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Eutectic Superalloys for Laser Powder Bed Fusion

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Abstract (150-250 words)

Due to the small freezing range of eutectic alloys, the Cotac-type alloys might be viable alternatives to conventional Ni-based superalloys when processed through additive manufacturing. Laser-pass assessment reveals that both Cotac-74 and Cotac-744 display improved cracking resistance when compared to the conventional Ni-based superalloy CM247LC. During laser powder bed fusion Cotac-74 displayed the highest cracking resistance, with no microcracking detected in the as-built or heat-treated microstructure. The promising

29 results presented for Cotac-74 highlight the possible use of this alloy for the additive
30 manufacturing of high-temperature aerospace components.

31 **Keywords:** nickel alloys; laser methods; electron microscopy; *in-situ* composites; additive
32 manufacturing; other

33 **Introduction**

34 Laser powder bed fusion (LPBF) is of tremendous interest to the aerospace industry, offering
35 opportunities for the production of geometrically complex components that may deliver
36 improved in-service performance. However, whilst low γ' (<30 vol.%) and γ'' superalloys can
37 be routinely and reliably manufactured using LPBF, significant challenges remain in the LPBF
38 processing of high γ' alloys [1, 2]. In particular, solidification and liquation cracking frequently
39 occur during fabrication, while higher γ' alloys may also experience strain-age cracking when
40 exposed to high temperatures in post-processing operations [3, 4]. The strain-age cracking
41 susceptibility of high γ' superalloys is believed to be a result of large residual stresses
42 developing within the material linked to the precipitation of the γ' phase. Consequently, to
43 improve the processability of these alloys, three key research strategies form the focus of the
44 majority of the open literature; the optimisation of process parameters during fabrication, the
45 chemical modification of the alloys, and the design of novel superalloy compositions that are
46 intrinsically resistant to both hot and strain-age cracking [4-8].

47 In this study, an alternative strategy is considered, namely the investigation of alloy systems
48 that exploit eutectic invariant reactions as a means of improving the cracking susceptibility of
49 high γ' superalloys without compromising the alloy performance. It has been reported that
50 controlling the freezing range can reduce, or in some instances eliminate, solidification
51 cracking [9-11]. As such, eutectic alloys, which possess an intrinsically narrow freezing range,
52 might enable the LPBF of alloys with high fractions of γ' . The systems Cotac-74 and Cotac-
53 744 are eutectic Ni-based superalloys containing γ , γ' and MC-type carbides that were
54 developed by ONERA during the 1970s to be used as directionally solidified composites for
55 turbine blades and nozzle guide vanes [12] [13]. These alloys offered a good combination of
56 mechanical performance and satisfactory oxidation resistance at temperatures in excess of 900
57 °C. The microstructures of these *in-situ* composites were based around the γ - γ' -MC eutectic,
58 with carbide fibres running through the microstructure along the solidification direction.

59 However, they did not achieve commercialisation due to the uneconomic furnace withdrawal
60 rates required to maintain a planar front during solidification.

61 To date, there has been no research into the additive manufacturing of either Cotac-74 or Cotac-
62 744, or indeed any other Ni-based eutectic alloys. The work herein, aims to present an initial
63 investigation of the amenability of the Cotac-74 and Cotac-744 alloys to LPBF, focusing
64 primarily on the cracking susceptibility of the alloys. Comparisons are made to the behaviour
65 of CM247LC. Particular attention has been given to the microstructural evolution of the alloys
66 during processing and post-built heat treatment.

67 **Experimental Methods**

68 The nominal compositions of the alloys investigated in this study are given in Table 1 [12, 14].

69 **Table 1** – Compositions of the alloys used in this study in wt %. The balance in Ni in each case.

Alloy	Al	Co	Cr	Hf	Nb	Mo	Ta	Ti	W	C	B	Zr
Cotac-74	4	20	10	-	4.9	-	-	-	10	0.6	-	-
Cotac-744	6	10	4	-	3.8	2	-	-	10	0.47	-	-
CM247LC	5.6	9.2	8.1	1.4	-	0.5	3.2	0.7	9.5	0.07	0.015	0.015

70

71 The alloy samples investigated in this study were produced via two routes; (i) vacuum arc-
72 melting and (ii) LPBF. This permitted analysis and comparison of the microstructure produced
73 by the two routes as well as an initial assessment of the propensity to cracking during surface
74 laser passes.

75 The surface laser passes were carried out using the bead-on-plate method on arc melted ingots
76 to determine the cracking tendency, similar to the bead-on-plate test carried out by Zhou *et al.*
77 [13]. For these tests, a laser was rastered across a flat surface that had been ground to a 1200
78 SiC grit finish. Conventionally cast CM247LC was included in this testing to provide a
79 benchmark for interpretation of the results. Three sets of laser-passes were performed on each
80 alloy with energy densities per unit area of 2.25 J/mm², 3.17 J/mm² and 4.04 J/mm², henceforth
81 referred to as low, medium and high respectively.

82 The assessment of cracking susceptibility was performed qualitatively from optical and
83 electron micrographs of the laser-scanned surface of the samples (shown as binary threshold
84 insets in Figure 1). The samples were subsequently cut in cross-section, mounted and prepared
85 for microscopy following standard metallographic preparation techniques culminating in a
86 final polishing step with 0.04 μm colloidal silica solution. This allowed the analysis of the laser
87 heat-affected zone (HAZ) with depth into the ingot surface to be assessed. Scanning electron
88 microscopy (SEM) was performed using a Zeiss GeminiSEM 300 fitted with an Oxford
89 Instruments X-MaxN 50 energy dispersive X-ray (EDX) detector for compositional analysis
90 of the microstructural features. Where required, processing the sample images was achieved
91 using the open-source ImageJ software.

92 LPBF samples were built using custom powder with a powder size of 15 μm - 45 μm . Samples
93 manufactured using LPBF were supplied by Rolls-Royce plc. As no process optimisation was
94 explored for this work, the lowest energy density of 2.25 J/mm^2 was chosen as appropriate
95 based on the laser passes investigated coupled with a bilinear raster scan strategy to produce
96 rectilinear columns. No additional hot isostatic pressing treatments were applied to the as-built
97 samples. However, in addition to microstructural evaluations of material in the as-cast and as-
98 built states, samples were also heat treated and aged following the guidelines reported by Khan
99 *et al.*[12] and modified based on differential scanning calorimetry results to ensure super-
100 solvus solution heat treatments were utilised. All samples were removed from the baseplate
101 using electro-discharge machining prior to heat treatments. Cotac-74 samples were
102 homogenised at 1125 $^{\circ}\text{C}$ for 1 hour and aged for 16 hours at 760 $^{\circ}\text{C}$, whereas Cotac-744
103 samples were homogenised at 1260 $^{\circ}\text{C}$ for 1 hour and aged for 16 hours at 850 $^{\circ}\text{C}$. For both
104 alloys, air cooling to room temperature was used between each heat treatment step. All samples
105 were heat treated in Ar-backfilled quartz ampoules to limit oxidation effects on the samples.
106 Henceforth the heat treatments will be referred to as “as-built” for no heat treatment and
107 “solution-aged” for the fully heat-treated condition.

108 Differential scanning calorimetry (DSC) was performed using a Netzsch 404 calorimeter on
109 disc-shaped samples of approximately 5 mm diameter and 1 mm thickness of each alloy.
110 Transition temperatures were obtained from the deviations from baseline of the first derivative
111 curves. Using this method, the γ' solvus and the material solidus temperatures were extracted
112 from the heating data whilst the liquidus temperature was determined from the cooling data.

113 X-ray diffraction (XRD) data were collected from Cotac-74 and Cotac-744 samples using a
114 Bruker D8 DAVINCI diffractometer fitted with a CuK α source and a Ni filter. Data were
115 acquired over a 2θ range of 20 to 100° with a step size of 0.05° and a dwell time of 3 seconds.
116 The diffraction data were analysed using full-pattern Pawley refinements in Topas-Academic.

117 Samples for transmission electron microscopy (TEM) were extracted from selected regions of
118 interest using focused ion beam milling (FIB) and were spot attached to a TEM grid. Electron
119 micrographs and selected-area diffraction patterns (SADP) were acquired from the FIB
120 samples using an FEI™ Tecnai Talos TEM operated at 200 kV. The scanning transmission
121 electron microscopy (STEM) mode was used to perform EDX for compositional analysis using
122 a Bruker XFlash detector in the same instrument.

123 **Results and Discussion**

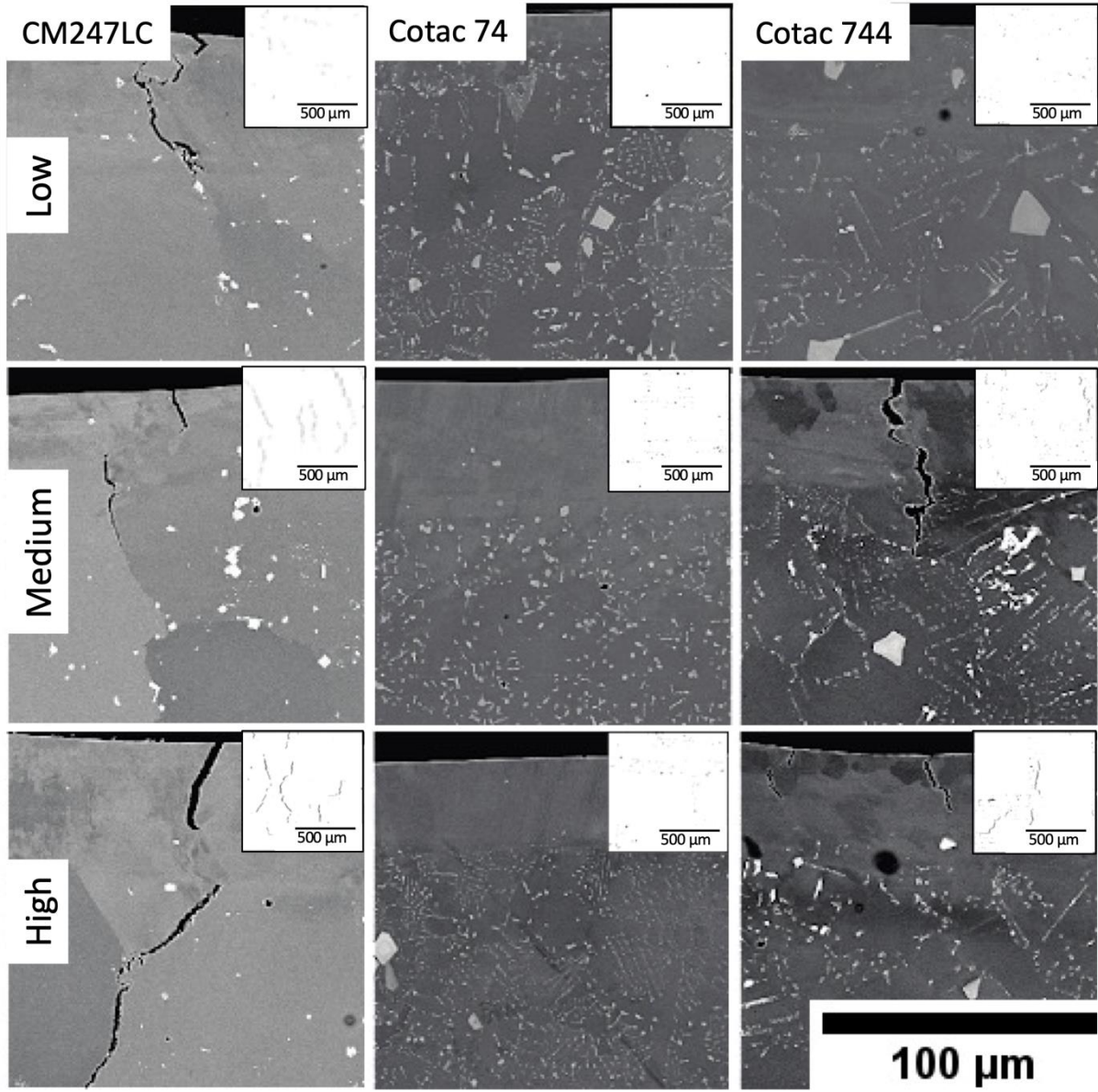
124 **3.1 Laser-pass Assessment**

125 The viability of the Cotac-74 and Cotac-744 for LPBF was determined through laser-pass
126 assessments on polished surfaces of the as-cast samples. Figure 1 shows cross-sectional
127 micrographs through the laser passes for Cotac-74 and Cotac-744 as well as CM247LC, which
128 was used as a benchmark material to assess the viability of the methodology utilised. In
129 addition, insets for each condition in Figure 1 show binary thresholded images of a larger area
130 of the laser pass surface, qualitatively highlighting the crack density for each material in each
131 condition. As expected, CM247LC exhibited cracking in all energy densities used, with an
132 increase in energy density leading to higher cracking susceptibility. In contrast, both alloys
133 Cotac-74 and Cotac-744 show reduced cracking densities. Cotac-744 showed no cracking at
134 low energy density, with some cracking being observed in the medium and high energy
135 densities, albeit this appeared to be of reduced severity when compared to CM247LC. Cotac-
136 74 was found to exhibit no visible cracking in any of the conditions assessed, consistent with
137 this material comprising a lower γ' fraction compared to Cotac-744.

138 In addition to the cracking susceptibility, the micrographs in Figure 1 also show the
139 microstructural changes of the material within the heat affected zone of the laser pass compared
140 to the as-cast structure. All samples show the development of a heat affected region where a
141 typical epitaxial structure with high levels of intragranular misorientation can be observed. Of
142 particular note is the dissolution of the finer carbide phases within the laser pass region in

143 Cotac-74 and Cotac-744, suggesting that optimisation of the microstructure of these materials
144 could indeed be possible in LPBF.

145

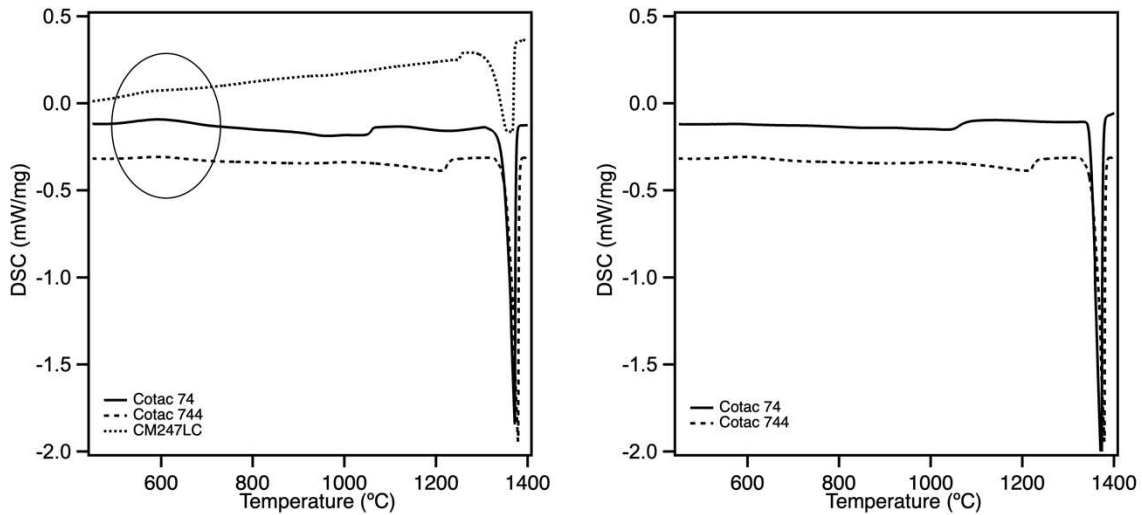


146

147 **Figure 1** – SEM cross-section images of the as-cast alloys CM247LC, Cotac-74, and Cotac-744 following laser-
148 pass assessment. Insets in each condition show a binary threshold image of the laser surface providing a clearer
149 representation of the cracking severity in each condition. No cracks were observed for Cotac-74 for any of the
150 three laser-pass conditions. Surface breaking cracks can be seen in all conditions for CM247LC, with cracking
151 observed in the medium and high-power regimes for Cotac-744.

152 **3.2 Thermodynamic Analysis**

153 To determine the solidification ranges and the solvus temperatures of the γ' phase for Cotac-
 154 74 and Cotac-744, DSC data were acquired from samples both in the as-built and as-cast state
 155 and compared against the equivalent conditions of CM247LC. The first heating curves of the
 156 alloys in the as-built state are shown in Figure 2. Table 2 summarises the key transition
 157 temperatures from all results in the as-cast and as-built states.



158
 159 **Figure 2** – Left: DSC first heating thermograms for the Cotac-74, Cotac-744 and CM247LC alloys in
 160 equivalent as-built conditions, Right: Equivalent DSC first heating thermograms of as-cast Cotac-74 and Cotac-
 161 744.

162 An exothermic event in the DSC heating data is present at approximately 500 – 700 °C for all
 163 as-built LPBF samples, but is notably absent in the as-cast samples. This event is commonly
 164 observed in AM processed superalloys and is thought to be associated with the precipitation of
 165 γ' [3, 15]. On second heating, this event was no longer observed in any of the conditions,
 166 confirming that it is the result of a microstructural feature related to the LPBF processing.

167 **Table 2** – Transition temperatures in degrees Celsius for the alloys used in this study, determined from analysis
 168 of the DSC data.

Thermal Events	CM247LC	Cotac-74		Cotac-744	
	LPBF	As-cast	LPBF	As-cast	LPBF
γ' solvus – Mid Point	1251.5	1061	1059	1230	1226

<i>Solidus Temperature</i>	1279	1333	1303	1321	1320
<i>Liquidus Temperature</i>	1364	1340	1345	1353	1363
<i>Approximate solidification range</i>	85	7	42	32	45

169

170 The solidification range of each alloy was calculated from their respective liquidus temperature
 171 obtained on cooling and their solidus temperature obtained on heating. The values obtained for
 172 Cotac-744 in both conditions and for the as-built Cotac-74 are similar, although the value for
 173 as-cast Cotac-74 is unexpectedly low. The calculated solidification range for CM247LC is
 174 approximately double that of the Cotac alloys, with the narrower freezing range of these alloys
 175 being a result of the eutectic solidification behaviour, which is theorised to lead to improved
 176 hot cracking resistance [9-11].

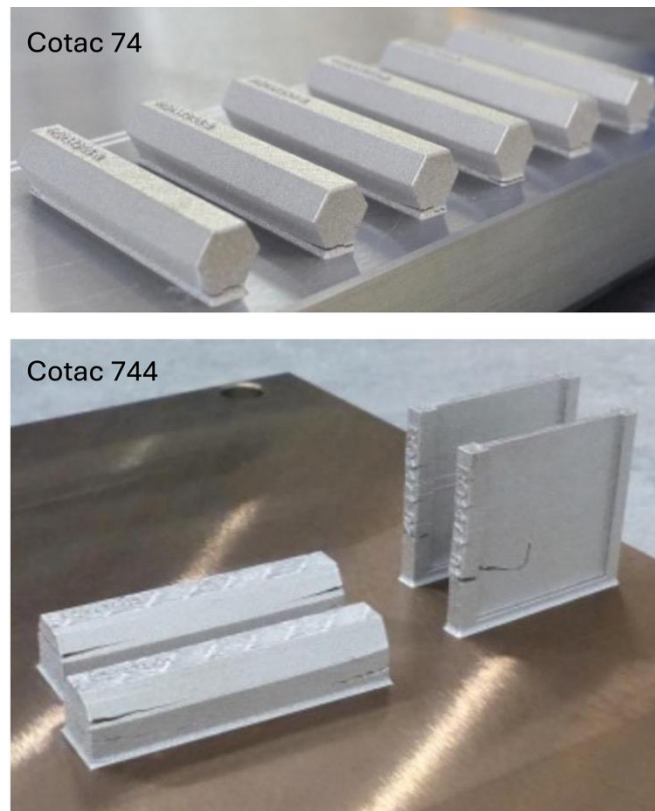
177 The γ' solvus temperature for all alloys is also reported in Table 2. Due to difficulties in
 178 determining the precise values of the onset and return to baseline, only the mid-point values
 179 corresponding to the point of maximum γ' dissolution are reported. Cotac-744 is shown to have
 180 a significantly higher γ' solvus temperature than Cotac-74 across both production routes and
 181 for all points of dissolution compared. This behaviour is to be expected due to the significantly
 182 higher Al content in Cotac-744 compared to Cotac-74 giving rise to both an increased γ' solvus
 183 temperature as well as a higher γ' volume fraction. The values for the solidus temperature and
 184 γ' solvus obtained in the LPBF condition for both alloys were found to be in line with values
 185 reported in the literature [12, 14].

186 Of particular significance to assess the material for LPBF suitability is the temperature range
 187 of the alloys between the γ' solvus and the solidus temperature. A larger temperature range is
 188 thought to be beneficial, reducing the cracking susceptibility of the material due to a reduction
 189 in the propensity for brittle, solute enriched films [16]. Based on the DSC thermograms
 190 obtained, this window is 20°C for CM247LC, 230°C for Cotac-74, and 80°C for Cotac-744,
 191 further suggesting the possibility of a reduced cracking susceptibility for the Cotac alloys.

192 **3.3 Microstructure and Cracking behaviour**

193 Macroscopic images of the as-built samples of the Cotac alloys, Figure 3, revealed significant
 194 macrocracking and base delamination in both the Cotac-74 and Cotac-744 alloys following

195 LPBF processing. This was believed to be a result of non-optimised build parameters [17], as
196 existing parameter sets commonly used for high γ' superalloys were chosen and no design of
197 experiments studies were performed to enable parameter optimisation. Whilst the observed
198 macrocracking is of concern, the results from the laser pass assessments suggest that
199 microcracking can be reduced or eliminated in these materials, and therefore, processing
200 optimisation may be feasible. Indeed, no microcracking was observed in samples of the Cotac-
201 74 alloy, Figure 4, in either the as-built or solution-aged conditions. In contrast, solidification
202 microcracks were visible throughout the microstructure of Cotac-744. This increased cracking
203 susceptibility was consistent with the higher γ' content in Cotac-744 compared to Cotac-74, as
204 well as the reduced temperature range between the terminus of γ' solvus and the solidus
205 temperature.



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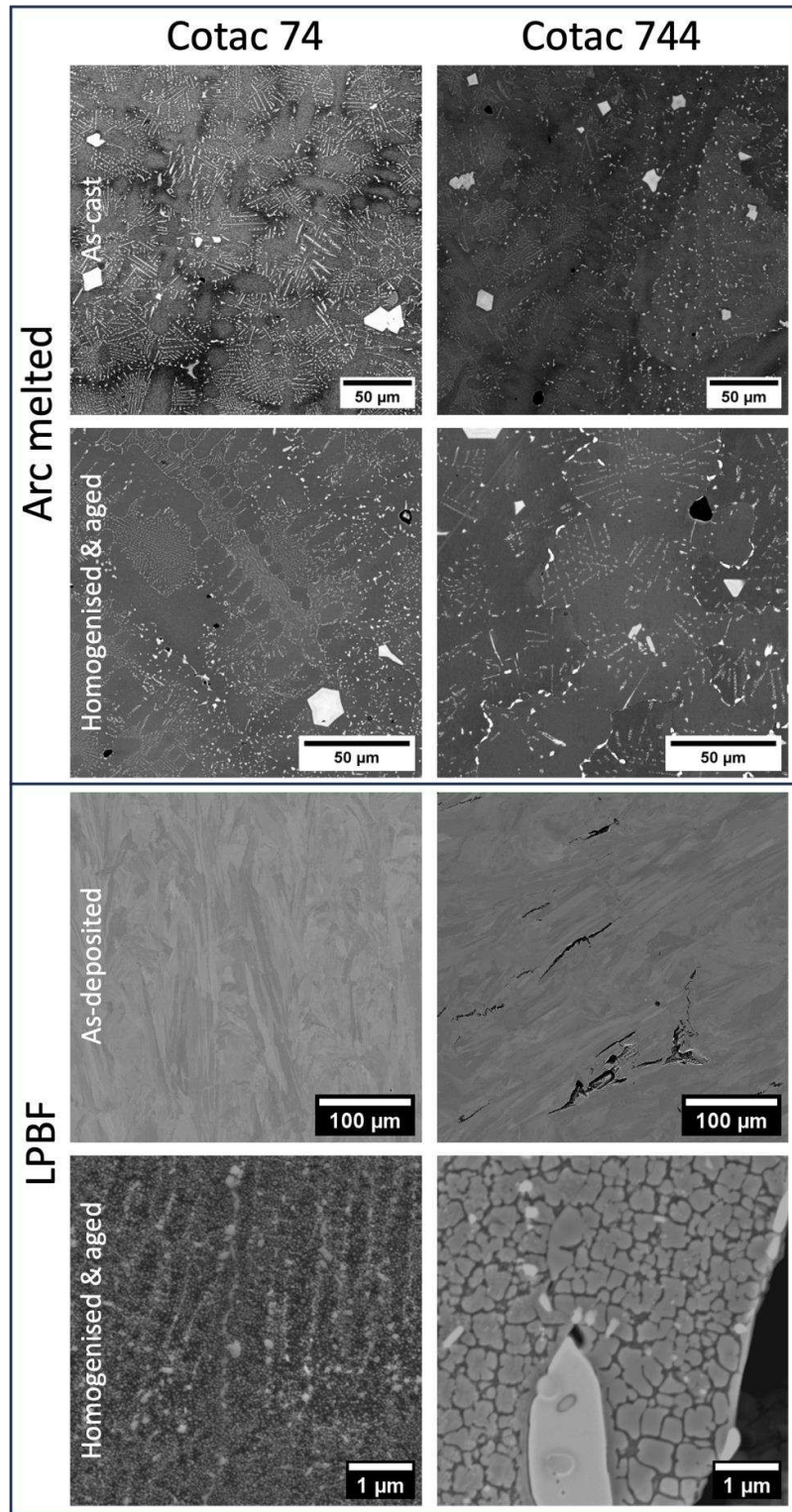
207 **Figure 3 – Photographs of the Cotac-74 (top image) and Cotac-744 (bottom image) builds exhibiting**
208 **macroscopic cracking behaviour and base delamination.**

209 Figure 4 further reveals the microstructures of the alloys in the as-built states and following
210 solution and ageing. In the as-cast state, both Cotac-74 and Cotac-744 alloys exhibited fine
211 eutectically formed MC carbides, with larger, blocky MC precipitates also forming. Upon
212 solution and ageing, the microstructure of Cotac-74 remained largely unchanged with only

213 minor spheroidisation of a small fraction of the fine eutectic carbide network observed. In
214 contrast, the eutectic carbide network in Cotac-744 was found to coarsen, with precipitation of
215 bright phases, also believed to be carbides, occurring at high angle grain boundaries.

216 In contrast to the as-cast states, the as-built microstructures for both Cotac-74 and Cotac-744
217 were found to solidify with the typical cellular structure observed in LPBF and no evidence of
218 the eutectic carbide networks. Instead, fine carbides were observed to form at cellular
219 boundaries in both alloys. Following solution and ageing, these carbides persisted but
220 additional coarse carbides were seen on the grain boundaries. Due to processing through LPBF,
221 the γ' precipitates were fine in both alloys, however larger precipitates were observed in Cotac-
222 744 due to the higher γ' content.

223 Examination of the as-built Cotac-74 microstructure produced via LPBF revealed a network of
224 fine carbides. After heat treatment the carbide network remained, with coarser precipitates
225 present. These were located primarily on the grain boundaries with a small amount of
226 additional intragranular precipitation. As in Cotac-74, a fine MC carbide network was seen in
227 the as-built material of Cotac-744. Following solution heat treatment and ageing these persisted
228 but additional coarse carbides were seen on the grain boundaries. The formation of γ'
229 precipitates was also observed following solution and ageing, with significantly finer γ'
230 particles observed in Cotac-74 compared to Cotac-744.



231

232

233

Figure 4 – Backscattered electron micrographs for Cotac-74 and Cotac-744 produced by arc melting and LPBF in the as-built states and following solution heat treatment and ageing.

234 3.4 Phase Analysis

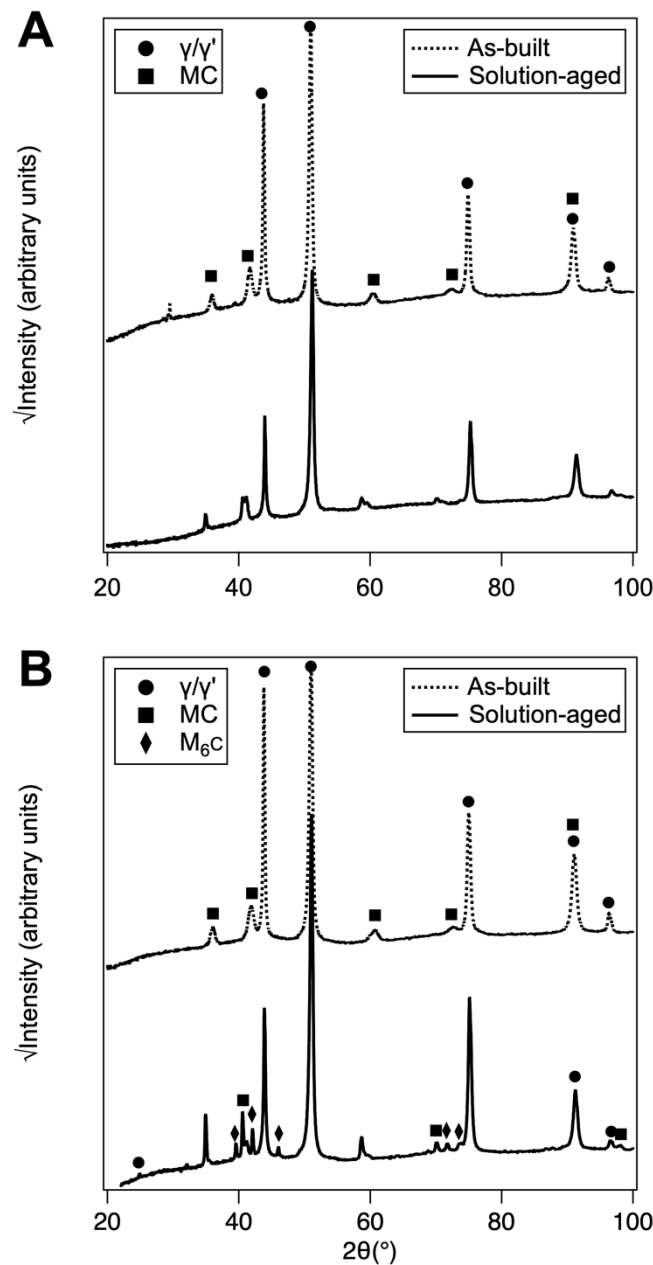
235 To further explore the microstructures of the Cotac alloys following LPBF, as well as
236 determine the crystallographic nature and elemental constitution of the precipitating phases,
237 XRD and TEM analyses were performed. Figure 5 summarises the XRD results obtained
238 whereas Figures 6 and 7 show STEM-EDX maps and selected area diffraction patterns
239 (SADPs) from the key phases from the solution and aged states.

240 Examination of the XRD data obtained from the LPBF material revealed the presence of γ/γ'
241 fundamental peaks and MC carbide peaks in the as-built condition for both alloys. The
242 associated lattice parameters of the phases obtained through Pawley refinements are shown in
243 Table 3. Due to the absence of superlattice γ' peaks, the difficulty in clearly separating distinct
244 γ and γ' contributions in the fundamental peaks, as well as the generally accepted theory of the
245 absence of γ' formation in the as-built condition for superalloys, only the lattice parameters for
246 the γ and MC carbide phases could be obtained for the as-built state.

247 As expected, for both Cotac alloys, peaks associated with MC carbides were observed in the
248 XRD traces. Based on the compositions of the alloys, these carbides should be nearly pure
249 NbC, as Nb is the only strong MC carbide former in both alloys. However, comparing the
250 lattice parameters obtained in the as-built state to that of pure NbC, which has a lattice
251 parameter of 4.470 Å [18], it is clear that Nb is not the only metal conjugate in the carbides
252 formed.

253 Following solution and ageing, the XRD results obtained differed for the two alloys. For Cotac-
254 74, no additional peaks were observed that would indicate the presence of additional phases.
255 However, the MC carbide peaks were seen to split into doublets suggesting the potential
256 formation of carbides with distinct compositions. This phenomenon was previously reported
257 by Divya *et al.* [19] and was believed to be due to the formation of non-equilibrium MC species
258 during the LPBF processing. Analysis of the lattice parameters of these carbides suggests that
259 one of the MC species approaches pure NbC, with the second species exhibiting a smaller
260 lattice parameter. The STEM-EDX analysis revealed the presence of both large and small
261 carbides rich in Nb. It is believed that the larger, more Nb-rich carbides formed from the
262 eutectic MC carbide particles, with more compositionally-complex finer carbides precipitating
263 during the subsequent ageing. In addition to the MC carbides, and despite no additional peaks
264 identified in the XRD patterns, STEM-EDX of the solution and aged Cotac-74 alloy indicated

265 the formation of strongly Cr-rich carbides, believed to be $M_{23}C_6$. Crystallographic confirmation
 266 of the presence of $M_{23}C_6$ was obtained through electron diffraction, which further revealed a
 267 $[0\ 0\ 1]//[0\ 0\ 1]$ orientation relationship between the $M_{23}C_6$ and γ phase. From the literature, it
 268 was reported by Khan *et al.* [12] that this phase evolves from the transformation of MC at
 269 temperatures in the range of 700 to 1000 °C, consistent with the ageing temperature of Cotac-
 270 74.



271

272 **Figure 5** – XRD traces for Cotac-74 (A) and Cotac-744 (B) in the as-built and solution-aged conditions. Note the
 273 split MC peaks in the solution-aged condition.

274 **Table 3** – Lattice parameters of the phases in Cotac-74 and Cotac-744, determined through Pawley refinement of

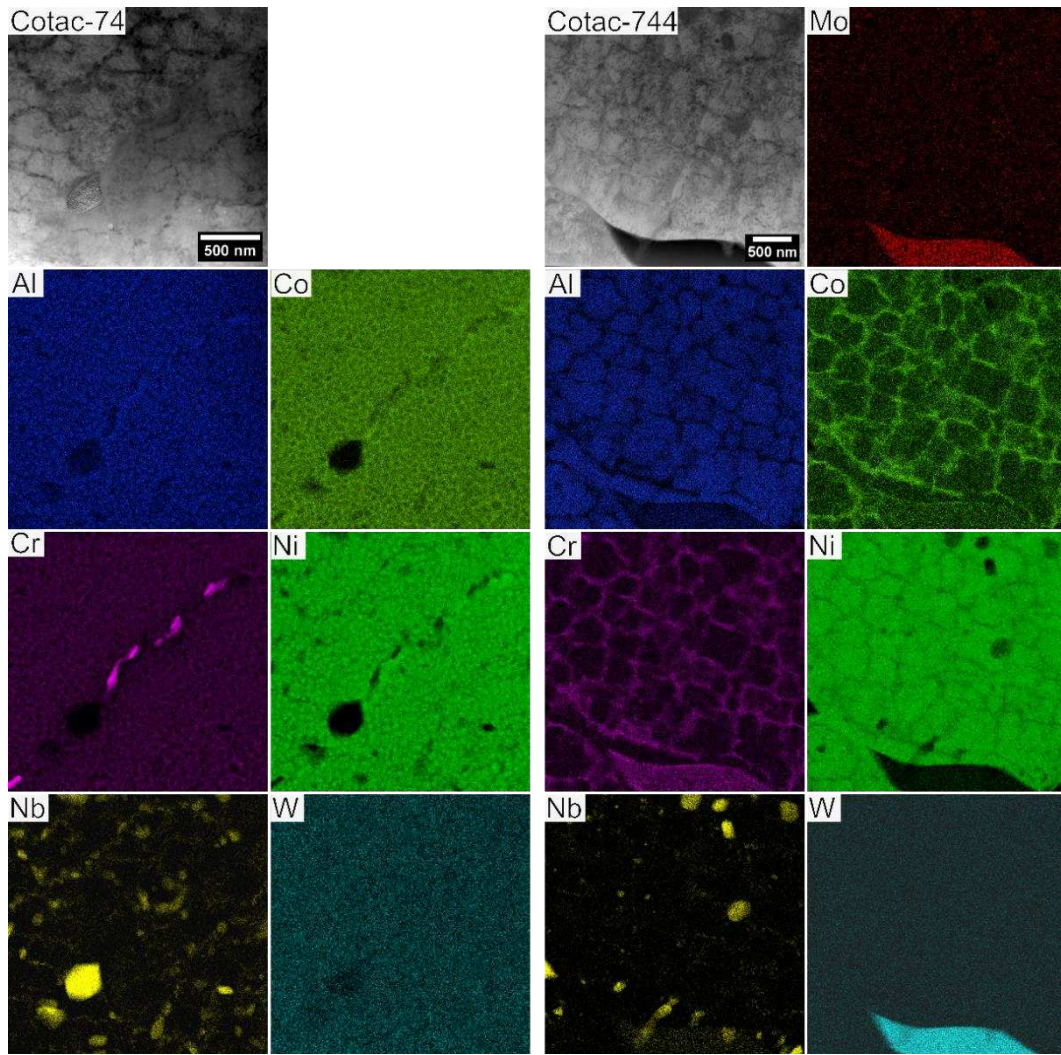
275 the XRD data.

Lattice Parameter / Å	Cotac-74		Cotac-744	
	As-built	Solution-aged	As-built	Solution-aged
γ	3.580	3.573	3.577	3.573
γ'	-	3.585	-	3.586
<i>MC Carbide - 1</i>	4.332	4.441	4.316	4.437
<i>MC Carbide - 2</i>	-	4.393	-	4.384
M_6C	-	-	-	11.151

276

277 Similarly to Cotac-74, the MC carbide peaks in the XRD patterns for Cotac-744 following
278 solution and ageing also showed splitting, enabling two distinct MC species to be identified;
279 one closer to pure NbC, and the other exhibiting a smaller lattice parameter. However, in
280 contrast to Cotac-74, the XRD patterns from the solution and aged Cotac-744 did also show
281 additional peaks not resulting from the γ/γ' and MC phases. These additional peaks were
282 identified to be due to the formation of the M_6C phase, which was also confirmed through
283 electron diffraction, Figure 7. The formation of the M_6C phase instead of the $M_{23}C_6$ phase was
284 believed to be due to the lower content of Cr and higher content of Mo in Cotac-744 compared
285 to Cotac-74 [12].

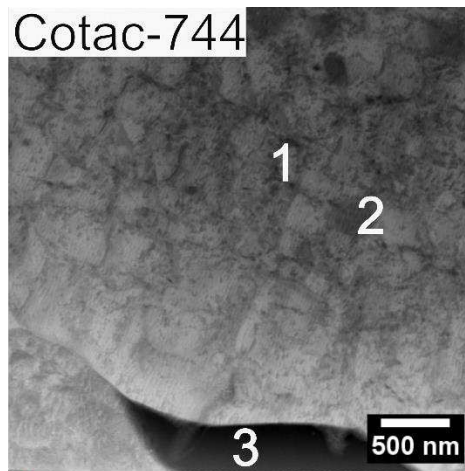
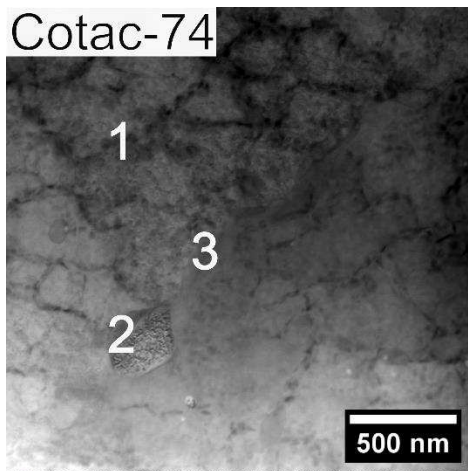
286 From STEM-EDX data, the M_6C phase was found to be rich in Mo and W. Though the M_6C
287 was not identified by Khan *et al.* [12], it was observed by Kachanov *et al.* [20] and Petrushin
288 *et al.* [21] in alloys with a similar composition. It was posited that this phase can form in
289 preference to $M_{23}C_6$ from the reaction of the γ and MC carbides at higher temperature. This
290 may arise as a result of the solidification induced microsegregation associated with LPBF
291 processing and may be further influenced by subsequent heat-treatments applied. It is therefore
292 likely that correct optimisation of heat-treatments specific to LPBF may be required to avoid
293 the occurrence of M_6C .



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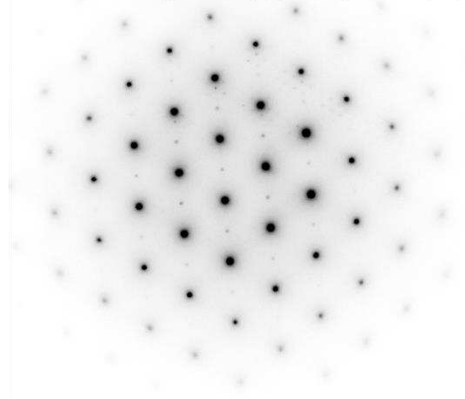
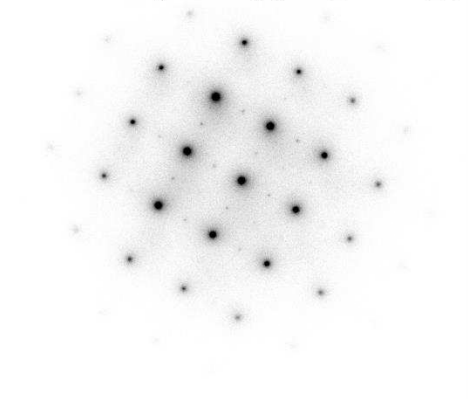
295 **Figure 6** – STEM-EDX analysis of solution-aged Cotac-74 and Cotac744. In each instance, the first image is a
 296 bright field electron micrograph. Individual elemental concentration maps have been provided for each of the
 297 major elements in the alloys.

298



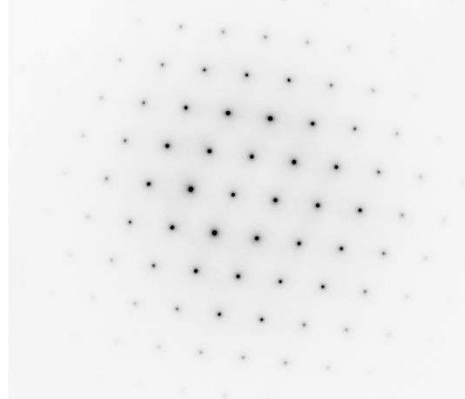
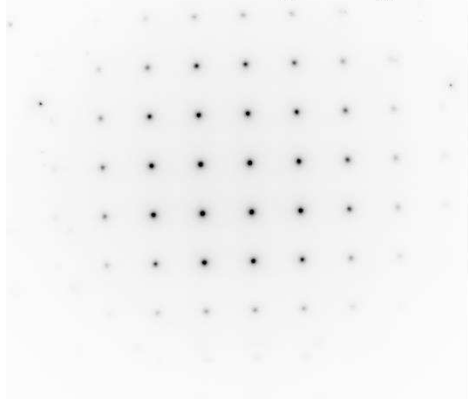
1 [001] γ' //[001] γ

1 [110] γ' //[110] γ



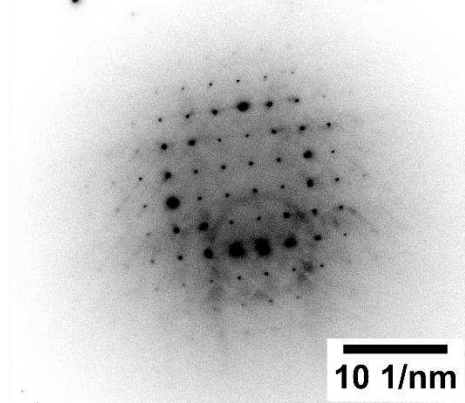
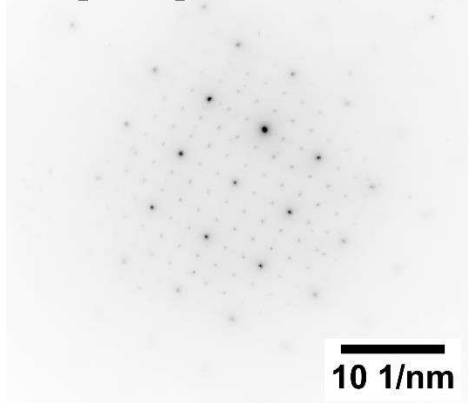
2 [001]MC

2 [011]MC



3 [001] $M_{23}C_6$ //[001] γ

3 [001] M_6C



300 **Figure 7** – TEM analysis of the solution-aged Cotac-74 and Cotac744. In each instance, the first image is a
301 bright field electron micrograph with numbered regions. The number corresponds to the regions where SADPs
302 were taken from. The specific SADPs have been provided below the bright field micrographs for each alloy. For
303 each SADPs the orientation and, if relevant, the orientation relationship have been provided. Due to the textured
304 nature of the samples it was not always possible to orient the cubic phases along the [100] planes. In both alloys
305 the γ' superlattice reflections are visible in the SADPs.

306 **Conclusions**

307 The results presented in this study highlight the potential advantage of using the γ - γ' -MC
308 eutectic superalloys for additive manufacturing. Both eutectic Cotac alloys studied herein
309 displayed increased cracking resistance in the laser-pass assessment when compared to
310 CM247LC. Indeed, Cotac-74 displayed no microcracking when processed through LPBF. In
311 addition, no deleterious or unexpected phases were detected in the Cotac-74 alloy following
312 processing through LPBF in either the as-built or heat-treated conditions. However, further
313 exploration of the process parameters and part geometry is required to eliminate the macro-
314 cracking and realise the increased temperature capability of these alloys above other crack-free
315 LPBF Ni-based superalloys. Additional research into the development of these non-traditional
316 Ni-based superalloys for additive manufacturing processing is therefore warranted.

317

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