Chosun Refractories

Investigation of Refractory Bricks and Oxide Materials Heated in Hydrogen Reduction Condition

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1 INTRODUCTION

- In order to achieve carbon neutrality, a lot of researches have been conducted to convert the iron ore reduction matter **from cokes to hydrogen gas.**

- Accordingly, refractory makers need to identify the reaction **of hydrogen gas with refractories** .

- We investigated phase changes, weight changes, color changes, and physical properties changes of refractory bricks when they are exposed to a hydrogen atmosphere at 1,100°C.

- And we also found out components of the raw material which cause theses changes of refractories

Fig. 1. fluidized hydrogen reduction reactor

Prediction of thermodynamic reactions in a hydrogen atmosphere

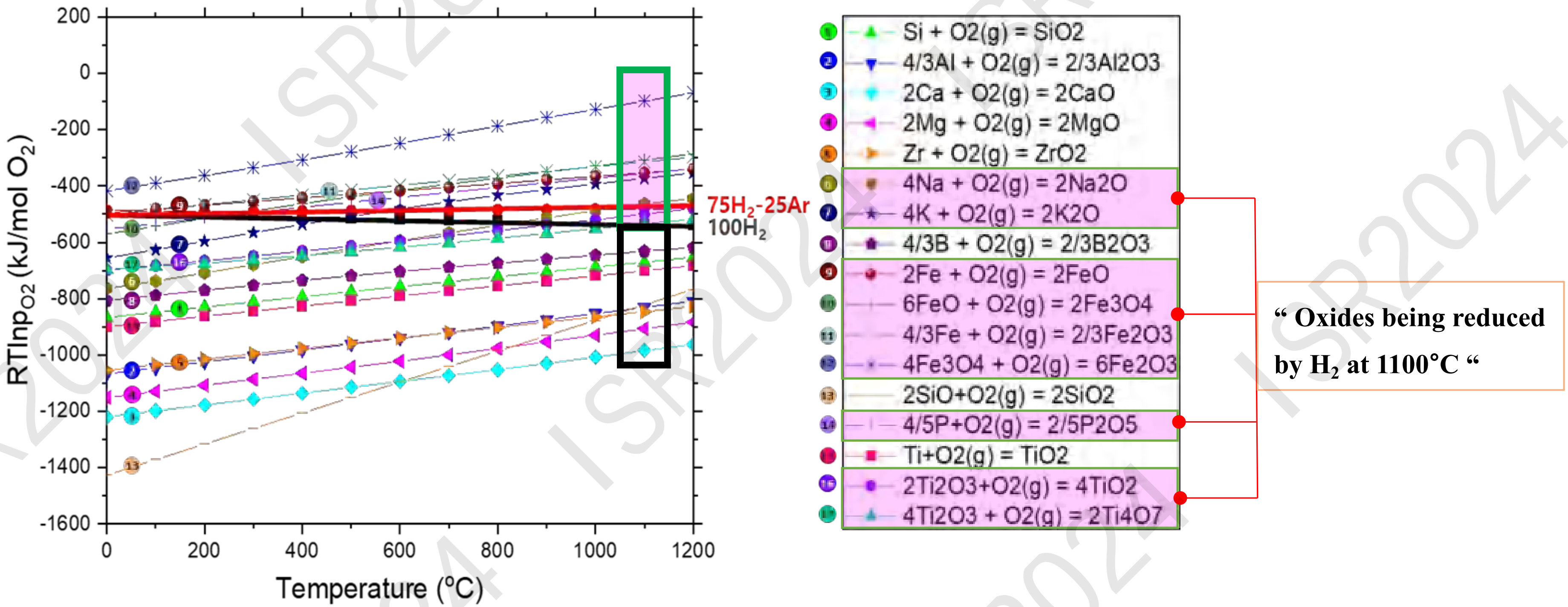


Fig. 2. Ellingham diagram

- Na_2O, K_2O, Fe_2O_3 and P_2O_5 are reduced by hydrogen at 1100°C among oxide materials,
- However, silica ,alumina,magnesia,calcia and zircona which are the main raw materials for refractories do not be reduced by hydrogen .

1 INTRODUCTION

The risk of hydration of raw materials in a H_2 atmosphere

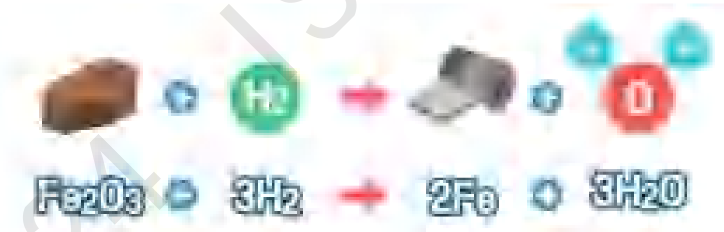
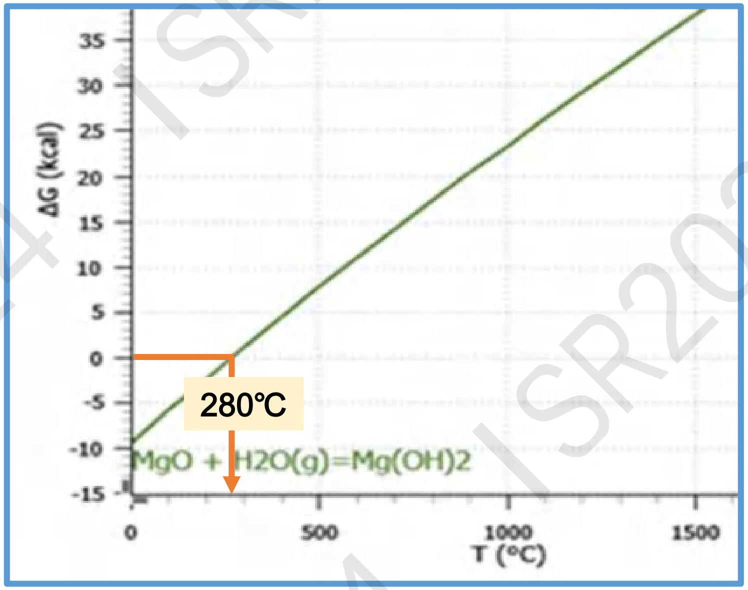


Fig.3. (a)Production of H2O by Fe2O3 reduction with hydrogen



(b) Predicted temperature of MgO hydrated by H_2O(g)

- When Fe_2O_3 is reduced by H_2 gas, The H_2O will be generated as a by-product .

- Even though MgO doesn't react with H_2(g), If H_2O came out there would be a risk of MgO slaking in the reduction furnace.
  Fig.3. (b) shows that the hydration of MgO can occur below 280 ℃ with H_2O gaseous state

Preparation of specimen

1. Alumina silica brick for the reaction test with H_2

Fig.4. Alumina silica brick

Raw material (particle size, mm)	Composition (wt%)
Andalusite (1~0.3)	30
Mullite chamotte (3~0.3)	60
Clay (1~0)	10
TOTAL	100

Tab.1. The raw materials & composition of brick

A refractory brick is composed of andalusite, mullite chamotte, and clay as raw materials. These raw materials were kneaded with binder in a mixer and the mixture was molded with a uniaxial pressing press, dried at 110°C for 24 hours, and heated at 1,350°C for 6 hours in the air.

2. MgO brick for the MgO hydration test by H_2O

The MgO brick is manufactured with only MgO raw materials.

And it is produced by the same way of the alumina silica brick.

Heat treatment conditions for a hydrogen reduction test

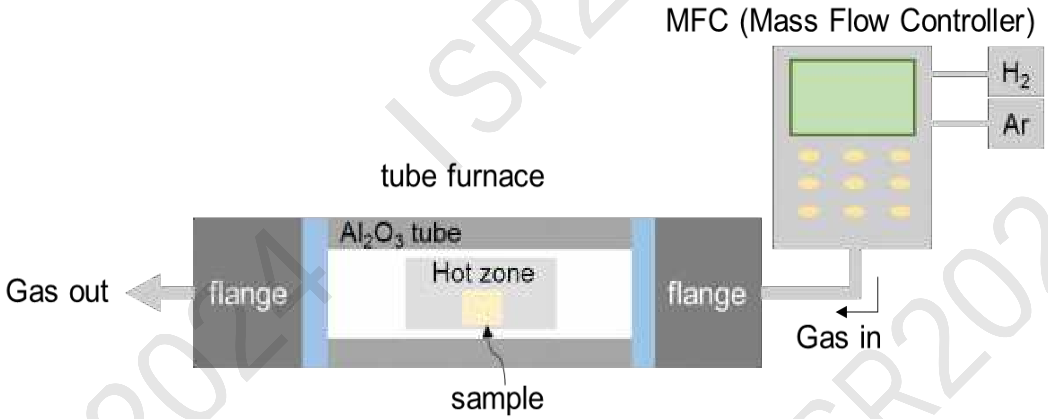


Fig. 5. Heat treatment equipment

Specimen	Al₂O₃-SiO₂ brick					MgO brick
	A	B	C	D	E	
	Fired at 1350℃*6hrs (Air atmosphere)					
Temp*time		at 1100℃*72hrs				at 400℃ *72hrs
Atmosphere		Air	H_2 : Ar			H_2
Gas ratio (Vol %)		100	25:75	75:25	100:0	100

Tab.2. The heat treatment conditions of the specimen

The specimen bricks are charged into an alumina tube furnace which is capable of controlling the atmosphere.

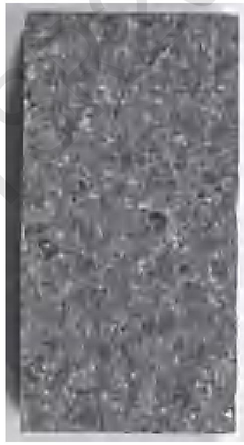
- Al_2O_3-SiO_2 bricks("B"~"E") are heated at 1100°C for 72 hours while injecting air, hydrogen and argon gas with a flow rate of 200cc/min. The heating rate is 5°C/min, and the pressure in the furnace is 1 bar.
- The MgO brick is heated at 400 ℃ for 72 hours while injecting hydrogen gas

3 RESULT AND DISCUSSION (Al_2O_3-SiO_2 bricks)

Color changes of refractory bricks in a hydrogen atmosphere

Reversible reaction

← Air H_2 →

Specimen	A	B	C	D	E
Atmosphere	-	Air	H_2 : Ar		
Gas ratio(%)	-	100	25:75	75:25	100
Picture					

After heated in a hydrogen atmosphere, the color of brick is changed to dark.
After that , when it is heated once more in the air, the dark color is returned to bright color like specimen "A"
This reversible phenomenon is considered that K_2O, Na_2O, and Fe_2O_3, are reduced to metal having dark color in a hydrogen atmosphere and oxidized again in the air to be bright color oxides.

Strength(M.O.R) changes of bricks in hydrogen atmosphere

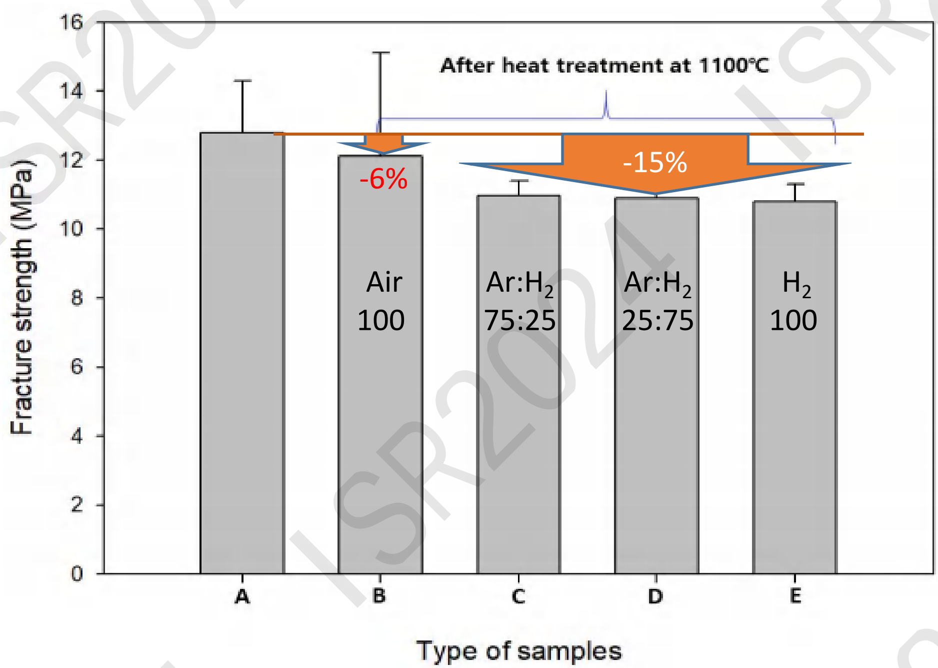


Fig. 6: Strength changes by heating atmosphere

- The strength of specimen "B" heat-treated in the air the strength is decreased slightly by 6% (1MPa), but the strength of specimen(C, D, E) heated in a H_2 atmosphere, are decreased by more than 15% (2MPa). This means that the strength of refractory is more vulnerable in a hydrogen atmosphere than in the air.
- The degree of strength changes at "C", "D", and "E" is almost same. It means that the strength is decreased by lack of oxygen not by hydrogen concentration.

3 RESULT AND DISCUSSION (Al_2O_3-SiO_2 bricks)

Phase changes of bricks in hydrogen atmosphere

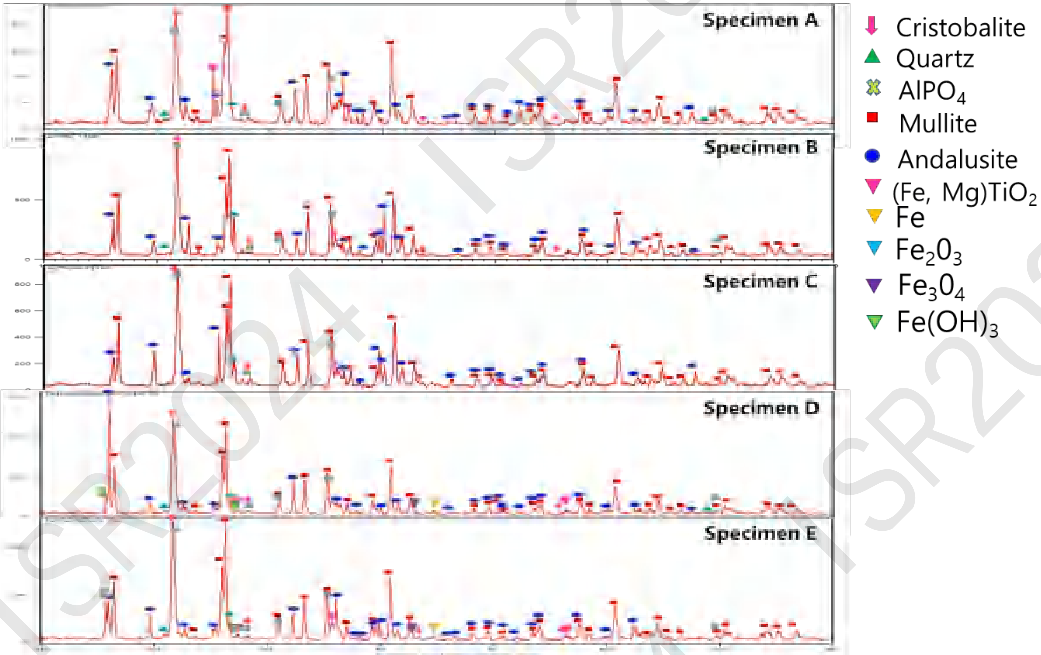


Fig. 7: XRD results by heating atmosphere

Tab.3. XRD results of refractory brick (main peak +++, traces +)

Specimen	A	B	C	D	E
		Air100	H_2:25	H_2:75	H_2:100
Mullite	+++	+++	+++	+++	+++
Andalusite	+++	+++	+++	+++	+++
Cristobalite	++	++	++	++	++
Quartz	+	+	+	+	+
Fe_2O_3	+	+			
Fe_3O_4		+	+	+	+
Fe			+	+	+
Fe(OH)3		+	+	+	+

- The phase of Fe_2O_3 in the brick was reduced to Fe_3O_4, Fe and $Fe(OH)_3$ phase after heat treatment.
- In particular, the metal Fe detected in specimens(C, D, E) could cause the specimen's color change after heat treatment in a H_2 atmosphere.

Color changes of raw materials in hydrogen atmosphere

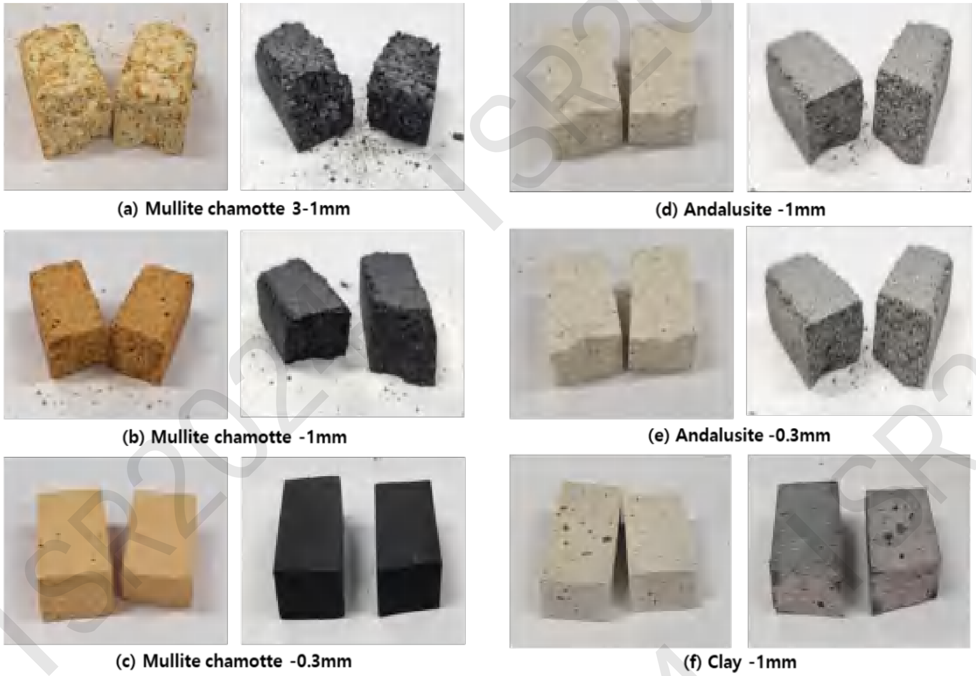


Fig. 8. Specimen before and after hydrogen heat treatment

Tab.4. Raw materials composition of refractory brick

Raw material (particle size, mm)	Composition (wt%)						
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	Na_2O	K_2O
(a) Mullite chamotte(3-1)	43.5	51.6	**1.2**	2.5	0.1	0.0	0.2
(b) Mullite chamotte(1)	43.9	50.8	**1.4**	2.5	0.1	0.0	0.2
(c) Mullite chamotte(0.3)	41.6	52.4	**1.4**	2.6	0.1	0.0	0.2
(d) Andalusite(1)	40.7	57.1	0.8	0.2	0.0	0.1	0.2
(e) Andalusite(0.3)	39.3	58.3	0.9	0.2	0.0	0.0	0.3
(f) Clay (1)	51.2	33.1	**1.2**	0.8	0.1	0.0	0.1

- As shown in Figure 8, the color changes were seen in all specimens after heat treatment in a hydrogen atmosphere. The color changes are more noticeable in Mullite chamotte with smaller particle sizes (specimen "C").
- Referring to Table 4, we found out the fact that the higher Fe_2O_3 content caused the color to be the more dark.

3 RESULT AND DISCUSSION (${Al_2O_3}$-${SiO_2}$ brick's raw materials)

Physical property changes of raw materials in a hydrogen atmosphere

Tab.5. Weight changes before and after heat treatment

Raw material (particle size, mm)	Weight (g)		△g (%)
	Before	After	
Mullite chamotte **(1)**	13.30	13.27	-0.22
Mullite chamotte **(0.3)**	9.76	9.73	-0.29
Andalusite **(1)**	13.65	13.62	-0.19
Andalusite **(0.3)**	8.77	8.75	-0.21
Clay (1)	6.97	6.97	-0.03

Tab.6. Strength changes before and after heat treatment

Raw material (particle size, mm)	M.O.R (MPa)		△σ (%)
	Before	After	
Mullite chamotte (1)	8.68	7.14	-18
Mullite chamotte (0.3)	34.63	23.87	-31
Andalusite (1)	5.50	4.38	-20
Andalusite (0.3)	8.40	8.25	-2
Clay (1)	26.27	36.68	40

- The weight loss was greater when the raw material's particle sizes were smaller.
- Table6 shows that the strength of mullite chamotte and andalusite was decreased .
- But In the case of clay, the strength is rather increased. that could be caused by the creation of mullite from clay components.

3 RESULT AND DISCUSSION (Al_2O_3-SiO_2 brick's raw materials)

XPS(X ray Photoelectron Spectroscopy) of Fe peak in mullite chamotte

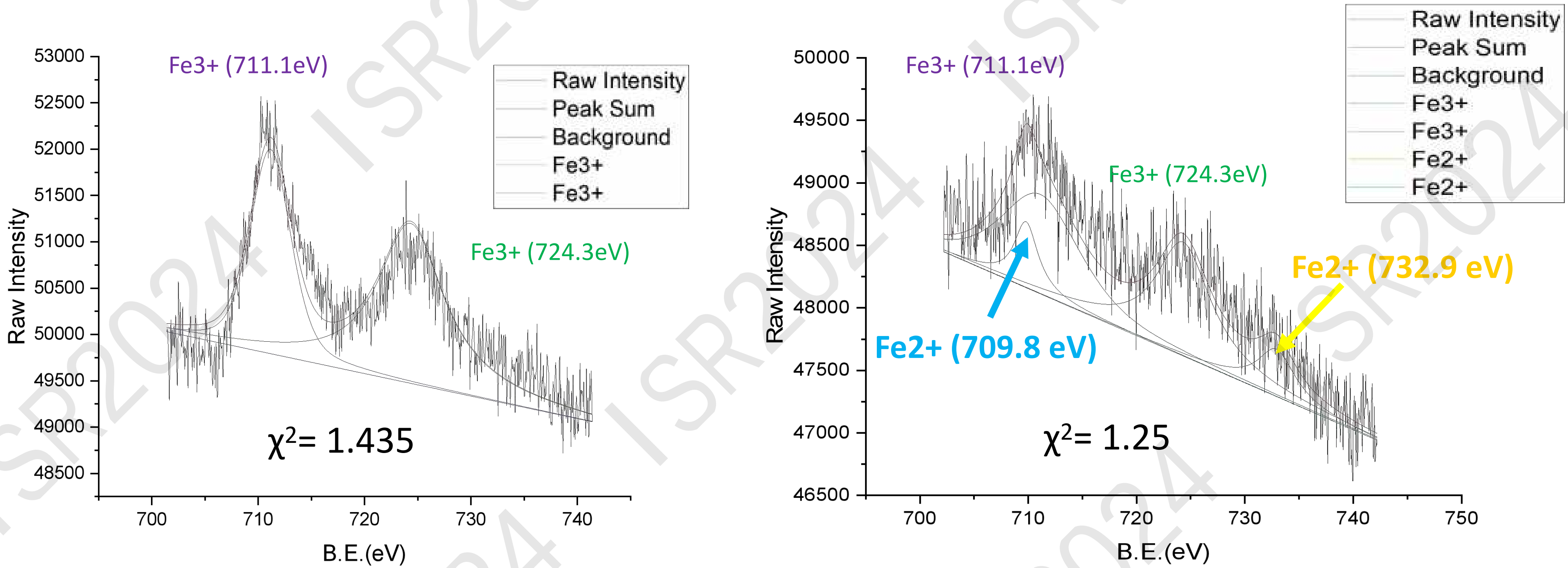


Fig. 9. XPS of Fe peak in mullite chamotte(0.3)
(a)Before hydrogen heat treatment (b)After hydrogen heat treatment

- Fig.9. shows XPS of Fe peak in mullite chamotte(-0.3mm) which contains 1.4wt% Fe_2O_3 as an impurity.
- After heat treatment, **the peaks of Fe^{2+} are detected**(blue & yellow line), and it shows that **Fe_3O_4 is produced t hrough a reduction of the Fe_2O_3 in a H_2 atmosphere.**

3 RESULT AND DISCUSSION (SiO₂ raw material)

Color changes of silica in hydrogen atmosphere

Fig. 10. Specimen before and after hydrogen heat treatment

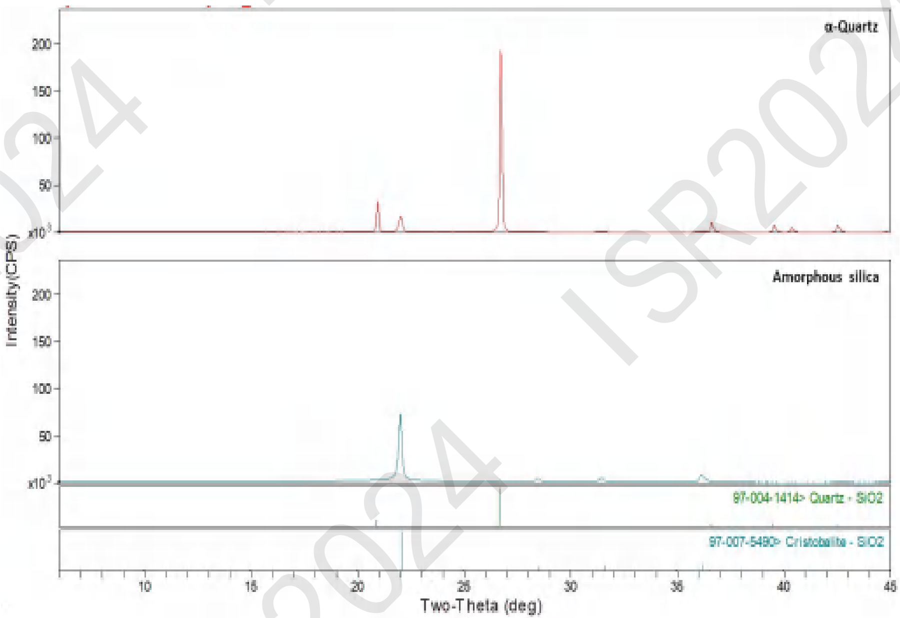


Fig. 11. XRD results before hydrogen heat treatment

Tab.7. Composition and content of silica

Material	Composition (wt%)				Phase (%)		
	SiO_2	Al_2O_3	Fe_2O_3	LOI	Quartz	Cristo balite	Amor phous
Amorphous	99.90	0.04	**0.01**	0.00	-	46	54
α-Quartz	99.05	0.34	**0.13**	0.13	88	12	-

- After heat treatment in a hydrogen atmosphere ,the color change is pronounced in α-Quartz specimen whic h has more Fe_2O_3 compound than amorphous specimen.

3 RESULT AND DISCUSSION (SiO_2 raw material)

Weight changes of silica in hydrogen atmosphere

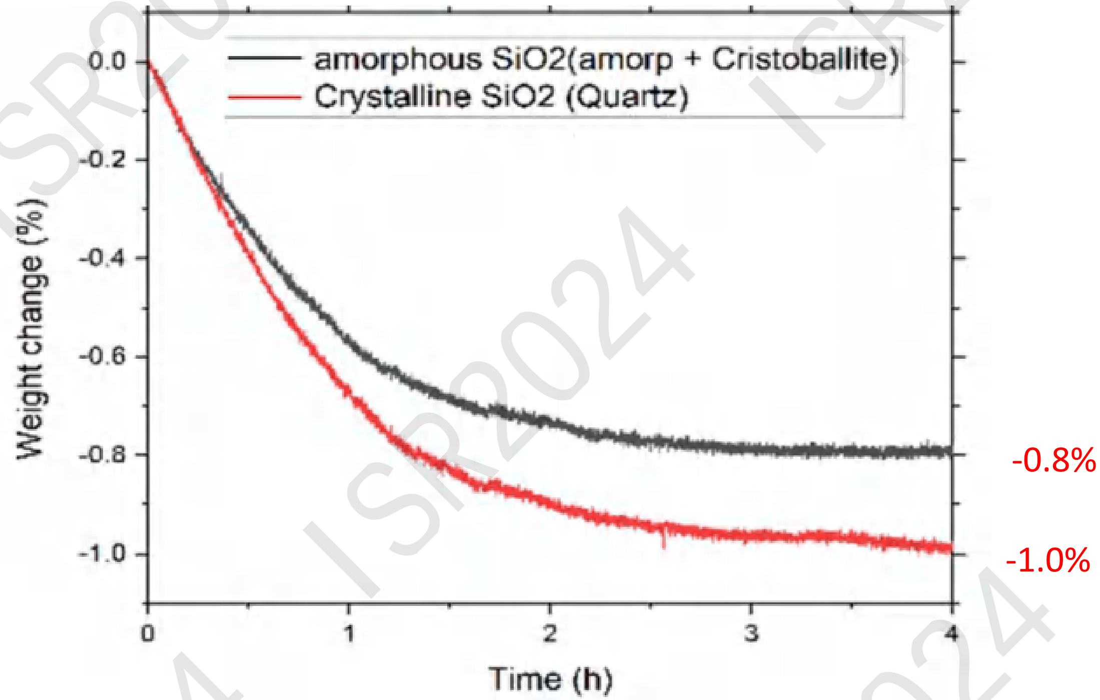


Fig. 12. TGA results of Silica

- TGA results of silica shows that the weight is decreased to 0.8wt% of amorphous silica and 1.0 wt% of quart z by keeping in hydrogen atmosphere at 1100℃
- In both cases, the weight loss was greater than the amount of impurities(0.13weight %) .
  It means that the weight loss of silica is **caused by the generation of SiO gas in a H_2 atmosphere**.

Calculation of silica volatilization loss in a hydrogen atmosphere

Assuming an equilibrium state with the Gibbs free energy for the volatilization reaction of silica[1],

Tab.8. Reduction reaction equation of silica

$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$	**(1) Direct reduction**
$SiO_2(s) \rightarrow SiO(g) + 1/2O_2(g)$	**(2) Indirect reduction**

$$\triangle G = -RT\ln K_{eq} = -RT\ln\frac{[SiO][H_2O]}{[H_2]}$$

According to reaction (1), ΔG = -219.71-170.09+661.48 = 271.68 (kJ/mol)

According to reaction (2), ΔG = -219.71+661.48 = 441.77 (kJ/mol)

Tab.9. Calculation of silica volatilization loss

	$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$				$SiO_2(s) \rightarrow SiO(g) + 1/2O_2(g)$					
	△G (J/mol)	exp(-G/RT)	D*[H2] = [SiO][H2O]	[SiO]=[H2O]	△G (J/mol)	exp(-G/RT)	[SiO][O2]^1/2	[O2]	[O2]^1/2	[SiO]
Cristobalite	271,680	4.61E-11	4.61E-06	**2.14E-03**	441,150	1.65E-17	1.65E-17	2.52E-20	1.59E-10	**1.04E-07**

[R] : 8.314J/molK [H2] : 100000 **[K] : 1373**

- The effect of **direct reduction by hydrogen is greater** than that of indirect reduction in a low oxygen partial pressure atmosphere.
- And, While the refractory is exposed to a hydrogen atmosphere at 1100℃. The deterioration of refractory will be accelerated by the volatilization of silica.

Microstructure changes of amorphous silica in a hydrogen atmosphere

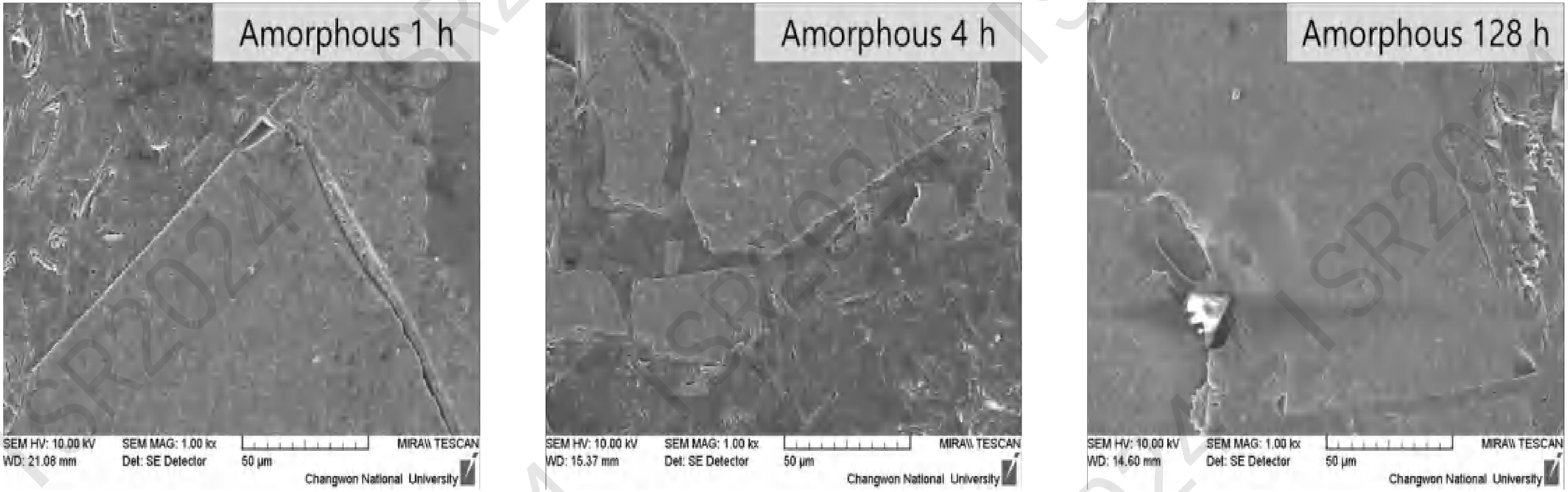


Fig. 13. SEM image of amorphous silica after hydrogen heat treatment

Amorphous silica keep their smooth surface after heating in a hydrogen atmosphere at 1100 °C for 128 hours

3 RESULT AND DISCUSSION (SiO$_2$ raw material)

Microstructure changes of crystalline silica in a hydrogen atmosphere

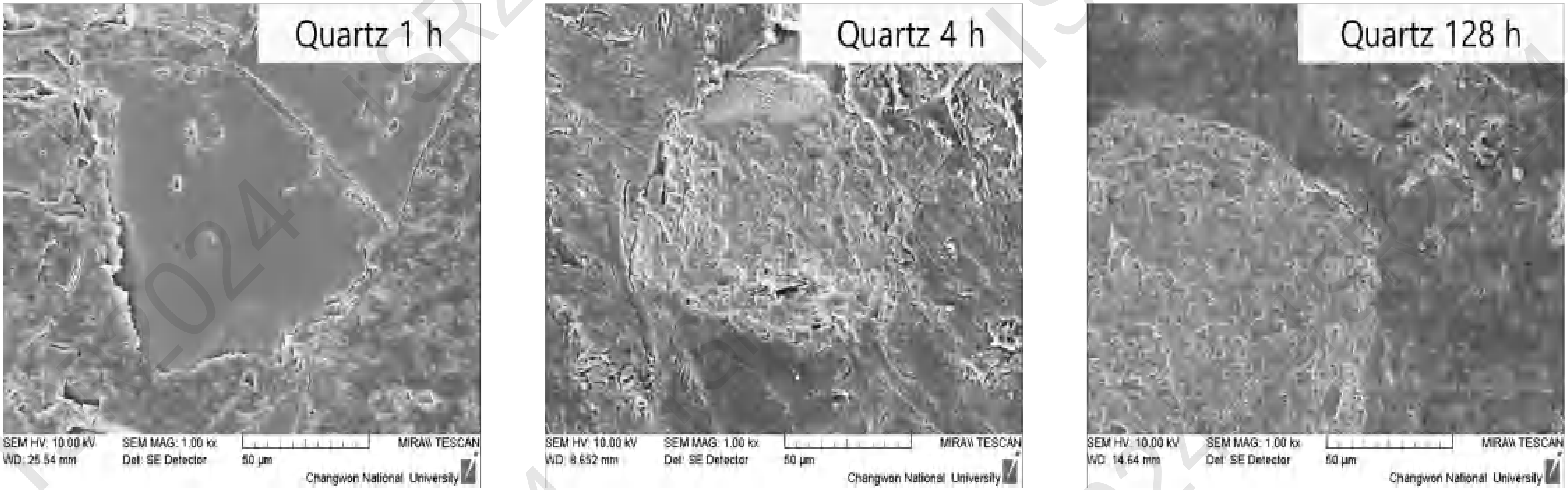
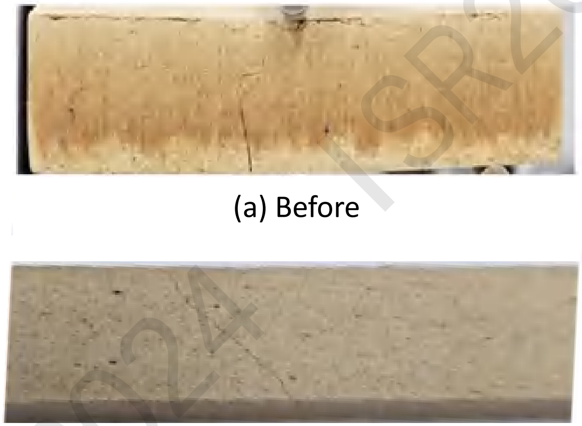


Fig. 14. SEM image of quartz after hydrogen heat treatment

- The quartz‘s original smooth surface turns into a rough surface after heating for more than 4 hours at 1100° C.
- These damage of quartz could reduce strength of refractory.

Color changes of MgO in a hydrogen atmosphere



(a) Before

(b) After

Fig. 15. Color of MgO specimens before and after heating at 400 ℃ in pure hydrogen atmosphere

Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	P_2O_5
W/%	0.34	0.05	0.55	97.70	1.20	0.04

Table 10. Chemical composition of MgO brick

- The color of the specimen is changed after heating, that means some reactions could occure even at 400 ℃ in a hydrogen atmosphere.
- Table 10 shows that MgO specimen has 0.55 weight % Fe_2O_3 which could be reduced by H_2 and produce H_2O in the specimen after heating.

3 RESULT AND DISCUSSION (MgO brick)

Physical property changes after heating in a hydrogen atmosphere

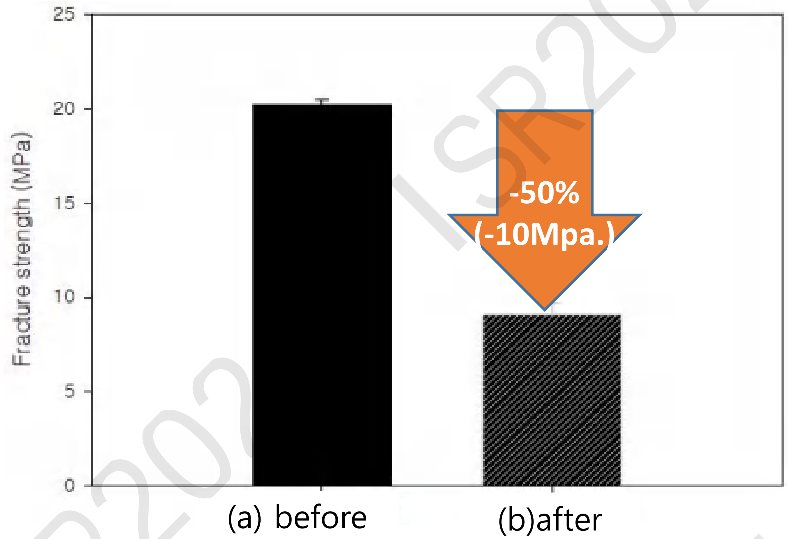


Fig. 16. Modulus of rupture of MgO specimens

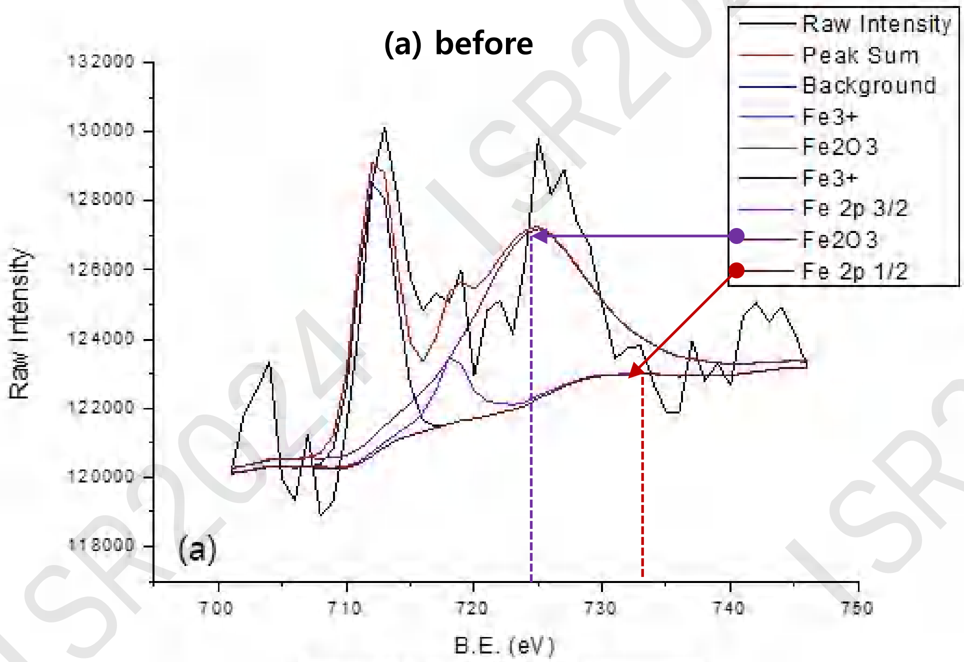
Specimen No.	Density (g/cm3)		△D (%)
	Before	After	
1	2.63	2.60	-0.9
2	2.62	2.61	-0.2
3	2.60	2.59	-0.6

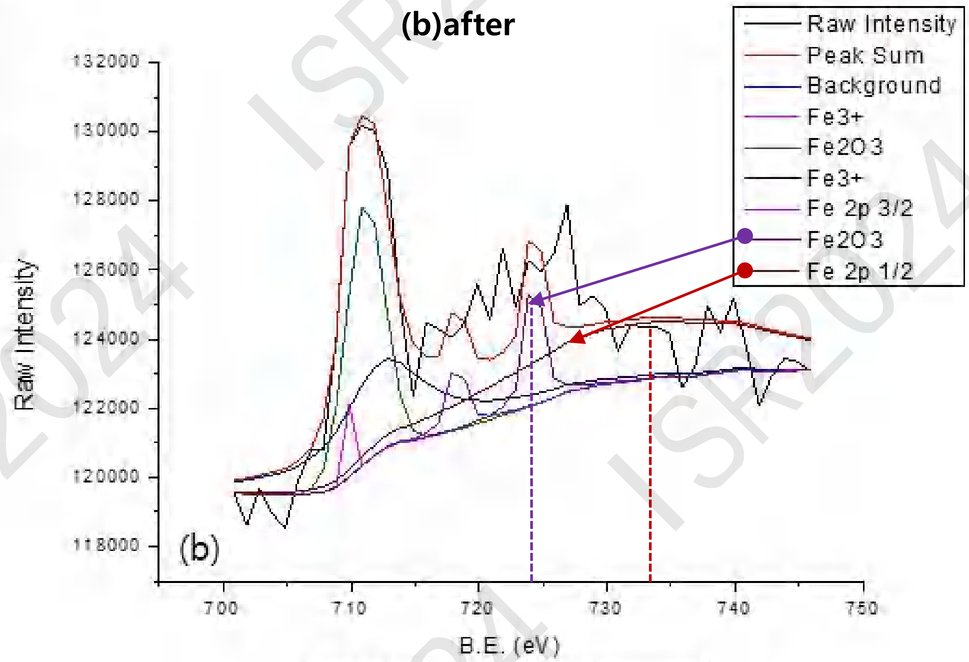
Table 11. Density of MgO specimens

- The strength of the MgO specimen is decreased by 50% (~10 MPa) after heated in 100% hydrogen atmosphere.
- This strength reduction is due to the generation of $Mg(OH)_2$ by the hydration reaction of MgO with H_2O.

RESULT AND DISCUSSION (MgO brick)

XPS results for Fe element in MgO brick





B.E. (eV)	(at. %)	
709.8	Fe3+	9.17391E-05
711.1	Fe2O3	9.17391E-05
712.3	Fe3+	26.995473
718.3	Fe 2p 3/2	8.141784038
724.3	Fe2O3	64.86246775
732.9	Fe 2p 1/2	9.17391E-05

B.E. (eV)	(%)	
709.8	Fe3+	1.395874
711.1	Fe2O3	21.987
712.3	Fe3+	28.30848
718.3	Fe 2p 3/2	3.793843
724.3	Fe2O3	7.369111
732.9	Fe 2p 1/2	37.1457

$3Fe_2O_3 + H_2(g) \rightarrow 2Fe_3O_4 + H_2O(g)$ --ΔG^o = -52984J/mol ,at 400℃

Generation of H_2O by Fe oxide in a H_2 atmosphere

$3Fe_2O_3 + H_2(g) \rightarrow 2Fe_3O_4 + H_2O(g)$ --(1)

$\Delta G^o = -RT\ln K_{eq} = -RT\ln(P_{H2O}/P_{H2})$

ΔG°=2-0.0817T(kJ/mol)				
ΔG°	[H2]	Temp(K)	exp(-G/RT)	[H2O]
-52984J/mol	100000	673	1.29 x 104	1.29 x 109

$MgO + H_2O(g) = Mg(OH)_2$ --(2)

- MgO refractories can be hydrated and weakened by H_2O generated by the reduction of Fe_2O_3 to Fe_3O_4 at 400°C.
- Since Fe_2O_3 exists as an impurity in the refractory, it is necessary to select a refractory with less Fe_2O_3 impurity to suppress hydration of the refractory.

4 CONCLUSION

1. The strength of refractory brick could be decreased by reduction of impurities such as Na_2O, K_2O, and Fe_2O_3 in a hydrogen atmosphere.

2. Refractory bricks show reversible color changes after heating in a hydrogen atmosphere. Fe_3O_4 and Fe, the reduction products of Fe_2O_3, were observed as major color change factors.

3. The strength of refractory is more vulnerable in a hydrogen atmosphere than in the air.

4. Silica components are prone to damage due to the evaporation of SiO, which leads to the weakening of refractory bricks.

5. The volatilization loss of silica by direct reduction with hydrogen is greater than that of indirect reduction at low oxygen partial pressure.

6. In a fluidized reduction furnace, where temperatures can be down to 400 ℃, there is a risk of slaking by hydration reactions in MgO materials. it is necessary to select a refractory with less Fe_2O_3 impurity to suppress hydration of the refractory.

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Thank you for your attention

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