Materials and Component Development for Advanced Turbine Systems - ODS Alloy Development

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23rd Annual Conference on Fossil Energy Materials

Pittsburgh, May 12-14, 2009

Project supported by NETL under RDS Contract DE-AC26-04NT41817.606.01.01

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Research Objective

The objective of this research task is to explore nickel-based ODS alloy and ODS coating development with the ODS powder mixtures prepared by the Hosokawa mechano chemical bonding (MCB) technology. The aims are:

(i) to produce ODS alloy with much reduced manufacturing cost,

(ii) to evaluate the applicability of ODS coating on superalloy substrate using suitable coating techniques such as Cold Spray or APS.

Four Research Activities:

1. Powder Mixtures Using Hosokawa MCB Technology

Through research collaboration with Hosokawa Micron Powder Systems at Summit, NJ, establish suitable processing conditions to achieve a homogenized ODS powder mixture comparable to that achieved with mechanical alloying.

2. ODS Coating Development

(Kazuhiro Ogawa, Tohoku University: Cold Spray)
(Kevin Klotz, Coatings for Industry: APS)

3. Processing Optimization and Heat Treatment

(Nick Wu, WVU and Gaylord Smith, Special Metals Inc.)

4. Mechanical Property Evaluation

(B. Kang) High temperature mechanical property and creep strength measurement of ODS alloys and coatings using WVU micro-indentation method

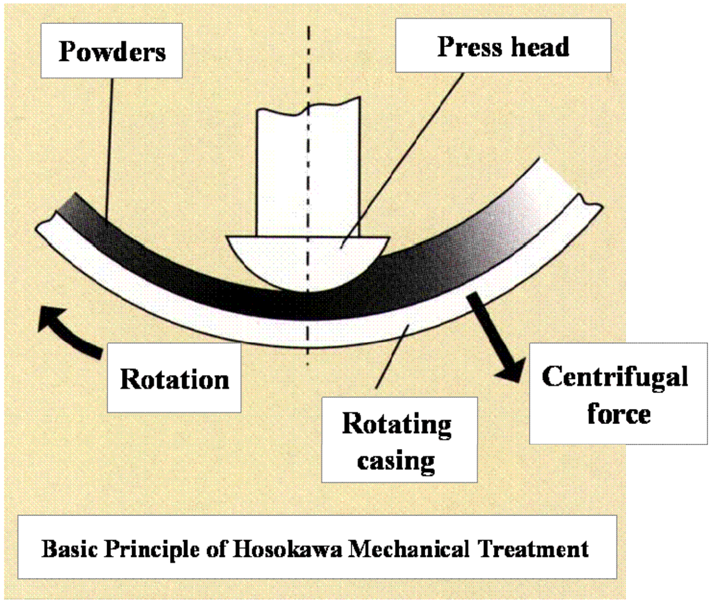
Presentation Outline:

Part I: ODS Poser Mixing Using Hosokawa MCB Technology

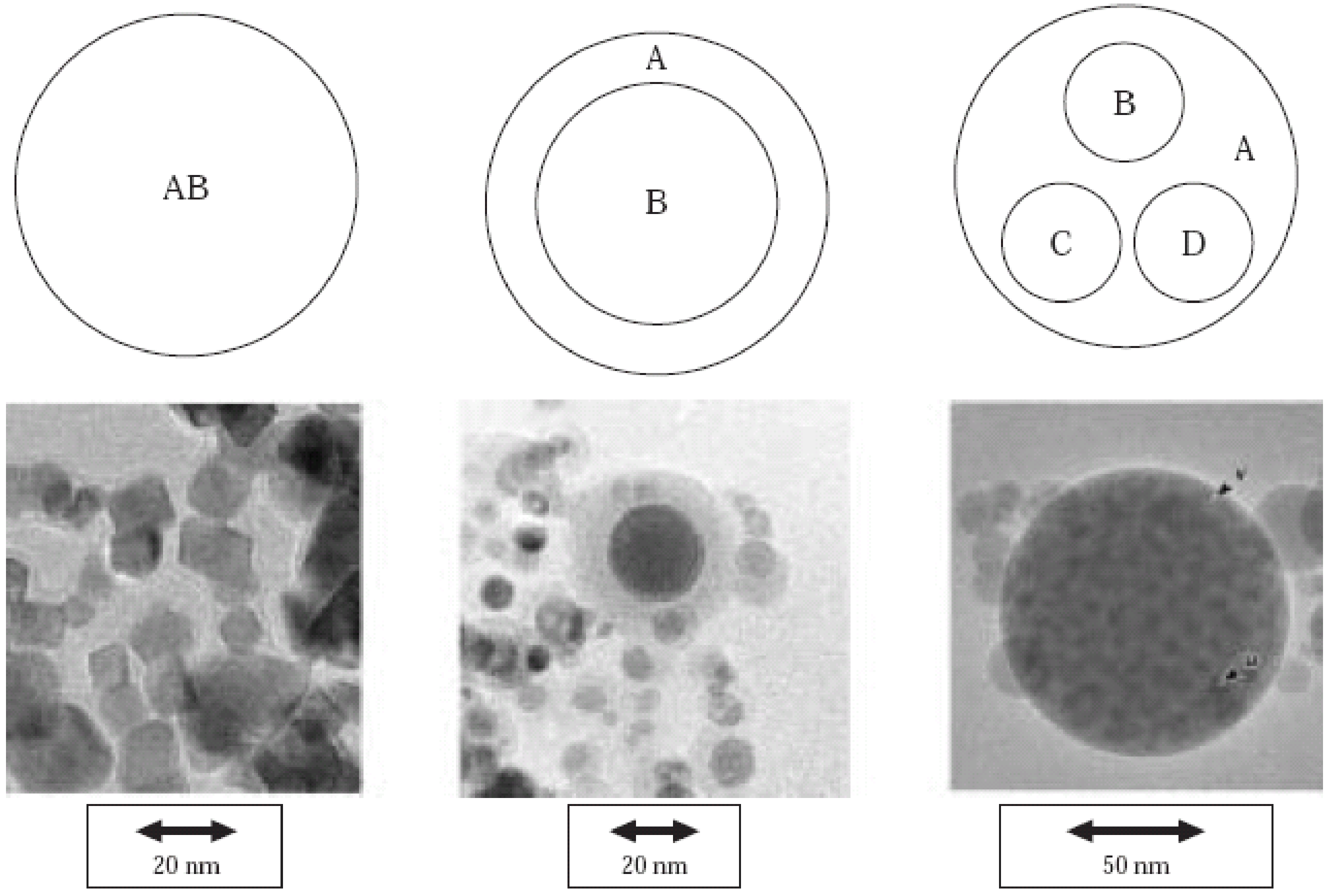
Part II: ODS Coating by Cold Spray

Powder Mixing Using Mechano-Chemical Bonding Technique

The powder mixture introduced into the internal cavity of the equipment is subjected to a centrifugal force which transports them to the inner wall of the rotating chamber. The powder mixture is then subjected to additional compression and shear mechanical forces as they rotate and pass through a gap between the chamber wall and a press head. This results in the smaller particles being dispersed and bonded onto the surfaces of larger base particles without using any binders. This technique can also be applied to improve particle sphericity and for precision mixing of nano and submicron powders.



The MCB technique can disperse submicron and nano-size particles and bonds them onto the surfaces of larger host particles, which may result in oxide dispersion effects, i.e. this technique is applicable to make alloy powders suitable for ODS alloys at much lower cost. Also, since the grain boundaries are pinned by the nano-oxide particles, grain growth will not occur during sintering, and therefore sintering of green compacts can proceed to full density. Also, the MCB process is much easier to scale up than ball mills.



a) Solid solution type (ZrO_2-CeO_2)

b) Core-shell type (ZrO_2-SiO_2)

c) Finely dispersed type (Al-Ca-Ti-Si-Zr oxide)

Structural patterns of nanocomposite particles

[T. Yokoyama and C. C. Huang, KONA No.23 (2005)]

ODS Powder Mixes using Hosokawa MCB Process

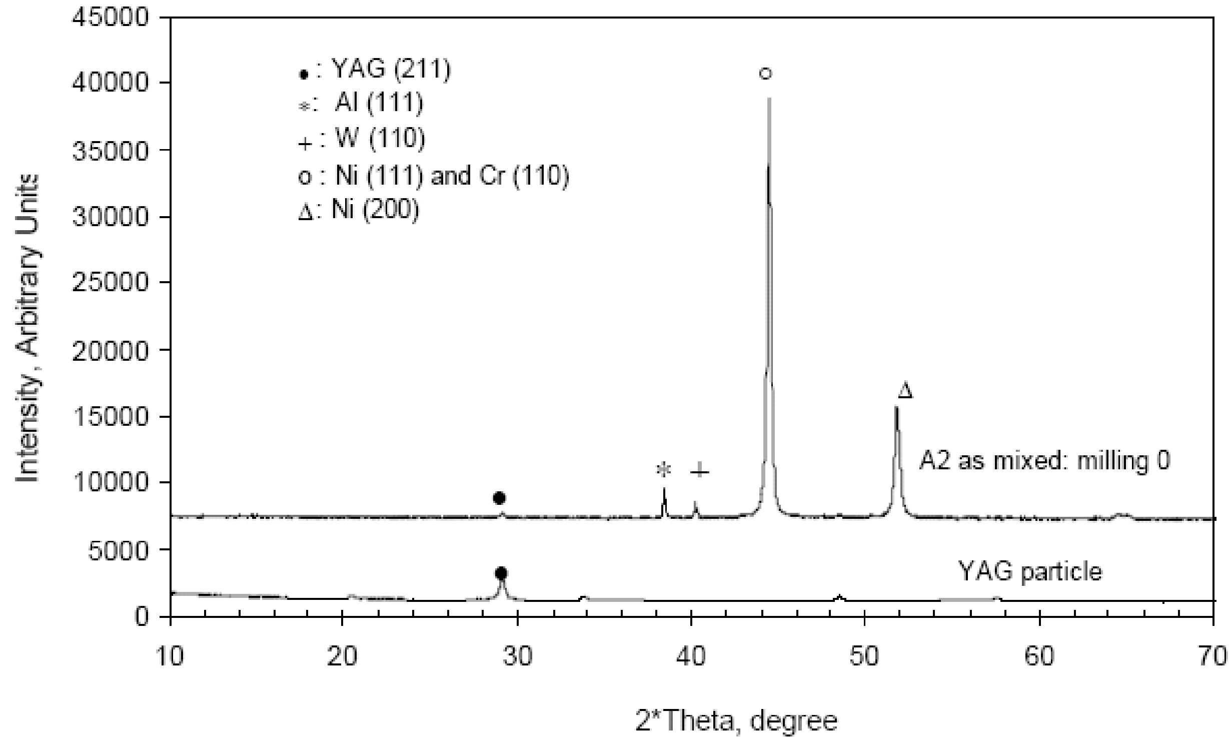
For each selected powder sample, the powder components were weighted (according to the designed weight %) and put in a bottle which is then sealed with argon gas. The MCB processes of these ODS powders were also carried out in argon gas environment.

The B samples (B1 and B2) are harder to process than A samples (A1 and A2). The aluminum particles seemed easier to fuse in the sample B formulation, which has larger nickel particles.

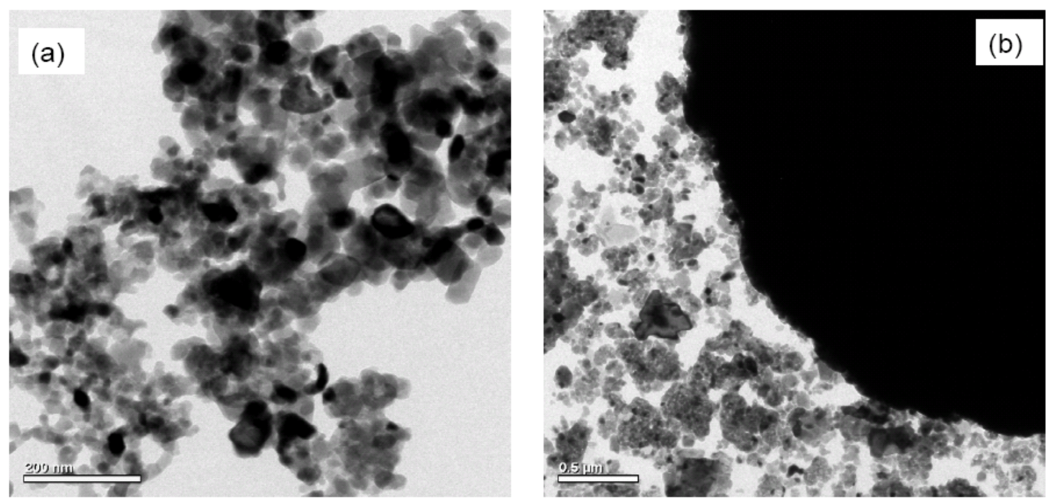
	Cr (7.5~10 µm)	Al (4.5 ~ 7 µm)	Y_2O_3 < 50nm	W (0.5~1 µm)	Ni (4 ~ 8 µm)
A1	20	5	1.5	0	73.5
A2	20	5	1.5	3	70.5

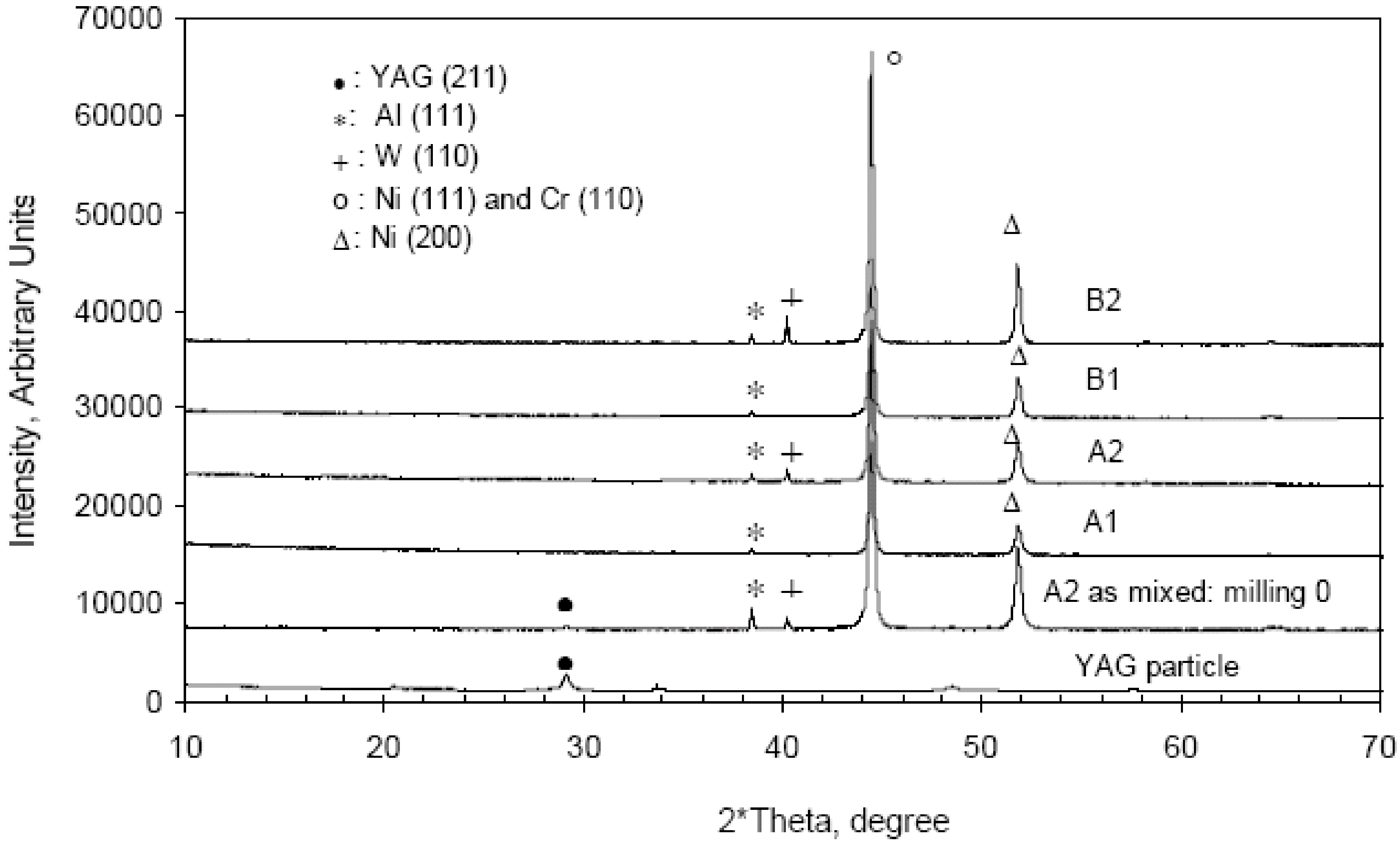
	Cr (8~12 µm)	Al (4.5 ~ 7 µm)	Y_2O_3 < 50nm	W (2~4 µm)	Ni (8~15 µm)
B1	20	5	1.5	0	73.5
B2	20	5	1.5	3	70.5

XRD patterns of two representative starting powders: Y_2O_3 and A2 sample powder before MCB processing

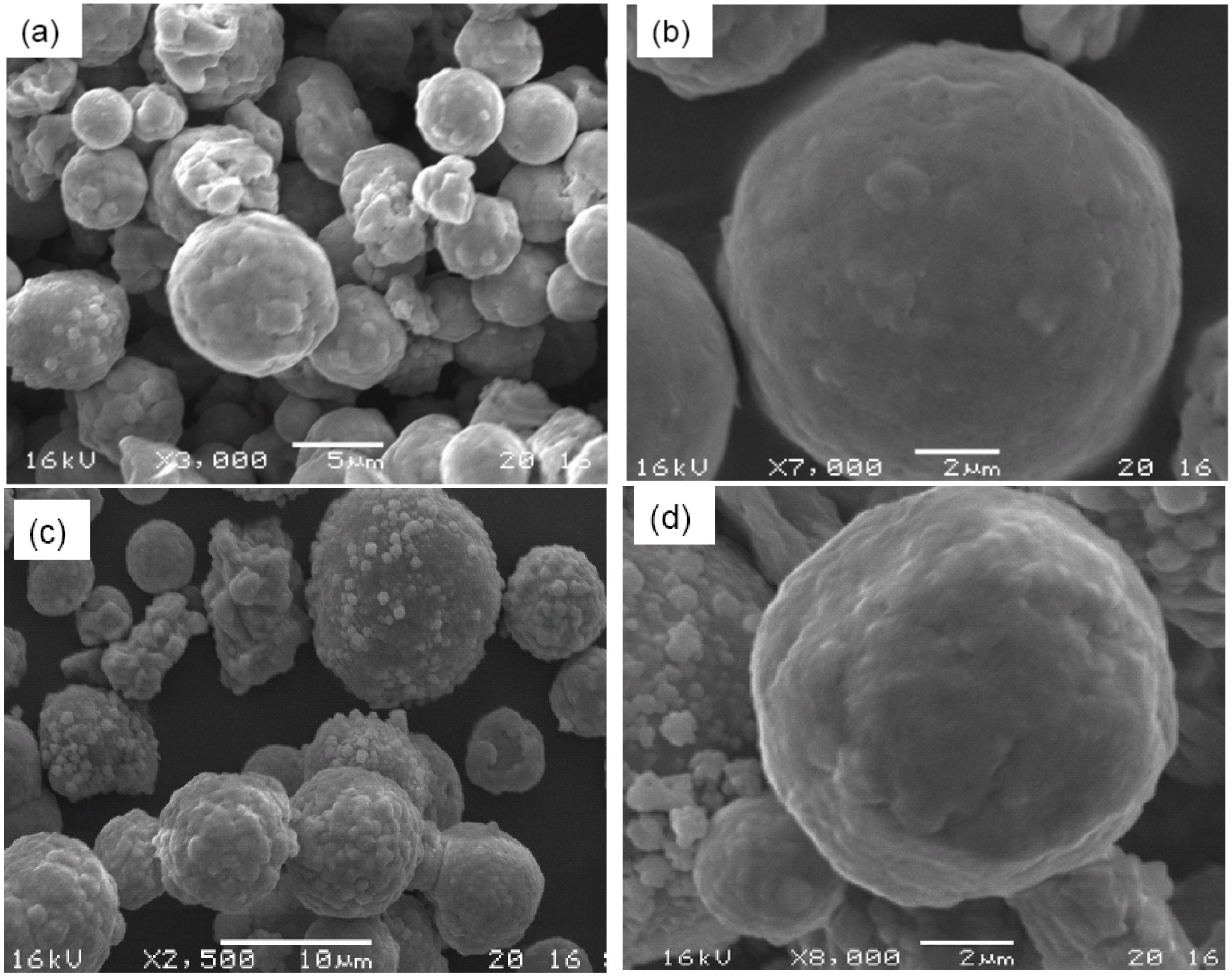


TEM micrographs of starting powders
(a) Y_2O_3 particle
(b) A2 sample powder before MCB processing

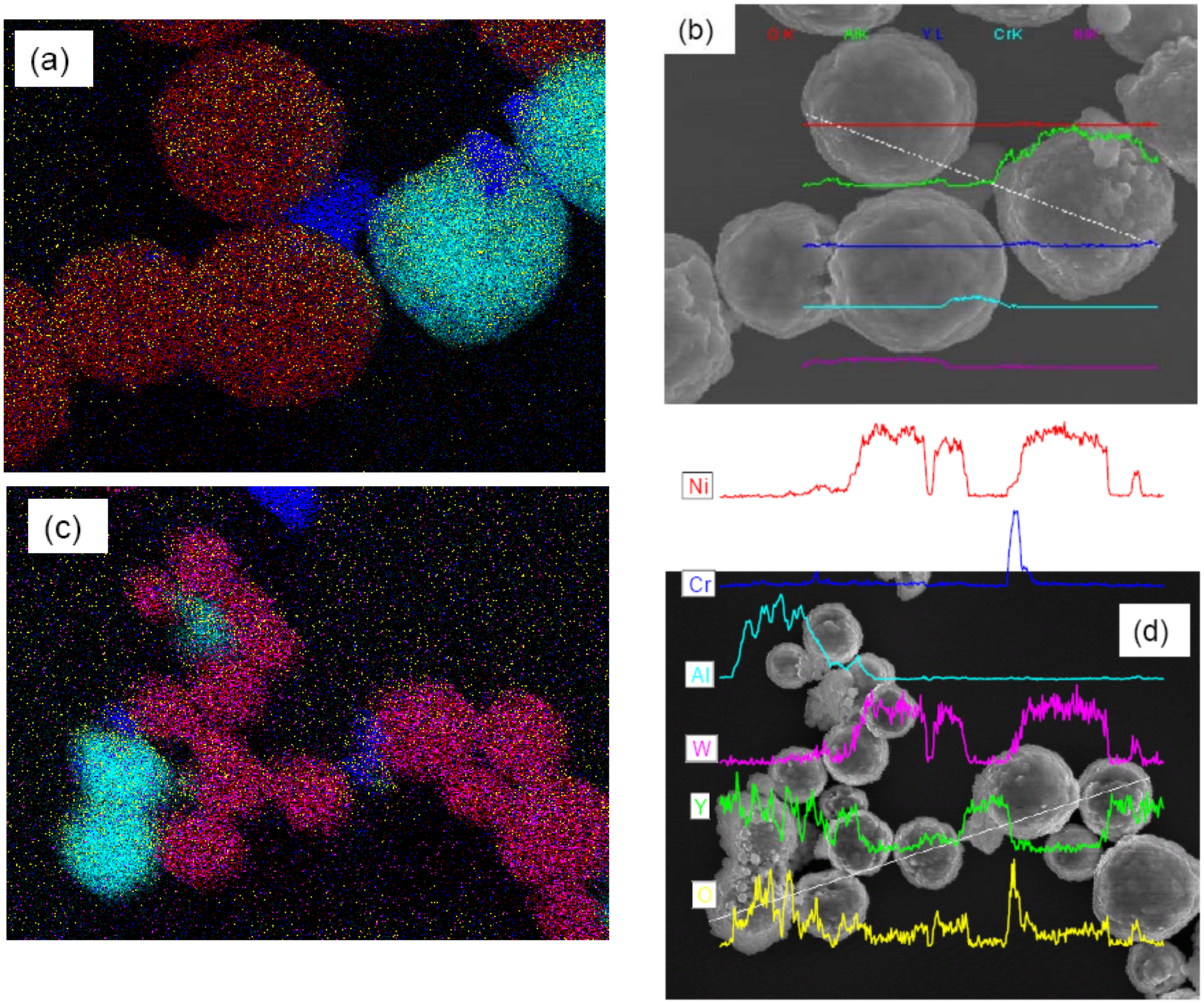




XRD patterns of starting and MCB processed powders



SEM micrographs of MCB processed powder sample A1 and A2
(a). Sample A1; (b) close view of (a); (c) sample A2; (d): close view of (c)



A1 Sample
Ni is red
Cr is blue
Al is cyan
O is yellow
Y is green

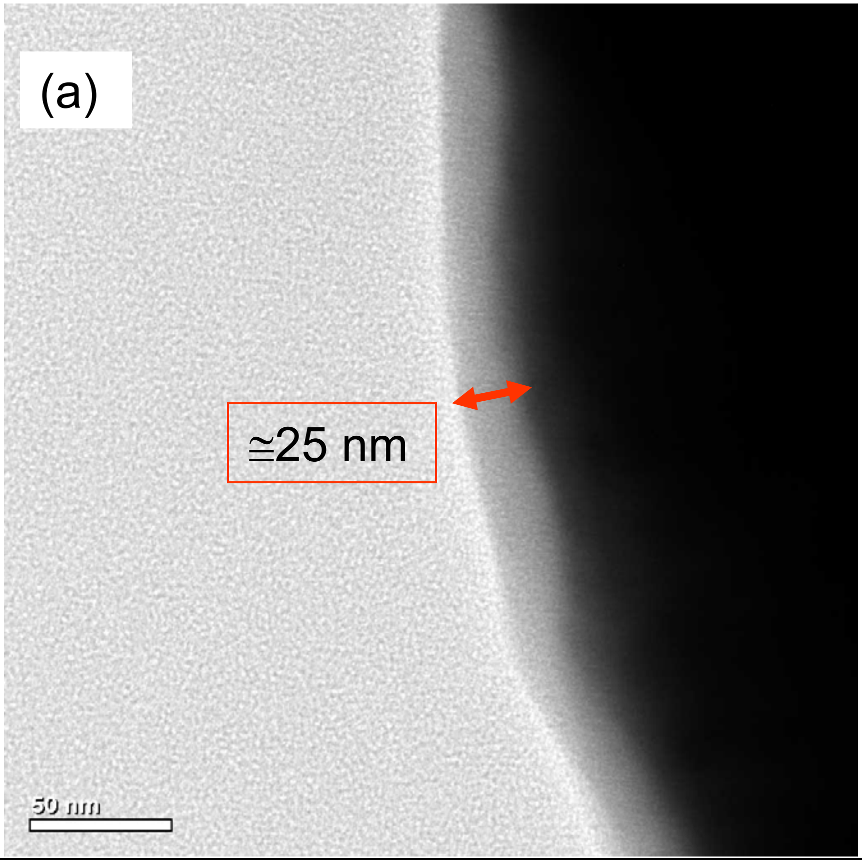
A2 Sample
Ni is red
Cr is blue
Al is cyan
O is yellow
Y is green
W is magenta

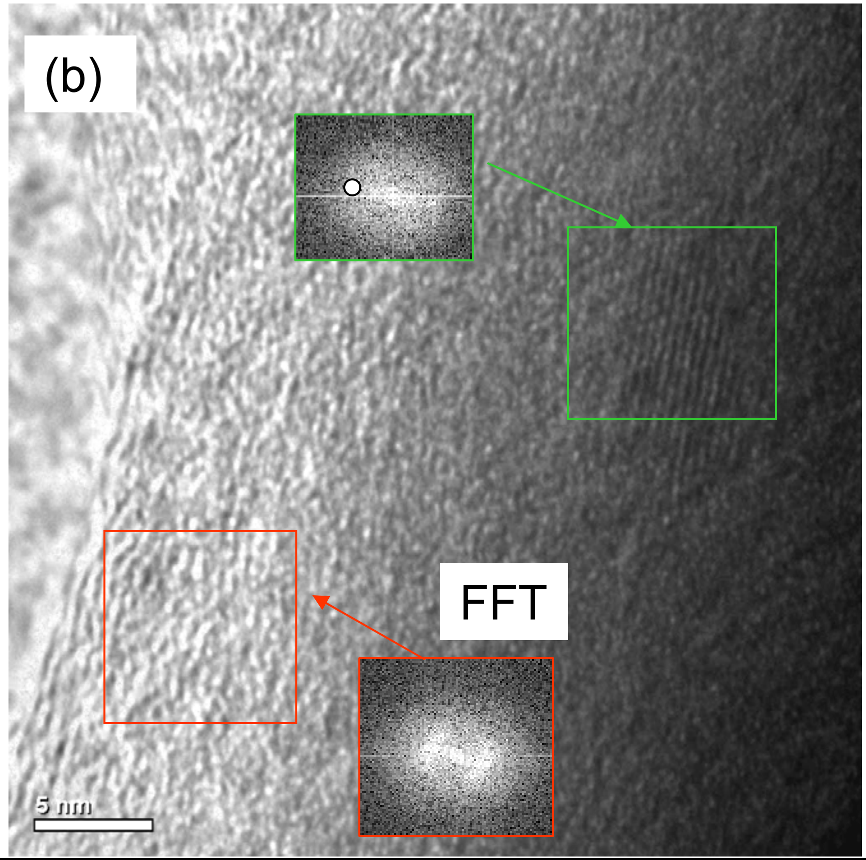
SEM EDX mapping micrographs and EDX line scanning profile of MCB processed powders (a). Sample A1; (b) line scanning of A1; (c) sample A2; (d): line-scanning of A2

TEM Sample Analyses

- Specimen preparation: Ultrasonic homogenization and solution-drop on carbon coated film grid
- Microscope: Tecnai F30 STEM/TEM
- Imaging mode: STEM (scanning transmission electron microscopy), FTEM (filtered transmission electron microscopy) BF mode (bright field), and HREM mode (high resolution electron microscopy)
- Spectroscopy mode: EDX (electron dispersed X-ray) with STEM with 0.2 nm probe size and drifting corrected line scanning

TEM BF and HREM imaging – A1 Sample



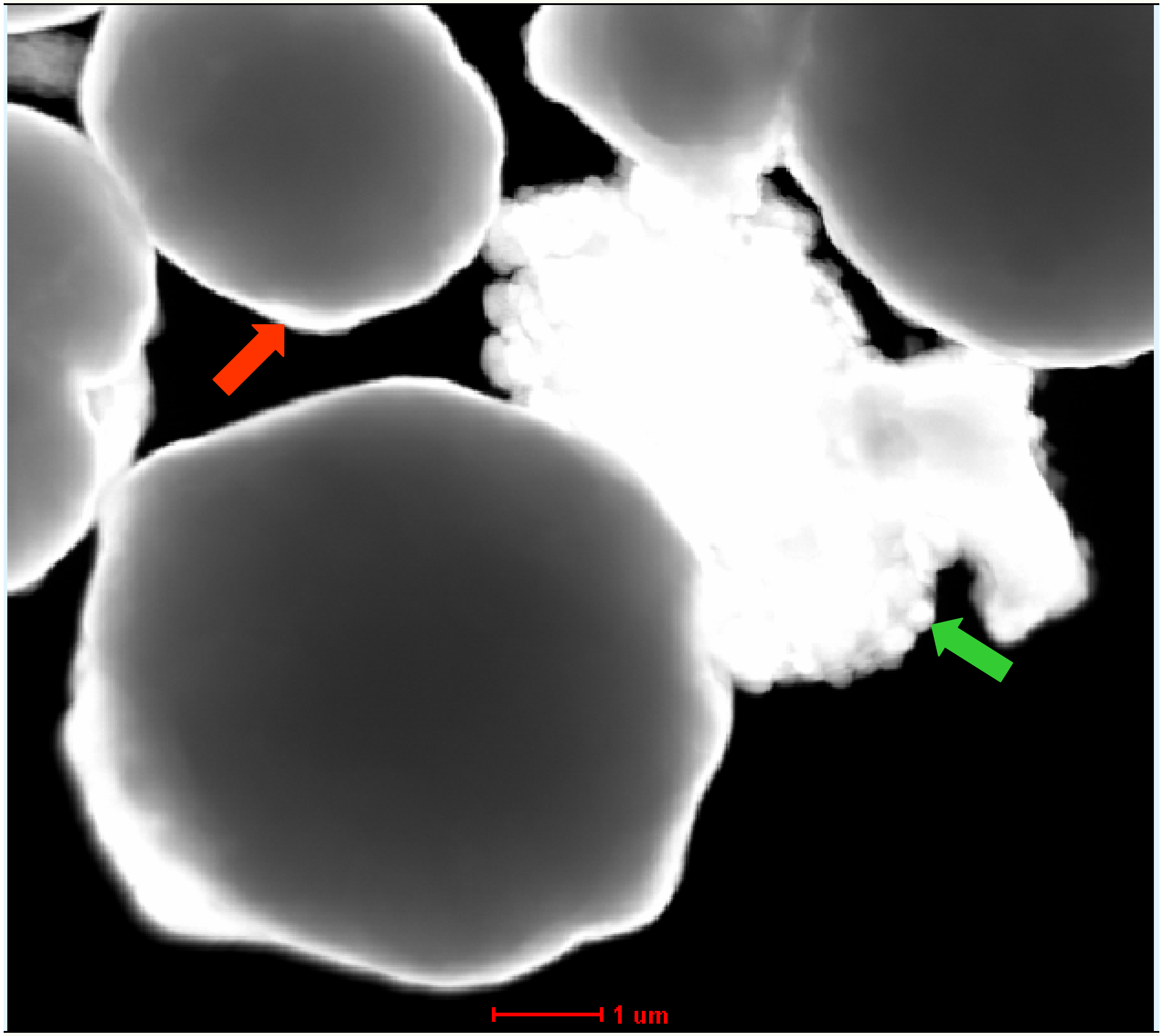


• TEM BF image (a) shows a layer of Y_2O_3 thin film with thickness about 25 nm around the edge of particle. The film thickness is relatively homogeneous

• HREM image (b) shows the fine structure of the thin film. Most area of the film is amorphous and the corresponding FFT (fast Fourier transform) image show the diffusive feature.

• There is crystal structure within film as FFT indicated. The embedded FFT shows the spots and image shows the one orientation fringe. The growth of film may involve crystallization of Y_2O_3

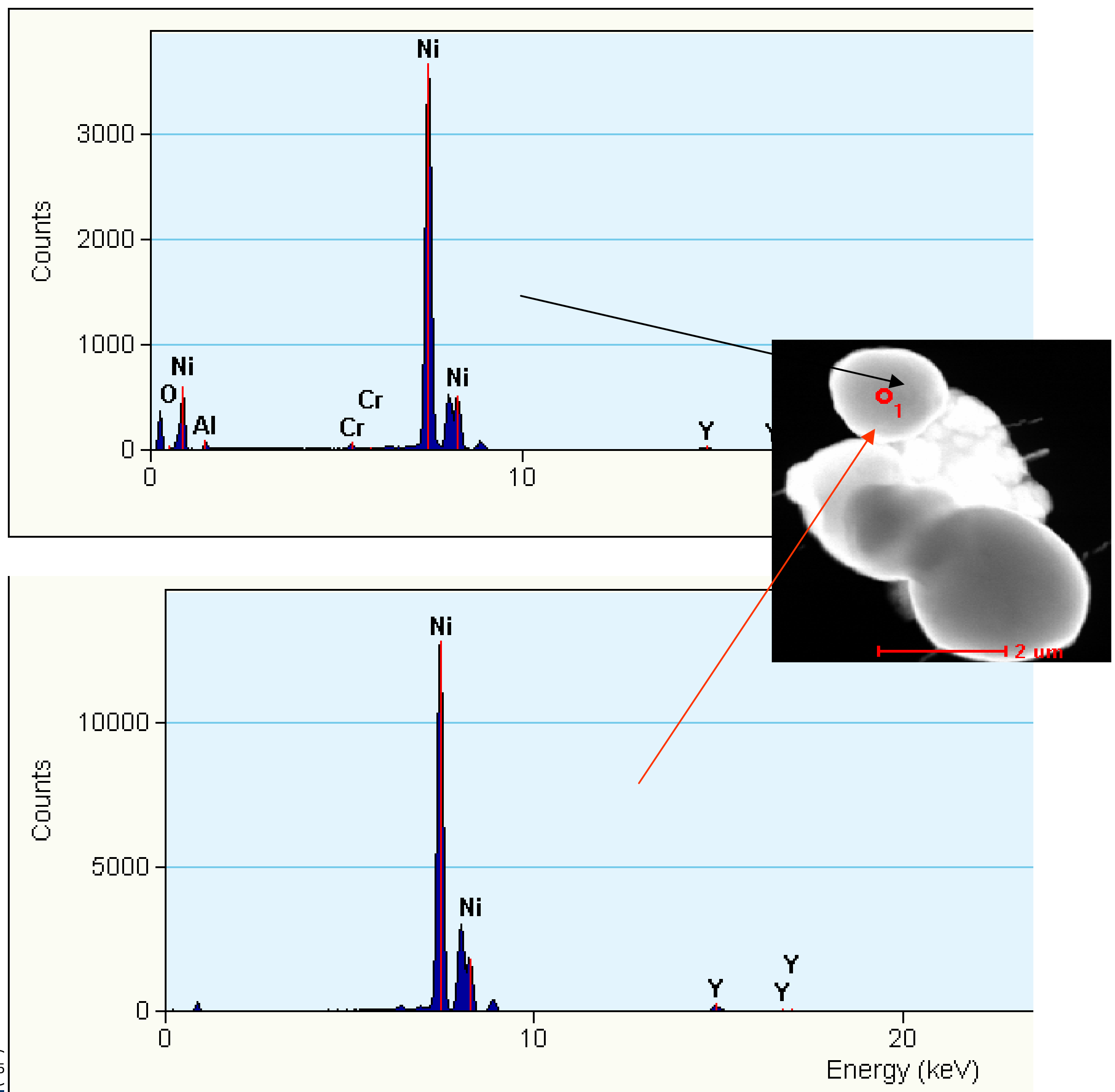
STEM Image showing Z-contrast – A1 Sample



STEM image

- showing Z-contrast of particles with 4-8 μm
- Dark contrast of particles is possibly arisen from poor electron transmission and low e-scattering due to low Z number. The carbon film shows the dark contrast in background.
- Bright contrast on the edge of particles, as indicated by red arrow, is arisen from the high e-scattering due to Z-number (Y_2O_3)
- Very tiny agglomerated particles are founded as indicated by green arrow and appearing bright contrast, which may be contributed by e-transmission and high Z number

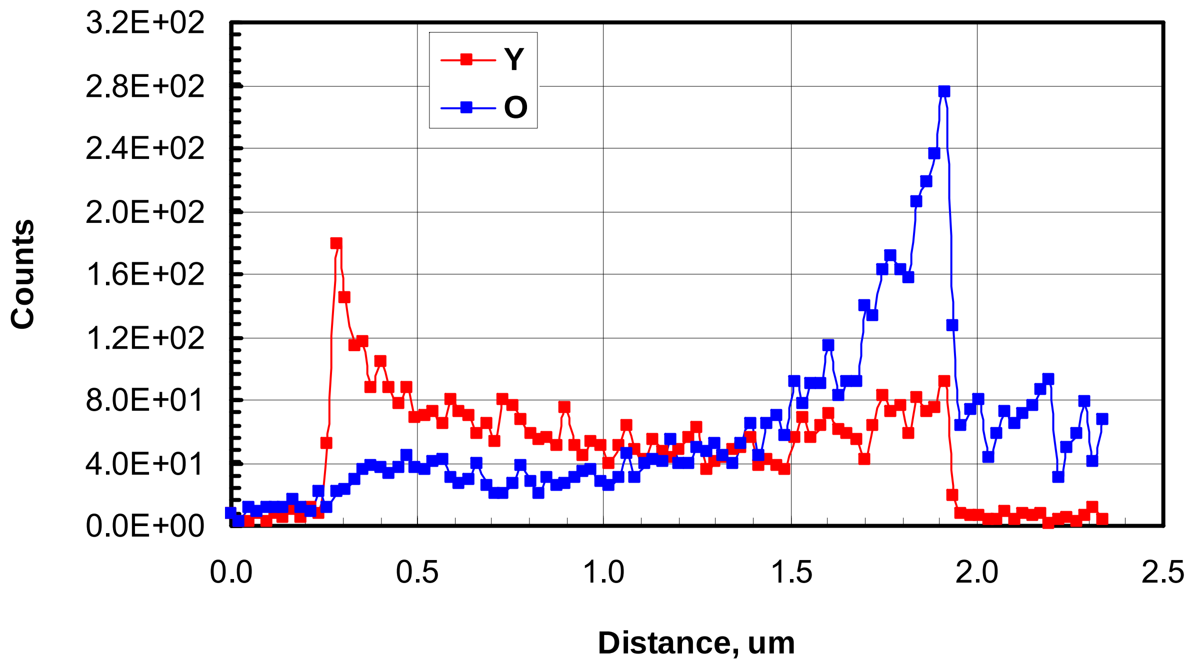
Nano Probe EDX showing chemical composition – A1 Sample



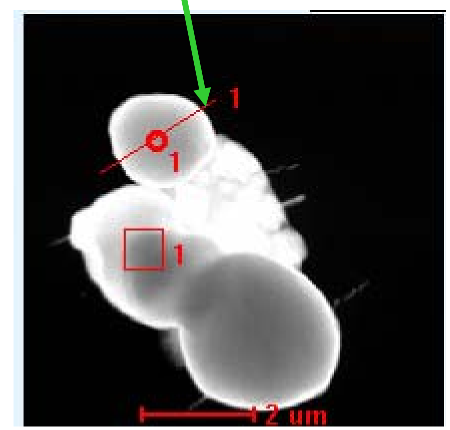
EDX for particle center and edge

- In particle center, EDX shows Ni-peak as major peaks and very small Y peak.
- On the edge of particle, Y peak is stronger than center indicating a layer of Y on edge. High counts relative particle center also shows e-transmission on the edge.

Drifting corrected EDX Line Scanning to Examine element composition distribution across the whole particle - A1 Sample



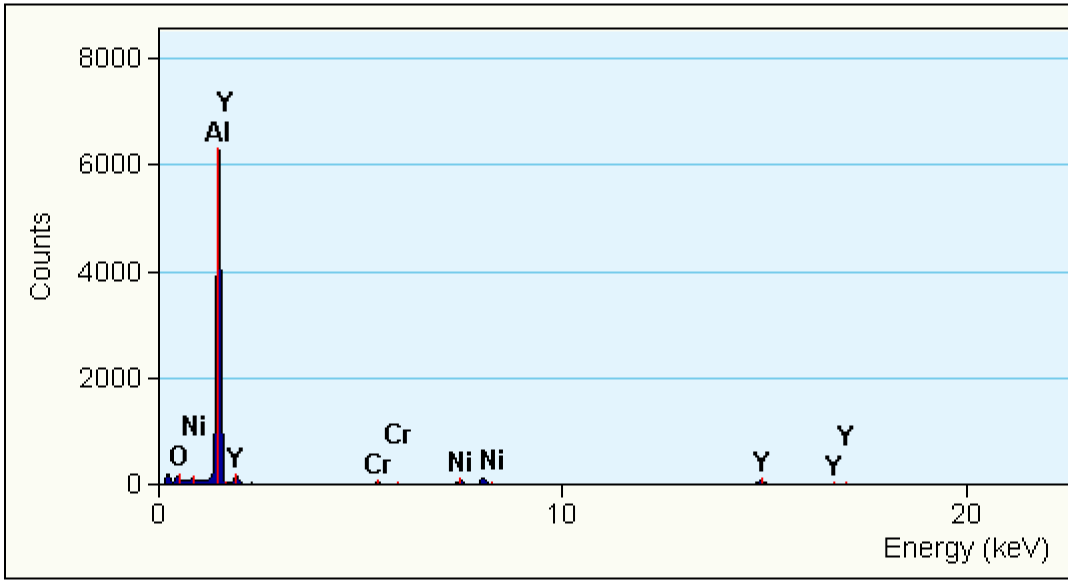
E-probe scanning along the line across particle

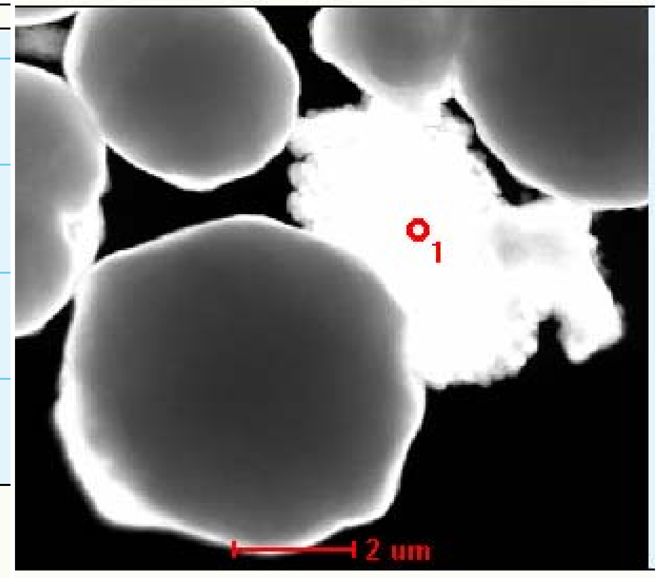


EDX Line Scanning across whole particle

- Y and O line scanning indicate that the significant increase of Y and O counts around edge of the particle showing Y and O concentration along particle edge
- Zero count indicates e-probe is outside the particle and there is some oxygen outside particle in the carbon film area.

Small Particle Analysis – A1 Sample



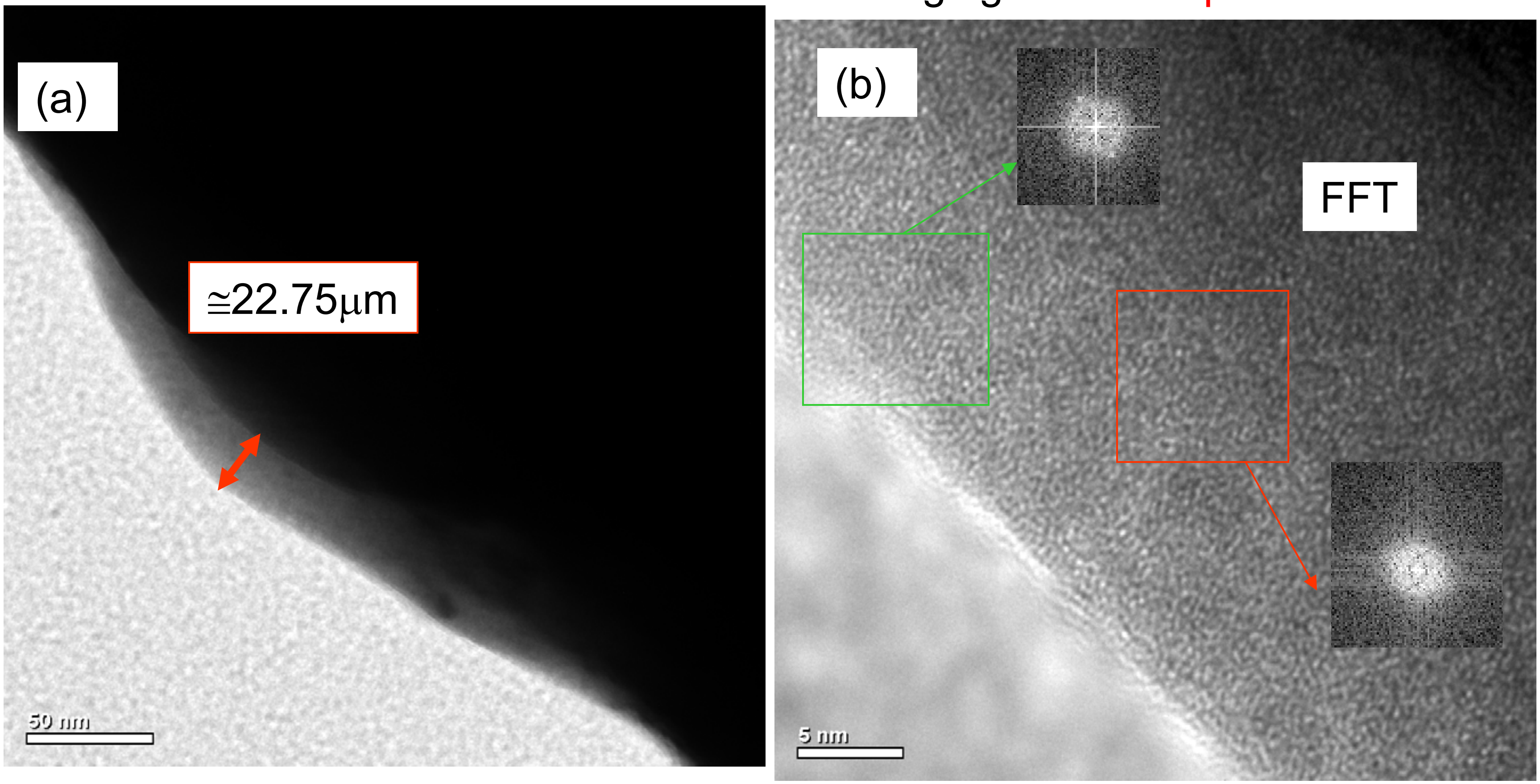


- EDX spectrum shows the small particles are aluminum particles, which are highly agglomerated.
- The Y and O are also detected on these small particles

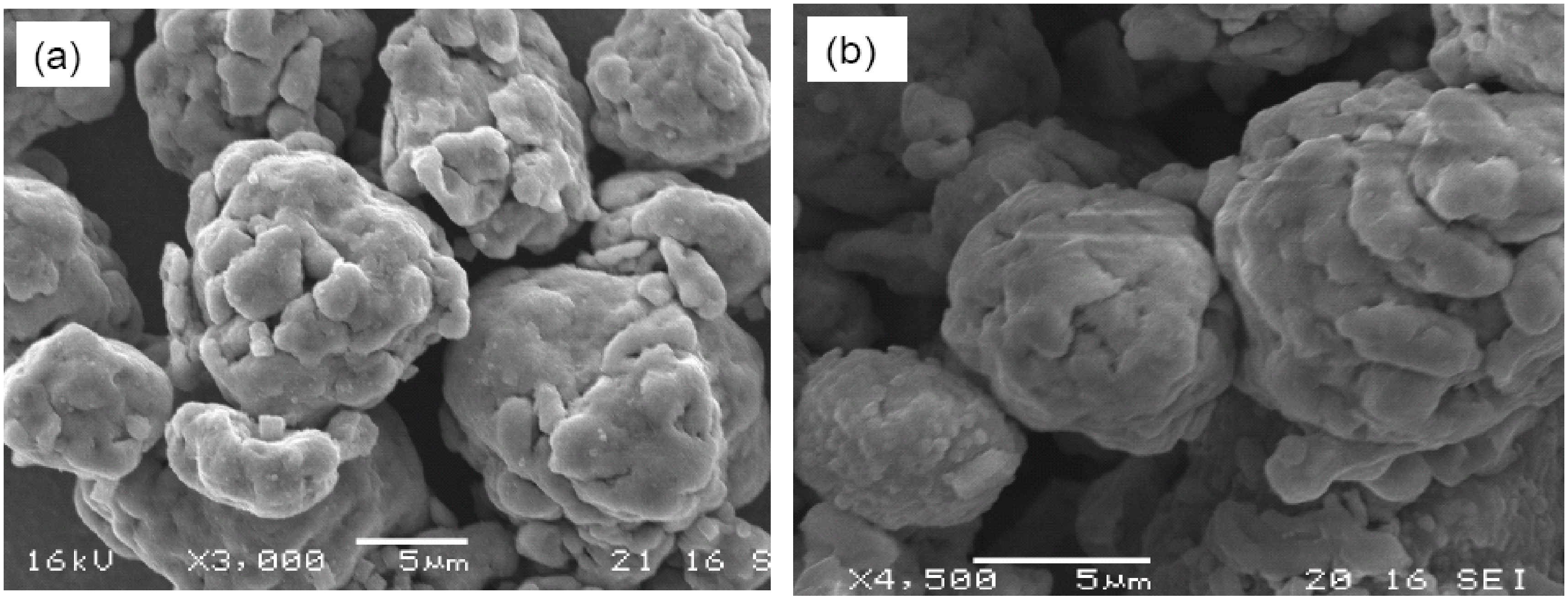
Summary of A1 sample

- A1 sample was examined by STEM, BF TEM, HRTEM and spectroscopy.
- The Ni-particles have average size of 4-8 μm and separately distribute and Al particles have 1-3 μm and appear to be agglomerated
- **STEM and TEM BF images show that there is a layer of thin film with a thickness of 23-25 nm on around the edge of Ni-particle. EDX line scanning indicated that the thin film mainly consists of Y and O.**
- **HREM image shows the structure of thin film includes amorphous and crystalline structure.**

TEM BF and HREM imaging – A2 Sample

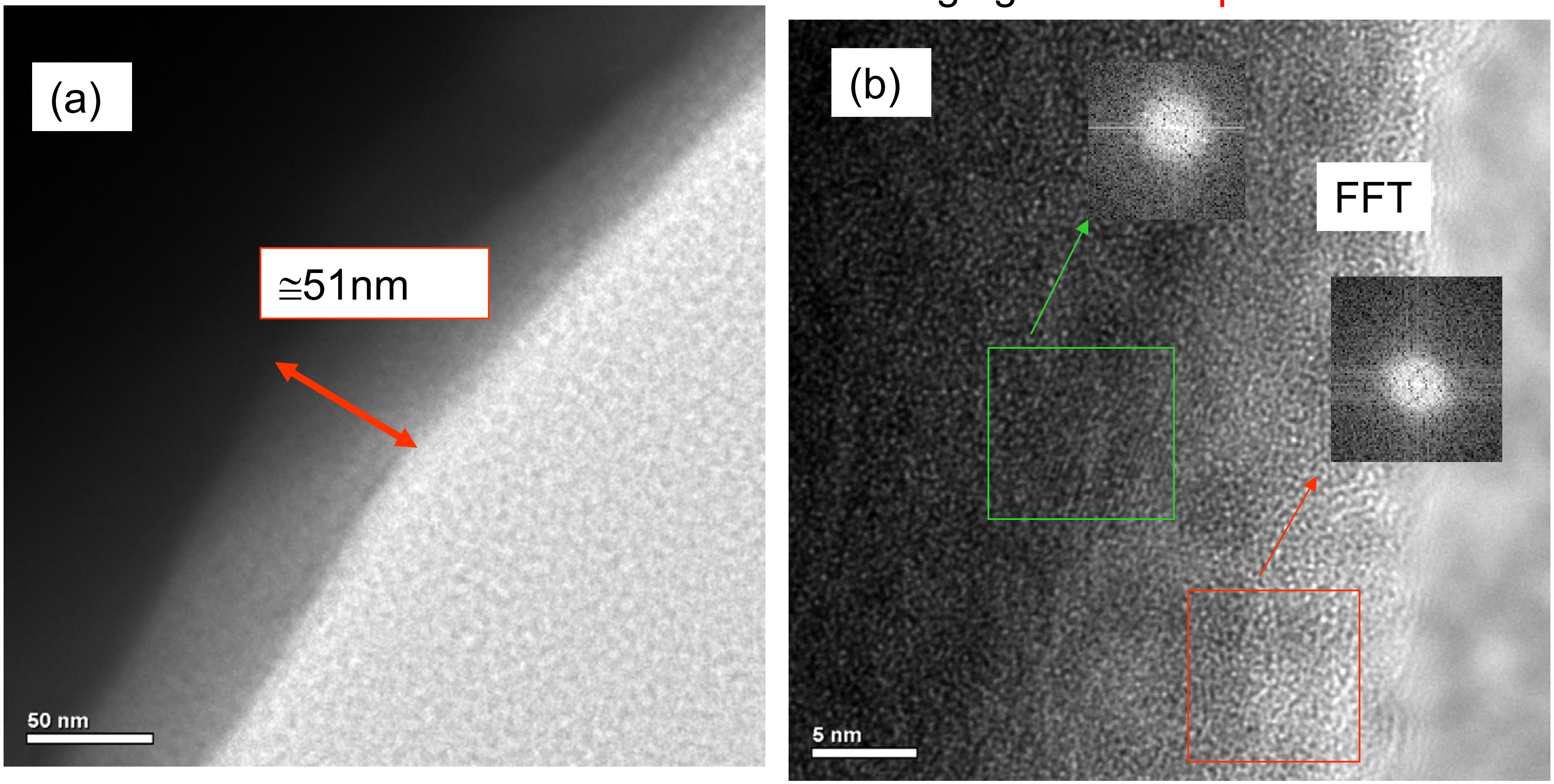


- TEM BF image (a) shows the dark contrast of particle due to thickness and a layer of thin film with thickness about 22.75 nm around the edge of particle.
- HREM image (b) shows the fine structure of the thin film. Most area of the film is amorphous and the corresponding FFT (fast Fourier transform) image show the diffusive feature.
- There is crystalline fringe within film as FFT indicated. The embedded FFT shows the spots and image shows the one orientation fringe. The growth of film may involve crystallization of Y



SEM micrographs of MCB processed powder sample B1 and B2
(a). Sample B1; (b) sample B2

TEM BF and HREM imaging – B1 Sample

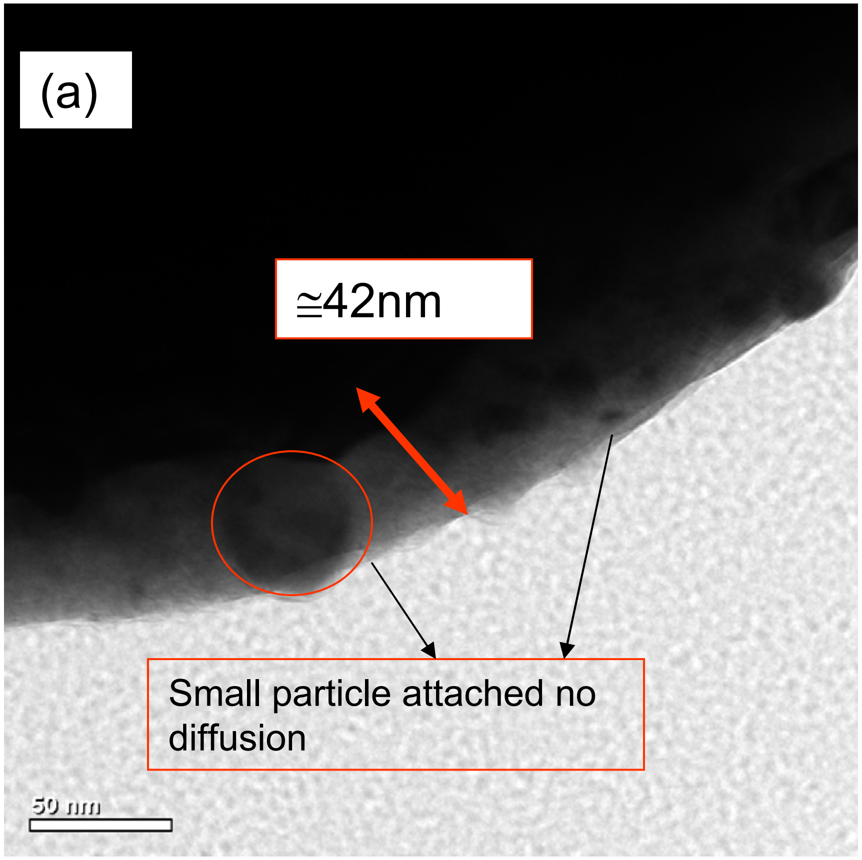


• TEM BF image (a) shows the dark contrast of particle due to thickness and a layer of thin film with thickness about 51 nm around the edge of particle.

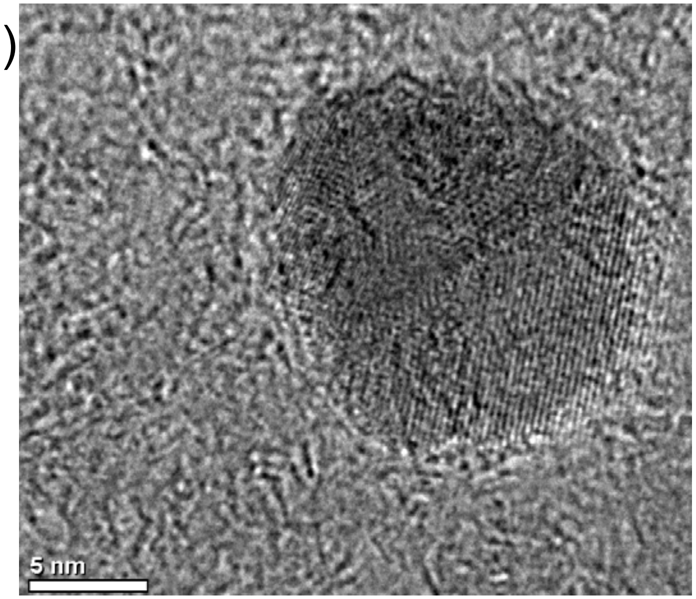
• HREM image (b) shows the fine structure of the thin film. Most area of the film is amorphous and the corresponding FFT (fast Fourier transform) image show the diffusive feature.

• There is crystalline fringe within film as FFT indicated. The embedded FFT shows the spots and image shows the one orientation fringe. The growth of film may involve crystallization of Y

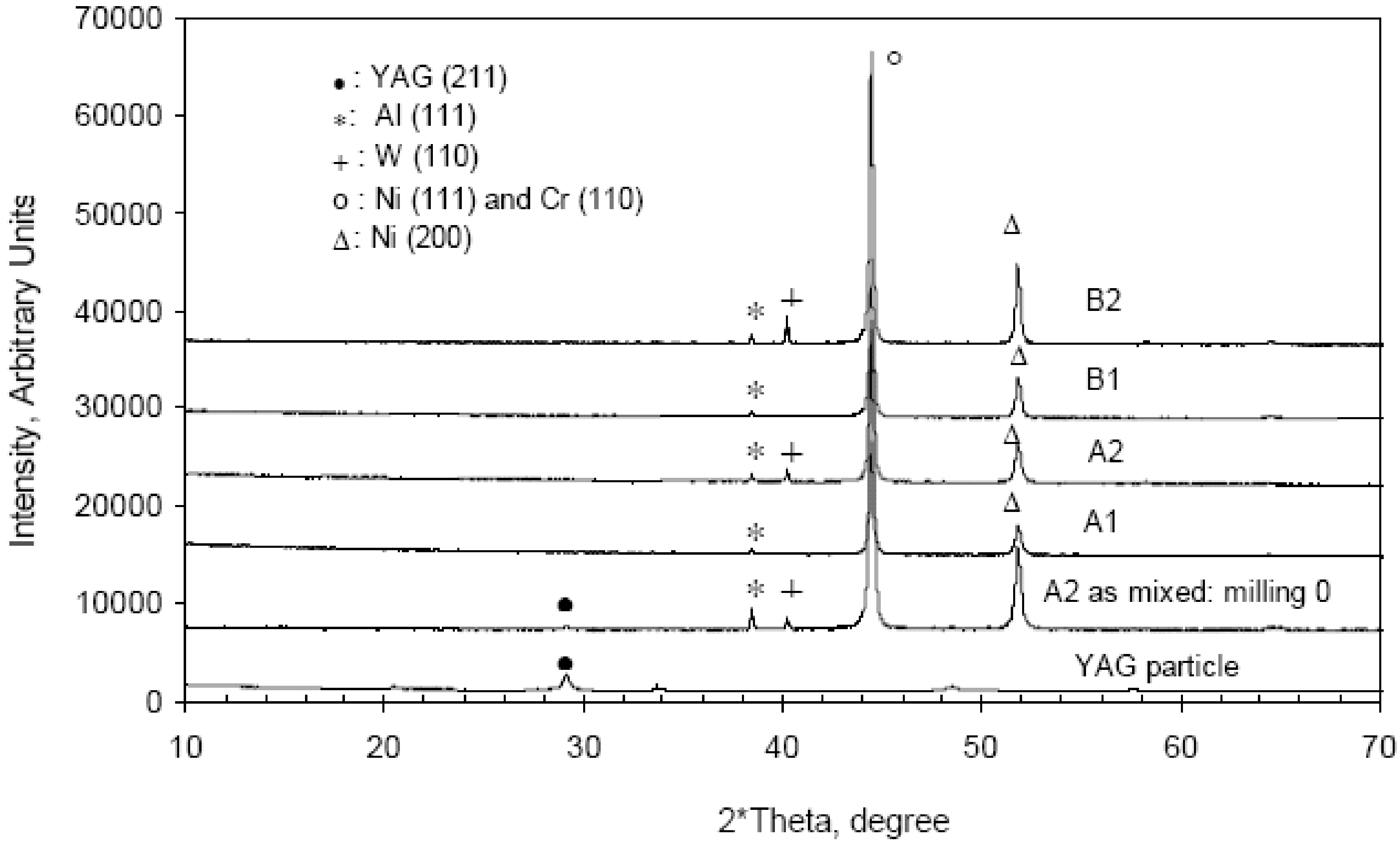
TEM BF and HREM imaging – B2 Sample



(b)



- TEM BF image (a) shows the dark contrast of particle due to thickness and a layer of thin film with thickness about 42 nm around the edge of particle.
- small particles were attached on the edge or individually present, indicating not well mixed.



XRD patterns of starting and MCB processed powders

Part I: Discussion and Summary

•The MCB process can form Y_2O_3 nano-sized amorphous layer on the larger Ni and Cr particles.

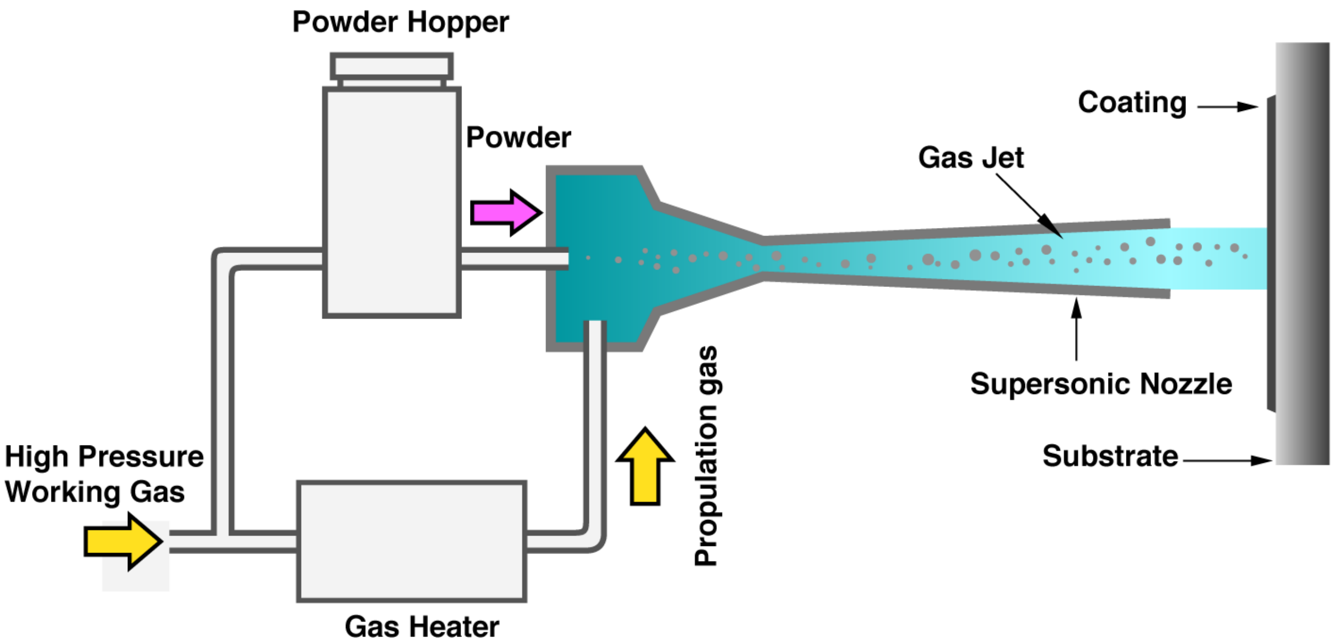
• All elements, Ni, Al, Cr, and W, appear well defined crystal structure. Only Y_2O_3 was formed amorphous layer around the particles

.

• W was not found in TEM image but in XRD. The reason is the density is low, and it may not be intercepted by grid during TEM sample preparation.

Part II: ODS Coating by Cold Spray

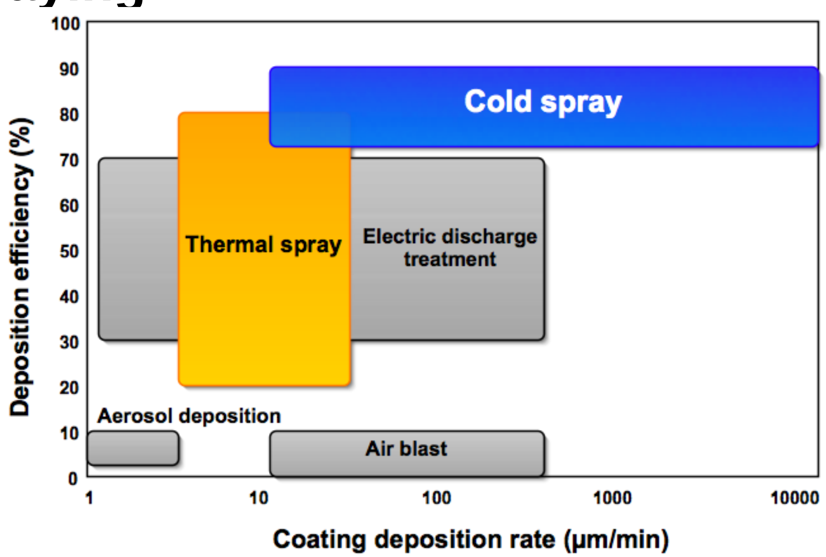
Cold-Gas Dynamic-Spray (Cold Spray)



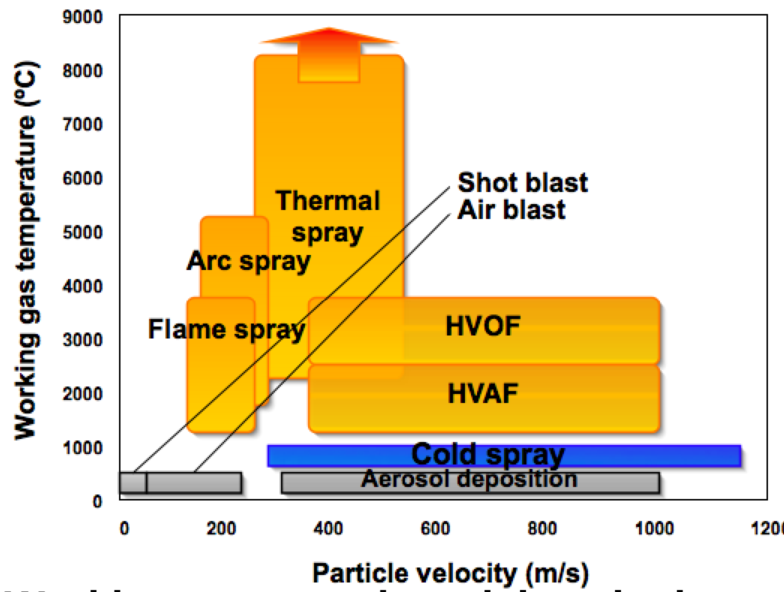
In conventional thermal spray technique, the coating material is heated to molten or semi-molten state. Therefore, thermal sprayed coatings have created some problems due to heating, i.e. high temperature oxidation and phase transformation. In the case of a cold spray technique, the particles are accelerated by the sonic/subsonic gas jet at the gas temperature, which is usually lower than melting temperature of powder materials.

Advantages of Cold Spray Technique

- **Low thermal effect** (oxidation, phase transformation)
  - small microstructural changes on substrate surface
  - applicable for thermally and oxygen sensitive materials (e.g. Cr, Al, Cu, Ti)
  - Nanophase, intermetallic and amorphous materials can be cold sprayed
  - formation of embrittled phases, macro- and micro-segregationn of the alloying elements (during solidification) can be avoided
- **Peening effect** - beneficial compressive residual stresses
- **Thick deposition**
- **Higher deposition efficiency and lower cost** compared with thermal spraying



Deposition efficiency and rate



Working temp. and particle velocity

Cold Spray

High Pressure Type

High particle velocity (500-1500m/s)
30-40 bar (430 – 580 psi)
Possible hard material, such as WC, Ni alloy etc.
Expensive

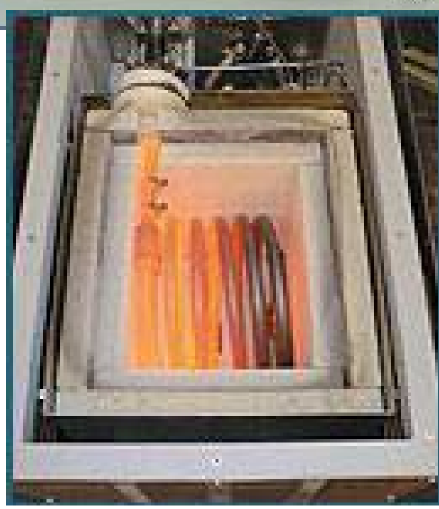
Low pressure type

Low particle velocity
5-6 bar
Portable
Possible soft materials only, such as Al, Cu etc.
Low price and low maintenance cost

HP Cold Spray

Gas temperature increases.

Nitrogen 800ºC, 40bar
Helium 600ºC, 40bar



Heater

Gun

Reference: Web site of CGT corp.

HP-Cold Sprayed MCRALY Coatings

MCrAlY Coatings

High temperature oxidation protection coating

TBC coated turbine blades
(Bond coat: MCrAlY)

MCrAlY

M (Ni and/or Co) + Cr, Al, Y

Excellent high temperature oxidation protection properties

MCrAlY coatings are produced by conventional thermal spray technique.
=> Higher cost, Low efficiency…

Required new coating procedure

Cold spray technique has a possibility to improve the deposition efficiency.
-As a result, coating producing cost can be reduce

Experimental Example

Material preparation

Coating material: CoNiCrAlY
(SULZER Metco AMDRY9951)

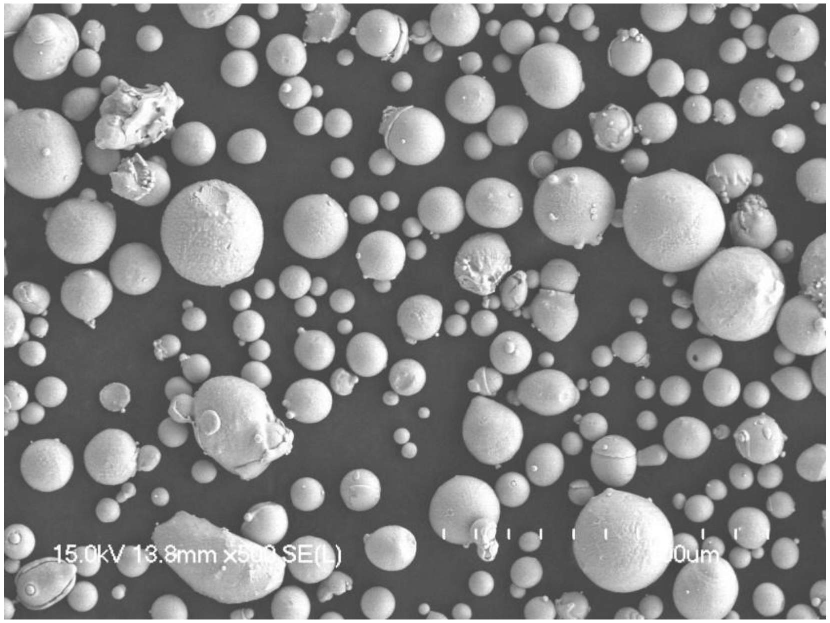
Co	Ni	Cr	Al	Y
Bal.	32	21	8	0.5

(wt.%)

Substrate: Inconel 625

Ni	Cr	Mo	Nb	Fe
Bal.	24	9	4	3.5

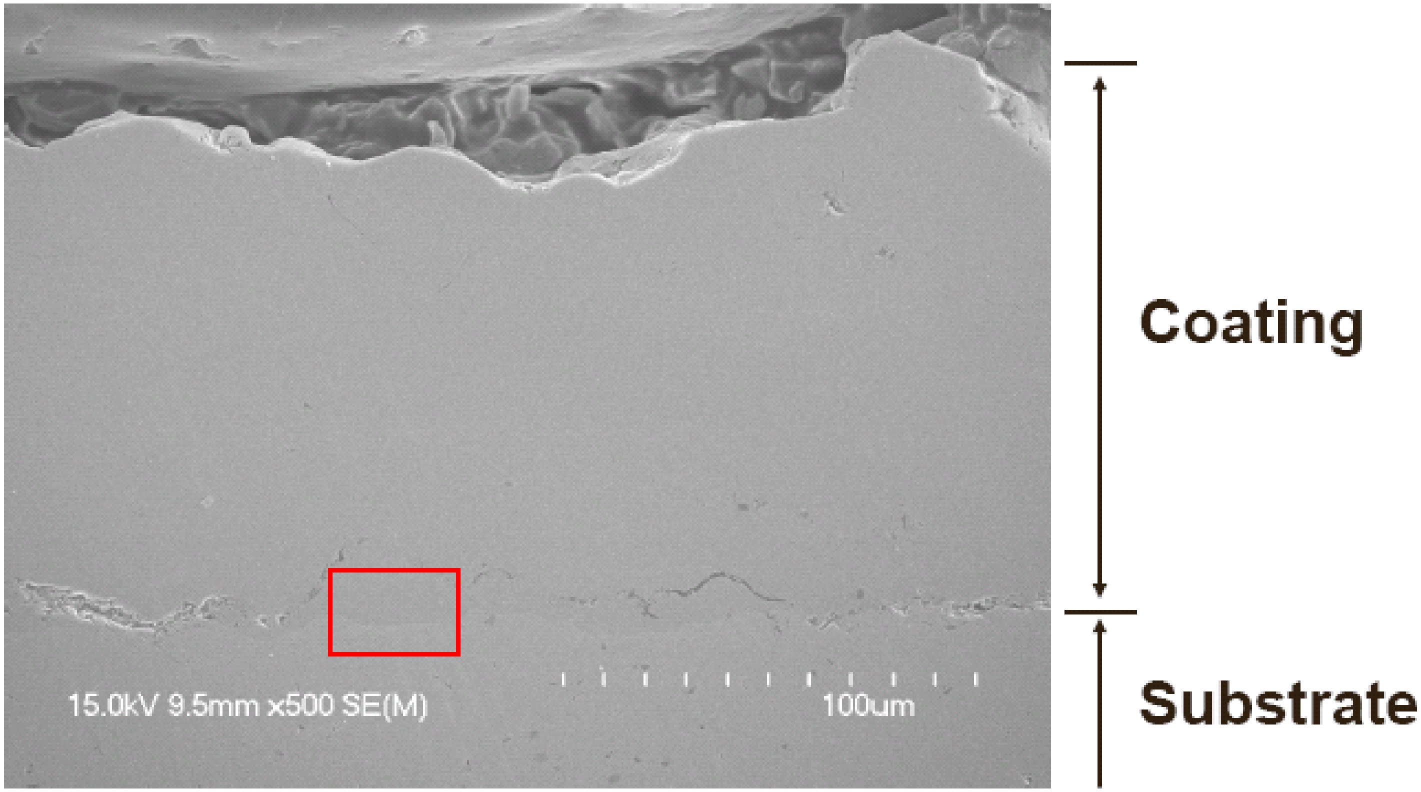
(wt.%)



SEM image of AMDRY9951 powder(-37+5.5μm)

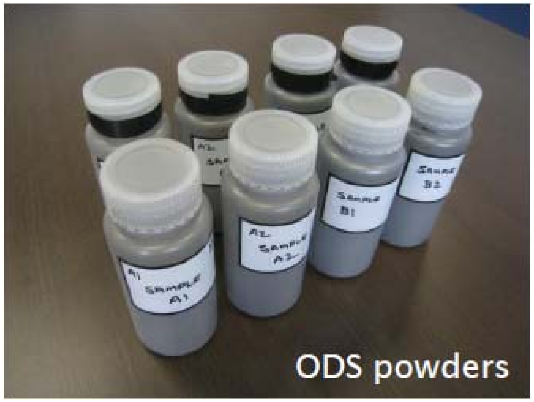
Facility: KINETIKS 3000 (CGT-Cold Gas Technology GmbH)
Gas: Nitrogen (3 MPa)

As-sprayed Coating



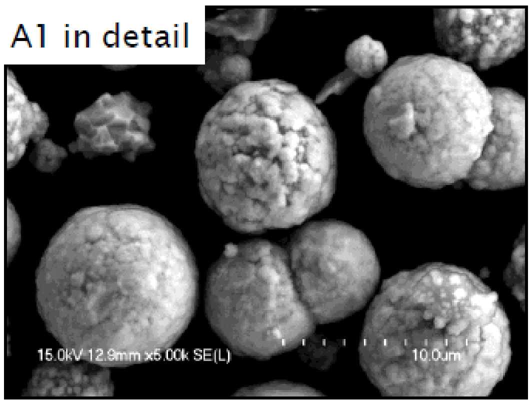
As-sprayed MCrAlY coating is high density due to high velocity impingements

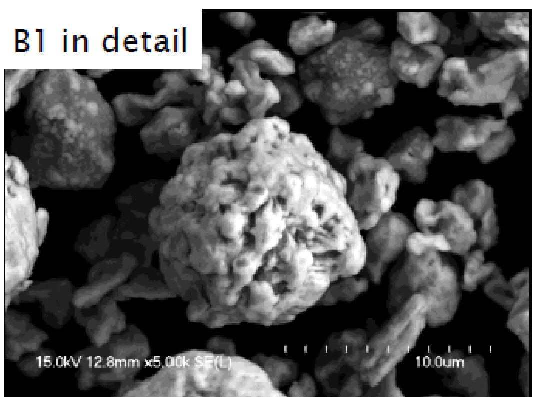
=> Higher magnified observation of interface between coating and substrate is required.

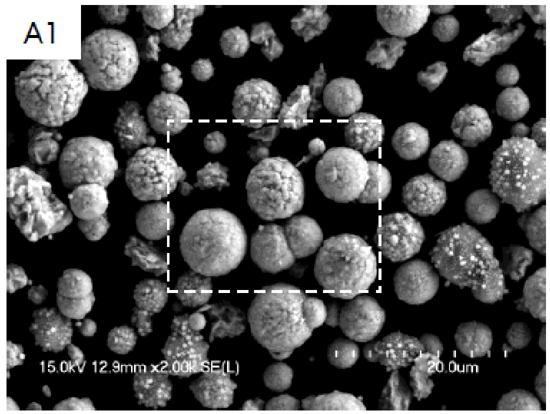


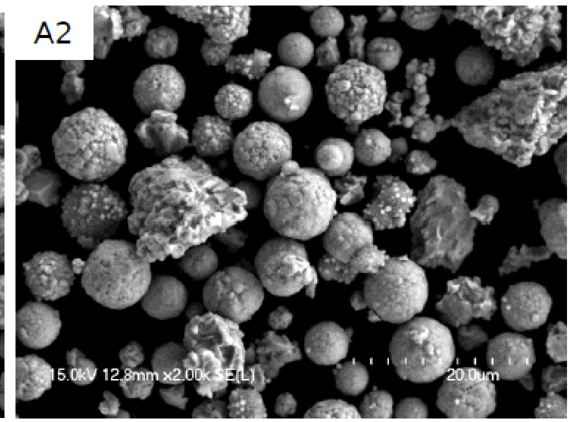
ODS in stock

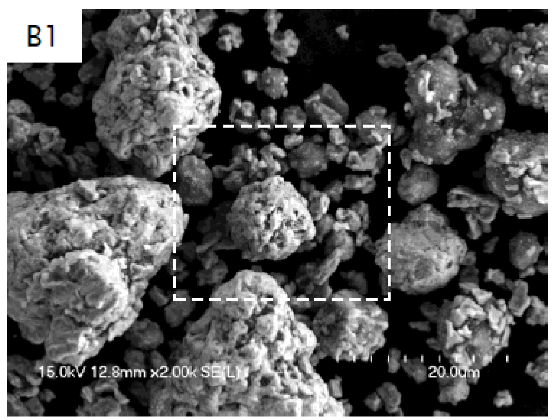
4-kinds (A1, A2, B1, B2), 400g per each powder pack.
Milled by Hosokawa MCB process.
73.5Ni-20Cr-5Al-1.5Y_2O_3 (sample A1) + W (only sample A2 & B2).

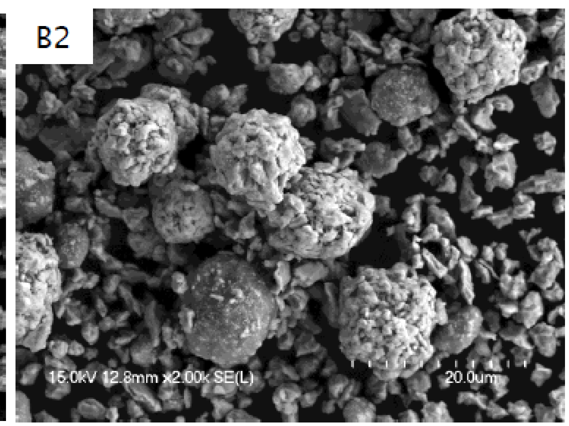






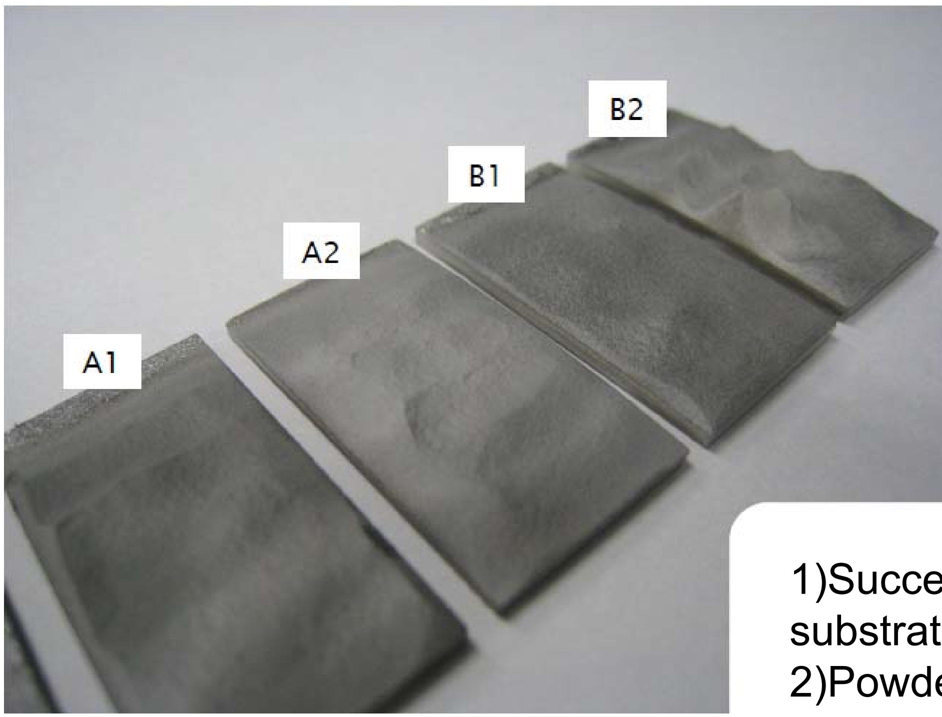




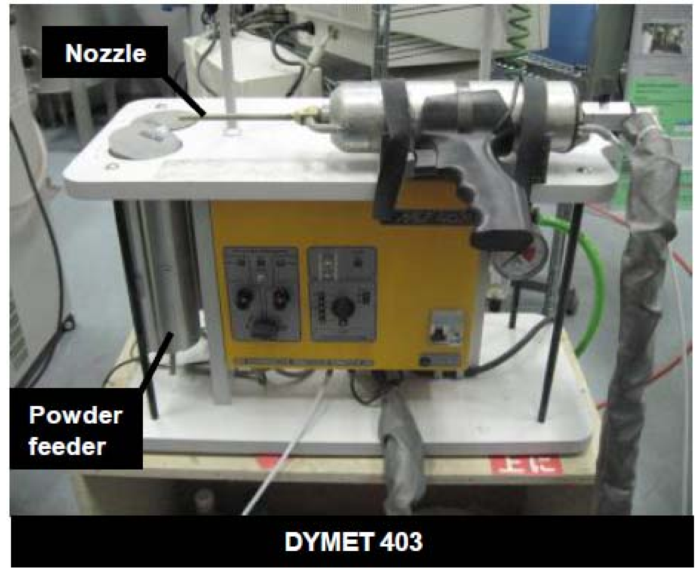


Trial Run of ODS Coatings on Inconel 625

Coating Conditions
A1, A2, B1, B2 coatings on sandblasted Inconel 625 by Dymet. Heating about 400deg.C; Powder Supply No. 8; 0.8MPa Air; 4 Pass; 10mm-off by Hands.



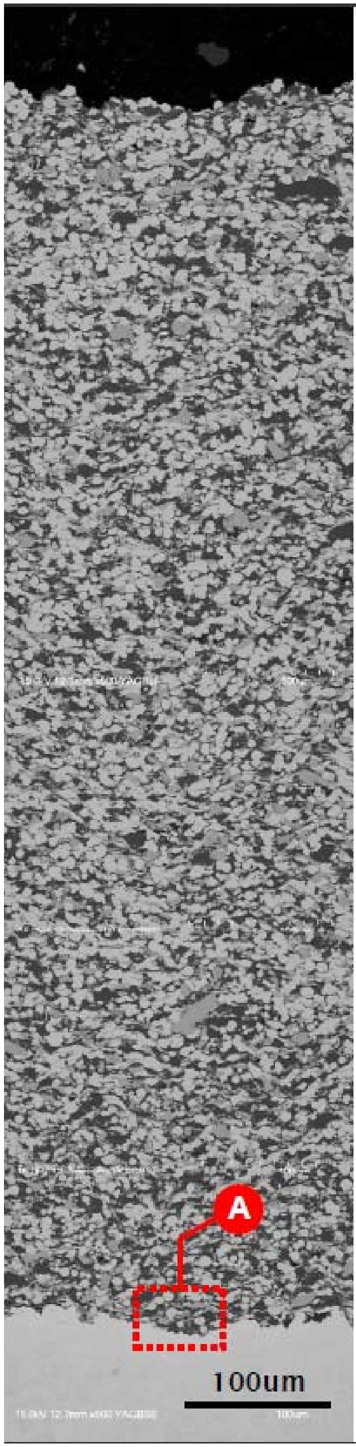
As-sprayed ODS coatings

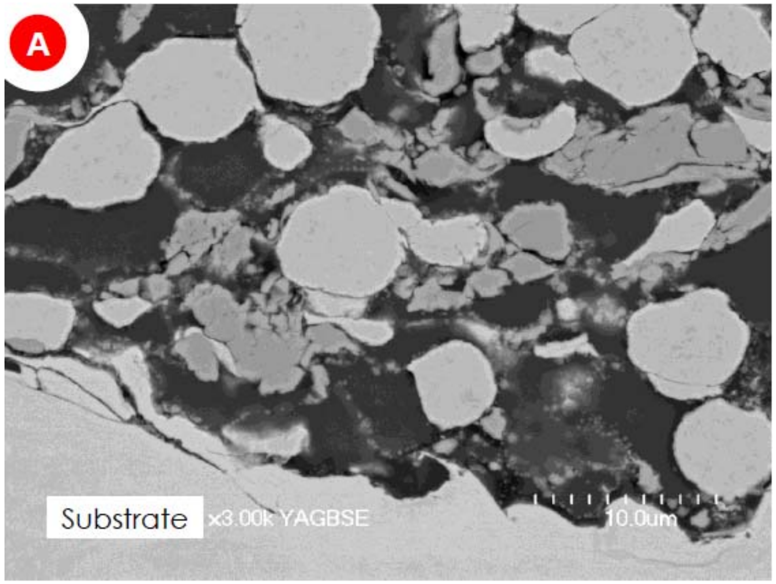


LP cold spray system used in this work

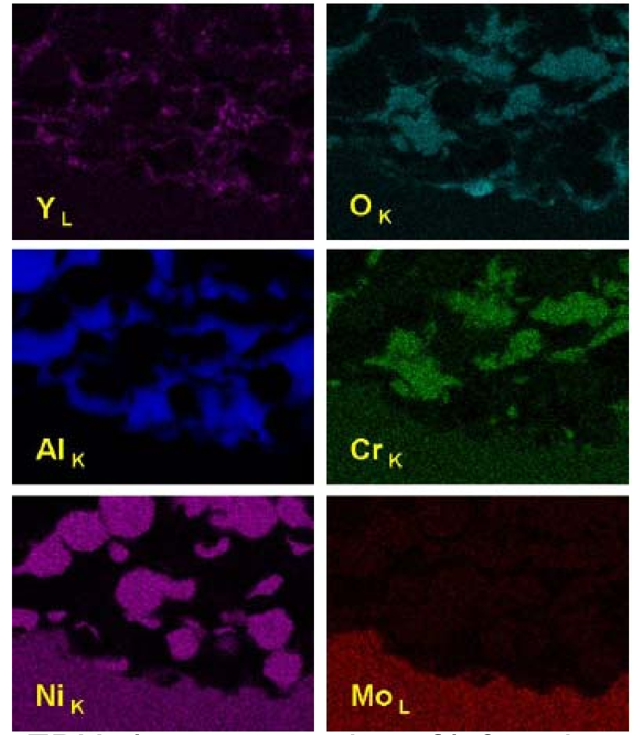
1)Successful in making a thick coating on hard substrate.
2)Powder feeding is not smooth, it shows a discontinuous flow. Powder dry process is desired additionally.

A1 coating & its EDX analysis



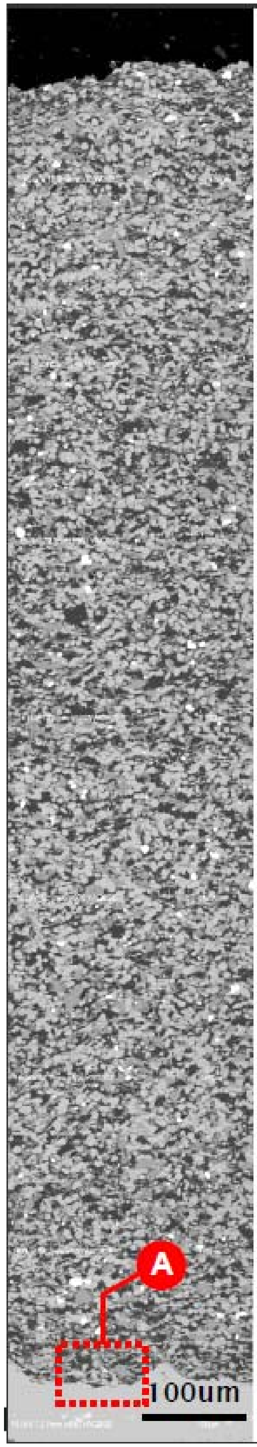


BSE image of region A, located at the coating/substrate interface

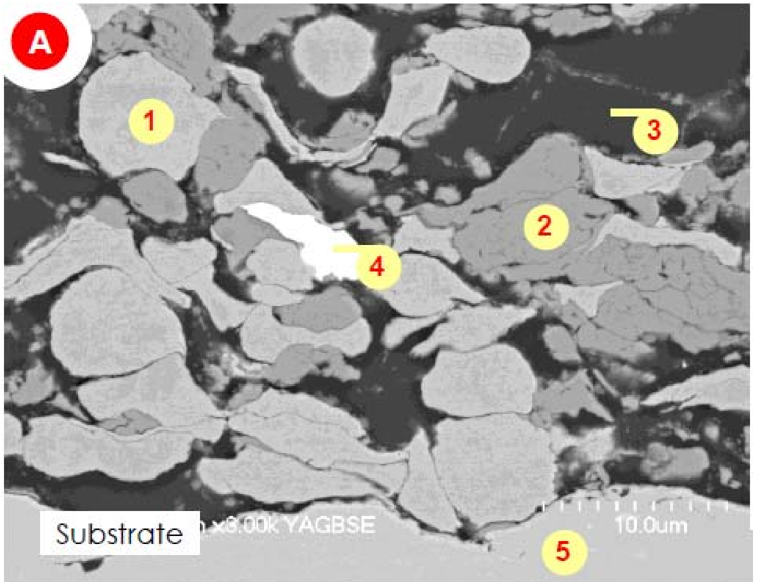


EDX element mapping of left region A

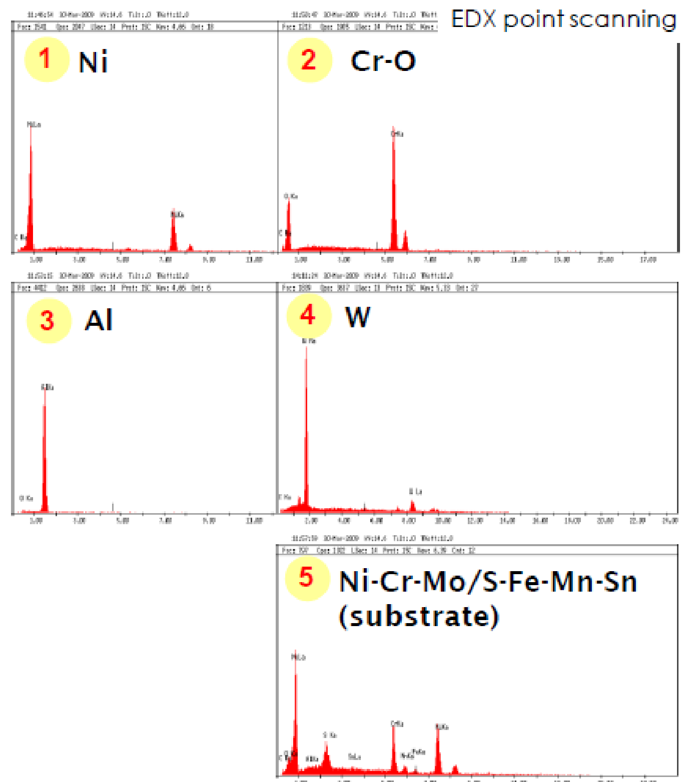
1)Coating is about 850um thick, dense, and well-adherent to each other particles. Most particles are well-distributed in whole coating layer, relatively uniform.
2)Most Al and Cr particles are full-deformed, especially the plastic deformation of Al particles may play an important role in the deposition mechanism.
3)Yttrium oxides are distributed uniformly at the interfaces among Al, Cr, Ni splats.
4)Most nickel particles keep their spherical shape with partial deformation only.
5)Chrome oxide showing in EDX maps results from the pre-holding compositions, may not from oxidizing in cold-spray gas stream.



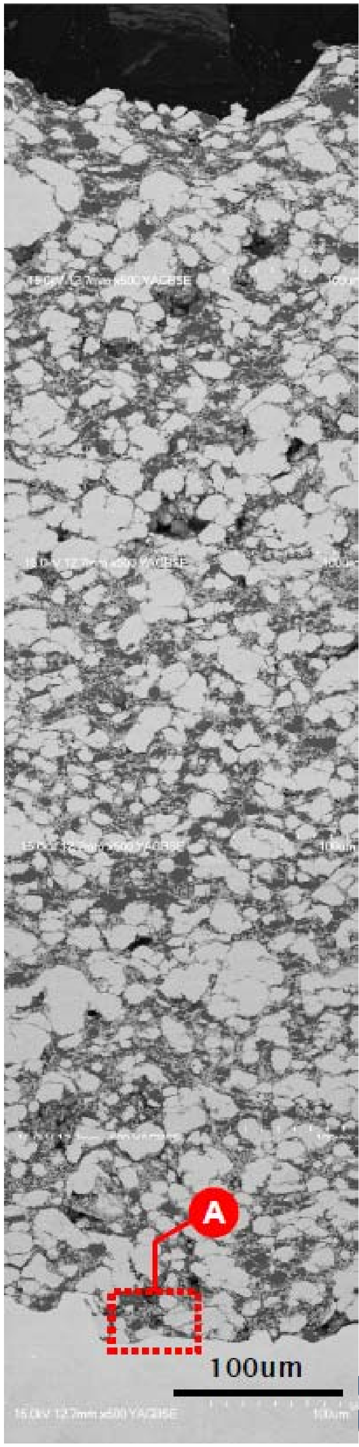
A2 coating & its EDX analysis



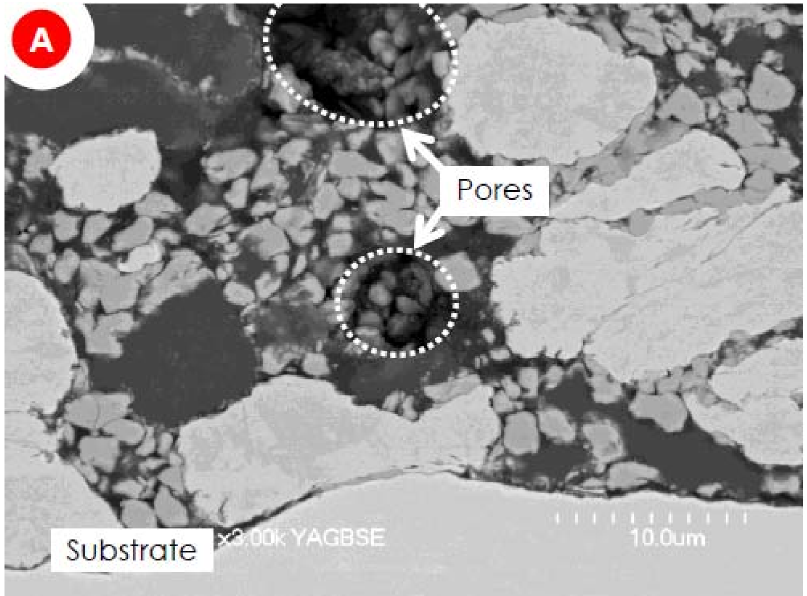
BSE image of region A, located at the coating/substrate interface.



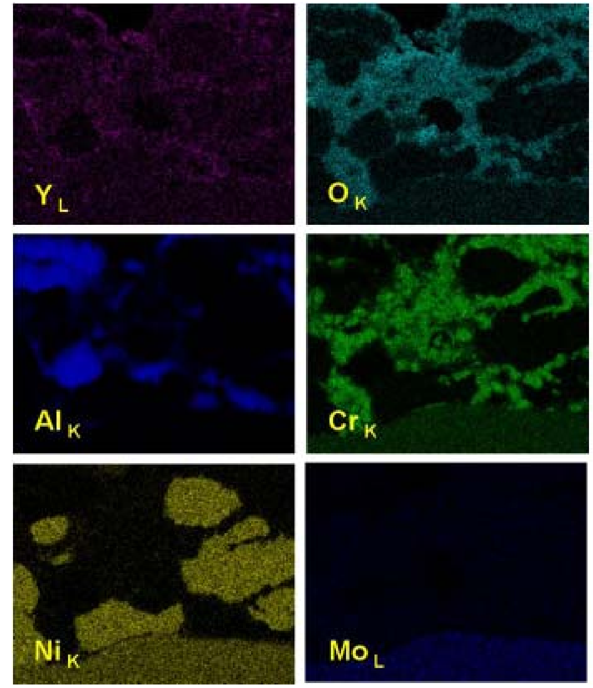
1)Coating is about 1,300 um thick, and its quality level seems to be similar with prior A1 coating, dense and well-adherent.
2)Most Al particles are full-deformed plastically and Cr particles are also well-deformed. Ni particle deforms more than Ni in A1 powder.
3)Few tungsten particles are observed with half-deformed form.



B1 coating & its EDX analysis



BSE image of region A, located at the coating/substrate interface.



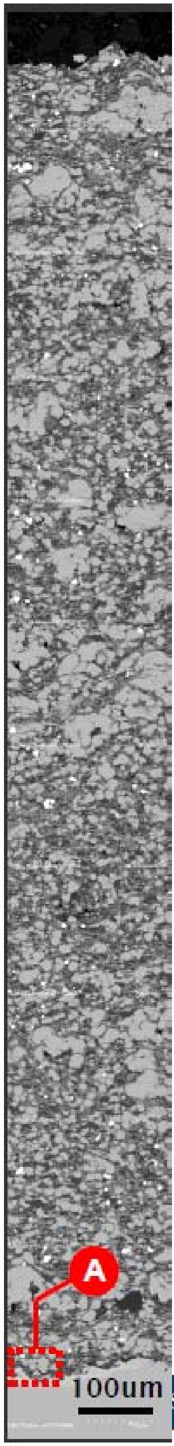
EDX element mapping of left region A

1)Coating is about 750um thick, and well-adherent to each other particles. Big pores are observed sporadically. It may be due to the relatively big, not-deformed Ni splats. But the interface (coating/substrate) adherence seems to be still good.

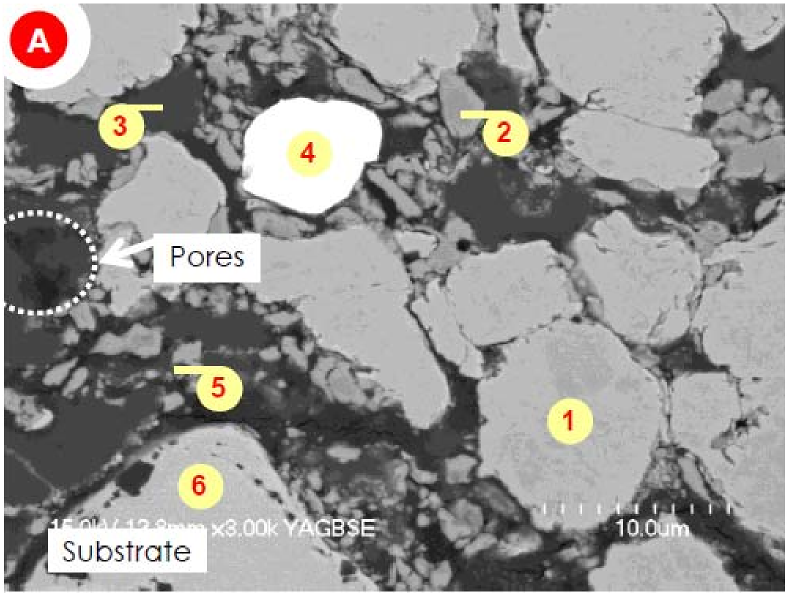
2)Most Al particles are full-deformed plastically. Crashed, tiny Cr particles are filled into the deformed Al splats, but Cr particles look to be not-deformed.

3)Yttrium oxides are also distributed well around the Al, Cr, Ni splats.

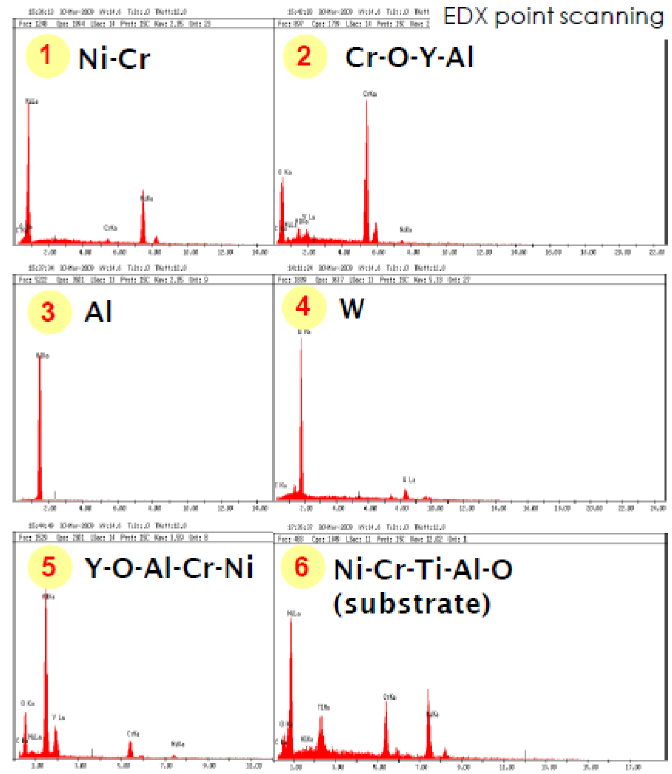
4)Nickel particles deform more than the A-series powders, many Ni splats adhere to the substrate directly. It may be due to the high kinetic energy caused by the heavy mass of Ni particle



B2 coating & its EDX analysis



BSE image of point A, located at the coating/substrate interface.



1)Coating is about 1,900um thick, and its quality seems to be similar level with prior B1 coating. Big pores are also observed.
2)Ni splats distribute uniformly, it may be one of reasons that there are many pores in side coating.
3)Few tungsten particles are observed with half-deformed form.
4)Interface (coating/substrate) adherence seems to be good

Part II: Summary

1. Successfully demonstrated ODS coatings on superalloy substrate by LP cold spray method. Thick and relatively uniform coating is possible with high deposition efficiency. Interface (coating/substrate) adherence also seems to be good.
2. Most Al and Cr particles are fully deformed, especially the plastic deformation of Al particles may play a main role in the deposition mechanism.
3. Yttrium oxides are also distributed well around the Al, Cr, and Ni splats.
4. In case of B1 and B2 coatings, pores are observed sporadically. It may be due to the relatively large, non-deformed Ni splats.
5. Few tungsten particles are observed with half-deformed form.
6. Additional powder dry process may provide better smooth, continuous feeding.
7. Joint provisional patent (Kang and Ogawa) on ODS coatings using HP and LP cold spray is in progress.

Planned Work

Old ODS Powder Mixes (in weight %) – 30 minutes MCB Processing

	Cr (7.5~10 µm)	Al (4.5 ~ 7 µm)	Y_2O_3 < 50nm	W (~1 µm)	Ni (4 ~ 8 µm)
A1	20	5	1.5	0	73.5
A2	20	5	1.5	3	70.5

	Cr (8~12 µm)	Al (4.5 ~ 7 µm)	Y_2O_3 < 50nm	W (2~4 µm)	Ni (8~15 µm)
B1	20	5	1.5	0	73.5
B2	20	5	1.5	3	70.5

New ODS Powder Mixes (in weight %) ~ 1.5 hours MCB Processing

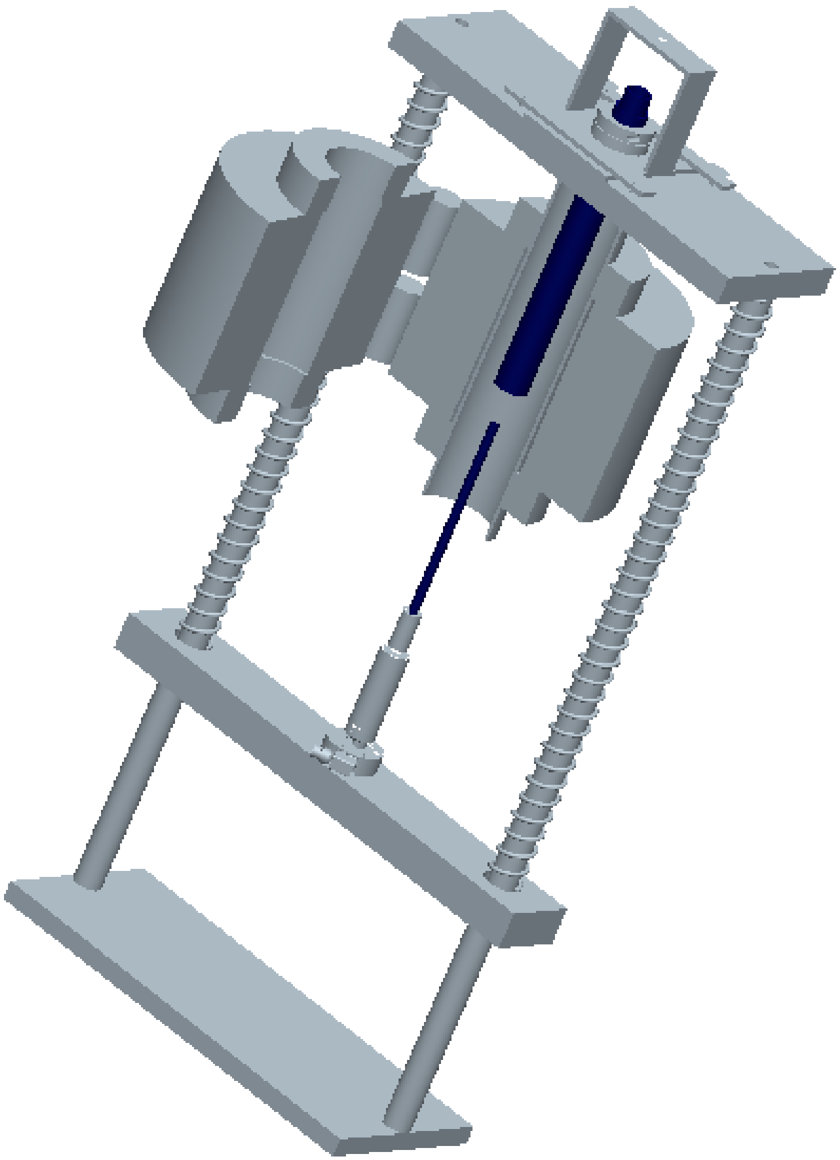
	Cr (7.5~10 µm)	Al (4.5 ~ 7 µm)	Y_2O_3 < 50nm	W (~1 µm)	Ni (4 ~ 8 µm)
A1*	20	5	1.5	0	73.5
A2*	20	5	1.5	3	70.5

	Cr (1~5 µm)	Al (1 ~ 3 µm)	Y_2O_3 < 50nm	W (~1 µm)	Ni (1~5 µm)
C1	20	5	1.5	0	73.5
C2	20	5	1.5	3	70.5

Mechanical Property Evaluation of ODS Coatings

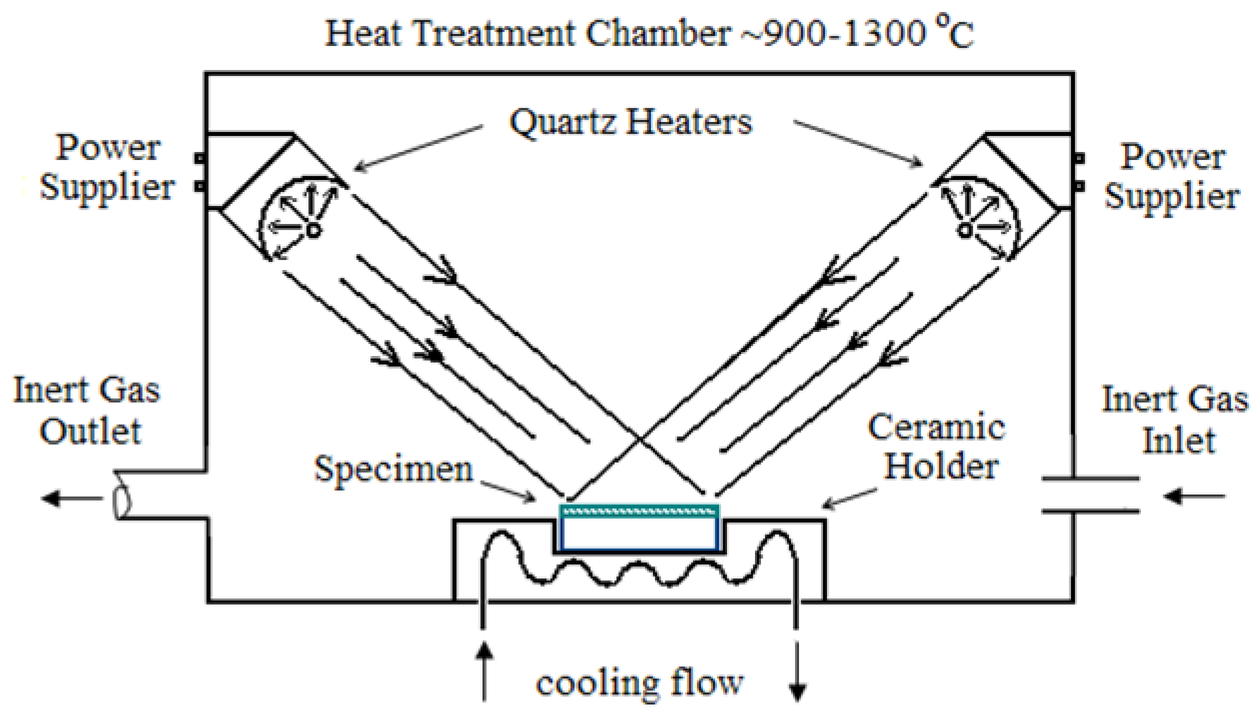
- **ODS Coatings subjected to isothermal and cyclic heating followed by RT micro-indentation testing**
- **High temperature mechanical property and creep strength measurement**

High Temperature Micro Indentation on ODS Coating



- *ATS Tube Furnace Capable of Temperatures to 1250°C (assembled, currently under proof testing)*
- *Inert Gas Testing Environment Equipped*
- *Inverted Indentation System Provides Minimal Thermal Drift*

ODS Coating Heat Treatment



Heat treatment of ODS alloys

- Optimize the grain size of alloy
- Control the precipitation of intermetallic compounds
- Examine the effect of oxides on the microstructure evolution at different temperature

Processes of Heat treatment of ODS alloys

- After any shaping process to achieve final or semi-final product configuration, the alloy of the present invention is heat treated in the solid state by solution annealing at 1275-1300°C, for one hour followed by air cooling.

- The alloys are then hardened by heating in the range of about 925-1000°C for about 1 to 12 hours, air cooling and then holding at a temperature of about 830-860°C for 12 to 60 hours followed by air cooling.

Evaluation of microstructure of ODS after heat treatment:

- Examine the microstructure by optical microscope
- Observe the size, shape and distribution of oxides and intermetallic compounds by atomic force microscope
- Further analyze the oxide and intermetallic compound by transmission electron microscope (TEM)
- Check the grain size by TEM and optical microscope

SEM/EDX, XPS, AFM, XRD, TEM are available at WVU

Thank You !