The role of advanced materials and performance-driven design criteria in the development of the EU Energy Industry

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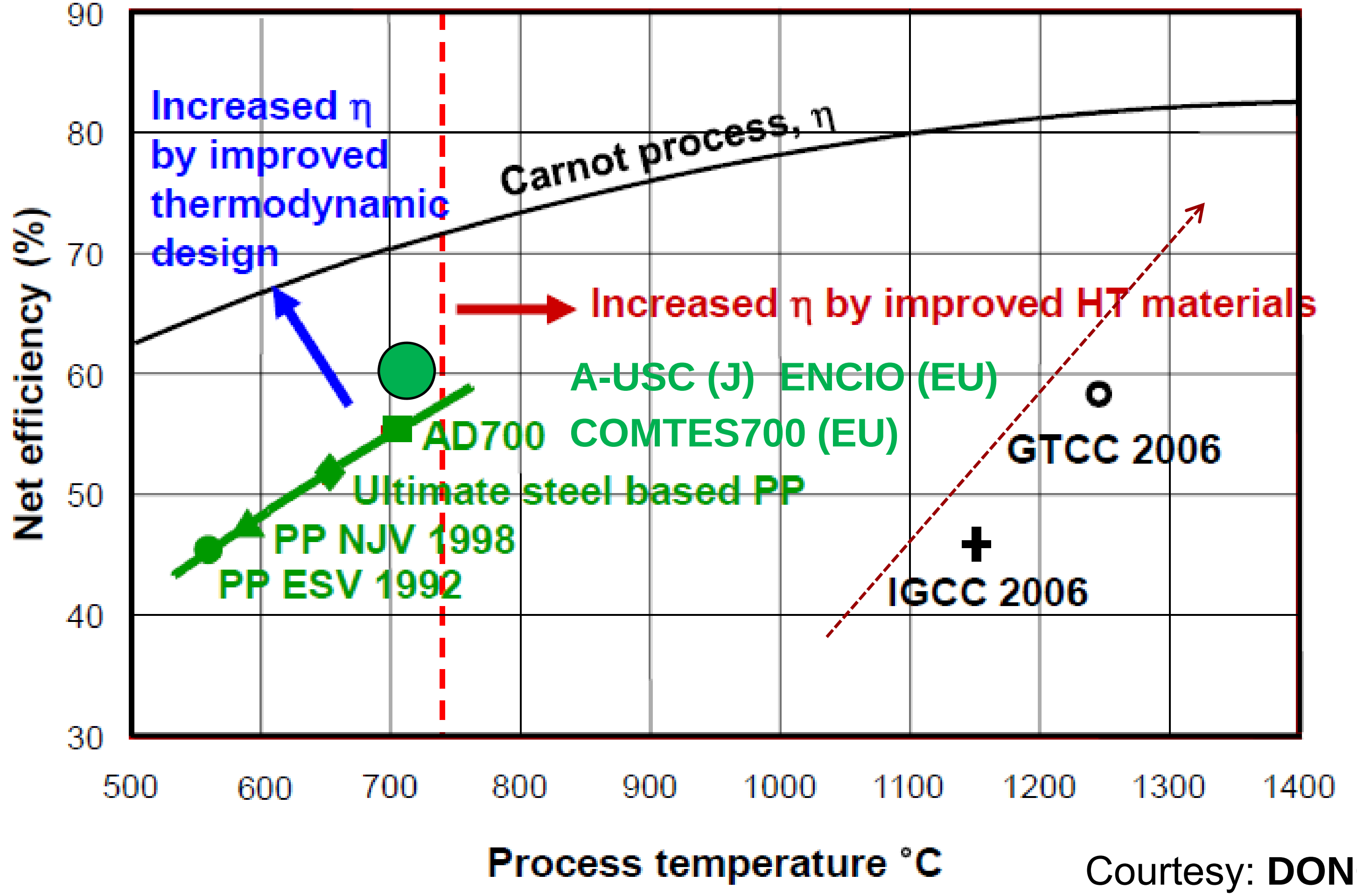
- Advanced High Temperature Structural Integrity design criteria and approach

- (EU and) National supporting initiatives

The role of advanced materials in the development of the EU Energy Industry

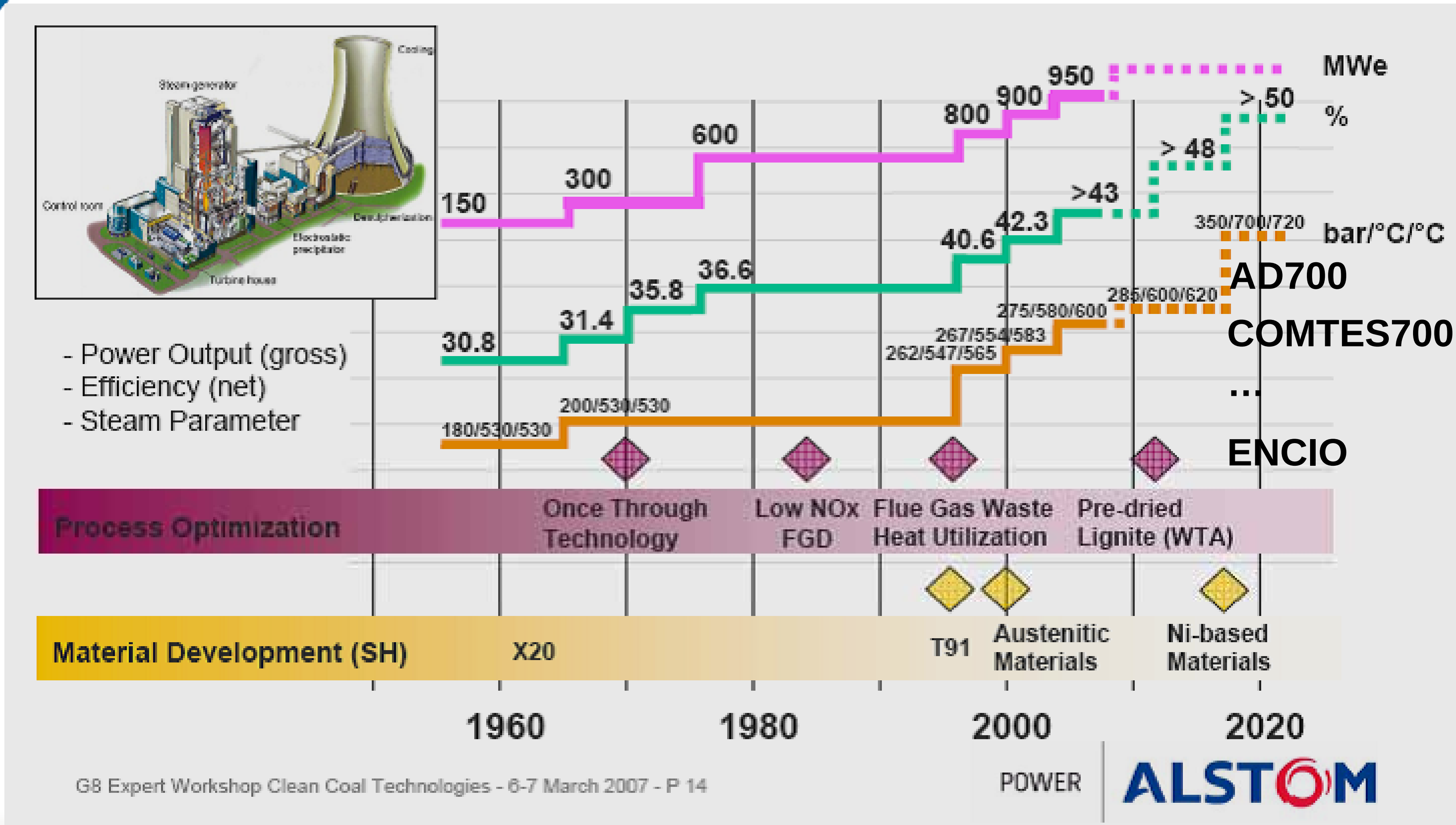
The role of advanced materials …

Efficiency Improvement, η

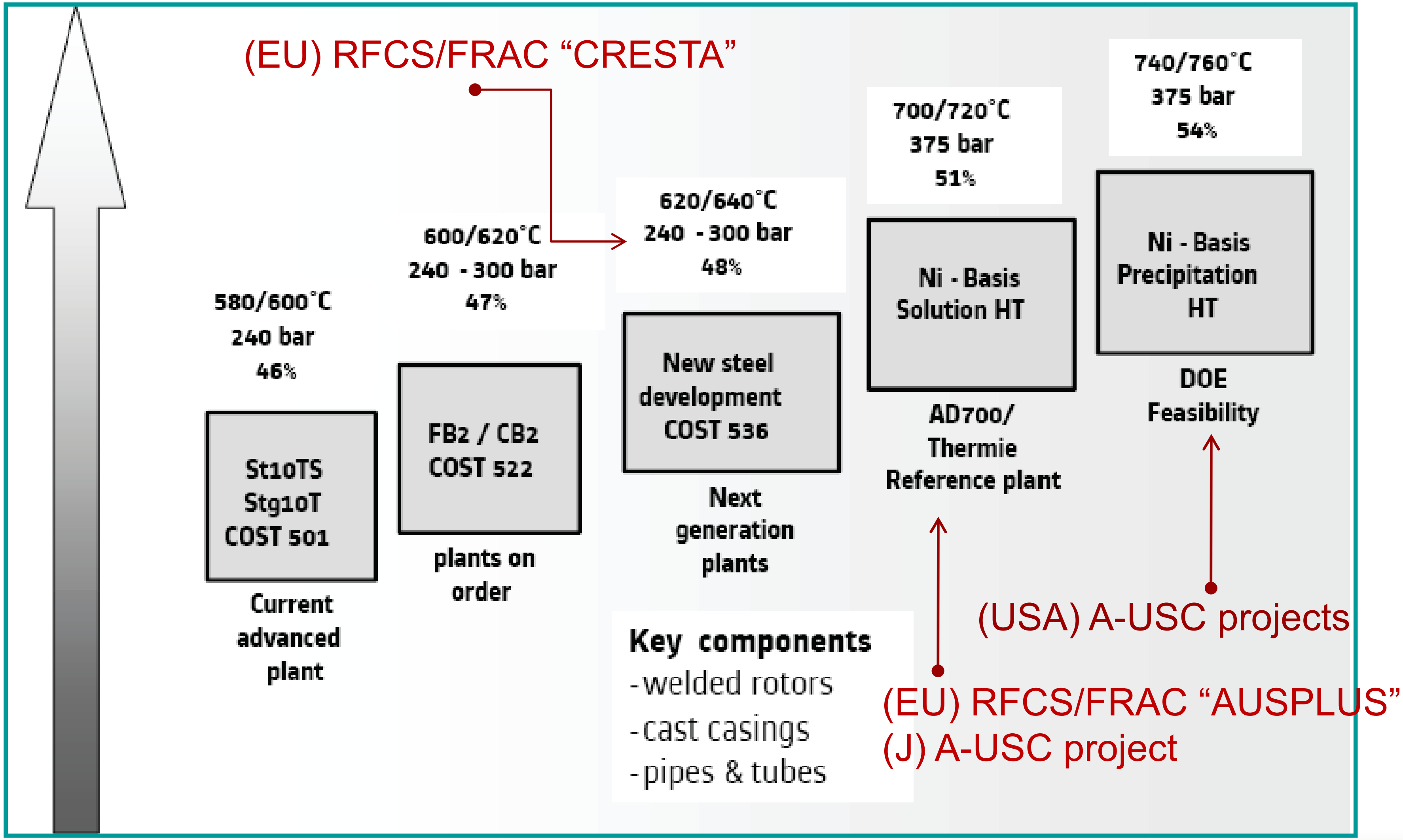


Courtesy: **DONG Energy**

The role of advanced materials …

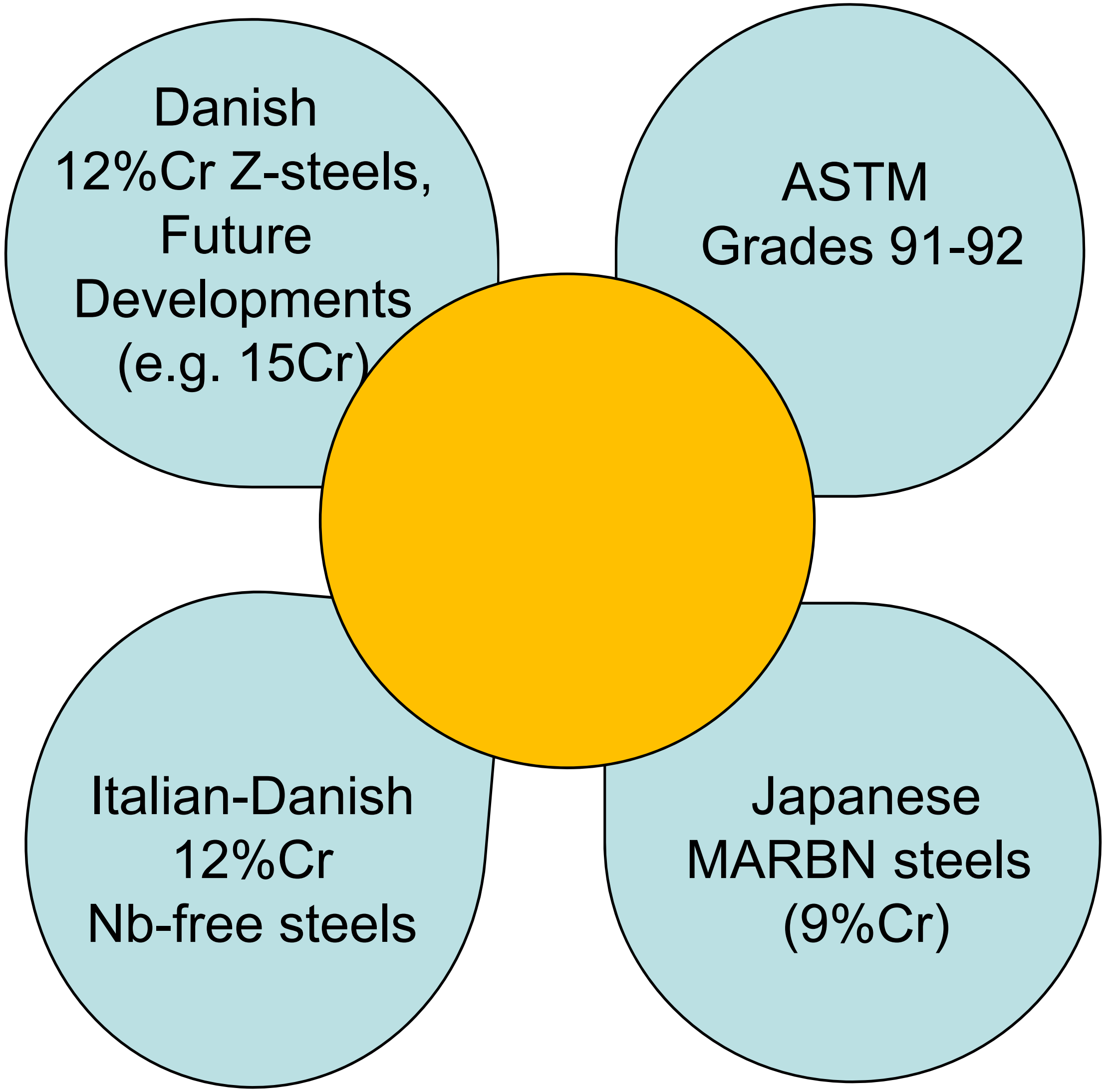


The role of advanced materials …



Courtesy: **ALSTOM Power**

Advanced creep strength … (A-CSEF)



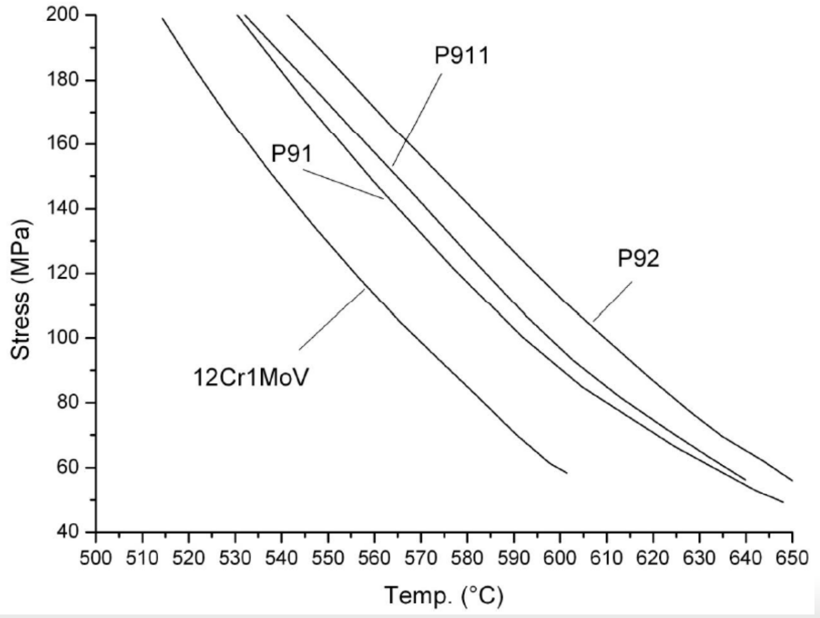
Advanced creep strength … (A-CSEF)

ASTM GRADES 91 & 92

- Currently ASTM **<u>Grades 91 & 92</u>** (and their fine tuned variants) are the most performant creep ferritic steels presently on the market.
- Recently new creep rupture assessments were performed within ECCC
  - Gr. 91: 600°C / 90MPa / 10^5 h by V&M and CSM in 2009
  - Gr. 92: 600°C / 113MPa / 10^5 h by V&M
- Max application temperature: 615°C

→ ENEL Units in Torrevaldaliga (Gr. 92)

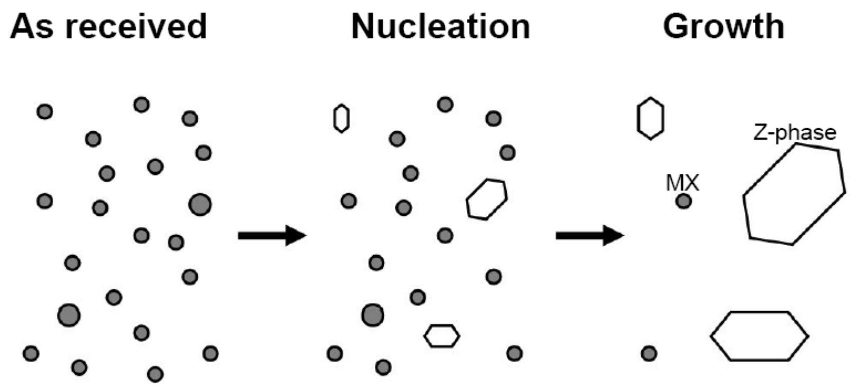
It is not possible to use Grades 91 and 92 for 650°C applications since 9%Cr amount does not guarantee enough resistance to oxidation.

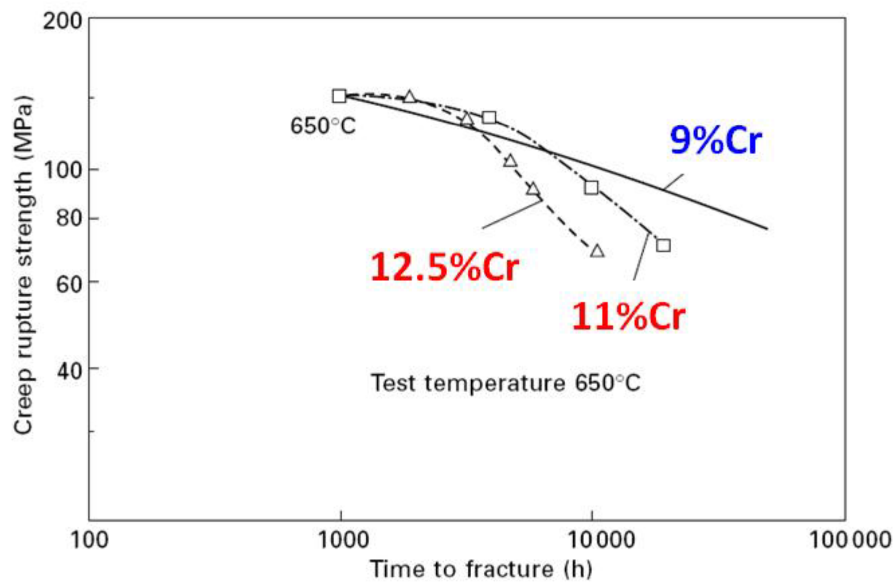


Advanced creep strength … (A-CSEF)

12%Cr vs (V,Nb)N: Failure of adv. 12%Cr steels

- Since now all efforts to combine superior oxidation resistance (12%Cr) with ferritic matrix strengthened by fine distribution of MX failed (e.g. P122)
- Indeed, recently it was demonstrated that the Nb- and V-nitrides (MN) transform into more stable Z-phase (CrVNbN) at 650^{o}C in 12%Cr steels
- Z-phase is a large and coarse phase. MX→Z-phase transformation causes creep resistance drop in 12%Cr steels



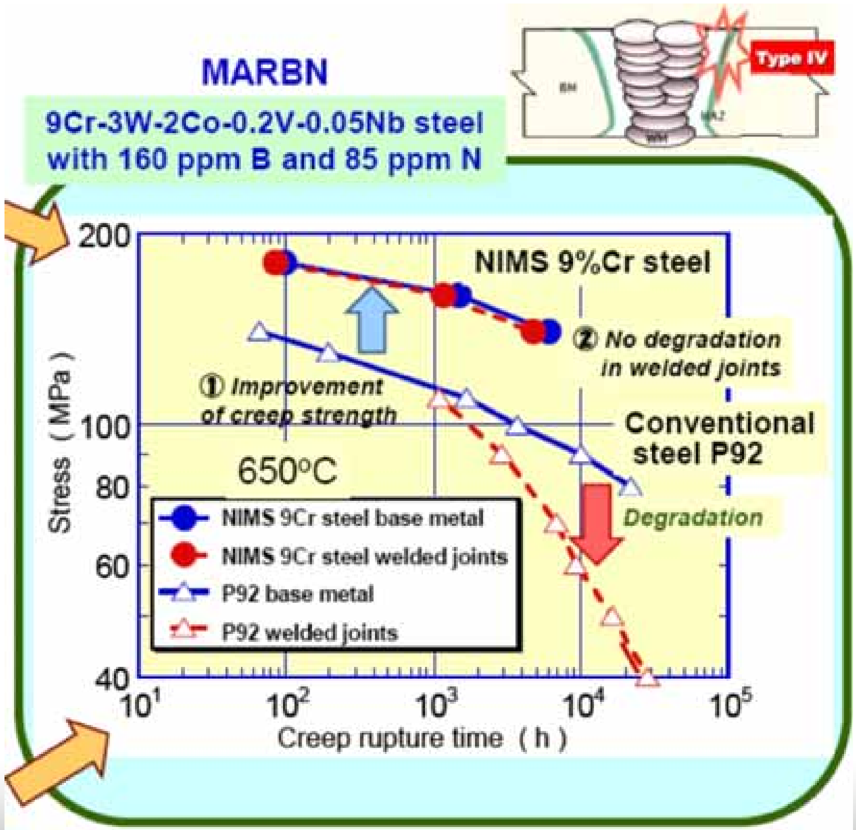


Advanced creep strength … (A-CSEF)

Japanese MARBN steels

- Recently Japanese researchers by NIMS developed an enhanced version of Grade 92 by addition of Boron and optimisation of B/N ratio
- MARBN steels → **<u>MAR</u>**tensitic microstructure and **<u>B</u>**oron/**<u>N</u>**itrogen control
- **Advantages**: Boron enhances creep resistance by lowering the coarsening rate of $M_{23}(C,B)_6$, no degradation in welded joint
- **Disadvantages**: 9%Cr amount, max application temperature 615-620°C.

Present best candidate:
9Cr-3W-2Co-Nb-V-N-B

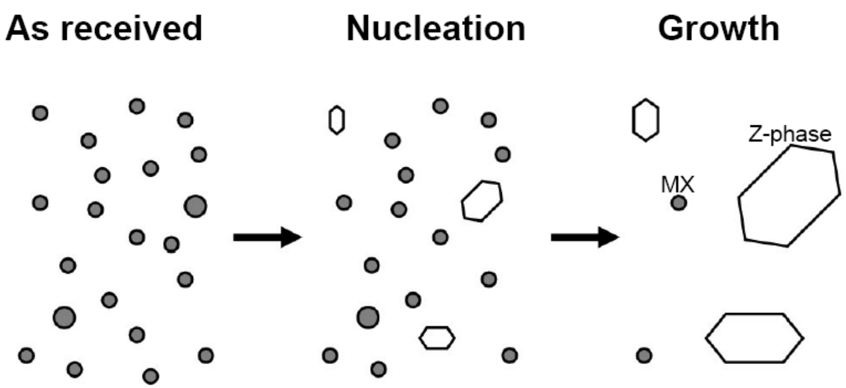


Advanced creep strength … (A-CSEF)

Danish Z-steels

- Danish researchers patented the ***Z-phase strengthening concept***
- ***If you cannot beat it, join it***. Since Z-phase causes the drop of creep resistance in **12%Cr steels**, then the innovative solution is to promote fast and abundant Z-phase precipitation in as-treated material to strengthen the matrix.

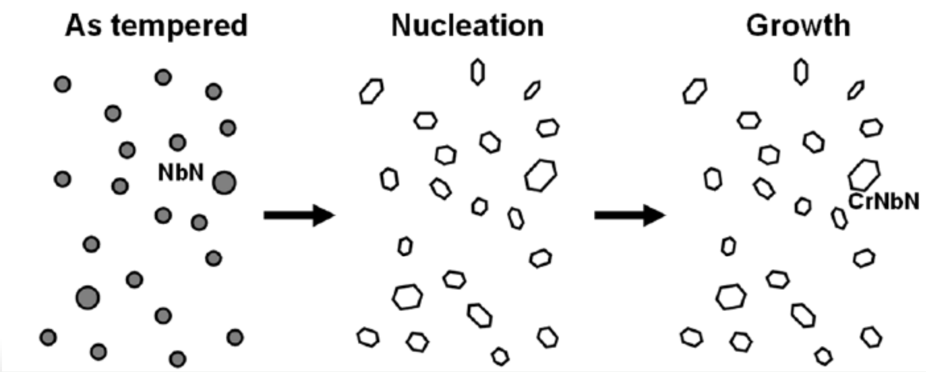
Old concept



Status
Currently under development

Advantage
12%Cr amount combined with Z-strengthening

New concept



Advanced creep strength … (A-CSEF)

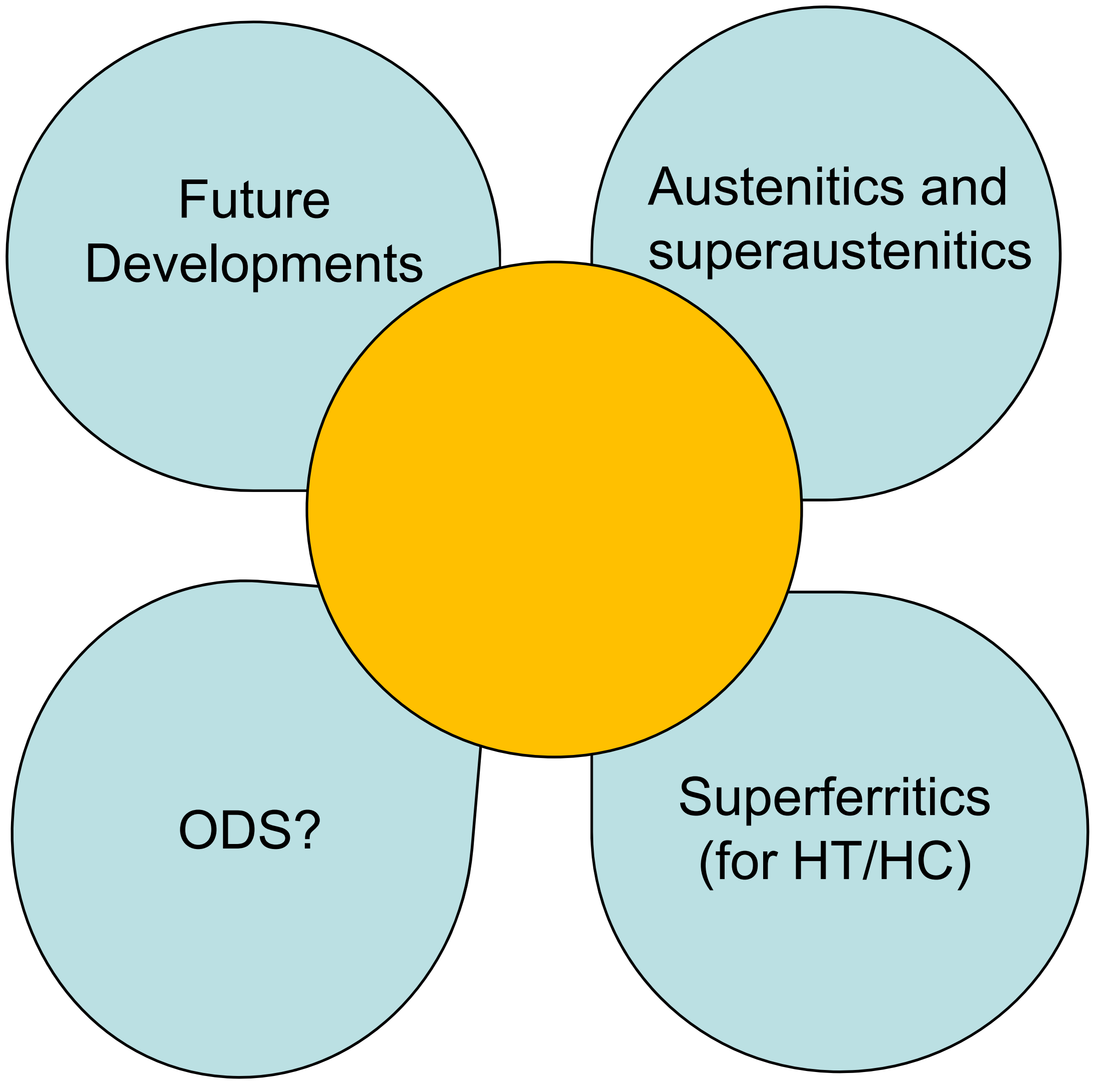
Italian-Danish Nb-free 12%Cr B-steels

• Most recently Italian-Danish researchers by CSM-DONG-DTU discovered that Nb has a high driving force for the formation of Z-phase in 12%Cr B-added steels.

New 12%Cr Nb-free steels are under development

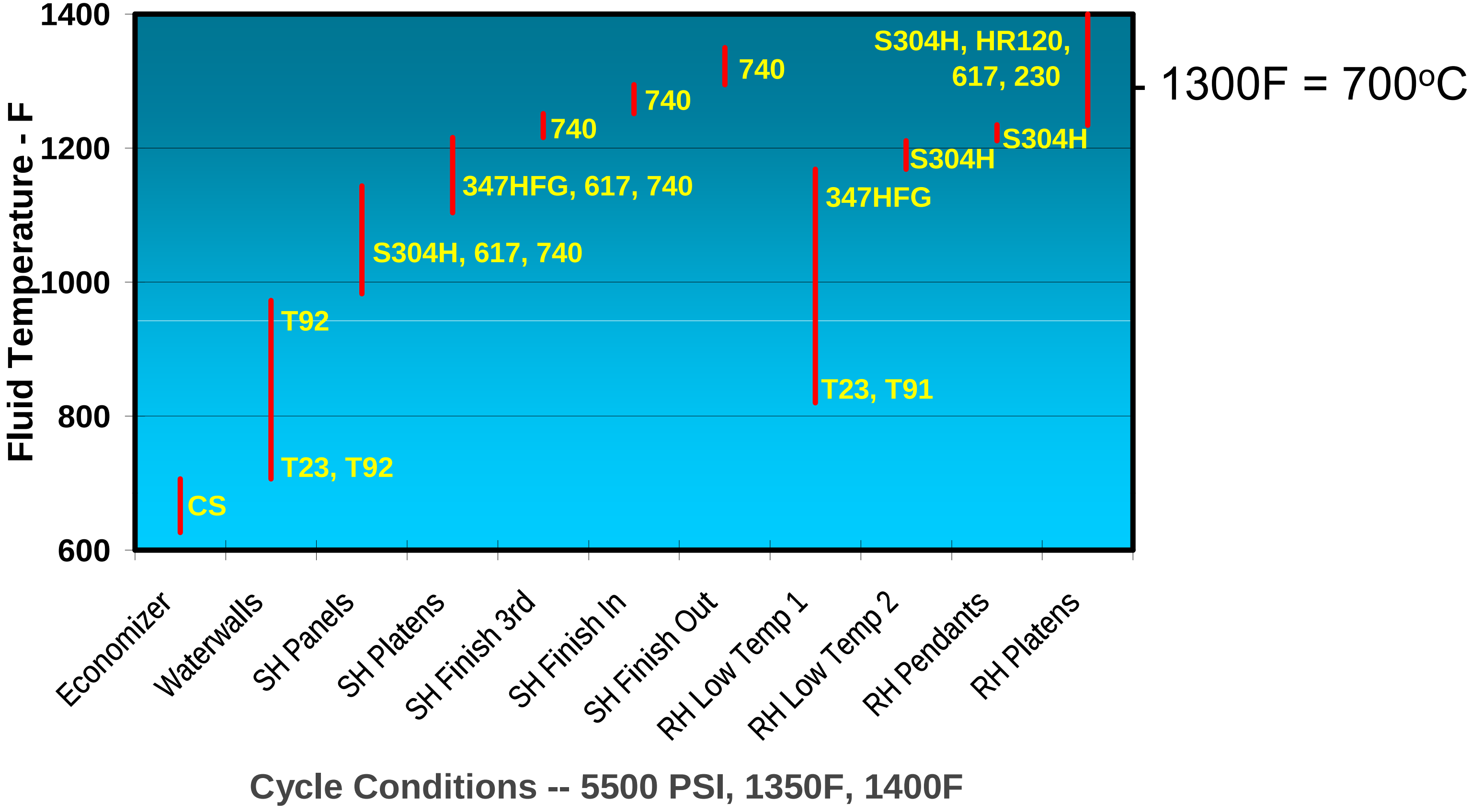
- **Advantages**: 12%Cr, strengthening by VN, Z-phase formation much delayed.
- **Disadvantages**: effect of absence of Nb? Coarsening of pure VN?
- **Status**: under development in the European project "CRESTA"

Creep strength enhanced … (CSES)



Creep strength enhanced … (CSEA)

USC Boiler Tubing Metallurgy



EPRI

Courtesy: **EPRI**

Creep strength enhanced … (CSEA)

- Austenitic (**A**) and SuperAustenitic (**SA**) steels for power generation are a valuable option to much expensive Ni-based alloys for 700°C applications.

- **Advantages**: superior oxidation and corrosion resistance (e.g. TEMPALOY A3, SANICRO25; up to 25%Cr, 18%Ni), high creep resistance up to 700/720°C (e.g. TEMPALOY AA1, S304H, 347HFG; up to 18%Cr, 10%Ni).

- **Disadvantages**: higher linear expansion coefficient than ferritic steels; not sufficient knowledge of microstructural evolution mechanisms; long-term creep properties to be much better investigated; chemical compositions not completely optimised, yet; more expensive than 12%Cr ferritic steels.

Creep strength enhanced … (CSESF)

• SuperFerritic (**SA**) steels for power generation are a valuable option to much expensive stainless steels and Ni-based alloys for HT/HC applications (e.g. waste inceneritors, biomass-riched fossile PG plants).

• **Advantages**: superior oxidation and corrosion resistance (e.g. SANICRO28; up to 30%Cr, 8%Ni), less expensive than stainless steels and Ni-base alloys, for applications in high temperature high corrosion (HT/HC) environments.

• **Disadvantages**: poor metallurgical knowledge of microstructural evolution; low creep resistance, creep properties to be explored and improved; chemical compositions not completely optimised, yet.

Creep strength enhanced … (CSEA)

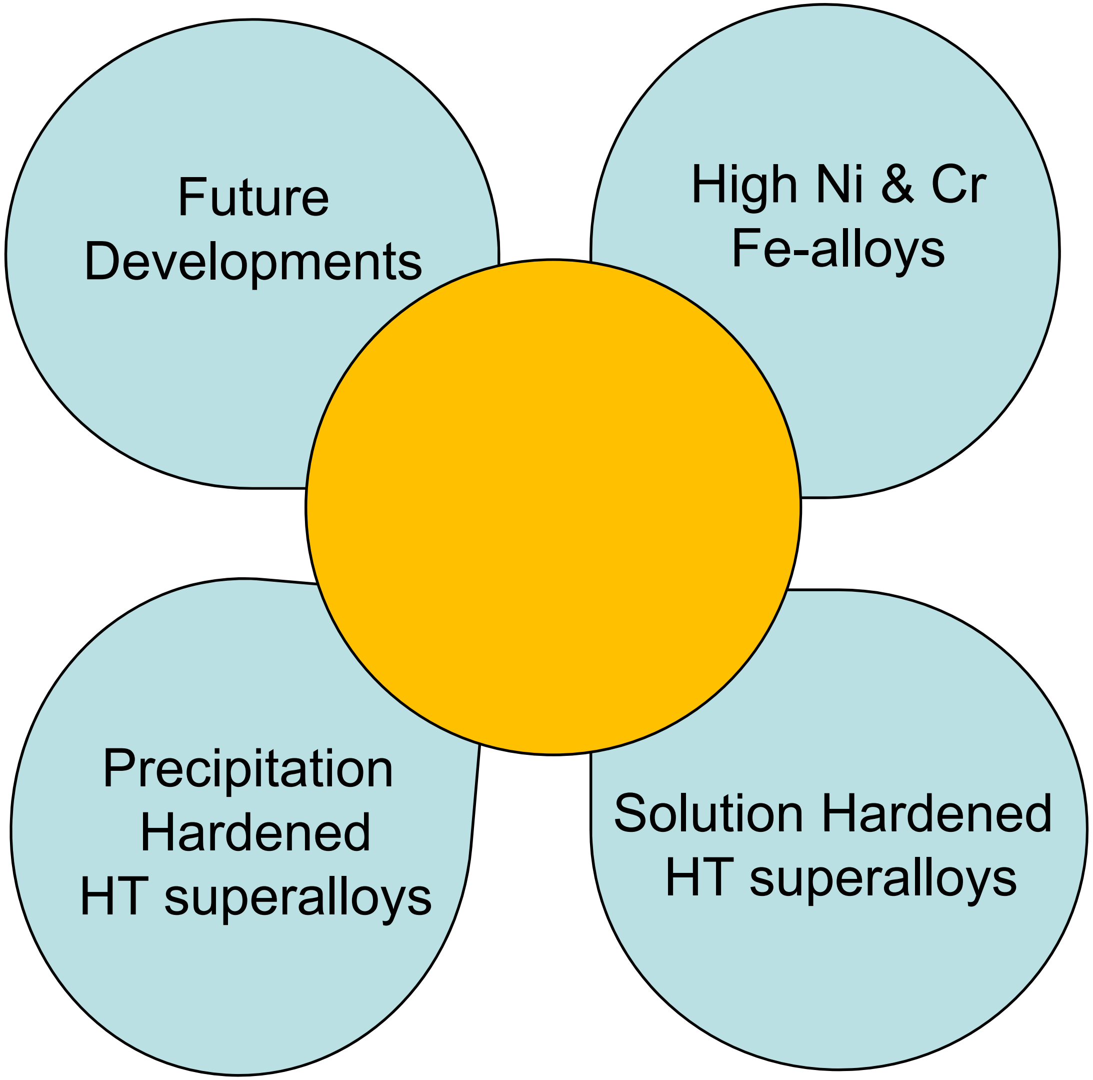
AUstenitic steels for complex and variable Stress-temperature, Pressure and environmentaL conditions of next generation Ultra Supercritical power plants (**AUSPLUS**).

The project financed by European Commission in the field of Research Fund for Coal and Steel (RFCS) is a 4 years project, starting from July 2010.
Many European Industries and major R&D Centres and Universities are involved: ***DONG Energy*** (Denmark), ***TUBACEX*** (Spain), ***Cogne Acciai Speciali*** (Italy), ***Salzgitter Mannesmann Stainless Tubes*** (Germany), ***Technical Research Centre of Finland*** (Finland), ***Chalmers University of Technology*** (Swedish), ***National Physical Laboratory*** (England), under the coordination of **Centro Sviluppo Materiali** (CSM).

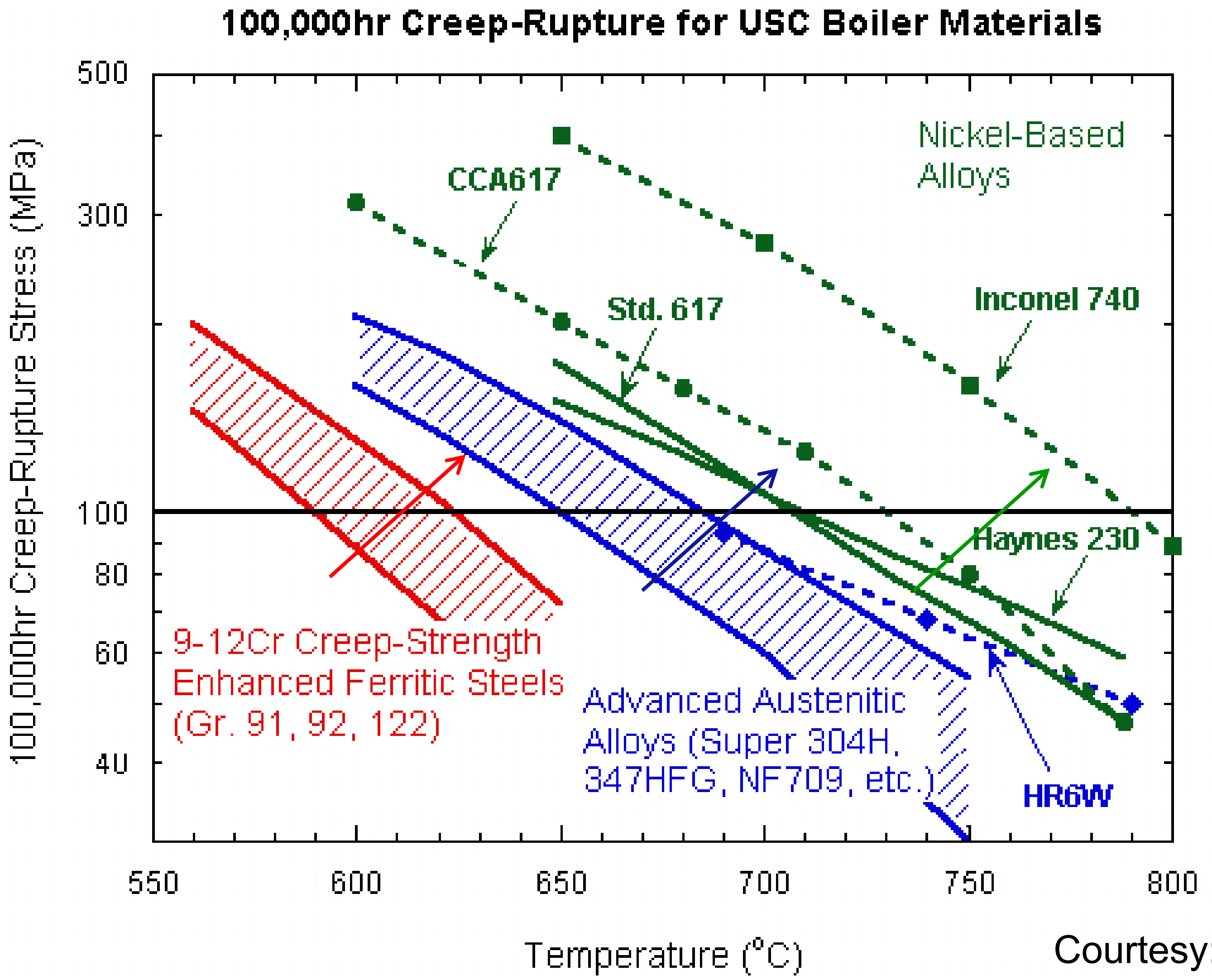
The main project deliverables are:

1. Alloy Design and Product Development of new creep resistant austenitic steel for A-USC PowerGen applications up to 700/720^{o}C
2. Production of pipe components in the most promising steel prototype, its characterisation and installation in a PP for long-term monitoring.

Ni-based solution and precipitation HT …



Ni-based solution and precipitation HT …



Courtesy: **EPRI**

Ni-based solution and precipitation HT …

High Ni/Cr Fe Alloys (i.e. HR6W): high cost respect to CSEA and performance not enough high to replace Ni-based alloys.

Solution hardened HT Ni-based superalloys:

• **617** (in its standard and CCA[1] version) is currently the most investigated material, but still to be optimised to reduce reheat cracking phenomena on thick welded components. Important outputs are awaited from COMTES700 and ENCIO programs,

• **625** is today the best candidate for the cast components.

Precipitation Hardened HT Ni-based superalloys: alloys 263, 740 and H282 are the USA candidates for the manufacture of thick pipes and forged components. Reference candidates for 375bar/740^{o}C/760^{o}C applications.

1] CCA 617: **C**ontrolled **C**ompositional **A**nalysis, a modified composition of Alloy 617

Ni-based solution and precipitation HT …

Main common problems for Ni-based alloys:

- high temperature and long time stability of the microstructure and mechanical and creep behaviour to be investigated in much more details

- manufacture procedures of thick welded components to be improved

- manufacture facilities for production of heavy components (pipes, valves and forged components) to be increased (segregation problems for ingots weight > 8-10 tons)

Nimonic 105®, H282®, IN740®, Udimet®720 and Waspaloy are candidate Ni-based superalloys for steam turbine rotor applications at T higher than 670-700^{o}C

Modified surface material-base solutions

HT components are exposed to both steamside oxidation and fireside corrosion mechanisms, affecting materials creep strength and reducing component lifetime in real service conditions.

At present, alloy design is focusing to answer all technological needs (i.e. creep strength, resistance to HT oxidation and hot corrosion) with a unique massive material solution.

Alternative pathways may on the contrary involve the possibility to develop and apply structural/functional coatings, able to cope with a specific application need (typically higher resistance to the environment).

The development of a particular coating strategy involves both materials and deposition technologies, normally to be specialised case by case.

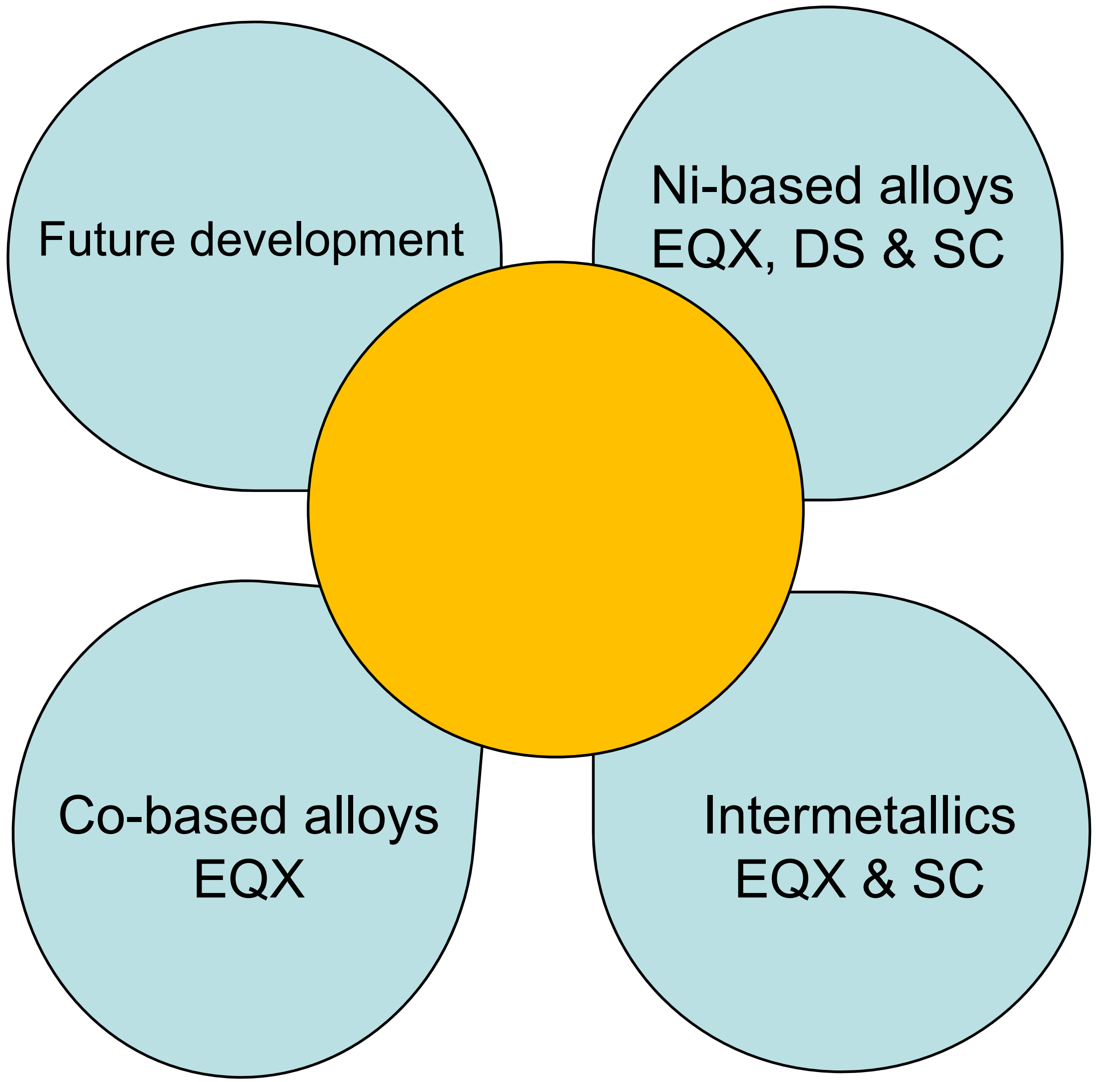
Modified surface material-base solutions

- shot blasting (in CSEA)
- weld overlays
- claddings,
- sprayed coatings (cold spray, HVOF),
- diffusion coatings (typically chromium, chromium-silicon, chromium-aluminum)
- nichel-chromium deposition by plasma-transferred arc (PTA) and laser welding

are the most commonly used techniques and materials to modify component surface, and improve steel response to the environment.

CSEF benefit most from coatings; CSEA may benefit. Ni-based alloys are not likely to need coatings at all.

Advanced alloys for GT blades



Advanced alloys for GT blades

Ni – base superalloys

EQX: i.e. **Renè80**, IN738. **DS:** i.e. **MAR-M002, IN6203**. **SX:** i.e. **CMSX4**, **PWA1480**

- Solution and precipitation hardened by γ' phase, high temperature strength and oxidation/corrosion resistance
- Grain boundaries parallel to major axis of blade: increase in the mechanical resistance and temperature capability
- Free from grain boundaries; further increase in mechanical properites and temperature capability

Main common problems:

- high temperature microstructure instability,
- manufacture costs increasing from EQX to SX, and SX component size.

Advanced alloys for GT blades

Co – base EQX superalloys

- Solution and precipitation hardened by carbides; hot corrosion resistance
- Used in the lower range of temperatures or lower stress ranges: vanes

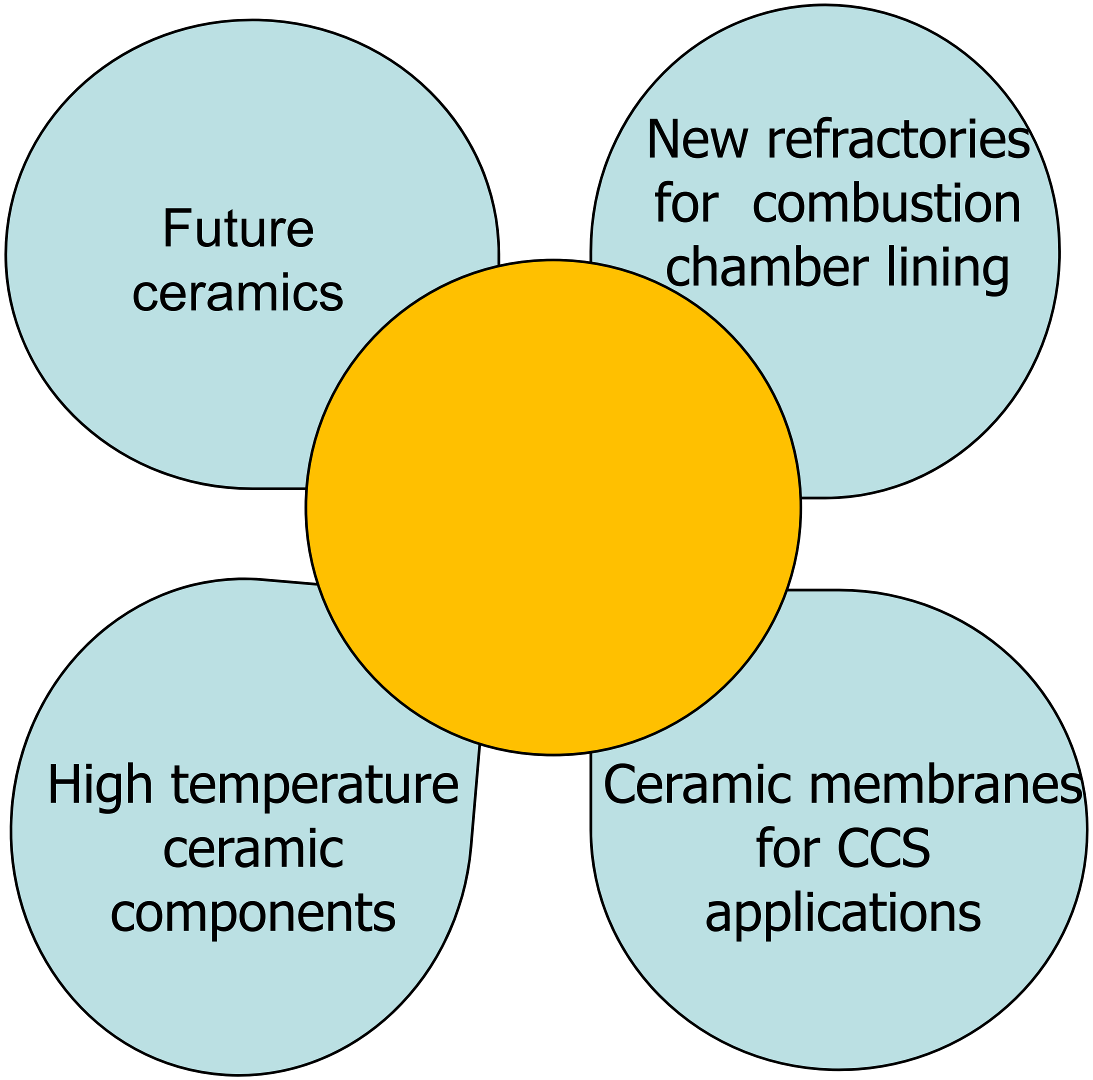
Main common problems:
- high temperature microstructure instability,
- high manufacture costs.

Intermetallics produced by thermomechanical or SX casting

- lower density, high mechanical and oxidation resitance, high temperature microstructue stability

Main problems:
- low ductility and toughness,
- high manufacture costs.

Non-metallic materials



Non-metallic materials

Ceramic material are recognised as "ideal" high temperature materials, since their overwhelming high temperature properties. The brittleness of these materials is their major drawback limiting the use to non structural applications.

New refractories for combustion chamber lining:

- high temperature ceramic bricks, outperforming the present products, able to withstand temperature up to 1700°C and aggressive environments due to coal quality;
- high temperature ceramic tiles for the annular combustion chamber in terrestrial turbo-gas power plants, able for service temperature up to 1600-1650°C.

Non-metallic materials

High temperature ceramic components

- Ceramic heat exchangers made of special ceramic designed for taking temperature up to 1300-1400^{o}C;
- Special wear resistant nozzles for pulverised coal burners.

Ceramic membranes for CCS applications

- Ceramic oxygen generators for implementing inexpensive and reliable methods of producing high purity oxygen;
- Molecular sieve for CO_2 sequestration.

Future Ceramics

- Fibre composites for structural applications (e.g. turbine components and blades).

Advanced High Temperature Structural Integrity design criteria and approaches

Premises

Materials technology and advanced criteria for both design and residual lifetime assessment of materials and components are fundamental tools for the realization of effective, affordable, more efficient and safe A-USC Power Generation Plants, including boilers, steam lines and steam turbine components and next generation nuclear power plants.

Advanced structural poly-crystalline materials and integrated material-component solutions for power generation applications are expected to operate at increasing service temperature and pressure, as well as cyclic loading conditions, coupled with demanding hot corrosion and oxidation environments. Moreover, new build designs have to meet future stringent environmental conditions whilst ensuring improvement during operation, long-term material safety and degradation behaviour, affordability and reliability of properties.

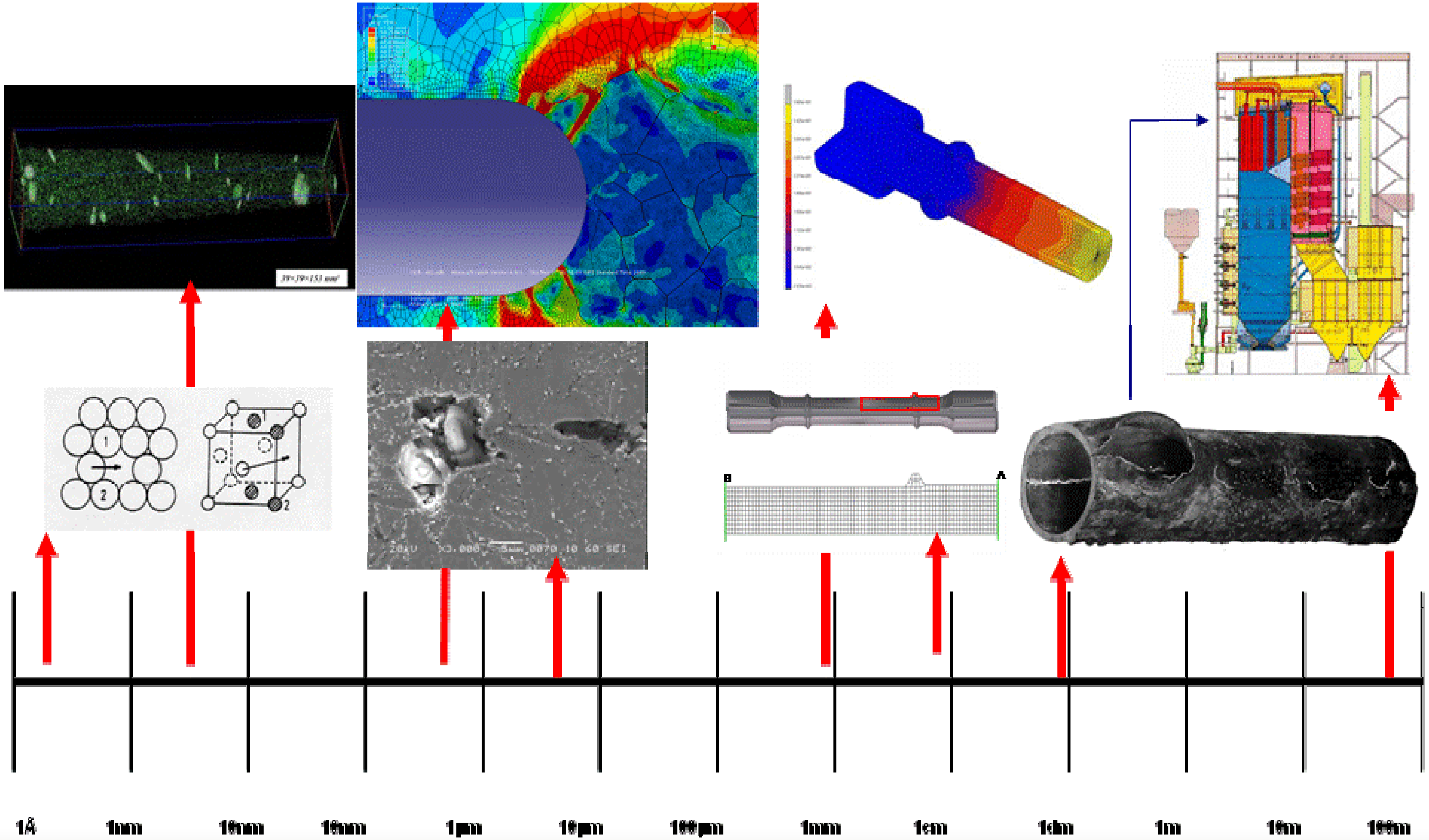
Premises

This scenario claims for an indispensable deep and comprehensive knowledge of failure mechanisms affecting and modifying materials response in real in-service conditions, in a strict deterministic rather than statistical/probabilistic approach. Independently, a link needs to be developed to identify relationships between **causes** (e.g. change in material behaviour and microstructure, loading history, environment) and **consequences** (e.g. crack formation, crack growth, creep/fatigue, wall thinning, leakage, failure, malfunction), and the way to assure the integrity of components.

A **methodological approach**, based on a **close description of metallurgical micro-mechanisms acting at different length scales**, coupled with **tailored small-to-large scale assessment of materials and components**, may represent the closest way to reach these goals.

The M*cube* approach

M*cube* = Multi-scale Multi-Material approach

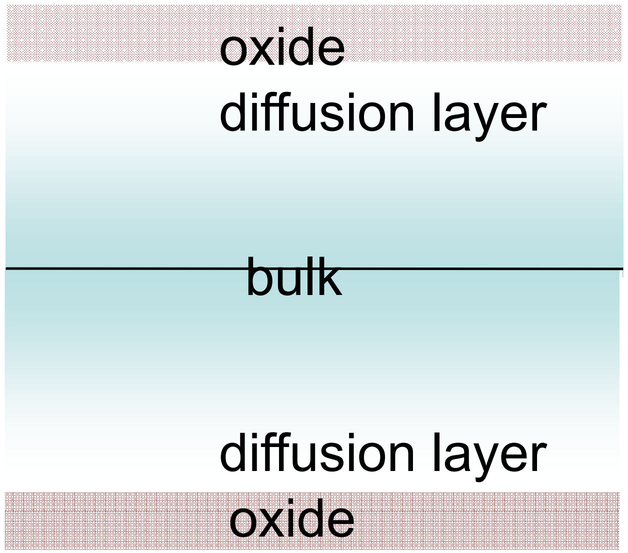


An example of complexity

Steel characteristics: steel grade (%Cr, %Ni, %Mn, …), grain size, surface finish

Steam condition: T, P, v, water chemical composition

steam oxidation conditions



- scale formation: thermodynamic and kinetic modelling → Oxide layer thickness, Oxide layer composition
- • diffusion modelling • thermodynamic modelling • precipitation modelling → phase distribution through the tube thickness: nucleation and growth modelling → mechanical properties modelling ↔ mechanical properties testing
- scale formation: thermodynamic and kinetic modelling → Oxide layer thickness, Oxide layer composition

Hot corrosion conditions

Hot flow gas conditions: T, v, chemical composition, ashes

(EU and) National supporting initiatives

OTP: "Energy Materials & Power Generation"

EM&PG

The iniziative, promoted and coordinated by Centro Sviluppo Materiali, has been started from 2008, with the following objectives:

- To create a permanent industrial network in the Energy Sector (material/component producers, engineering companies, final users, research);
- To improve the dissemination within the Network of the best national and international know-how in the Energy Materials and PG-related processes and technologies;
- Make easier the exchange of information and expertise with relevant European and extra-EU entities, while promoting join initiatives for R&D, technical exchange and scientific growth.

OTP: “Energy Materials & Power Generation”

EM&PG

- Today OTP_EM&PG Partners:

CSM, Flame Spray, LucchiniRS, Ansaldo Nucleare, ASO Siderurgica, ENEL, Cogne Acciai Speciali (CAS), E.ON Italia, Europea Microfusione Aeronautiche (EMA), Società delle Fucine (SDF), Technip KTI, ISPESL, Techint Engineering&Construction (E&C), University of Cassino, Tecnopolo Castel Romano

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Stefano Martelli (*Non-metallic materials*)
Luciana Intiso, Nicoletta Zacchetti (*Oxidation & Hot Corrosion*)
Tommaso Coppola, Paolo Lombardi (*Mechanical modelling and HT Structural Integrity*)