Precipitation in an as-atomized nickel-based superalloy powder

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The microstructure of argon-atomized René 95 powder has been characterized by a combination of transmission and scanning-transmission electron microscopy, and energy dispersive X-ray analysis. Specimen preparation techniques have been developed in order to obtain samples suitable for such analyses, and similar but complementary microstructural features are revealed by each technique. Dendritic and cellular structures, both on the surface of the powder particles and in the interior, are delineated by fine precipitates. These have been identified as MC-type carbides, containing Nb and Ti, with some Cr, Ni, Mo and W.

1. Introduction

The microstructures of metal powders are often characterized using the scanning electron microscope [1], but the information is limited to surface features which may not be easily related to structures within the powder. This method also gives little data on the phases present, either at the surface or in the interior. In order to obtain such information, transmission electron microscopy has been employed on the foils of powders [2–3, 4]. Such specimens are extremely difficult to prepare, but do permit identification of precipitates within the powder. Examination of similar precipitation at the particle surface, however, has not been reported. A combination of extraction replication and thin-foil microscopy is shown here to yield information from both powder surface and interior.

2. Experimental procedure

Argon-atomized René 95 powder was screened to a size range of − 270/+ 325 mesh (45 to 53 μm). This alloy has a composition of Ni–13 wt% Cr– 8 wt% Co–3.5 wt% Mo–3.5 wt% W–3.5 wt% Al–3.5 wt% Nb–2.5 wt% Ti–0.05 wt% Zr–0.01 wt% B–0.06 wt%C. Specimans prepared by the techniques described below were examined using an Hitachi H600 transmission electron microscope (TEM) operated at 100 kV, and a JEOL JSEM-200 scanning transmission electron microscope (STEM)

operated at 200 kV. Energy dispersive X-ray spectra (EDS) were obtained with a Nuclear Semiconductor detector and a Tracor Northern NS880 analyser equipped with a Digital PDP11 computer.

Three different sample preparation techniques were used. One of these was extraction replication on powder particles which were mounted, polished metallographically, and etched in a 10 vol% bromide–90 vol% methanol solution for 30 sec. Instead of extracting by direct carbon replication [5], where the etching rate is sometimes difficult to control, a two-stage acetylcellulose tape technique was used. Only carbon was evaporated onto the replica tape, since no contrast was needed, and no X-ray signal from the replicating medium was desired. This method results in good extraction replicas from cross-sections of the particles.

In order to extract precipitates from the powder surface, it is necessary to hold the particles in a material which is relatively impervious to the etchant, yet exposes the powder surfaces to the etching action. The technique devised used Barco Bond epoxy resin, which was mixed from two tubes onto a glass slide cut to dimensions of approximately 25 mm × 25 mm. The mound of epoxy nearly covered the glass, and was about 4 mm in height. It was allowed to cure slightly (15 to 20 min in this case) and then powder was poured onto the middle portion in a circle of
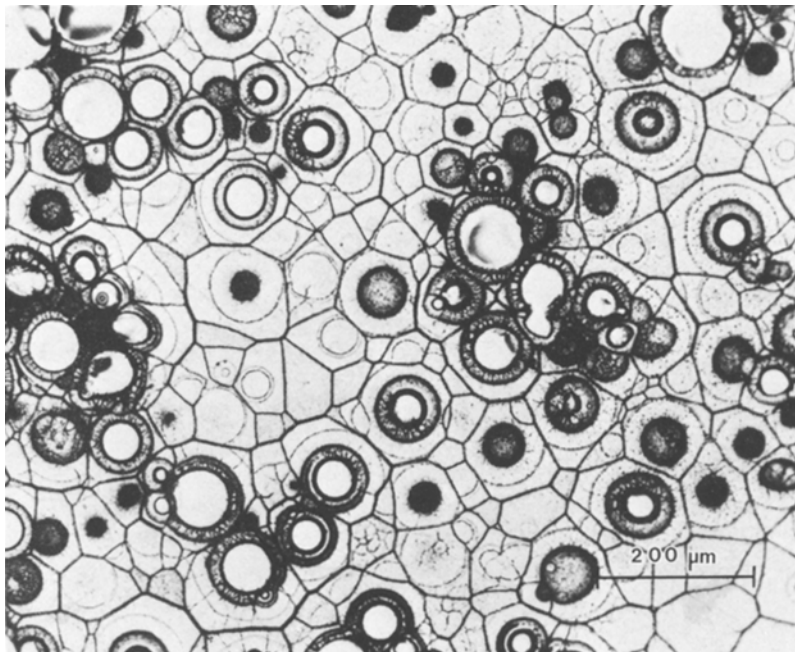
about 13 mm in diameter. Most of the powder sank into the epoxy, but as the epoxy cured, the settling of the powder slowed. The final sample, which had been dried for 24 h, consisted of a loose layer of powder on top of a layer partially embedded in the epoxy. Some of the loose powder was removed by tapping the sample lightly. The rest of the loose powder was stripped-off onto a piece of replicating tape, which was applied with acetone and allowed to dry. The remaining sample contained the partially-exposed powder, as well as powder completely covered by epoxy. These exposed surfaces were etched for 1 min in the bromine solution, and an extraction replica was made using the two-stage technique.

In order to obtain thin foils of the powder, a method similar to that used by Field and Fraser [3], but different in several stages, was employed. A piece of Cu foil 0.05 mm thick was cut to 25 mm x 25 mm and spread thinly with a Cu-paint solution. This was lightly covered with the powder and dried, after which loose powder was tapped off. The powder side was then electroplated with 0.05 mm of Ni. This sheet of Ni was then ripped from the Cu foil, taking most of the powder with it. The Ni–powder composite was soaked in acetone for 24 h to remove the Cu paint, and 0.05 mm of Ni was electroplated onto the previously unplated side of the powder. The resulting sandwich was about 0.15 mm thick, and

could be punched into 3 mm diameter discs. No jet-machining, or dimpling, of these discs was necessary, such as had been required by the 0.38 mm thick discs used in [3]. It was further found that sufficient electron-transparent area could be obtained only if the discs were abraded by 400 or 600 grit Al_2O_3 paper in order to smooth the surfaces. If this was not done, the specimens tended to thin in the interparticle pockets of Ni electroplate.

Since the Ni–powder sandwich was brittle, the edges of the discs were uneven, and Pt apertures were used during electropolishing to limit edge erosion. The electropolishing was carried out in a 20 vol% perchloric acid–80 vol% methanol solution, at 30 V and a temperature of $-50°$ C, using a Fishione twin-jet apparatus. The first holes which appeared in the specimen were generally numerous and small, and had little thin area around them. By allowing the holes to grow and coalesce, at least one, and often more, powder particle contained some thin area.

A typical disc was electropolished, but not perforated, and etched in the bromine solution for 15 sec. As can be seen in a light optical micrograph of the sample (Fig. 1), there is a high density of powder particles in the Ni. The particles appear white in this micrograph, due to their high reflectivity, and each particle is surrounded by a ring of Ni electroplate.
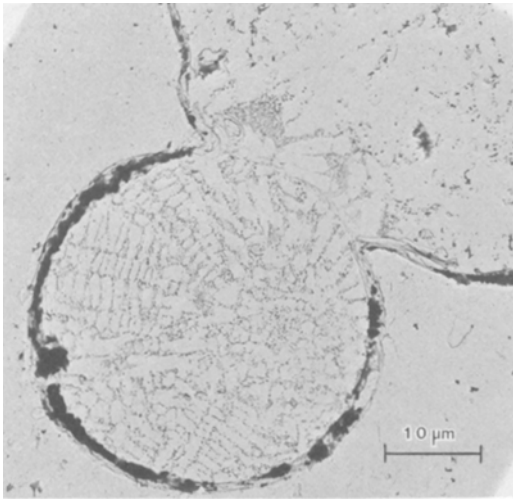
Figure 2 Extraction replica of metallographically-polished powder, with dendrites and cells outlined by extracted precipitates.

3. Results and discussion

In the extraction replicas of metallographically-polished cross-sections of powder, cells and dendrites within the powder are clearly outlined by small precipitates (Fig. 2). There is a large variation in the size of these, although diameters of 25 nm and 200 to 500 nm are the most frequently observed. High concentrations of these former very fine precipitates are seen in the smaller of the two particles attached to the surface of a large one (see Fig. 3a), and in the large particle in areas immediately adjacent to the two small ones (see Fig. 3b). While this is only a plane section, the dendrite—cell spacing in each particle

supports the size differences observed. Precipitates of a similar size are observed in protrusions from essentially spherical powder particles (Fig. 4). This suggests that the average size of the precipitates, as well as the dendrite size and spacing, may be related to the cooling rate experienced by the region containing them. Work on splat-cooled layers in IN–100 powder [1] reports no precipitation within these layers; however, the authors do not specify the type of replication used in their analysis, and no micrographs of replicas are shown. It is possible that extraction replication might reveal precipitates similar in size to those observed here in the René 95 powders.

The larger precipitates are of a fairly convoluted shape, and those which have been fully extracted are of a multi-branched morphology, which will be referred to as "spidery" (Fig. 5). This morphology is so unusual, that the first impression is that they must be an etching artifact, particularly in the case of a deeply-etched powder surface, where the prolonged etch might be expected to have left residue (Fig. 6). However, selected area electron-diffraction studies on these, and on the extracted fragments on the polished powder cross-section, have identified them as MC-type carbides, with a lattice parameter of approximately 0.44 nm and a fcc crystal structure. The very fine precipitates seen in Fig. 5 are also MC carbides.

X-ray powder diffraction was carried out on extracted residues of powder. After the bulk of the extracted matter had been removed from the glass vial, in which the residue had been centrifuged, it was noticed that a film of very fine par-
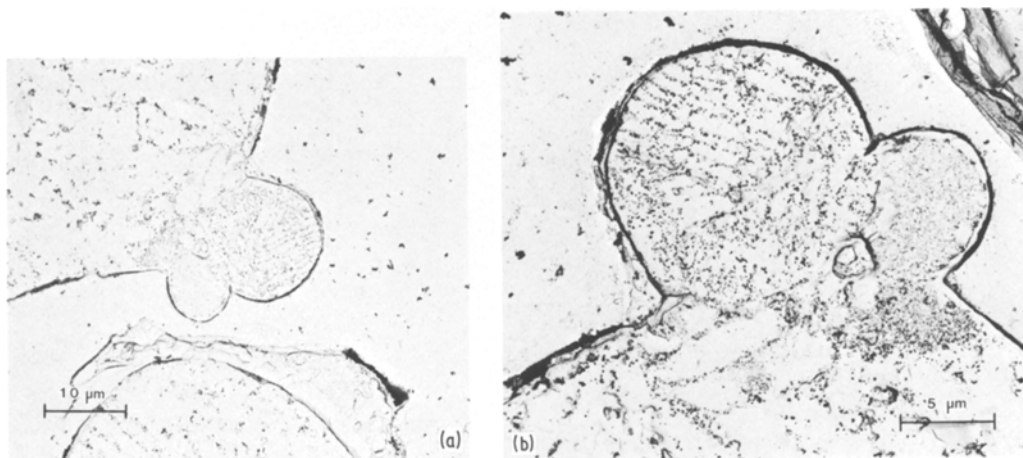

Figure 3 (a) Extraction replica of metallographically-polished powder, showing large particle with two smaller particles attached to it. (b) Increased magnification of the three particles in (a) shows size range of interdendritic precipitates.
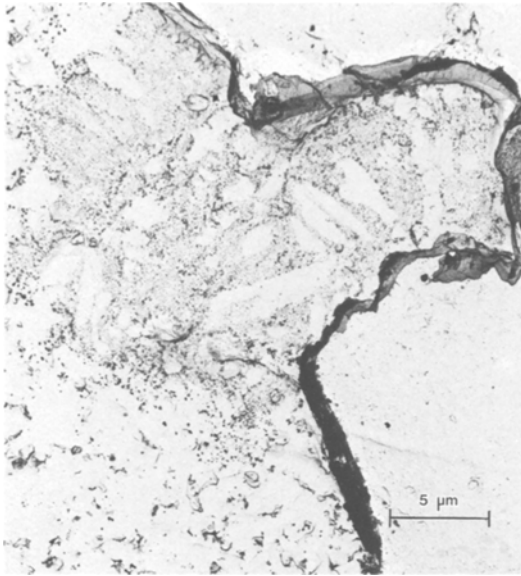
Figure 4 Extraction replica of metallographically-polished powder, with very fine precipitates observed in protrusion from the particle.

Figure 6 Extraction replica of deeply-etched particle surface, showing numerous, fully-extracted precipitates of spidery morphology.

ticles remained on the sides of the glass. Patterns from the bulk residue revealed the presence of MC carbides with a lattice parameter of 0.442 nm, and the very fine precipitates were shown to be MCs as well, but with a smaller lattice parameter of $a_0 = 0.438$ nm. Faint lines of other, as yet unidentified, phases were also detected, but the MCs are the dominant precipitate found by this method. The result is corroborated by the TEM—STEM data.
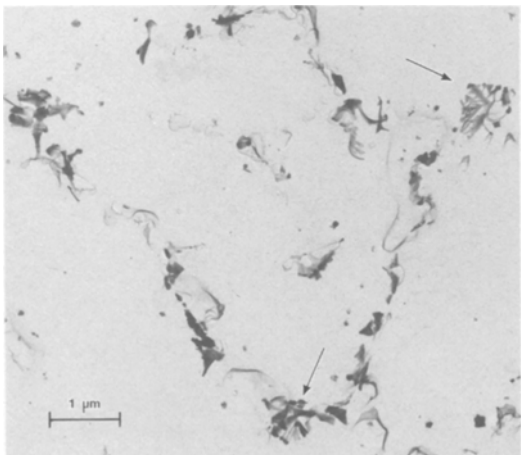
Energy dispersive spectra taken on the precipitates on the extraction replica indicate that they contain primarily Nb and Ti, with varying amounts of Cr, Ni, Mo and W (Fig. 7). It should be noted that, due to the complex chemistry of these precipitates, it is not possible to distinguish between MC and M(C, N, O) phases in this alloy. NbC has a larger lattice parameter than NbN, the a_0 value for TiC is less than either, and that of TiN is the smallest. All values of a_0 lie within a range of 0.42 to 0.45 nm. The addition of Nb to a TiC would then tend to increase the lattice parameter, while addition of O and N would decrease it. Certainly, the difference in a_0 for the two sizes of precipitate, as measured by the Debye—Scherrer patterns, indicates a difference in composition, but it is not possible to quantify this. Because of the compositional uncertainty, these compounds will be referred to as MCs, but the possibility of N and O substitution for C must be considered.

Figure 5 Extraction replica of metallographically-polished powder in which the twisted morphology of many of the larger interdendritic precipitates appears. Fully-extracted, "spidery" precipitates are indicated by arrows.
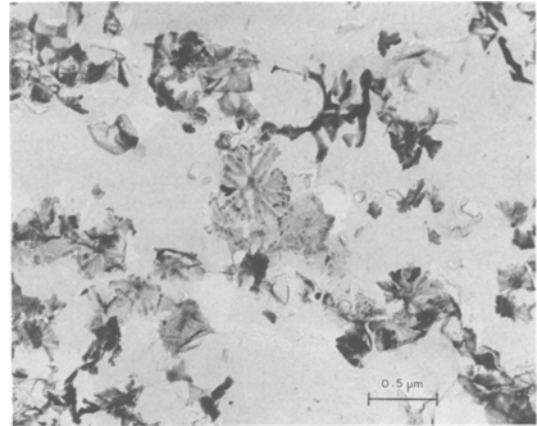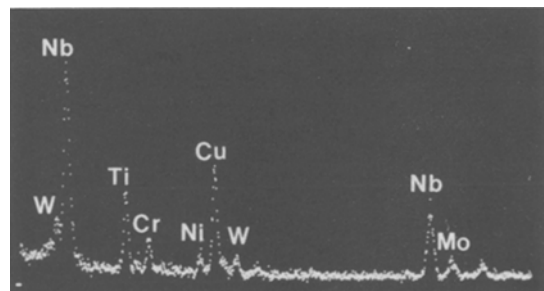

Figure 7 Energy-dispersive X-ray spectrum from extracted interdendritic precipitate. Note that Cu peaks are from replica support grid.
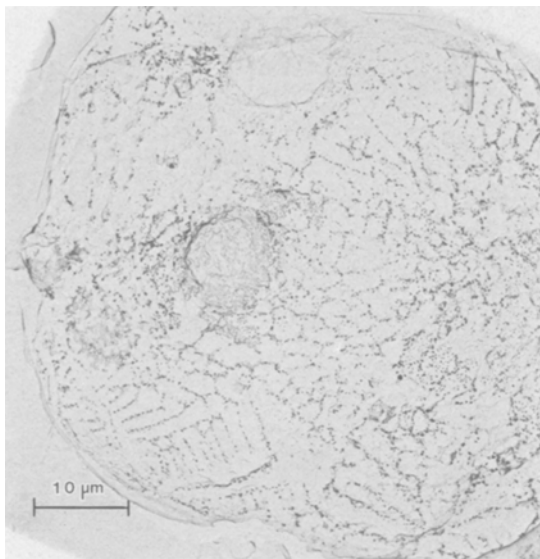
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Figure 8 Extraction replica of particle surface, showing precipitates in interdendritic–intercellular regions. The large particle has smaller one on its surface, and precipitates in smaller one are of much finer size than those in the larger particle.

Examination of replicas from the powder surface shows that the precipitates also lie in the interdendritic or intercellular regions (Fig. 8), and that their morphology is often not of the spidery type found in the particle interior, but instead is usually flake-like (Fig. 9). The flakes often have small protrusions, but these are not developed into the twisted shape of the spidery precipitates. The particle surface phases are also MC carbides, of similar composition to those inside the particle. No other compounds, such as simple oxides, were
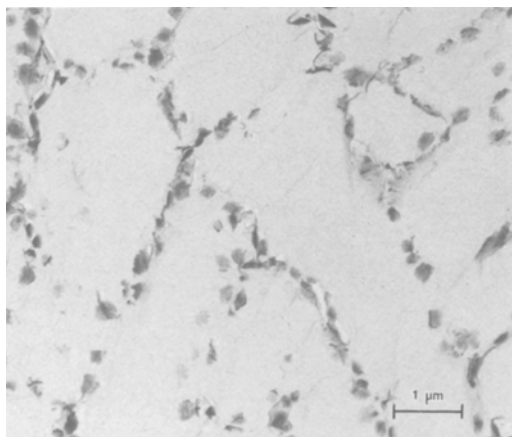

Figure 9 Extraction replica of powder surface, on which interdendritic precipitates are of flake-like morphology.
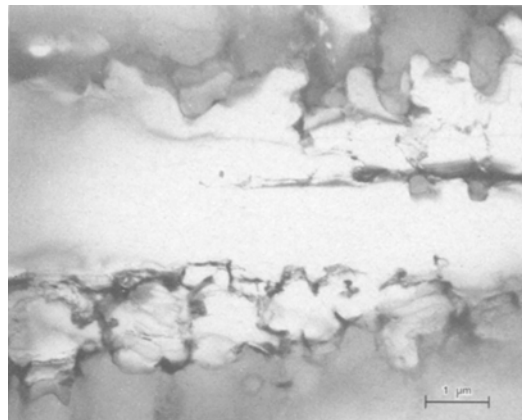

Figure 10 Thin foil of powder, showing dendrites in powder interior.

found at the particle surfaces, although a lack of evidence does not definitely establish the absence of such phases. If the size of other precipitates were very small (< 10 nm), or if they were present as a thin film, even a light etch might be sufficient to remove them from the surface. Very short-time etches were tried in an attempt to extract possible fine phases, but were unsuccessful. It is possible that they were washed off into the several rinsing solutions necessary to remove all of the bromine solution. Long etching times were also used, in case other compounds were more tightly bound to the surface than the MCs. The result of this procedure was to extract not only the surface MCs, but some of those from the interior, identifiable by their shape. No other phases, however, were extracted and, as will be discussed below, no clearly identifiable precipitates, other than MCs, were observed on the powder surfaces in thin foils.

Micrographs from thin foils of powder clearly show the dendrites (Fig. 10) and cells (Fig. 11), with highly convoluted boundaries. At higher magnifications, the interdendritic regions are observed to contain the spidery precipitates (Fig. 12), as well as a much higher density of dislocations than the dendrite cores, which are nearly dislocation-free. It is interesting to note the apparent absence of γ'-precipitates in the γ-matrix, both in the dendrite cores and interdendritic regions. A fine mottled structure seen at some orientations (Fig.13), and the presence of extremely faint (100) superlattice spots in diffraction patterns, suggests that γ'-phase has precipitated in the matrix, but is of very small size, perhaps less than 5 nm, due to the fast quenching rate.
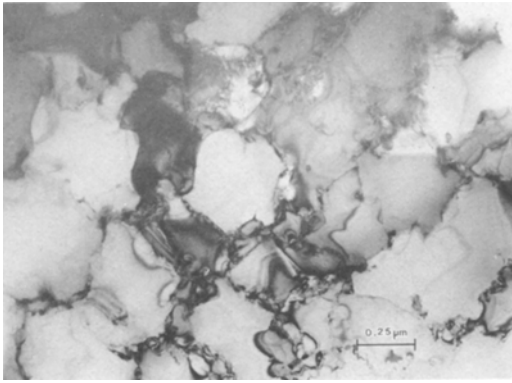
Figure 11 Thin foil of powder particle containing cells.

Figure 13 Faint mottled appearance of γ-matrix at some orientations, indicating presence of very fine γ'-precipitates; note absence of resolvable γ'-phase in all thin foil micrographs.

Suppression of γ'-precipitation in a laser-melted nickel–base material has been reported [6], but the micrograph provided in support of this is of an extraction replica at a magnification of 2000. At this magnification, γ'-precipitates of 100 nm in diameter would be 0.2 mm across, and therefore just barely visible; therefore fine γ'-precipitates of approximately an order of magnitude smaller in size, could not be detected by such a technique. As has been seen in the powder examined here, however, fast quenching will result in very small γ'-particles, and the suppression of any larger γ'-particles.

Fig. 14 shows the interface between a powder particle and the Ni electroplate, which appears as a very fine-grained structure. There is generally good cohesion between the plating and powder, and no excessive preferential attack at the interface by the electropolishing solution. Again, no obvious phases except the MC carbides were seen
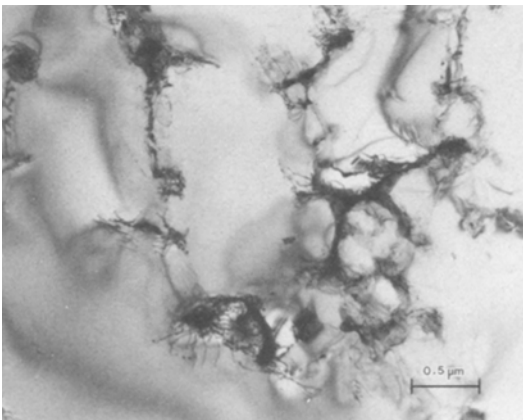
at the powder surface examined in this foil, although small precipitates could easily be obscured by the fine-grained nature of the plating. High spatial resolution spectra taken at several points along the interface showed no increase of possible oxide formers such as Al or Zr, or Ti except in conjunction with strong Nb peaks. If the possible oxides were less than 10 nm in diameter, however, their mass could be insufficient to generate an X-ray signal that would not be obscured by that of the matrix. The existence of such oxides on the powder surface, then, has not yet been proved or disproved.

Energy dispersive spectra from the interdendritic precipitates in the thin-foil specimens show greatly enhanced Nb and Ti contents, relative

Figure 12 Thin foil of powder dendrites, with spidery precipitates and high dislocation density in interdendritic regions.
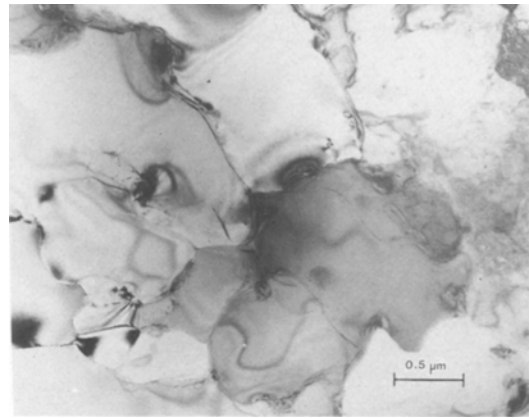

Figure 14 Interface (indicated by arrows) of powder and Ni electroplating, as seen in thin foil. Possible fine precipitates at powder surface are largely obscured by small grains of Ni plating.

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to the matrix. Minor constituents of the carbides, such as Cr, Mo and especially Ni, are difficult to detect in thin foils, since it is not easy to eliminate contributions to the spectra from the surrounding matrix. Some work using a computer program for peak subtraction has attempted to do this [3]. Spectra taken on extracted precipitates are much more reliable, however, especially for precipitates of low mass with respect to the matrix, and containing small amounts of minor elements.

Differences in morphology between the interdendritic precipitates in the powder interior and those on the surface can be attributed to different constraints imposed during solidification. The cooling rate of the powders from the molten state has been shown to be rapid enough to suppress the growth of large amounts of the γ'-phase. Solidification of dendrites, or cells, causes rejection of strong γ' formers, such as Nb and Ti, which lower the melting point of nickel, to the interdendritic regions. The liquid is forced into the twisted configuration of the dendrite interstices by stresses generated by the cooling of the solidified material and transformation of the solute-rich regions to MC carbides results in precipitates of a convoluted morphology. Liquid in the interdendritic regions which intersect the particle surface experiences less constraint, and the resulting precipitates generally achieve the flake-like morphology.

MC carbides have been observed at the prior-particle boundaries (PPBs) of material which has been compacted and heat-treated. Some data for IN–100 indicates that MCs nucleate on oxides already existing at the PPBs of extruded and annealed samples [7]. Menzies et al. suggest that, were such oxides not present, it might be possible to suppress precipitation of the MCs at the PPBs. These results are thus judged not to be applicable to René 95, in which, as has been shown in the above discussion, the carbides at the powder surface are present due to segregation during solidification. Others [8, 9] have also observed oxycarbonitrides of Ti at PPBs in as-HIP (hot isostatic pressed) René 80 and IN–100; but it is not known, for these alloys, whether the precipitates formed during the HIP cycle or on atomization. Certainly the semi-continuous nature of the MCs observed by Larson in IN–100 [9] is quite different from the distribution of phases found on René 95 powder surfaces. In general, then, it is difficult to extrapolate observations made on consolidated material to as-atomized, or as-solidified powder.

4. Conclusions

The preparation of René 95 powder for TEM and STEM, using several specialized techniques, has been successful; the examination of such samples has yielded precise information on the location and morphologies of precipitates in the powder. Identification of the precipitates by selected-area electron diffraction, coupled with microchemical analysis by energy dispersive X-ray spectrometry, provides data on the distribution of solute during solidification of the powder. Application of these preparation and analysis methods to powder formed by other processes such as rotating electrode, spinning disc, melt explosion, etc., could also be fruitful, as would a comparison of phases present in René 95 powder to those in consolidated product.

Acknowledgements

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