#### MHD coating, understanding and status

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Understanding and status:

Basic knowledge

Candidates

Procedure for improvement

Enhanced understanding

Critical issues

# Thermodynamic property of ceramic materials being contact with Li and V alloy (V-Cr-Ti)

Thermodynamic database shows possible ceramics for MHD coating material.



• Oxides : Small number of rather little-experienced oxides will be stable in Li.

Coating material candidates are strictly limited.
 → Search for new candidates materials are important.

## Scoping of bulk ceramics





Pint, ISFNT-6 Suzuki, ISFNT-6

## Improvement : CaZrO3 as an example

#### Advantage of mixed oxides

• Mixed oxides is sometimes thermodynamically more stable than that of the average of each oxide.

 $\varDelta G(CaZrO_3) < (\varDelta G(CaO) + \varDelta G(ZrO_2)) / 2$ 

- Mixed oxide is sometimes used to improve coating properties.
- CaZrO3 as a possible stable oxide to be used with CaO (in-situ coating)

#### Improvement of CaZrO3

- Reduction of ZrO2 impurity
- Increase the density by addition of Sc

## CaZrO<sub>3</sub> grain itself is compatible with liquid Li.

## Effect of ZrO<sub>2</sub> impurity in CaZrO<sub>3</sub> on corrosion behaviors

CaZrO<sub>3</sub> is a stable chemical form among mixture of CaO and ZrO<sub>2</sub>. However, a small amount of  $ZrO_2$  may remain while coating fabrication  $\rightarrow ZrO_2$  may be a main impurities for CaZrO<sub>3</sub>.

ZrO<sub>2</sub> is thermodynamically unstable in liquid Li.



## Dependence of long-term compatibility on the density of CaZrO<sub>3</sub>

•  $CaZrO_3$  (low density) with 76 % of theoretical density of  $CaZrO_3$  was sintered in Li at 773 K for 108 days.

• CaZrO<sub>3</sub> (high density) with 91 % of theoretical density of CaZrO<sub>3</sub> was sintered in Li at 773 K for 126 days.

• CaZr(Sc)O<sub>3</sub> was made by addition of small amount of Sc as a binder. Sc was selected because  $Sc_2O_3$  is thermodynamically more stable than  $Li_2O$ . CaZr<sub>0.95</sub>Sc<sub>0.05</sub>O<sub>3-x</sub> with 98 % of theoretical density of CaZrO<sub>3</sub> was sintered in Li at 773 K for 84 days.



CaZrO<sub>3</sub> (high density) with 91 % of theoretical density of CaZrO<sub>3</sub>

Liquid Li invade into ceramic bulk through open grain boundary.
The grains near the surface are about to remove.



 $CaZrO_3$  (high density) with 91 % of theoretical density of  $CaZrO_3$  after the sintering test at 773 K for 126 days. CaZr(Sc)O<sub>3</sub> with 98 % of theoretical density of CaZrO<sub>3</sub>

- Liquid Li invading into ceramic bulk was reduced.
- Lithium hydro-oxide with water molecules remain near the surface.



 $CaZr(Sc)O_3$  with 98 % of theoretical density of  $CaZrO_3$  after the sintering test at 773 K for 84 days.

## High temperature compatibility of CaZrO<sub>3</sub> samples with high density

 $CaZrO_3$ ,  $CaZr(In)O_3$ , and  $CaZr(Sc)O_3$  was sintered in Li at up to 1073 K.

At 823 K, The samples were sintered for about 100 h. At the other temperatures, the samples were sintered 10 for 1000 h. Weight increase (mg/cm<sup>2</sup>) 0  $10\,\mu$  m -10 -20  $CaZrO_{3}(91\%)$ 0  $CaZr_{0.95}Sc_{0.05}O_{3-x}$  (98%) -30  $CaZr_{0.95}In_{0.05}O_{3-x}$  (98%) Δ -40Broken into grains at 973 K -50Broken into grains at 823 K -60800 850 1050 950 1000 1100 900 Temperature (K)

Mass change after the sintering test.

CaZrO<sub>3</sub> samples (with 91 % of its theoretical density) decreased their weight significantly above 873K. This is due to the grains leaving from the surface.

In contrast,  $CaZr(Sc)O_3$  (with 98 % of theoretical density of  $CaZrO_3$ ) containing only about 1 at% of Sc showed a small mass change up to 973 K. However,  $CaZr(In)O_3$  (with 98 % of theoretical density of  $CaZrO_3$ ) containing only about 1 at% of In was broken into powder even at 823 K due to thermodynamically unstable  $In_2O_3$  in Li.

Addition of Sc to CaZrO<sub>3</sub> significantly improve the compatibility with Li.

## In-situ coating method

In-situ coating method is a kind of CVD method using Liquid instead of Vapor.



In case of CaO, a small amount of O is introduced near the surface of V alloy. And a small amount of Ca is dissolved in the liquid Li. O and Ca react to form insulating CaO at interface ( the surface of V alloy)

## CaO coatings formed on NIFS-HEAT-2



Images of SEM-EDS analysis on the cross section of the interface area show successful demonstration of CaO formation on the NIFS-HEAT-2.

Typical SEM image of the cross section

SEM-EDS analysis on a 2200 wppm-O sample after 50 h exposure to Li+2.8wt%Ca



Coating thickness ; 5.4µm

V impurity at CaO coatings ; V/(Ca+V) = 40%

SEM-EDS analysis on a 6300 wppm-O sample after 50 h exposure to Li+2.8wt%Ca



Coating thickness ; 15.8µm

V impurity at CaO coatings ; V/(Ca+V) = 18%

# Change of depth profile of oxygen concentration during oxidation and CaO formation



of the samples before exposure test

of the 2200-3100 wppm-O samples before and after exposure to Li+Ca

Micro-Vickers Hardness test provides oxygen profile in the specimen

Understanding and status:

Basic knowledge

Extending thermodynamic database

Candidates

New candidates showing good performance as bulk specimens

Procedure for improvement

Clear direction obtained for some materials and further improvement expected

Enhanced understanding

Oxygen transportation during in-situ CaO formation

Critical issues

Optimization of coating methodology Irradiation test technology

#### MHD coating, ongoing activity and plan

T. Muroga (NIFS, Japan)

Coating development

Test plan of Radiation-Induced Conductivity

## **RF-Sputtering**

Sawada, Terai, Suzuki, Muroga



Controlled parameters : Target composition, Substrate temperature, Composition and pressure of atmospheric gas, Input RF power

## AlN



 $0.5 \sim 2.0 \text{ E} + 09 \text{ ohm-m}$ 

## $Y_2O_3$



0.9~3.0 E+09 ohm-m

## $Er_2O_3$



#### Filtered Arc-source Plasma Vapor Deposition Device (IPP-Garching)

Suzuki, Maier, Bolt



High density · Highly crystallized · Low impurity coating Very high coating rate on wide area expected

## Er<sub>2</sub>O<sub>3</sub> Coating



#### SEM

In a  $7 \times 10^{-4}$  [Pa]O<sup>2</sup> environment, Er vapor was produced by arcing and ionized Er were introduced into SiC(600C) substrate using magnetic filter. O/Er>1.45 and no impurity was detected by EDS

### Future Plan of the Coating Test

Coating on V-4Cr-4Ti substrates Sintering test (static) Low temperature (<500C) in Japan (present facility) High temperature (>500C) in Japan (improved facility) or in the US Dynamic test by JUPITER-II collaboration

#### Transient phenomenon :

Drift of charges induced by recoil and nuclear reactions Radiation Induced Conductivity (RIC)





Radiation Induced Electrical degradation (RIED)



Neutron Effect on Insulating Coating Material

### Experiment at FNS/JAERI



Experimental Arrangement at FNS (Fusion Neutron Source) Facility



Photograph of Tritium Target and Measurement Chamber

#### Previous Results for Al<sub>2</sub>O<sub>3</sub> and the Test Plan

