE 1 : EXPERIMENTAL MATERIALS : COMPOSITION (WT. Z), BALANCE NICKEL

HIP Conditions : 1 = 4 h 1140 °C, 100 MPa ; 2 = 4 h 1170 °C, 100 MPa ; m.d. = not determined

With the exception of C, S, O and N, chemical analyses were made on melt samples for the AA materials and on the electrode stubs in the case of RE products. Carbon and sulphur were determined on the powders, whereas oxygen and nitrogen were analysed on the consolidated billets. No trace of argon could be detected in the densified materials, neither by micrographic examination after annealing for 24 hours at 1175°C, nor by the presence of blisters on an electron-beam-cut surface. The sensitivity of the latter technique is approximately 2 p.p.m. All mechanical testing was carried out after heat-treating

4h 1160°C AC + 4h 1080°C AC + 24h 850°C AC + 16h 760°C AC

MECHANICAL PROPERTIES

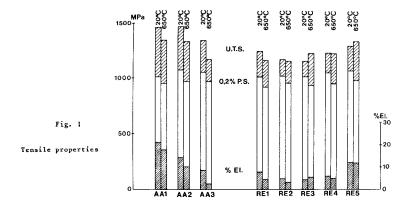
Charpy V-notch impact tests were carried out at room temperature. The results, together with the type of rupture observed, are given in table 2. In the AA material, the impact strength is lower at the higher carbon level and further decreases when the oxygen content rises. At the same time, the proportion of prior-particle boundaries (p.p.b.'s) visible on the fracture surface increases, particularly in the oxygen-rich billet. Elsewhere, the rupture is transgranular and ductile in nature. In the RE products, the toughness values are considerably lower than for AA materials of equivalent composition. The deleterious effect of higher carbon contents is again evident, while the oxygen levels in this case do not differ significantly from one billet to another. No influence of sulphur can be detected in the limited range of compositions studied. Comparison of the values obtained for alloys RE 4 and RE 5, prepared from the same powder batch, shows the advantage of the smaller mean particle size. All of the RE fracture surfaces contain a large proportion of p.p.b.'s, the remainder having a strong tendency to be intergranular.

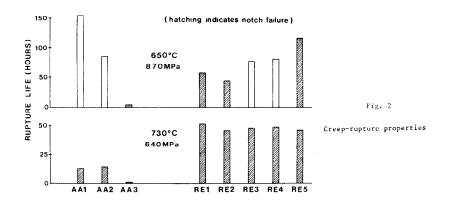
Tensile tests were carried out at room temperature and at 650°C, at an average strain rate of 2 x 10-3 5-1 on specimens with a 15 mm gauge-length, 3 mm in diameter. The results are shown in figure 1. It can be seen that the elongations vary in exactly the same manner as the impact strengths. The yield strength values of the different materials are fairly close to one-another, but tend to be slightly greater at higher carbon contents. In almost all cases, both the ductility and the proof-stress are lower at 650°C than at room temperature. The types of fracture obtained at 20°C are similar to those observed on the impact specimens. At 650°C however, while the percentage of p.p.b. 's remains approximately the same, there is little evidence of intergranular failure in the KE test-pieces.

Creep tests were performed on mixed, notched-and-plain, specimens, at 650°C and 730°C. The results, illustrated in fig. 2, are not as clear-cut as for the tensile and impact tests. There is a strong tendency for notch failure, particularly at 730°C. The most significant observations are the deleterious effect of the high oxygen content in AA 3 and the superiority of the RE materials at 730°C.

TABLE 2 - IMPACT STRENGTH

Billet	Compos	ition (p.p.m.)	Impact strength	Rupture type					
N°	c s		0	(J. cm ⁻²)	Prior particle boundaries	Elsewhere				
AA 1	150	40	80	36 - 36	absent	100 % transgranular				
AA 2	350	30	70	23 - 25	∼ 10 % of the surface	№90 % transgranular				
AA 3	360	42	120	i2 - i2	∼100% of the surface					
RE I	180	14	50	16 - 18	№ 80 % of the surface	~50 % intergranular				
RE 2	480	16	50	12 - 10	∼ 90 % of the surface	∼100 % intergranular				
RE 3	440	40	40	12 - 11	N100 Z of the surface					
RE 4	420	60	50	12 - 12	№ 90 % of the surface	~ 50 % intergranular				
RE 5	420	60	40	14 - 16	№90% of the surface	?				
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MICROSTRUCTURE OF CONSOLIDATED PRODUCTS

Optical Micrography

The microstructure of the consolidated products has been studied by optical microscopy on polished and etched sections. The following description will be confined solely to the decoration of prior-particle boundaries and to the distribution of carbides. Fig. 3 shows the structures observed in both the heat-treated and as-MIP conditions, after a permanganate etch. The extent of p.p.b. decoration is determined principally by the mode of powder production and by the carbon content. It is also increased by a higher oxygen concentration (alloy AA 3), whereas within the range of compositions studied, sulphur and nitrogen have me appreciable influence. Vitually mo p.p.b. precipitation is observed in the low-carbon gastonised material (AA 1), either as-BIP or after beat-treatment, the carbides being uniformly distributed throughout the alloy. At the higher carbon level (AA 2), a slight decoration appears in the as-BIP condition and isfurther accentuated after heat-treatment. The microstructure of the RE products is much coarser and a principal feature is the heterogeneous distribution content and explains the fact that p.p.b. decoration is quite marked even in the low-carbon alloy (RE 1). Heat treatment further enhances the decoration and also produces considerable grain-boundary carbide precipitation in the RE materials.

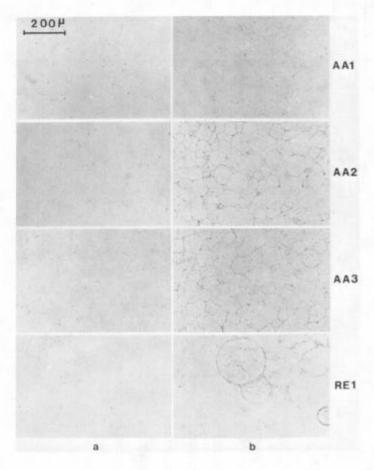


Fig.) Microstructure = (a) as-HIP (b) heat-treated

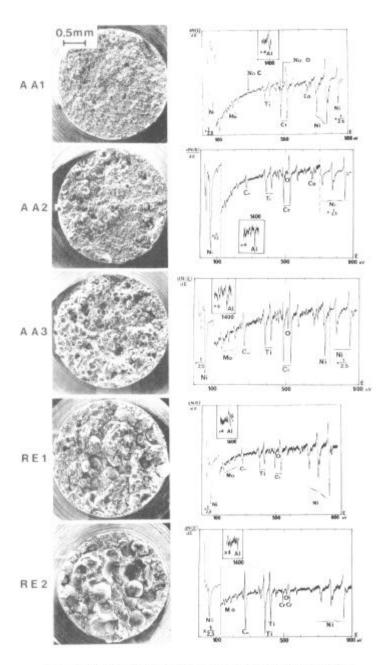


Fig. 4 Morphology and Auger electron spectra of as-HIF fracture surfaces

OBSERVATION AND ANALYSIS OF FRACTURE SURFACES

Fracture surface analysis has been carried out by Auger electron spectroscopy (AES), using a primary beam diameter of 15 μ m, on specimens broken by impact inside the apparatus, that is, in a vacuum of at least 10-9 torr (1.3 x 10-7 Pa). The AES apparatus is equiped with an ion-sputtering system which enables cleaning of the specimen surface and the determination of depth-concentration profiles. Sputtering is performed under a pressure of 5 x 10-5 torr (6.5 x 10-3 Pa) of argon. In the conditions employed, the erosion rate can be estimated at \sim 20 Å. mn⁻¹. However, this value is only approximate, since it depends on the nature of the surface constituents. After analysis, the same fracture surfaces were examined by scanning electron microscopy (SEM).

Figure 4 shows the influence of composition and powder production process on the morphology of the fracture surfaces for the as-HIP condition. For the alloy AA 1, the entire rupture surface is transgranular. At higher carbon content (AA 2), some p.p.b.'s appear, covering roughly 10 % of the surface. In the case of the RE materials, interparticular failure is observed even at the low carbon content of 180 p.p.m. (RE 1), rapresenting about 20 % of the total aera. At 480 p.p.m. C (RE 2), more than 90 % of the fracture occurs along particle boundaries. Cracking occurs indifferently at the boundaries of both large and small particles, and this is confirmed by the results obtained on the billet consolidated from fine powders (RE 5). Comparison of the fracture surfaces of alloys AA 2 and AA 3 shows that a high oxygen content also enhances p.p.b. failure, the rupture being entirely interparticular for the latter material. On the contrary, within the range of compositions studied, no effect of sulphur or nitrogen could be detected.

Heat treatment changes neither the extent nor the appearance of the interparticular rupture zones. In contrast, the transgranular regions, which are ductile in the as-HIP condition, become brittle and intergranular in the RE products, due to the extensive precipitation of carbides at grain boundaries. These observations are in agreement with the rupture morphologies seen on the impact specimens (table 2).

When the fracture surface is transgranular, the composition determined by AES is essentially the same as the nominal values for the principal constituents of the alloy (Ni, Co, Cr, Ti, Al, Mo). The carbon concentration is variable and generally greater than the nominal alloy content, but does not exceed 5 at %. No correlation could be found between the concentration of carbon and that of any other alloying element. However, the increase in carbon content must correspond to the presence of precipitates, and not to atomic segregation, since it is not eliminated rapidly by sputtering. For the other materials, in the interparticular zones, the carbon and titanium concentrations increase simultaneously, and can attain very high local values, greater than 20 and 10 at % respectively . Oxygen is systematically detected on the rupture surface of alloy AA 3 (between 1 and 2 at 7). In the other specimens, the spectra are difficult to interpret, since, even in the very high vacuum, oxygen contamination cannot be avoided. However, when all the analyses are considered together, there seems to be a definite correlation between high carbon and titanium contents and the presence of oxygen. The analytical sensitivity is insufficient to detect small quantities of sulphur and nitrogen, but it can be affirmed that their surface concentrations are less than 0,5 at. Z. A similar observation can be made in the case of boron, for which detection by AES is as easy as for carbon. Contrary to the conclusions of a recent investigation on the same alloy (2), boron does not appear to form borides either at particle surfaces or at grain boundaries.

STRUCTURE AND COMPOSITION OF NON-CONSOLIDATED POWDER PARTICLE SURFACES

Extraction Replicas

Carbon extraction replicas were made on powder particle surfaces, using a technique which will be described in detail elsewhere (8). The phases present were identified by electron differaction and by energy-dispersive X-ray micronallysis (EDAX). However, it should be noted that the replication technique was only effective for either very large or very small particles, with the result that in the case of AA powders, observations were restricted to particles less than about 20 µm in diameter.

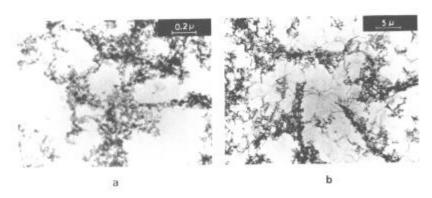


Fig. 5 Carbon extraction replicas of powder particle surfaces (a) AA 1 (b) RE 1

Figure 5 a shows the microstructure observed on AA I powders. The precipitates are distributed in a network corresponding to the interdendritic regions. Electron diffraction and microanalysis shows that the principal constituent is MG-type carbide, rich in titanium, chronium and polybdenum ($a_0 = 4.32$ Å) The RF | powder surfaces have x different appearance.Fig. 5 b. The carbide clusters are much nore extensive and the precipitates are globalar in form. As in the AA powder, they are distributed in the interdendritic spaces. These carbides were found to be of the MgC type ($a_0 = 11.4$ Å), containing chronium and polybdenum. Another, such less absordant phase, with lamellar corphology, was also observed, situated at the powder surfaces, and was shown to be a titanium and molybdenum rich MC carbide ($a_0 = 4.3$ Å).

AUGER ASMLYSIS

The analysis conditions were the same as those indicated for the fractographic examination. Because of their small diameters, the AA powders were fixed in a ring-shaped holder by a simple slight compression, whereas the RE particles were embedded in the surface of a low melting point alloy (Youd's metal). No trace of contamination due to the mode of mounting could be detected.

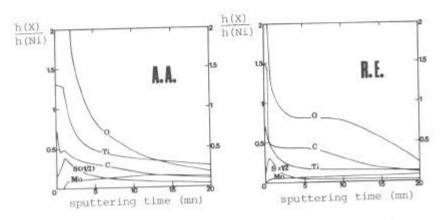


Fig. 6 AES spottering profiles determined ou powder particle auffaces. Peak height ratios of 5150, %0186, 6272, Tig87 and 0512 with respect to Sigsa

Sputtering profiles obtained on AA 3 and RE 1 powders are represented in fig. 6. The ordinate scale corresponds to the ratio of peak heights between the element concerned and nickel. Although it would be possible to determine atomic concentration profiles, these could have little real meaning given the irregularity of the surfaces and the differences in sputtering rates; the analyses are best considered as being qualitative in nature. Whatever the mode of powder production, the particles are covered with a large amount of amorphous carbon and oxygen. Considerable quantities of titanium and sulphur are also observed, although their signals are attenuated by the layer of carbon and oxygen. The carbon is partly in amorphous form and partly associated with titanium, since the spectrum for the latter is typical of the carbide. Although the concentrations of these elements are independent of their nominal contents, differences are observed between the two types of powder. The amount of amorphous carbon at the surface is greater (\sim 40 %) in the RE powders than in those produced by gas-atomisation (\sim 27 %). While the quantities of oxygen and sulphur are comparable, the concentration of titanium is much higher in the AA powders (N 16 % as against ~ 5 % for the RE ponders). The levels of all of the elements vary rapidly from the earliest stages of sputtering, but in the majority of cases, the nominal alloy contents are only attained after several tens of minutes. For certain elements, such as carbon and molybdenum, even after long sputtering times, the estimated concentrations still exceed the nominal values, due to the selective erosion of the matrix compared to the carbides. The variations of the carbon, titanium and molybdenum profiles indicates the presence, beneath the contamination layer, of a considerable quantity of titanium carbide, together with more complex, molybdenum -rich carbides in the underlying metal. However, the amounts of carbides detected cannot be related with certainty to the carbon contents of the alloys. The concentration of sulphur increases during the first few minutes of sputtering, due to the disappearance of carbon and oxygen, reaching a maximum of ~3 at. Z, but again there is no correlation between this value and the sulphur content of the alloys. No trace of nitrogen could be detected.

MASS SPECTROMETRY

Powder specimens were placed in an ultra-high-vacuum chamber of known volume, connected to a mass-spectrometer through a micro-leak valve. As the temperature of the chamber was gradually raised to 900°C, the total quantity of gas desorbed was determined by the increase in pressure in the chamber and its composition was analysed by the spectrometer.

The results obtained for two types of powder (AA I and RE 2) are shown in fig. 7. In both cases the desorbed species are the same and the desorption temperatures are similar. The quantity of gas per unit mass is roughly 5 times greater for the AA powder than for those produced by the RE process. However, taking into account the difference in particle size distributions, the amounts per unit surface area are comparable. No significant difference is observed between the various powders produced by the same process. Water vapor desorbs between 100 and 500°C, with a maximum around 400°C for AA powders and 200°C for RE materials. CO2 and CO are evolved between 150 and 800°C with a maximum towards 600°C. Desorption of CH4 and argon begins ar about 150°C, that of hydrogen at around 400°C, and thenincrease with temperature. The existence of maxima for H2O, CO and CO2 is due to re-combination

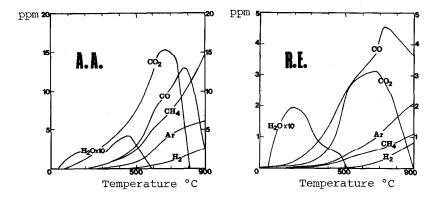


Fig. 7 Quantity of desorbed gaseous species expressed as the weight of gas per unit weight of powder

with the alloy at high temperature. This phenomenon is irreversible; during a second heating cycle no desorption of these gases is observed. In the case of argon, the concentrations determined are almost certainly greater than the real values, since its elimination from the mass-spectrometer (by means of an ion-pump) is less efficient than for the other gases. One significant difference between the two types of powder concerns the amount of CH4; the quantity desorbed from the AA powders is greater than that evolved from the RE materials, even taking into account the difference in specific surface area.

DISCUSSION AND CONCLUSIONS

In accordance with previously published work (9), the observations on the consolidated materials demonstrate the essential role of p.p.b. decoration in determining the mechanical properties of PM superalloys, particularly as concerns the ductility and toughness. This effect is especially marked for the RE products.

It is generally agreed that for a given carbon content, the degree of segregation increases with particle size, since the carbides are concentrated in a relatively smaller area. The coarse particle size of the RE powders could therefore be the cause of the decoration observed even at low carbon content. This reasoning implicitly assumes that all the carbon contained in the particles migrates to the surface. In fact the surface carbides draw carbon only from a limited depth, depending almost certainly on the densification and heat-treatment conditions, but which can be estimated at 20 to 30 µm. If this is the case, the degree of surface segregation should be independent of particle size for diameters above about 60 µm. It is more probable that the most important factor is the size of defect created. The results obtained on alloy RE 5, produced from finer powder, support this view.

In the consolidated products, the interparticular decoration is comprised principally of TiC-type carbides. The complex M6C-type carbides observed in the RE powders do not therefore intervene directly in the phenomenon. Contrary to recently published work (2), no evidence was found for surface enrichment of chromium, molybdenum or boron. As has been shown by several investigations (10), the most important parameter is the nominal carbon content. It is probable that in the low-carbon AA powders all the carbides are taken into solution at the consolidation temperature, in contrast to the higher carbon materials. In the case of RE powders, resolutioning is not complete in certain particles, due to the heterogeneity. The interparticular carbides which remain undissolved at high temperature represent preferred precipitation sites, thus explaining the enhanced decoration after heat-treatment. Surface contamination of the powders by carbon and oxygen must also play an important part in the segregation phenomenon since, in the regions of p.p.b. fracture, high concentrations of carbon and titanium are generally associated with the presence of oxygen (0.5 to 2 %). At the beginning of densification, the large amount of oxygen adsorbed at the powder surfaces (20 to 30 %) should favour the coupled migration of titanium and carbon towards the surface by fixing them in the form of a stable oxy-carbide (TiCl-xOx). The oxygen content subsequently decreases by diffusion into the alloy, but the titanium and carbon remain at the surface in the form of TiC containing a few percent of oxygen. Sulphur, which also segregates to the powder surfaces, could have a similar action, but this cannot be confirmed, due to its low concentration. Nitrogen, which was never detected, probably has no effect.

The work which has been described shows the combined influence of alloy composition and powder surface contamination. That is, for a given nominal carbon content, the extent of p.p.b. decoration will depend on the amount of adsorbed carbon and oxygen. This contamination, which persists at room temperature, even after long times in ultra-high vacuum, shows the interest of either preventing contact of the powders with air or of applying a dynamic vacuum-degassing treatment, carried out at an intermediate temperature (400 to 600°C), or possibly both.

In this temperature range, the amount of desorption measured by mass spectrometry corresponds to the contamination layer estimated by Auger spectroscopy. At higher temperatures the carbon and oxygen recombine irreversibly with the alloy.

ACKNOWLEDGEMENTS

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