



The Influence of Adding Recycled Refractories on The Mechanical Strength and Thermal Shock Resistance of Al_2O_3 -C Refractory Formed by Isostatic Pressing

Zhi GAO*, Lei PAN, Zuochuang WANG, Qin YANG

1 Puyang Refractories Group Co., Ltd., China



CONTENTS



Introduction

Experimental Procedures

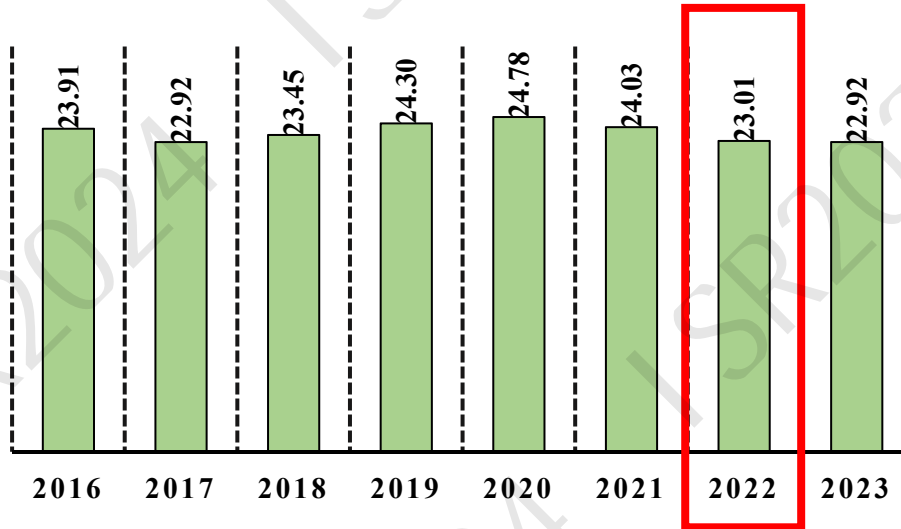
Results and Discussions

Conclusions

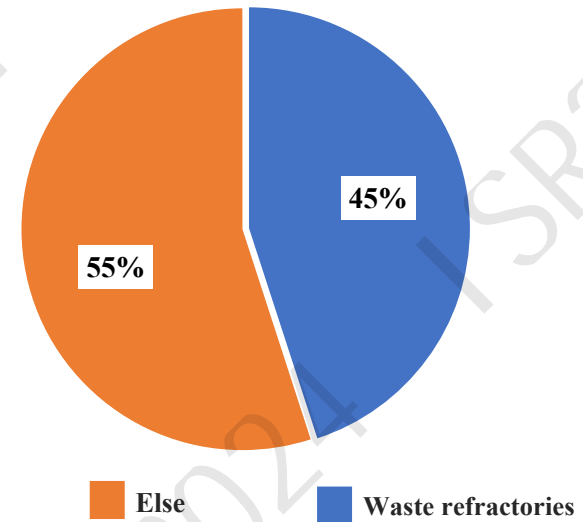
1. Introduction

Production of waste refractories in China

Change of refractory production in China (Mt)



Total consumption of refractory materials in 2022



- In China, annual production of refractory exceeds 22 million tons, and over 9 million tons waste refractories were produced each year.

1. Introduction

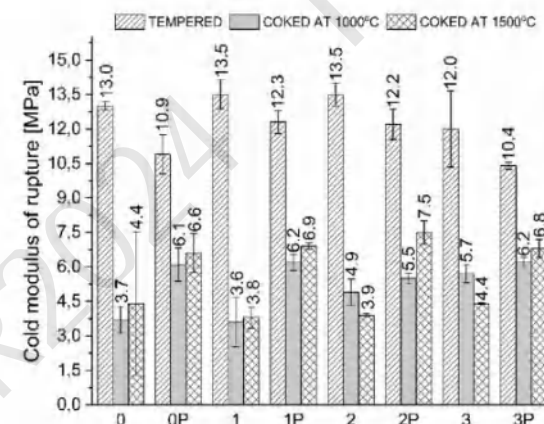
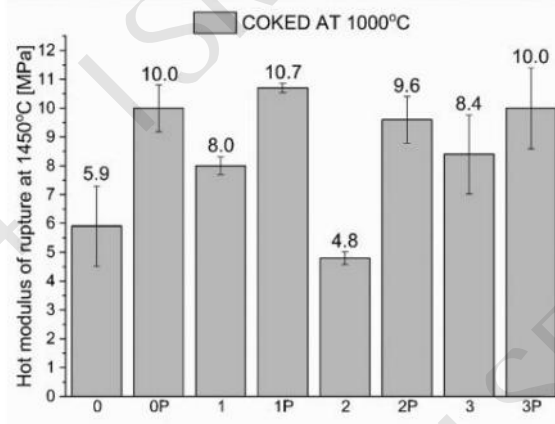
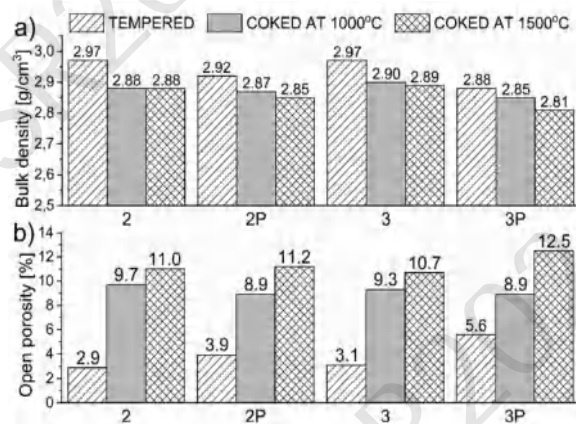
Recycling of MgO-C refractory

MgO-C brick with 30 wt% recycled refractories

Table 1
Designations of the samples.

Description	Content of recycled aggregate, [wt%]			
	0 (reference)	10	20	30
Sample without MgO _p	0	1	2	3
Sample with MgO _p	0P	1P	2P	3P

MgO_p – powder fraction of fused MgO (<0.125 mm).



➤ Adding 30wt% recycled refractories has little effect on the performance of MgO-C bricks, but greatly saves costs.

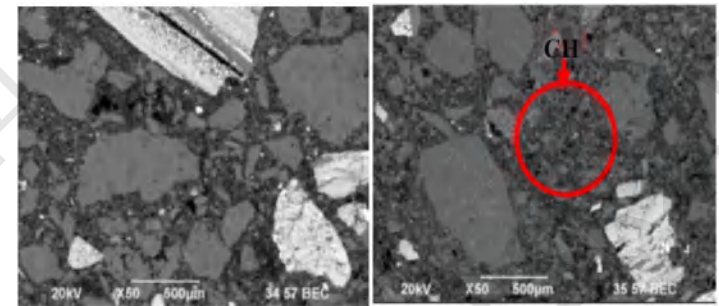
1. Introduction

Recycling of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-C}$ refractory

$\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-C}$ sliding nozzle with 50 wt% recycled refractories

Table 1 Composition of experiment formulation %

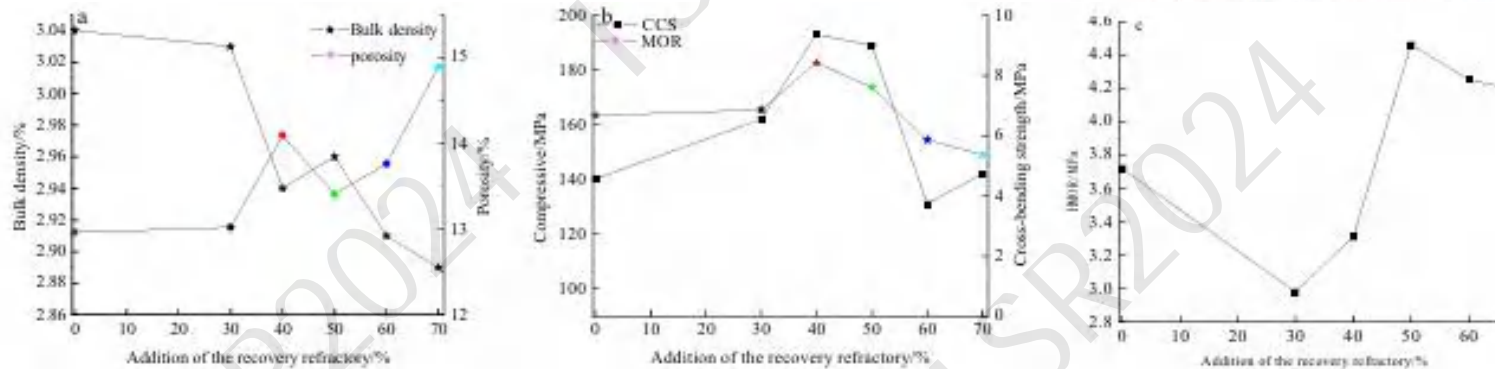
Ingredients	Formulation					
	1#	2#	3#	4#	5#	6#
Recovery refractory	0	30	40	50	60	70
Carbon	7	5	4	3.5	3	2
Corundum	55	42	33	25.5	17	10
ZAS	15	11	10	8	7	5



A normal sliding nozzle

B recovery sliding nozzle

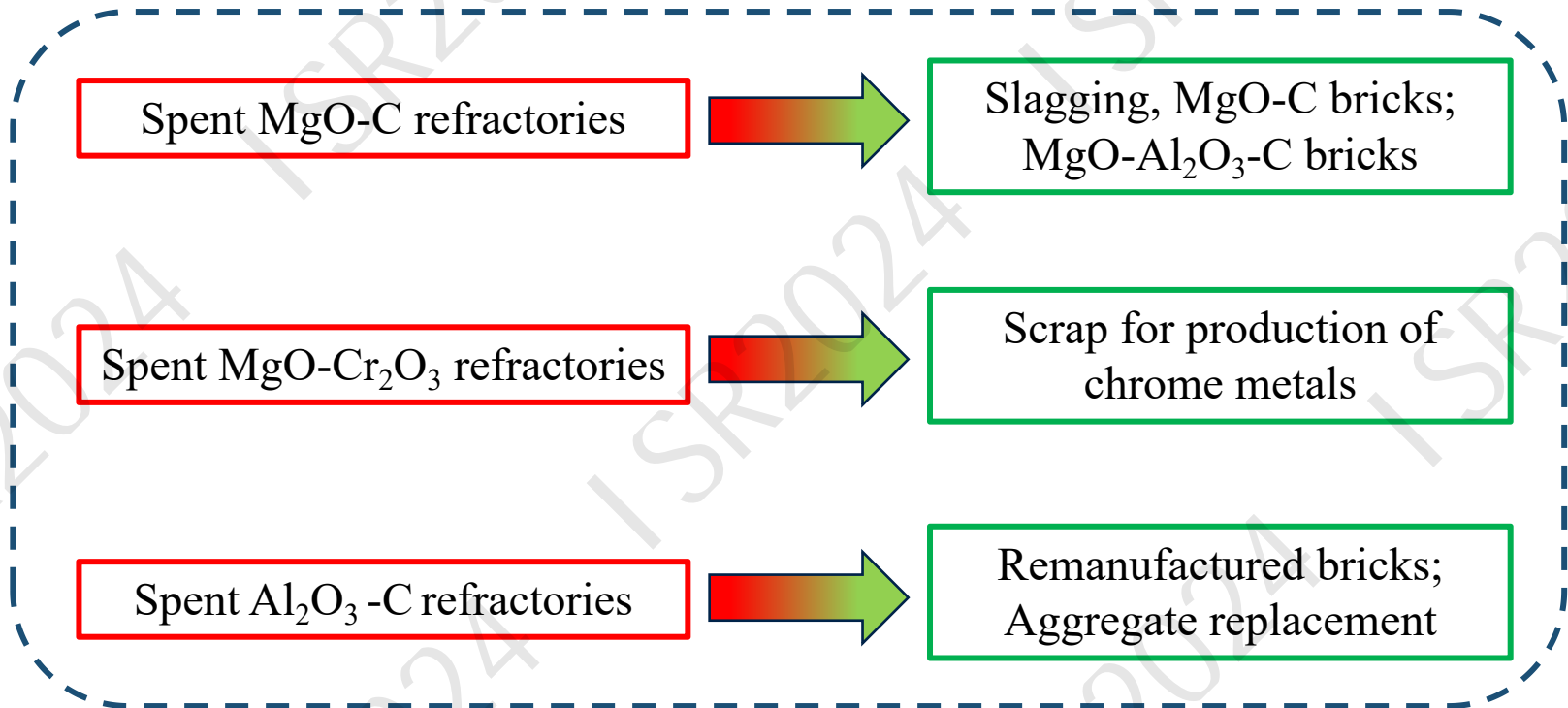
Fig 3 The photograph of microstructure



➤ Adding 50wt% recycled refractories enhances the performance of $\text{MgO-ZrO}_2\text{-C}$ refractory.

1. Introduction

Research situation



- **The recycling of isostatic pressing products (mainly composed of Al₂O₃ and C) has better economic value.**

1. Introduction

Isostatic Pressing Products

Submerged Entry Nozzle



Tundish Stoppers



Ladle Shrouds



Tundish Nozzle



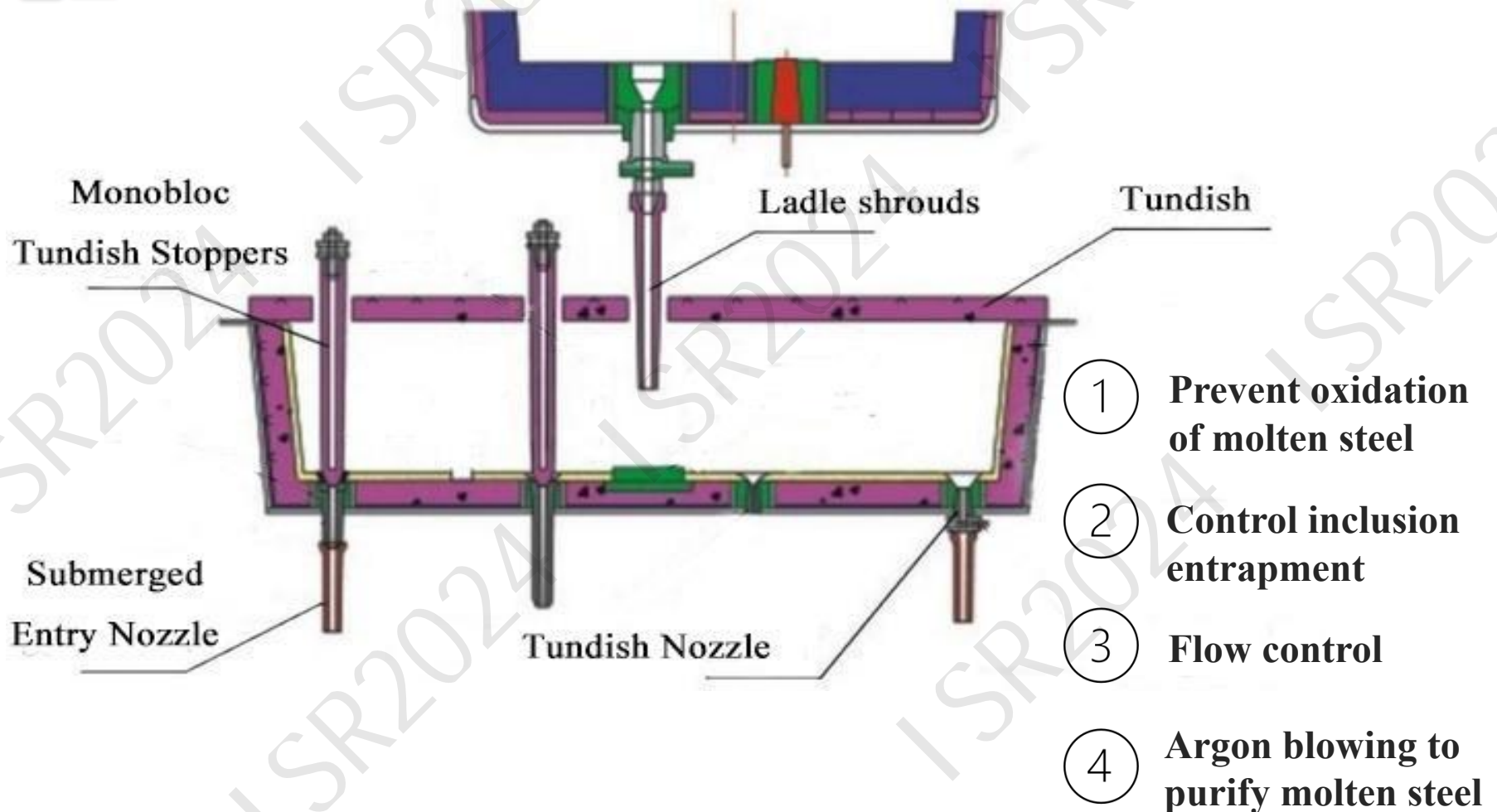
High quality raw materials:

1. fused corundum
2. fused quartz
3. high purity flake graphite

**Complex process
and
High production cost**

1. Introduction

Working condition



1. Introduction

After Used



The body of Ladle Shrouds



Inner layer of stoppers



The body of nozzles

➤ **These parts have not been contaminated by molten steel and have high recycling value**

1. Introduction

» Causes and difficulties

External factors

- ① Unclassified processing after used
- ② Difficulty in cleaning up
- ③ Low consumption and low attention



Intrinsic factors

- ① Decline of aggregate grade
- ② Introduction of metal impurities

➤ If the recycled refractories can be reasonably utilized in isostatic pressing products, it will be beneficial for reducing costs and carbon cycling.

2. Experimental Procedures

➤➤ Indicators of recycled refractories

Particle size distribution of recycled refractories (mm)

Particle size range	≥1.5	1.5~1	1~0.5	0.5~0.2	0.2~0.1	≤0.1
Mass fraction (wt%)	1.4	15.9	22.01	43.67	9.83	8.15

Chemical composition of recycled refractories (wt%)

	SiO ₂	Al ₂ O ₃	SiC	Si	C	ZrO ₂	Others
Content	8.90	56.22	1.71	1.00	20.58	3.63	7.96

- Recycled refractories also contain a small amount of MgO, CaO, Na₂O, K₂O impurity.

2. Experimental Procedures

➤➤ Procedure

Raw materials

Binder and solvent

Recycled refractories



Material-mixing



Mold



Isostatic pressing



Slicing



Sintering



Stoving

2. Experimental Procedures

Analysis and Testing



Cold modulus of rupture



Bulk density & Apparent porosity



Cold compress strength



Hot modulus of rupture



Thermal Shock Resistance

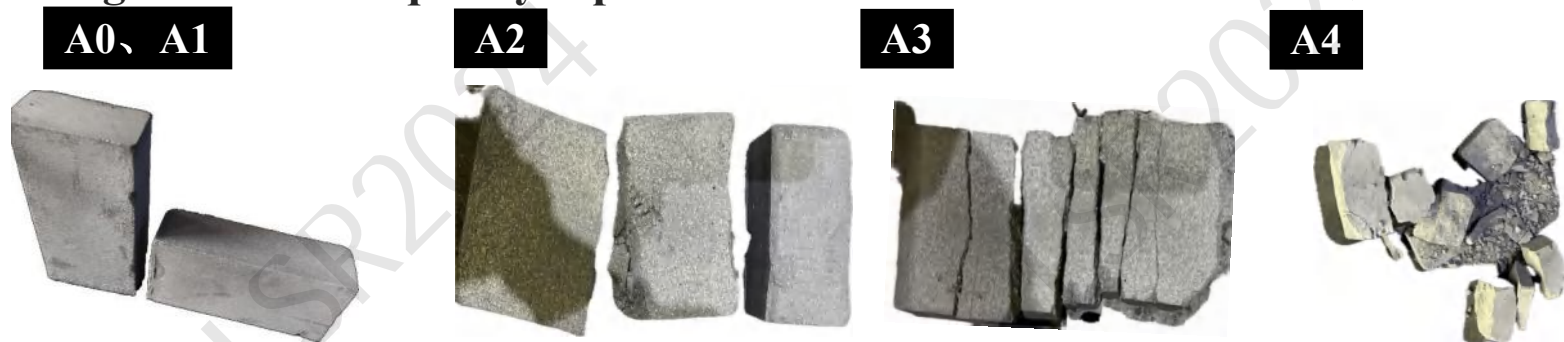
3. Results and Discussions

1. The influence of the quantity of recycled refractories added

Basic formula of samples (wt%)

Raw material	A0	A1	A2	A3	A4
Tabular alumina (<2 mm)	65	58.5	52	45.5	39
Mixed powder	25	22.5	20	17.5	15
Flake graphite	10	9	8	7	6
Solid phenolic resin	+4.5	+4.5	+4.5	+4.5	+4.5
Recycled refractories	0	10	20	30	40

Forming results after quality replacement:



3. Results and Discussions

1. The influence of the quantity of recycled refractories added

Chemical composition of each sample

	SiO ₂	Al ₂ O ₃	ZrO ₂	SiC	C	Si
A0	4.86	82.60	0.04	-	10.07	0.52
A1	5.49	78.33	0.65	-	12.25	0.65
A2	5.47	75.13	1.30	0.47	13.34	0.54
A3	5.88	72.62	2.03	0.60	14.51	0.55
A4	6.63	68.52	3.00	0.77	16.25	0.51

- ✓ The replacement of quality will cause changes in the particle size distribution and composition of the system.
- ✓ Based on the above molding results and chemical composition, sample A3 is selected for subsequent experiments.

3. Results and Discussions

2. Effect of particle size distribution

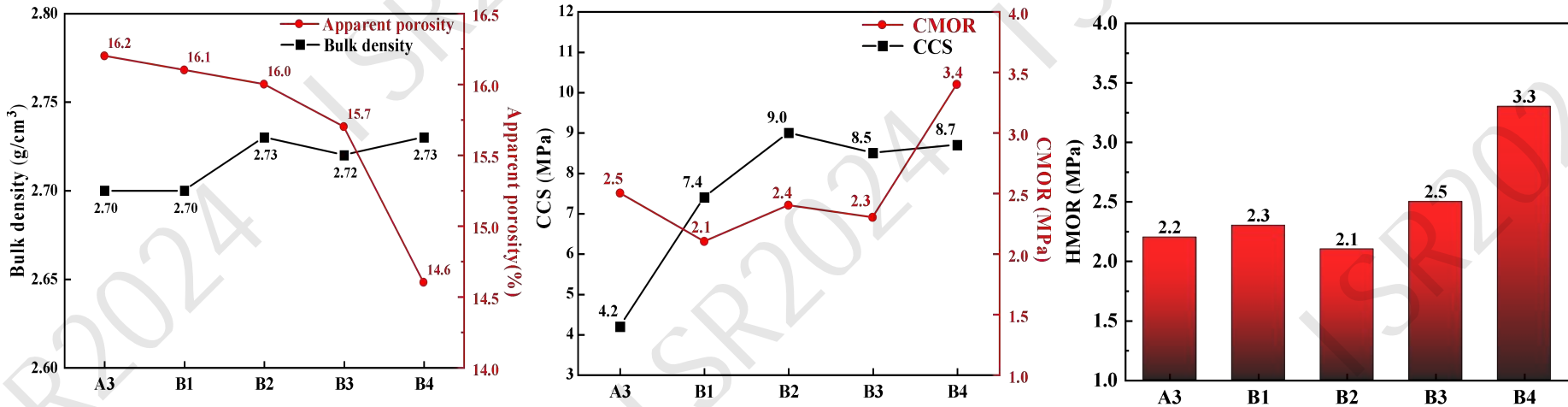
Sample ratio for particle grading experiment (wt%)

Raw material		A3	B1	B2	B3	B4
Tabular alumina	2-1 mm	10.5	15.5	10.5	10.5	15
	1-0.5 mm	17.5	12.5	25	10	18.5
	0.5-0 mm	17.5	17.5	10	25	11.5
Mixed powder		17.5	17.5	17.5	17.5	17.5
Flake graphite		7	7	7	7	7
Solid phenolic resin		+4.5	+4.5	+4.5	+4.5	+4.5
Recycled refractories		30	30	30	30	30
Forming result		Layered cracking				No cracks



3. Results and Discussions

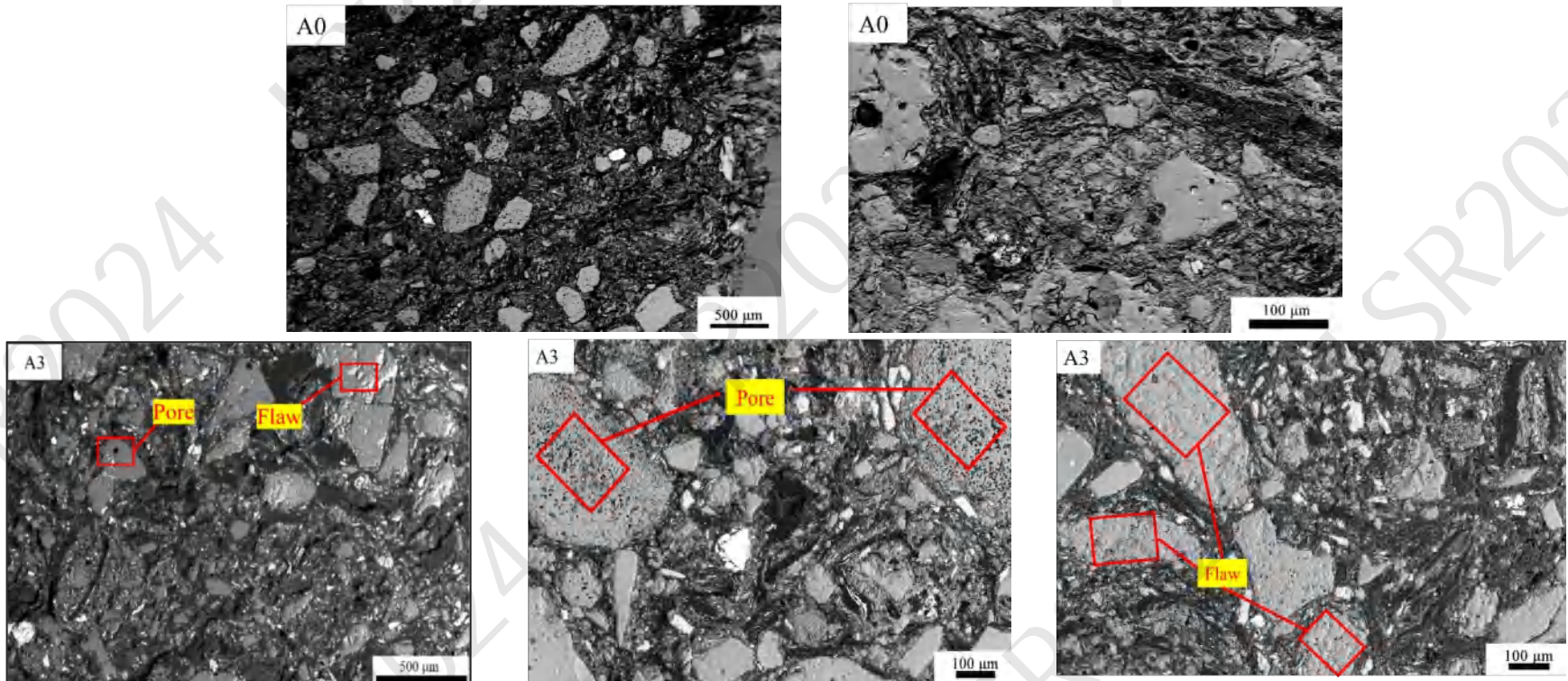
a) Physical properties



- Adjusting the particle size distribution by increasing the proportion of large particles can significantly improve molding results.
- Room temperature strength and hot modulus of rupture are improved but do not meet the conditions for industrial.

3. Results and Discussions

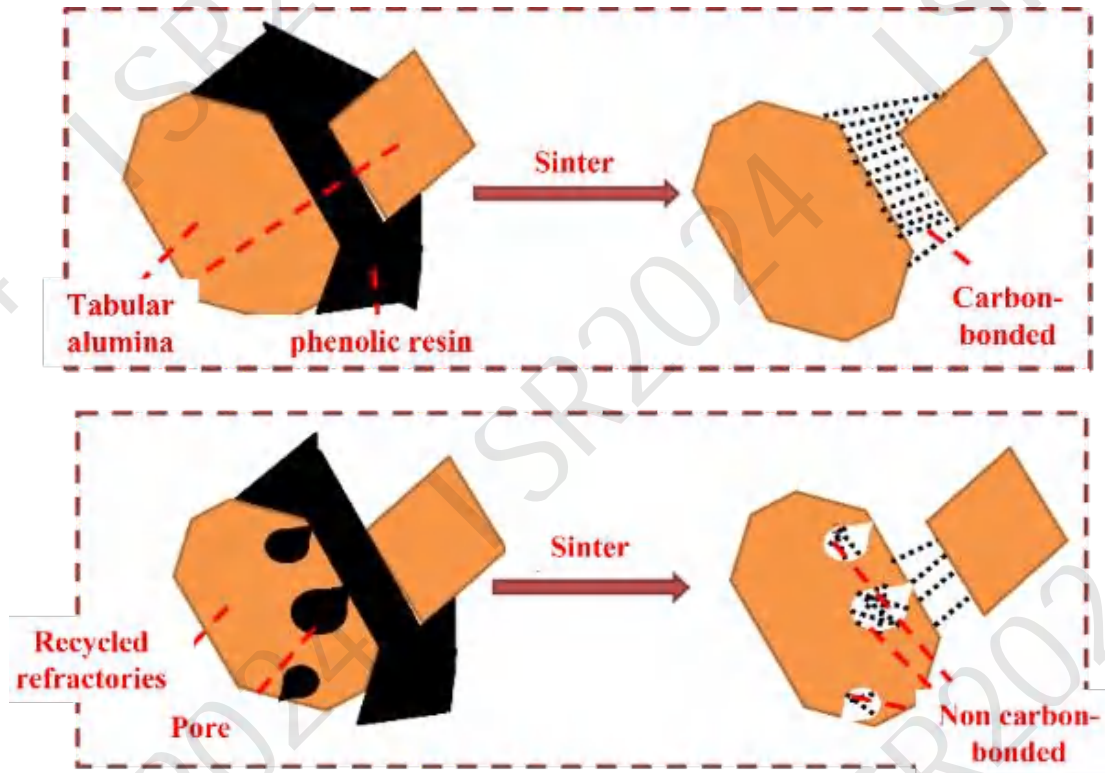
b) SEM micrographs



- The recycled aggregate particles have many cracks and pores compared with tabular corundum.

3. Results and Discussions

c) Schematic diagram of carbon network formation



- Some resin fills into these pores, preventing it from participating in the subsequent formation of the carbon bonded

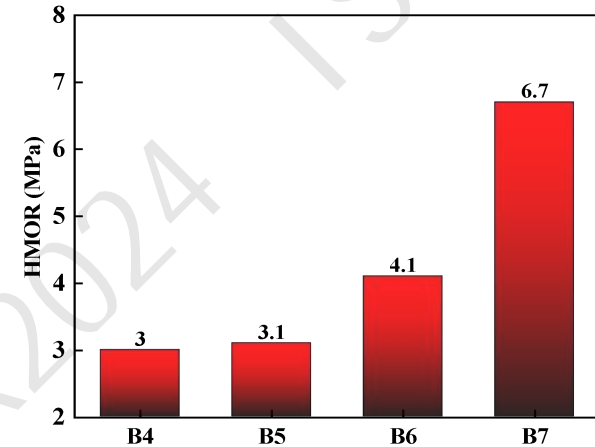
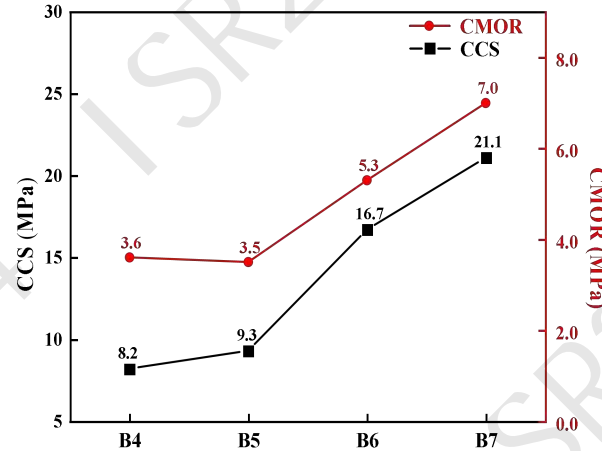
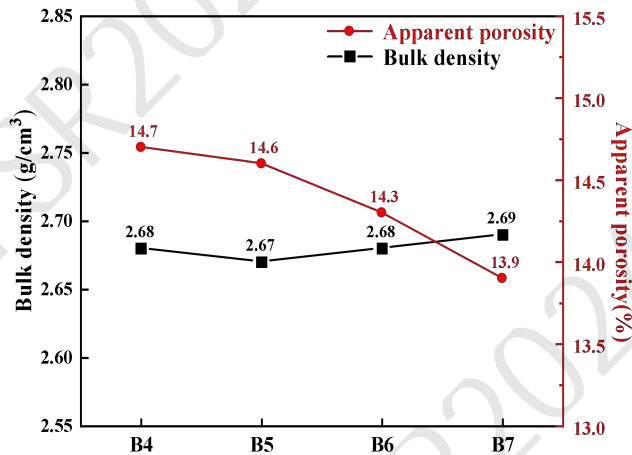
3. Results and Discussions

3. Influence of binder addition on the strength of samples

Amount of binder added (wt%)

Sample	B4	B5	B6	B7
Addition amount of solid phenolic resin	+4.5	+5	+5.5	+6.0

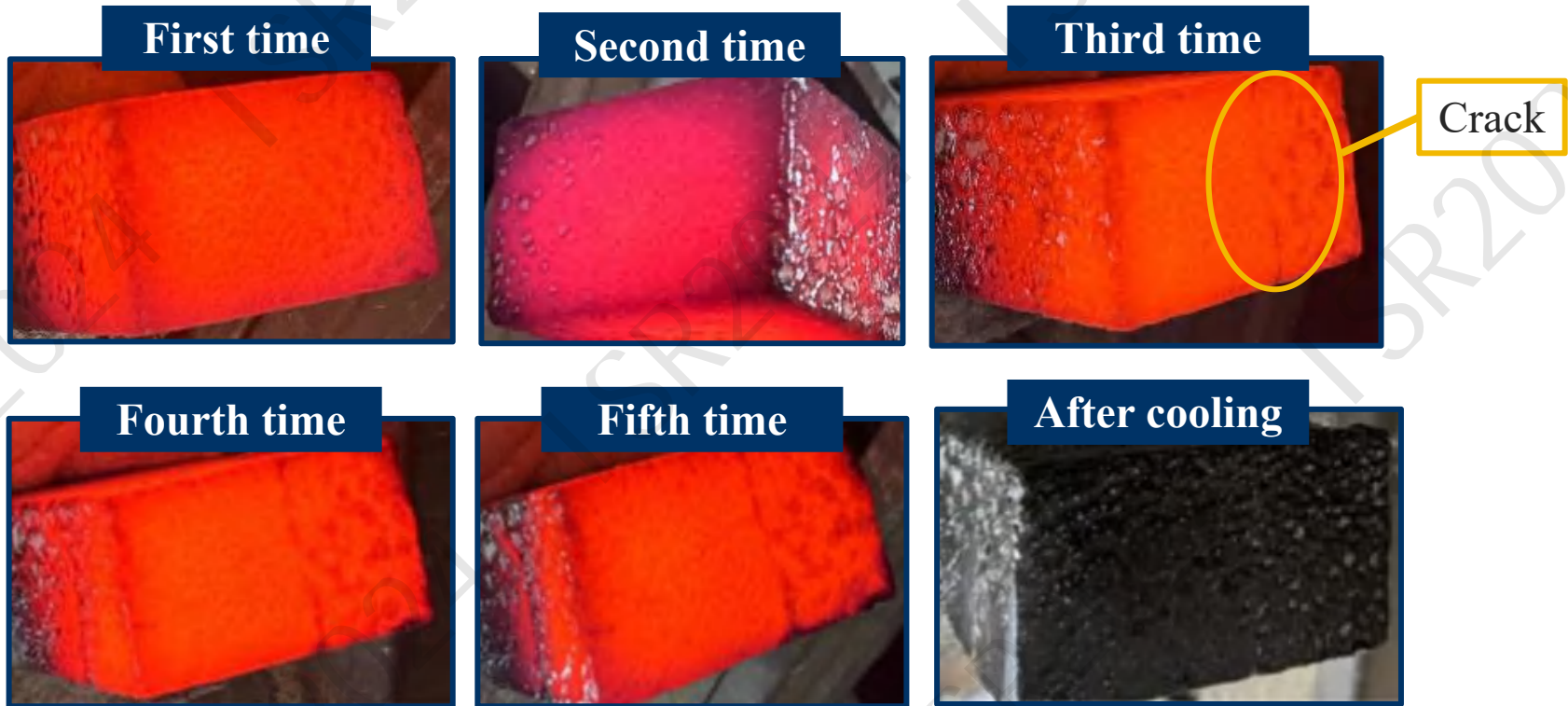
a) Physical properties



➤ By supplementing 1.5wt% resin, the strength at room temperature and high temperature were increased by about 1 times

3. Results and Discussions

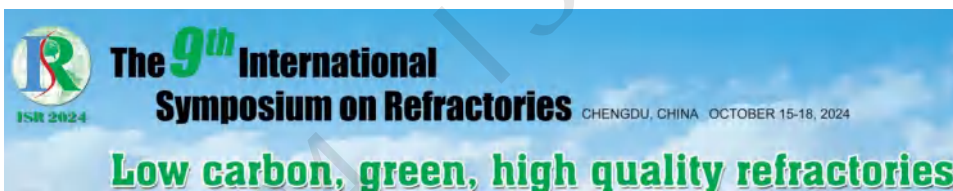
» 4. Thermal Shock Resistance



- After two cycles of water cooling, the surface of the sample B7 showed no cracks, and after five cycles of water cooling, there was no spalling

» Conclusions

- Using recycled refractories instead of raw materials will lead to a reduction in strength. Due to the irregularity, wide particle size range, high impurity content and contain numerous pores of recycled refractories, these factors hinder the formation of carbon networks involving certain binders.
- After adjusting the particle size distribution, the forming strength of $\text{Al}_2\text{O}_3\text{-C}$ refractory has been enhanced. However, there is only a marginal increase in strength after sintering.
- Appropriately increasing the amount of binder can significantly improve the strength of $\text{Al}_2\text{O}_3\text{-C}$ refractory. Additionally, thermal shock resistance is also ensured to a certain extent.



Thanks for Your Attention!