Influence of Chemistry on the Tensile Yield Strength of Nickel-Based Single Crystal Superalloys

Pierre CARON¹, a, Frédéric DIOLOGENT²,b and Stefan DRAWIN¹,c

¹ONERA/DMSM, avenue de la Division Leclerc 29, BP72 92322 Châtillon Cedex, France
²Applied Materials Switzerland SA, Route de Genève 42, 1033 Cheseaux, Switzerland

¹pierre.caron@onera.fr, b frederic_diologent@amat.com, c stefan.drawin@onera.fr

Key words: Superalloy; Single Crystal; Yield Strength.

Abstract. The tensile yield strength of AM1 and MC-NG single crystal superalloys with a γ’ precipitate size close to 300 nm were compared within the 20-1050°C temperature range. The room temperature yield strength of the fourth generation MC-NG superalloy is about 200 MPa less than that of the AM1 first generation one. Inversely, at higher temperatures (T > 800°C), the tensile strength of MC-NG is higher than that of AM1. These results are discussed by taking into account the elementary deformation mechanisms and the respective strengths of the γ and γ’ phases. Experiments on a modified MC-NG alloy show that reinforcing the γ’ phase by increasing the contents of Ti and Ta is an efficient way to recover a higher tensile strength at low temperatures. Rhenium addition and increase of the γ’ solvus temperature are suggested to be beneficial for the high temperature tensile strength. Data published on various other single crystals are in agreement with these hypotheses.

Introduction

For more than thirty years the development of nickel-based superalloy chemistries suited for single crystal (SC) turbine blade applications was mainly driven by the need for improved high temperature creep strength in order to satisfy the requirements for a continuous raise of the gas turbine inlet temperature. Addition of increasing levels of rhenium in successive generations of SC superalloys was thus demonstrated to be an efficient way to attain this objective especially within the temperature range 900°C-1000°C. In the same time much less attention was paid to the effect of alloy chemistry on the tensile behaviour of these materials. And yet a rapid survey of the published data reveals that significant tensile strength differences may exist from one alloy to the other especially within the low temperature regime (T < 800°C). This is not without consequence because lowering the yield strength may affect the strain controlled low cycle fatigue (LCF) behaviour or thermo-mechanical fatigue (TMF) behaviour by increasing the plastic deformation amount for a given applied stress or total deformation and therefore reduce the number of cycles to rupture. As an example, Zhou et al. [1-3], by comparing the behaviours of TMS-75 and TMS-82+ alloys during TMF cycles between 400°C and 900°C, suggest that the higher tensile strength at 400°C of TMS82+, as compared with TMS-75, can account for its better TMF rupture life. The purpose of this paper is mainly to compare the tensile behaviour of a first generation SC superalloy AM1 [4] with that of the fourth generation SC superalloy MC-NG [5] from room temperature (RT) up to 1100°C and to show how chemistry modification of MC-NG can improve its tensile strength.

Experimental Procedure

The nominal compositions of AM1 and MC-NG superalloys are reported in Table 1 together with those of other SC nickel-based superalloys considered for the sake of comparison. TMS-75 [3] and TMS-138 [6] are respectively third and fourth generation SC superalloys developed in Japan and EPM-102 is a fourth generation alloy developed in the USA [7]. All these alloys exhibit a face-centred cubic Ni-based γ-matrix containing a high volume fraction (65-70% at room temperature) of...
Ni$_3$Al-type $\gamma'$ phase submicronic strengthening precipitates. A modified MC-NG alloy (MC-NG Mod) was also designed by increasing the Ti and Ta contents at the expense of Al in order to reinforce the $\gamma'$ strengthening phase where these alloying elements partition preferentially. The sum $x_{\text{Al}} + x_{\text{Ti}} + x_{\text{Ta}}$, where $x_{\text{Al}}$, $x_{\text{Ti}}$, and $x_{\text{Ta}}$ are the atom fractions of Al, Ti and Ta, respectively, is nearly the same as in MC-NG in order to maintain a similar volume fraction of $\gamma'$ phase. The $(x_{\text{Ti}} + x_{\text{Ta}})/x_{\text{Al}}$ ratio has thus been increased from 0.171 for MC-NG up to 0.380 for MC-NG Mod. For the sake of comparison the value of the $(x_{\text{Ti}} + x_{\text{Ta}})/x_{\text{Al}}$ ratio is 0.346 for AM1.

Table 1 – Nominal compositions of SC superalloys (wt%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Re</th>
<th>Ru</th>
<th>W</th>
<th>Al</th>
<th>Ti</th>
<th>Ta</th>
<th>Hf</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1</td>
<td></td>
<td>7.8</td>
<td>6.5</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>5.7</td>
<td>5.2</td>
<td>1.1</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MC-NG</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>0.5</td>
<td>5</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>MC-NG Mod</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4.8</td>
<td>1.2</td>
<td>7.7</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>TMS-75</td>
<td>Base</td>
<td>12</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>TMS-138</td>
<td>Base</td>
<td>5.8</td>
<td>3.2</td>
<td>2.8</td>
<td>5</td>
<td>2</td>
<td>5.9</td>
<td>5.9</td>
<td>-</td>
<td>5.6</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>EPM-102</td>
<td>Base</td>
<td>16.5</td>
<td>2</td>
<td>2</td>
<td>5.95</td>
<td>3</td>
<td>6</td>
<td>5.55</td>
<td>-</td>
<td>8.25</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Cylindrical tensile specimens (gauge length: 30 mm and gauge diameter: 4mm) with orientations within 5° off a <001> direction were machined from AM1 and MC-NG SC cylindrical rods provided by Snecma and from MC-NG Mod SC rods directionally cast at ONERA from a small-scale laboratory heat. The SC rods were first fully solution heat treated and subsequently aged using the respective procedures listed in Table 2. As previous works have shown that the $\gamma'$ precipitate size may have an influence on the tensile behaviour of the SC superalloys [6-8], adequate ageing treatment have been selected for each alloy in order to produce similar $\gamma'$ precipitate sizes and to be able to discriminate between the possible effects of chemistry and microstructure. Only the first ageing treatment conditions were varied, the last ageing treatment being the same for both alloys. MC-NG Mod SC rods experienced the same heat treatment procedure as MC-NG that gives a similar $\gamma'$ precipitate mean size (Table 2).

The tensile tests were performed in air at room temperature (RT) and under argon at high temperatures, at a constant crosshead speed corresponding to an initial strain rate of $1.1 \times 10^{-4}$ s$^{-1}$.

Table 2 – Heat treatment procedures applied to AM1, MC-NG and MC-NG Mod alloys (AC: air cooled) and resulting mean $\gamma'$ precipitate sizes.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution heat treatment</th>
<th>Ageing heat treatment</th>
<th>$\gamma'$ mean size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1</td>
<td>1300°C/3h/AC</td>
<td>1000°C/2h30min/AC + 850°C/24h/AC</td>
<td>300</td>
</tr>
<tr>
<td>MC-NG</td>
<td>1310°C/3h, ramp at 3°C.h$^{-1}$, 1340°C/3h/AC</td>
<td>1100°C/4h/AC + 850°C/24h/AC</td>
<td>310</td>
</tr>
<tr>
<td>MC-NG Mod</td>
<td>1320°C/3h, ramp at 3°C.h$^{-1}$, 1350°C/3h/AC</td>
<td>1100°C/4h/AC + 850°C/24h/AC</td>
<td>310</td>
</tr>
</tbody>
</table>

Experimental Results and Discussion

Variations with temperature of the 0.2% yield strength (YS) of AM1 and MC-NG alloys are reported in Fig. 1, together with data obtained on MC-NG Mod at RT, 750°C and 1050°C. The yield strength of AM1 is almost constant between RT and 650°C, reaches its maximum value at 750°C, and then decreases rapidly when temperature increases above 750°C. For MC-NG, the evolution of the yield strength with temperature follows a comparable trend, but with significant differences in strength level and strength peak temperature. Indeed the YS of MC-NG is about 200 MPa lower than that of AM1 between RT and 750°C. The position of the strength peak is shifted by about 50°C
towards higher temperatures as compared with AM1. The two curves cross each other at 800°C and the yield strength of MC-NG is therefore higher than that of AM1 at high temperatures. At RT, the YS of MC-NG Mod is in-between those of the two other alloys. At 750°C and 1050°C, MC-NG Mod exhibits a slightly, but significantly, higher yield strength than MC-NG.

![Graph](image)

**Fig. 1 – Variation with temperature of the YS of AM1, MC-NG and MC-NG Mod SC alloys.**

The evolution with temperature of the YS of both AM1 and MC-NG alloys is comparable to those previously reported for other SC superalloys with γ' precipitate sizes within the range 300-500nm, as CMSX-4 [8], PWA1480 [9], SRR99 [10] or CMSX-2 [11]. Several factors are generally reported to have an influence on the Y.S. behaviour of such alloys. Apart from the effect of crystallographic orientation which is out of the scope of the present study and obviously apart from the effect of temperature, the γ' precipitate size [8-10] and morphology [12, 13] and the strain rate [14-16] have been reported to influence the YS behaviour of this class of materials, whereas the effect of alloy composition has been only scarcely discussed.

During a tensile test in the low temperature regime, from RT up to 750-800°C, the matrix dislocations first move through the γ phase channels by ½<110>{111} slip, then cut the γ' precipitates as pairs bounded by an antiphase boundary (APB) [11]. The deformation is generally concentrated in intense slip bands which progressively multiply till the tensile specimen is completely deformed and before it can consolidate. Transmission electron microscopy analyses have shown numerous γ' precipitate shearing events in MC-NG and AM1 tensile specimens after 2% of plastic deformation at RT together with a high density of matrix dislocations in the γ channels [17]. In the high temperature regime (T > 800°C), the matrix dislocations propagate between the γ' precipitates by thermally activated glide/climb processes, and only a few γ' shearing events are observed, that promotes a homogeneous deformation. In these conditions, the tensile strength is therefore essentially linked to the mobility of the matrix dislocations between the precipitates.

The comparison of the YS evolution for the three alloys at given γ' precipitate size and strain rate strongly suggests that the alloy chemistry influences the tensile behaviour independently of the microstructure. Indeed, in the low temperature regime, where no significant solutioning of the γ' phase is observed, similar γ' phase volume fractions and γ' precipitate sizes determine comparable γ
channel widths in the three alloys. The Orowan stress for bowing the a/2<110> matrix dislocations between the γ' particles is therefore supposed to be almost the same in the three alloys. Modifications of alloy composition are thus inferred to affect mainly the levels of solid solution strengthening of both γ and γ' phases, the APB energy (APBE) of the ordered γ' phase which controls the shearing of the γ' precipitates by pairs of ½<110> dislocations and the γ/γ' lattice parameter mismatch which induces coherency strain hardening. All this parameters are known to affect the mobility of the dislocations and consequently the YS.

Measurements of the γ/γ' lattice mismatch, defined as $\delta = 2(a_{\gamma'} - a_{\gamma})/(a_{\gamma'} + a_{\gamma})$, where $a_{\gamma'}$ and $a_{\gamma}$ are the lattice parameters of the γ' and γ phases, gave a value of -0.5 × 10^{-3} in AM1 at 760°C [17] and in MC-NG at 750°C [18]. The YS difference between AM1 and MC-NG in the low temperature regime can therefore not be attributed to a difference in lattice mismatch.

In order to estimate the level of solid solution hardening in both γ and γ' phases of AM1 and MC-NG, the respective increases of plastic flow at 77 K of pure nickel and Ni3Al due to multiple alloying have been evaluated for these two alloys [19] by taking into account the chemistries of the γ and γ' phases determined by atom-probe analyses (Table 3) [17]. The resulting values of plastic flow increase as compared with pure nickel and pure Ni3Al are 302 MPa and 392 MPa for the γ matrix, and of 233 MPa and 185 MPa for the γ' phase, in AM1 and MC-NG respectively. The higher strength of the γ' phase in AM1 as compared with MC-NG results from the increased levels of Ti and Ta which substitute for Al. Moreover, substitutions of Ti or Ta for Al in Ni3Al were reported to increase the APBE of this ordered phase [20] thus rendering more difficult the shearing of the γ' precipitates by pairs of matrix dislocations.

At temperatures below 800°C, the higher YS of AM1 compared with MC-NG can be unambiguously attributed to the better resistance of the γ' precipitates against shearing. When compared with the MC-NG alloy, the increased YS obtained with the MC-NG Mod alloy, which exhibits Ti, Ta and Al contents close to that of AM1, is in agreement with this conclusion.

Table 3 - Chemical compositions (at. %) of γ and γ' phases in AM1 and MC-NG single crystal superalloys [17].

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Ru</th>
<th>Al</th>
<th>Ti</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-AM1</td>
<td>Bal.</td>
<td>11.1</td>
<td>26.1</td>
<td>2.5</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>γ'-AM1</td>
<td>Bal.</td>
<td>2.1</td>
<td>2.1</td>
<td>0.7</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>15.2</td>
<td>2.1</td>
<td>3.7</td>
</tr>
<tr>
<td>γ-MC-NG</td>
<td>Bal.</td>
<td>-</td>
<td>11.3</td>
<td>1</td>
<td>1.62</td>
<td>4.6</td>
<td>5.6</td>
<td>2.9</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>γ'-MC-NG</td>
<td>Bal.</td>
<td>-</td>
<td>2</td>
<td>0.56</td>
<td>1.7</td>
<td>0.4</td>
<td>1.8</td>
<td>17</td>
<td>0.8</td>
<td>3</td>
</tr>
</tbody>
</table>

When the temperature increases above 800°C, the enlargement of the γ channel associated with the continuous solutioning of the γ' precipitates must be considered when analysing the difference in YS between AM1 and MC-NG. For example the residual amount of γ' phase at 1050°C was measured to be higher in MC-NG than in AM1, i.e. 62% and 52% respectively [21], thanks to a higher γ' solvus temperature, i.e. 1292°C as compared with 1265°C [17]. By taking a volume fraction at RT of 70% of 300 nm edge length cubical γ' precipitates perfectly aligned along the <001> directions [17], a simple calculation gives a γ channel width of 38 nm at RT in both alloys. Partial solutioning of the γ' precipitates at 1050°C increases the γ channel width up to 66nm and 49nm in AM1 and MC-NG respectively. Consequently, a significantly higher Orowan stress (+26%) in MC-NG as compared with AM1 can explain, at least partly, the higher YS observed at high temperatures. The intrinsic properties of the γ phase, linked to its chemistry, may also play a role in the mobility of the dislocations which propagate by combined slip and climb mechanisms. The presence of rhenium in the matrix of MC-NG can thus slow down the climb rate as compared with AM1, as this alloying element was demonstrated to be the one characterized by the lowest diffusion rate in nickel-based superalloys [22]. Finally, the higher solid solution strengthening effect estimated for the MC-NG matrix compared with AM1 is a supplementary argument to explain its greater YS in the high temperature range.
It must be pointed out that the YS of MC-NG Mod at 1050°C is also significantly higher than that of AM1, which confirms the beneficial effect of the rhenium addition, and even slightly higher than that of MC-NG. This small advantage could be due to the addition of Ti and Ta which partition only weakly to the γ matrix, but which could however bring a supplementary effect of solid solution strengthening.

Comparison of the data obtained on AM1 and MC-NG with those available on TMS-75 [23], EPM-102 [7] and TMS-138 [23] SC superalloys confirms our hypotheses. The three latter alloys behave in the same way as MC-NG, with a YS below that of AM1 between RT and about 800°C, and above when the temperature exceeds 800°C. These three superalloys are characterized by a \((x_{Ti}+x_{Ta})/x_{Al}\) ratio of 0.149, 0.222 and 0.142 respectively, therefore significantly lower than that of AM1 and close to that of MC-NG. At temperatures above 800°C, all rhenium containing alloys exhibit a higher YS as compared with rhenium-free alloys. In addition to the beneficial effect of this low diffusion rate alloying element, the third and fourth generation alloys are characterized, as MC-NG, by elevated γ’ solvus temperatures, for example 1283°C for TMS-75 and 1300°C for TMS-138 [23]. This ensures a higher γ’ volume fraction at high temperatures and consequently a higher tensile strength.

![Graph showing variation of 0.2% yield strength with temperature for various SC alloys](image)

**Fig. 2 –** Variation with temperature of the 0.2% yield strength of various SC alloys.

**Conclusions**

Third and fourth generation SC superalloys containing high levels of rhenium exhibit a significantly lower yield strength between room temperature and 800°C, as compared with rhenium-free first generation superalloys. This is suggested to be due to their lower contents of γ’-strengthening alloying elements such as titanium and tantalum, that decreases the antiphase boundary energy and the intrinsic strength of the γ’ phase and facilitates γ’ precipitate shearing by pairs of matrix dislocations. On the other hand, at temperatures above 800°C, addition of rhenium which slows down the thermally activated glide/climb mechanisms controlling the yield strength and the increase of the γ’ solvus temperature which retards the solutioning of the γ’ phase can explain the improved tensile strength of these third and fourth generation SC superalloys.
Acknowledgments

The authors acknowledge Snecma for having provided AM1 and MC-NG SC rods. They are also grateful to Snecma and to the French Ministry of Defence for funding of this work.

References