A New Single Crystal Superalloy For Power Generation Applications

J.J. Moverare\textsuperscript{1,2}, A. Sato\textsuperscript{3}, M. Hasselqvist\textsuperscript{1}, F. Karlsson\textsuperscript{1} and R.C. Reed\textsuperscript{3}

\textsuperscript{1} Siemens Industrial Turbomachinery AB, Finspång, Sweden
\textsuperscript{2} Linköping University, Dept. of Management and Engineering, SE-58183, Linköping, Sweden
\textsuperscript{3} Dept of Metallurgy and Materials, University of Birmingham, UK

Acknowledgements

The authors are grateful to Siemens Turbomachinery for sponsoring this work. The invaluable advice and full support of Helena Oskarsson, Leif Berglin and Dr.Xin-Hai Li at Siemens Turbomachinery AB in Sweden, Prof.Hugh Evans, Dr.Mary Taylor, Dr.Yu-Lung Chiu at the University of Birmingham and Dr. Cathie Rae at the University of Cambridge, Prof. Emmanuelle Marquis in the University of Michigan is acknowledged. Peter Cranmer at the University of Birmingham for casting, Dr. Edward Oliver at the ISIS facility at Rutherford Appleton Laboratory and Dr. David Dye at Imperial College London for in-situ neutron diffractometry are thanked for their invaluable assistance.
Background of this project

Oxidation resistant

US Patent: 20050194068Al

highest (Ta/Al) ratio line

lowest (Ta/Al) ratio line

Target properties

Oxidation : CMSX-4 level
Hot corrosion : IN738 level
Creep : IN792 level
Objectives

Evaluate STAL15 in terms of...

- Processing
- Mechanical properties
- Oxidation performance
- Phase stability

Find the relationship between...

- Microstructure vs. mechanical performance (such as creep, fatigue…)
- Chemical composition vs. oxidation performance
- Effect of silicon additions on the above.
Nominal Composition

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Ta</th>
<th>Hf</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAL15</td>
<td>5</td>
<td>15.5</td>
<td>1.0</td>
<td>4.0</td>
<td>4.55</td>
<td>8.0</td>
<td>0.1</td>
<td>Ce: 200ppm</td>
</tr>
</tbody>
</table>

Single Crystal Casting

Mould temp: 1570°C
Atmosphere: up to 4−1Pa
Withdrawing speed: 229mm/hr
Castability: 92% -> SX

Heat treatment

Solution treatment: 1280°C 1hr -> 1300°C 5hrs, followed by air cooling (window: ~120°C)
First ageing treatment: 1080-1160°C for 4-48 hours, followed by air cooling
Second ageing: 850°C 20 hours, followed by air cooling

Neutron Diffraction

Shape of sample: Ø8, h = 20mm
Machining company: Marsden Limited, Nottingham
Place: Engin-X, ISIS, Digcot
Temperature range: 800-1000° C
Measurement time: >20mins
Interval period for obtaining data: Every 2mins
Lattice parameter & Misfit

γ' Vf for STAL15

Good agreement between calculation and experiment

average lattice misfit \( \delta \)

800°C : -0.09±0.03%
900°C : -0.10±0.03%
1000°C : -0.20±0.07%
From the Vf...

Microstructure chosen for mechanical testing

1100°C 6hrs
Uniform Microstructure1

1120°C 24hrs
Large primary $\gamma'$ Microstructure2

1160°C 4hrs
More secondary $\gamma'$ Microstructure3
Creep testing
Specimen: 24.5 mm gauge length and 5 mm diameter
Temperature/Stress:
850°C/275MPa, 850°C/225MPa
750°C/520MPa, 750°C/455MPa

OP-TMF testing
Specimen: 22 mm gauge length and 6 mm diameter
Temperature range: 100-950°C
Strain controlled (R = ε_{min}/ε_{max} = -∞)
Mechanical Strain range: -0.6 ~ -0.9%

Isothermal/Cyclic oxidation testing
Temperature: 900°C-1000°C
Isothermal oxidation testing: up to 300 hours
Cyclic oxidation testing: 65hrs/cycle up to 4550 hours

Phase stability
Temperature: 900°C, 1000°C
Exposure time: Up to 10000 hours -> No TCP phase
Creep rupture life

- Uniform microstructure performs best in creep

- Bimodal microstructure performs best in TMF

TMF life

- STAL15 ≈ IN792
- STAL15 ≈ CMSX-4
To understand TMF...

Shearing of primary $\gamma'$

Good agreement with TMF life results. Higher volume fraction or larger $\gamma'$ is good.
To understand TMF...

Shearing of primary $\gamma'$

Shearing resistance is...

$$\propto \sqrt{\gamma_{APB}fr}$$

Volume fraction of $\gamma'$
Radius of primary $\gamma'$


Good agreement with TMF life results. Higher volume fraction or larger $\gamma'$ is good.
Isothermal Oxidation

1000°C  950°C  900°C

More oxidation at 900°C
Oxidation: 0.25Si < 0.5Si < 0Si
Cross-sectioned oxidized superalloys after 100 hours

(1) Higher temperature
(2) With greater Si: \( \alpha-\text{Al}_2\text{O}_3 \) is continuous
Theoretical Analysis of Composition/Oxidation Relationship – Modelling Approach

\[
\frac{4}{3}\text{Al (in superalloy)} + \text{O}_2(\text{gas}) \rightarrow \frac{2}{3}\text{Al}_2\text{O}_3 \text{ (solid)}
\]

\[
k_t = -\frac{\sigma (t_a + t_c)t_{el}}{z_c^2 z_a^2 e^2} \Delta G_f
\]

Nernst-Einstein relation...

\[
\frac{c_o z_a^2 e^2}{kT} D_o
\]

when n-type...

\[
\sigma \left( t_a + t_c t_{el} \right) \frac{z_c^2 z_a^2 e^2}{0}
\]

\[
\Delta G_f = \Delta G_0 + RT \ln \left( \frac{a_{2/3}}{a_{4/3} P_{O_2}} \right)
\]

thermodynamical calculation

\[
0.2193 \times T -1127.3137 \text{ (kJ/mol)}
\]

~Oxidation rate~

1. \( f(\Delta G_f) \)
2. \( f(\text{impurities factor}) \)

Oxidation Diagrams

Good agreement between modelling & experiment

Oxidation Diagrams

Good agreement between modelling & experiment
Cyclic Oxidation

- STAL15: better than CMSX-4
- Good cyclic oxidation resistance at 900°C or above.
Summary and Conclusions

1. A new single crystal superalloy STAL15 has been developed specifically for use in industrial gas turbine applications. It displays a good balance of environmental and mechanical properties.

2. In laboratory-based casting trials, single crystal superalloys have been produced reliably and consistently, with no evidence of casting defects such as freckles. The solutioning window for heat treatment is wide, and optimised primary ageing treatments have been identified.

3. The isothermal and cyclic oxidation resistance is superior to most other superalloys, specifically on account of its high Cr content, reasonable Al content and absence of Ti. The evidence indicates that it is an alumina former, particularly at temperatures of 1000°C or beyond. The alumina scale formation capability can be enhanced by doping with small quantities of Si.

4. The creep performance is comparable to that of the alloy IN792, which it is intended to replace. The TMF performance is superior to it and is indeed comparable to CMSX-4, despite the absence of Re. This seems to be in part due to creep relaxation processes in compression which occur during out-of-phase thermal cycling.

5. We believe STAL15 to be one of the first single crystal superalloys to be designed by making extensive use of computer-based modelling methods, which have allowed the isolation of its composition with a rather small number of make/test iterations in the laboratory.