γ' Precipitation Study of a Co-Ni-Based Alloy

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- 1 Title page
- 2 γ' precipitation study of a Co-Ni-based alloy
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10 Abstract:

11 A Co-Ni-based alloy strengthened by γ' -(L1₂) precipitates was utilized to investigate the
12 precipitation evolution after various cooling rates and several aging conditions. In this study, the
13 precipitate size and volume fraction have been studied *via* scanning electron microscopy and
14 transmission electron microscopy. The influence of the precipitation evolution was measured *via*
15 microhardness tests. The cooling rate study shows a more sluggish γ' precipitation reaction
16 compared with that observed in a Ni-based superalloy. Following a rapid cooling rate, the
17 application of appropriate double aging treatments allows the increase of the γ' volume fraction as
18 well as the control of the size and distribution of the precipitates. The highest hardness values reach
19 those measured on supersolvus cast and wrought Ni-based superalloys. The observed γ'
20 precipitation behavior should have implications for the production, the heat treatment, the welding
21 or the additive manufacturing of this new class of high temperature materials.

22 I. Introduction

23 The mechanical properties and especially the tensile strength of γ/γ' superalloys strongly depend on
24 the fraction, distribution and size of the γ' phase precipitates. Regarding high γ' fraction wrought Ni-
25 based superalloys, the γ' precipitation is predominantly controlled by the cooling rate ^[1,2,3,4,5] after
26 the solutioning heat treatment. Generally, one or two aging treatments are then applied to adjust the
27 γ' precipitate characteristics ^[6,7,8].

28 Recently, several research teams have found that Co-based alloys can possibly be strengthened by
29 the precipitation of a L1₂- γ' phase based on Co₃(Al,W). This new phase is the subject of numerous
30 studies since the article of Sato *et al.* ^[9]. More recently, Indian researchers published a series of
31 articles on Co-based alloys strengthened by the precipitation of the Co₃(Al,Mo,X) phase (where X
32 is Ta or Nb) ^[10,11,12,13,14]. Even more recently, a novel Co-Ti-Cr alloy was shown to be strengthened
33 by γ' precipitates ^[15]. All these results have attracted great attention of several research groups. Most
34 of the studies on Co-Al-W alloys are dedicated to the improvement of their mechanical properties
35 and environmental resistance by means of alloying in relation to the microstructure. Only few
36 studies focused on the γ' -Co₃(Al,W) phase precipitation and more precisely on the coarsening
37 behavior ^[16,17,18,19,20,21].

38 The present work was performed on a Co-Ni-based alloy, the composition of which was derived
39 from that of a quaternary model alloy studied by Shinagawa *et al.* ^[22]. The Ni substitution for Co
40 promotes the widening of the γ/γ' domain, the increase of the γ' solvus temperature and the decrease
41 of the lattice parameter mismatch between the γ and γ' phases.

42 The objective of the present study was to investigate the mechanism of the γ' precipitation during
43 various heat treatments. We firstly studied the influence of the cooling rate on the γ' precipitation
44 and the results were compared to those obtained jointly on a Ni-based superalloy. In a second time,
45 we investigated the effect of three aging parameters to optimize the γ' precipitation and
46 consequently the strength of this Co-Ni-based alloy.

47 II. Experimental procedure

48 The Co-GP-1 Co-Ni-based alloy contains 30 at% of Ni, 7 at% of Al and 10 at% of W ^[22]. Minor

elements (C, B and Si) were added to control the grain size and to improve the grain boundary properties (Table I). The alloy was melted from raw elements by vacuum induction melting and then poured into a metallic mold. A cylinder was machined from the ingot, encapsulated in a steel can, held at 1250°C for 3 hours (supersolvus homogenization heat treatment) and then extruded with a reduction ratio of 10:1. Once the steel was removed, cylindrical samples (10 mm diameter and 10 mm length) were machined from the extruded billet and solution heat-treated for cooling rate or aging studies.

A Ni-based alloy was used for the cooling rate study as a reference material. Alloy N18 (Table I) is a powder metallurgy Ni-based superalloy used for production of high pressure compressor and turbine disks of the M88 turbofan for the Dassault Rafale fighter ^[5]. Cylindrical samples (10 mm diameter and 10 mm length) were machined out of an isothermal forging disk provided by Safran Aircraft Engine. These N18 samples belong to the same disk studied by Boittin *et al.* ^[23].

All the heat treatments were conducted in horizontal resistance furnaces. Microstructural investigations were carried out at the center of the specimens. Samples used for scanning electron microscopy (SEM) imaging were polished to a 0.25 µm diamond finish and to a 0.02 µm colloidal silica suspension in a vibratory polisher (Buehler VibroMet 2). Transmission electron microscopy (TEM) samples were prepared via mechanical grinding and polishing of 3 mm diameter disks. These samples were thinned by electropolishing in a Struers Tenupol-3 polishing unit. The solution used for Co-GP-01 thin foils is (5 % perchloric acid + 95 % methanol) at 243 K and 10-20 V and the one used for N18 thin foils is (45 % acetic acid + 45 % butylcellosolve + 10 % perchloric acid) at 273 K and 10-14 V. Observations were performed using a Zeiss DSM982 Gemini or a Zeiss MERLIN FEG-SEM and a FEI CM20 or a Zeiss Libra 200 FE TEM at 200 kV. The images used for the quantification of the precipitate size and their area fraction are either TEM dark field images with a <001> zone axis or SEM images acquired near a {100}-type plane. These images were converted to binary images via a combination of manual and automatic coloring techniques using the GIMP-2 and the ImageJ software packages. As the images used for the precipitate size measurement originate from different techniques (SEM secondary electron (SE) or back-scattered electron (BSE) and TEM micrographs) and as the precipitate morphology varies, the precipitate size is determined on a different sampling: from 100 area measurements for the study related to the effect of the cooling rate and up to 275 to 1800 area measurements for the study related to the effect of aging. The precipitate size is defined as the weighted mean equivalent particle diameter. The weight of each precipitate is the volume of the spherical particle of same equivalent diameter ($\frac{\pi d^3}{6}$). This weighting technique is necessary to ensure the relevance of the size measurements in terms of contribution of the precipitates to the size distribution. Vickers microhardness tests were conducted at room temperature on a Buehler OmniMet MHT tester (4.9 or 9.8 N). The hardness value is the average of 48 measurements on about 6 mm².

III. Results and discussions

A. Influence of the cooling rate on the γ' precipitation

The cooling rate study was carried out on both alloys Co-GP-01 and N18 to directly compare the γ' precipitation behavior of a Co-Ni-based alloy with that of a Ni-based superalloy. Alloy N18 was selected as a reference alloy because of its high γ' volume fraction as a wrought Ni-based superalloy (55-60%) which approaches the one estimated for alloy Co-GP-01 (60-70%). As the supersolvus

91 heat treatment window is narrow for alloy N18 (1195-1230°C^[23]) and wide for alloy Co-GP-01 (~
92 1035-1440°C^[22]), samples of both alloys were solution heat treated for one hour at 1200°C. This
93 supersolvus solution treatment was followed by ice water quenching, air cooling, furnace cooling or
94 slow cooling to produce a wide range of cooling rates. As the samples were not instrumented, the
95 precipitation model adapted by Boittin to the supersolvus N18 alloy^[24] was used to estimate the
96 various cooling rates from the mean size of the γ' precipitates. As both N18 and Co-GP-01 samples
97 were cooled together, we estimate the same value of cooling rate for both materials. These results
98 are presented in Table II. The precipitation model is understood to be accurate in a range of cooling
99 rates from 5 to 700 K/min^[25], so that it should not be surprising that the precipitate size resulting
100 from a 0.33 K/min cooling rate has been calculated by the precipitation model as it was resulting
101 from a 0.16 K/min rate. This factor 2 in terms of cooling rates corresponds to a factor 1.4 in
102 precipitate size, which is quite satisfactory given the fact that the cooling rate is far beyond the
103 accuracy range of the model. Therefore, the estimations concerning the other cooling rates can be
104 regarded as relevant.

105 A.1 Microstructure

106 The mean grain size is in the range 40-50 μm for alloy N18 and is larger for alloy Co-GP-01 (200-
107 250 μm). This difference is mainly due to the material processing. Alloy Co-GP-01 was cast and
108 extruded whereas alloy N18 was powder metallurgy processed. This later process leads to limited
109 grain size growth even after supersolvus solution heat treatment due to prior particle boundaries
110^[26,27].

111 TEM was used to characterize γ' precipitates in ice water quenched and air cooled samples of both
112 alloys due to the fine size precipitation in Co-GP-01 alloy whereas the other microstructures were
113 investigated using SEM. Examples of the γ' precipitate distribution in N18 and Co-GP-01 alloys are
114 shown in Figure 1.

Fig. 1 – Typical γ/γ' microstructure in Ni-based N18 (on the left) and in Co-Ni-based Co-GP-01 (on the right) after: an ice water quenching (a,b), an air cooling (c,d), a furnace cooling (e,f) or a 0.33 K/min cooling (g,h). TEM images (dark field- $\langle 001 \rangle$ zone axis (a-d) and BSE SEM images (e-h)).

115

116 The mean equivalent particle diameters of the γ' precipitates for both alloys and for the four cooling
 117 conditions are compared in Table III. In ice water quenched N18 (Figure 1a), three populations of γ'
 118 precipitates are observed. The largest population presents a low number density and a particle size
 119 of around 150 nm. A second burst of precipitation leads to a high fraction of a second population of
 120 finer precipitates (20-40 nm) and a third population of very fine precipitates is observed near the
 121 larger ones. In ice water quenched Co-GP-01 alloy (Figure 1b), only one very fine population of γ'
 122 precipitates is detected. For the air cooling condition, two populations of γ' precipitates are present

123 N18: a larger population having a mean size of 218 nm and a high particle fraction, and a second
 124 population of very fine precipitates (around 10-20 nm). For that same cooling condition, the Co-GP-
 125 01 sample contains only one dense and fine population of precipitates. For the slower cooling rates,
 126 the same trend is noticed, i.e. the precipitate size is always significantly smaller in the Co-Ni-based
 127 alloy (Figure 2). No second population of γ' precipitates is observed for both alloys after the furnace
 128 cooling. On the other hand, sparse fine precipitates are observed in the large γ channels in N18 and
 129 numerous very fine precipitates are present in the narrow γ channels in Co-GP-01.

Fig. 2 – Effect of cooling rate from solution heat treatment (1200°C) on Ni-based N18 and Co-Ni-based Co-GP-01 precipitate mean size.

130

131 As far as the precipitate morphology is concerned, the first population of precipitates (first burst) in
 132 N18 presents a cuboidal shape for the fastest cooling conditions (ice water and air cooling). When
 133 decreasing the cooling rate, the N18 precipitates evolve to octocubes (furnace cooling) and finally
 134 to complex irregular shapes (0.33 K/min cooling) (Figure 1). For the Co-GP-01 alloy, the
 135 precipitates are nearly spherical for the fast cooling conditions, and then tend to change to cuboidal
 136 shape for the furnace cooling condition and with a tendency for splitting from the slowest cooling
 137 rate.

138 In some studies of the coarsening behavior of γ' -Co₃(Al,W) precipitates, the observation of the γ'
 139 precipitation was not carried out after the cooling following the solution heat treatment but rather
 140 after the aging treatment^[16,20]. After water quenching, no γ' precipitation was noticed by Sauza^[19]
 141 in Co-8.8Al-7.3W and Co-9.7Al-7.1W-2.1Ru (at%) alloys and by Xue^[28] in two Co-Al-W-Ti-Ta
 142 alloys, using a SEM. However, very fine γ' precipitates were observed in a water quenched sample
 143 of Co-10Al-10W (at%) using TEM (2-10 nm)^[17] and in a water quenched sample of Co-9.3Al-
 144 7.4W (at%) using TEM and atom probe tomography investigations (3-8 nm)^[21]. The same result
 145 was also observed on quenched Co-10Al-5Mo-2Nb (at%) using TEM^[11]. Our TEM investigation
 146 on Co-GP-01 ice water quenched sample confirms these observations (mean diameter of 10 nm). As
 147 for high γ' fraction wrought Ni-based superalloys, a rapid cooling condition does not prevent the
 148 nucleation (and certainly the growth) of the γ' -Co₃(Al,W) precipitates in these new alloys, even in
 149 very thin samples (300 μ m thickness)^[21]. However, this first study to examine the influence of
 150 cooling rate (in a wide cooling rate range), clearly shows that the γ' -Co₃(Al,W) precipitation

151 kinetics are sluggish and leads to a distribution of more dense and finer precipitates than those
 152 observed in the reference Ni-based superalloy at a given cooling rate. Indeed, the interdiffusion
 153 coefficients close to the precipitation onset temperature are lower for the Co-Ni-based alloy because
 154 of its lower γ' solvus temperature. Other parameters such as γ/γ' interface energy or elastic strains in
 155 both phases (due to differences in misfit) could also affect the precipitation kinetics.

156 A.2 Hardness

157 Hardness tests were performed on samples of both alloys for the four cooling conditions. The
 158 results of these measurements are presented in Figure 3. Once again, it is worth mentioning that the
 159 Co-GP-01 alloy behaves differently to the Ni-based superalloy. For alloy N18, the hardness is
 160 superior to 400 HV for the highest cooling rates. Then, as the cooling rate decreases, the
 161 strengthening decreases. In contrast, for the Co-Ni-based alloy, the hardness value is very low for
 162 the fastest cooling condition (< 250 HV) and increases to a maximum of 390 HV for the furnace
 163 cooling condition. For the slowest cooling rate, the Co-GP-01 hardness drops close to 350 HV. It is
 164 worth noting that Co-GP-01 hardness is superior to that of N18 when the cooling rate is less than 10
 165 K/min.

Fig. 3 – Effect of cooling rate from solution heat treatment (1200°C) on Ni-based N18 and Co-Ni-based Co-GP-01 room temperature hardness.

166 A.3 Discussion

167 The influence of the cooling rate on the γ' precipitation and on the hardness of a Co-Ni-based alloy
 168 is presented for the first time. These results are directly compared to those jointly obtained for a Ni-
 169 based superalloy.

170 For the N18 superalloy and high cooling rates, the γ' precipitation kinetics are fast enough to lead to
 171 a distribution of precipitates with appropriate sizes to reach high strengthening. As the cooling rate
 172 decreases, the hardness substantially drops. It may be assumed that this behavior is due to the
 173 observed precipitate coarsening and change of morphology. Their morphology changes from cubes
 174 to octocubes after the furnace cooling and to complex shapes after the slowest cooling rate. These
 175 changes lead to large matrix corridors containing few fine precipitates, which promote easier

176 dislocation motion.

177 In contrast, for the Co-Ni-based alloy and high cooling rates, the γ' precipitation kinetics are
178 sluggish and lead to a distribution of a high density of very fine precipitates. For the ice water
179 quenching, the low hardness value can be attributed to the presence of precipitates with a mean
180 diameter smaller than 10 nm, which are easily sheared by the matrix dislocations. It can be assumed
181 that the γ' fraction at the end of the quenching is not at equilibrium as observed by Azzam^[21]. As
182 the cooling rate decreases, the γ' precipitates coarsen but their size is significantly smaller than the
183 N18 ones (3 to 7 times smaller) and their morphology remains close to the cube even after the
184 slowest cooling rate. It can be also assumed that the γ' fraction at the end of the slower cooling
185 conditions is closer to the equilibrium fraction. The hardness level increases to reach its highest
186 value after the furnace cooling. Up to that cooling rate, the precipitates shearing should become
187 harder (due to the increase of γ' fraction and to the coarsening of the precipitates), whereas after this
188 point, the dislocations should more easily bypass the coarse precipitates.

189 In comparison with Ni-based superalloys, alloy Co-GP-01 shows after quenching a more sluggish
190 γ' phase precipitation reaction associated with low hardness. There are benefits of such behavior
191 during the production, the heat treatment, the welding or the additive manufacturing of this new
192 class of high temperature materials to be considered. Firstly, in high γ' fraction wrought Ni-based
193 superalloys, the application of a rapid cooling, in particular in massive components supersolvus heat
194 treated, could result in quench-cracking or severe shape distortion phenomena^[29,30]. These issues
195 are partly attributed in these alloys to the impossibility to avoid or to limit the strengthening γ' phase
196 precipitation during the severe quench. The nucleation and growth of extensive cooling γ'
197 precipitates result in high strengthening and, depending on the part geometry, can act as tensile
198 stresses responsible for quench cracking. Such quench cracks were observed in N18 specimens after
199 oil or water quenching^[25]. Secondly, Ni-based superalloys with high contents of Al and Ti are
200 regarded as non-weldable materials^[31,32]. As the additive manufacturing can be assimilated to a
201 multilayer welding process, its applicability to high precipitation hardened Ni-based superalloys is
202 deemed to be very challenging^[33,34]. In particular, the susceptibility to strain-age cracking during
203 post-welding heat treatments, is promoted by high content of γ' forming elements (such as Al, Ti,
204 Ta and Nb)^[31,35] which results in high γ' fraction. In such alloys, as IN738LC^[36] or N18, the
205 precipitation kinetics is fast, and as a consequence high cooling rates cannot prevent the nucleation
206 and the growth of a significant percentage of precipitates. The resulting high precipitation hardening
207 can then lead to strain-age cracking. In contrast, alloy 718 is considered to be less prone to this
208 phenomenon due to the more sluggish precipitation kinetics of the strengthening γ'' phase^[31,37,38].
209 This sluggish precipitation in alloy Co-GP-01 can be partly explained by a higher γ/γ' interface
210 energy than in Ni-based superalloys. The γ/γ' interface energy evaluated in model Ni-Al-Cr alloys is
211 generally in the 10-20 mJ·m⁻² range^[21], whereas the γ/γ'' interfacial energy was evaluated at 95
212 mJ·m⁻² in alloy 718^[39]. This value was found equal to 48 mJ·m⁻² in a low supersaturated Co-Al-W
213 alloy^[21]. Moreover, the interface energy increases as the γ - γ' lattice parameter misfit becomes larger.
214 Reported lattice misfit values in Co-Al-W alloys are generally larger than in Ni-based superalloys.
215 This allows the high γ' coarsening rate to be explained^[17]. But as previously mentioned, the
216 equilibrium γ' fraction is not attained at the end of the quenching, so the alloy will still undergo
217 nucleation and growth processes during initial stage of aging. A high interface energy will inhibit
218 the increase of γ/γ' interface surface and thus impede the γ' nucleation and growth processes^[18].

219 B. Influence of the aging step on the γ' precipitation

220 From the first part of the present study, it appears that the γ' precipitation in the Co-Ni-based alloy
221 Co-GP-01 is more sluggish than in the Ni-based superalloy N18. The second part of this work
222 focuses on the influence of the aging conditions on the γ' precipitation in the Co-Ni-based alloy. As
223 the γ' precipitation in the Co-Ni-based alloy is less dependent on the cooling rate than in N18, the
224 aging conditions become more deciding for the adjustment of the mechanical properties. Hardness
225 tests and microstructural observations were conducted to investigate the effect of aging temperature
226 and duration or of the application of a double aging treatment.

227 The aging study was carried out only on the Co-Ni -based alloy Co-GP-01. For this reason, it is no
228 longer necessary to conduct the solution heat treatment at 1200°C which leads to a large grain size
229 (200-250 μm). For the aging study, all the samples were solution heat treated at 1050°C for four
230 hours and ice water quenched. All the aging treatments were also followed by an ice water
231 quenching. A recrystallized microstructure with a mean grain size close to 50 μm was thereby
232 obtained. The same sample geometry was used as in the cooling rate study and as no γ' precipitation
233 was observed after quenching using SEM investigation, it is expected that the γ' precipitates are
234 very fine (close to 10 nm).

235 B.1 Effect of the aging temperature

236 After solution heat treatment, a single aging treatment was carried out in the 650-1000°C range for
237 24 hours. The strengthening of the material was assessed by Vickers hardness testing with a 1 kg
238 load (Figure 4). These results show that the hardness peak is reached at 800°C for an aging duration
239 of 24 hours.

Fig. 4 – Influence of the aging temperature on Co-GP-01 room temperature hardness (24 hours aging treatment).

240

241 These hardness data were completed with TEM and SEM observations of the γ' precipitation
242 (Figure 5). It appears that the γ' precipitates undergo an extensive range in terms of particle size,
243 shape and fraction. For the lowest aging temperatures (650-750°C), the γ' precipitates present a size

244 of few dozen of nanometers with a spherical morphology and a high fraction. Beyond 900°C, the γ'
 245 fraction begins to diminish and the precipitates coarsen to several hundreds of nanometers with
 246 rounded cube shape. In the 800-900°C range, the γ' fraction is still high but the precipitate size
 247 increases to few hundreds of nanometers. The precipitates have generally a cuboidal shape but
 248 lower order of symmetry morphologies are observed like "L" or more complex "Tetris-like" shapes
 249 (Figures 5b and 5c).

Fig. 5 – Typical γ/γ' microstructure in Co-GP-01 after 1050°C/4h /ice water quench solution treatment and: 700°C/24h (a), 800°C/24h (b), 900°C/24h (c) or 1000°C/24h (d) aging treatment. TEM image (dark field- $\langle 001 \rangle$ zone axis) (a) and BSE SEM images (b-d)).

250

251 The γ' area fraction and precipitate size were measured on samples aged between 800 and 1000°C
 252 for 24 hours (Figure 6). The precipitate size (mean diameter) increases from 112 nm at 800°C to
 253 545 nm at 1000°C whereas the γ' area fraction decreases from 63% to 31%.

Fig. 6 – Influence of the aging temperature on Co-GP-01 γ' area fraction and precipitate size (24 hours aging treatment).

254 B.2 Effect of the aging duration

255 The influence of the hold time of aging was studied at 800, 900 and 1000°C on samples previously
 256 solution heat treated (1050°C for four hours and ice water quench). The aging duration was 24, 96
 257 and 192 hours. The evolution of the hardness for these different aging states is presented in Figure 7.

Fig. 7 – Influence of the aging time and duration on Co-GP-01 room temperature hardness.

258 SEM-FEG observations were carried out to investigate the γ' precipitation stability and the
 259 evolution of the γ' fraction and precipitate size (Figure 8 and Figure 9).

Fig. 8 – Influence of the aging duration on Co-GP-01 γ' area fraction.

Fig. 9 – Influence of the aging duration on Co-GP-01 precipitate size.

260 The microstructure essentially consists of γ' precipitates embedded in the γ matrix and some fine
 261 precipitates (bright in BSE imaging) are noticed in grain boundaries. A preliminary analysis of
 262 these intergranular particles (in a Zeiss Libra® 200 FE equipped with energy-dispersive X-ray
 263 spectroscopy and electron energy loss spectroscopy) points out a W-rich phase with boron. No new
 264 phase was detected after 96 or 192 hours compared with the 24 hour aging. At an aging temperature
 265 of 800°C, the precipitate size and the γ' fraction both slightly increase with time. The influences of
 266 these two phenomena balance each other out and lead to a stable hardness level. At 900°C, the
 267 precipitate coarsening is accelerated but here the γ' fraction increase is not sufficient to avoid the
 268 hardness decline. For the highest aging temperature, both the decrease of the γ' fraction and the
 269 rapid rise of the precipitate size are observed. However, the hardness value is unchanged on this
 270 time range. It seems that for these severe conditions, the precipitation hardening is no more

271 effective and that this hardness level matches with the matrix strengthening.

272 B.3 Effect of a double aging

273 For the great majority of studies on Co-based γ/γ' alloys, a single aging treatment is applied after the
 274 solution heat treatment. A double aging treatment was identified in only one article ^[40] but without
 275 studying its influence on the microstructure or on the strengthening. For polycrystalline Ni-based
 276 superalloys, up to four aging treatments are industrially carried out ^[41]. Generally, two aging
 277 sequences are applied with the second aging treatment temperature below or above the first one. In
 278 order to further increase the strength of alloy Co-GP-01, we applied double aging treatments with
 279 the second aging treatment temperature 100°C or 150°C below the first one (Table IV). The first
 280 aging temperature is in the range 800-1000°C. The aging duration of each aging treatment is of 24
 281 hours. The hardness data for these different double aging treatments are presented in Figure 10.

Fig. 10 – Influence of a single aging treatment and of double aging treatments on Co-GP-01 room temperature hardness.

282 The application of a double aging treatment systematically leads to an increase of the hardness
 283 compared with the related single aging treatment (Figure 10). When the second aging is carried out
 284 100°C below the temperature of the first aging treatment, the hardness increase is in the range 10-
 285 20%, this benefit goes up to 10-30% when the second aging treatment is applied at - 150°C
 286 (especially for the high temperature first aging treatment). The double aging treatment "850°C/24h
 287 + 700°C/24h" gives the highest hardness value of 427 HV which is close to those measured on
 288 supersolvus C&W (cast and wrought) Ni-based superalloys. SEM-FEG or TEM observations of the
 289 γ' precipitation were performed on some double aging specimens (Figure 11).

Fig. 11 – Typical γ/γ' microstructure in Co-GP-01 after 1050°C/4h /ice water quench solution treatment and: 800°C/24h (a), 800°C/24h + 700°C/24h (b), 950°C/24h (c), 950°C/24h + 800°C/24h (d), 1000°C/24h (e) or 1000°C/24h + 850°C/24h (f) aging treatment. BSE SEM images.

290

291 The γ' fraction and precipitate size were measured on samples double aged "800°C/24h +
 292 700°C/24h", "950°C/24h + 800°C/24h" and "1000°C/24h + 850°C/24h" (Figure 12). For the low
 293 temperature aging treatment, the γ' precipitate morphology is unmodified (Figures 11a and 11b) and
 294 their size and fraction slightly increase compared with the microstructure observed after a single
 295 aging treatment (Figure 12 – 800°C first aging temperature). Fine γ' precipitates were detected by
 296 means of TEM observations only for treatment with a first aging at 900°C and higher (not
 297 presented). At 900°C and 950°C, very few and fine precipitates were observed in the largest matrix
 298 channels. After a first aging treatment at 950°C, the coarse γ' precipitates are rounded cuboidal
 299 shaped (Figure 11c). The application of a second aging treatment at lower temperature leads to
 300 notable differences: first, the γ' fraction increases significantly and the precipitates present a more
 301 aligned and regular distribution (Figure 11d). A slight decrease of their mean size is measured
 302 (Figure 12).

303 A more dramatic evolution is noticed between the single aging treatment at 1000°C and the related
 304 double aging treatment (second aging at 850°C) (Figures 11e and 11f). The area fraction of coarse
 305 precipitates evolves from 31% for the 1000°C/24h aging treatment to 46% for the 1000°C/24h +
 306 850°C/24h aging treatment. Moreover, the application of the second aging at 850°C produced a

307 microstructure with a γ' bimodal precipitation. This second population in the large γ channels has a
 308 mean size of 120 nm and an area fraction of 16%. The coarse and fine precipitates have a total γ'
 309 area fraction of 62%. This is equal to that obtained after a single aging treatment at 850°C for 24
 310 hours. And this is twice the area fraction measured after a single aging treatment at 1000°C for 24
 311 hours. Again, the coarse precipitate population exhibits a more aligned and regular distribution after
 312 the application of the second aging treatment.

Fig. 12 – Influence of double aging treatments on Co-GP-01 γ' area fraction and precipitate size.

313

314 B.4 Discussion

315 In this second part of this work, the influences of the temperature and duration of a single aging
 316 treatment were investigated as well as that of a double aging treatment. Hardness measurements
 317 were collected and, when possible, correlated to microstructural investigations. The γ' area fraction
 318 and precipitate size were quantified. High γ' fraction and fine precipitate size are required for high
 319 mechanical strength. It is assumed that the mobility of the dislocations is governed by the width of
 320 the matrix γ channels^[7,42]. When this dimension is large, dislocations can move easily by glide
 321 through the matrix channels resulting in poor mechanical properties. In contrast, when the channel
 322 width becomes smaller, dislocations have to propagate by γ' shearing processes which are more
 323 energy requiring processes. In order to quantify the effect of the width of the matrix channels on
 324 hardness, this dimension was calculated through a basic assumption. A two-dimension pattern of
 325 perfect cube-shaped γ' particles was used to calculate the mean channel width for each aging
 326 treatment (only microstructure without fine second precipitation observed). With this geometrical
 327 arrangement, the channel width L is defined as

$$L = e(f^{-\frac{1}{2}} - 1)$$

328 Where e is the average edge length of the γ' precipitates (calculated from the particle area) and f is
 329 the γ' area fraction. Despite this basic approach, the link between hardness and the channel width is
 330 clearly established (Figure 13). A rapid decrease is noted between channel width of 10 and 100 nm
 331 which is experimentally observed in the aging temperature and in the double aging studies. For the

aging duration study, the steady hardness level noticed at 800°C can be directly linked to the slight variation of the channel width (17 to 26 nm). At 900°C, the channel width almost doubles and the hardness moderately decreases (8 %). At 1000°C, the channel widening is even more marked, but the hardness level remains relatively constant. As the γ' solvus temperature of Co-GP-01 is 1035°C, it is assumed that at 1000°C, the precipitation strengthening is no more effective and only the matrix hardness is measured.

Fig. 13 – Influence of the γ channel width on the hardness of Co-GP-01 alloy.

338

The γ' fraction was extracted from the calculated phase diagram of Co-GP-01 alloy without minor elements, using Thermo-Calc software with TCNI8 database. As this new family of materials seems not well-documented in the database, it was necessary to consider only γ and γ' as possible stable solid phases for the calculation. The temperature was also shifted of 65°C to fit the experimental γ' solvus temperature (Figure 14).

Fig. 14 – Experimental (192 hours aging treatments) and calculated γ' fraction vs temperature for Co-GP-01 and N18 alloys.

The calculated curve fits well with the experimental values obtained for the longest aging treatment (aging duration of 192 hours). It is worth noting that the γ' fraction curve drops more noticeably for the Co-Ni-based alloy than for the Ni-based superalloy. It means that Co-GP-01 alloy keeps a higher γ' fraction as the service temperature comes close to its γ' solvus temperature than N18 alloy. Finally, this calculation shows that the equilibrium γ' fraction between 750 and 850°C is 65-67%. This computed value is close to the area γ' fraction measured after a single aging treatment applied in this temperature range (Table V) or after a double aging treatment with the second step in this temperature range.

IV. Conclusions

The γ' precipitation evolution and hardness behavior of the Co-Ni-based alloy Co-GP-01 after different heat treatments have been examined. Regarding the cooling rate and the aging parameters, the following conclusions can be drawn based on the obtained results:

- 1/ In comparison with a high γ' fraction wrought Ni-based superalloy, the application of a high cooling rate to a Co-Ni-based results in much finer γ' precipitates. This more sluggish γ' precipitation reaction is related to a low hardening. This precipitation behavior should give benefits during the production, the heat treatment, the welding or the additive manufacturing of this new class of high temperature materials.
- 2/ After a rapid cooling rate, high hardness can be reached through appropriate single or double aging treatments. These hardness values are similar to those measured on supersolvus C&W (cast and wrought) Ni-based superalloys. A monomodal or a bimodal γ' population can be achieved according to the aging parameters. In the same way, the total area γ' fraction can reach 60 to 70 %. The γ channel width can be then adapted to reach the target mechanical properties. These results show that the microstructure and so the hardness can be adjusted through the aging parameters. It is easier to control the microstructure, in particular for large components, because

369 the Co-Ni-based alloy is much less sensitive to the cooling rate.

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Fig. 1 – Typical γ/γ' microstructure in Ni-based N18 (on the left) and in Co-Ni-based Co-GP-01 (on the right) after: an ice water quenching (a,b), an air cooling (c,d), a furnace cooling (e,f) or a 0.33 K/min cooling (g,h). TEM images (dark field- $\langle 001 \rangle$ zone axis (a-d) and BSE SEM images (e-h)).

Fig. 2 – Effect of cooling rate from solution heat treatment (1200°C) on Ni-based N18 and Co-Ni-based Co-GP-01 precipitate mean size.

Fig. 3 – Effect of cooling rate from solution heat treatment (1200°C) on Ni-based N18 and Co-Ni-based Co-GP-01 room temperature hardness.

Fig. 4 – Influence of the aging temperature on Co-GP-01 room temperature hardness (24 hours aging treatment).

Fig. 5 – Typical γ/γ' microstructure in Co-GP-01 after 1050°C/4h /ice water quench solution treatment and: 700°C/24h (a), 800°C/24h (b), 900°C/24h (c) or 1000°C/24h (d) aging treatment. TEM image (dark field- $\langle 001 \rangle$ zone axis) (a) and BSE SEM images (b-d)).

Fig. 6 – Influence of the aging temperature on Co-GP-01 γ' area fraction and precipitate size (24 hours aging treatment).

Fig. 7 – Influence of the aging time and duration on Co-GP-01 room temperature hardness.

Fig. 8 – Influence of the aging duration on Co-GP-01 γ' area fraction.

Fig. 9 – Influence of the aging duration on Co-GP-01 precipitate size.

Fig. 10 – Influence of a single aging treatment and of double aging treatments on Co-GP-01 room temperature hardness.

Fig. 11 – Typical γ/γ' microstructure in Co-GP-01 after 1050°C/4h /ice water quench solution treatment and: 800°C/24h (a), 800°C/24h + 700°C/24h (b), 950°C/24h (c), 950°C/24h + 800°C/24h (d), 1000°C/24h (e) or 1000°C/24h + 850°C/24h (f) aging treatment. BSE SEM images.

Fig. 12 – Influence of double aging treatments on Co-GP-01 γ' area fraction and precipitate size.

Fig. 13 – Influence of the γ channel width on the hardness of Co-GP-01 alloy.

Fig. 14 – Experimental (192 hours aging treatments) and calculated γ' fraction vs temperature for Co-GP-01 and N18 alloys.