Understanding of microstructural evolution of Ni alloys during service and effects on long-term properties

Oriana Tassa, Arianna Gotti, Sandro Notargiacomo

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IEA CLEAN COAL CENTRE
3RD WORKSHOP
ADVANCED ULTRASUPERCRITICAL POWER PLANT
13-14 DECEMBER 2017, ROME
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Understanding of microstructural evolution of Ni alloys during service and effects on long-term properties

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OUTLINE

- Background
- Fabrication route and relevant metallurgical issues
- Microstructure evolution
- Influence on mechanical properties
- Microstructure optimization

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Reference Framework

LIMITS ON CO_2 EMISSIONS
FOSSIL FUEL AS MAIN SOURCE FOR POWER GENERATION
FOSSIL IS A NON-RENEWABLE RESOURCE

- **UTILIZATION OF FOSSIL FUEL IN HIGHLY EFFICIENT PLANTS**
  Increase T & P Steam parameters:
  - **> 750 °C**
  - **> 100 MPa / 100kh.**

Key factor

Reliable high temperature materials

- **NI SUPERALLOYS**

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Background

Ni superalloys

Nickel base alloys are candidate for higher temperature applications:

- high creep rupture strength
- high temperature corrosion resistance against coal ash corrosion
- steam oxidation resistance.

The candidate Ni based alloys have been fundamentally developed for aeronautic applications, where service times are limited.

The use in power plant at 700/750°C opens several questions, particularly:

✓ Process route have to be optimized to produce **large components**

✓ Very long-term applications under increasingly severe service conditions request to assess properties: creep, fatigue, toughness….

➢ **Understanding of microstructure stability**

Metallurgical design concepts

- Solid solution strengthening: Co, Mo, W, Fe
- Precipitation strengthening: coherent intermetallic precipitate (fcc) called γ' having composition $Ni_3(Al,Ti)$. Increasing Al+Ti increases γ' fraction and mechanical and creep strength. High γ' fractions can reduce ductility of the alloys.
- Carbide formation: mostly $M_{23}C_6$, some M_6C and Ti(C,N).
- Additional phases: undesirable and brittle phases, TCP (Topologically Close-packed Phases), η, σ, μ, G, Laves phase,… can be formed during heat treatment or service.

1. Chemical composition defined to:

- Increase γ' fraction.
- Increase microstructure stability: γ' evolution and formation of TCP phases.
- Assure adequate fabricability.

Ni alloys candidates for boiler components

1. Alloy A617 / 617B
2. Alloy 263
3. Alloy 740/740H

Alloy	C	Cr	Mo	Co	Al	Ti	Nb	Mn	Fe	Si
617	0,08	22,00	9,00	12,50	1,00	1,00		0,10	0,50	0,10
617B	0,06	21,90	8,90	12,00	0,84	0,41	0,06	0,01	0,97	0,15
263	0.05	20,00	5,80	19,50	0.50	2.10		0.35	0.50	0.10
740	0.03	25,00	0.50	20,00	0.90	1.80	2,00	0.30	0.70	0.50
740H	0.03	25,00	0.50	20,00	1.35	1.35	1.50	0.30	0.70	0.15

Fabrication route and relevant metallurgical issues

The nickel base superalloys have a very complex chemical composition, with high content of alloying elements, causing stable/metastable phase precipitation.

The production process of Ni based superalloys results expensive:

1) Selected raw materials, metal alloys and scraps in order to limit the amount of impurities and trace elements that can strongly influence the ductility and the performances of the final products.
2) Remelting processes, in order to control the segregation, and to narrow windows requested for hot working.

Ingot production

- ✓ Primary melting, by EAR, IM or VIM
- ✓ Remelting by ESR or VAR

Thermomechanical process:

- ✓ Forging (square or round bar)
- ✓ Hot extrusion
- ✓ Hot rolling
- ✓ Cold rolling

Heat treatments

- ✓ Solution
- ✓ Aging

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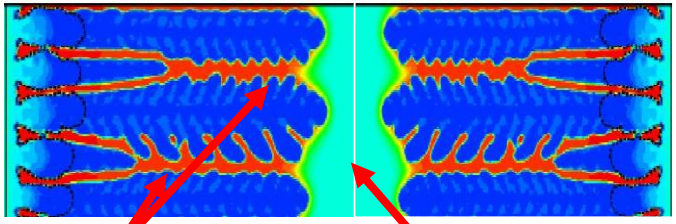
Fabrication

Fabrication route and relevant metallurgical issues

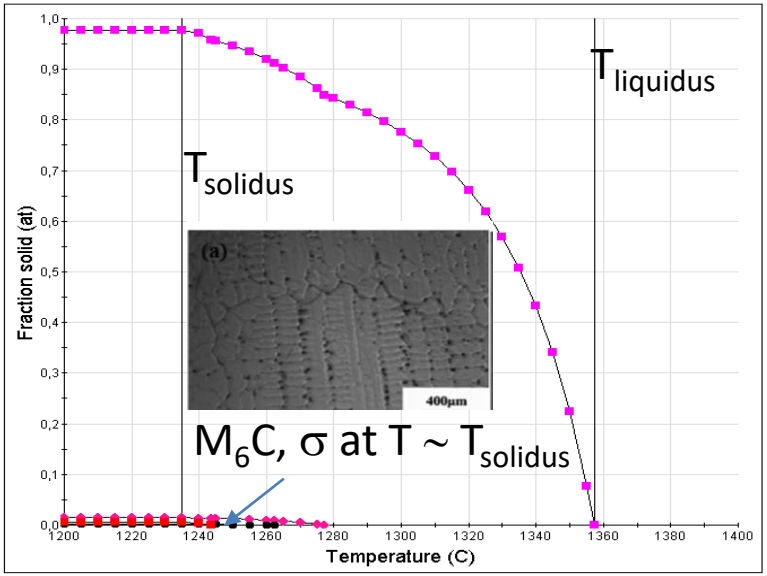
Solidification behaviour: micro and macrosegregation

Alloy 617: Scheil solidification diagram

Formation of non equilibrium phases at the solidification end.

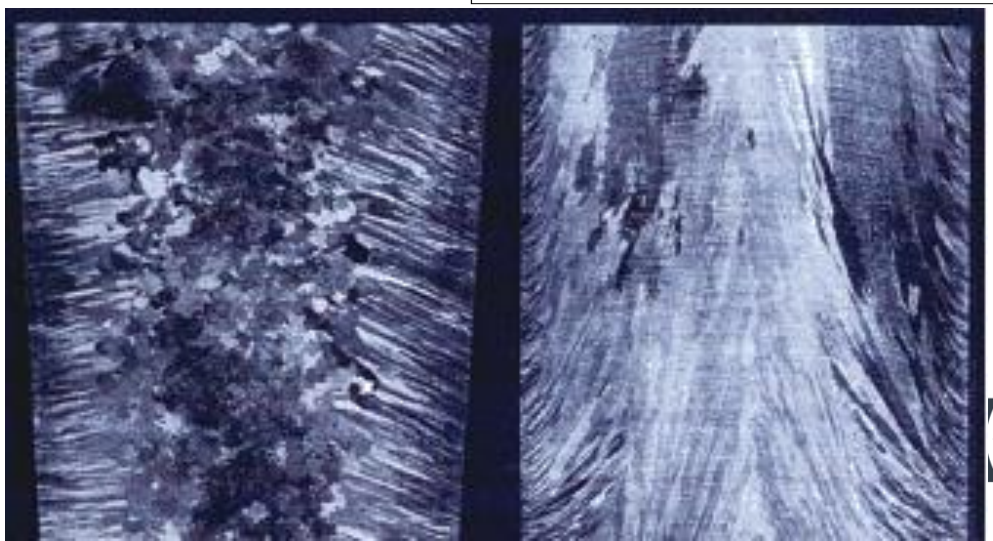


Micro Macrosegregation



1) Ingot fabrication: remelting refines microstructure and macrostructure

Conventional Ingot



VAR Ingot

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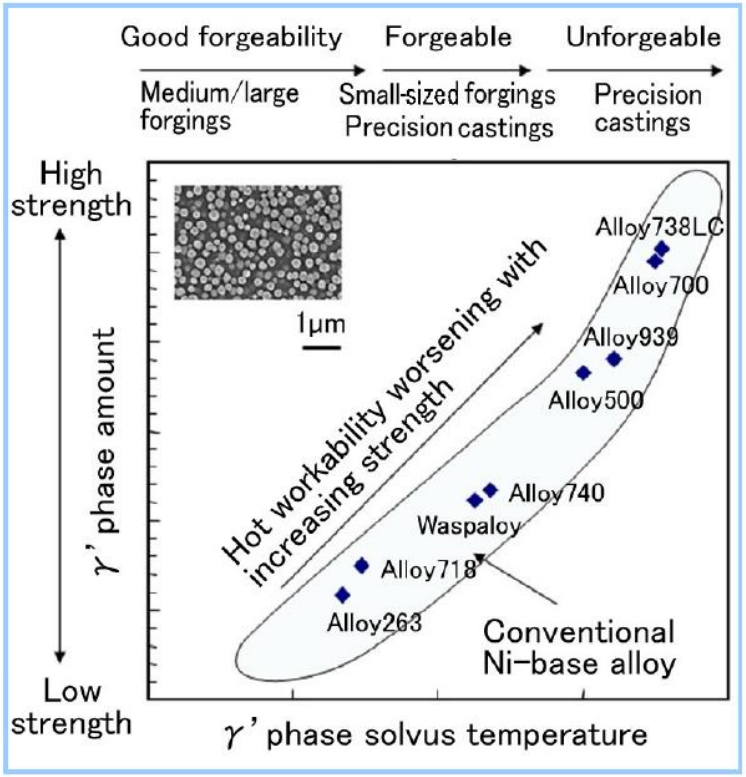
Fabrication

Fabrication route and relevant metallurgical issues

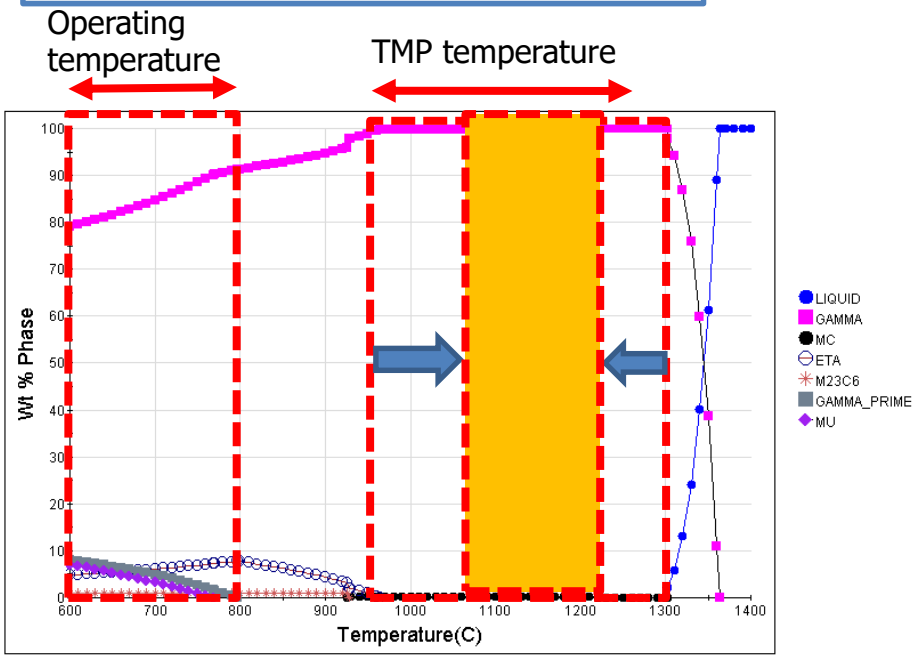
Metallurgical window ΔT: hot deformation temperature range.

Tsolidus – Tsolvus.

Segregation reduces locally ΔT: homogemization treatments (up to several days) are requested before hot working operations to reduce segregation and solubilize eutectic metastable phases.



Alloy 263:



S. IMANO et al. *Mitsubishi Heavy Industries Technical Review Vol. 52 No. 2 (June 2015),* 32

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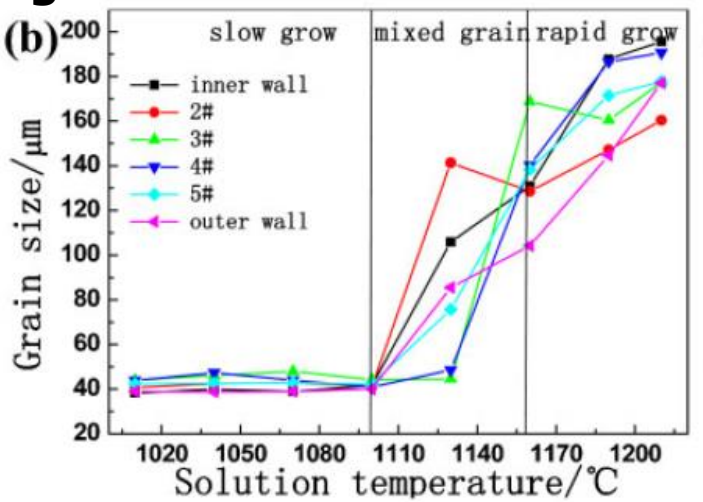
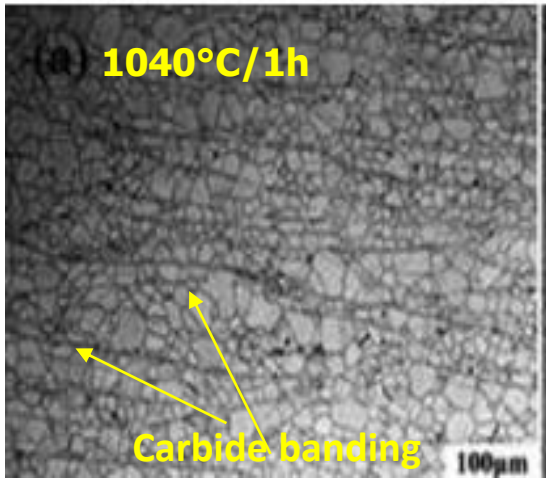
Fabrication route and relevant metallurgical issues

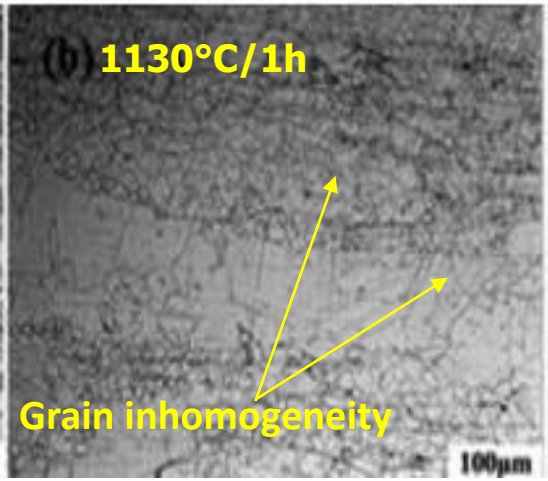
Heat treatment: solution annealing

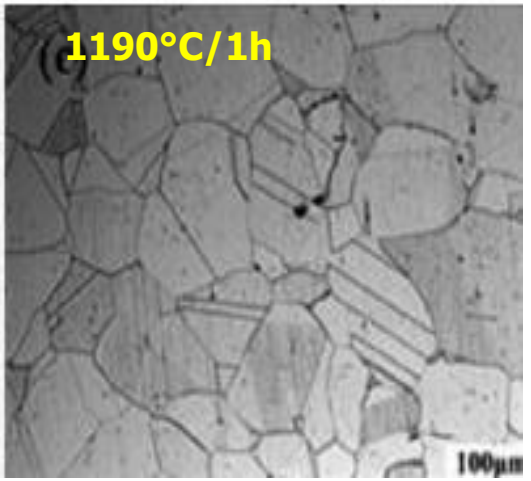
1) To reduce segregation and precipitate stringers
2) To optimize grain size

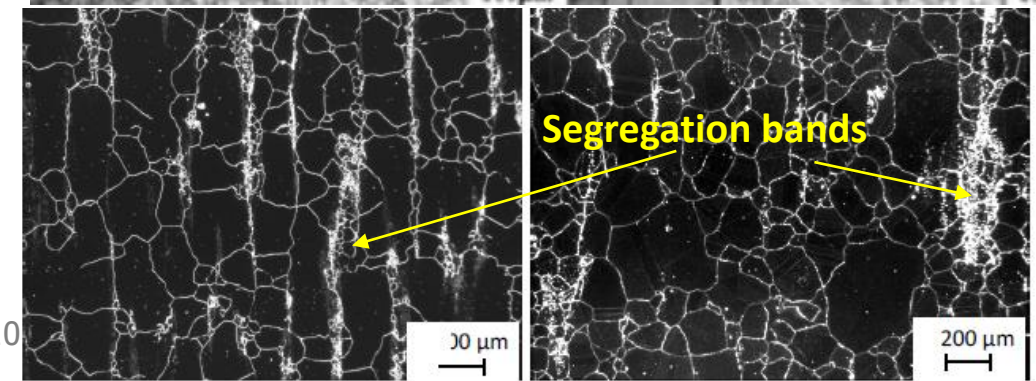
➢ **Alloy 617**











Segregation bands can be still observable after long term aging: 700°C/20000h
Effect on precipitation kinetics.

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Jiang, Materials Research Innovations 2014 VOL 18 SUPPL 4 S4-369

Fabrication

Microstructure evolution
Results from MACPLUS Project

Precipitation status of Ni alloys: A617, IN740, Nim263, to define:

- Precipitate type and fraction
- Morphology and location
- Quantitative particle size distribution
- Precipitate reactions
- Evolution of precipitates composition and size

Main results

- Complex precipitation status and reactions
- γ' phase is present in all the alloys: 740 > 263> 617
- Precipitation of brittle Ni_3Ti (η) in 740

  η not observed in 263 alloy for ageing up to 10kh, even if it's thermodinamically stable: fractions < 2-3% don't affect creep properties

Microstructure

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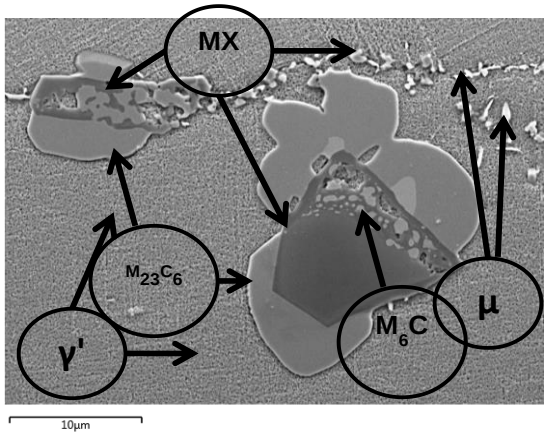
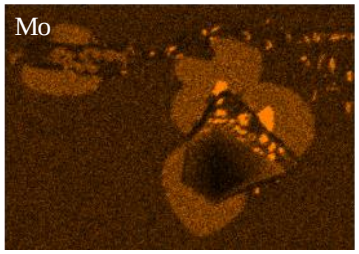
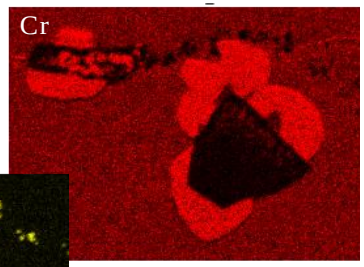
Microstructure evolution

Complex precipitation status and reactions of Ni alloys

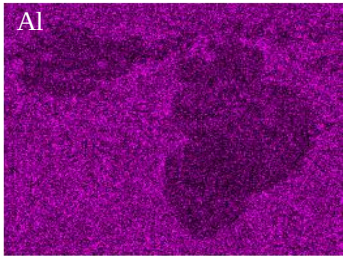


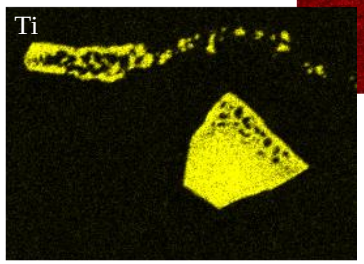


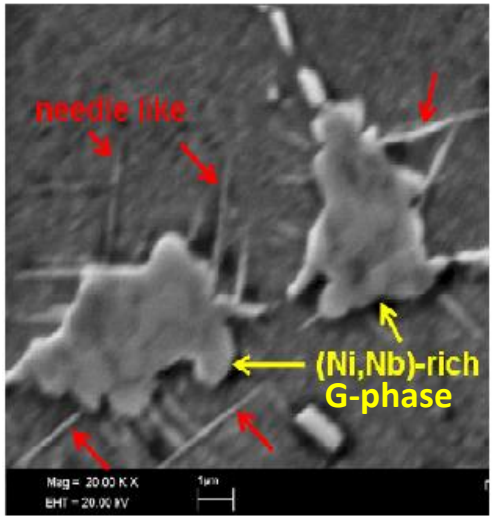
Alloy 617
700°C/~20kh

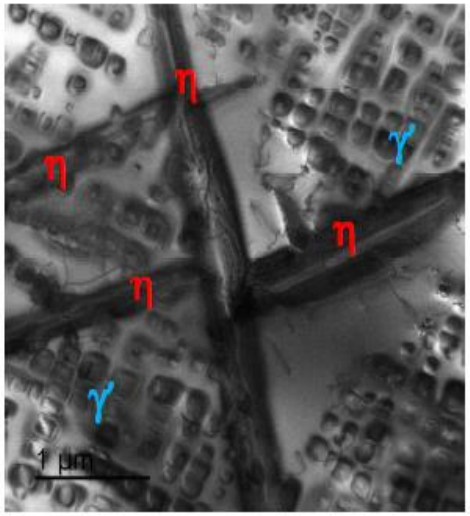


740 Alloy
725°C/~20kh









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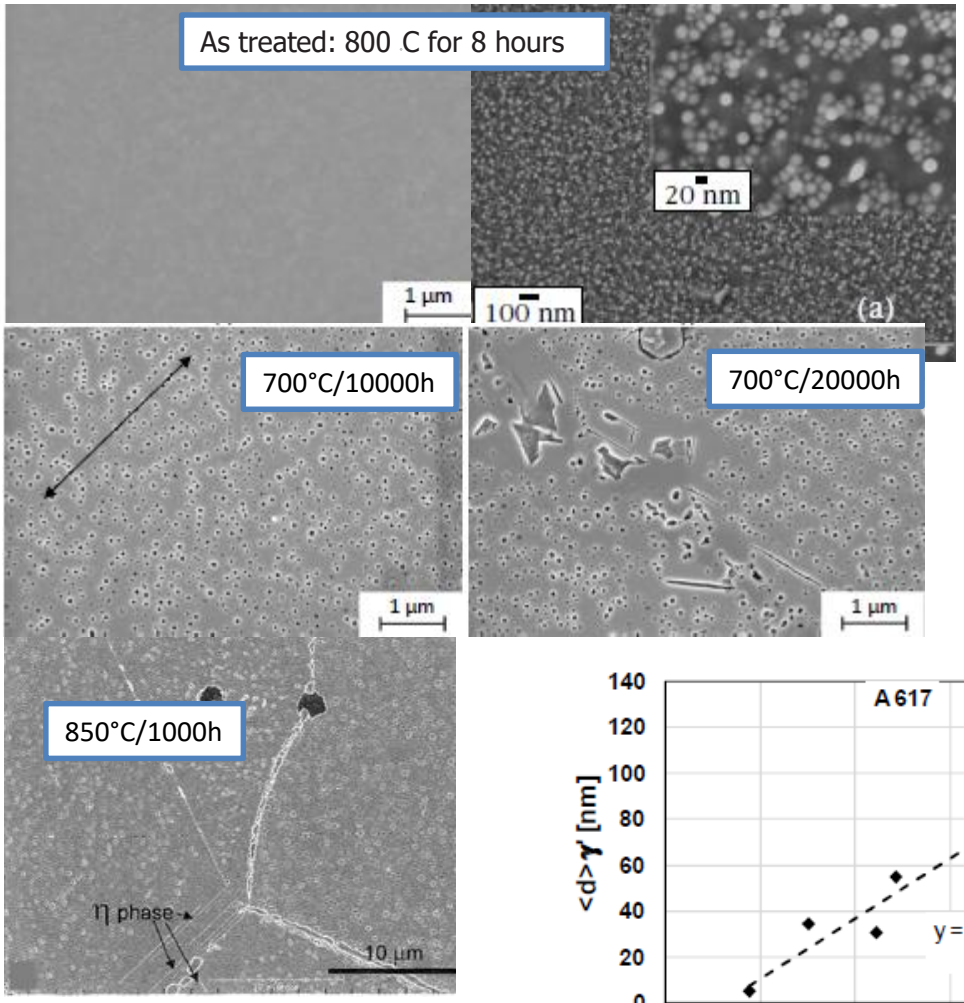
Microstructure

O. Tassa et al.: MACPLUS PROJECT

Microstructure evolution

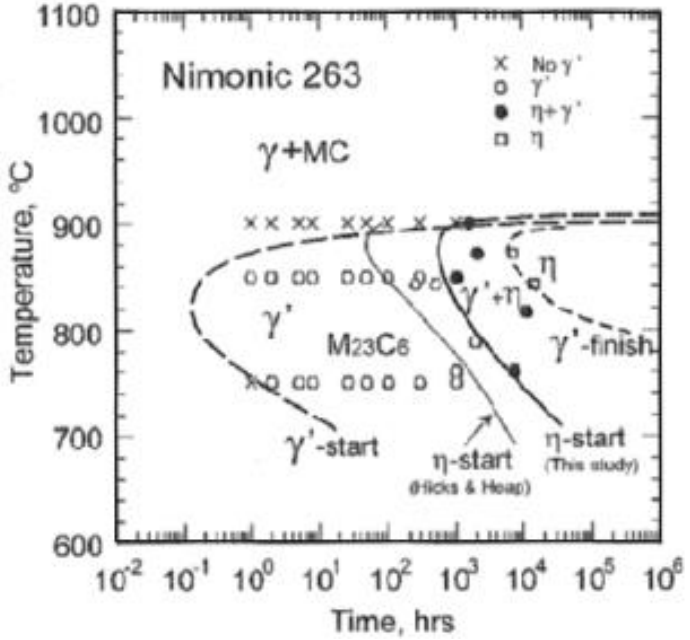
γ′ evolution:

1) Particle size growth
2) η formation

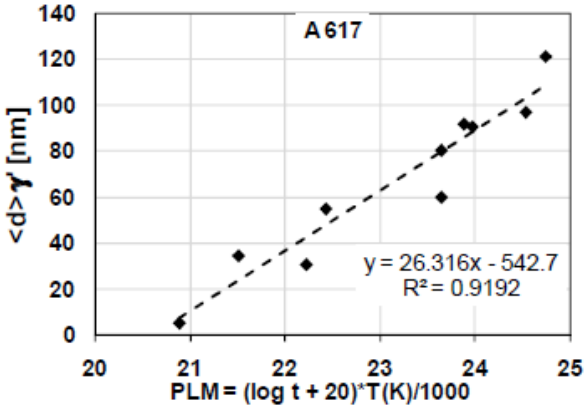


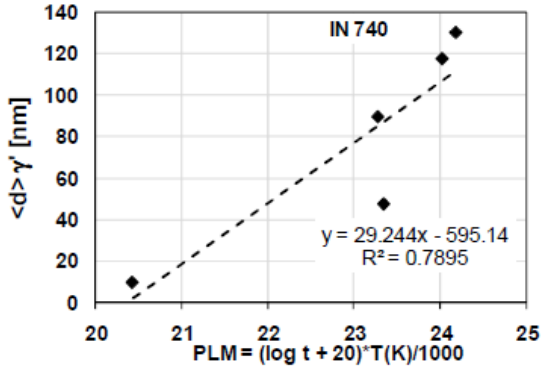
C. Crozet et al. Eurosuperalloys 21014

Alloy263



1) γ′ growth formation





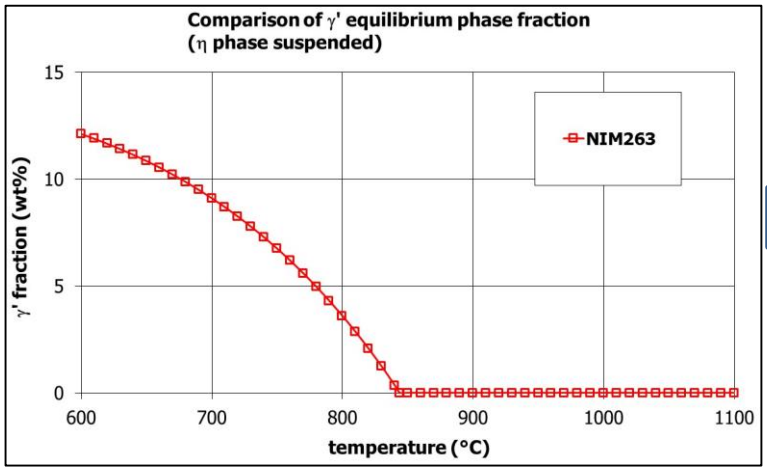
O. Tassa et al. Proc. Liege 2014

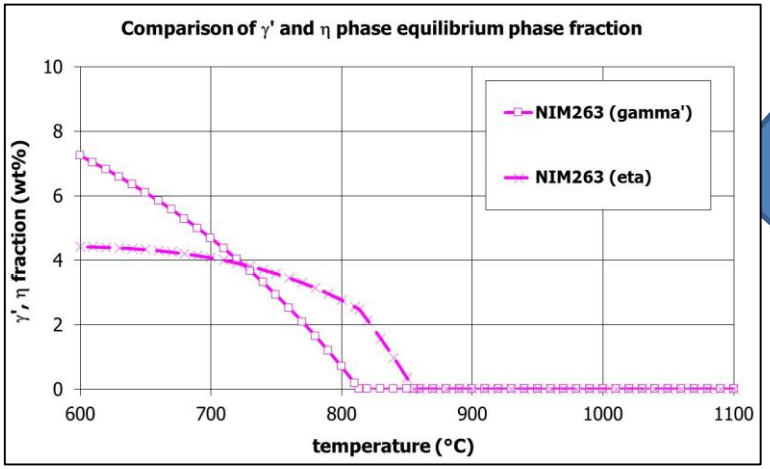
Microstructure evolution

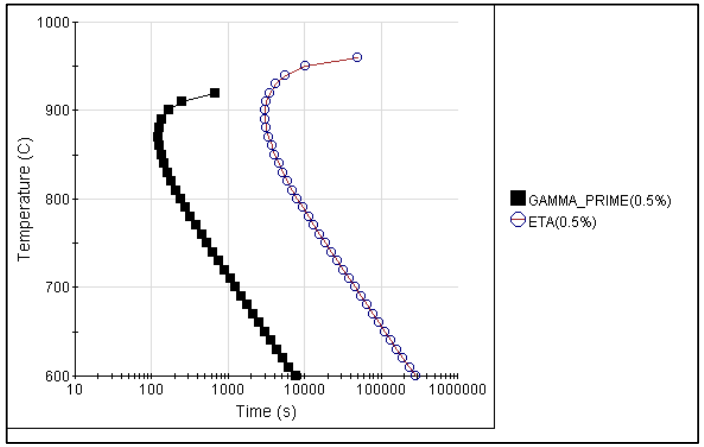
ALLOY 263

1) γ′ precipitation: high creep strength

2) Transformation γ′ → η: reduction of creep strength and toughness







Microstructure

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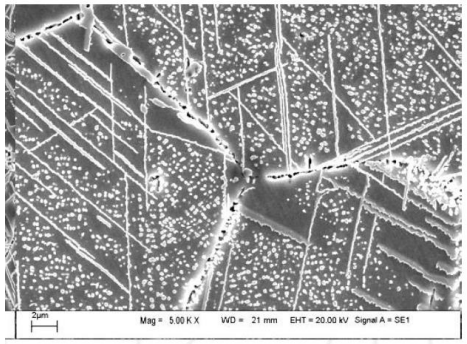
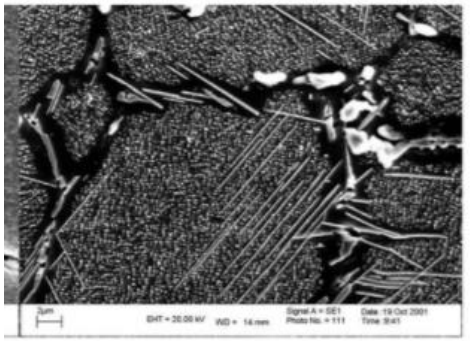
Microstructure evolution

Degradation mechanism:

1) γ' denuded zone forms around the grain
   - Grain boundaries decorated with $M_{23}C_6$ and intermetallic TCP phases will deplete the adjacent matrix of elements including: Cr, C, Nb, Si, and
   - Ti. Nb and Ti are elements that are incorporated in the gamma prime phase in and their reduction may reduce the local stability of the gamma prime.
   - A γ' denuded region consisting of only a gamma matrix will be much weaker than the grain interior which is strengthened by the well-known creep strengthening effect of gamma prime.
   - Analysis of the notched-bar creep data shows that the rupture behavior is controlled by the effective stress, which requires grain boundary sliding (cavity initiation).
2) Formation of the eta phase platelets.
   - η phase precipitates form on grain boundaries after an incubation period and then grow into the grain interior as a function of time.
   - Creep crack growth investigation in alloy 706 demonstrated that the creep-crack growth resistance increased (growth rate decreased) with heat-treatments that caused precipitation of eta phase platelets extending into the grains, but when 'film-like' eta phase formed on the grain boundary and grew in a direction parallel along the grain boundary, the resistance decreased.

Alloy 263:
775 °C/115MPa/12601h





aged at 760 °C for 2000h

IN740: 760°C/2000h

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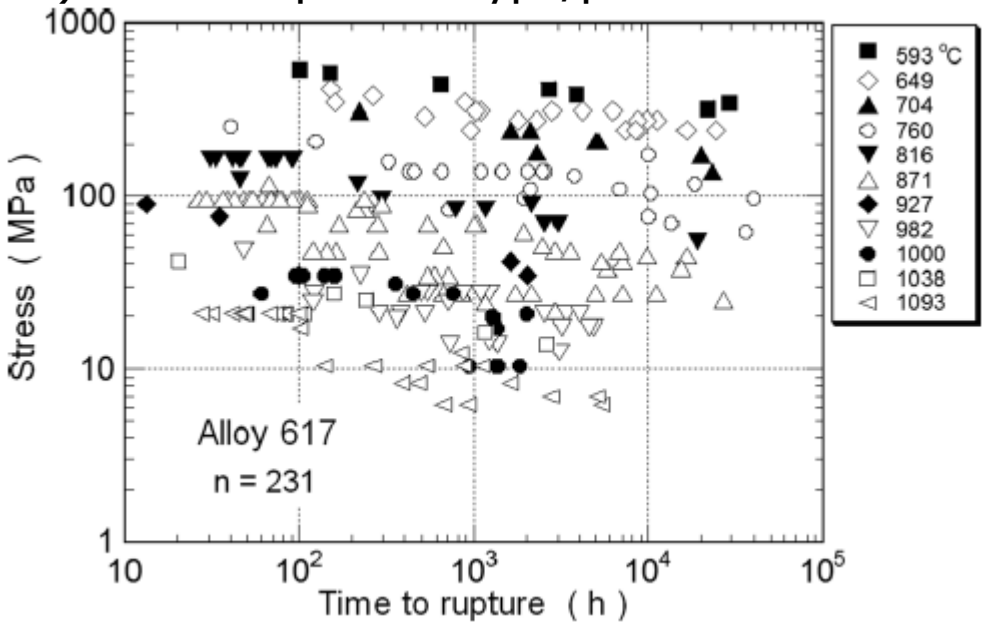
Microstructure

Creep behaviour

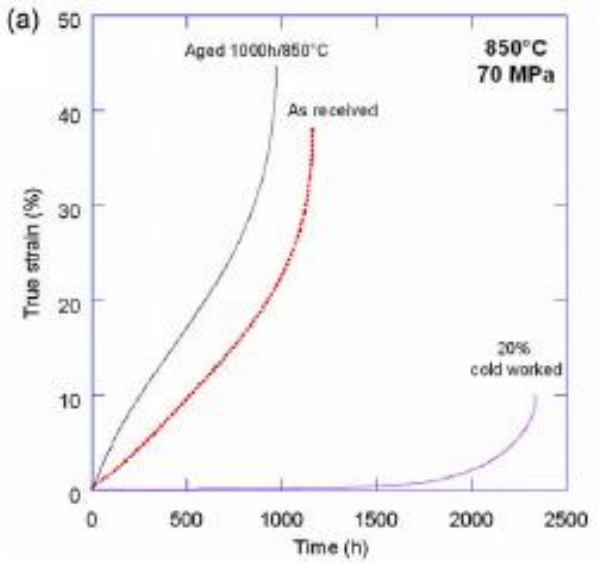
Alloy A617: wide scatter band

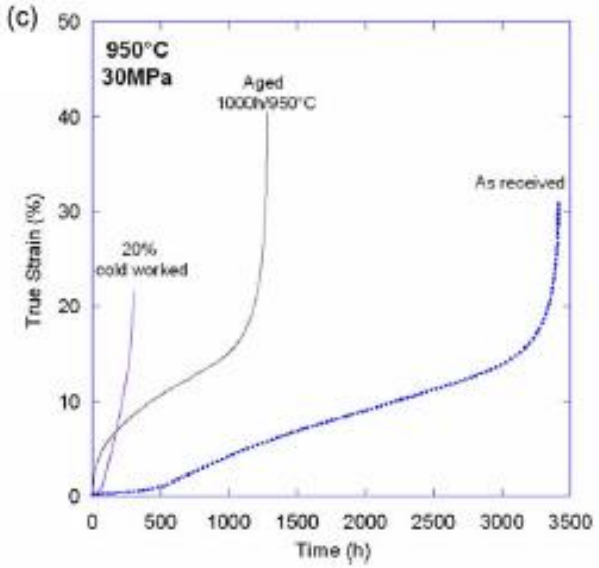
1) Effect of composition
2) Effect of product type/process route



Under further investigation within ECCC

- ✓ Effect of ageing: lower rupture times
- ✓ Effect of cold work: effect of stress induced precipitation depending on temperature





F. Abe et al., J. Pressure Vessel Technology ASME FEBRUARY 2017, Vol. 139 / 011403-1

S. Chomette et al. http://oatao.univ-toulouse.fr/

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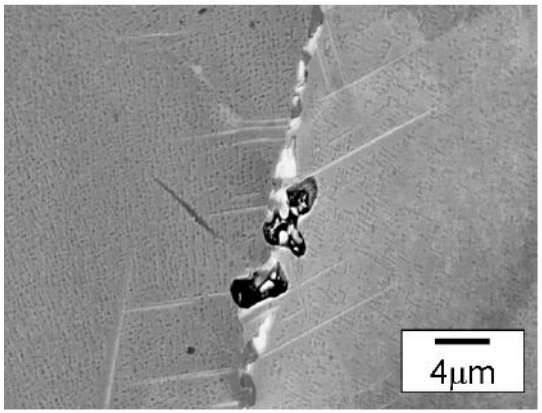
Creep

Creep behaviour

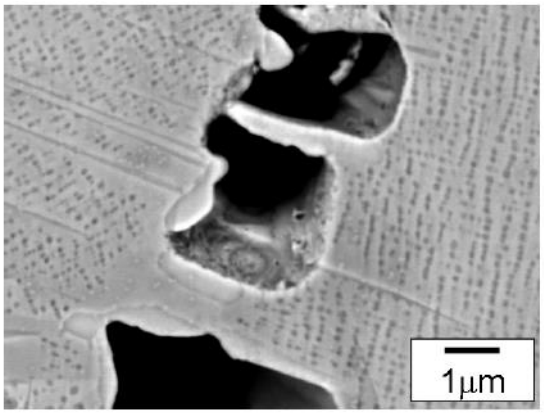
Mechanisms of creep damage

Alloy 740

- ✓ Grain boundary creep cavities nucleated on η particles.
- ✓ η precipitation is accelerated by stress
- ✓ Presence of PFZ (Precipitate Free Zone)

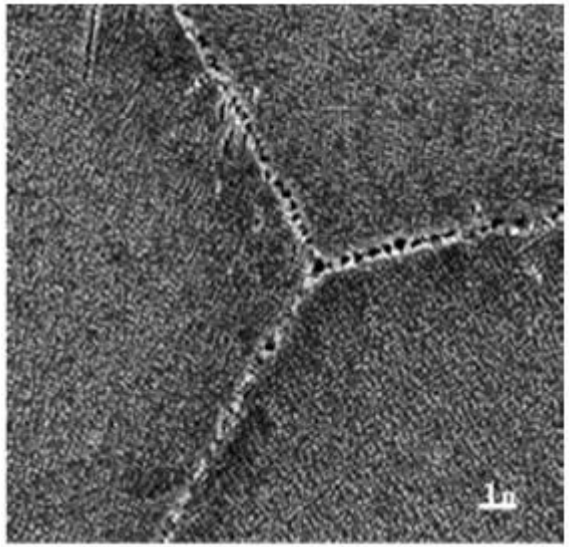


750°C / 180 MPa



750°C / 320 MPa

Alloy 740H:
No η precipitation
No PFZ



750°C / 280 MPa.

J. P. Shingledecker, PhD diss., 2012

J. J. de Barbadillo, 4th Inte. Symp. - Supercritical CO2 Power Cycles September 9-10, 2014, Pittsburgh

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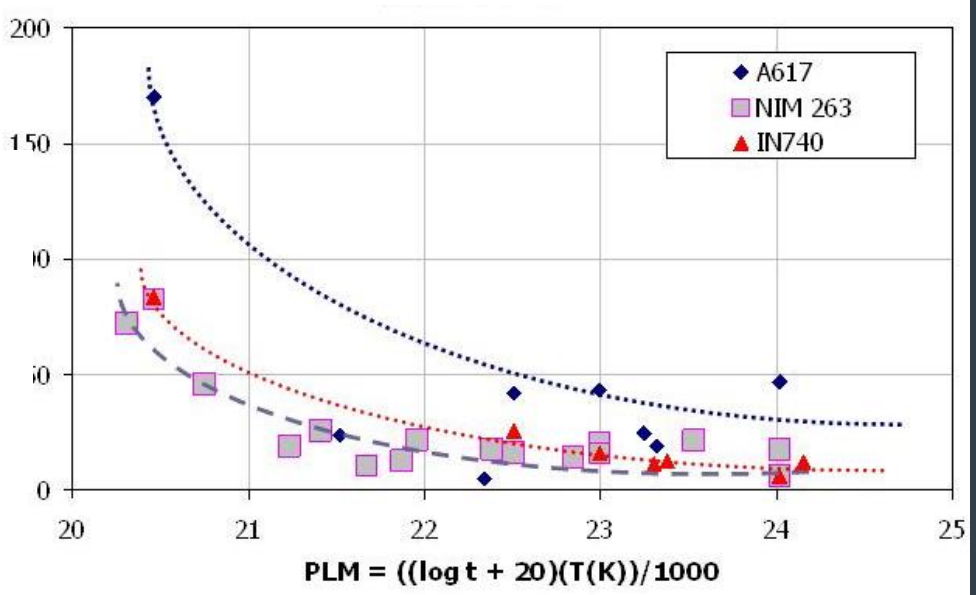
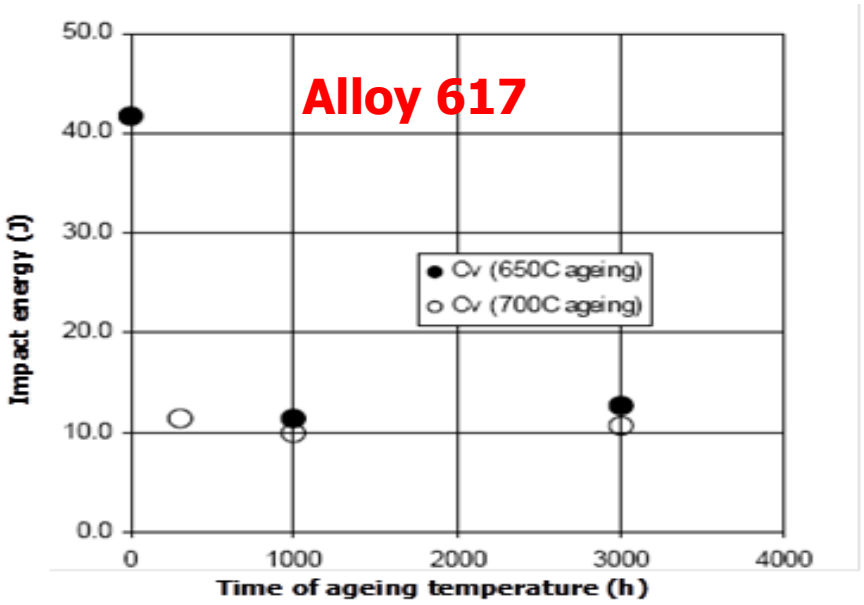
Mechanical properties

Detrimental effect on the alloy properties of grain boundary precipitation and η formation after high temperature exposure.

Dramatic Charpy toughness decrease





O. Tassa et al.: MACPLUS PROJECT

R. Blum et al . Proc. EPRI Conf. (2004)

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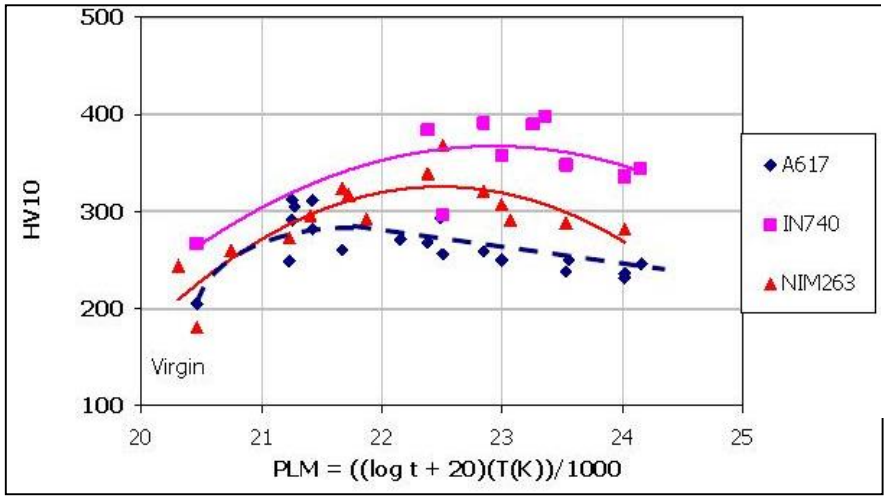
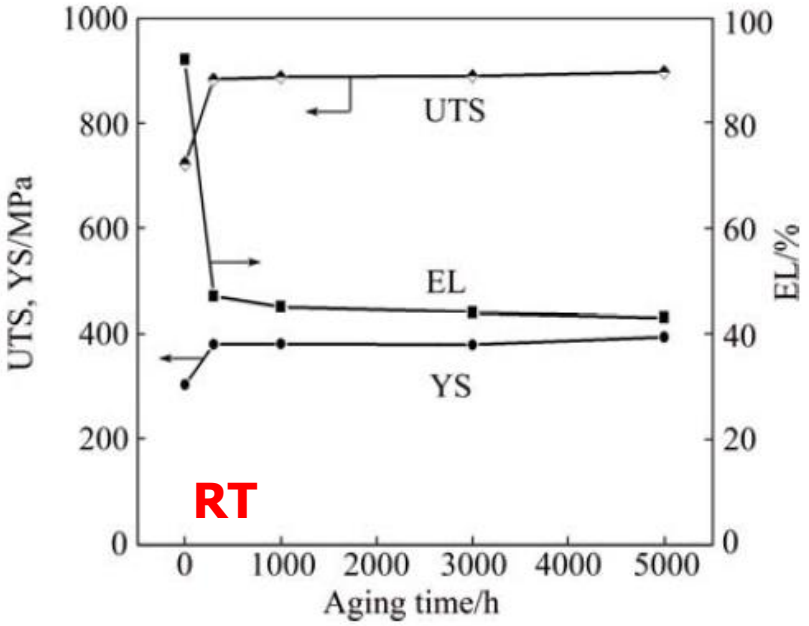
Mechanical properties

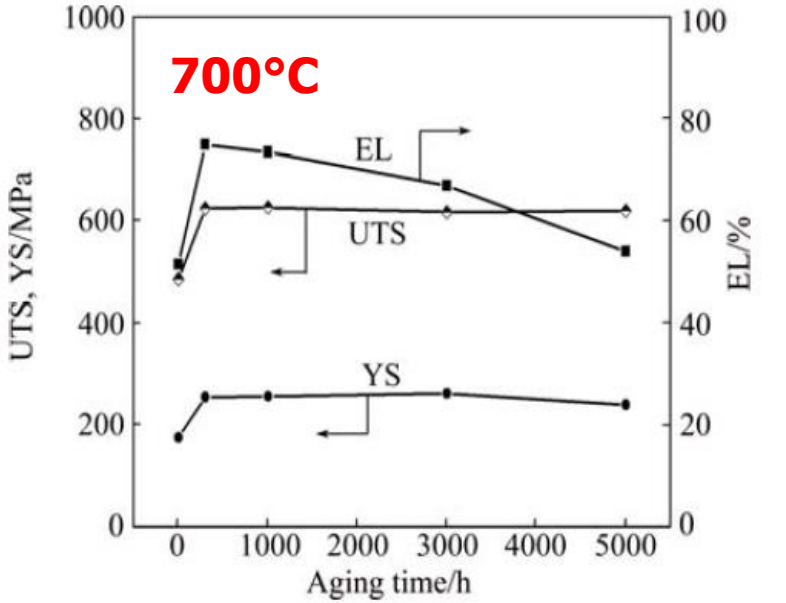
Alloy 617B

- ✓ Tensile strength increases in the first 1000 hours, then remains stable.
- ✓ Ductility decreases.

Hardness increases within the first 1000 h followed, generally, by a stabilisation. This effect is thought to be due to grain boundary precipitation







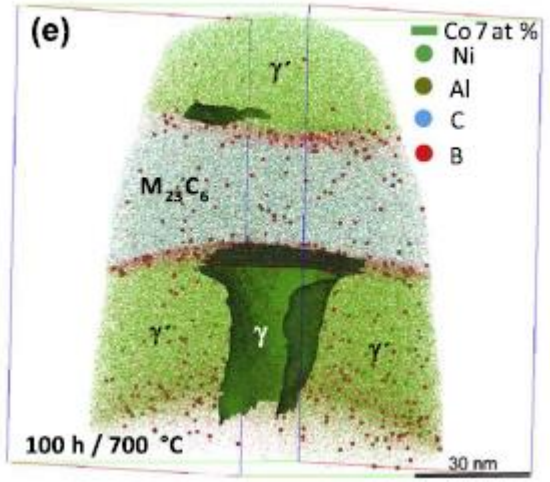
Y. Guo, et al / Trans. Nonferrous Met. Soc. China 25(2015) 1106−1113

Microstructure optimization

1) Alloy 617B

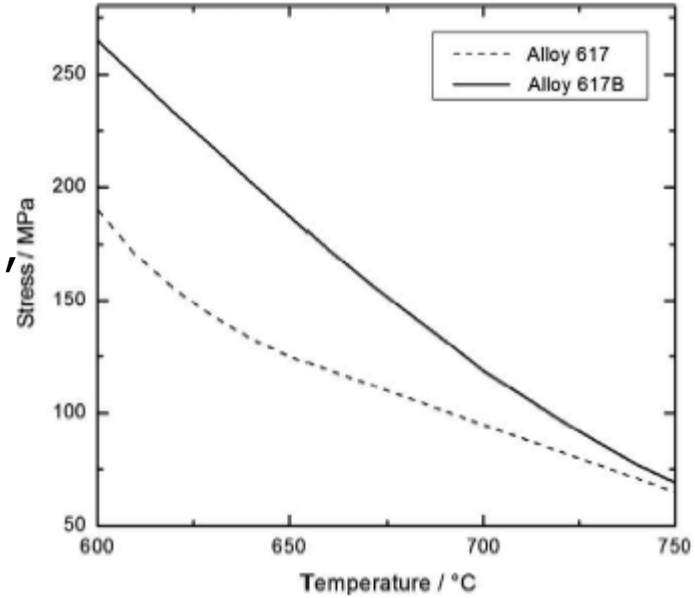
Controlled B addition to stabilize $M_{23}C_6$ carbide at grain boundaries.

Interfacial B enrichments and γ′ formation at $M_{23}C_6$ are believed to slow down the growth of $M_{23}C_6$ particles preserving a stable precipitation network of coherent particles

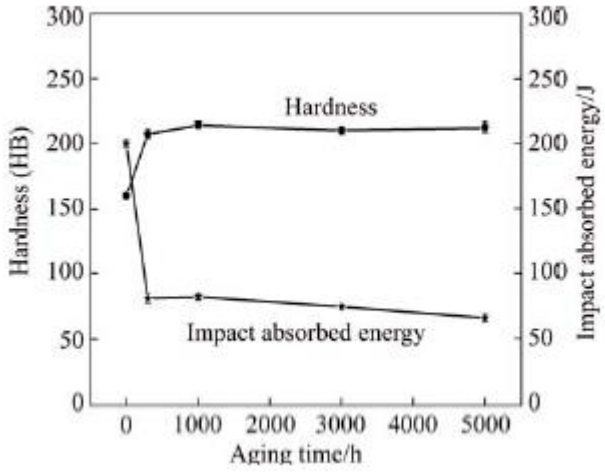


APT data and concentration profiles across $M_{23}C_6$/c interfaces

- ***Higher creep rupture strength (10^5h)***
- ***Lower toughness reduction***



D. Tytko et al. Acta Materialia 60 (2012) 1731–1740



Y. Guo et al., Trans. Nonferrous Met. Soc. China 25(2015) 1106−1113

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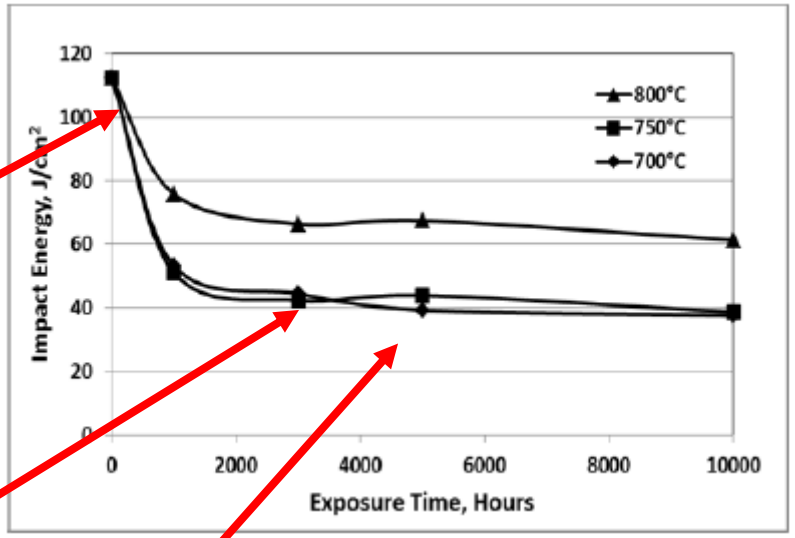
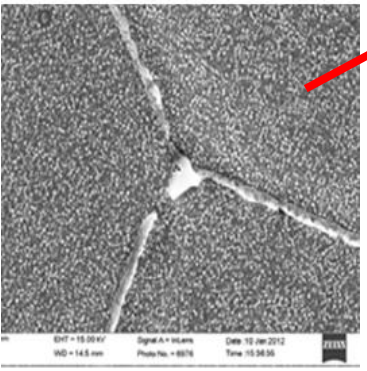
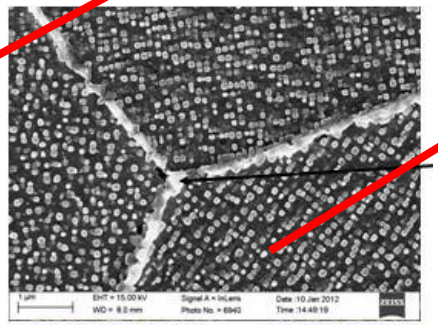
Microstructure optimization

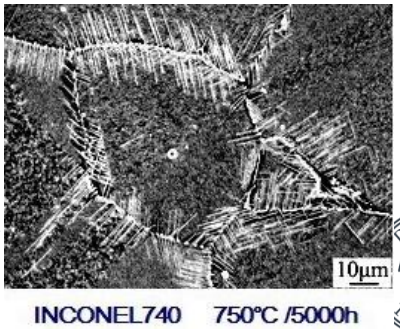
2) **Alloy 740H**
Increased γ′ stability against η formation: > Al/Ti

- ***No PFZ***
- ***No η formation***
- ***Toughness reduction is limited: E > 40J.***









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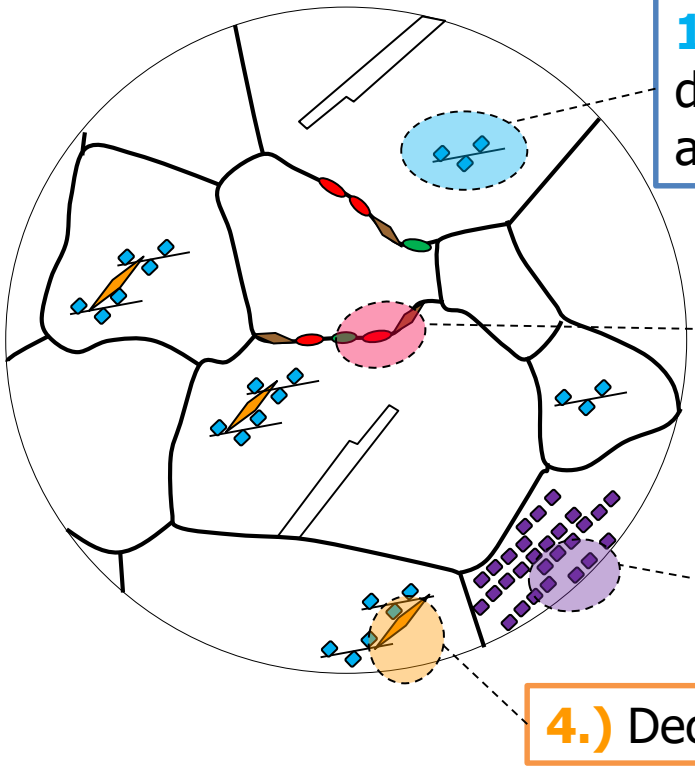
Microstructure optimization

Microstructure optimisation by Kinetic modeling:
Target for the optimisation



1.) Increasing the phase fraction and decreasing the size of **$M_{23}C_6^{ig}$** inside grain to avoid dislocation movement

2.) Decreasing precipitates size of grain boundaries precipitates (**$M_{23}C_6^{gb}$, σ, μ...**) on grain boundaries to avoid grain boundary movement

3.) Increasing the phase fraction and decreasing the size of precipitate inside grains to avoid dislocation movement: γ`

4.) Decrease phase fraction of **η-Phase** (in Ni alloys)

MatCalc simulations to predict precipitate evolutions as function of chemical composition: solidification + heat treatment + ageing

Optimization by modeling

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O. Tassa et al.: MACPLUS PROJECT

Microstructure optimization

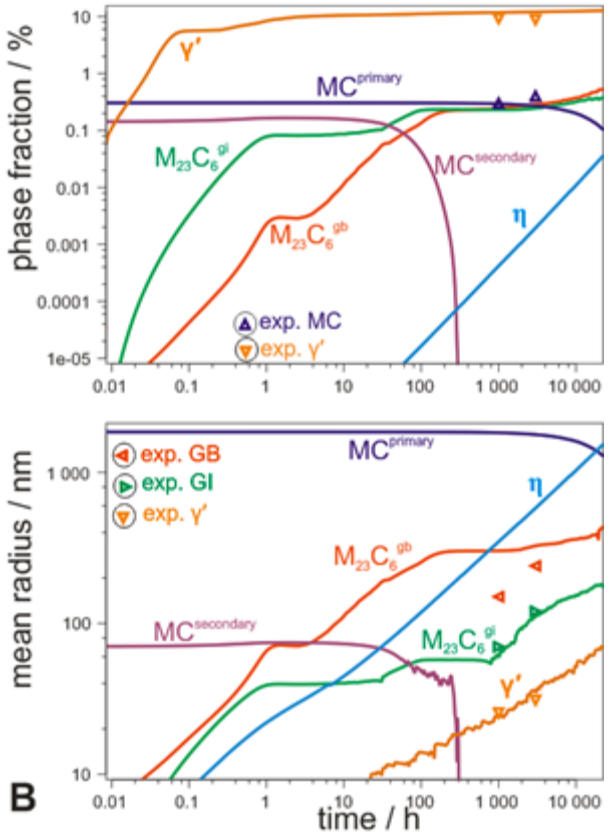
Chemical composition optimization **Alloy263:** : **MACPLUS Project**

- ***Model calibration by experimental results on long term aged alloys.***

1. VAR1: inside standard

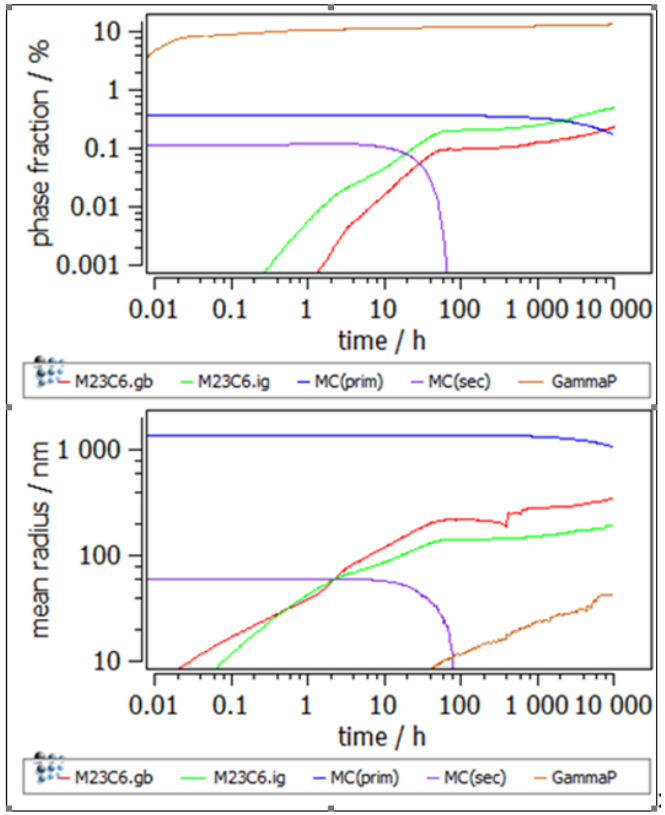
2. VAR 2 outside standard:

- ✓ ***higher Al/Ti***
- ✓ ***higher γ′ fraction***
- ✓ ***higher Cr content to increase corrosion behaviour***



Standard 263/750°C

η not formed



VAR2/750°C

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Optimization by modeling

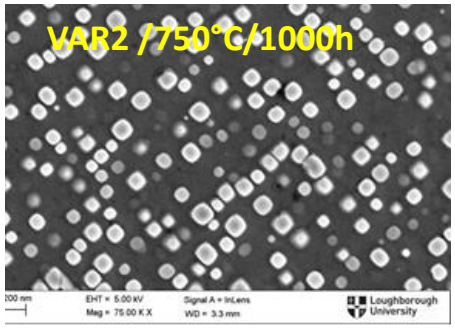
Microstructure optimization

Chemical composition optimization: **Alloy263**

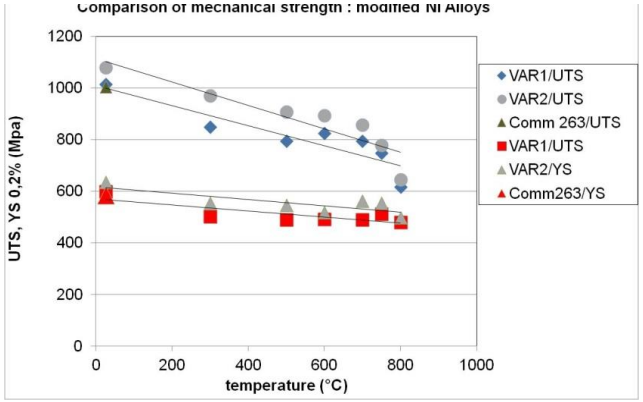
MACPLUS Project: VAR2

Optimization by modeling

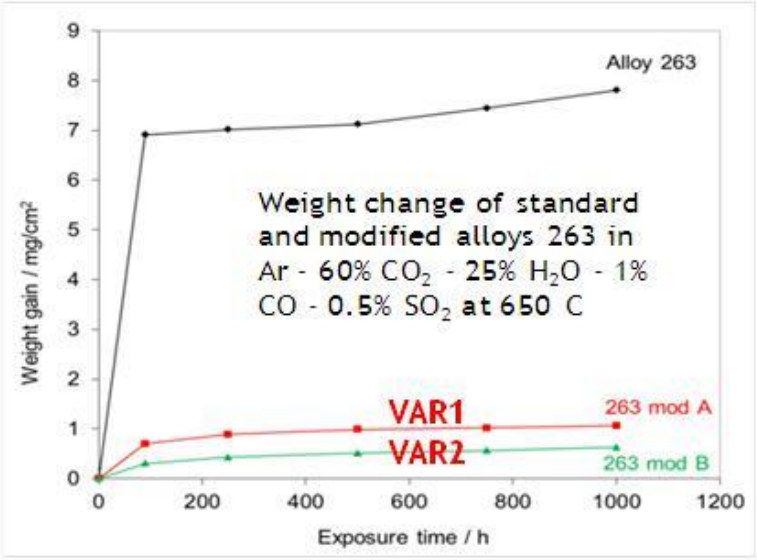
❖ High γ′ stability



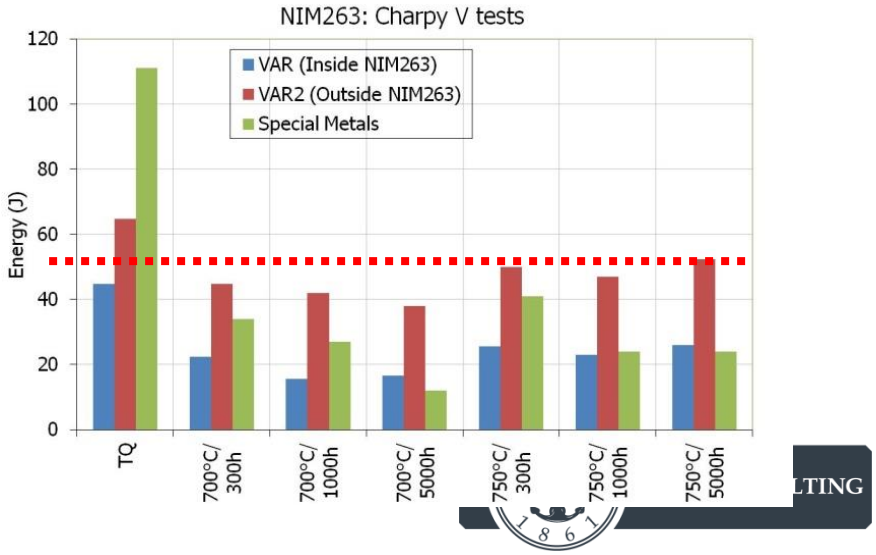
❖ Higher mechanical strength



❖ Higher corrosion resistance



❖ Limited toughness drop



Concluding remarks

- The candidate Ni based alloys have complex composition.
- Due to the high content of alloying elements, remelting process is requested to reduce segregation, to refine microstructure and to control trace elements.
- Process route influences strongly the quality and performance of the materials.
- Exposure at high temperatures causes evolution of the initial microstructure:
  - coarsening of γ', precipitation of η phase, precipitation and coarsening of carbides and TCP intermetallic phases.
- Drop of material properties is strictly associated to the precipitation evolution.
- Optimization of chemical composition can prevent or control material evolution, limiting the drop of properties.

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Thank you very much for your attention

oriana.tassa@rina.org

RINA Consulting S.p.A.
Via San Nazaro, 19
16145 GENOVA – Italy
Tel. +39 010 3628148
Fax +39 010 3621078

RINA Consulting Centro Sviluppo Materiali S.p.A.
Via di Castel Romano, 100
00128 ROMA – Italy
Tel. +39 06 50551
Fax +39 06 5055204

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