Symposium C31; Abstract No. 1826

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High temperature stability of MGC gas turbine components in combustion gas flow environments

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EUROMAT 2005
5 –8 September 2005
Prague, Czech Republic

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(1) Final targets of MGCs applied gas turbine system
(2) High-temperature stability of the trial components
(3) Possibility of low-cost process technology by near-net shape casting
(4) Basic exposure test in combustion gas flow environment

3. Improvement of high-temperature strength characteristics:

(1) The refinement of the binary MGCs microstructure
(2) Introduce of recently developed the new ternary MGC

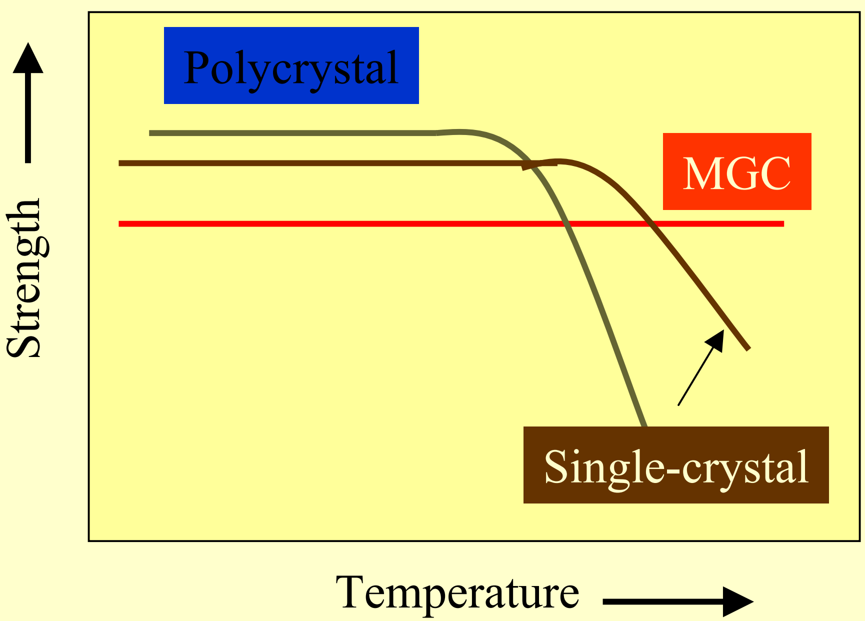
4. Another applications to making use of composition and properties MGCs

Background

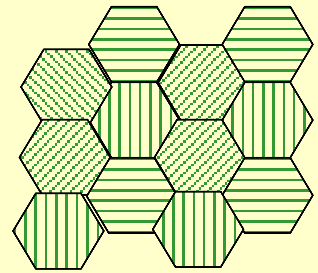
1. Global warming prevention & Energy-saving

2. Thermal efficiency improvement;
Develop high-performance structural materials
→Stable remain at 1500 ºC or higher in air
→ improvement of microstructure oxide

MGC's microstructure have superior high temperature strength that overcome polycrystal and single-crystal materials.



Polycrystal

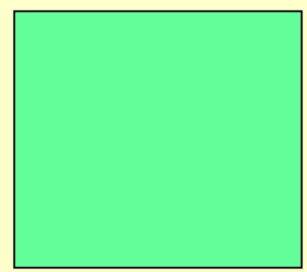


- Micro grain superplasticity due to grain-boundary sliding or rotation at high temperature

↓

- Remarkable decrease of high temperature strength of oxide ceramics

Single-crystal



- No barrier (interface) to disturb dislocation motion

↓

- Gradual decrease of high temperature strength

MGC

- No grain-boundary sliding or rotation (against polycrystal)
- Interface prevent dislocation motion (against single-crystal)

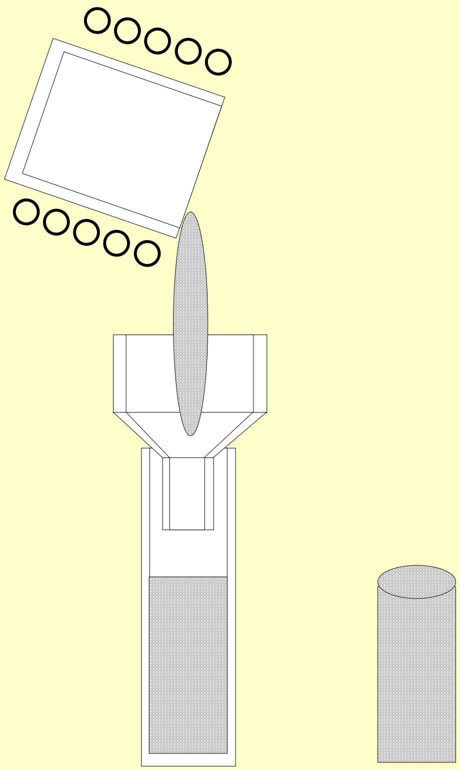
↓

- Excellent high temperature strength

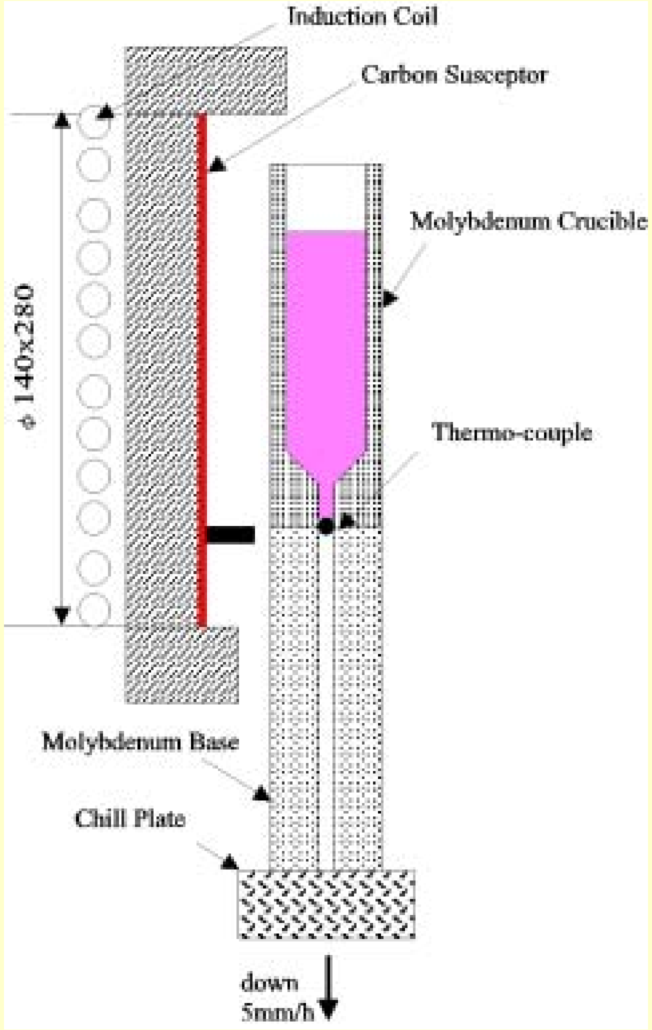
Fabrication Process

Commercially available Al_2O_3 powder and Y_2O_3 powder or Gd_2O_3 powder were mixed for the mole ratio of eutectic composition. Preliminary melting is performed by high-frequency induction heating and casted into to a molybdenum crucible to obtain an ingot. Unidirectionally solidification was carried out by using the Bridgman type furnace.

○Al_2O_3／YAG :
Al_2O_3／Y_2O_3＝82/18 mole % ratio
○Al_2O_3／GAP :
Al_2O_3／Gd_2O_3＝78/22 mole % ratio

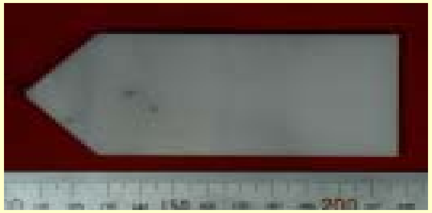


Ingot making



Unidirectional Solidification

Molybdenum divided mold

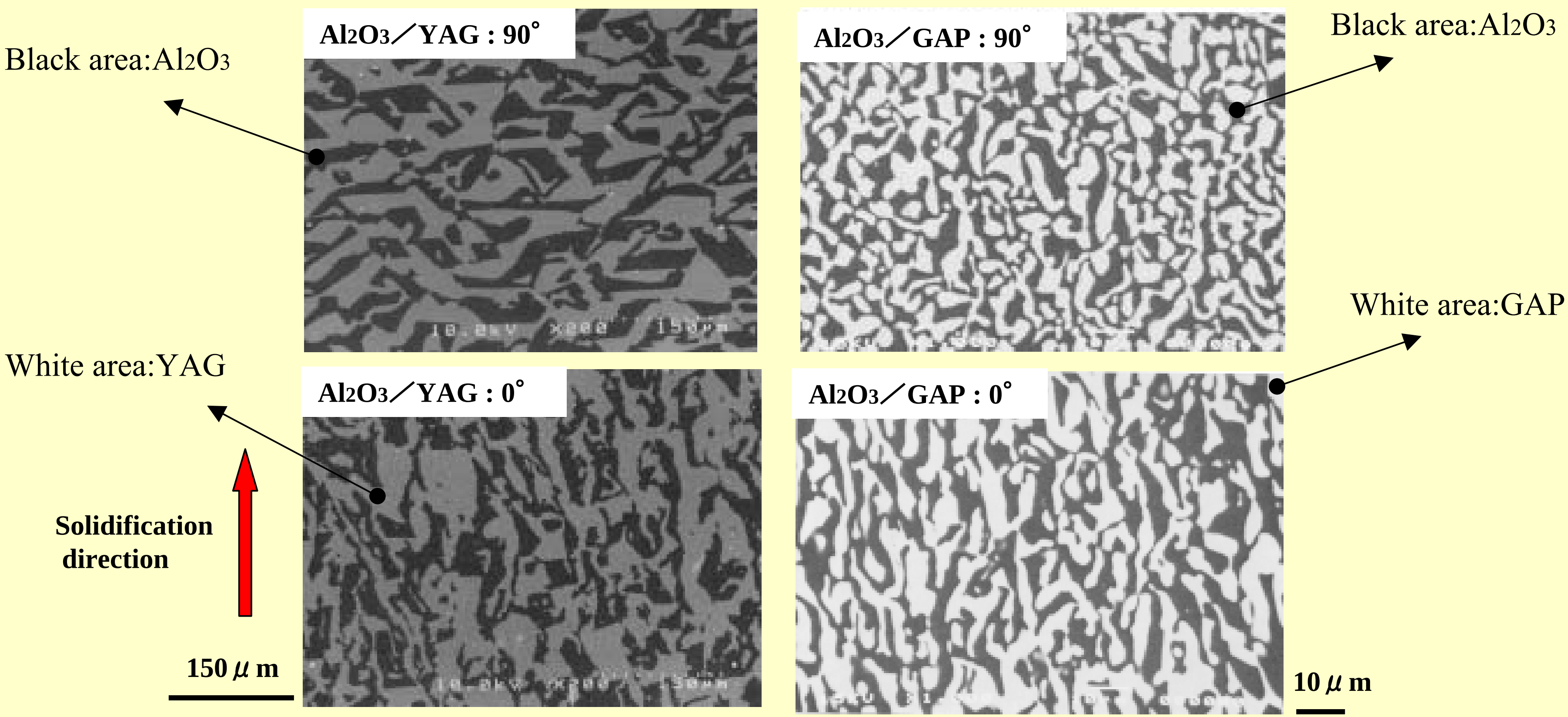


Al_2O_3/YAG plate (45*90*6)

Al_2O_3/GAP rod (Φ53 mm)

Microstructures

The MGC materials have new microstructures, which are composed of continuos network of single-crystal Al_2O_3 phases and single-crystal oxide compounds (YAG, GAP) without grain boundaries.

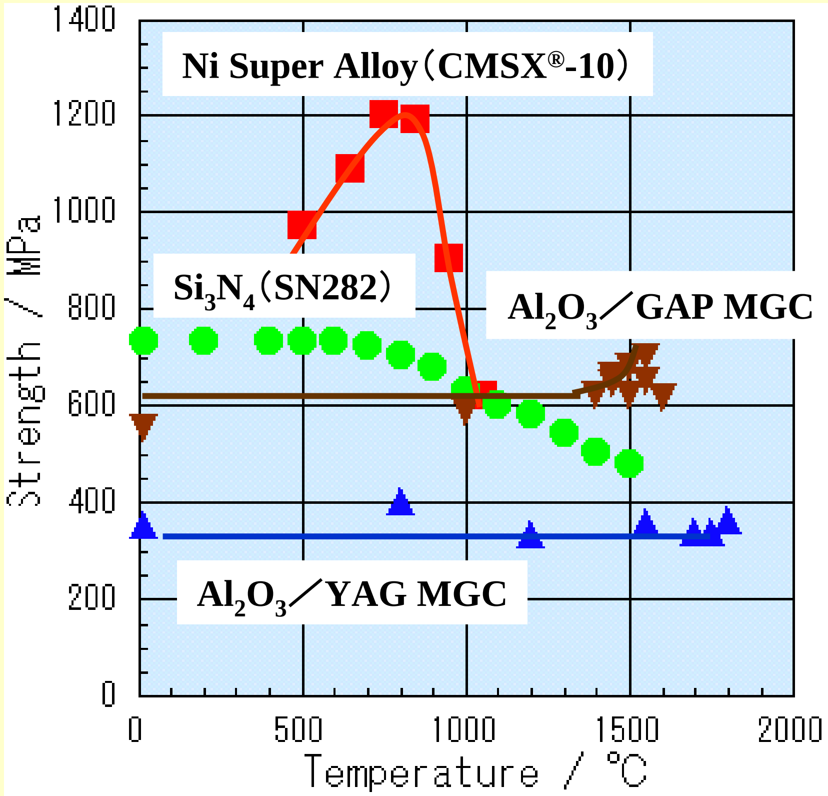


SEM images of the microstructures of cross section perpendicular (90º direction) and parallel (0º direction) to the solidification direction of the MGC materials.

$Y_3Al_5O_{12}$ (YAG : Yttrium Aluminum Garnet) , $GdAlO_3$ (GAP : Gadolinium-Aluminum-Perovskite)

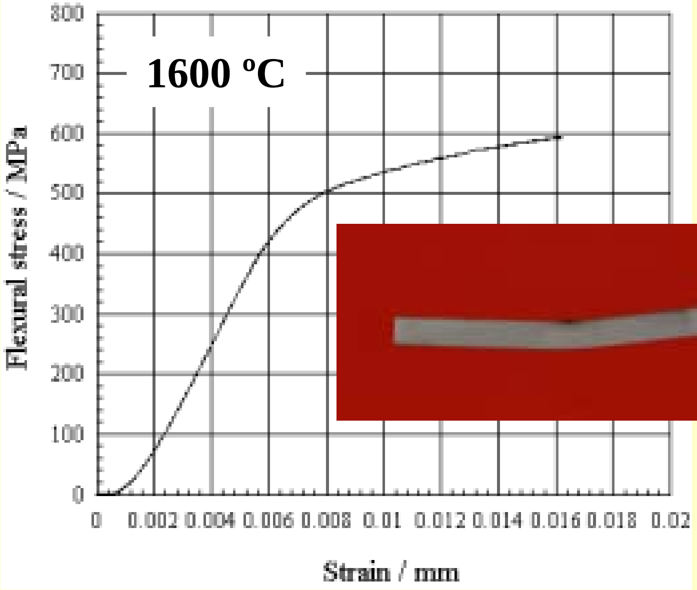
High Temperature Strength Characteristics

The Al_2O_3/YAG binary MGC maintains its room temperature strength up to about 1700 ºC, with flexural strength in the range of 300 - 350 MPa. The Al_2O_3/GAP binary MGC shows approximately 600 MPa from 1400 ºC to 1600 ºC. Ni-based superalloys shows a large drop in strength above around 800 ºC.
And Si_3N_4 has the higher than the Al_2O_3/GAP MGC, but its strength decreases gradually above 800 ºC.



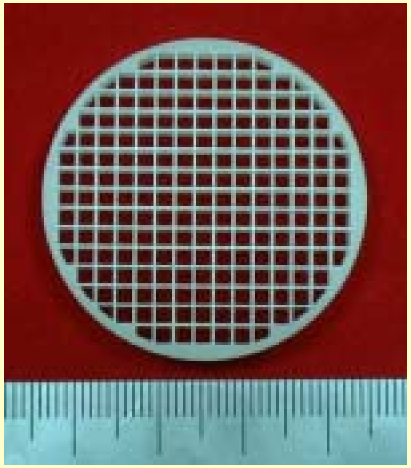
Temperature dependence of the strength in representative high temperature structural material.
*Ni super alloy: Tensile strength

The Al_2O_3/GAP MGC shows yielding behavior under high stress above 1600 ºC, with a flexural yield stress of around 600MPa.



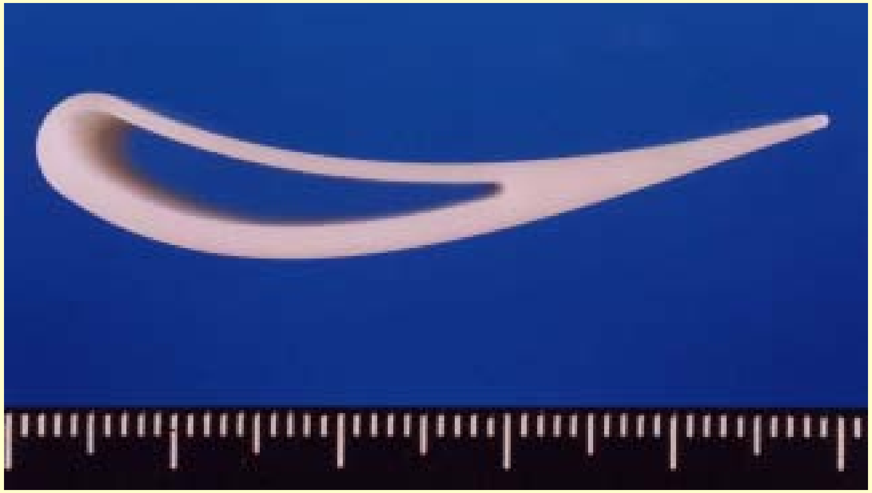
Typical stress-displacement curve of the 4-point flexural test of Al2O3/GAP MGC at 1600 ºC.

Machinability

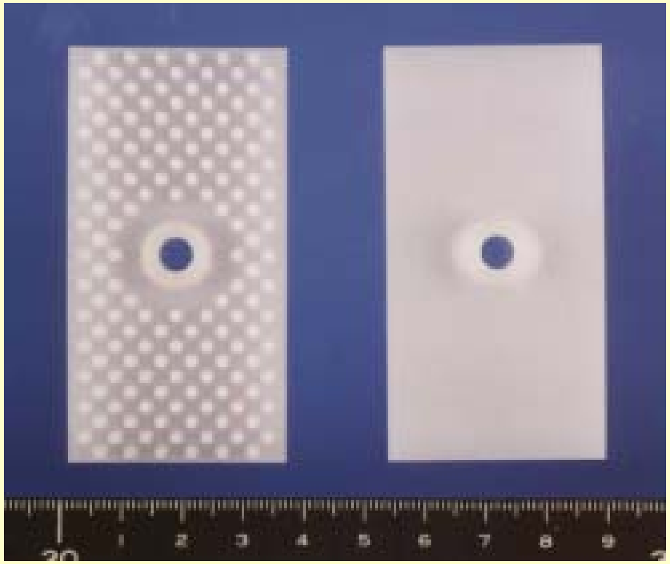


Filter

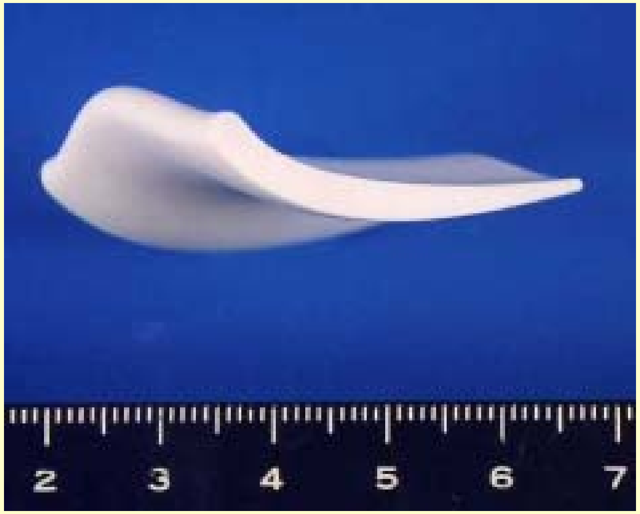
Volts



Hollow type turbine nozzle vane



Heat shield panels of combustion liner



Bowed stacked turbine nozzle vane

Motivations

1. Directionally Solidified Eutectic Ceramics;

* Improve the microstructure and the mechanical properties using unidirectional solidification
ex. Binary System; $Al_2O_3/Y_3Al_5O_{12}$(YAG), $Al_2O_3/GdAlO_3$(GAP), $Al_2O_3/Er_3Al_5O_{12}$(EAG)
Ternary System; $Al_2O_3/Y_3Al_5O_{12}$(YAG)/ZrO_2 , $Al_2O_3/Er_3Al_5O_{12}$(EAG)/ZrO_2

2. MGC's Advantages;

* High mechanical strength up to melting point temperature
* High creep resistance and oxidation resistances
* Good machinability and productivity to fabricate complex shape components

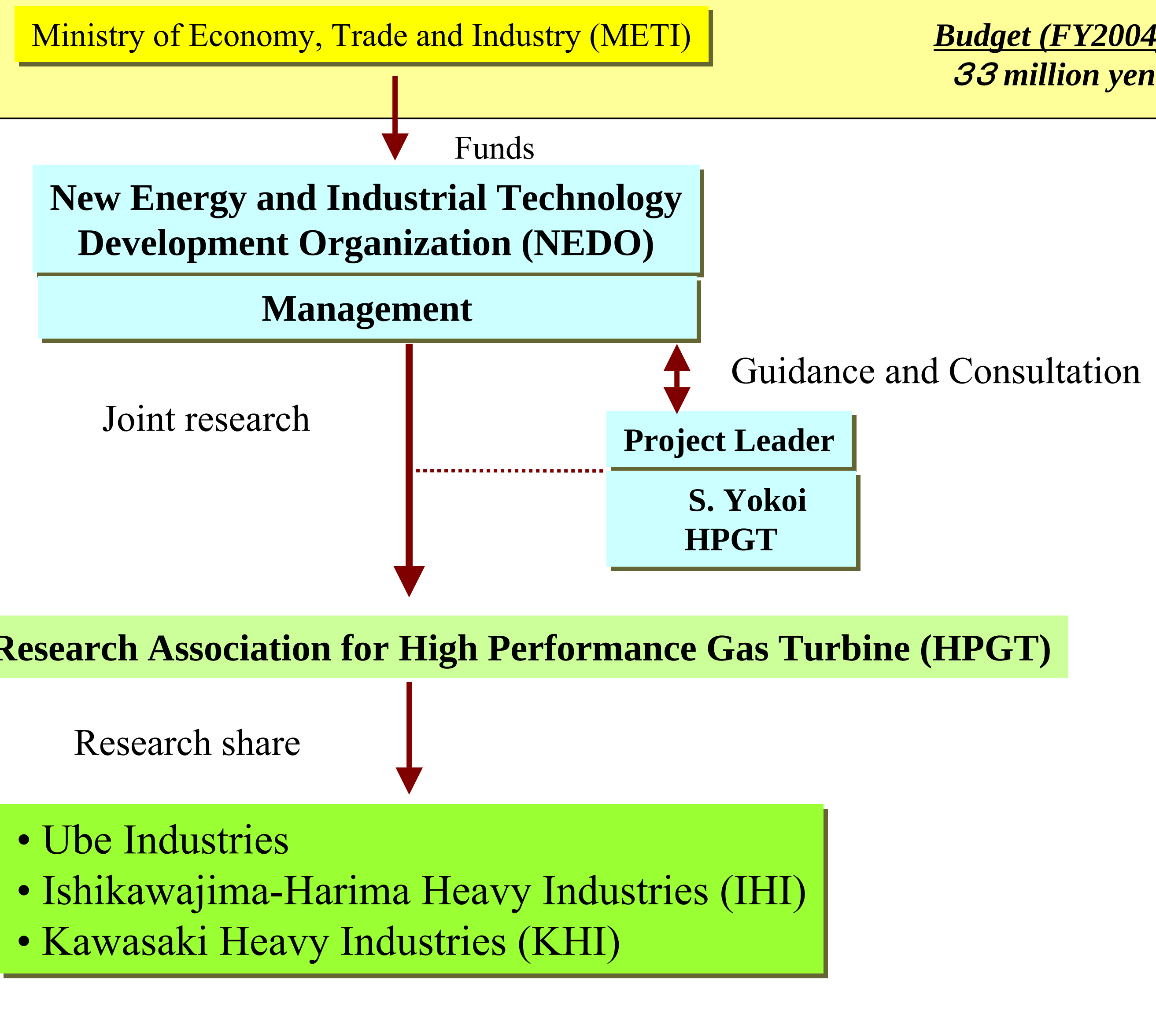
NEDO Project (FY2001-05)
Research and Development on
MGC Applied Gas Turbine System

Basic technologies to apply the high temperature section for a gas turbine
* System Integration Technology : IHI & KHI
*** Materials & Process Technology : UBE**

Implementation

Project term
FY2001-2005

Budget (FY2004)
33 million yen



Outline of Research and Development on Processing Technology for Superior Heat-Resistant Melt Growth Composites (MGC)

Processing Technology

<u>R&D on Innovative Process & Manufacturing Technology</u>

1. Near-net shape casting of complex shape components

2. Improvements of materials reliability & long-term durability under severe Environments
(highly water vapor Pressurized at ultra-high temperature)

3. MGC’s application technology to the high temperature section of the gas turbine system

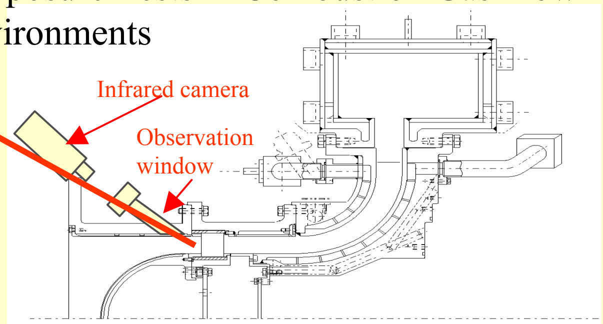
<u>Goals</u>

• Development of near-net shape casting technology
• Thermal stability: ~1,700 °C

Application Technology to the hot section of the gas turbine

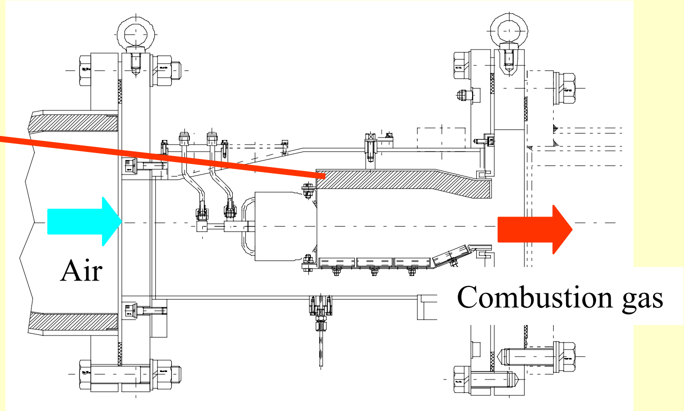
MGC turbine nozzle vane

• Improving Design Technology
• Exposure Tests in Combustion Gas Flow Environments



Cross-section drawing of the high temperature nozzle rig

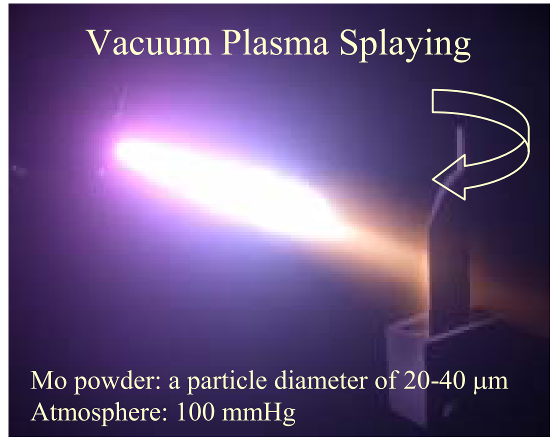
MGC heat shield panel for Combustor liner



1/4 sector combustor rig

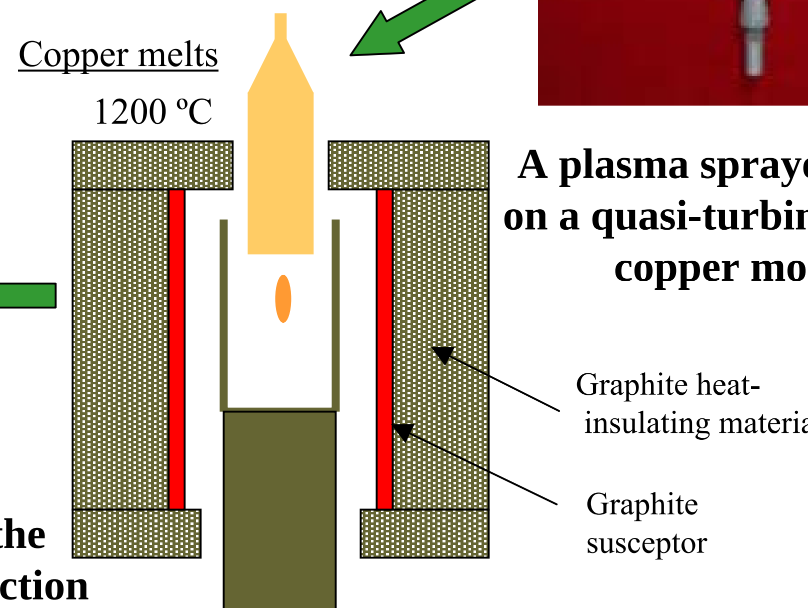
1. Fabrication process of plasma sprayed quasi-turbine nozzle mold for near-net shape casting for MGC components

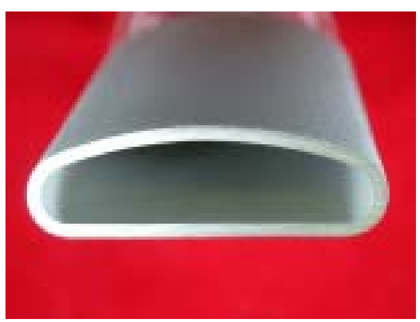
Quasi-turbine nozzle copper model



Thickness of wall of mold: 2-3 mm

A plasma sprayed mold on a quasi-turbine nozzle copper model





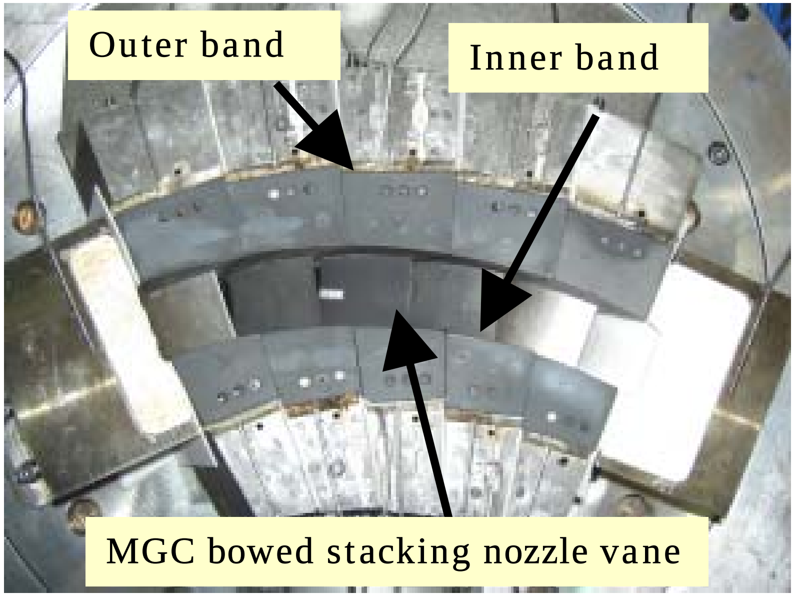
Cross-section diagram of the plasma sprayed mold at the middle of the longitudinal direction

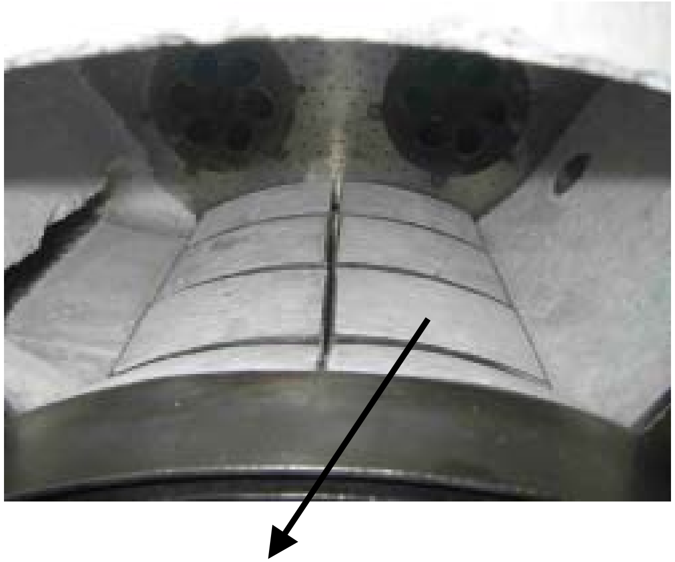
Al_2O_3/GAP sample

2. MGC turbine nozzle test rig

The high temperature nozzle rig (maximum temperature ~1700°C) have been improved to measure continuous temperature distribution on the nozzle surface by using an infrared camera.

We are now planning the test rig at an inlet gas temperature level of 1700°C in order to ensure the structural integrity under the steady-state and thermal shock conditions.



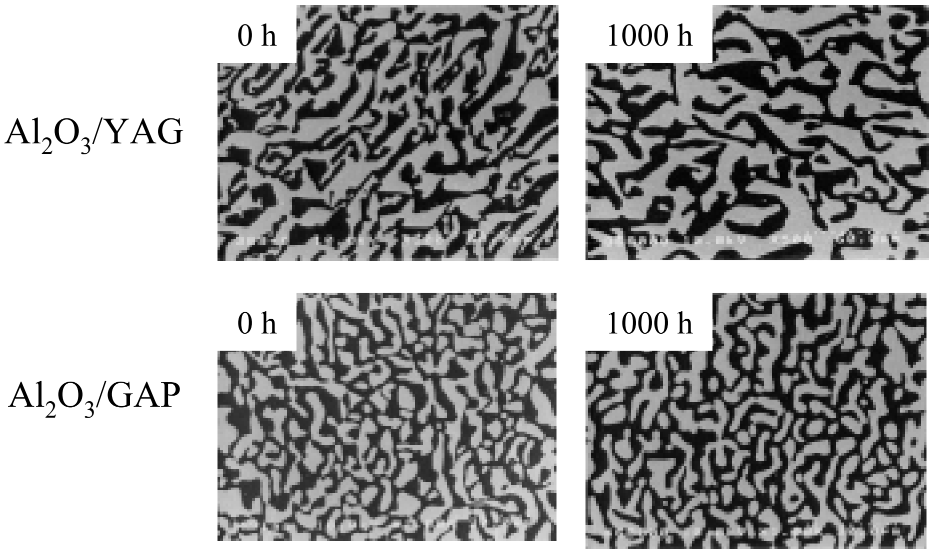


MGC heat shield panel

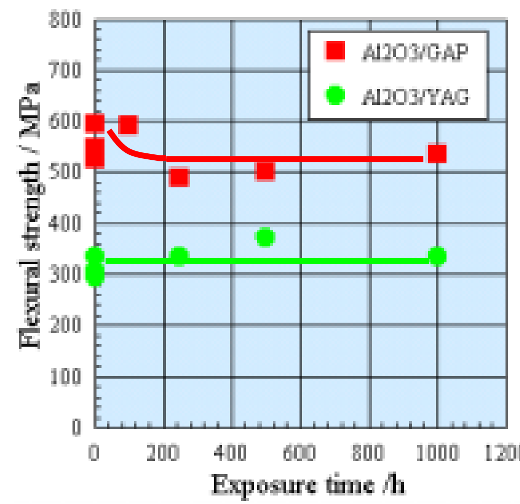
- Completed successfully 1500 °C steady-state condition test
- Confirmed no damage in MGC nozzle vane and MGC heat shield panel

Thermal Stability of MGC Components

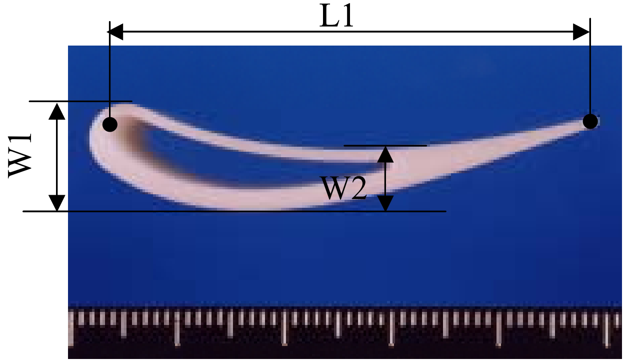
Even after 1000 hours of exposure test at 1700 ºC in an air atmosphere, no grain growth was observed in the microstructures. The MGC components have excellent oxidation resistance with no change in weight and surface roughness after 1000 hour at 1700 ºC in an air atmosphere.



SEM images of the microstructures of MGC after 1000 hours of exposure at 1700 ºC in an air atmosphere.



Relationship between 4 point flexural strength at room temperature and time of heat treatment at 1700 ºC in air.



Hollow turbine nozzle vane

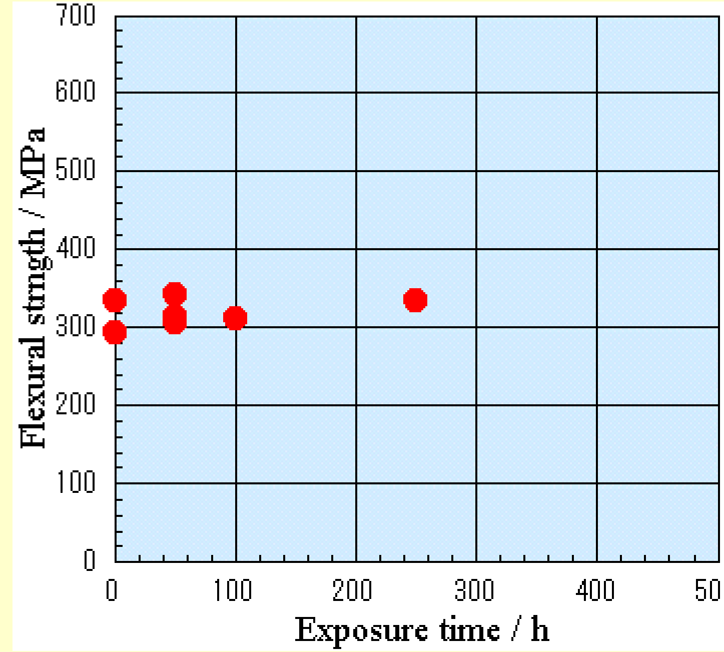
Table.1 Difference of the MGC nozzle vane after exposure test for 1000 hours at 1700 ºC in an air atmosphere.

Length	0 h	500 h	1000 h	Dimensional change
L1 (mm)	43. 971	43. 977	44. 000	0. 029
W1 (mm)	10. 614	10. 614	10. 598	—0. 022
W2 (mm)	5. 389	5. 385	5. 371	—0. 019
Weight (g)	26. 194	26. 232	26. 227	—0. 019
Rouphness (Ra/ μ m)	0. 46	0. 78	0. 75	0. 29

Materials Reliability & Mid-term Durability

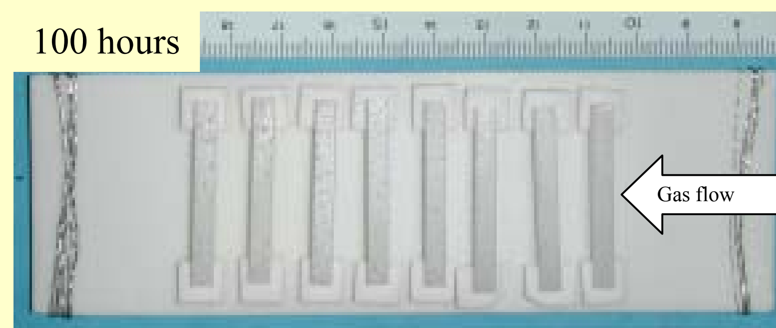
Hot corrosion resistance

No weight-loss and strength-reduction were observed even after exposure for 250 hours at1700ºC in addition to 30 wt.% moisture environments.
MGC materials also displayed very superior hot corrosion resistance



Residual 4-point flexural strength after hot corrosion test at 1700ºC.

Appearance of the hot corrosion testing equipment

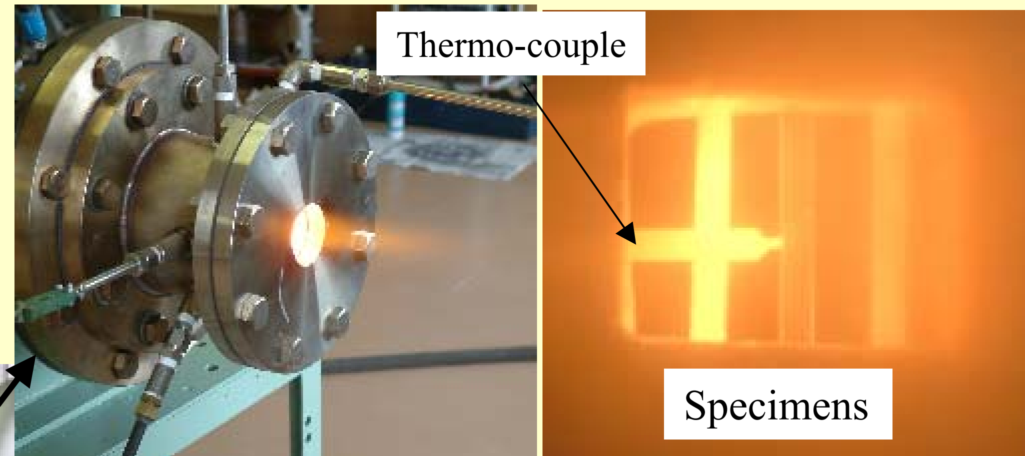


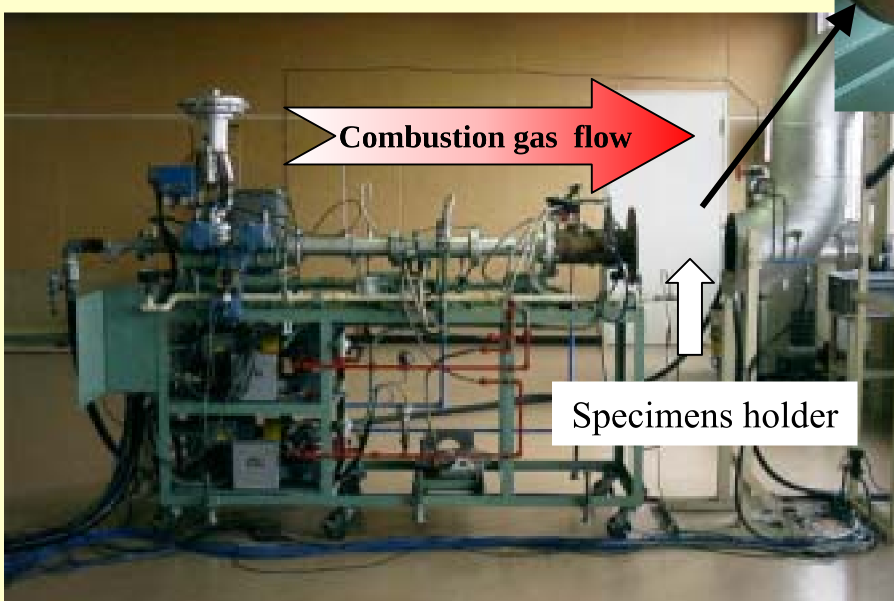
Appearance of the MGC specimens after hot corrosion test

Exposure tests in combustion gas flow environment

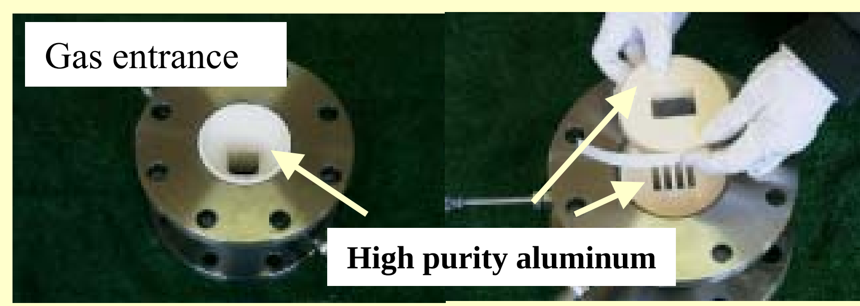
Recently, it has been reported that the recession of conventional ceramics such as Si_3N_4, SiC and Al_2O_3, mainly caused by water vapor is progressing under the combustion gas flow.
We have just stared exposure tests to evaluate the influence of combustion gas flow environment on MGCs.

Test machine specification
*Fuel : kerosene
*Combustion gas exit temperature : 1,600 ºC
*Combustion gas pressure : 0.3MPa
*Combustion gas speed : 500 m/s
* Vapor partial pressure : 45KPa
*Specimen size : 3*4*50 mm



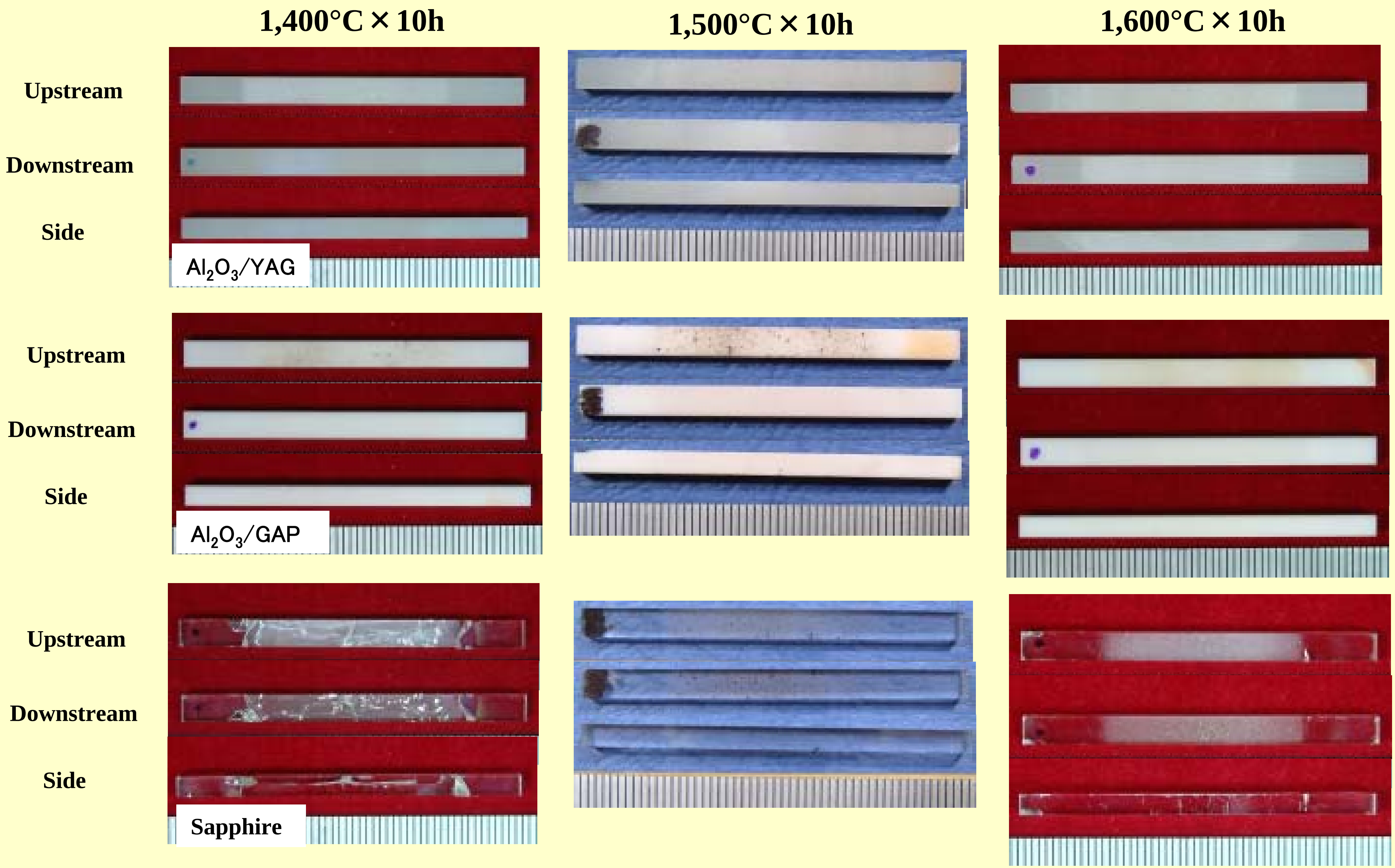


Appearance of combustion gas flow testing apparatus



Specimen holder

External appearance of the specimens
(T=1,400 - 1,600°C, P_{H20}=15kPa, t=10h)

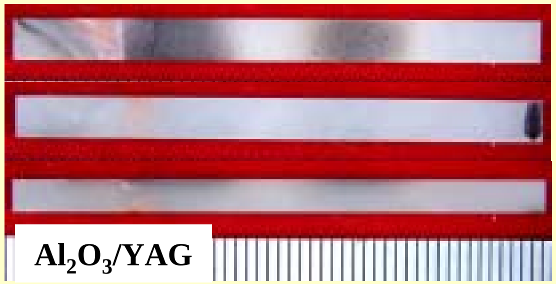


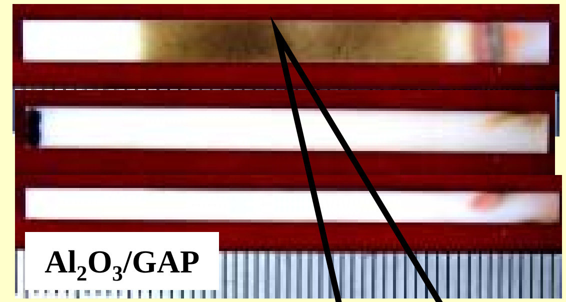
External appearance of the specimens
(T=1500°C, P_{H2O}=45kPa, t=10h)

Upstream

Downstream

Side





Upstream

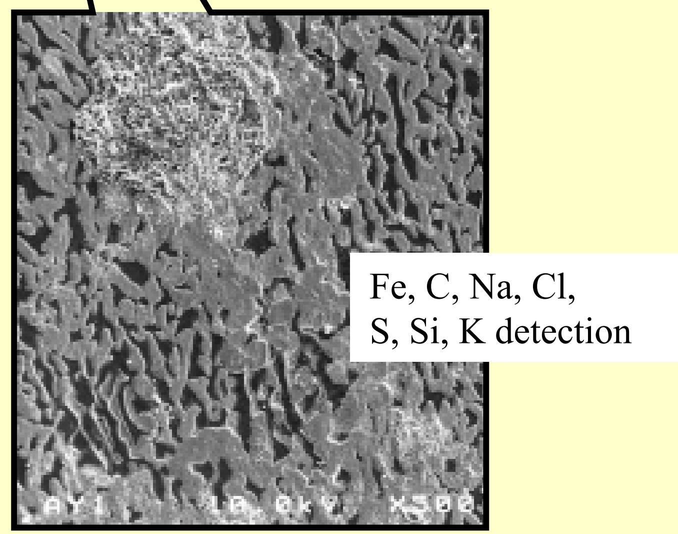
Downstream

Side

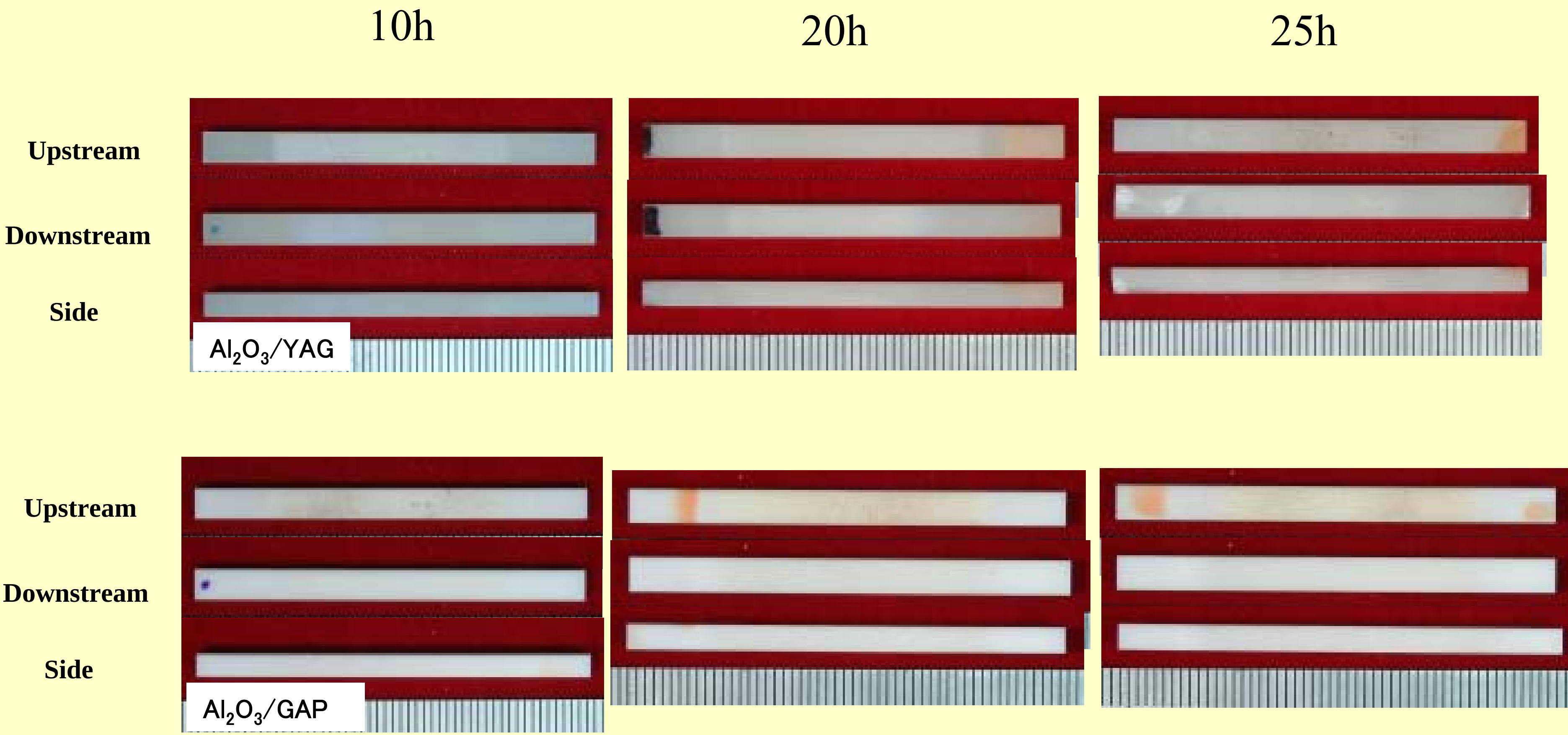
Upstream

Downstream

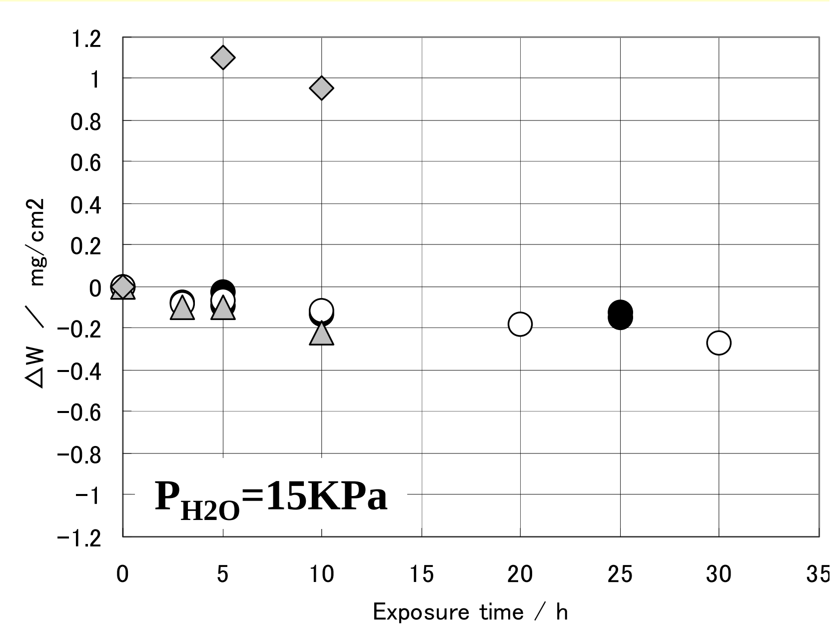
Side



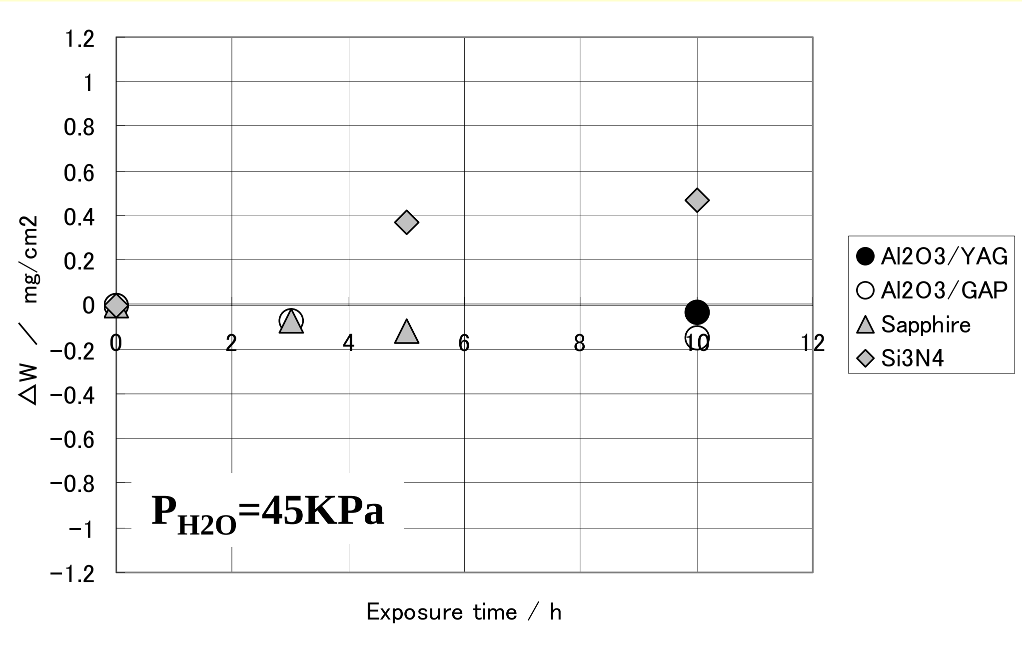
External appearance of the specimens
(T=1,500°C, P_{H2O}=15kPa, t= 0 - 25h)



Weight change
(T=1500°C, P_{H2O}=15, 45kPa, t=0 - 25h)



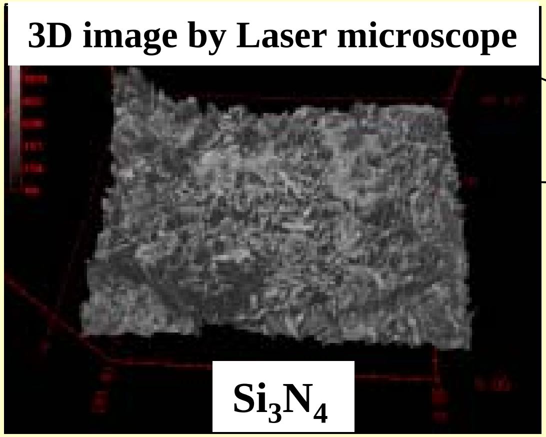
Relationship between exposure time and weight change

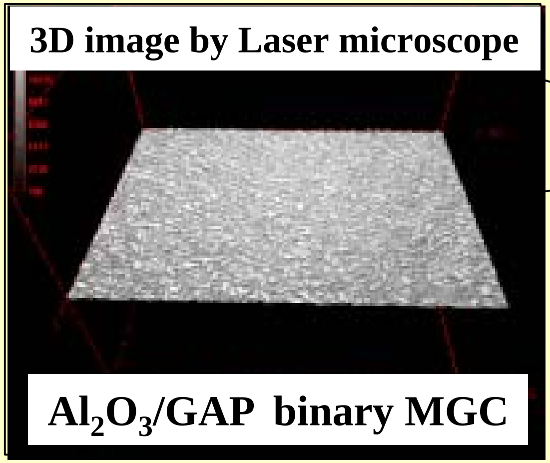


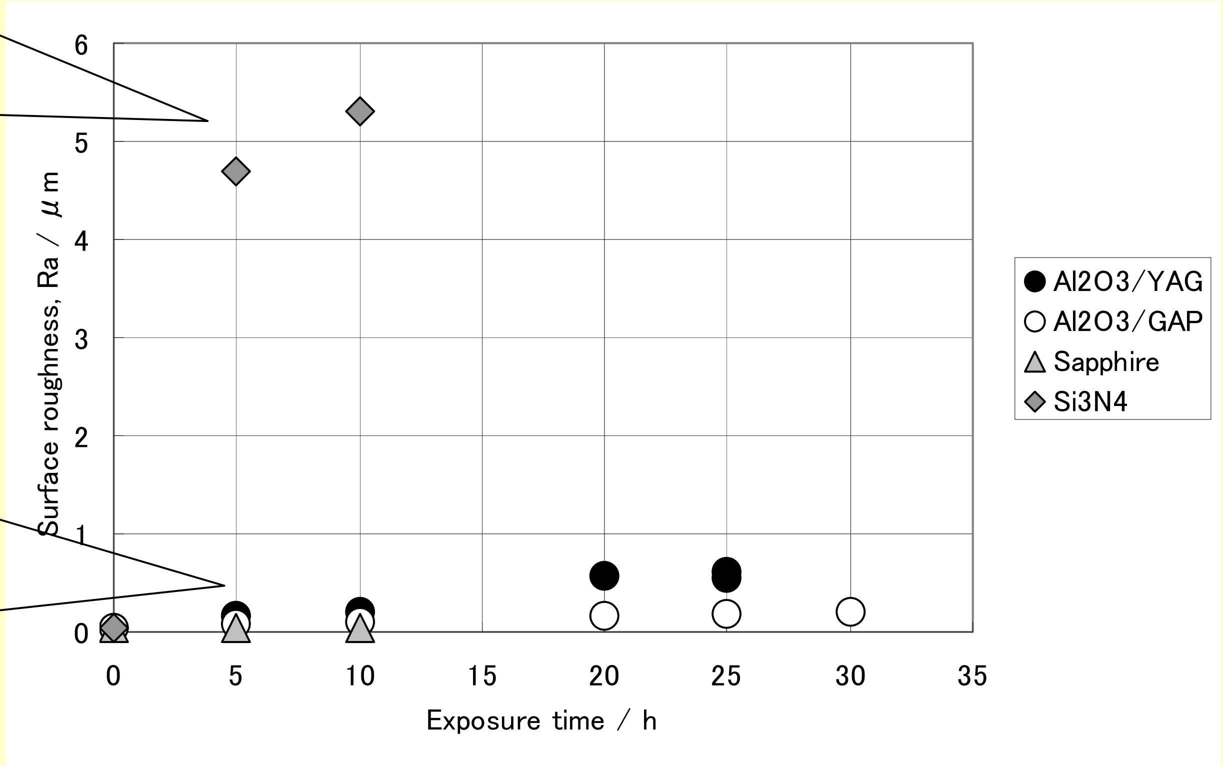
Relationship between exposure time and weight change

MGC showed 0.2 mg/ cm^2 barely weight loss after 30 hours with the vapor partial pressure of 15KPa. However, the change quantity hardly changes even if vapor partial pressure becomes 45KPa.
The weight loss of Al_2O_3 single crystal showed 0.2 mg/cm^2 more than MGCs after 10 hours.
Si_3N_4 showed 1.1 mg/cm^2 weight gain after 10 hours with the vapor partial pressure of 15KPa.
Furthermore, Si_3N_4 showed 0.5 mg/cm^2 weight gain in 45KPa.

Surface roughness change of downstream side
(T=1,500°C, P_{H2O}=15kPa, t= 0- 30h)



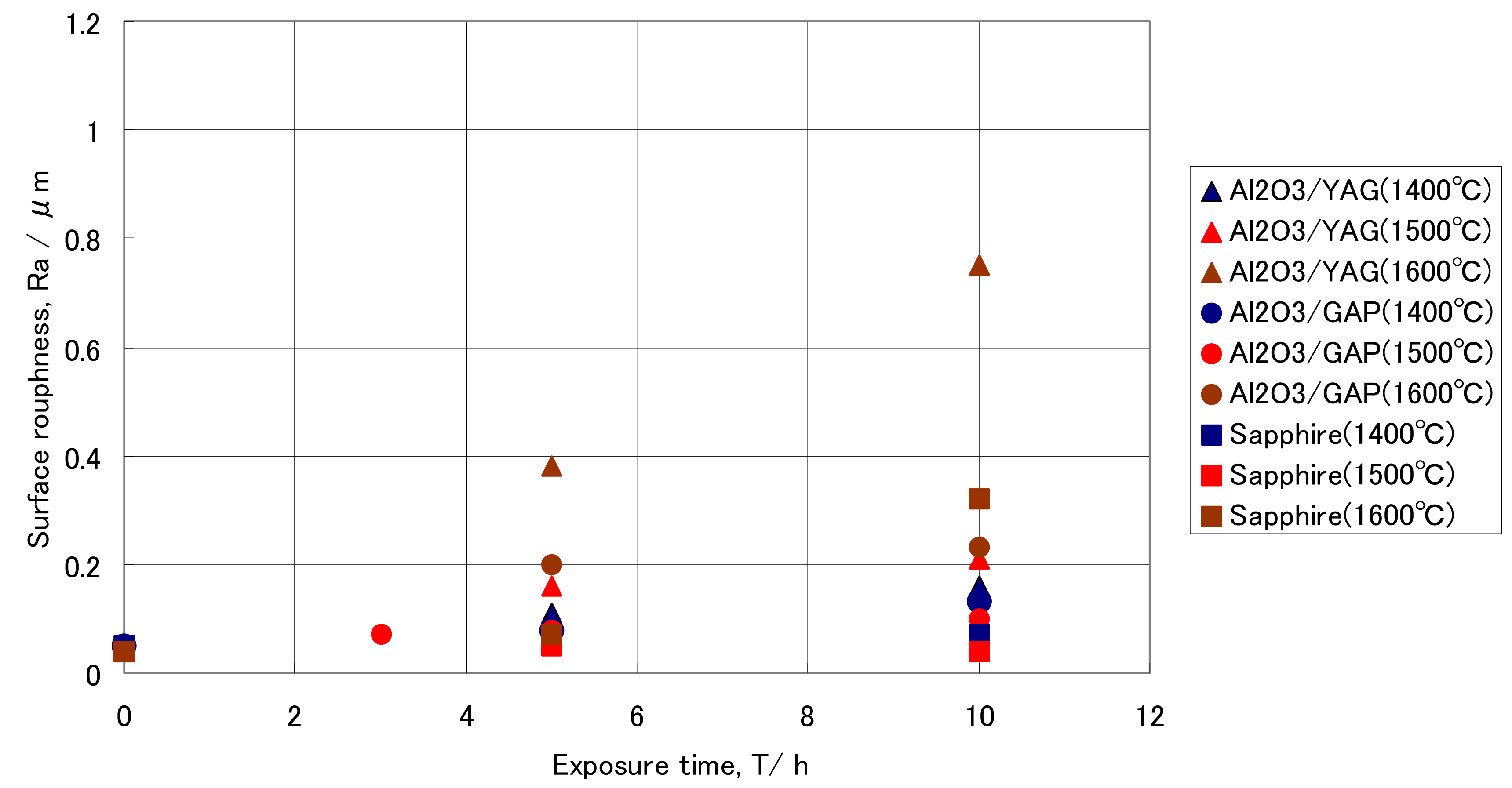




MGC and sapphire show the change of the surface roughness like only 0.1- 0.2 μm after exposure test until 30 hours with the vapor partial pressure of 15KPa in combustion gas flow.

On the other hand, Si_3N_4 shows obvious change of the surface roughness of 5.4 μm after exposure test in 10 hours with the vapor partial pressure of 15KPa. This phenomena is caused by oxidation and scattering of an oxide layers.

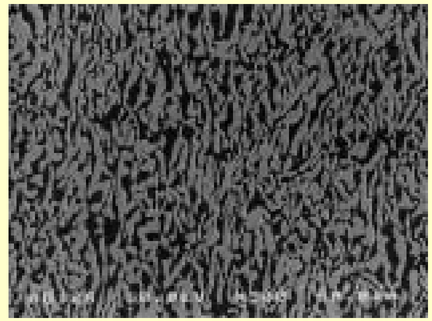
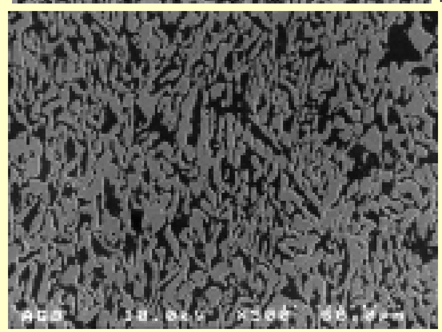
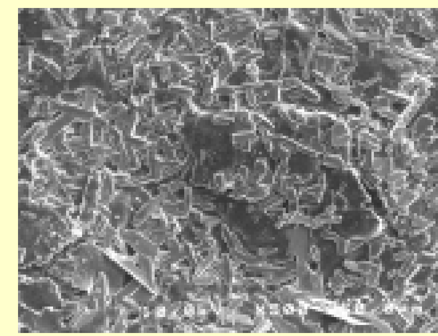
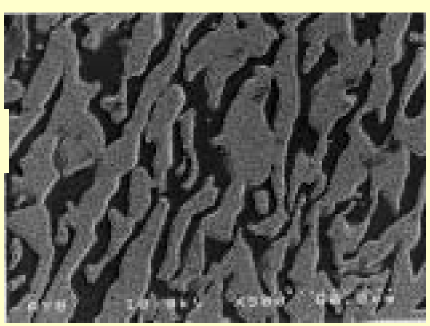
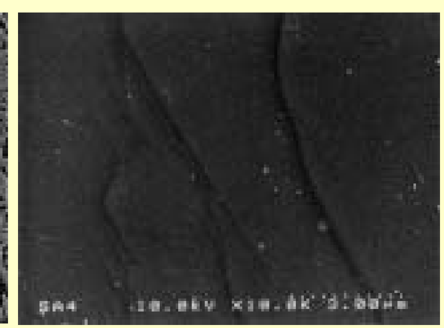
Surface roughness change of downstream side (T=1,400 - 1,600°C, P_{H2O}=15kPa, t=10 h)



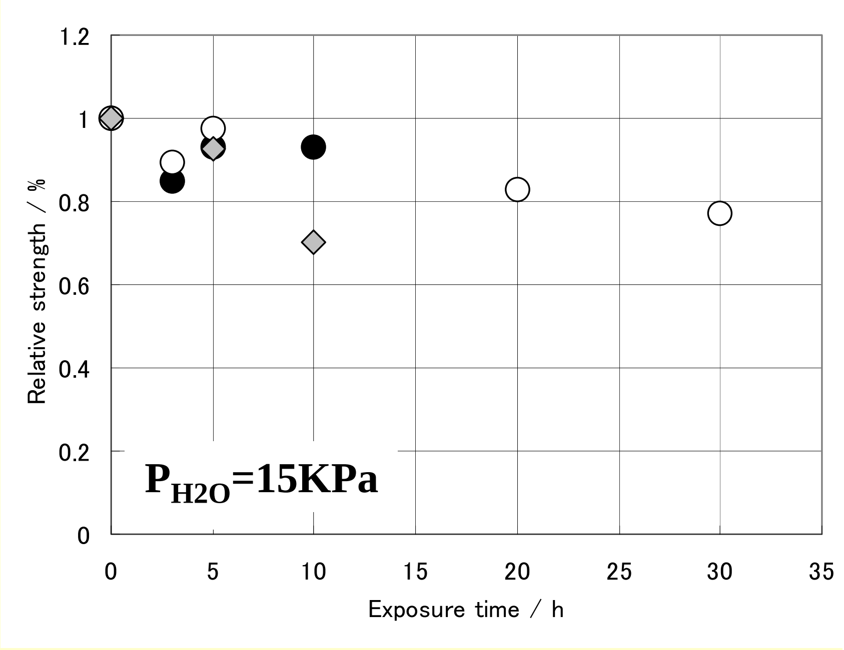
Temperature dependence of surface roughness change after the exposure test in combustion gas flow environment at 1400 – 1600 °C.

Al_2O_3/GAP binary MGC show the change of the surface roughness like only 0.2 μm after exposure test until 10 hours with the vapor partial pressure of 15KPa in combustion gas flow at 1400 – 1600 °C.

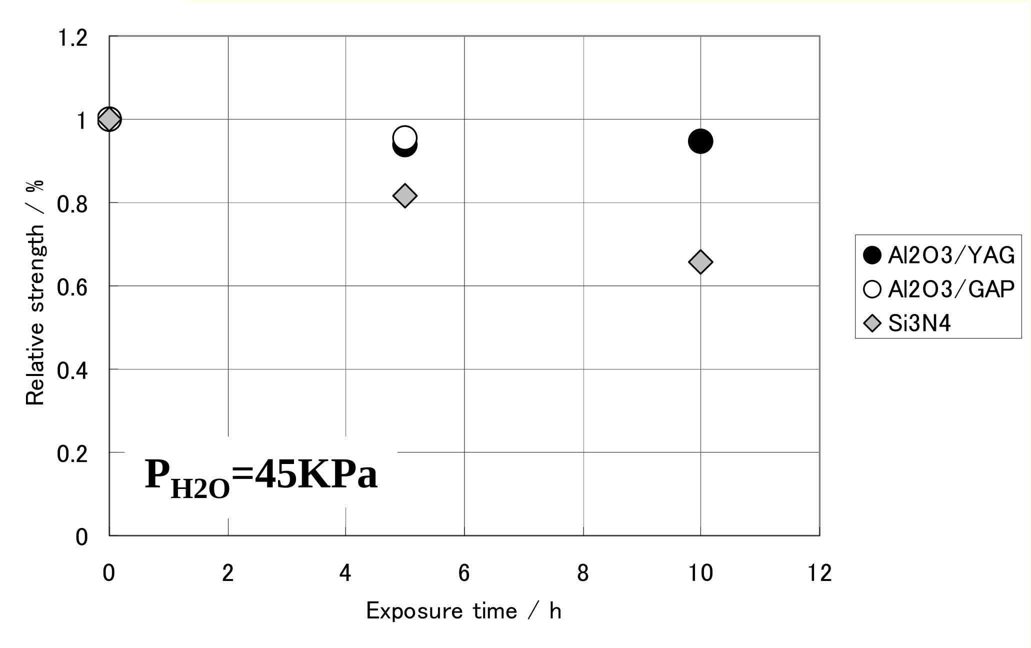
SEM images of the downstream side surface
（T=1,400 - 1,600°C, P_{H20}=15kPa, t=10h）

	Al_2O_3/YAG	Al_2O_3/GAP	Sapphire	Si_3N_4
1,400°C				
1,500°C				
1,600°C				

Residual strength
(T=1500 ºC, P_{H2O}=15, 45kPa, t=0 -30h)



Relationship between exposure time and residual strength

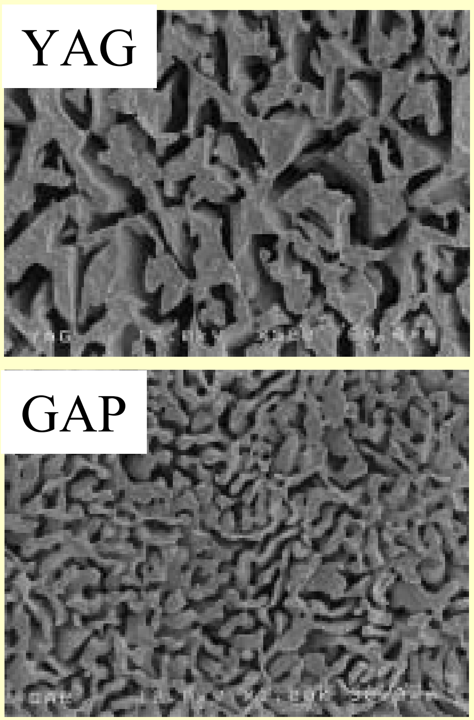


Relationship between exposure time and residual strength

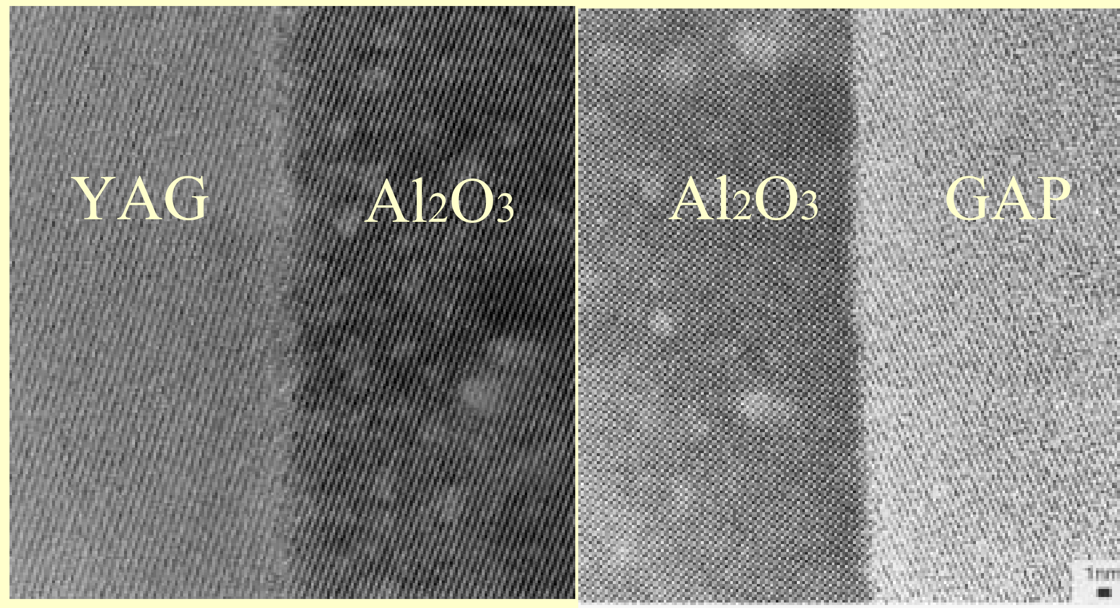
MGC does not show an obvious strength drop after exposure test until 30 hours in combustion gas flow with either vapor partial pressure of 15KPa and 45KPa.
On the other hand, Si_3N_4 shows 30% of strength drop after exposure test in 10 hours with the vapor partial pressure of 15KPa. Furthermore, Si_3N_4 shows 35% of strength drop in 45KPa.

Cause for thermal stabilities characteristics

1. MGC has a microstructure consisting of three-dimensionally continuous and complexly entangled single-crystal Al_2O_3 and single-crystal $Y_3Al_5O_{12}$ or $GdAlO_3$.
2. No amorphous phase were formed at the interfaces between the Al_2O_3 and $Y_3Al_5O_{12}$ or $GdAlO_3$ phases.
3. Relatively compatible interface is formed.



These photograph of three-dimensional YAG and GAP phase with only the Al_2O_3 phase extruded, after the eutectic composite was heated in graphite powder for one hour at 1600 ºC.



High resolution TEM image of the interface between Al_2O_3 and $GdAlO_3$ phase of the MGC materials.

Conclusions

1. The MGC materials also displayed superior thermal stability of microstructure, strength and oxidation resistance until 1000 hours after heat treatment at 1700 ºC in an air.

2. MGC does not show strength drop, weight loss and surface roughening among 10 hours after exposure tests in combustion gas flow environment at 1400 ºC.

3. MGC does not show an obvious strength drop, weight loss and surface roughening among 30 hours after exposure tests in combustion gas flow environment at 1500 ºC.

4. These excellent high-temperature characteristics are closely linked to such factors as:
   (1) the composite consisting of a single-crystal Al_2O_3 phase and single-crystal YAG or GAP phase with no grain boundaries, no amorphous phase at the interface boundary,
   (2) the phases being connected three-dimensionally having a complex interlocking structure.

The present MGCs have some advantages as ultra-high temperature structural materials.

The MGCs are expected to be widely used in mechanical engineering at very high temperatures in the future.

Acknowledgement

The authors would like to express their thanks to the New Energy and Industrial Technology Development Organization (NEDO) and the Ministry of Economy, Trade and Industry (METI), who gave them the opportunity to conduct " Research on Technology for MGC Ultra high-Efficiency Gas-turbine System".