SYNTHESIS AND APPLICATION OF HEAVY-DENSITY CALCIUM HEXALUMINATE

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Difficulties of densification and sinter of heavy-density CA6, most papers have studied the light-density CA6 & insulation.

This paper investigates the synthesis of heavy-density CA6 including

Additive and sintering temperatures.

Properties of alumina-CA6 composite materials including bricks and castables

Optimized in field applications, working linings in steel ladles, EAF roofs, slide gates, purge blocks, RH furnaces, checker bricks & regenerators, glass-making furnaces, cement kilns.

HIGIANT PRODUCTS

1. Tabular alumina
2. Sintered spinel
3. Ultrafine alumina and spinel powders
4. Hydratable alumina powders
5. Dispersant
6. CA6 and CA2

- Calcium hexaluminate or hexaaluminate (CA6), unique & excellent characteristics and properties[.
- Heavy-density CA6 possesses tabular crystal structure, micro-pore within crystal grains, good thermal shock resistance
- Stable in reducing atmosphere at high temperatures.
- Excellent resistance against high-basicity steel slags, CA6 widely used in metallurgy, aluminum-making,
- Excellent resistance against Na_2O –rich gas, checker bricks & regenerators, glass-making and waste incineration.

In binary CaO-Al_2O_3 system, C3A, C12A7, CA, CA2, CA6

CA6, refractoriness 1850°C,

CA6, highest alumina content Al_2O_3 91.6%

CA6, highest density, theoretical density 3.82.cm.

Compatibility, thermal expansion coefficient of CA6 is 8.0×10-6/°C, in comparison with pure Al_2O_3 (8.6×10–6/°C)

Complementarity, rigid & stiff alumina vs. flexible & soft CA6

Table 1 Composition and properties of main raw materials.

Heat treatment	Chemical composition， w/%					Particle size/ um			Pack density /g.cm^{-3}
	Al_2O_3	CaO	Na_2O+ K_2O	SiO_2	Fe_2O_3	D10	D50	D90	
Industrial alumina	/	/	0.32	0.01	0.01	1.49	8.17	29.23	0.68
Q-calcium carbonate *	0.86	97.77	0.03	0.31	0.18	0.91	2.86	6.08	0.55

*： Chemical composition of calcium carbonate was based on 1100°C treatment.

1. Experimental

1.1 Raw Materials

- Additive material X was doped with addition of 0a, 1a, 2a, 3a and 4a respectively to promote the sinter of CA6 after high temperature firing.
- Additives can be a lot options
- Calcium carbonate and industrial alumina powders were mixed stoichiometrically, i.e. CaO 8.38%, Al_2O_3 91.62%,
- Pressed to tablets

1.2 Lab Experimental Procedures and Measurements

- Sintered at 1400℃、1500℃、1600℃、1650℃、1700℃、1750℃, holding for 3 hours。

2. Lab Results and Discussions

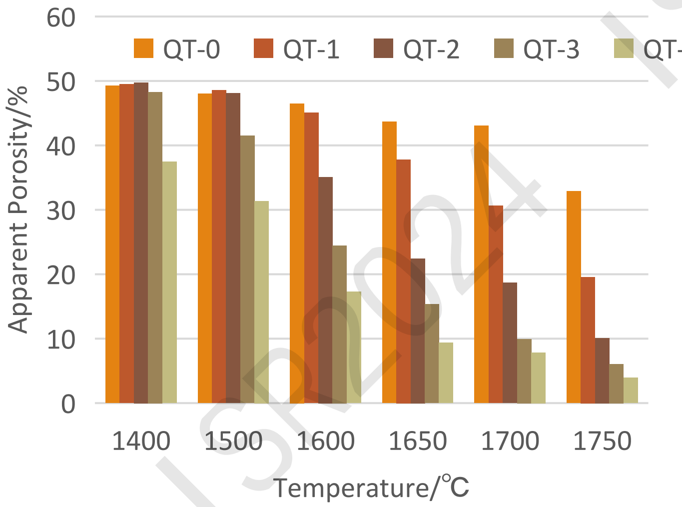


Fig.1 Apparent porosity vs temperature of QT samples

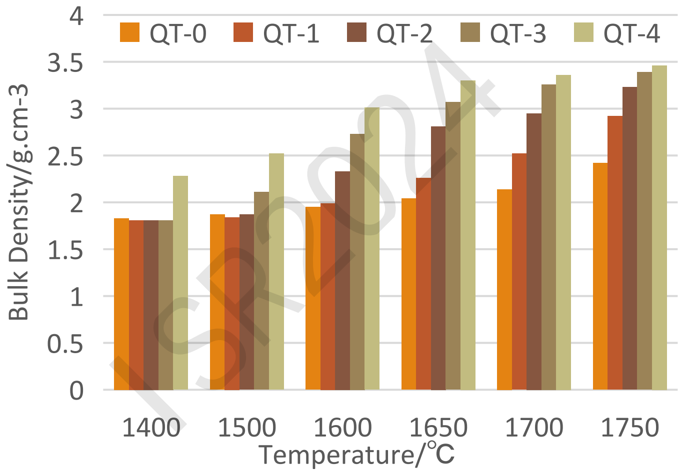


Fig. 2 Bulk density vs temperature of QT samples

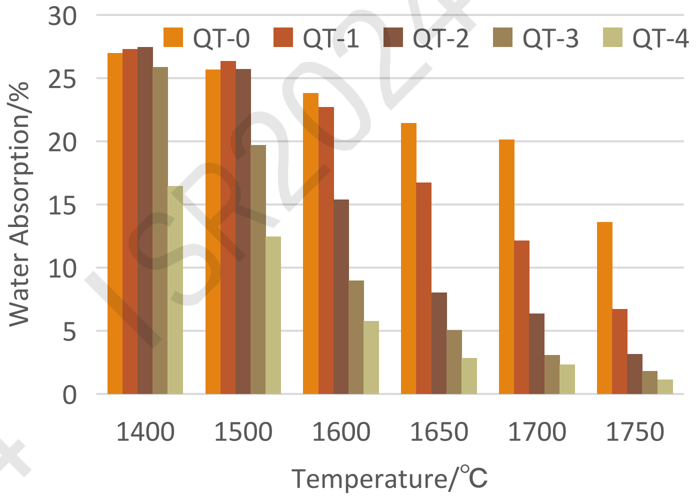


Fig. 3 Water absorption vs temperature of QT samples

Table 2 Physical properties of QT-3 after different temperature treatment

	Apparent porosity/%	Bulk Density/g.cm^{-3}	water absorption /%
1400℃×3h	48.29	1.81	25.86
1500℃×3h	41.48	2.11	19.69
1600℃×3h	24.47	2.73	8.96
1650℃×3h	15.33	3.07	5.05
1700℃×3h	9.96	3.26	3.05
1750℃×3h	6.08	3.39	1.79

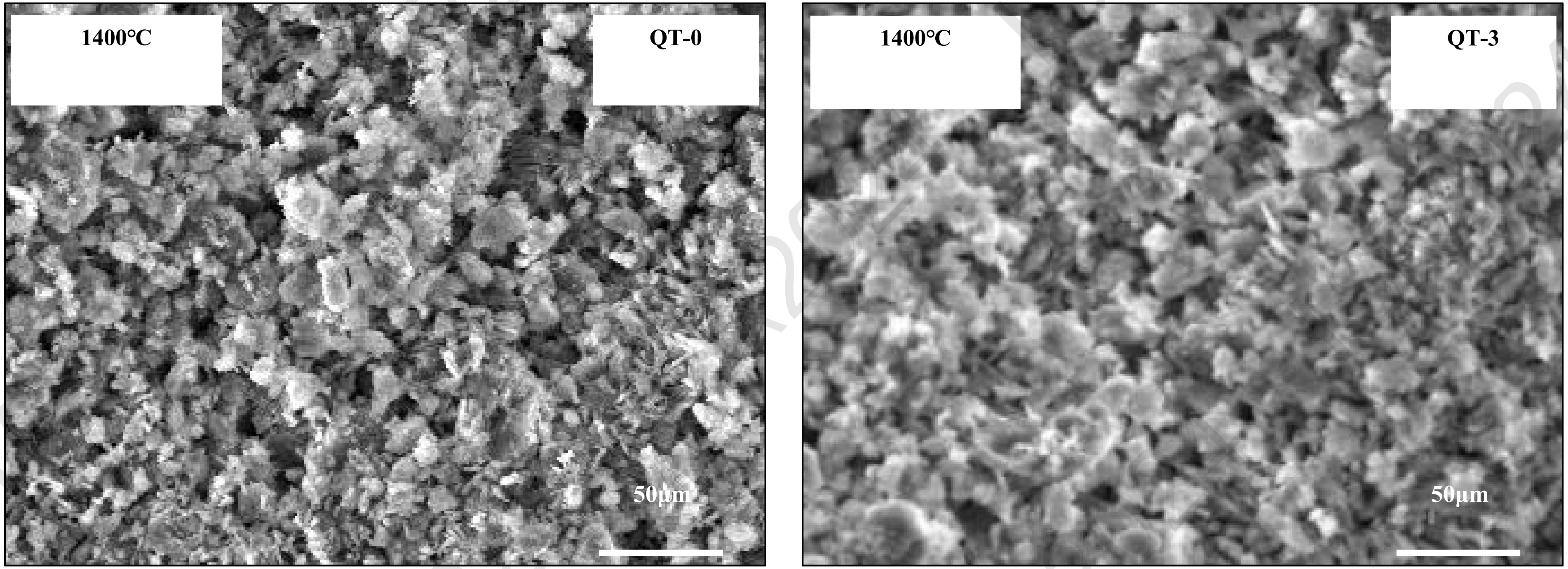


Fig. 4 Microstructure of QT-0 and QT-3 after 1400℃×3h firng

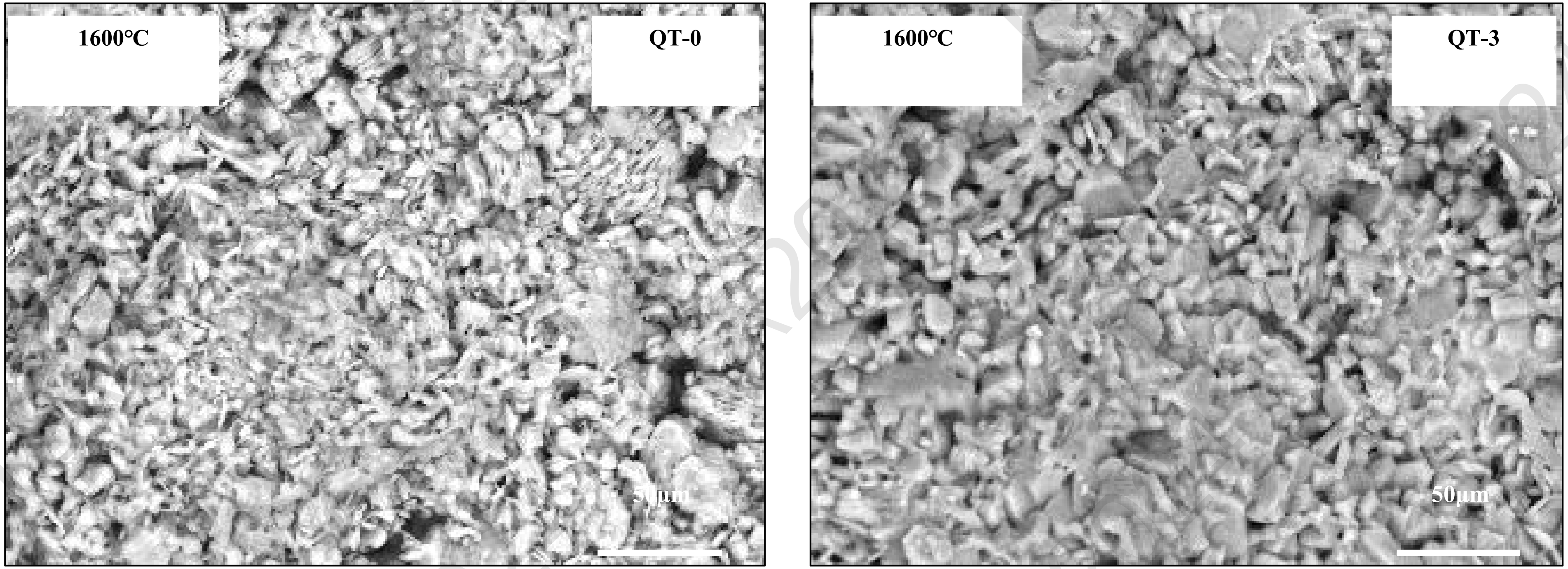


Fig. 5 Microstructure of QT-0 and QT-3 after 1600℃×3h firng

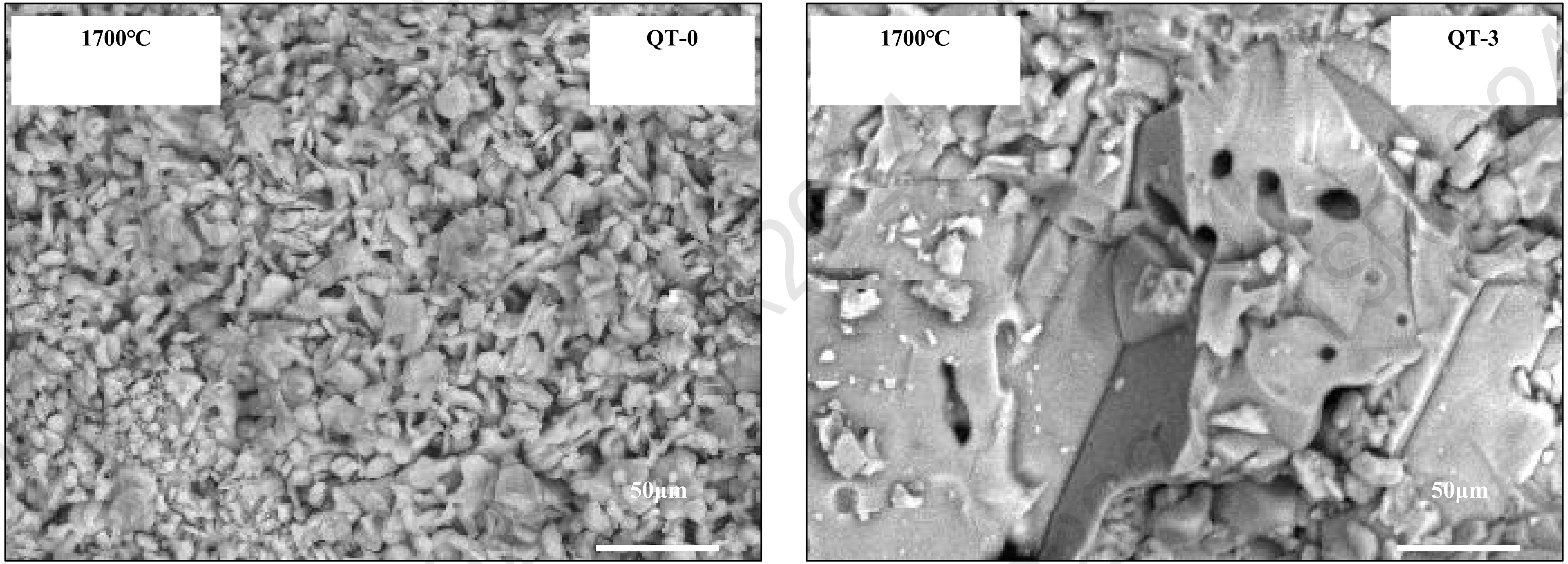


Fig. 6 Microstructure of QT-0 and QT-3 after 1700℃×3h firng

- CA6 phase dominated, minor corundum and trace CA2 available.
- Actually sintered at 1400℃, almost all CaO and Al_2O_3 were reacted to CA6, easy to synthesize CA6, but difficult to densify.

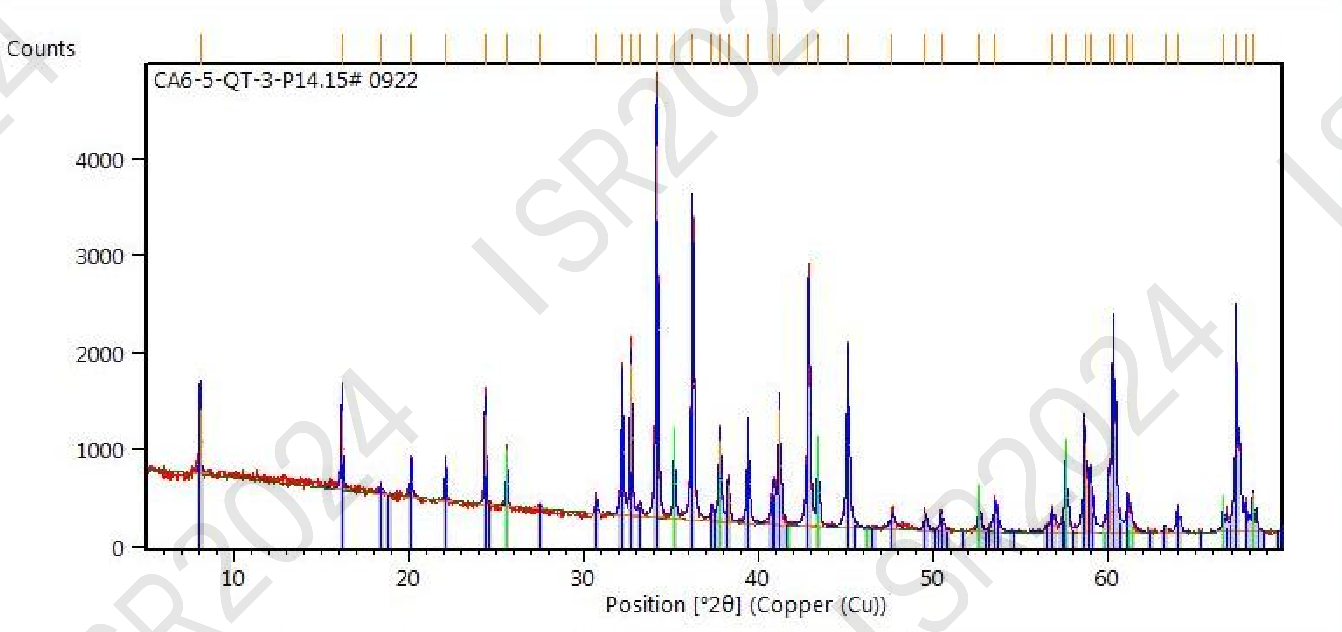
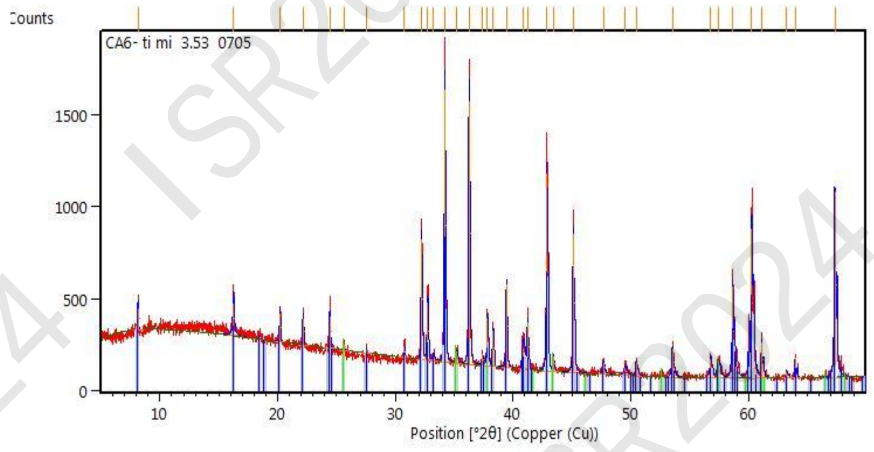


Fig. 7 XRD phase diagram of QT-3 after 1700℃×3h firing

3. Industrial Production of CA6

- Based on the previous lab results and recipe of QT-3,
- Raw materials were pelletized
- Fired in high-temperature shaft kiln for industrial production of tabular alumina
- Bulk density of final CA6 could reach 3.40-3.55g/cm³.



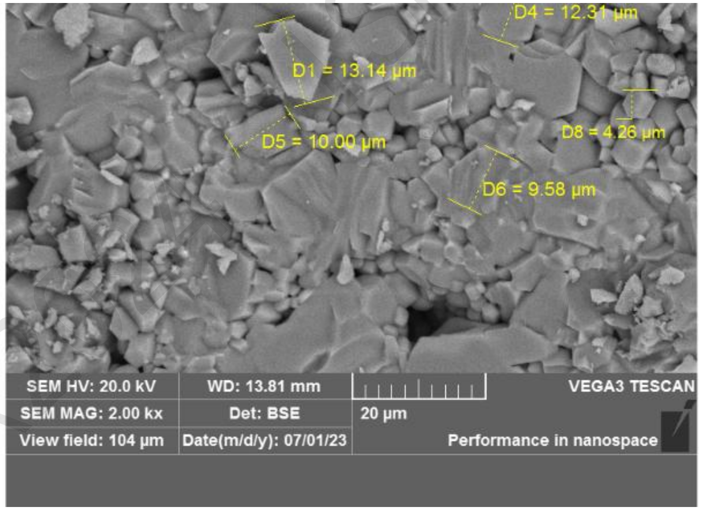


Fig. 8 XRD phase diagram of QT-3 by industrial production

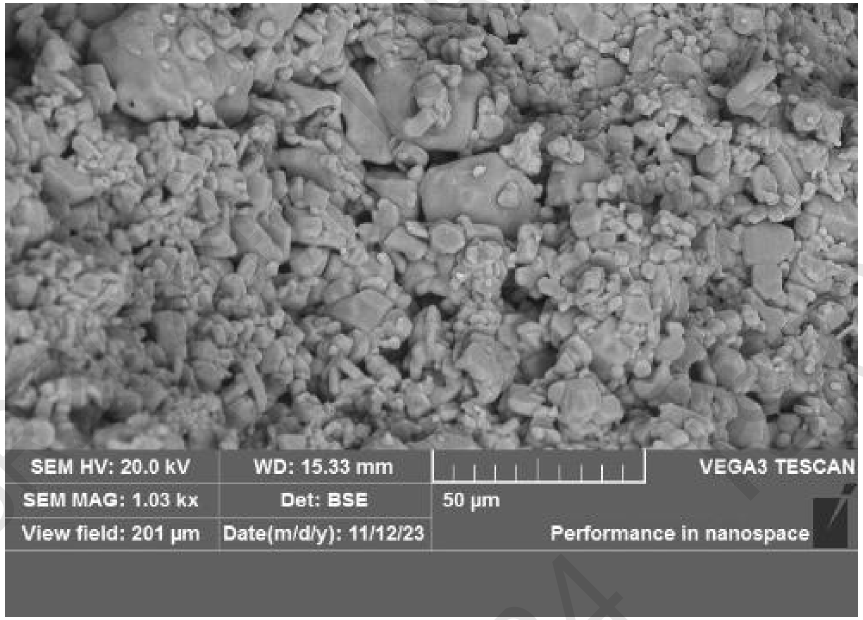
Fig. 9 Microstructure of QT-3 by industrial production

4. CA6 Brick and CA6 Castable Test

4.1 Comparison of Alumina Brick and CA6 brick

Table 3 Comparison of of alumina brick and CA6 brick

	Al_2O_3 /%	CaO /%	Sinter temp. /℃	AP /%	BD /g.cm^{-3}	CCS /MPa	RUL,/℃(0.2MPa, T0.6)	HOMR /MPa
Alumina brick	99		1650	16	3.30	97	>1700	-
CA6 Brick (92%CA6+2%CA cement+6% alumina)	91	8	1570	16.7	3.12	117	1686	2.9Mpa (1500℃*30min)



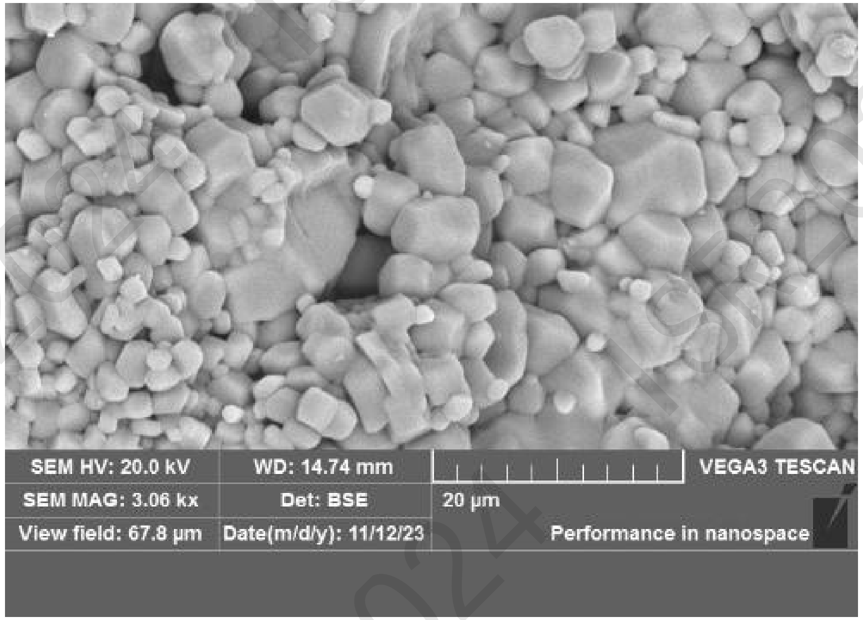


Fig. 10 SEM microstructure of CA6 brick

4.2 Comparison of Alumina Castables and CA6 Castables

Table 4 Recipes of alumina castables and CA6 castables

		0#	1#	2#	3#	4#
Tabular Alumina	0-5mm	88%	65%	40%	20%	0%
CA6	0-5mm	0%	23%	48%	68%	88%
Cement	CA	5%	5%	5%	5%	5%
Ultrafine alumina	BL-2	7%	7%	7%	7%	7%
Dispersant	HDA-1	+0.7%	+0.7%	+0.7%	+0.7	+0.7

Table 5 Properties of alumina castables and CA6 castables

Items	Heat treatment	0#	1#	2#	3#	4#
BD /g.cm^{-3}	110℃*24h	3.22	3.24	3.20	3.12	3.11
	1000℃*3h	3.20	3.21	3.18	3.10	3.09
	1350℃*3h	3.22	3.21	3.15	3.05	3.04
	1600℃*3h	3.19	3.20	3.17	3.14	3.09
CMOR /MPa	110℃*24h	19.5	17.5	15.5	16.5	17.2
	1000℃*3h	18.9	18.8	17.4	18.3	19.9
	1350℃*3h	>20	>20	>20	>20	>20
	1600℃*3h	>20	>20	>20	>20	>20
CCS /MPa	110℃*24h	75	59	70	62	65
	1000℃*3h	65	65	61	68	73
	1350℃*3h	>200	114	100	94	68
	1600℃*3h	>200	119	104	>200	>200
HMOR /MPa	1500C*0.5h	15.5	4.4	3.2	3.1	3.0

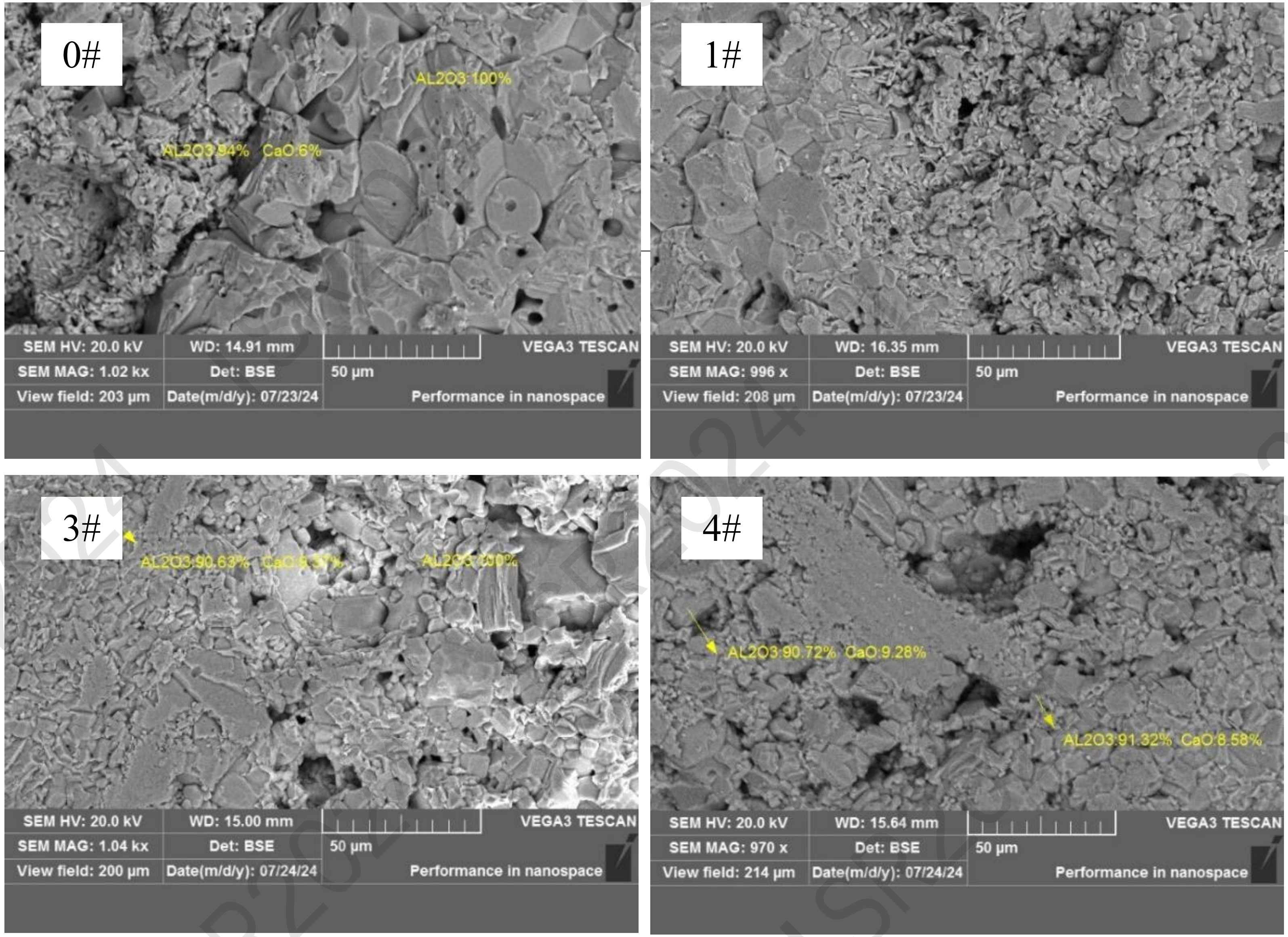


Fig. 11 SEM microstructure of Al_2O_3-CA6 castables after 1600°C*3h

5. Conclusions

- (1) Higher sintering temperatures and additive X could be conducive to densification of CA6 synthesis and appropriate crystal size.
- (2) In the lab work, additive X is doped at 3a, QT-3 fired at 1700℃×3h could achieve bulk density no less than 3.2 $g.cm^{-3}$， phase composition was almost CA6, with proper grain crystals, similar to that of tabular alumina.
- (3) When CA6 was produced in production shaft kiln, bulk density higher than 3.4 $g.cm^{-3}$ could be achieved.
- (4) Different size CA6 particles, being crushed and milled from sintered CA6 sphere, were optimized to achieve comprehensive properties. Actually alumina-CA6 bricks and alumina-CA6 castables have been used successfully in purge blocks, steel ladles, EAF roof blocks, glass-making furnaces, checker bricks & regenerators, etc.

THANK YOU FOR YOUR ATTENTION!