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Relationship of Preparation Parameters and Chromatic Properties of Zircon-Encapsulated Carbon Black Ceramic Pigment Prepared with a Sol-Gel-Spraying Method

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Abstract

Zircon-encapsulated carbon black is prepared as a black ceramic pigment by means of the sol-gel-spraying method. It is proposed that the dense zircon coating around the pigment is formed as a result of the fast transformation from sol into gel caused by the rapid extraction of solvent. To realize this, the preparation conditions are optimized as follows: the spray-drying temperature is 600 °C, the concentration of the ZrO_2 sol is 0.8 mol/L, the mass ratio of the ethanol/water is 1:1, the mole ratio of the Si/Zr is 1.5 and the calcining conditions are 1250 °C with a holding time of 30 min. With these conditions, the chromatic value of the obtained pigment is L^*=21.40, a^*=-0.21, b^*=-3.31. It is verified that the microstructure of tetragonal ZrO_2 dispersed and distributed in amorphous SiO_2 is necessary for the black ceramic pigment.

Keywords: Ceramic pigment, zircon, encapsulated pigment, sol-gel-spraying

I. Introduction

Black inorganic pigment is used to obtain dignified, elegant decorative effects in ceramic decoration [1]. Black (Fe, Mn, Co)-containing ceramic pigment used up to now is very sensitive to the glaze composition owing to the chemical reaction between the pigment and the glaze. Recently, zircon-encapsulated carbon black pigment has attracted more attention owing to its advantages, such as low cost, environmental compatibility and stability in glaze [2,3]. Moreover, carbon black provides a pure black hue that is not affected by the glaze composition [4]. However, carbon black used as a pigment in glaze must be covered completely with a dense coating because carbon black is easily oxidized [5–7]. If not, the pigment becomes gray, even white, revealing the color of the zircon [8–10].

Many methods have been reported for the preparation of the dense coating of zircon-encapsulated carbon black, such as the non-hydrolytic sol-gel method [3,4], co-precipitation method [5] and sol-gel method [6]. However, the results are unsatisfactory. The obtained zircon-encapsulated carbon black pigment is gray after calcining in air (L^* >30, $a^*\approx0$, $b^*\approx0$).

Zircon-encapsulated carbon black prepared with the sol-gel-spraying method has been reported in our previous works [2]. The L^* value of the pigment is down to 19. The microstructure of tetragonal ZrO_2 dispersed and distributed in amorphous SiO_2 is considered the key to the pigment remaining black. The purpose of the present work is to demonstrate the relationship between this special structure and the preparation conditions, such as spray-drying temperature, alcohol/water ratio, sol concentration, calcination temperature and holding time.

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II. Materials and Methods

(1) Preparation of pigments

All the chemical reagents were reagent-grade and did not undergo any further purification before the experiment.

In the special experiment, 51.56 g $ZrOCl_2{\cdot}8H_2O$ was dissolved into 100 ml alcohol-water mixed solution (1:1 mass ratio). 17.94 g hexamethylenetetramine ($C_6H_{12}N_4$,) was dissolved into another 100 ml alcohol-water mixed solution. The $C_6H_{12}N_4$ solution was dropped into the $ZrOCl_2$ solution under vigorous stirring. The mixed solution was aged for 3 h at room temperature. ZrO_2 sol was obtained.

SiO_2 sol and carbon black suspension were obtained from commercial sources.

Finally, SiO_2 sol, ZrO_2 sol and carbon black suspension were directly mixed together. According to the previous work [3], the molar ratio of Si/Zr was 1.5:1 and the weight ratio of carbon black/zircon was 1.3:1.

The mixture was sprayed into a tubular furnace. The temperature was 400 °C, 600 °C or 800 °C. The precursors (ashes) were collected and calcined at 1250 °C for 30 min in Ar, the encapsulated pigments were obtained. The pigment was then calcined at 900 °C for 2 h in air to remove the uncoated carbon black.

(2) Characterization

XRD data of the pigments were collected on a Rigaku D/max-(β) X-ray diffractometer using a graphite monochromator and Cu *K*α radiation (λ = 0.15418 nm) with the scanning range (2θ) of 5 – 70°.

The microstructure and morphology of the pigment particles were observed with a transmission electronic microscope (TEM, JEOL-2010, Japan).

CIE lab parameters *L**, *a**, *b** were measured with a spectraphotometer (HunterLab Miniscan MSXP 4000, 400 – 700 nm, white-glazed tile reference *x* =31.5, *y* = 33.3). In this context, *L** is the lightness axis [black(0)~white(100)], *b** is the blue(-)~yellow(+) axis, and *a** is the green(-)~red(+) axis.

III. Results and Discussion

The microstructure of tetragonal ZrO_2 dispersed and distributed in amorphous SiO_2 is considered the key factor affecting the color performance of carbon black. The low *L** value in CIE lab parameters indicates that the dense zircon coating exists and the visible light is absorbed by carbon black. Therefore, the effects of the preparation conditions on the chromatic value of the pigments were discussed, which can indirectly characterize the special structure.

(1) Spray-drying temperature

Table 1 shows the chromatic value of the pigments prepared at different spray-drying temperatures. It can be seen that the pigment has the lowest *L** value of 21.40 at the spray temperature of 600 °C. Carbon black is the only color agent for the pigment. Zircon is white and carbon black is black. If carbon black is oxidized and lost, the pigment is white, not black. Therefore, the coverage of carbon black can be estimated based on the *L** value. The higher the *L** value is, the lower the coverage of carbon black. The lowest *L** value of 21.40 at the spray temperature of 600 °C indicates the highest coverage of carbon black. In other words, the zircon coating is the densest under this condition.

Table 1: Chromatic value of the pigments prepared at different spray-drying temperatures.

Number	Spray-drying temperature/°C	*L**	*a**	*b**
1	400	52.48	-0.55	-3.34
2	500	39.82	-0.04	-5.68
3	600	21.40	-0.21	-3.31
4	700	42.76	0.18	0.54
5	800	46.36	0.57	-0.12

Note: The samples were calcined at 1250 °C for 0.5 h in Ar and the concentration of ZrO_2 sol is 0.8 mol/L, the mass ratio of ethanol/water is 1:1, the mole ratio of Si/Zr is 1.5.

To understand the relationship between the coverage of carbon black and *L** value, the precursors prepared at different spray-drying temperature were characterized with TEM. Fig. 1 shows the TEM images of the precursors with the spray-drying temperatures of 400 °C, 600 °C and 800 °C. To distinguish carbon black from ZrO_2 or SiO_2 gel, the TEM image of carbon black is also shown in Fig. 1.

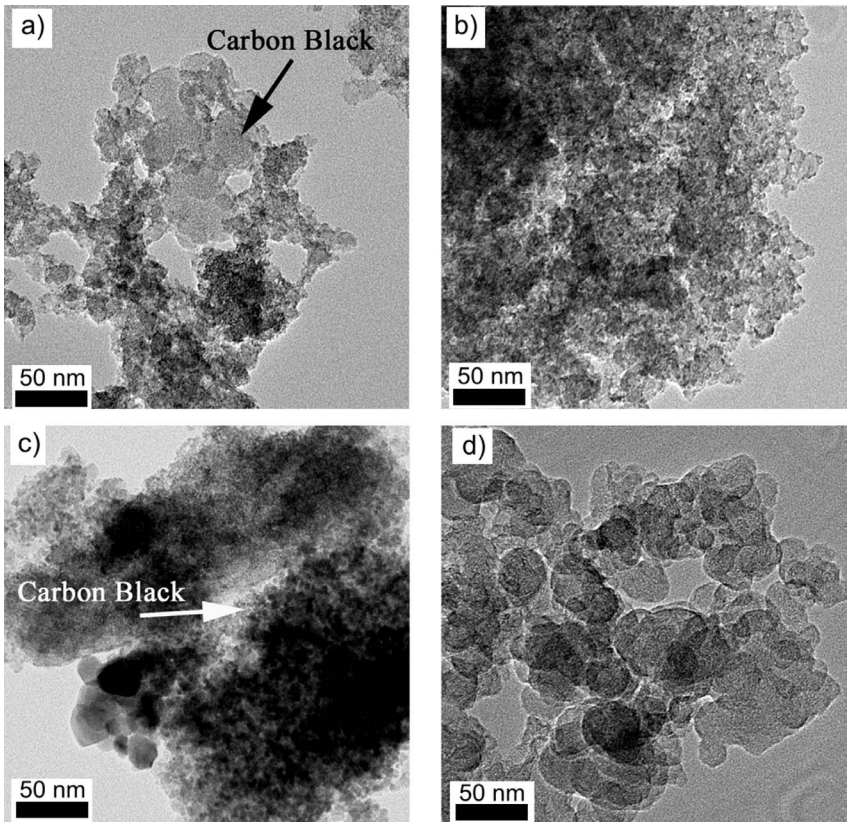

Fig. 1: TEM images of the precursors prepared at different spray-drying temperature a) 400 °C, b) 600 °C, c) 800 °C and of d) carbon black.

It can be seen that most of carbon black particles are naked if the spray-drying temperature is 400 °C. The carbon black is seldom encapsulated by zircon aerogel. Obviously, those carbon black particles will be oxidized during subsequent calcination in air. If the spray-drying temperature is 800 °C, carbon black is also seldom encapsulated by the crystallized zircon. The precursor particles are in a serious aggregation state. Some of zircon aerogel particles are crystallized and their particle sizes are smaller than that of the carbon black. When the spray-drying temperature is 600 °C, the zircon aerogel particles have the suitable particle size and mix homogeneously with carbon black. The carbon black is encapsulated and then the zircon aerogel is crystallized and coarsened.

The precursors are further calcined at 1250 °C in Ar following 900 °C in air, the TEM images of which are shown in Fig. 2. It can be seen that when the spray-drying temperature is 600 °C, the carbon black is encapsulated by the dense dried gel. After calcination, the carbon black is protected completely, as shown in Fig. 2 (B). This can be explained by the fact that the sol particles transform into gels in a very short time. No solution is consolidated into the gel, and therefore no pores remain in the dried gels in this process. After calcination, the carbon black is fully protected. In comparison with Fig. 2 (B), naked carbon black is observed in Fig. 2 (A) and Fig. 2 (C). The solution may not evaporate fully before the dried gel is formed when the spray drying temperature is 400 °C. Many pores exist in the gel. A similar structure is also formed when the spray-drying temperature is 800 °C. The difference is that the formation velocity of the dried gel is faster than the evaporation of the solution. To sum up, the optimized spraying temperature contributes to the formation of a dense coating on the carbon black.

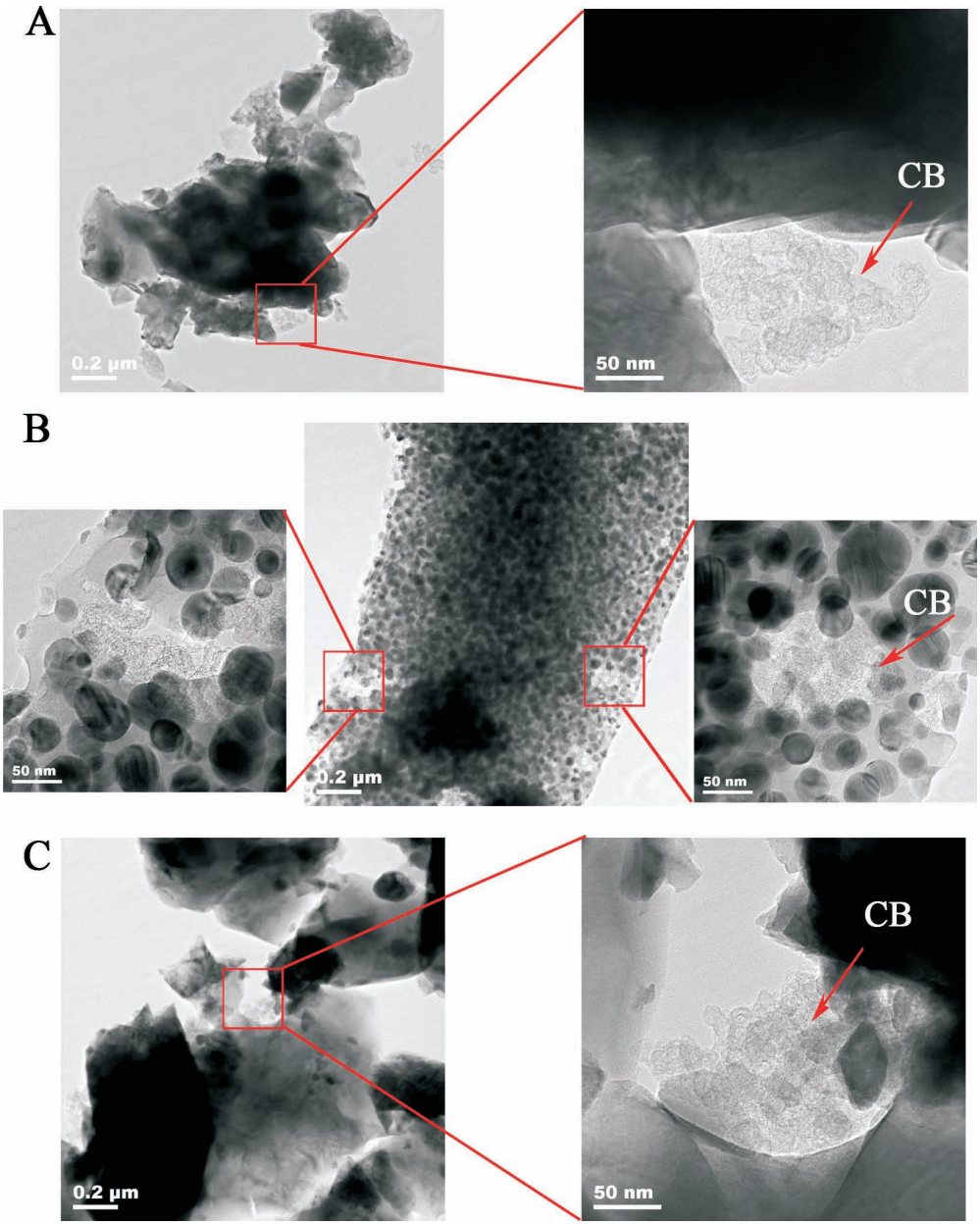

Fig. 2: TEM images of the encapsulated pigments with different spray-pyrolysis temperature calcined at 1250 °C (A) 400 °C, (B) 600 °C, (C) 800 °C.

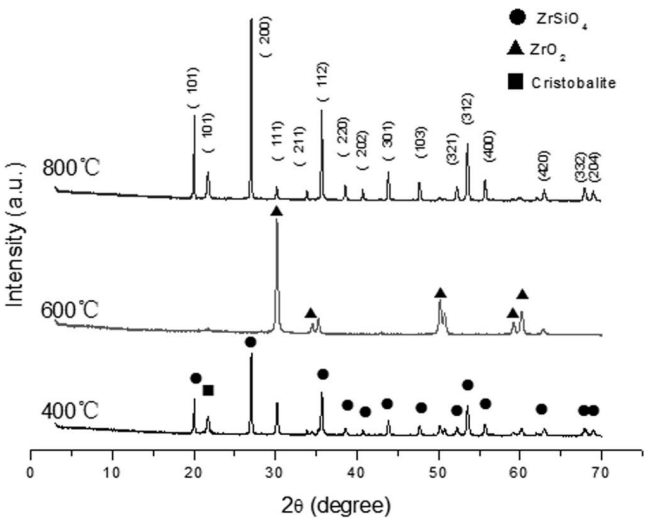

Fig. 3: XRD patterns of the pigments calcined at 1250 °C in Ar following 900 °C in air at different spray-drying temperature.

Fig. 3 shows the XRD patterns of pigments calcined at 1250 °C in Ar following 900 °C in air at different spray-drying temperatures. Fig. 3 shows that zircon is the main crystal phase for the pigment prepared at the spray-drying temperatures of 400 °C and 800 °C. However, zirconia is the main crystal phase when the spray drying temperature is 600 °C. This difference may originate in the structures of the precursors prepared at different spraying temperatures. As shown in Fig. 1, the dried gel particles are in the aggregation state at the spraying temperature of 400 °C and 800 °C. This indicates a short transport distance for sintering. Therefore, the aggregation contributes to the coarsening and the crystallization of zircon [11]. Some of crystal phase even exists in the precursor powders at 800 °C. However, the uniform mixture of zirconia and silica gel particles obtained at 600 °C may have a negative effect on the formation of zircon. Zirconia particles are isolated by silica particles because the Zr/Si molar ratio is 1:1.5. The fine zirconia can exist among silica particles if its particle size is less than the critical dimension (< 50 nm) [12]. It is further verified that the special microstructure obtained at the spray-drying temperature of 600 °C is the key to obtaining the black-encapsulated carbon black pigment.

(2) ZrO_2 sol concentration

Table 2 shows the chromatic value of the pigments prepared with different ZrO_2 sol concentration. The L^* value decreases with increasing ZrO_2 sol concentration. As discussed above, a low L^* value indicates a high coverage of the carbon black. Actually, the high-concentration ZrO_2 sol has a low water content. The full solution is evaporated before the transformation of the sol into a gel. No solution is consolidated into the gel. Therefore, a dense coating is generated with a microstructure similar to that shown in Fig. 1 (B). However, the higher the ZrO_2 sol concentration is, the faster the ZrO_2 gel forms. This causes trouble with the mixing of the ZrO_2 sol and SiO_2 sol.

(3) Ethanol/water ratio

Table 3 shows the chromatic value of the pigments with different ethanol/water ratio. It can be seen that the addition of ethanol into the solution contributes to a decreasing L^* value if the ethanol/water ratio is no more than 1:1. The addition of ethanol has two functions in the spray-drying process: (1) increasing the evaporation rate of the solvent and (2) accelerating the gelation process with an instant high temperature generated by the ethanol combustion. The effect of the ethanol/water ratio on the microstructure is similar to that of the ZrO_2 sol concentration. However, the L^* values of the pigments increase if excess ethanol is added. The reason is that the solution evaporation is so fast that the gel particles have no time to rearrange, resulting in a porous structure of the coating. The ethanol/water ratio has a similar effect as the spraying temperature.

Table 2: Chromatic value of the pigment prepared with different ZrO_2 sol concentrations.

Sample label	ZrO_2 sol concentration (mol/L)	L^*	a^*	b^*
1	0.4	31.30	-0.03	-3.16
2	0.6	23.50	-0.30	-2.04
3	0.8	21.40	-0.21	-3.31

Note: The samples were prepared at the spraying temperature of 600 °C, and calcined at 1250 °C with 0.5 h in Ar following 900 °C in air, the mass ratio of ethanol/water is 1:1, the mole ratio of Si/Zr is 1.5.

Table 3: Chromatic value of the encapsulated pigments prepared with different ethanol/water ratios.

Sample label	Ethanol/ water ratio	L^*	a^*	b^*
1	0:1	47.51	0.91	2.33
2	0.5:1	27.43	-0.13	-2.11
3	1:1	21.40	-0.21	-3.31
4	2:1	41.81	0.02	-2.64
5	3:1	45.72	0.49	-0.74

Note: The samples were prepared at the spraying temperature of 600 °C, and calcined at 1250 °C for 0.5 h in Ar following 900 °C in air, the ZrO_2 sol is 0.8 mol/L, the mole ratio of Si/Zr is 1.5.

(4) SiO_2/ZrO_2 ratio

Table 4 shows the chromatic value of the encapsulated pigments with different SiO_2/ZrO_2 ratio. As can be seen, the minimum L^* value of 21.40 is obtained when the SiO_2/ZrO_2 ratio is 1.5:1. This can be explained with reference to the microstructure, as discussed in Section III(1).

Table 4: Chromatic value of the encapsulated pigments with different SiO_2/ZrO_2 ratios.

Sample label	SiO_2/ZrO_2 ratio	L^*	a^*	b^*
1	1.2:1	42.21	-0.53	-4.93
2	1.4:1	35.47	-0.23	-1.50
3	1.5:1	21.40	-0.21	-3.31
4	1.6:1	26.12	0.37	-3.93
5	1.8:1	29.32	0.06	-2.05

Note: The samples were prepared at the spraying temperature of 600 °C, and calcined at 1250 °C for 0.5 h in Ar following 900 °C in air, the ZrO_2 sol is 0.8 mol/L, the mass ratio of ethanol/water is 1:1.

(5) Holding time

Table 5 shows the chromatic value of the pigment calcined at 1250 °C with different holding times. The minimum L^* value of 21.40 is obtained when the holding time is 30 min. As discussed above, the processor with this structure, as shown in Fig. 1 (B), has been obtained before the calcination under the condition that the concentration of ZrO_2 sol is 0.8 mol/L, the mass ratio of ethanol/water is 1:1, the mole ratio of Si/Zr is 1.5 and the spray-drying temperature is 600 °C. In other words, the calcination does not change the mixing of the ZrO_2 particles, SiO_2 particles and carbon black. Therefore, the changes in the L^* value have no relationship to the calcination temperature.

To explain the change of the L^* value, the XRD patterns of the pigments calcined at 1250 °C for different holding times without mineralizer added are shown in Fig. 4. As can be seen, ZrO_2 and SiO_2 are the main crystal phases if the holding time is less than 30 min. Under this condition, the fine zirconia can exist among silica particles because its particle size is less than the critical dimension, as shown in Fig. 2 (B). When the holding time is more than 30 min, zircon is the main phase in the pigment. However, the L^* value increases. As zircon is white, the higher the coverage of carbon black by zircon is, the higher the L^* value is. In view of the high chemical stability, the formation of zircon is desirable. However, the encapsulated carbon black pigment may change from black to gray, and even white, which is far removed from the desired black pigment.

Fig. 5 shows the TEM images of the pigments. The pigment has the structure that the transparent silica phase is situated as the outer coating thus keeping the zircon particles separated from each other, which permits visible light to penetrate circuitously through the pigment and shows the color of carbon black if the holding time is less than 30 min. When zircon is formed, the pigment loses the dispersive structure, as shown in Fig. 5 c) and d). The longer the holding time is, the higher the crystallization degree of zircon is. Under this condition, zircon reflects the light. Less visible light can be absorbed by carbon black, therefore, the pigment becomes gray, even white [13].

Table 5: Chromatic value of the encapsulated pigments with different holding times.

Sample label	Holding time/min	L^*	a^*	b^*
1	0	24.02	0.31	-1.97
2	30	21.40	-0.21	-3.31
3	60	24.22	-0.54	-5.26
4	90	32.26	0.25	-0.60
5	120	35.30	-0.55	-2.52
6	180	37.77	-0.66	-2.18
7	240	38.98	0.04	-2.22

Note: The samples were prepared at the spraying temperature of 600 °C, and calcined at 1250 °C in Ar following 900 °C in air, the ZrO_2 sol is 0.8 mol/L, the mass ratio of ethanol/water is 1:1, the SiO_2/ZrO_2 ratio is 1.5:1.

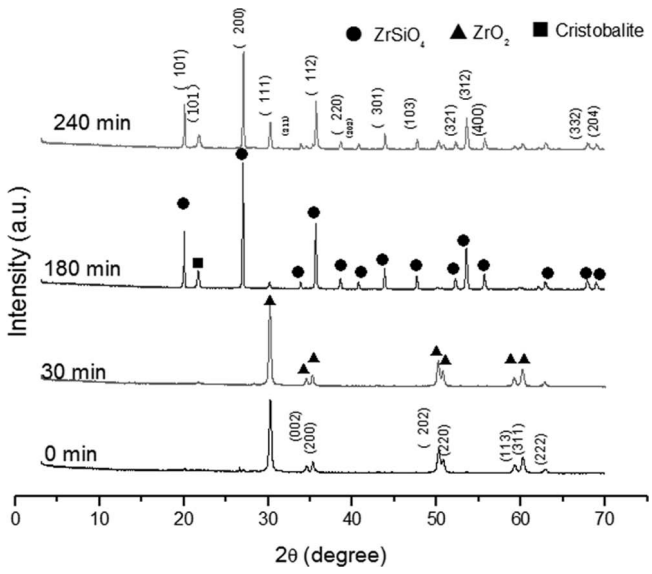

Fig. 4: XRD patterns of the pigments calcined at 1250 °C in Ar with different holding time (A, 0 min, B, 30 min, C, 90 min, D, 240 min).

Fig. 6 shows the image of the pigment prepared under the condition that the concentration of ZrO_2 sol is 0.8 mol/L, the mass ratio of ethanol/water is 1:1, the mole ratio of Si/Zr is 1.5 and the spray-drying temperature is 600 °C. The CIE coordinates are: L^*=21.40, a^*= -0.21, b^*=-3.31. The pigment looks black.

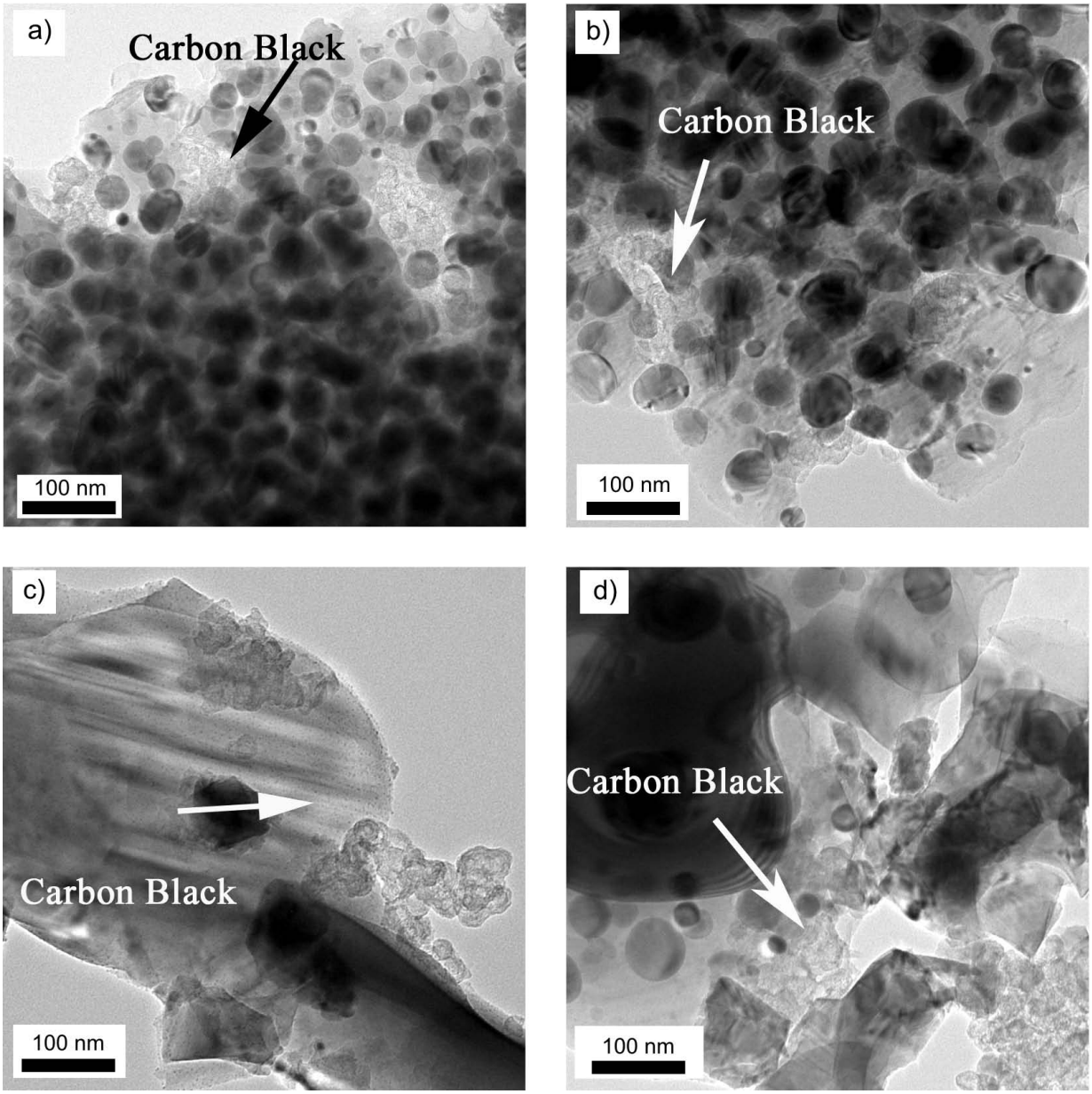

Fig. 5: TEM image of the pigments with different holding time calcination for 1250 °C, a), 0 min, b), 30 min, c), 90 min, d), 240 min.

Fig. 6: Photo of the zircon-encapsulated carbon black pigment.

IV. Conclusions

The black ceramic pigment of zircon-encapsulated carbon black is synthesized with the sol-gel-spraying method. The pigment has the L^* value of 21.40 with the structure that tetragonal ZrO_2 is dispersed among the amorphous SiO_2. In the black pigment, the dense coating layer on the carbon black is formed owing to the fast transformation from sol into gel caused by the rapid extraction of solvent. The pigment can be obtained under the following conditions: the spray-drying temperature is 600 °C, the ZrO_2 sol concentration is 0.8 mol/L, the mass ratio of ethanol/water is 1:1, the mole ratio of Si/Zr is 1.5 and the calcining temperature is 1250 °C held for 30 min.

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