

## PHASE RELATIONSHIPS IN RENE' 95

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*Rene' 95 samples with various carbon levels and stages of processing were studied. Loose powder was found to contain an MC type carbide which transforms to the cast-wrought MC during HIP'ing. Variations in gamma prime solvus in powder and HIP powder from that in cast-wrought material are discussed. Understanding of the carbide and gamma prime phases in powder may lead to improvement of the parameters used for HIP'ing.*

### INTRODUCTION

Rene' 95 was introduced approximately 12 years<sup>(1)</sup> ago as a cast and wrought superalloy. As applications matured, process technology progress stimulated a gradual shift toward powder metallurgy for manufacture of components. Throughout this period, chemical composition has remained relatively unchanged except for reductions in carbon and chromium which were made to enhance phase stability and ductility.

#### Rene' 95 Nominal Composition, Weight %

<u>C</u>	<u>Al</u>	<u>Co</u>	<u>W</u>	<u>Zr</u>
0.15 to 0.04	3.5	8.0	3.5	0.05

<u>Cr</u>	<u>Ti</u>	<u>Nb</u>	<u>Mo</u>	<u>B</u>	<u>Ni</u>
15.0 to 13.0	2.5	3.5	3.5	0.01	.Bal.

Although structures and phases were described from time to time in the literature, phase relationship data are sparse, somewhat conflicting, and frequently not correlated with process parameters. The existence of actual

quantitative phase relationship information is indeed rare. This investigation identifies all reported phases, indicates inconsistencies, quantifies some phase content, and provides insight to some phase relationships. This study is limited in scope to consideration of structures of cast ingot, atomized powder, cast-wrought material, and HIP'ed powder.

#### MATERIALS

Two 8-inch diameter VIM-VAR ingots, one containing 0.16 C, 13.7 Cr, and 3.6 Nb and one containing 0.04 C, 13.1 Cr, and 3.1 Nb were characterized. Argon atomized powder containing 0.07 C, 13.0 Cr and 3.6 Nb, and discerned to yield fractions ranging in size from -35 to -325 mesh was analyzed.\* All other elements in the above specimens are consistent with the nominal composition given in the introduction.

#### PHASES

At specific stages of manufacture, Rene' 95 is reported to contain one or more of the phases described in Table I. Either herein or previously, the authors have identified all listed phases except sigma. This phase still eludes confirmation and is reported only in early works (1,2).

The MC type carbide is found only in cast ingots or in wrought or HIP'ed alloy. However in loose powder a new M'C type carbide was identified. Only under certain conditions of thermal treatment and microchemical segregation is the M<sub>6</sub>C type carbide found in Rene' 95. The occurrence of M<sub>6</sub>C is considered rare. In the temperature range 760°C (1400°F) to 927°C (1700°F), the M<sub>23</sub>C<sub>6</sub> type carbide forms directly from carbon in solution or from decomposition of MC, depending upon process or thermal exposure parameters.

Both Laves and delta are considered to be transition phases which likely form as a result of microchemical segregation. They are either rare or nonexistent in a truly homogeneous structure which has a proper balance between carbon and niobium. Mu phase exists only as a terminal phase if the alloy is subjected to overaging, especially near 871°C (1600°F).

\*All powder had less than 70 ppm oxygen.

TABLE I

$\gamma'$	$\text{Ni}_3(\text{Al, Ti, Nb})$	MAJOR	FCC SUPERLATTICE
MC	$(\text{Ti, Nb})\text{C}$	MAJOR	FCC
MC'	$(\text{Nb, Ti, Cr, W})\text{C}$	MAJOR	FCC
$\text{M}_{23}\text{C}_6$	$(\text{Cr, Mo, W})_{23}\text{C}_6$	TRACE	COMPLEX CUBIC
$\text{M}_3\text{B}_2$	$(\text{Mo, Cr, Ni})_3\text{B}_2$	TRACE	TETRAGONAL
LAVES	$\text{Co}_2\text{Mo}(\text{type})$	TRACE	HCP
$\delta$	$\text{Ni}_3(\text{Nb, Ti})$	MINOR	ORTHORHOMBIC
$\mu$	$\text{Ni}_7\text{Mo}_6(\text{type})$	MINOR/TRACE	RHOMBOHEDRAL
$\sigma^*$	$(\text{Cr, Mo})_x(\text{Ni, Co})_y$	TRACE	TETRAGONAL
$\text{M}_6\text{C}$	$(\text{Ni, Co})_x(\text{Cr, Mo, W})_{6-x}\text{C}$	TRACE	COMPLEX CUBIC

\* REPORTED BY OTHERS

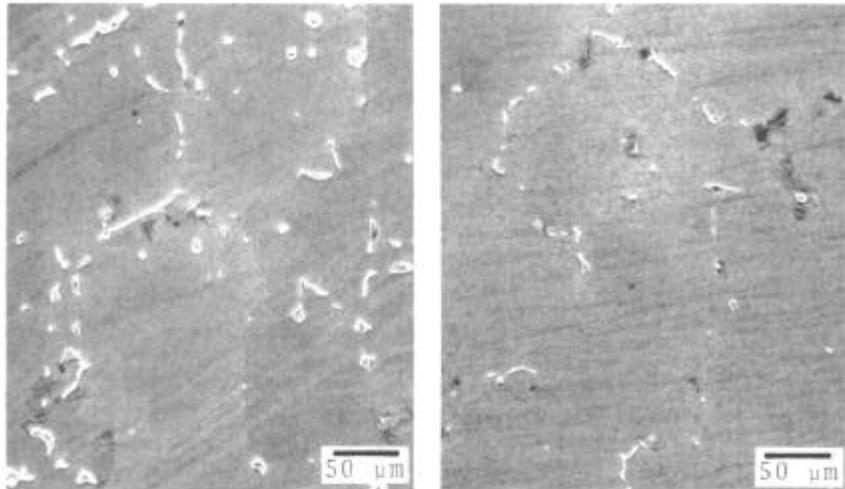
The  $\text{M}_3\text{B}_2$  phase is produced either during solidification or as a solid state precipitate under certain conditions of processing. Although not listed in Table I nor reported in the literature, a fine precipitate of zirconium and/or aluminum rich particles has been found outlining some prior particle boundaries in powder products. While no structural identification has yet been made, these are thought to be oxides originating in some stage of processing from the zirconium and/or aluminum rich areas of surface films which encase some atomized powder particles.

As described later, gamma prime appears in two forms. The gamma prime generated during processing which remains after thermal treatment below the maximum gamma prime solvus is defined as primary gamma prime. That which forms as a result of an aging heat treatment is defined as secondary gamma prime. As yet, specific compositional and/or lattice parameter differences have not been investigated.

Hereafter, the discussion shall concentrate mainly on carbon-carbide phase relationships and thermal analysis data as it relates to process parameters.

#### DISCUSSION

INGOTS: Typical as-cast Rene' 95 ingot structures are illustrated in Figure 1. The extremes in carbon content,



a) 0.16 C

b) 0.04 C

Figure 1. SEM micrographs of as cast ingots.

0.04 and 0.16%, produce significant differences in phase relationships. The composition of the MC type carbide in both alloys as determined by x-ray energy dispersive spectroscopy (EDS) appears similar. The "M" portion is mainly niobium and to a lesser extent titanium. A trace of tungsten was also found in the "M" portion. Aside from the obvious lower MC content in the 0.04% carbon alloy, an increase in a plate-like phase is observed.

Details of the cast ingot structure are revealed in Figure 2. The bright white phase in this scanning electron microscope (SEM) photo are the MC type carbides. The larger irregular shaped gray phases adjacent to the carbides are  $M_3B_2$  type borides. The very large plate-like phase is delta phase ( $Ni_3(Nb,Ti)$ ) and the much smaller dark matrix phase is primary gamma prime. Although not shown in this photo, eutectic gamma prime pools are common in cast ingots. There is a definite relationship between the quantity of eutectic gamma prime pools and carbide content, with less gamma prime pools observed as carbon increases. The secondary dendritic arm spacing (DAS) for this type of ingot, regardless of carbon content, averages about 100 microns.

POWDER: Typical spheres in -180 microns (-80 mesh) and -106 microns (-150 mesh) argon atomized powder are compared in Figure 3. These SEM photos show the range of particles present and clearly reveal characteristic satellite particles of gas atomized powder. Internal structure is related to particle size which in turn is related to particle solidification rates. For example, the average secondary DAS in the 35 micron particle depicted in Figure 4 is 1 micron. The authors and other workers<sup>(3)</sup> have studied DAS in various size particles, and have determined that the average secondary DAS ranges from about 1 micron in 35 micron (400 mesh) particles to about 3 microns in 155 micron (100 mesh) particles. Formation of delta phase and other intermetallics in powder particles is restricted by the rapid cooling rate.



Figure 2. 0.16C as cast.

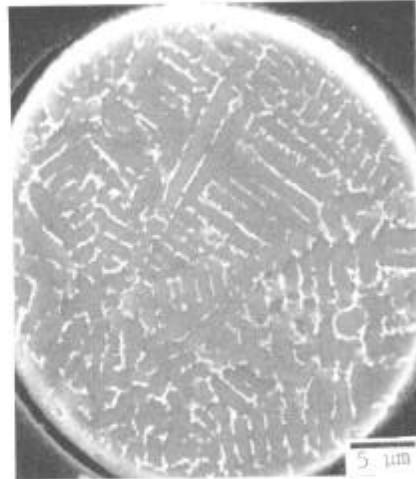
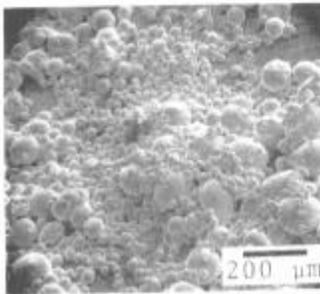
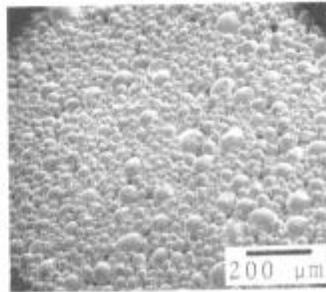


Figure 4. 35µm particle.



a) -80 mesh



b) -150 mesh

Figure 3. Argon atomized powder.

The MC type carbides in powder are much smaller than those detected in ingot products, and range in size from less than 0.1 micron to about 1 micron depending upon particle size, whereas the MC type carbides in ingot products are in the order of 10 microns.

**CARBON PARTITIONING:** The carbon partitioning data were obtained by digestion of loose powder and ingot material in a solution of 10 volume percent bromine in methanol. This reagent dissolves matrix and gamma prime plus any  $M_3B_2$ ,  $M_23C_6$  or TCP phases present, leaving a residue which is essentially 100% MC. The fraction of carbon combined as other carbides is negligible in samples of this investigation as determined by electrolytic hydrochloric acid-methanol extraction. Carbon partitioned as MC is determined by dividing the carbon in the MC by the total carbon of the sample. Such data are presented in Table II. The percent of total carbon in the alloy present as MC varies with particle size and appears, at least for ingots, relatively independent of carbon level of the sample.

The composition of the "M" portion of the MC carbide is dependent upon the sample from which the carbide is extracted. The smaller carbides extracted from rapidly cooled powder particles contain Nb, Ti, W, and Cr whereas the larger carbides extracted from slower cooled ingots contain mainly Nb and Ti with a trace of W. A steady reproducible decrease in MC lattice parameters with particle size was observed. This decrease was accompanied by a decrease in the weight percent carbon in the MC residues. The larger atomic weight and the smaller atomic volume of tungsten and chromium as opposed to titanium could account for the carbon analysis and lattice parameter shifts respectively. Due to the observed differences in the carbides extracted from the powder particles, they have been designated as M'C type carbides in this work.

TABLE II

	LATTICE PARAMETERS (Å)	CARBON PARTITIONING, % C AS MC	MC METALLIC CONTENT	W%C IN MC
INGOT, HIGH CARBON	4.42	85	Nb, Ti	11.4
" , LOW CARBON	4.42	87	Nb, Ti	11.9
POWDER, -35 MESH	4.393 ± .001	73	Nb, Ti, W, Cr	10.3
" , -80 "	4.390 ± .001	64	Nb, Ti, W, Cr	9.4
" , -150 "	4.389 ± .001	60	Nb, Ti, W, Cr	9.3
" , -325 "	4.374 ± .001	38	Nb, Ti, W, Cr	8.3

Figure 5 shows the hyperbolic nature of the carbide partitioning function. Here the percent of total carbon as MC is plotted versus the maximum particle size in each sieve fraction analyzed. If narrower ranges of sieve fractions had been chosen, one would expect the +325 to -35 portion of the curve to be shifted toward higher percent values. Nevertheless the percent carbon as MC approaches zero asymptotically for infinitesimally small powder particles. Likewise, the percent carbon as MC is expected to approach 100 percent for an infinitely large ingot. For practical purposes, the percent carbon as MC in reasonable ingots is expected to be about 85 to 90%.

**DIFFERENTIAL THERMAL ANALYSIS:** The techniques employed have been described previously (4,5). Typical on-heating thermograms in Figure 6 show the gamma prime solvus is higher for loose powder than for either ingot, while the opposite is true for the solidus, MC solvus and liquidus. Table III shows that after HIP'ing, all reactions occur at temperatures similar to those of ingots, except gamma prime solvus which requires remelting. This apparent difference in gamma prime may be accounted for by the higher solidification rate of the powder.

% OF C  
AS MC

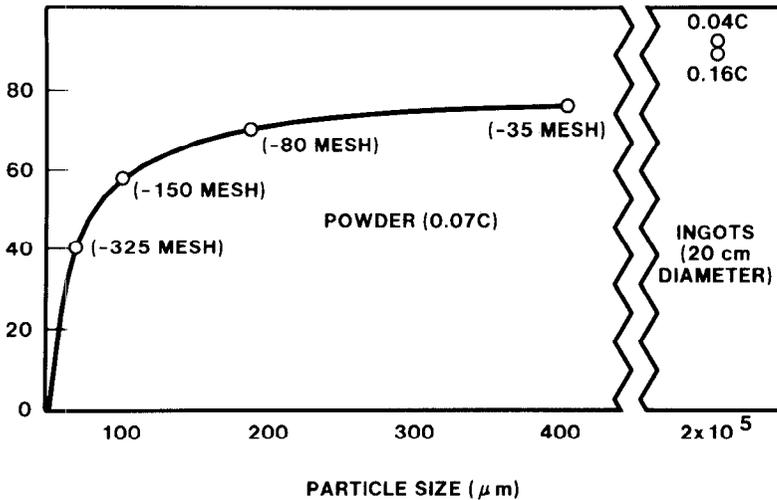


Figure 5. Carbon partitioning vs. particle size.

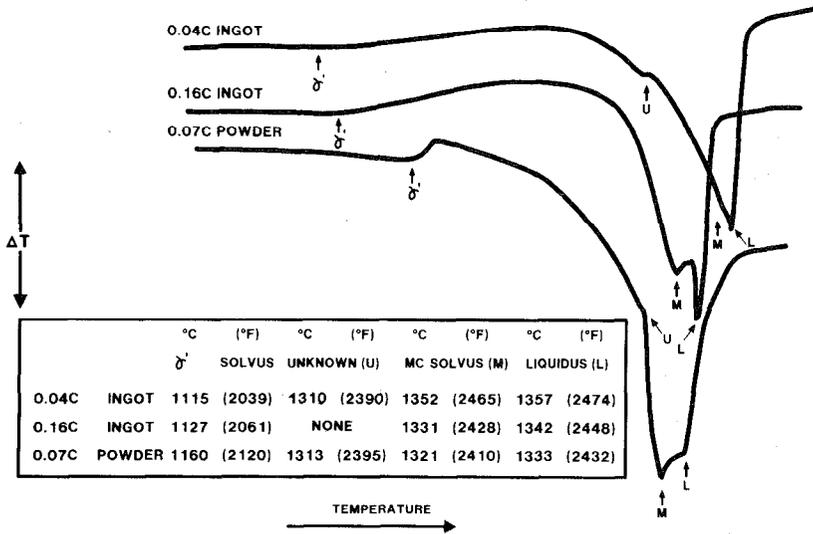


Figure 6. Typical thermograms.

TABLE III

	$\gamma'$ SOLVUS	SOLIDUS	UNKNOWN REACTION	MC SOLVUS	LIQUIDUS
INGOT, HIGH CARBON, EDGE	1144	1292	NONE	1331	1339
" , " , MID-RADIUS	1135	1295	NONE	1333	1343
" , " , CENTER	1127	1293	NONE	1331	1342
" , LOW CARBON, MID-RADIUS	1115	1277	1310	1352	1357
POWDER, -150 MESH	1160	1246	1310	1324	1333
" , HIP'ed	1166	1282	1317	1329	1346
" , REMELTED	1139	1274	1313	1334	1342

The gamma prime solvus of the high carbon ingot shows an edge to center effect, reflecting the increased dendritic segregation towards the center. A similar effect, not shown in Table III, was found for low carbon ingot. Also observed for the ingots, and not unusual, is the depression of the liquidus and MC solvus by carbon increase.

A more subtle phenomenon is the weak reaction detected between the solidus and MC solvus in all but the high carbon ingot. This "unknown" reaction is very likely the melting of eutectic gamma prime which is more abundant in low carbon material. The explanation appears to be linked to competition between MC and other phases for niobium.

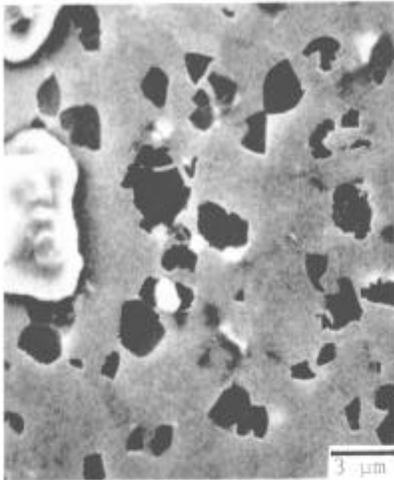


Figure 7. SEM micrograph of cast-wrought R95.

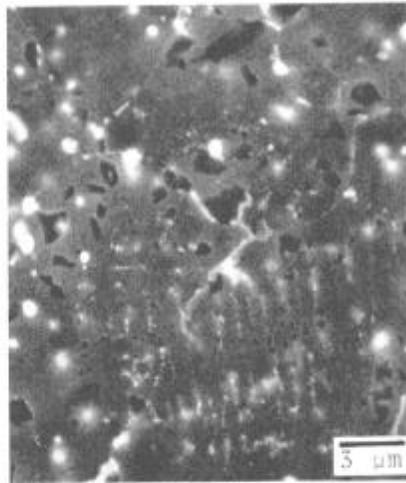


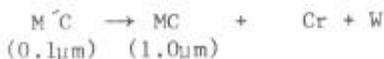
Figure 8. SEM micrograph of HIP R95 powder.

Interestingly enough, this reaction is observed for loose powder, although eutectic gamma prime and delta are not expected to form as large, well defined areas during solidification.

**CAST WROUGHT:** Material converted from the ingots previously described was studied. The typical microstructure in Figure 7 shows that hot working has caused partial homogenization, dissipated delta, and coarsened the primary gamma prime.

Carbon partitioning and DTA reaction temperatures were identical to those of ingots for respective carbon levels. The MC carbides of wrought and ingot have identical size, lattice parameters, wt% carbon and energy dispersive spectra.

**HIP'ed POWDER:** The scanning electron micrographs in Figure 8 show an even MC distribution and MC size of about one micron. 100% of carbon present partitions to the MC phase, with lattice parameters and wt% carbon in MC identical to those of wrought and ingot. MC is similar to wrought and ingot MC in composition, but without the usual trace of tungsten. This indicates a reaction at the HIP'ing temperature of 1121°C (2050°F).



## CONCLUSIONS

1. A new transition carbide M'C was detected in Rene' 95.
  - M'C is found only in loose powder, where the percent of total carbon partitioning to this phase depends on particle size. M'C size is about 0.1 micron.
  - M'C converts to MC during HIP'ing at 1121°C with outward diffusion of chromium and tungsten, as all carbon present partitions to the MC phase.
2. New relationships were detected near the solidus.
  - Delta and eutectic gamma prime are more common in low carbon cast and cast-wrought, probably due to niobium partitioning.
  - Differential thermal analysis shows a subtle endothermic reaction, in addition to MC solvus, in low carbon Rene' 95.
3. The main terminal phases in Rene' 95, MC and gamma prime are affected by process methods.
  - Cast-wrought MC is similar to HIP'ed powder MC but particles are larger (10 microns vs. 1 micron) and less evenly distributed.
  - Gamma prime solvus is dependent on solidification mode.
  - Gamma prime size, morphology, distribution and volume fraction appear dependent on conversion practices (cast wrought vs. HIP) as well as heat treatment.

## ACKNOWLEDGEMENTS

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