HKIAS Distinguished Lecture Series

Alloy Design of Structural Materials from Simple to Complex Alloy Systems

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Outline of my presentation

- Briefly mention the basic atomic and lattice structures of metallic materials
- Briefly mention the general mechanical Behavior of metallic structural materials

- Alloy design of Ir-base alloys for spacecraft system applications at ultra-high temperatures
- Alloy design of ordered intermetallic alloys for applications at elevated temperatures
- Alloy design of nanostructured steels with high strengths for structural applications at ambient temperatures
- Alloy design of high-entropy alloys (HEAs) containing multiple principle elements for structural applications at all temperatures

The importance of material development

Those who dominate materials dominate technology

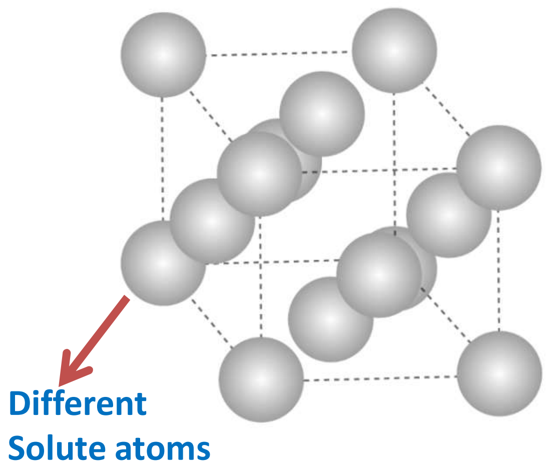
(科技之进展取决于材料之開发**)**

T. Sekimoto

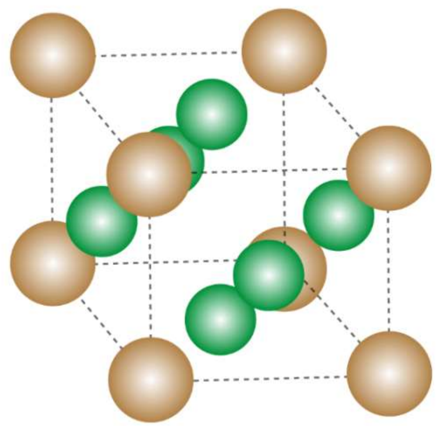
President of the NEC Corporation, Japan

Lattice structures for fcc metallic materials

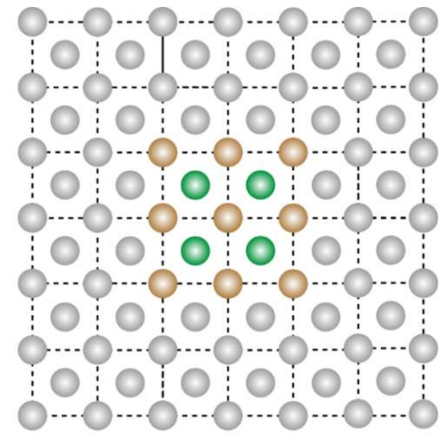
Two basic fcc lattice structures



Disordered fcc structure
(solid solution alloys)



Ordered fcc structure
(ordered $L1_2$ intermetallic alloys)



(fcc+$L1_2$) two-phase
alloy structure

Three types of metallic alloys

- **Ordered intermetallic alloys: Alloys with completely ordered lattice structures**
- **Solid solution alloys: Alloys with essentially disordered lattice structures**
- **Two-phase alloys: Alloys having a mixed ordered and disordered lattice structures**

General mechanical behaviors of different metallic alloys

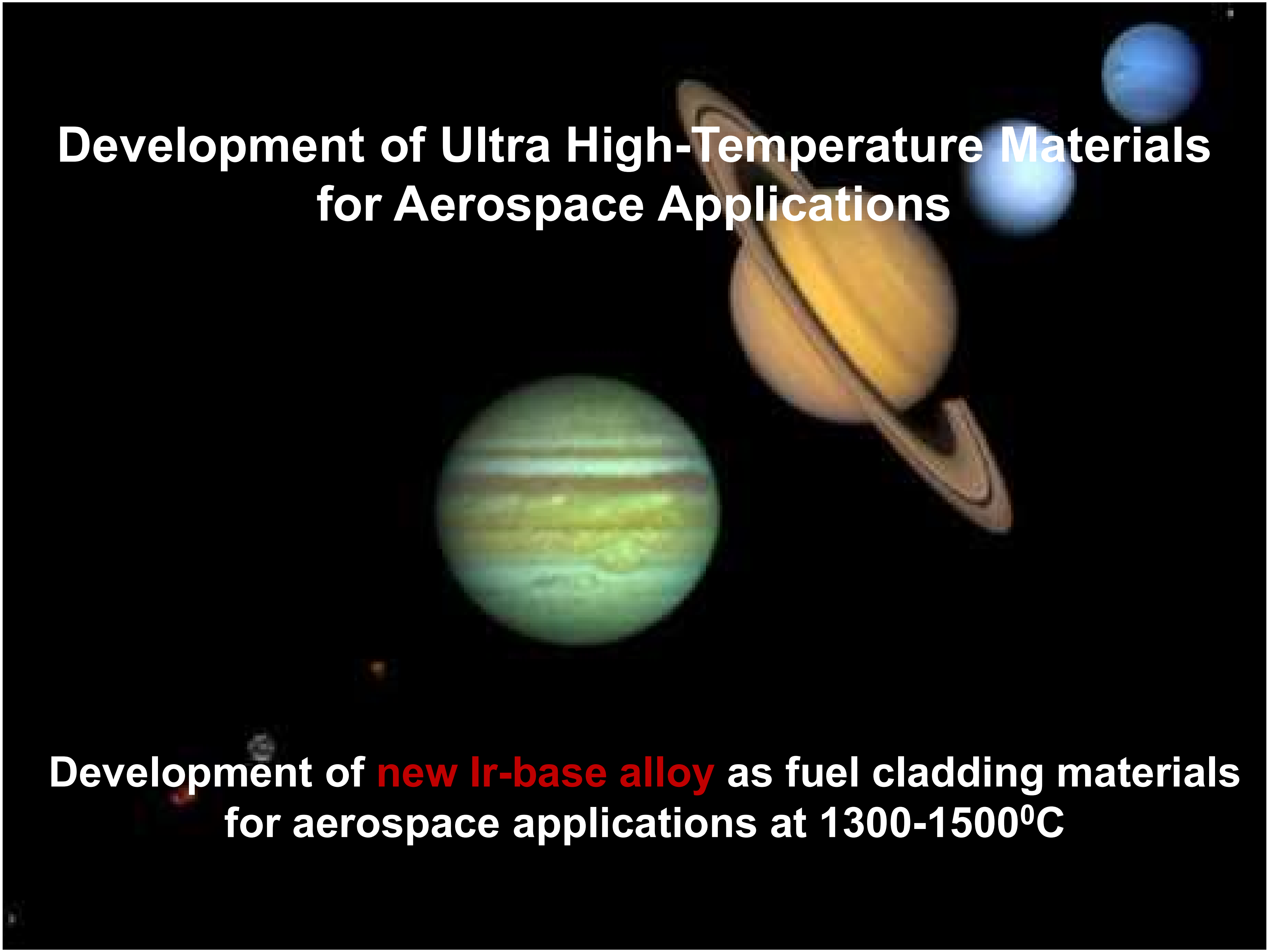
- **Solid solution alloys: These alloys are generally ductile, but lack of sufficient strength at elevated temperatures**
- **Ordered intermetallic alloys: These alloys are generally strong at elevated temperatures, but lack of sufficient ductility at ambient and low temperatures**

- **Two phase alloys: These alloys are generally have enhanced mechanical strengths, but with a relatively lower ductility (as compared with solid solution alloys)**

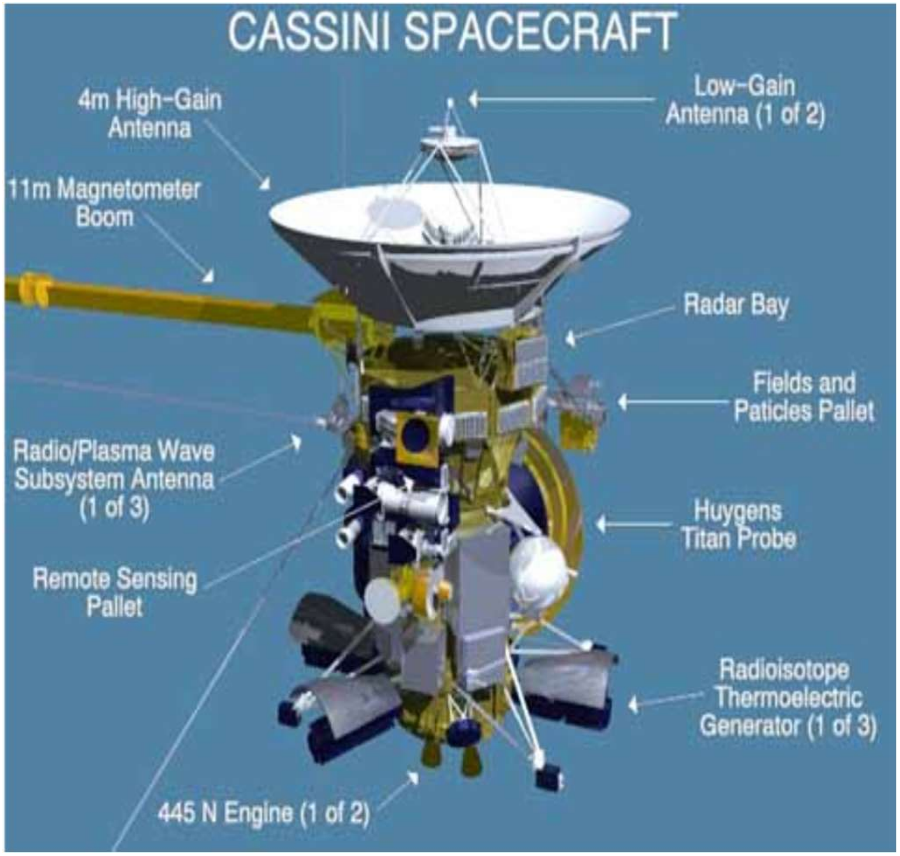
Alloy-design efforts are focusing on enhancing the mechanical properties of different structural alloys

- Many structural alloys show grain-boundary weakness; as a result, they generally lack a sufficient ductility due to brittle intrinsic or extrinsic intergranular fractures with limited ductility.
- Most structural alloys a lack sufficient strength at elevated temperatures for structural applications.

- Thus, alloy design efforts are necessary for enhancing both the strength and ductility of structural materials at different temperatures and work conditions

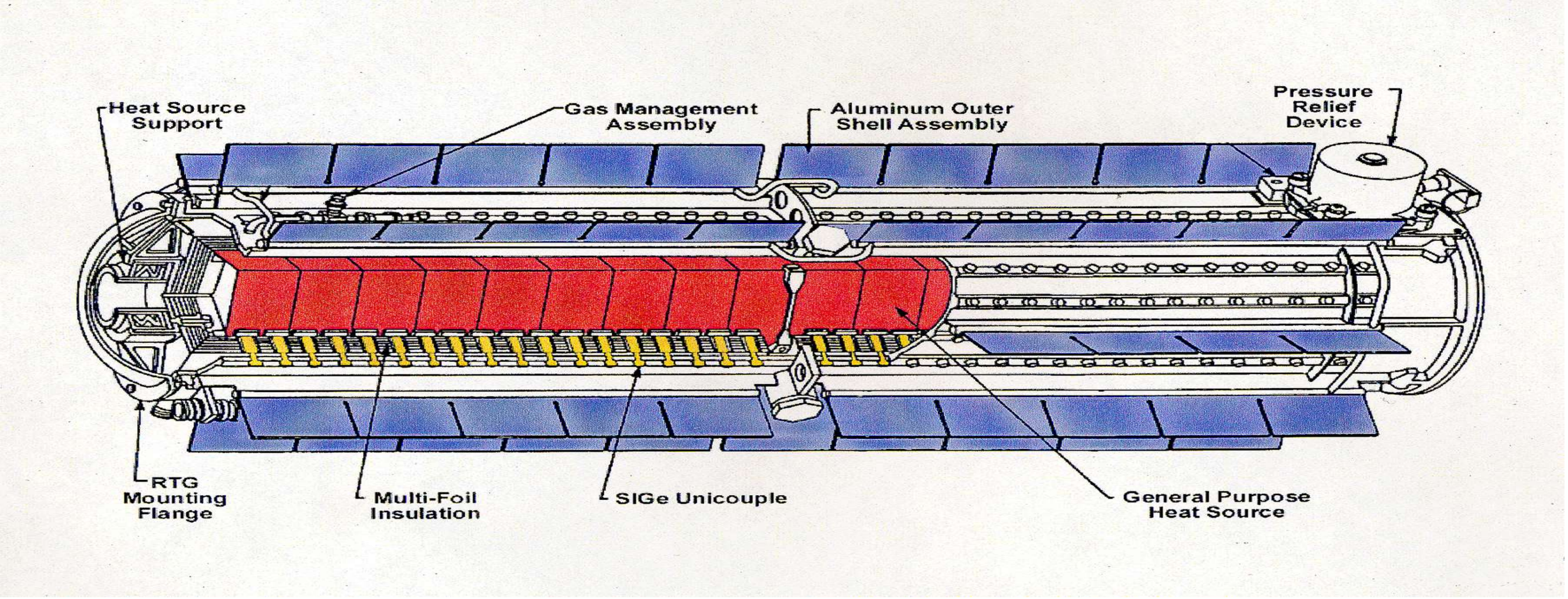

Development of Ultra High-Temperature Materials
for Aerospace Applications
Development of new Ir-base alloy as fuel cladding materials
for aerospace applications at 1300-1500⁰C

Electric generators for spacecraft required to operate at 1300-1500C for missions of 15-20 years



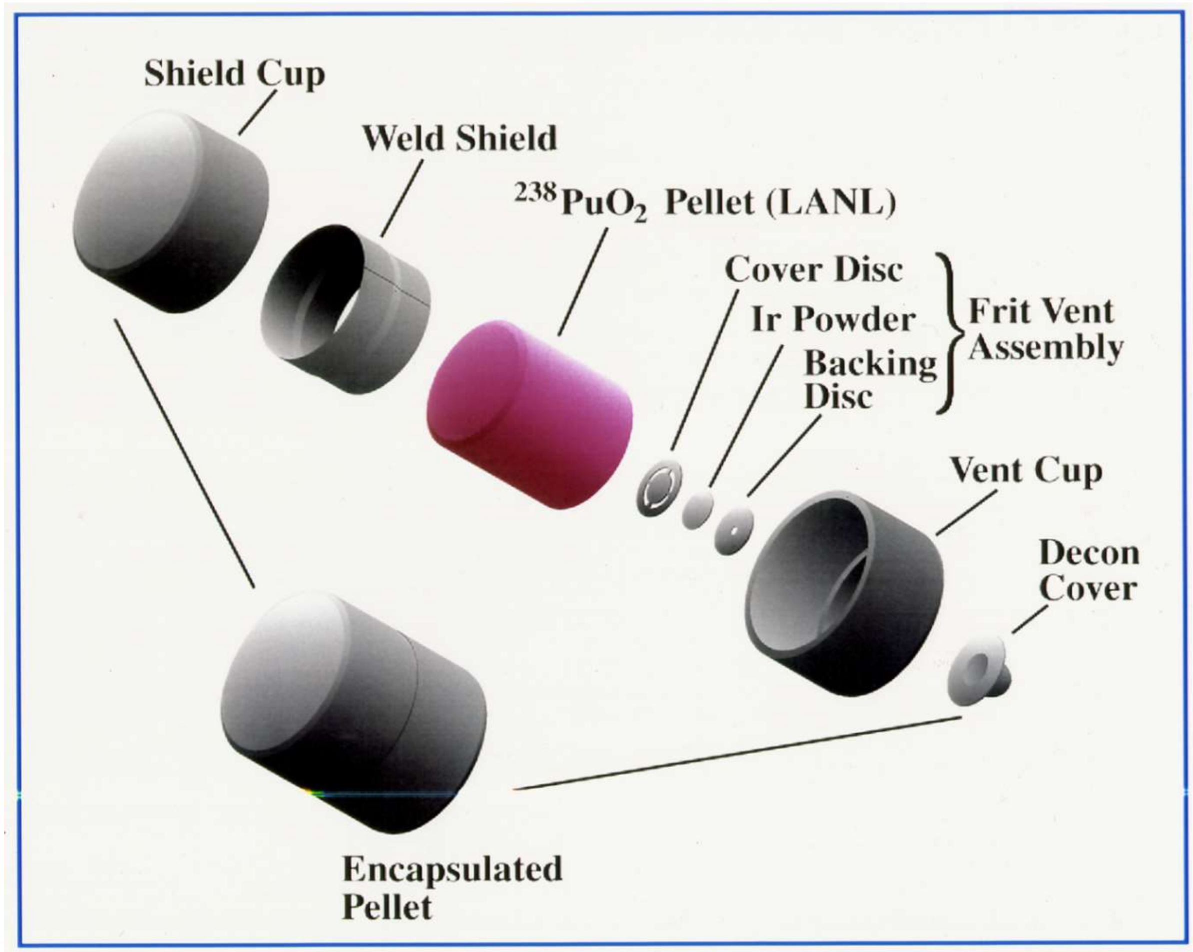
- The electricity for the Cassini Spacecraft is provided by three radioisotope thermoelectric generators (RTGs)

Inside the RTGs (Radioisotope Thermoelectric Generator), the heat source is provided by red fuel boxes which contain Pu oxides as the hot junction

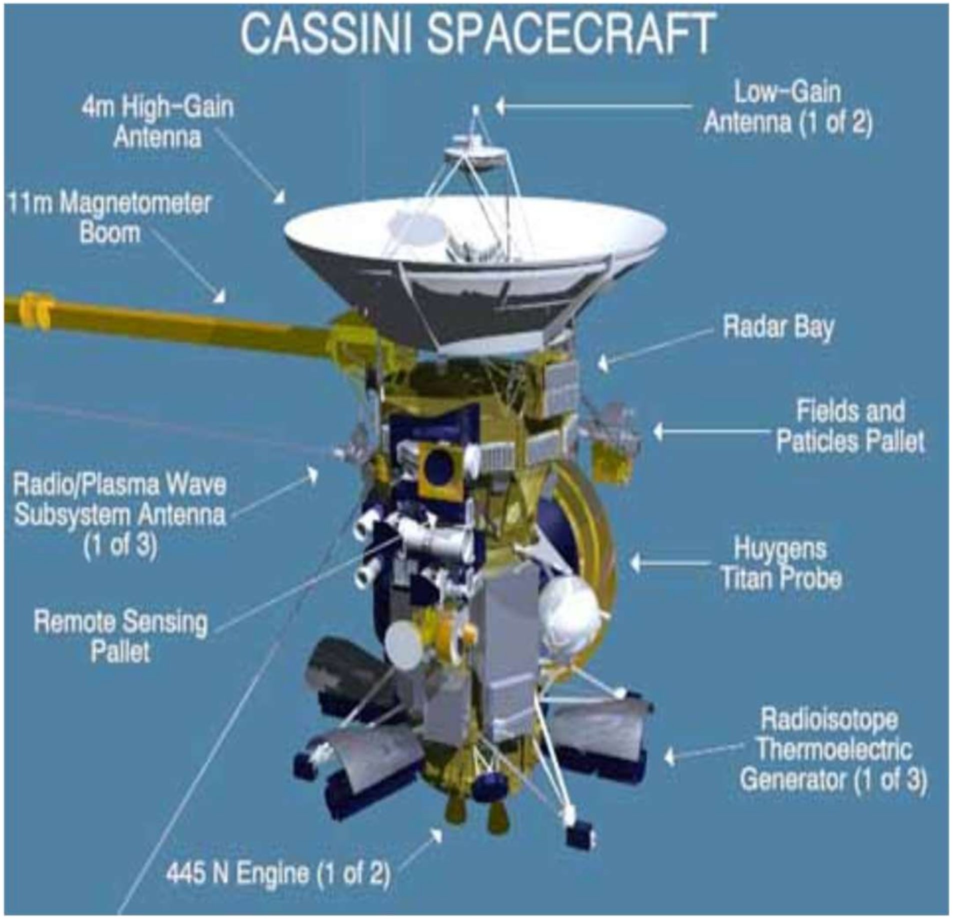


- The electricity is generated by both the hot and cold junctions
- It is important that these red boxes containing PuO_2 have to survive possible re-entry impacts at 85 m/s at temperatures 1300-1500°C.

The hot PuO_2 pellet inside the red box is encapsulated by a metallic material



The metallic capsule used for the fuel cladding in the RTG has to survive reentry impacts at 1300-1500C during any conditions



The metallic material used here has to encapsulate the radioactive fuel PuO_2 pellets at all conditions, including reentry impacts.

Then what material can be used here?

Iridium (Ir) metal was chosen as the base material for alloy development, because of

- High melting point (2450°C)
- Good corrosion and oxidation resistances at high temperatures
- Decent strength and ductility at elevated temperatures

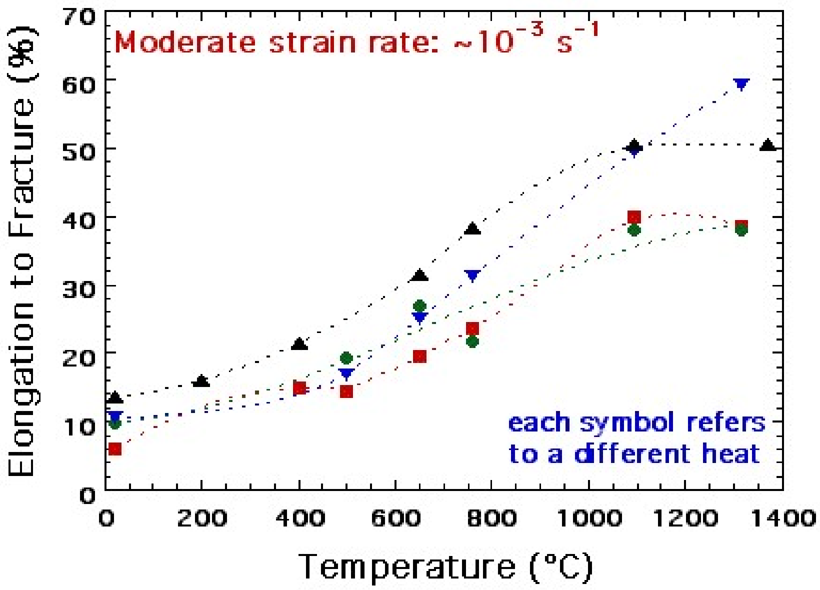
Problems for the use of pure Ir as cladding material

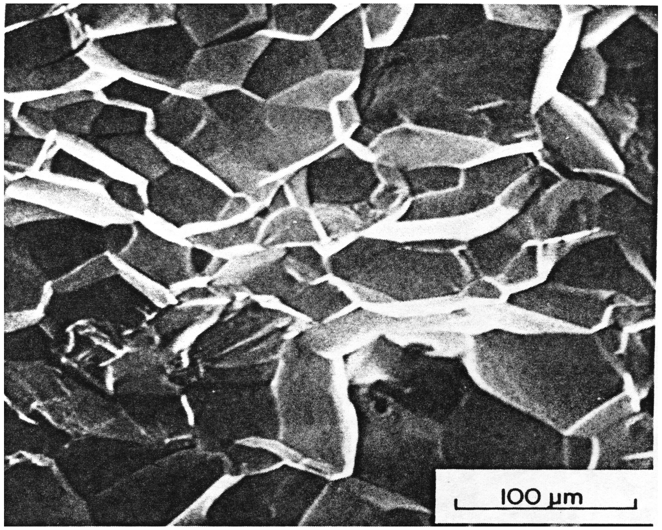
- Brittle grain-boundary fracture below 600C
- Strain-rate sensitivity: Ir shows brittle grain-boundary fracture when impact tests even at high temperatures (>900C)
- Ir metal shows only limit strength at high temperatures

Thus it was necessary to develop a **new Ir-base alloy** for the fuel cladding. This new material must be compatible with nuclear fuels and it has adequately impact properties at 85 m/s (300 ft/s) at 1300-1500C.

Development of new Ir base alloy

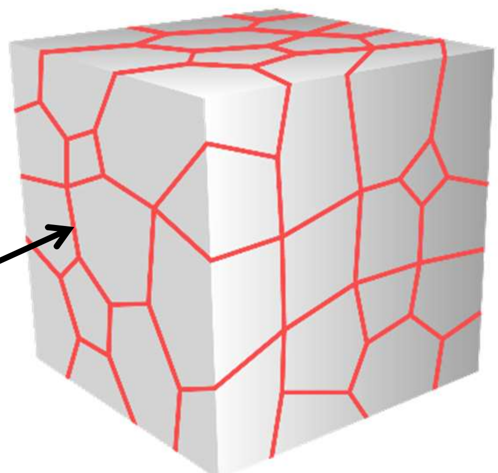
- Iridium metal is ductile when tested at temperature >800C at conventional strain rates.
- Furthermore, Ir metal shows brittle grain-boundary fracture with a low ductility when impact tests at high strain rates even at 1000^{0}C.
- Thus we had to find ways to strengthen Ir GBs and to eliminate brittle intergranular fracture during high-velocity impact tests at elevated temperatures.



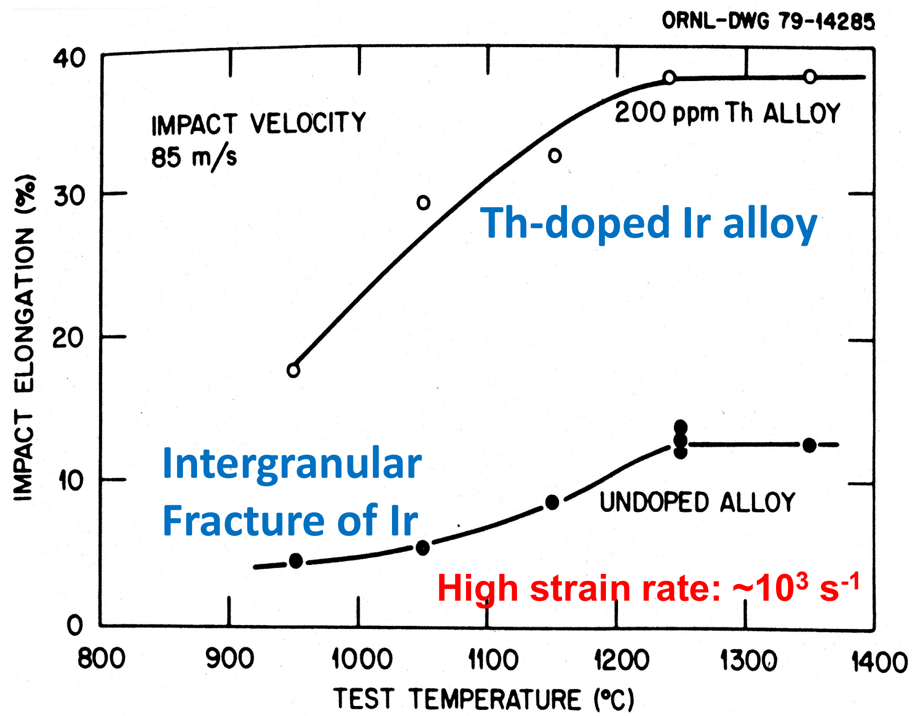


Our alloy-development effort led to discover that the Th element was able to segregate strongly to Ir grain boundaries and to strengthen Ir GBs effectively

Th at 0.1% segregates strongly at grain boundaries

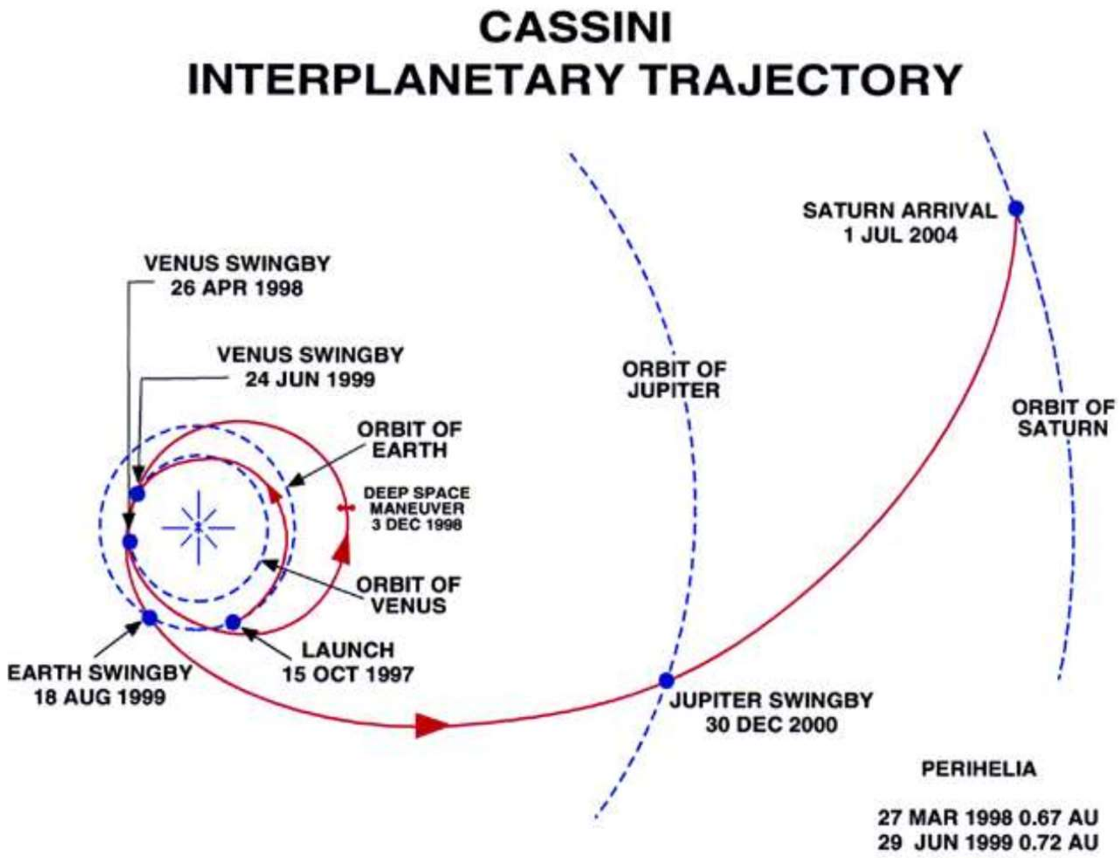


Grain structure of Ir metal



- Ir-0.3% W alloy doped with Th has the excellent impact resistance at elevated temperatures.
- Th-doped Ir alloy has successfully used as the container material for RTGs on board to a number of spacecraft systems.

The Cassini Spacecraft containing our Th-doped **Ir alloy** capsules was launched in 1997 and had arrived at Saturn (土星) after 7 years (2004)



For development of the new Ir alloy for the US space missions, I was rewarded with the E.O. Lawrence Award (a US Presidential Award).

- The photo shows that I received the award from the secretary of the Department of Energy, USA

Receive a NASA Group Award in 1999

Photo with US Astronauts

Design of ductile ordered Ni and Fe aluminides (Intermetallics) for structural applications

- Both ordered nickel aluminides (Ni_3Al, NiAl) and iron aluminides (Fe_3Al, FeAl) have excellent oxidation/corrosion resistances and good strength at elevated temperatures.

- However, these aluminides generally show brittle grain-boundary fracture with low ductility at ambient and low temperatures.

- My alloy-development effort was mainly focused on the understanding of the brittle fracture mechanism and the development of ductile ordered aluminides for structural applications.

General properties of ordered aluminides

Advantages

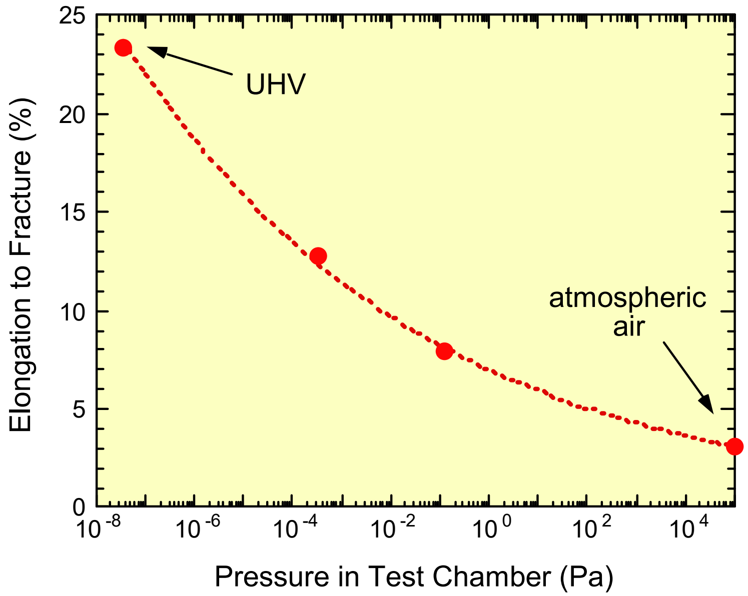
- Good strength at elevated temperatures
- Excellent oxidation and corrosion resistance at ambient and elevated temperatures
- Light weight

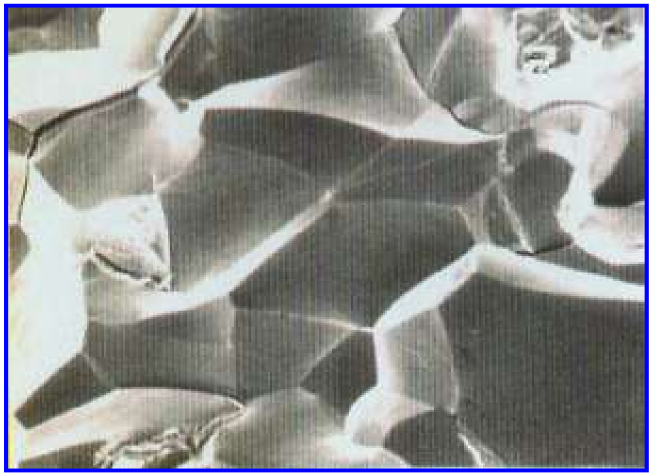
Alloy development efforts focusing on two areas:

- To improve the ductility of aluminides at all temperatures
- To further develop new structural materials based on nickel and iron aluminides

The ductility concern of nickel aluminide based on Ni_3Al

- Ni_3Al shows brittle grain-boundary fracture and low tensile ductility when tested in air at room temperature
- **Our study reveals that the brittle grain-boundary fraction is not intrinsic, and it is due to moisture-induced embrittlement (environmental embrittlement)**





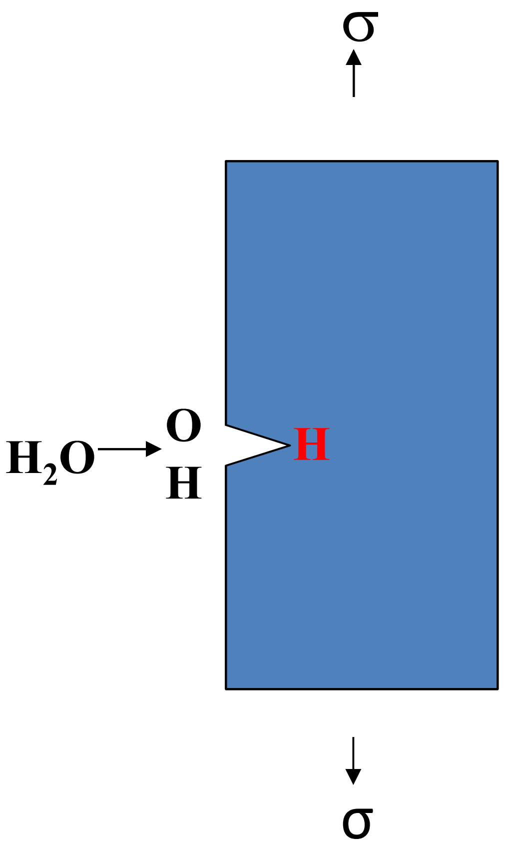
•Ni_3Al ductility at RT is extremely sensitive to moisture in air

Ni_3Al shows brittle grain boundary fracture with a low ductility at RT in air (containing moisture)

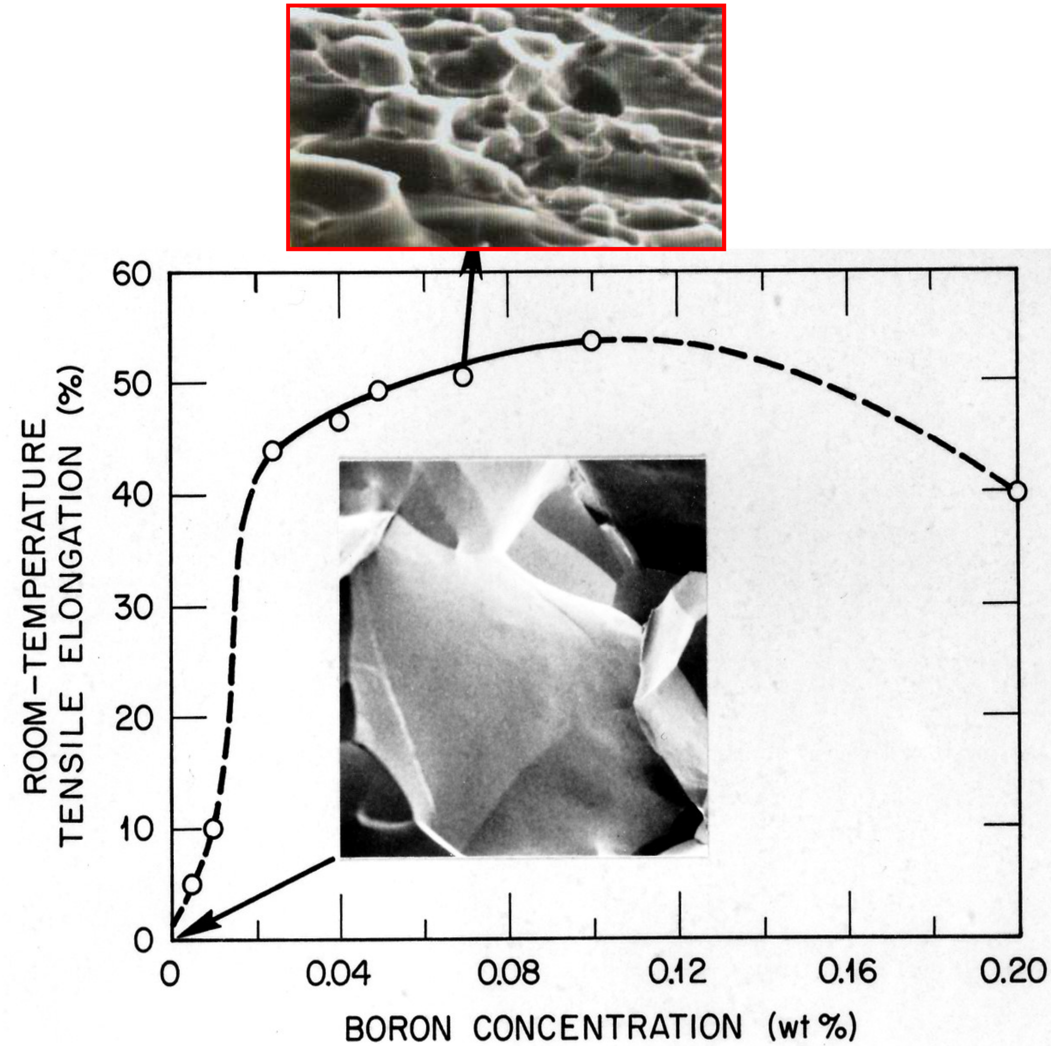
Ni_3Al can be embrittled by moisture-induced hydrogen in air at room temperature

- $Ni_3Al + H_2O \text{ (air)} \Rightarrow \text{Al-(OH)} + \text{Ni-H}$
  $\Rightarrow \text{Al-O} + \text{Ni-H}$

- **Embrittlement is caused by H atoms which penetrate into alloys through grain boundaries, resulting in hydrogen-induced grain-boundary embrittlement**



We discover that small B additions strongly segregate to grain boundaries and dramatically improve the tensile ductility of Ni_3Al at room temperature



- **B-doped Ni_3Al (24%Al) is even more ductile than common steels**

Benefical effects of B on Ni_3Al alloys

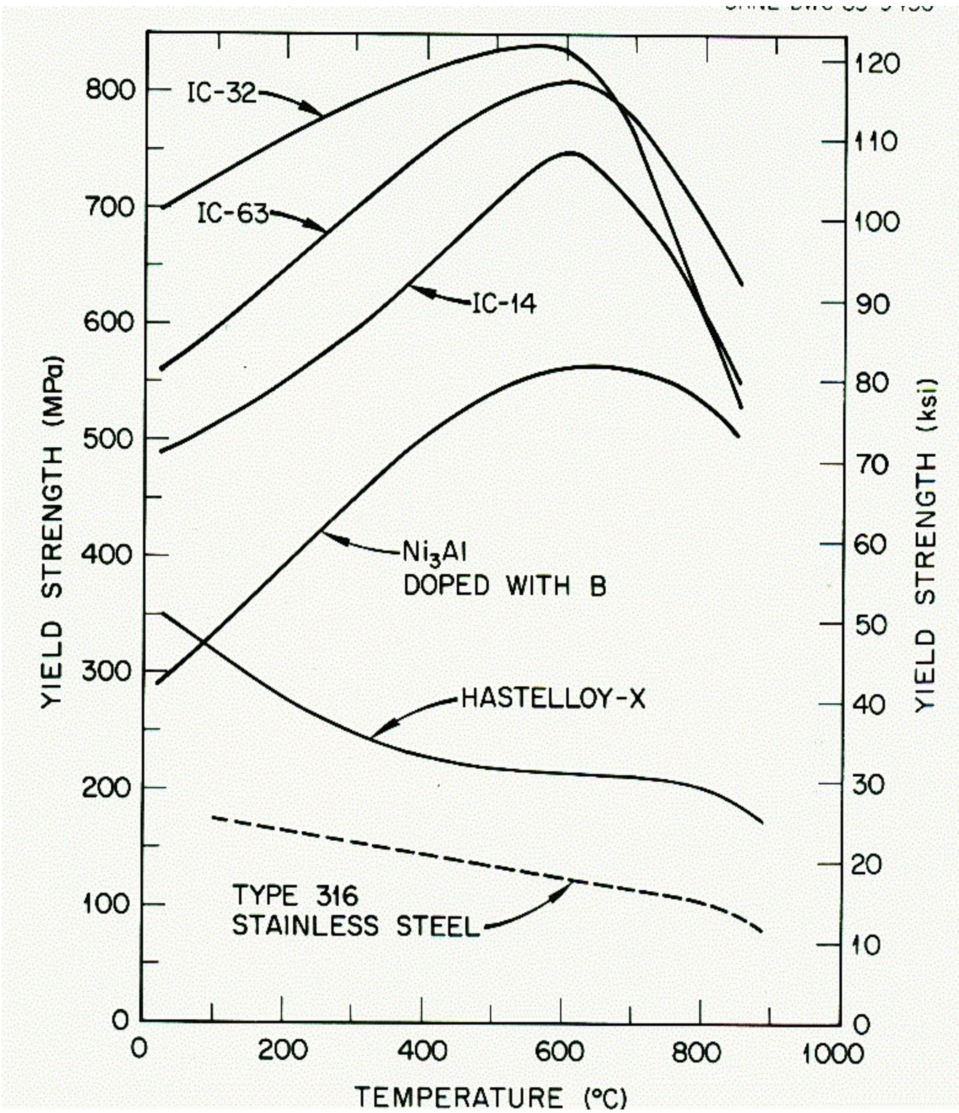
- Auger-electron-spectrum(俄歇电子能谱) analyses indicate that B has a strong tendency to segregate to grain boundaries in Ni_3Al (24%Al).
- B segregation enhances the cohesive strength of grain boundaries and also slows down the H-atom penetration along grain boundaries.

- Effect of the Al concentration in Ni_3Al on B segregation: Our studies reveal that B segregation depends strongly on the Al concentration. B segregates much less to grain boundaries in Ni_3Al with >24%Al, resulting in a much less beneficial effect on the ductility of aluminides.
- Thus, for the ductility improvement by B, it is very important to control the Al level in Ni_3Al.

Development of ductile and strong Ni_3Al aluminides for structural uses

Alloying effort on Ni_3Al

B: For RT ductility
Cr: For elevated-temperature ductility and oxidation resistance
Mo, Zr: For strengthening

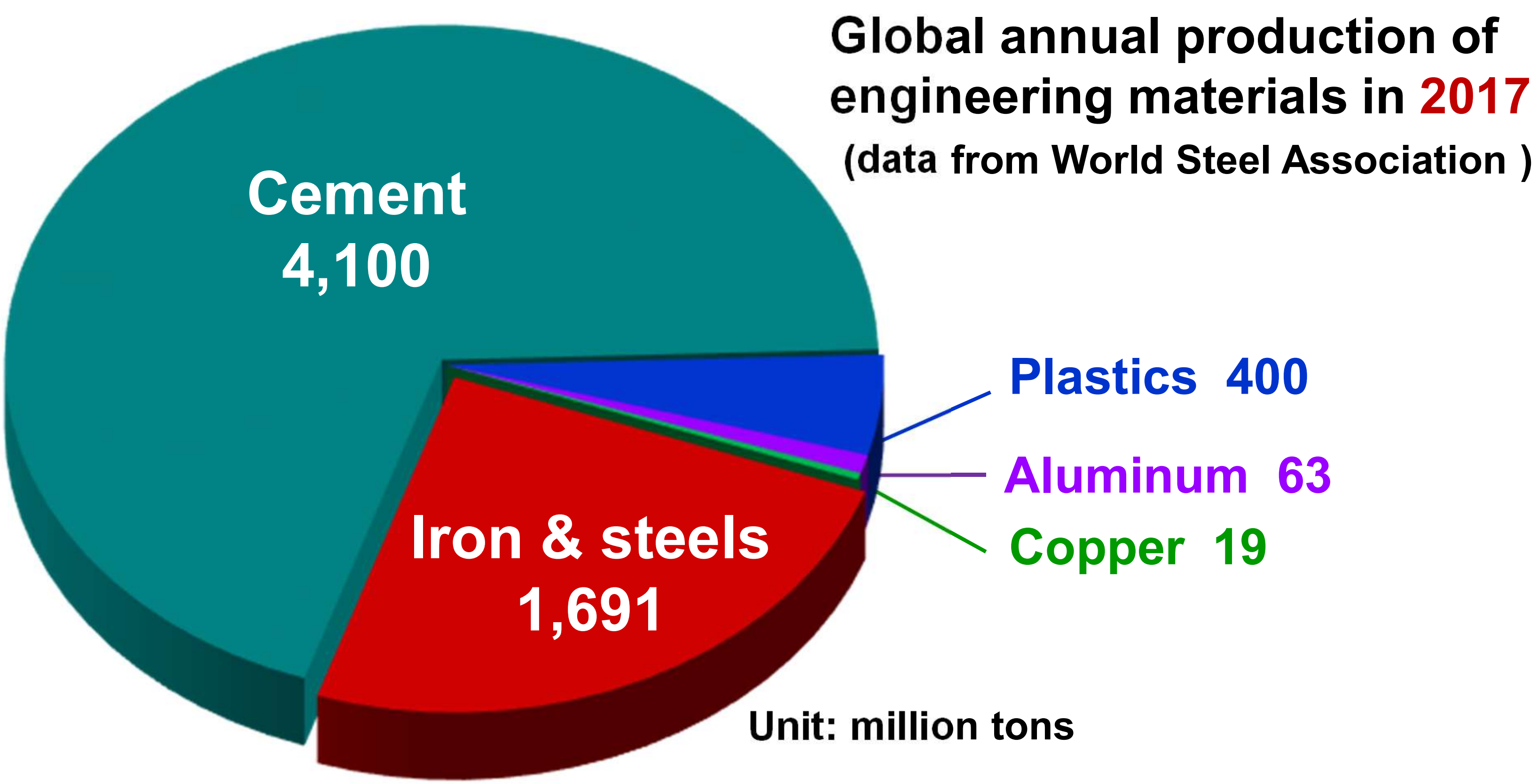


B-doped Ni_3Al alloys have been used as high-temperature transfer rolls for steel fabrication at elevated temperatures

- The performance of Ni_3Al rolls is tremendously better than that of commonly used **HU rolls** (Ni-42.45Fe-18Cr-0.55C, wt%)

Development of ultra-high strength steels hardening with nanoscale precipitates for structural applications

Iron and steels are the most widely used metallic materials in the world



- The massive production of steels causes some serious concerns in China

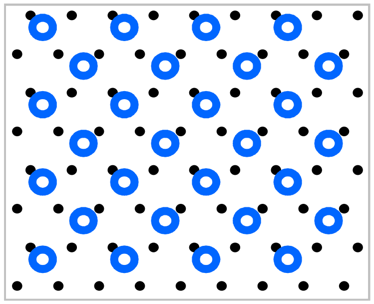
Steel production causes the energy consumption and air pollution in China

- In 2018, the energy used for steel production in China is equal to the burning of 452 million tons of coals
- In China, the steel production is accountable for more than 10% of the total energy consumption (4,360 million tones of coals)
- The large production of steels results in serious air pollution and smog concerns in China
- An effective way to reduce the steel production and energy consumption is to develop ultra-high strength steels for structural uses

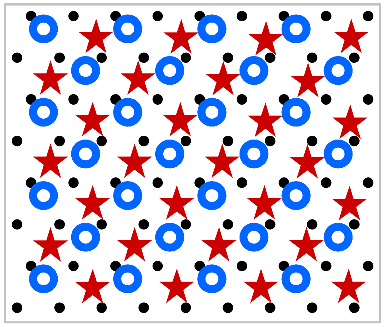
Common steels Hardened by

- Solid-solution hardening
- Grain-size refinement
- Strain-induced hardening
- Carbide hardening

Our efforts on development of high-strength steels by precipitation of nanoscale particles



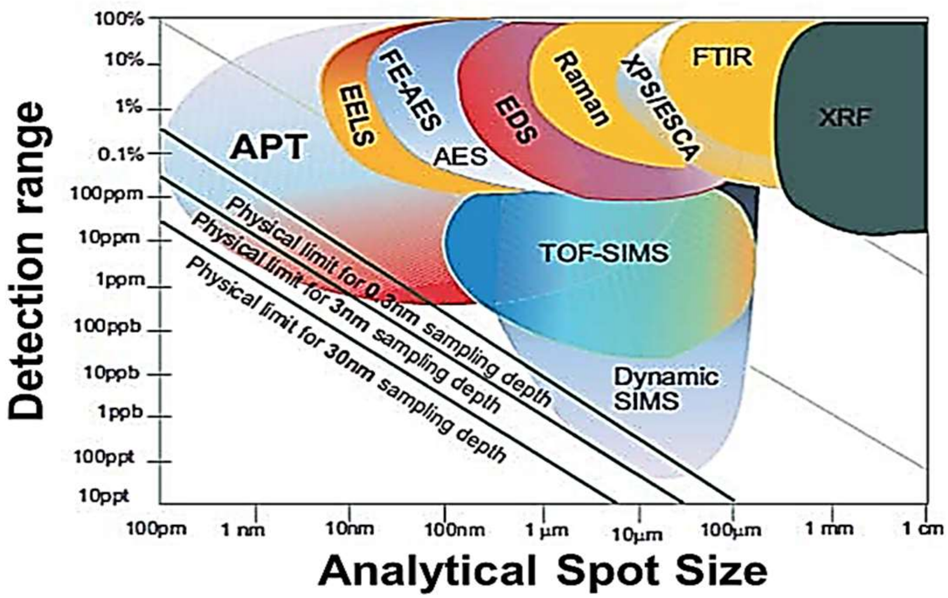
Hardening by precipitation of nanoscale Cu particles



Additional hardening by precipitation of nanoscale intermetallic NiAl particles

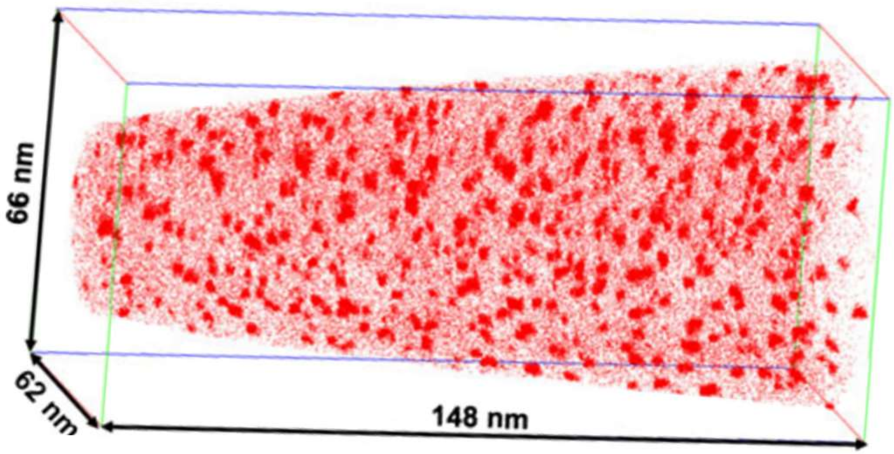
3D Atom Probe Tomography (APT) at CityU is an idea tool to characterize nanoscale particles

LEAP-5000 used for both 3D imaging & chemical analyses of nanoscale particles



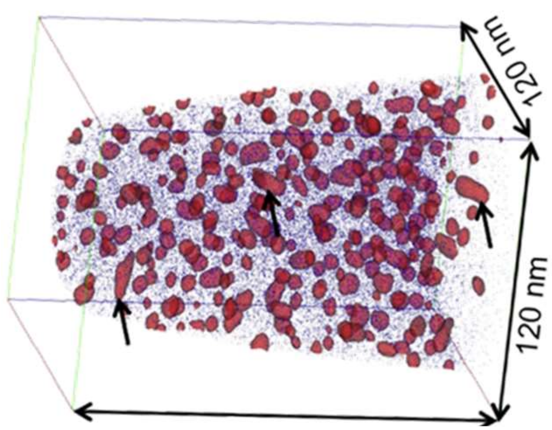
- ❑ High analytical sensitivity (1 nm spot size)

APT analyses of **nanoscale particles** containing Cu, Ni, Al and Mn elements in oue high-strength steels developed at CityU



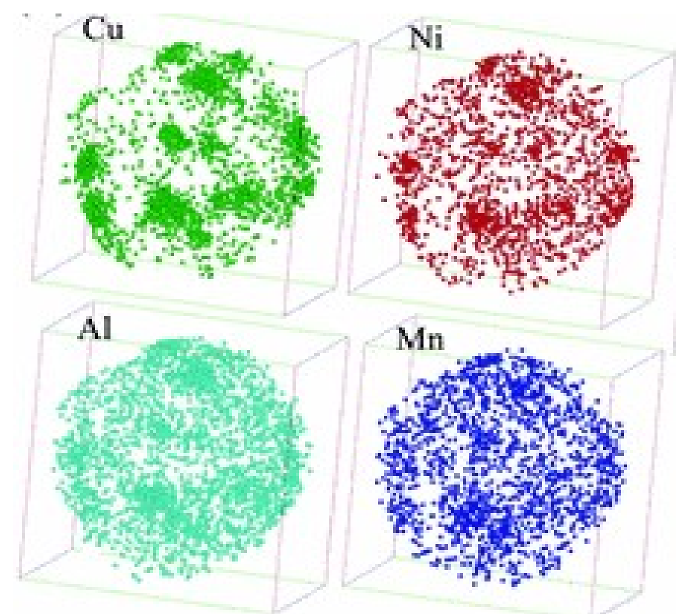
Zhang, Liu, et al. PRB, 2011

Cu-rich nanoparticles *ME Fine, MMT, 2010*

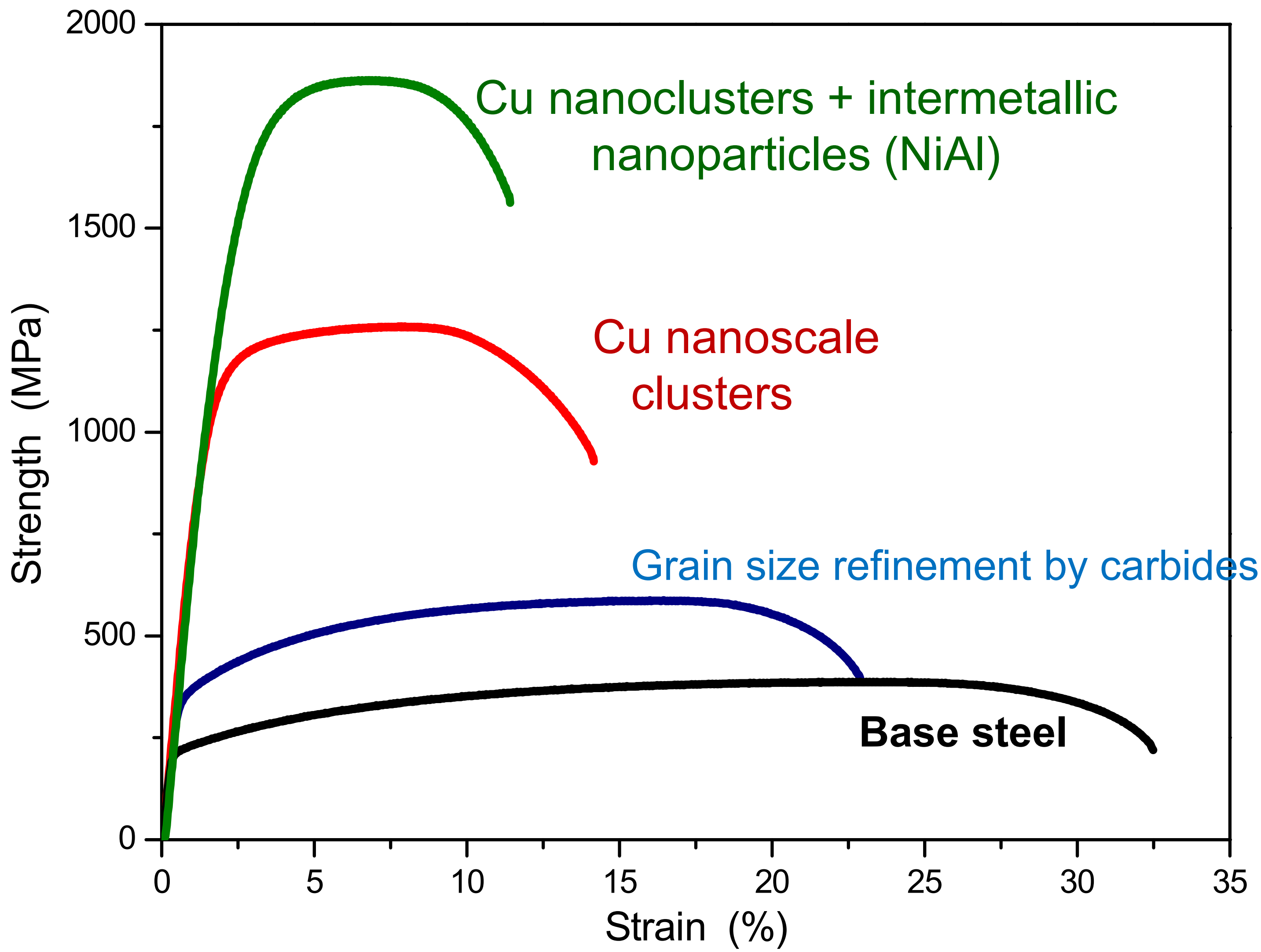


Kapoor, Chung, et al, Acta Mater, 2014

Our study of multi-component particles in steels



Tensile properties of steels hardening by nanoscale particles at room temperature



Superior properties of the high-strength steels we have developed at CityU

- YS : 1100-1500 MPa
- UTS: 1200- 1800 Mpa
- Elongation (延伸率): 13-16%; RA (断面收缩率) : >40%

- Impact energy : 100-250 J at-20C
- Better corrosion resistance than that of common steels
- Easy cold & high fabrications, and easy to production
- Ready to produce by mass productions and low costs
- East to make cast parts with good mechanical properties
- Good weldability (有优良的焊接性能)
- Several large steel companies in China are interested in mass production of these high-strength steels

Many potential uses of our high-strength nanostructured steels

Shipping container

40 feet in length;
4 tons in weight

Oil rig chain

2.5 km in length;
350 tons in weight

Ship

Welding constitutes 30% of the total building cost.

High-speed train

120 million tons of steels in 12th Five-year plan (110 million tons in the 13th plan)

Construction

0.1 million tons of steels in the Taipei 101 Tower

Bridge

0.8 million tons of steels in Hangzhou Bay Bridge

Wind energy

350 tons of steels in a wind turbine

Nuclear RPV

RPV constitutes 14% of a nuclear power plant in cost

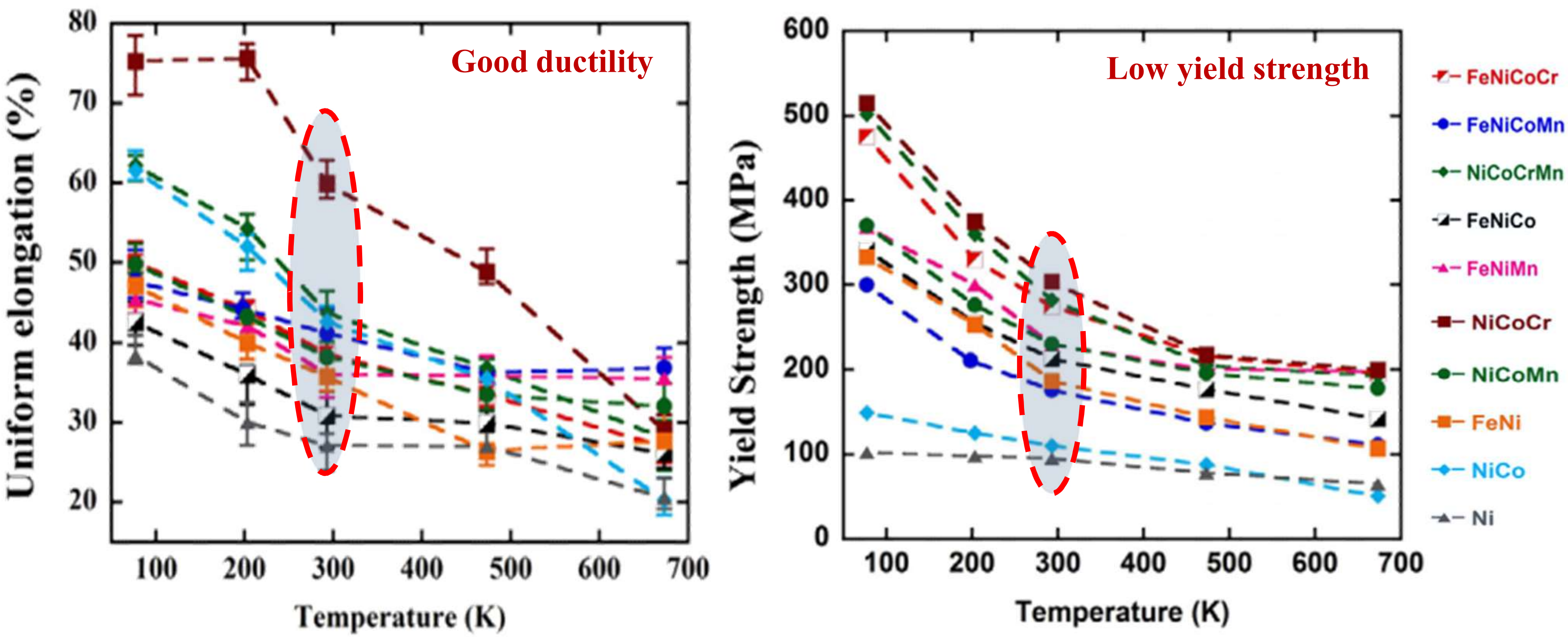
Recent development of High Entropy Alloys (HEAs) containing multiple-Principle alloying elements

- **Conventional alloys generally contain a single-principle element**
- **HEAs are designed based on multiple-principle alloying elements (new alloy-design concept)**

Currently we are working on fcc-base high-entropy alloys (HEAs) hardening by precipitations

- Principle alloying elements in the fcc base HEAs:
  Ni, Co, Fe, Cr, Mn, Cu…….
- Elements used for precipitation-hardening in HEAs
  Al, Ti, Nb, Mo, Ta, Zr, Hf,….

Single-phased FCC HEAs generally show good ductility, but limited strengths at ambient and elevated temperatures



- FCC HEAs generally have a good ductility but limited strength at ambient and elevated temperatures
- FCC HEAs can not be hardened effectively by solid solution atoms

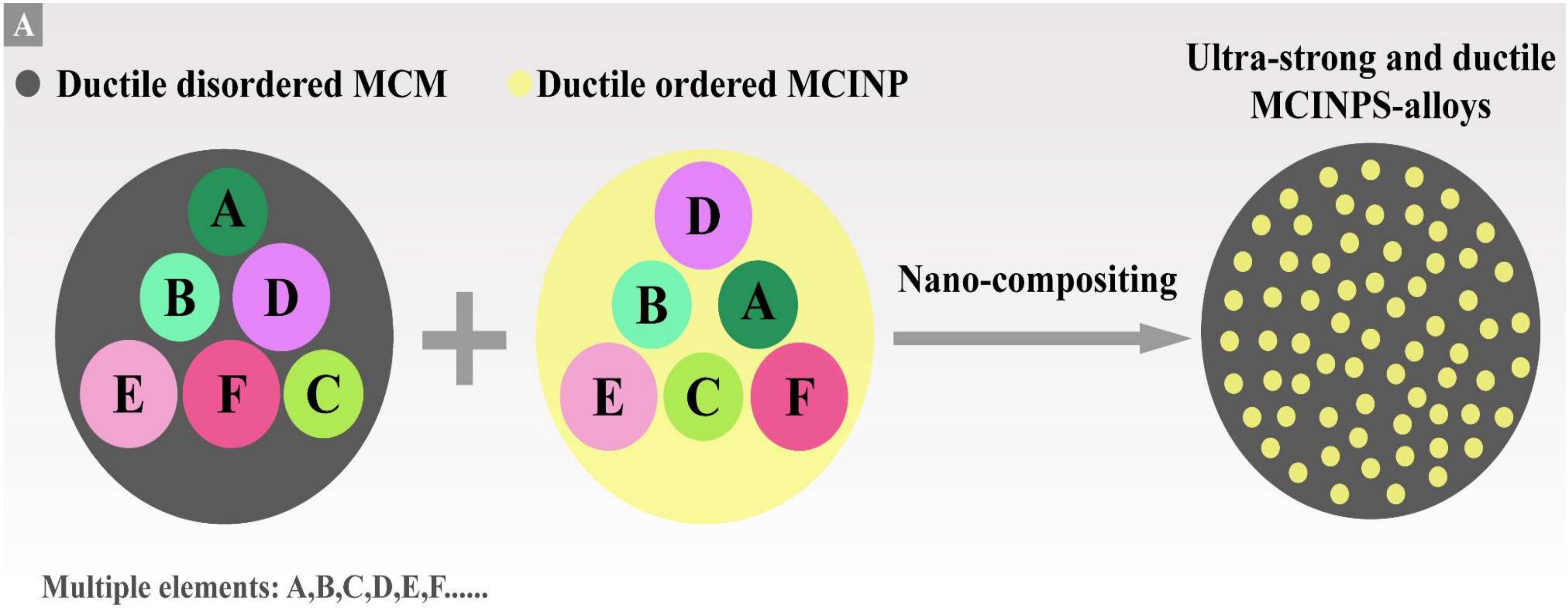
Z. Wu, E. George, et al. Acta Materialia. 2014.

Our current alloy design effort has focused on the hardening of HEAs by precipitations

- Currently we are working on the hardening of HEAs with the precipitation of $L1_2$ ordered intermetallic particles in nanoscales.

- Our development goal is to achieve an effective hardening without any significant loss of the ductility of these HEAs at ambient and elevated temperatures

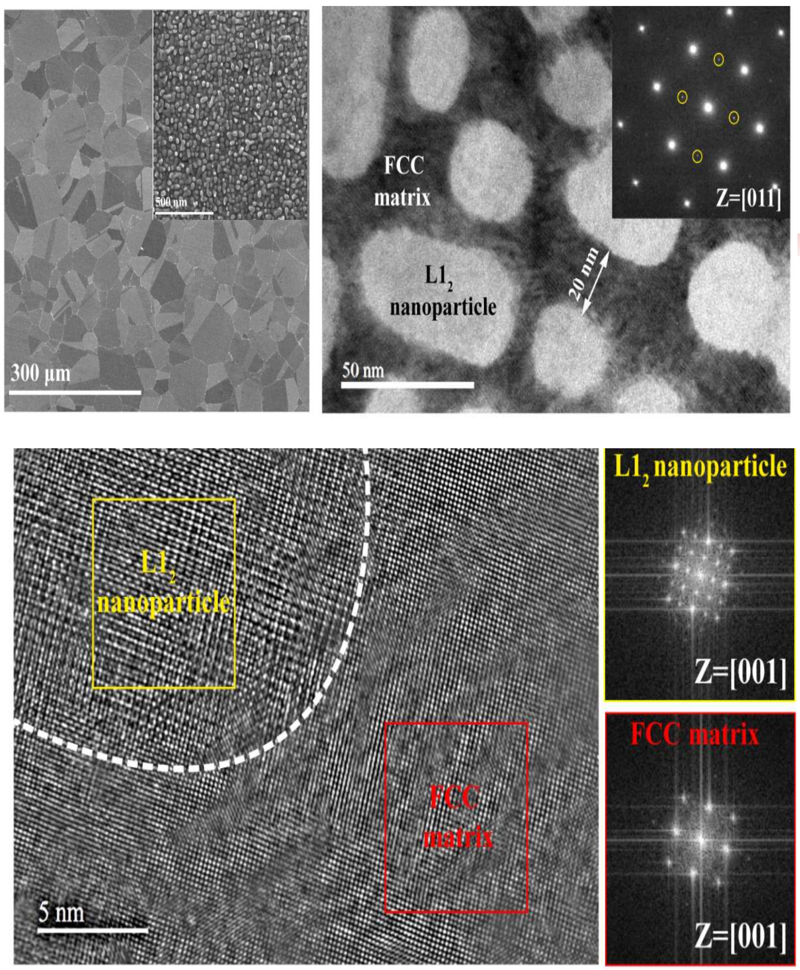
In our HEAs, the matrix contains multi-component elements, and the matrix is hardened by precipitation of multi-component ordered intermetallic particles



- In order to get nanoscale particles, physical metallurgy has been used to control the precipitation of high-density and nanoscale $L1_2$ ordered particles in HEAs.

Dense precipitation of nanoscale $L1_2$ precipitates formed in the $NiCoFeAl_7Ti_7$ HEA we designed

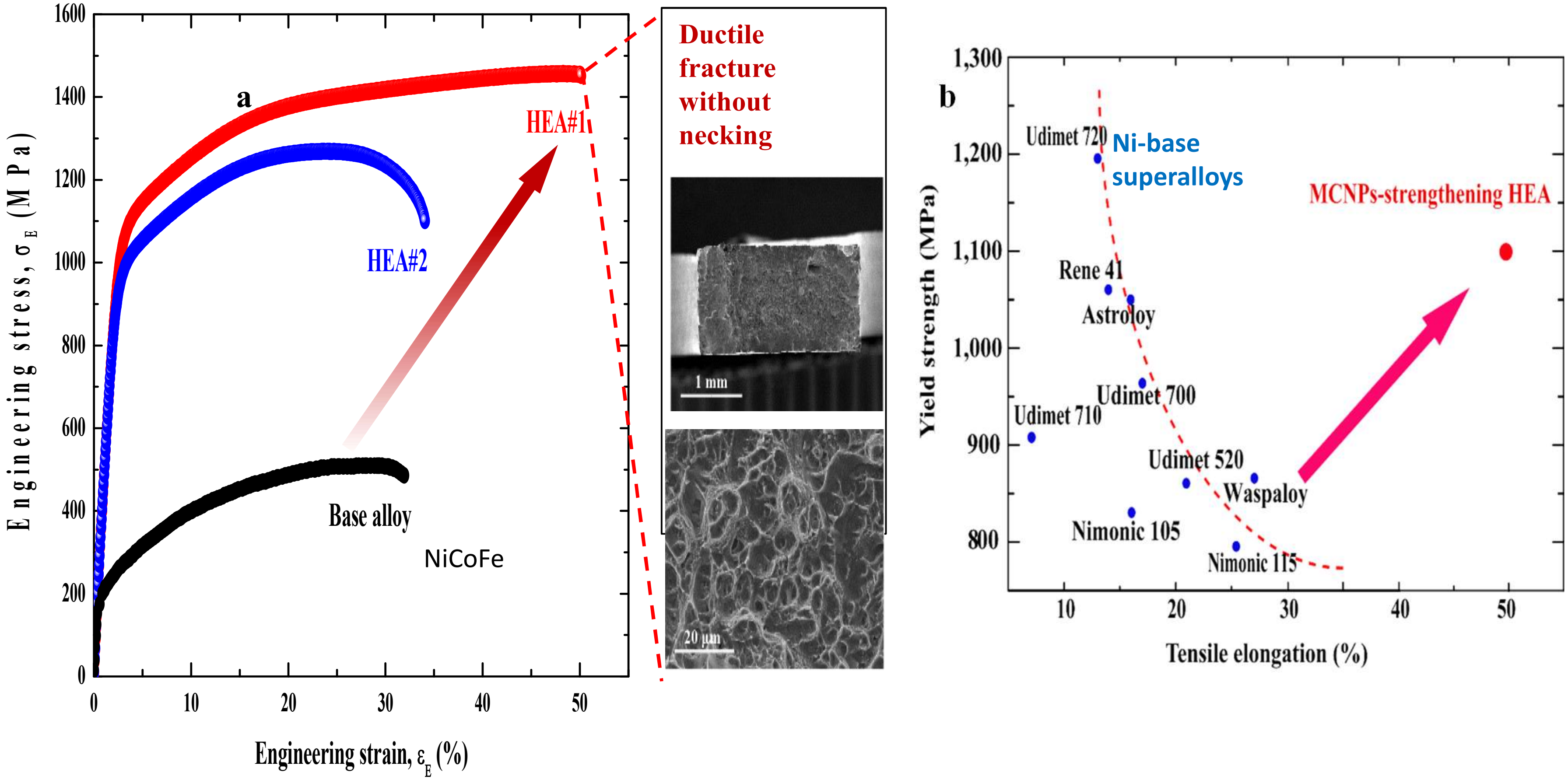
1150 ℃-solid solution/780℃-aging



1. Nano-meter size (~30-50 nm)
2. High volume fraction (~60%)
3. Very uniform distribution
4. Coherent with the matrix

- These particles have the complex ordered alloy composition of $(NiCoFe)_3(AlTiFe)$
- They are much more ductile and harder than simple Ni_3Al particles

Mechanical properties of the **NiCoFeAl$_7$Ti$_7$** HEA with ordered L1$_2$ intermetallic particles



- The particle-strengthened HEA has a superb combination of both the strength and ductility, which significantly outperforms the strength of superalloys at ambient temperature

At present time, we are working on HEAs with the complex matrix compositions of (Co, Ni, Fe, Cr) being hardened by precipitate of nanoscale particle (Al, Ti, Mo, Zr, W).

Conclusions: Four advanced alloys for structural applications have been successfully developed

- Alloy design of Ir-base alloys for aerospace applications at temperature to 1500C.
- Understanding and design of ductile ordered Ni and Fe aluminides for structural applications at elevated temperatures.
- Design of ductile ultra-high strength steels by nanoscale precipitates for structural applications.
- Recent development of particle-strengthening high-entropy alloys for structural applications at all temperatures.

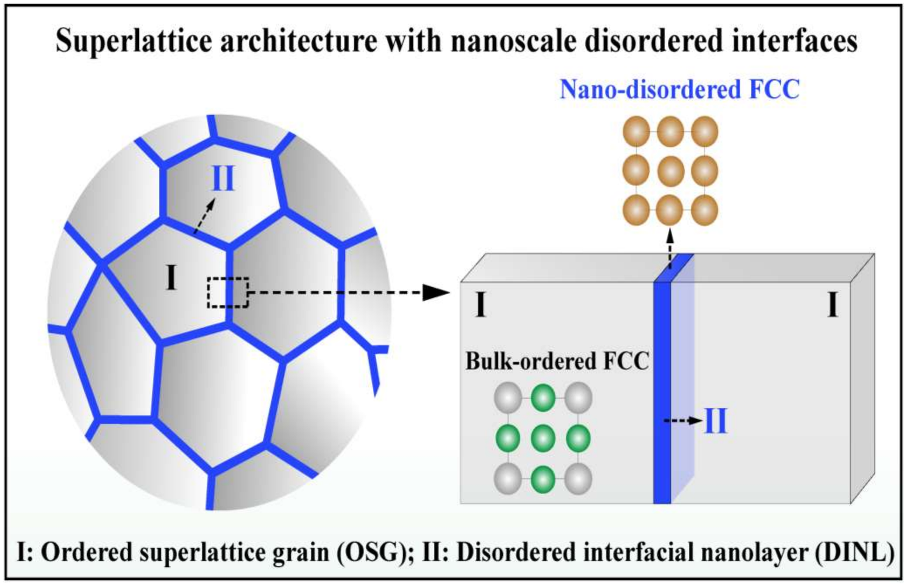

Thanks for your attention!

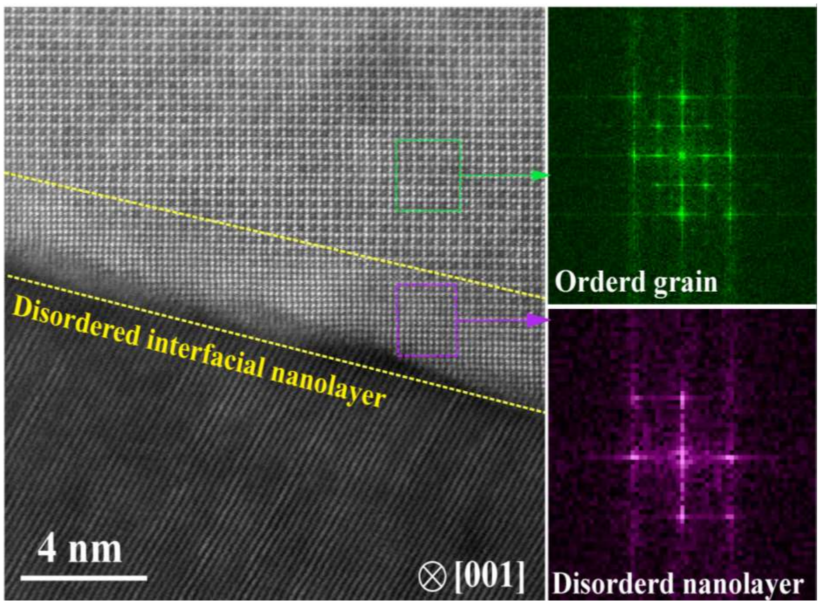

Acknowledgement

Thanks to Drs. Tao Yang, HJ Kong, WH Liu, ZB Jiao, BX Cao, and JH Luan for their helps in alloy design and development at CityU.

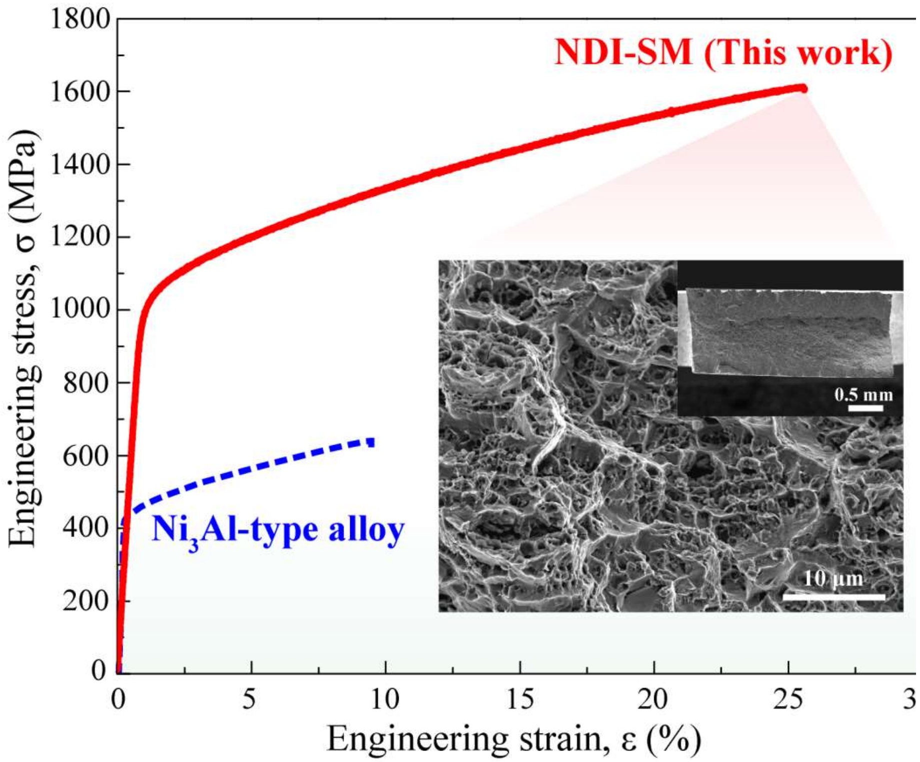
Our recent study discvers a new structural feature in the multi-component ordered intermetallic HEA ($Ni_{43.9}Co_{22.4}Fe_{8.8}Al_{10.7}Ti_{11.7}B_{2.5}$)

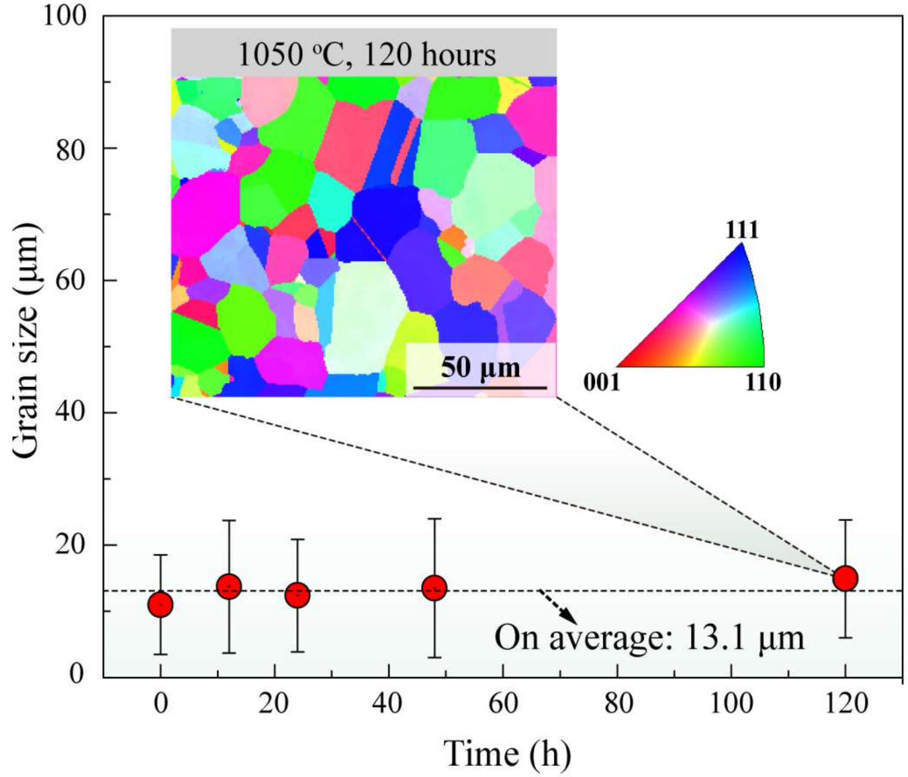
- This ordered intermetallic alloy is based on Ni_3Al, but with the complex composition of $(Ni,Co,Fe)_3(Al,Ti,Fe)$
- In this HEA, its grain boundaries are coated with a nanoscale disordered layer of 4 nm, as shown below





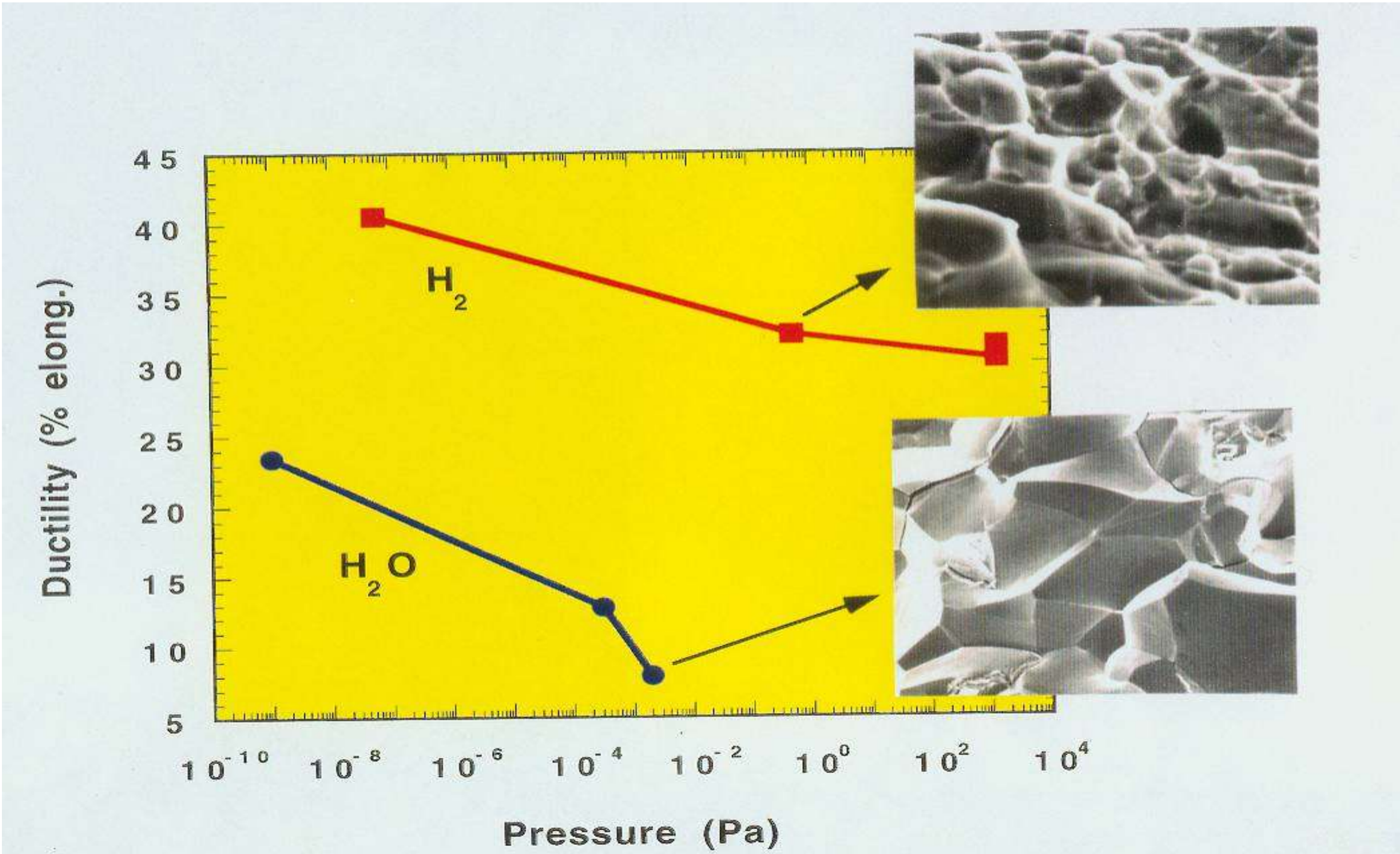
This nanoscale grain-boundary layer has a dramatic effect on enhancing (1) the strength at ambient temperature and (2) The thermal stability of this multicomponent HEA at 1050^0C





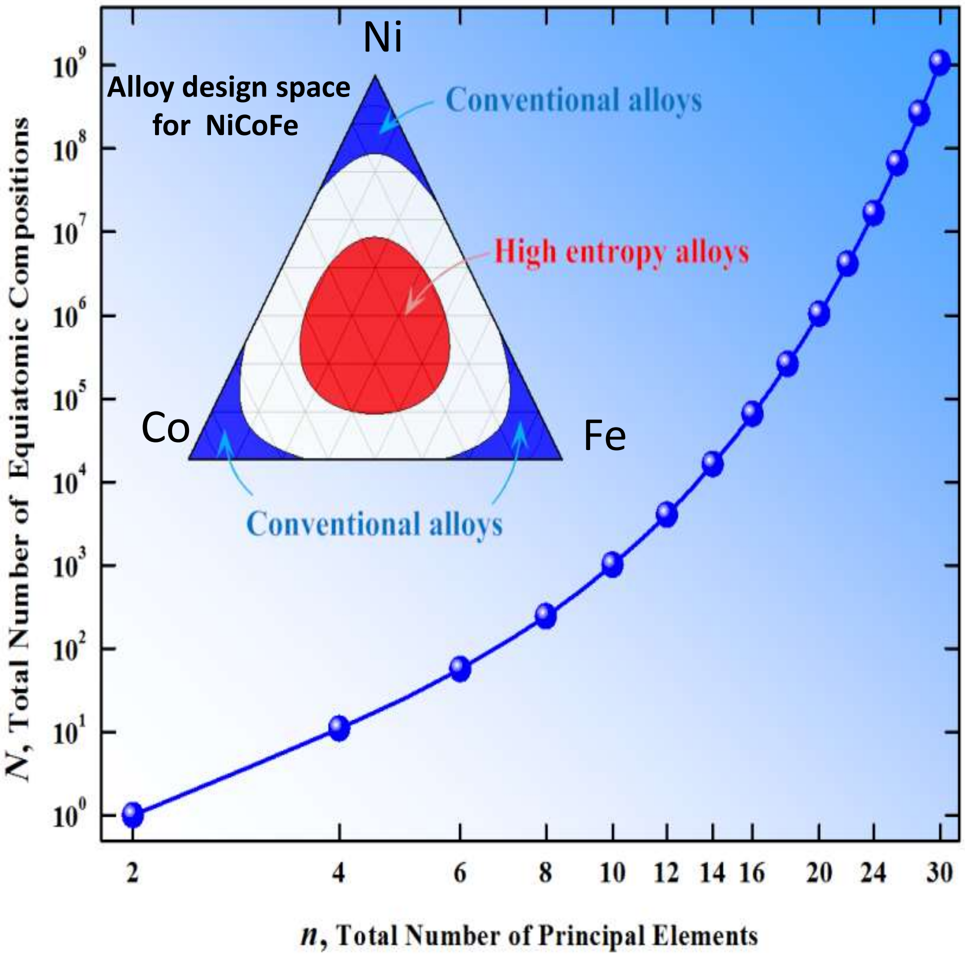
- **All these data indicate that this unique HEA has superior properties at both ambient and high temperatures**

Tensile ductility is extremely sensitive to moisture level



- As compared with H_2O, H_2 gas causes much less embrittlement at RT

High Entropy Alloys (HEAs) open a new alloy design strategy



Y. F. Ye, Y. Yang, Mater. Today, (2015).

- **HEAs pen up a huge new alloy design space for tailoring microstructures and properties.**