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Al계 준결정 분말의 제조 및 응용

제3회 최신분말제품 응용기술 workshop

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Contents of talk

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What is quasicrystals ?

- ► Crystal : periodic sharp diffraction pattern showing
  2, 3, 4, or 6 rotation symmetry
  Periodic distribution of atoms translation & rotation order
- ► Quasicrystals : sharp diffraction pattern but with aperiodic
  distribution of diffraction spots with 5, 8, 10 or 12-fold
  rotation axis
  Aperiodic distribution of atoms with rotation order
- ► Amorphous : diffuse halo pattern
  Random distribution of atoms

•1991, International Union of Crystallography
"crystal" : *any solid having an essentially discrete diffraction diagram*

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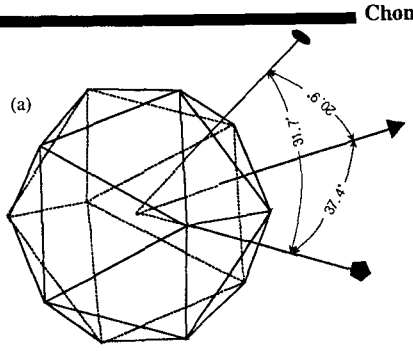
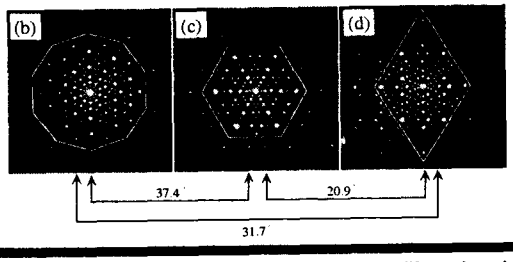
Icosahedral phase

1984 by D. Schechtman
Al-Mn alloy (RSP)



Stable I phase
Al-Cu-Fe,
Mg-Zn-Y,
Ti-Ni-Zr etc.



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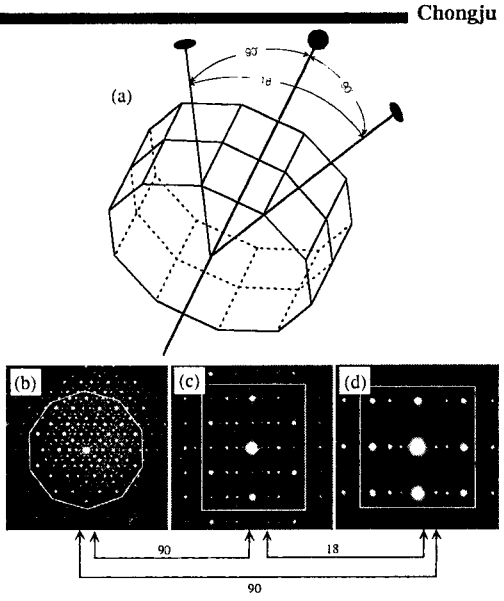
Decagonal phase
- 2D quasicrystal

Al-Ni-Co,
Al-Cu-Co etc



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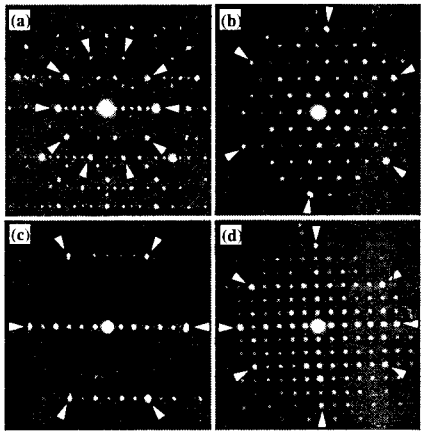
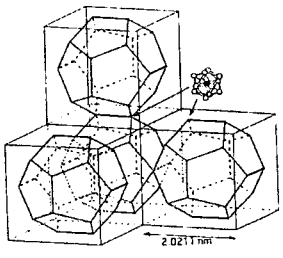
Cubic approximant phase in the Al-Cu-Fe-Si system





(a) pseudo 5-fold axis
(b) pseudo 3-fold axis
(c) another pseudo
3-fold axis
(d) pseudo 2-fold axis

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Comparison of properties of Quasicrystals with others

		Density (g/cm^3)	Thermal conductivity (W/mK)	Thermal expansion ($10^{-6} K^{-1}$)	Adhesion energy (mJ/m^2)	Electrical resistivity ($\mu\Omega cm$)
Quasicrystals	Al-Cu-Fe	3.5-4.5	1.8	14-19	57-67	2500
	Al-Co-Fe-Cr	3.5-5.0	2.3-4.0	14-19	62-72	-
Metals	Al alloy	2.7	202-243	24	97.8	2.65
	Cu	9.0	387	17	105	1.7
	Steel	7.8	62-90	12-20	98	9.7
Ceramic oxides	Al_2O_3	3.5-3.9	3.4-3.5	8.4	120	>100000
	ZrO_2 + 8%Y_2O_3	5.6-6.0	1.8-2.7	7-9	-	>10000

Comparison of properties of Quasicrystals with others

		Young's modulus (GPa)	Fracture strength (MPa)	Elongation at rupture (%)	Micro-hardness (kg/mm^2)	Coefficient of friction
Quasicrystals	Al-Cu-Fe	130-140	250-690	0.35-1.10	715-750	0.12
	Al-Cu-Fe-B	140	595-1010	0.65-0.85	670-850	0.15
Metals	Al alloy	72	325	15.0	87	0.37
	Copper	130	235	45	48	0.42
	Low carbon steel	205	620	32	120	0.32
Amorphous alloys	Al-Zr-Ni	80.4	800	1.4	340	-
	Al-Y-Ni	71.2	1140	1.6	300	-

Physical properties of Al-Cu-Fe icosahedral phase

Young's modulus : 61-110 Gpa
Elongation at fracture : 0.35-1.1 %
Microhardness Hv : 7.15 GPa
Thermal conductivity : 1.8 W/mK
Thermal expansion coefficient : 14-19 x 10^{-6} K^{-1}
Low friction coefficient : 0.05-0.4
High corrosion resistance
Electro-optical property
Low surface energy : 24-25 mJ/m^2
Fracture toughness : 1 $MPam^{1/2}$

Physical properties of the Al-Ni-Co(-Si) decagonal phase

- ✓ Young's modulus : 165 GPa
- ✓ Elongation at fracture : 0.9 %
- ✓ Microhardness Hv : 8.3 GPa
- ✓ Thermal conductivity : 2-6 W/mK
- ✓ Thermal expansion coefficient : 14-19 x 10^{-6} K^{-1}
- ✓ Low surface energy
- ✓ Low friction coefficient
- ✓ Good oxidation/corrosion resistance
- ✓ Electro-optical property

Potential application of I phase

- ▶ Structural application
  Composite material consisting of ductile phase : ex-situ or in-situ
  - ► High-strength Al alloys : Al with I precipitation
  - ► Surgical tools, electric shavers : Maraging steel with I precipitation
  - ► Mg alloy strengthened by I phase
- ▶ Functional application :
  Thin film or thick film applications :
  Thermal barrier coating (low thermal conductivity)
- ▶ Wear resistance coating (low friction coefficient)
  - ► Coating of powertrain tools
- ▶ Non-stick coating (low surface energy)
  - ► Cookware
  - ► Non-stick, wear resistant tire mold coatings
  - ► Injection molding cavity surface enhancements

Composites :
quasicrystalline particles + crystalline/amorphous matrix

Fabrication :
PM method : Al-Cu-Fe + alloy powder
Casting : mixture of Al-Cu-Fe + alloy melt
→ But the microstructure is thermally unstable

Nano composites by solid state transformation or
controlled cooling for specific alloys
→ But it needs consolidation process

In-situ composites by casting

Advanced Al alloys using quasicrystalline particles*

High elevated temperature strength alloy : Al-Fe-Cr-Ti system.
Hot extrusion of gas atomized powder
: 400 nm sized I-phase and 500 nm sized Al grain.

σ_F = 400-460 MPa at 473 K

σ_F = 350-360 MPa at 573 K.

Excellent thermal stability : 200 h at 573 K

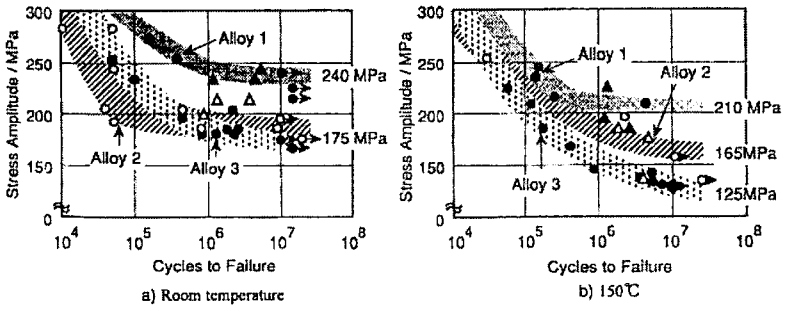
Ductile Al alloys : Al-Cr-Ce-Co alloys
Hot extrusion of gas atomized powder
: I-phase + Al

σ_f = 500-600 MPa with 12-30 % of plastic elongation

⇨ **Composites is a route to solve brittleness problem of I-phase**

* A. Inoue, Progress in Materials Science, 43(1998), 365

Nanoquasicrystalline particles in Al-based system

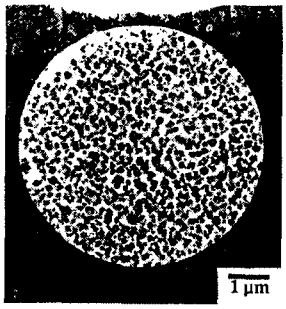


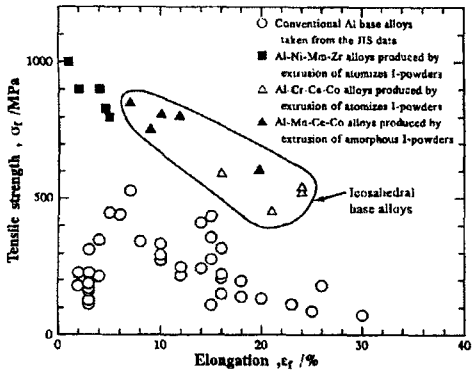
Fatigue testing results—S–N curves (○: normal fracture; △: fretting fracture).

Alloy 1: Al-4.35Cr-2.96Co-4.68Mn-3.06Zr (α_{Al}+QC)
Alloy 2 : Al-4.35Cr-2.96Co-4.68Mn-3.06Zr + 5% SiC
Alloy 3 : Al-11.8Si-4.22Cu-0.63Mg

Nanoquasicrystalline particles in Al-based system

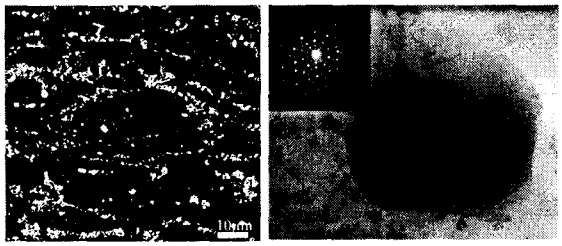
➢ Extrusion of atomized icosahedral powders





Typical bright field TEM image and SADP $Mg_{86}Zn_{12}Y_2$ alloy.

Mg-Zn-Y alloys in-situ composites

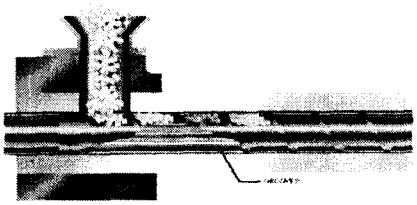


Alloy	Grain size μm	Vol. fraction of 2nd phase	Yield Stress ($s_{0.2}$), MPa	UTS, MPa	Elongation %
AZ31	17.6		152	275	22.0
AZ61	9.9		175	320	19.8
AZ91	13.4		225	395	18.2
$Mg_{96}Zn_{3.4}Y_{0.6}$	7.8	0.08	210	355	23.4
$Mg_{95}Zn_{4.3}Y_{0.7}$	7.7	0.09	220	370	19.7
$Mg_{94.8}Zn_{4.3}Y_{0.7}Zr_{0.2}$	7.8	0.09	180	325	23.5

Structural	Functional
Dispersion of fine icosahedral phase in Al solid solution in Al-Li-Cu-Mg alloy (Sainfort et al., 1987)	Non-sticking quasicrystalline coatings (Dubois et al., 1991) commercial cookware
Precipitation of icosahedral structure in maraging steel (Nilson et al., 1998 Sandvik Steel) commercial maraging steel used in razor blade and surgical tools	Selective light absorber (Eisenhammer et al., 1994)
High strength Al-based alloy reinforced by nano-quasicrystalline phase (Inoue et al., 1999)	Hydrogen storage in Ti-ZrNi icosahedral quasicrystal (Kelton et al., 1997)
Polymer composite reinforced by Al-Cu-Fe quasicrystalline particles for biomedical applications (Sheares, 1999)	Thermoelectric power generation (Cyrot-Lackmann, 1997)
Quasicrystalline particles as strengthening phase in Mg-Zn-Y alloys (Kim et al., 2000)	Quasicrystals as precursor of catalyst (methanol steam reforming) (Tsai et al., 2001)

Potential applications of QC coatings

- Plastic injection machinery : barrel and mold : low friction, no-sticking and wear properties,



- Blades in paper industry and in printer : low friction, no-sticking and wear properties,
- Metallic tubes currently used in power plant, chemical plant, petroleum plant and maritime applications to insulate and/or to protect against oxidation/corrosion.

Powder making

- **Casting and crushing**
- **Gas atomization**
- **Mechanical alloying**

Quasicrystal formation by MA/ heat treatment

Al-Cu-Fe system : stable I phase
Ti-Zr-Ni system : stable I-phase up to around 838 K.

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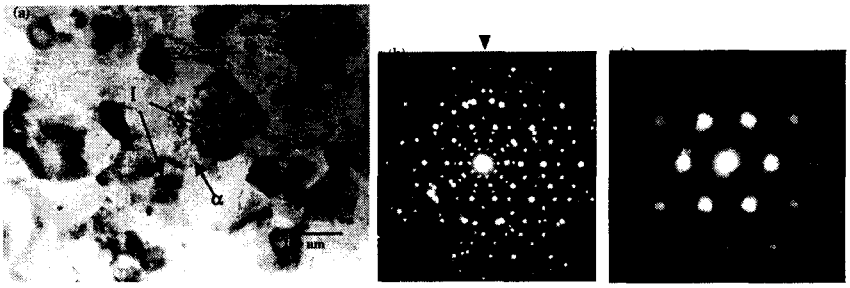
TEM of the bulk $Ti_{41.5}Zr_{41.5}Ni_{17}$ sample, annealed at 807 K for 15 hrs



Formation of nanocomposites consisting of I-phase+α phases.

The bulk specimen shows microhardness around 6.2 GPa and much more ductile characteristics than the single I-phase sample.

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Gas atomization

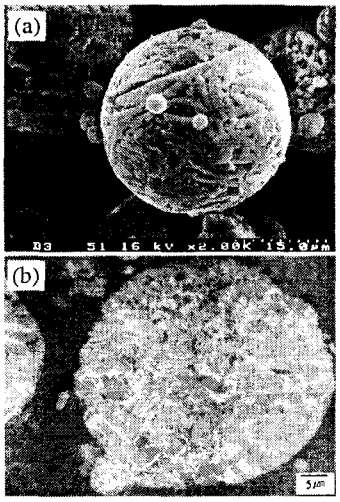

Fig. Gas atomized Al-Ni-Co-Si powder

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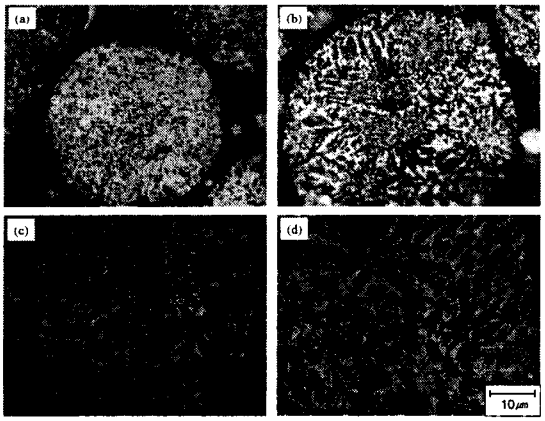
Microstructual change with powder size in Al-Cu-Fe powder



(a)+400mesh, (b)+325mesh, (c) +200mesh, and (d) +100mesh

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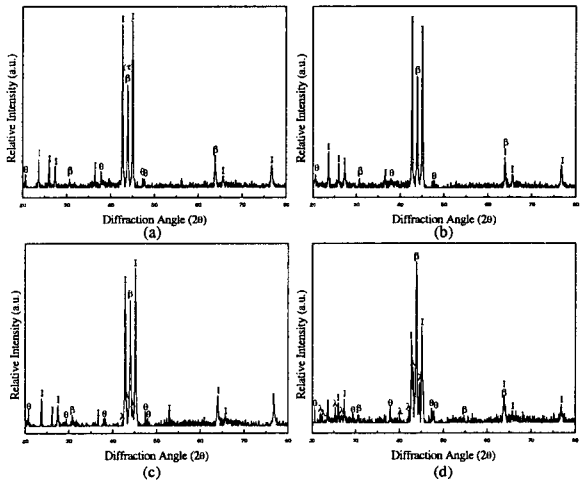
XRD trace of $Al_{62}Cu_{26}Fe_{12}$ gas-atomized powders



(a)+400mesh, (b)+325mesh, (c)+200mesh, and (d)+100mesh

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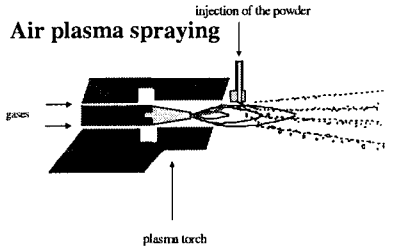
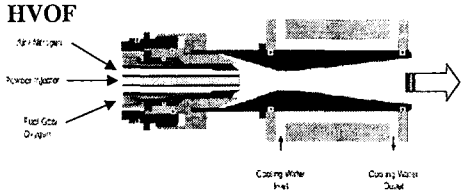
Comparison between APS vs. HVOF

Air plasma spraying



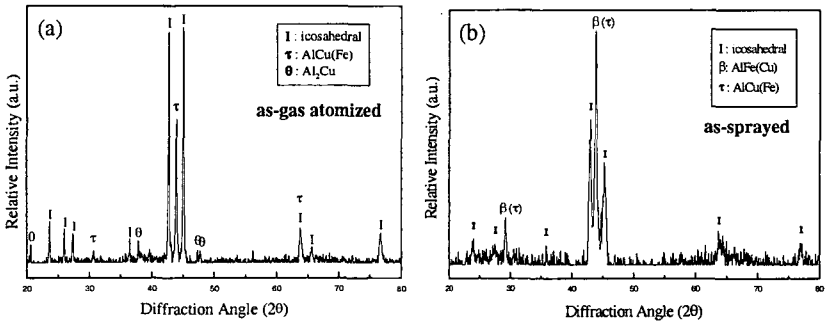
High temperature plasma ~ 15000℃,
Velocity of the plasma gas ~ 650 m/s,
Length of plasma flame : short (~ 3 cm),
Large temperature gradient in particles,
Porosity level between 8 to 16%.

HVOF



Temperature of flame zone : ~3000 ℃,
Velocity of the gas ~2000 m/s,
Length of the flame : long (~20 cm),
Low temperature gradient in particles,
Porosity level less than (<5 %),
Wider window for process optimization.

Al loss during gas atomization and APS processes



Condition	gas-atomized powder	coating run A (300A)	standard condition (400A)	coating run B (500A)
Composition	$Al_{62}Cu_{26}Fe_{12}$	$Al_{59.9}Cu_{24.5}Fe_{15.6}$	$Al_{58}Cu_{25.7}Fe_{15.7}$	$Al_{58.5}Cu_{25.8}Fe_{15.7}$
Al recovery	99.2 %	95.8 %	93.8 %	93.6 %

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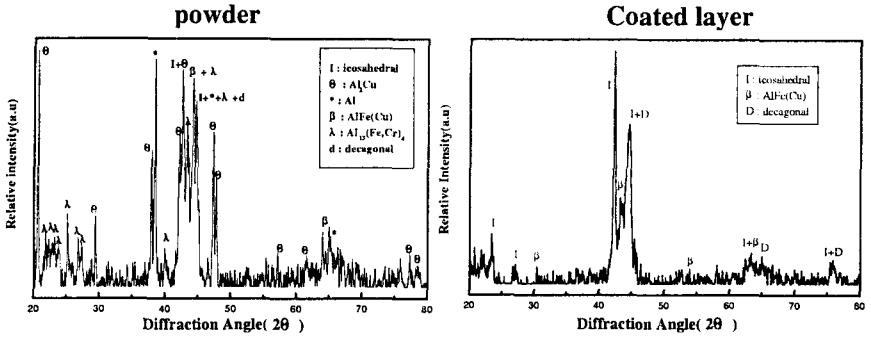
Target alloy composition : $Al_{70}Cu_{10}Fe_{13}Cr_7$



Complex phase distribution in powders is due to excess Al content
Coated layer consisted of expected phases

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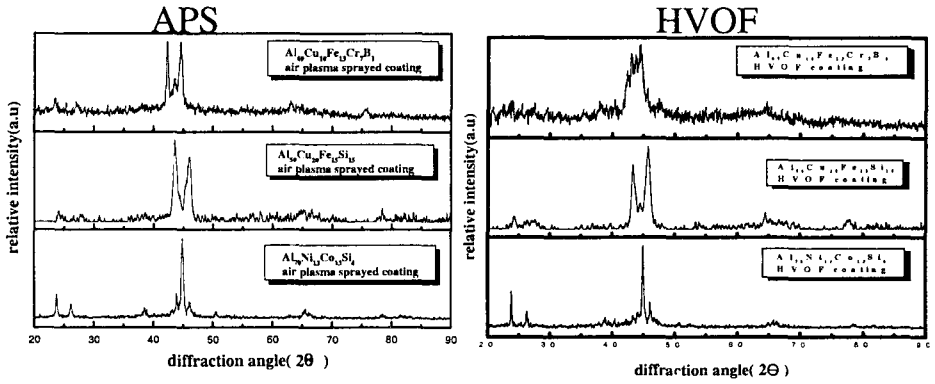
XRD results of various specimens



No significant difference in microstructures between
APS and HVOF specimens

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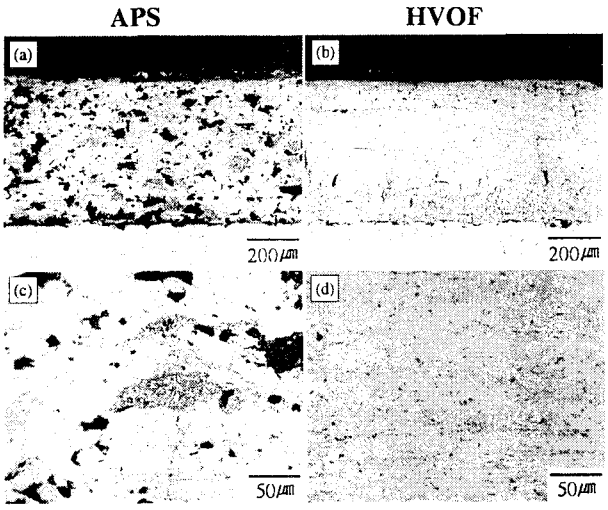
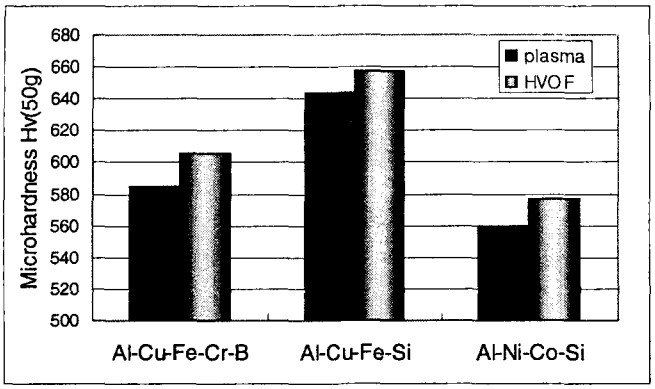
Optical microstructure of Al-Cu-Fe-Si doposites



Comparison of microstructure in APS and HVOF coatings

APS	HVOF
Partially melted particles : - large temperature gradient in powder - different particle trajectories owing to the particle injection perpendicular to the plasma flame.	- Low porosity level in coatings due to high particle velocity, -small temperature gradient in particle due to long flame zone.
Porosity level : between 10 to 15 %.	Porosity level : between 2 to 4 %
Suitable for thermal barrier coating	Suitable for wear resistance application

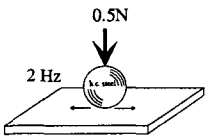
Plasma and HVOF coatings: microhardness



Tribological tests

- Polisding : Ra < 0.2μm.
- ultrasonic cleaning in ethyl alcohol for 10 min.

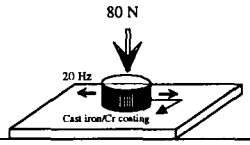
pin-on-plate experimental device



- Load = 0.5 N, pressure = 160 MPa
- Sliding velocity = 0.08 m/sec,
- Sliding distance = 80 m
- Counterpart material = high carbon steel, WC

Small contact area

flat-on-plate experimental device



- Load = 80N, pressure = 0.7 MPa
- Sliding velocity = 0.56 m/s,
- Sliding distance = 560 m.
- Counterpart material = cast iron/Cr coating

Large contact area

Similar contact pressure and sliding velocity to those of piston motion in auto engine.

Why friction coefficient is so different ?

Scratch test :
. ~ 0.22 (Al-Cu-Fe deposit)
. ~ 0.19 (Al-Cu-Fe-Cr-Si deposit)
~ 0.05 (Al-Cu-Fe against diamond)
~ 0.15 (Al-Cu-Fe against WC)

Pin on disk : steel ball Ø 6.3 mm
. ~ 0.15 (Al-Cu-Fe ingot)
0.1-0.15 (Al-Cu-Fe-X deposit)

Pin on disk : flattened ball
0.2-0.35 (Al-Cu-Fe-X deposit)

Flat on disk : flat Ø 8 mm
0.35-0.45 (Al-Cu-Fe-X deposit)

The variation of friction coefficient is sensitive to contact area :

Large contact area is favorable for formation of stable intermediate layer,

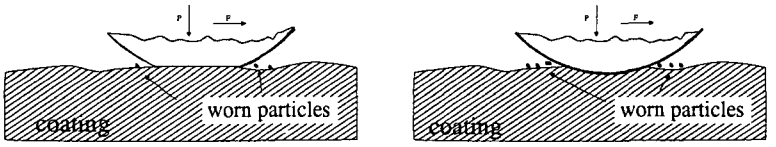
Friction coefficient between two intermediate layers are measured

Influence of indenter geometry and contact area on friction

Small tip radius

soft indenter

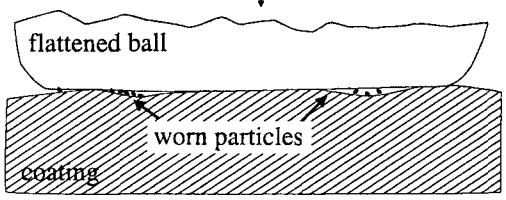
hard indenter



Dominant friction mechanism : adhesion

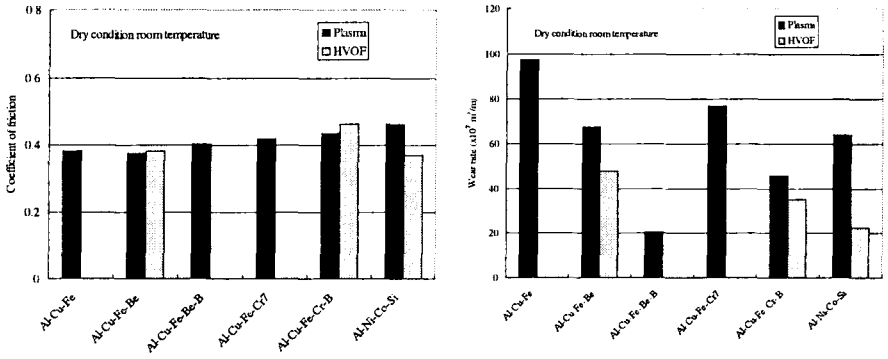
Friction mechanisms : adhesion and plowing

Flattened ball



Friction mechanisms : adhesion (with transfer?), and abrasion

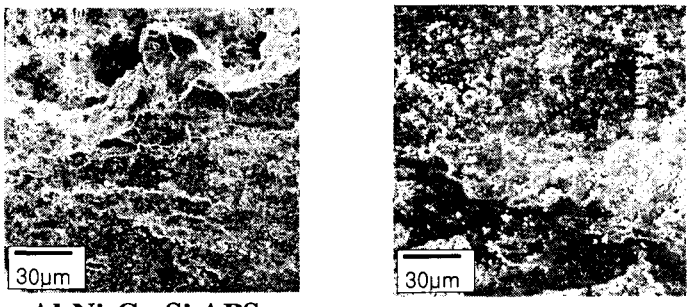
Friction coefficients and wear rates of coatings



Dry condition, RT, Flat on plate

SEM image of worn surface

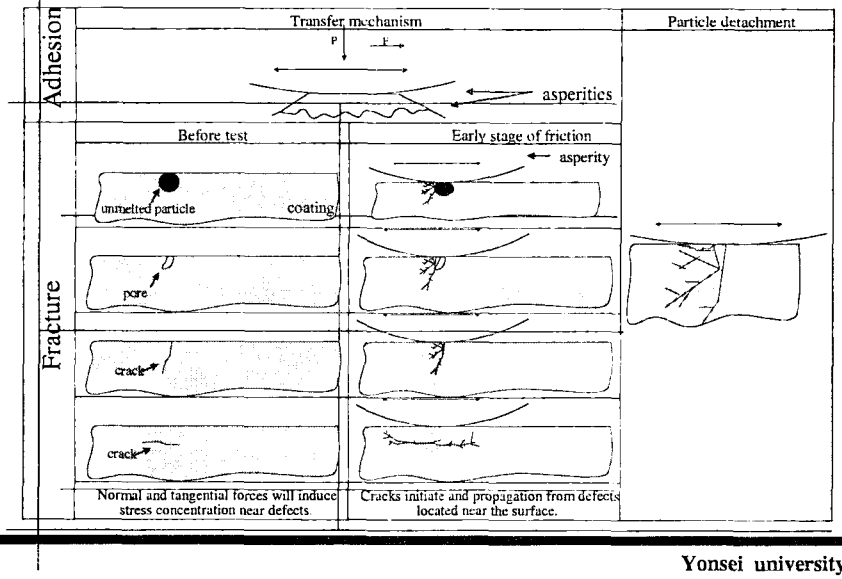
Sliding direction



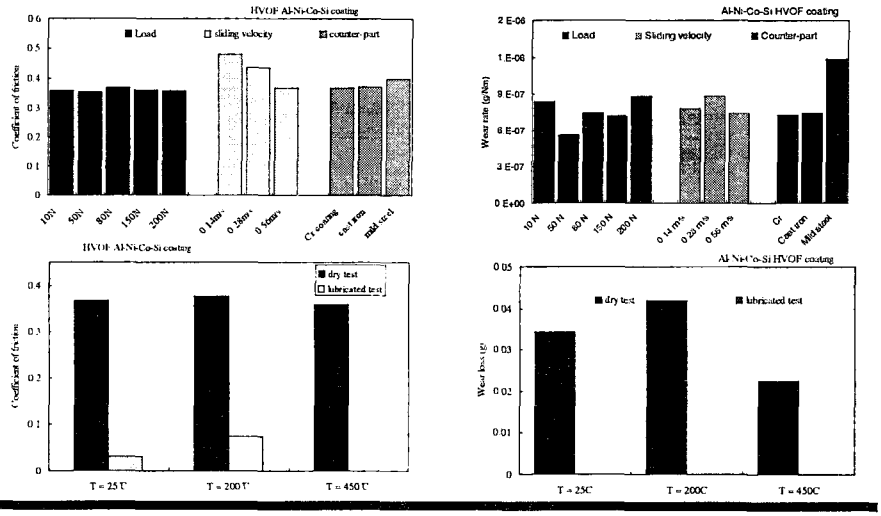
Al-Ni-Co-Si APS **Al-Ni-Co-Si HVOF**

Higher wear loss in APS coating due to
high porosity and inhomogeneous microstructure

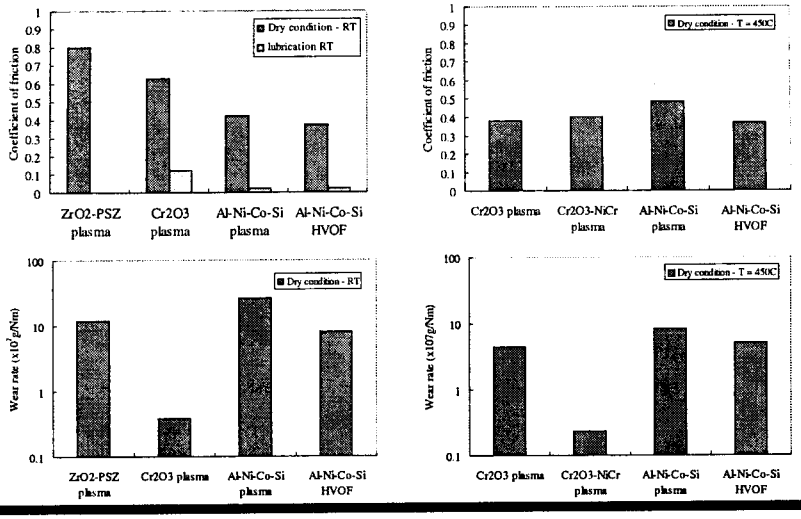
Wear mechanisms



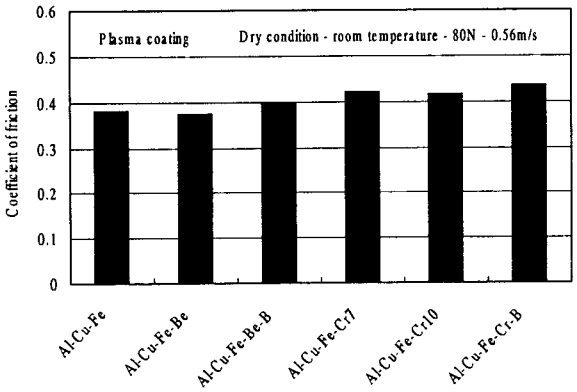
Influence of test conditions on friction coefficients



Comparison with ceramic coatings



Coefficient of friction (dry condition at RT)



Brass	0.56
Mild Steel	0.67
SUS	0.52
Plasma PSZ	0.78
Plasma Cr_2O_3	0.61

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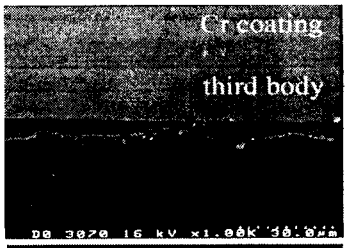
Intermediate layer formation on flat and coating surfaces

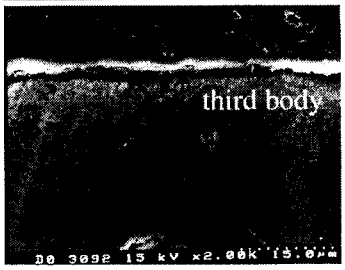
Al-Ni-Co-Si HVOF coating (at room temperature)

flat



intermediate layer on flat surface

Coating layer



Dense intermediate layer on surface

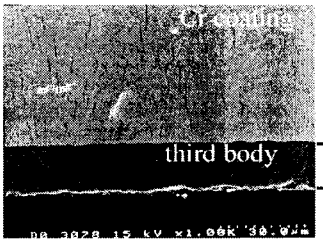
Arrow indicates the formation of lateral crack for detachment

Chongju university

Intermediate layer formation on flat and coating surfaces

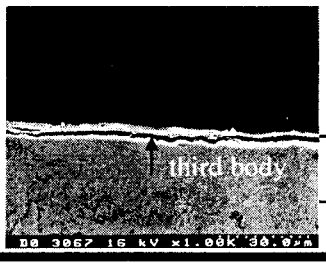
Al-Ni-Co-Si HVOF coating (at 450 K)

flat



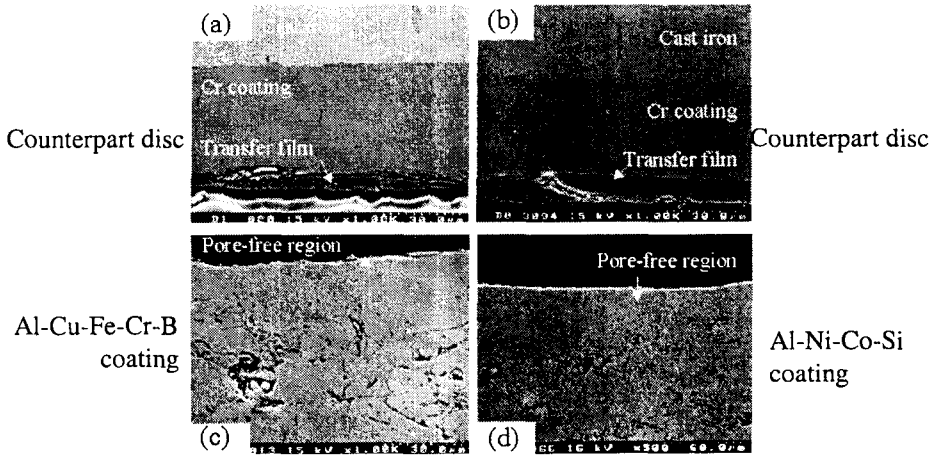
intermediate layer on flat surface

Coating layer



Dense intermediate layer on surface

Evolution of the contact surface after friction tests
APS coatings of Al-Cu-Fe-Cr-B and Al-Ni-Co-Si alloys



Amorphous powder coating

Amorphous structure : homogeneous, wear and corrosion resistance

Precursor to nanostructure : suitable heat treatment

Armacor powder (LMT)
- **Fe-Cr-B-Ni-Mo powder coating**
- **Glass coating by twin wire arc spraying**
- **HVOF spraying : glass fraction is very low**

Super-hard steel coating (DOE's INEEL)
- **Fe based amorphous coating**
- **A tough, low cost, wear and corrosion resistant coating**
  - **Hardness : up to 16 GPa**
  - **one of top 100 technologies (2001)**

Summary

1. Quasicrystalline powders shows exotic physical and mechanical properties
2. Applications :
   structural application : strengthening particles for composites
   Coating application : wear resistance, low friction coefficient
3. For thermal spaying : material loss during process should be considered to control chemical composition of deposit
4. Friction coefficient is strongly dependent on contact geometry
   Friction coefficient from pin on plate : 0.1-0.2
   Friction coefficient from flat on plate : about 0.46.
5. Quasicrystalline materials show lower friction coefficient but higher wear rate than corresponding values of Cr_2O_3 coated layer.
6. Amorphous coating seems to be promising