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Production of coloured zircon pigments from zircon

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Abstract

Zircon ($ZrSiO_4$) pigments are commonly used in the ceramic industry for glazes due to their high chemical stability and superior resistance to the dissolution during firing in glazes. These pigments are made by calcining a mixture of SiO_2, ZrO_2, a dopant ion which produces the colour and mineralizer. In the present work, synthesis of coloured zircon ceramic pigments from intermediate products obtained by decomposing zircon sand with NaOH was undertaken. After decomposing zircon with NaOH at around 850 °C, decomposed products (Na_2ZrSiO_5 and Na_2ZrO_3) were used as raw materials to produce zircon pigments and Pr, Fe and V oxides were used as colouring agents. The crystalline phases formed after decomposition and pigment production steps were determined by using X-ray diffraction (XRD) technique. XRD analysis showed that Na_2ZrSiO_5 and Na_2ZrO_3 phases were formed after decomposition and when these products used as a raw material, zircon containing colouring ion can be obtained. Prepared pigments were used in transparent glazes and porcelainized tile and their colour properties were determined. As a result in this work it was shown that it is possible to obtain zircon pigments from zircon sand instead of using pure ZrO_2 and SiO_2.

Keywords: Colour; Optical properties; Zircon; Powders-solid-state reaction

1. Introduction

Zircon ($ZrSiO_4$) pigments are commonly used in the ceramic industry for glazes due to their high chemical stability and superior resistance to the dissolution during firing in glazes. These pigments are made by calcining a mixture of SiO_2, ZrO_2, a dopant ion which produces the colour and a mineralizer.[1] Turquosie blue zircon pigments containing vanadium, yellow pigments containing praseodymium and pink pigments containing iron are produced commercially. During the reaction, silica is attacked by the mineralizer such as sodium floride (NaF) and transported to the ZrO_2 where $ZrSiO_4$ is formed. The dopant ion is trapped in the lattice during the formation process. Several studies showed that the colouring ion must be present at the time of $ZrSiO_4$ formation.[2–4] Recently, it was reported that these pigments can also be prepared by non-conventional methods such as aerosol hydrolysis,[5] sol–gel[6,7] and coprecipitation routes[8] at lower temperatures than solid-state methods.

Zircon pigments cannot be made from the mineral zircon itself. There is thus the unusual circumstance that natural zircon is processed to produce zirconium oxide, which is then reconverted to zircon while making the colour.[1] Since ZrO_2 is obtained by complex and expensive purification process from zircon sands, synthesis of a pigment by using zircon or intermediate in the process of making ZrO_2 might have a significant economical advantage. Several numbers of patents have claimed that intermediate products in the process of making ZrO_2 from zircon can be used to produce zircon pigments, which has more regular and intense hue. Sodium silico-zirconate frit ($Na_2O{\cdot}SiO_2{\cdot}ZrO_2$) prepared from zircon sand by fusion with alkali oxides such as Na_2CO_3 at about 1000 °C were mixed with extra SiO_2 to make up the correct molar proportioning and calcined at 800–1000 °C together with a vanadium for blue and iron compound for pink colour.[9,10]

In previous studies, zircon pigments were prepared from mineral zircon, as the starting raw material. Zircon was decomposed with waste KOH/NaOH mixtures and decomposed products were used to produce pink–violet zircon pigments by adding iron compounds[11] and blue–green pigments by adding CrOOH and $PbCrO_4$.[12] Naga et al.[13] also reported that green zircon pigments containing Cr_2O_3 were prepared with zircon sands dissociated with fluoride salts.

In recent years, studies have focused on the synthesis and characterisation of zircon pigments obtained from a non-conventional mixture of precursors. Bondioli et al.[14] reported that it is possible to obtain a zircon hematite inclusion pigment from the mixture containing FeOOH and Li_2O–ZrO_2–SiO_2 glass that was prepared with lithium carbonate, zirconium sil-

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icate and quartz and melted at 1500 °C. In another study,[15] Pr-yellow and V-blue zircon pigments were prepared by the direct use of plasma dissociated zircon sand.

In this work, synthesis of blue (V-containing), pink (Fe-containing) and yellow (Pr-containing) zircon ceramic pigments from zircon sands decomposed to intermediate products with NaOH were undertaken in order to reduce the cost of the pigments. Also, colour properties of the pigments used in transparent glazes and porcelainized tile were determined and compared with the pigments obtained from pure zirconium dioxide.

2. Experimental procedure

2.1. Decomposition of zircon into intermediate products

It is known that zircon is decomposed at high temperatures in a reducing media.[16] The decomposition temperature is lowered if a fluxing agent such as NaOH, Na_2CO_3 or $CaCO_3$ is used. In this study, to decompose zircon sand, NaOH was chosen as a fluxing agent due to the fact that the decomposition reaction is occurred at a lower temperature than in the case of Na_2CO_3 or $CaCO_3$ addition.

About 1 mol zircon (industrial grade) was mixed with 4 mol NaOH pellets (Merck) in agat mortar. Thermal treatment was carried out at temperatures between 600 and 950 °C for 5 h. Then, the decomposed intermediate products were washed with water or 1–5% H_2SO_4 solution in order to remove Na based compounds formed during process.

2.2. Preparation and characterisation of pigments

To produce zircon pigment by using intermediate product obtained from decomposed zircon with NaOH, intermediate products were mixed with excess SiO_2 (Merck) together with NH_4VO_3 (Aldrich) for blue, $FeSO_47H_2O$ (Merck) for pink and Pr_6O_{11} (Org.Panc.) for yellow colour. NaF (Merck) and NaCl (Merck) mixture was used as a mineralizer in all the pigment compositions. Also, pigments were prepared by using pure zirconium dioxide ZrO_2 (Merck), SiO_2 and other oxides in order to compare colour properties of pigments produced from zircon sand. The prepared pigment compositions are given in Table 1.

The mixtures were ground in water in a ball mill for 3 h to obtain homogeneous slurries. The slurries were then dried at 100 °C. Calcination were carried out in an electric furnace between 900 and 1100 °C temperature range for 3 h by applying a heating rate of 2 °C/min.

The calcined pigment products were ground in water in a ball mill for an hour and washed with water to remove undesirable soluble salts that have negative effects during the glazing.

In order to test colour properties of prepared pigments in the ceramic glaze and bodies, 5 wt.% pigments were added to a frited transparent glaze and applied to an engobed single firing ceramic biscuits. Finally, the colour-glazed biscuits were fired at 1125 °C for 45 min. About 5 wt.% pigments were also added to a porcelainized tile body and fired at 1210 °C. The ceramic tile biscuits, glazes and porcelainized tile granules were supplied from a ceramic factory (Toprak San. and Tur. A.Ş) in Eskişehir, Turkey.

To identify the crystalline phases present in the raw materials and pigments, XRD patterns were obtained using conventional powder diffraction technique in a RIGAKU diffractometer with Ni-filtered, Cu Kα radiation with a goniometer speed of 1°/min. The chemical analysis of raw materials and pigments were carried out by using an energy dispersive X-ray spectrometer (EDX) (LINK ISIS 300) attached to a scanning electron microscopy (SEM) (CAM SCAN S4).

The IR spectra were measured in the wavenumber range from 380 to 2000 cm^{-1} with a Fourier transform infrared (FTIR) spectrometer (BRUKER TENSOR 27). The potassium bromide (KBr) pellet method was employed and the pigment powders were diluted in the KBr.

Table 1
Pigment compositions prepared with zircon product decomposed with NaOH at 850 °C (wt.%)

Code	Type of washing	T_D (°C)	DP	ZrO_2	SiO_2	NH_4VO_3	$FeSO_47H_2O$	Pr_6O_{11}	NaF	NaCl	T_C (°C)
VO	–			59	30	8	–	–	5	2	1000
V1	–	850	89	–		8	–	–	5	2	1000
V2	Water	850	60	–	25	8	–	–	5	2	1000
V3	Water	950	60	–	25	8	–	–	5	2	1000
V4	1% H_2SO_4	850	64	–	21	8	–	–	5	2	900
V5	1% H_2SO_4	850	64	–	21	8	–	–	5	2	1000
V6	1% H_2SO_4	850	64	–	21	8	–	–	5	2	1100
V7	1% H_2SO_4	850	66	–	22	5	–	–	5	2	1000
V8	1% H_2SO_4	850	67	–	23	3	–	–	5	2	1000
V9	5% H_2SO_4	850	66	–	19	8	–	–	5	2	1000
FO	–	–	–	56	28		9	–	5	2	1000
F1	1% H_2SO_4	850	51	–	26	–	16	–			1000
F2	1% H_2SO_4	850	61	–	20	–	9	–	3	7	1000
PO		–	–	59	29	–	–	5	3	4	1000
P1	1% H_2SO_4	850	59	–	29	–	–	5	3	4	1000
P2	1% H_2SO_4	850	66	–	22	–	–	5	3	4	1000

DP, decomposed zircon product, T_D, decomposition temperature and T_C, pigment calcination temperature.

$L^*a^*b^*$ colour parameters and spectral curve of coloured glazes were measured with an spectrophotometer (MINOLTA 3600 d). These parameters were measured for an illuminant D65, following the CIE-$L^*a^*b^*$ colourimetric method recommended by the CIE (Commission Internationale del'Eclairage). In this system, L^* is the degree of lightness and darkness of the colour in relation to the scale extending from white ($L^* = 100$) to black ($L^* = 0$). a^* is the scale extending from green ($-a^*$) to red ($+a^*$) axis and b^* is the scale extending from blue ($-b^*$) to yellow ($+b^*$) axis.

3. Results and discussion

3.1. Decomposition of zircon with NaOH

Zircon sand powders were mixed with NaOH and heated at temperature between 600 and 950 °C for 5 h and their XRD patterns were taken to find out present phases at different temperatures (Fig. 1). These diffraction patterns showed that the reaction was not complete at temperatures below 850 °C and the reaction products contained Na_2ZrO_3, Na_2SiO_3 and unreacted zircon. At around 850 °C, zircon phase disappeared, Na_2ZrSiO_5 formed and Na_2ZrO_3 phase content increased. Although temperature was increased to 900 and 950 °C, zircon was observed with other phases. It is apparent from Fig. 1 that zircon decomposed completely to intermediate products with NaOH at around 850 °C

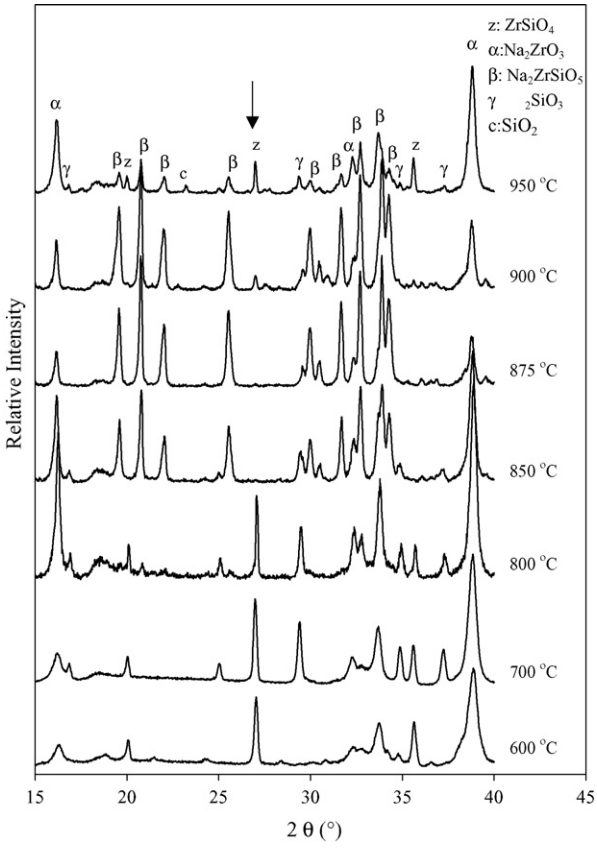

Fig. 1. XRD patterns of products obtained after decomposition of zircon at different temperatures.

Table 2
EDX analysis of decomposed products used throughout this study obtained by converting elemental EDX analysis to oxides (wt.%)

Decomposed product	Na_2O	MgO	Al_2O_3	SiO_2	CaO	ZrO_2
Unwashed product	38.6	–	0.6	20.5	–	40.1
Washed with water	7.1	0.8	0.9	8.9	1.2	81.0
Washed with 0.5 wt.% H_2SO_4	6.5	0.7	0.3	13.2	0.8	78.5
Washed with 1 wt.% H_2SO_4	3.0	0.3	–	9.1	–	87.7
Washed with 5 wt.% H_2SO_4	1.0	–	–	15.8	–	78.3

and small amount of decomposed products re-crystallised to form synthetic zircon at 900 °C. As a consequence of this, decomposition temperature for zircon into intermediate products was selected to be 850 °C.

The chemical analyses of decomposed products determined by using EDX are given in Table 2. As shown in this table, decomposed intermediate product contains large amount of Na_2O (about 38.6 wt.%), which is in the form of Na_2ZrSiO_5, Na_2ZrO_3 or Na_2SiO_3 as determined from XRD analysis. To reduce Na_2O based phases, decomposed product was washed with water or H_2SO_4 solution. XRD patterns of decomposed product showed that mainly Na_2ZrSiO_5 remain after washing process, while the water-soluble α (Na_2ZrO_3) and γ (Na_2SiO_3) phases were removed (Fig. 2). Removed phases were confirmed by XRD analysis of the dried powders obtained from washing solutions. It was found that a 1 wt.% H_2SO_4 solution was most effective in the removal of Na_2O from the decomposed products. Na_2O can be fully eliminated from decomposed products at higher acid concentration (5 wt.% H_2SO_4) but amount of ZrO_2

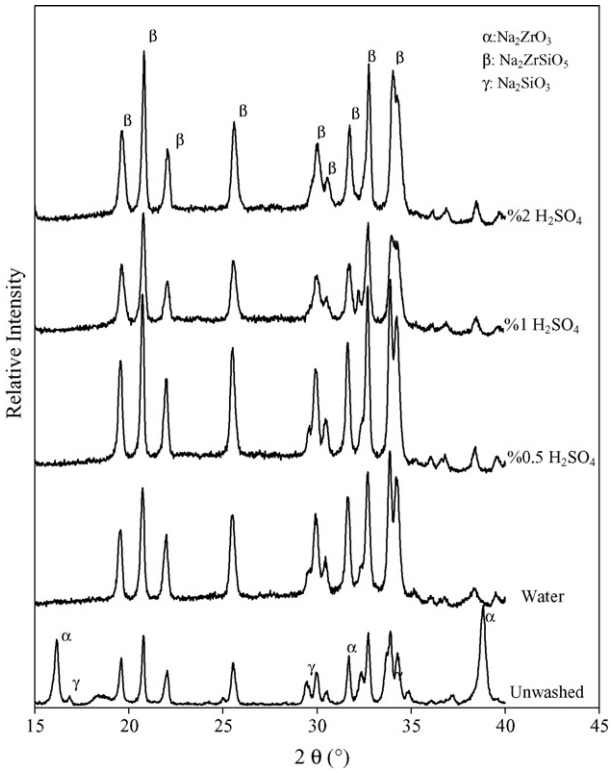

Fig. 2. XRD patterns of differently treated products decomposed at 850 °C.

decreased in the product (Table 2). Although, chemical composition of decomposed product changed by washing with different H_2SO_4 solution (Table 2) there was no differences observed in the XRD patterns (Fig. 2). This result can be explained by ion exchanges between decomposed product and acid solution without any variation in the structure.[12]

3.2. Production and characterisation of pigments

3.2.1. V–zircon blue pigments

In Table 3, $L^*a^*b^*$ values of glazes containing pigments prepared with decomposed products and calcined at different temperatures are given in comparison with that of an industrial V–zircon pigment (CP) and pigment prepared with pure oxide (VO). Pigment prepared with decomposed product washed with water has no colour as given in Table 3. When decomposed product washed with H_2SO_4 solution, the colour of pigments visually changes from white to blue. The $-b^*$ values that indicate blueness increased when decomposed product washed with H_2SO_4 solution, while $-b^*$ decreases with increasing calcination temperatures. The blue colours on the tiles containing pigments prepared in this study are less intense in comparison to the industrial pigment but is comparable with that colour exhibited when the pigments prepared with pure oxide is used.

Table 3
The $L^*a^*b^*$ values of V, Fe and Pr-containing pigments in transparent glazes and porcelainized tiles

Code	Transparent glaze			Porcelainized tile		
	L^*	a^*	b^*	L^*	a^*	b^*
VT	70.1	−16.7	−19.6	64.3	−8.9	0.4
VO	74.5	−17.4	−13.7	66.5	−10.7	0.5
V1						
V2	92.2	−0.01	2.5			
V3	91.8	−0.01	2.6			
V4	79.9	−13.1	−11.6	69.1	−6.1	3.6
V5	81.0	−12.3	−10.4	70.2	−5.7	4.0
V6	85.9	−7.1	−3.5			
V7	84.8	−9.2	−5.7			
V8	86.9	−7.4	−3.6			
V9	79.9	−9.9	−2.1			
FT	60.5	26.1	24.2	57.3	11.1	8.11
FO	61.1	20.9	23.5	59.8	10.3	9.7
F1	76.8	15.1	26.2	53.0	9.5	10.6
F2	76.7	17.6	24.5	56.9	8.7	13.6
PT	84.5	−10.2	41.9	62.1	−1.6	23.1
PO	87.3	−8.9	39.2	64.7	−0.9	21.6
P1	88.1	−7.3	51.2	75.5	−2.2	29.8
P2	89.2	−6.5	49.3	76.9	−1.6	25.8

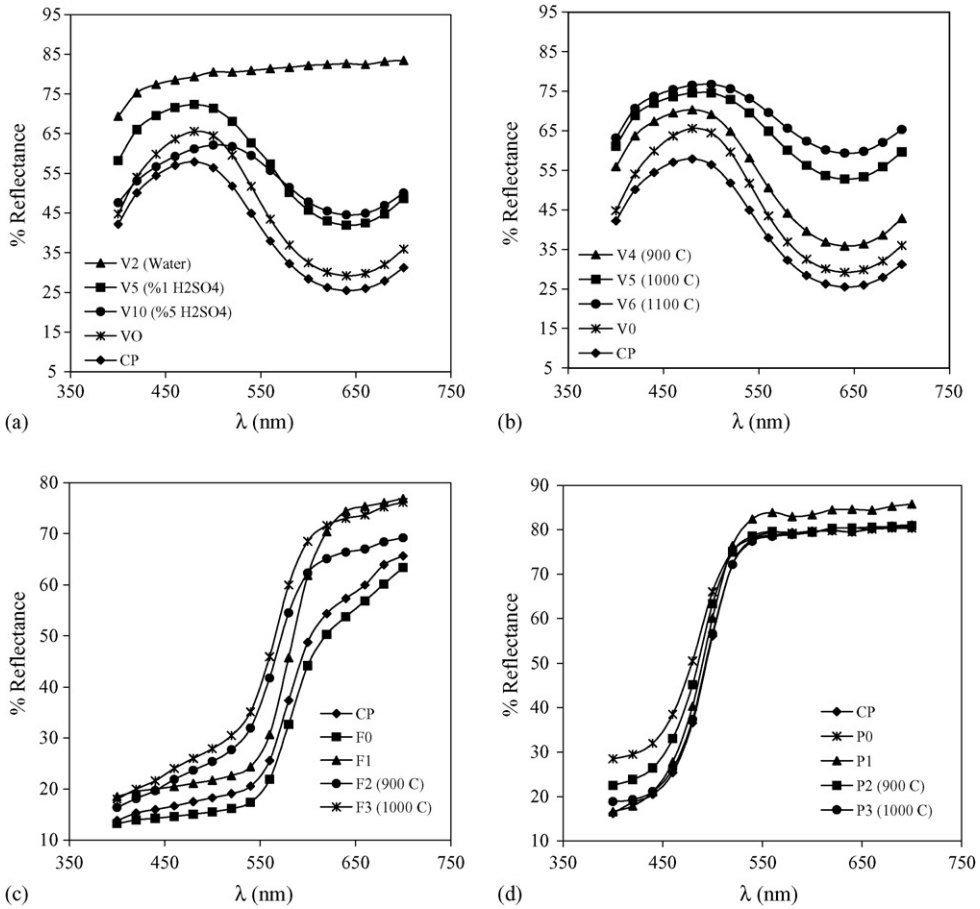

Fig. 3. Reflectance curves of glazed tiles containing (a) V–zircon blue pigments showing the effect of washing process, (b) V–zircon blue pigments showing the effect of temperatures, (c) Fe–zircon pink pigments and (d) Pr–zircon yellow pigments all calcined at different temperatures showing the effect of colouring agent and temperature.

Spectral reflectance curves of glazed tiles coloured with pigments prepared with decomposed products or pure oxides calcined at different temperatures are given in Fig. 3. As expected, there was no absorption in glaze containing pigment prepared with decomposed product, washed with water and has no colour. In contrast, the absorption is above 500 nm and the wavelength of absorption is centred in yellow–red region in the glaze containing pigments prepared with decomposed product washed with H_2SO_4 solution. Reflectance curves or colour properties of pigments prepared with decomposed product and pigment made from pure oxides are very similar.

The $L^*a^*b^*$ values of coloured porcelainized tiles containing pigments are given in Table 3. It is clear that the intense blue colours were obtained in porcelainized tiles containing 5 wt.% pigment. Although colour intensity is less than pigments prepared with pure oxide, decomposed zircon as a raw material can safely be used to produce pigments and reduced the pigment production cost if higher amount of pigment is used in a final product.

The XRD patterns of V-containing blue pigments produced from decomposed zircon with excess SiO_2, NH_4VO_3 and mineralizer mixture and calcined at different temperatures are shown in Fig. 4. Decomposed zircon products of Na_2ZrSiO_5 and Na_2ZrO_3 react with excess SiO_2 and crystallise as zircon at the calcination temperatures. Small amount of an intermediate compound, Na_2ZrSiO_{11} were also observed at 900 °C while this phase completely disappeared at 1000 and 1100 °C. Although commercially available blue V–zircon pigment contains quartz (SiO_2) and baddeleyite (ZrO_2) apart from the zircon (Fig. 4), all the peaks of the pigments prepared with decomposed zircon product were identified as zircon. Since, unreacted V compound were not observed in the XRD patterns of pigments, it is thought to be solid solution occurring between V-compound and zircon and V^{4+} and V^{5+} ions replaced both Zr^{4+} and Si^{4+} ions in the zircon lattice as reported at several previous studies.[5,17]

Infrared spectra of the V-containing blue pigments are shown in Fig. 5. The wavenumber of the main IR absorption peak were observed at around 1000, 900, 615 and 435 cm^{-1}. These peaks are associated with zircon as indicated in previous studies.[18,19] The structure of zircon can be described as consisting of chains of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra running parallel to the *c*-axis.[20] In general the tetrahedral SiO_4 unit in silicates exhibits the vibrational spectra at 800–1000 cm^{-1}.[21,22] The main observed IR absorption peak at around 1000 cm^{-1} is Si–O–Si stretching vibration. IR absorption of V4 pigments was shifted to lower wavenumber position probably due to the fact that V4 pigments contain small amount of Na_2ZrSiO_{11} phases that was observed in the XRD pattern. The weak absorption peak (at 803 cm^{-1}), which is present in vanadium containing zircon and its intensity increased as the vanadium content increased,[5] was not clearly distinguished in the prepared pigment. The 615 cm^{-1} band may be associated with the ZrO_8 group in which the Zr(IV) ion is found in a

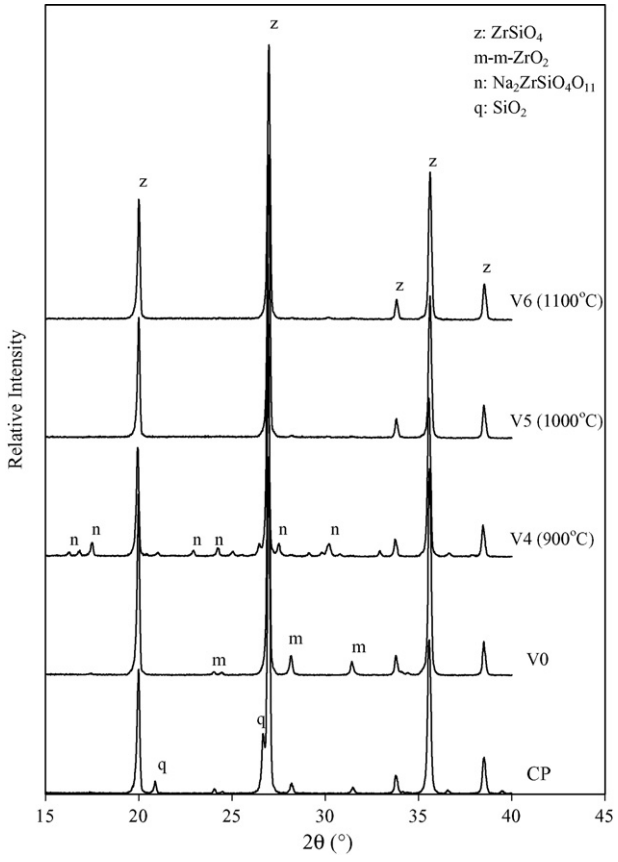

Fig. 4. XRD patterns of V–zircon pigments.

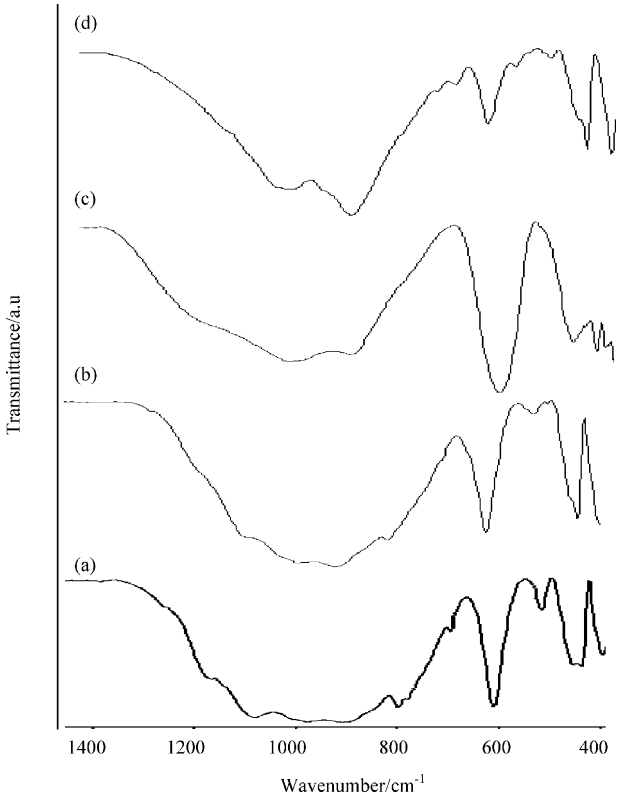

Fig. 5. Infrared spectra of V–zircon pigments: (a) commercial pigment, (b) pigments prepared with pure oxide, (c) V5 pigment (1000 °C) and (d) V4 pigment (900 °C).

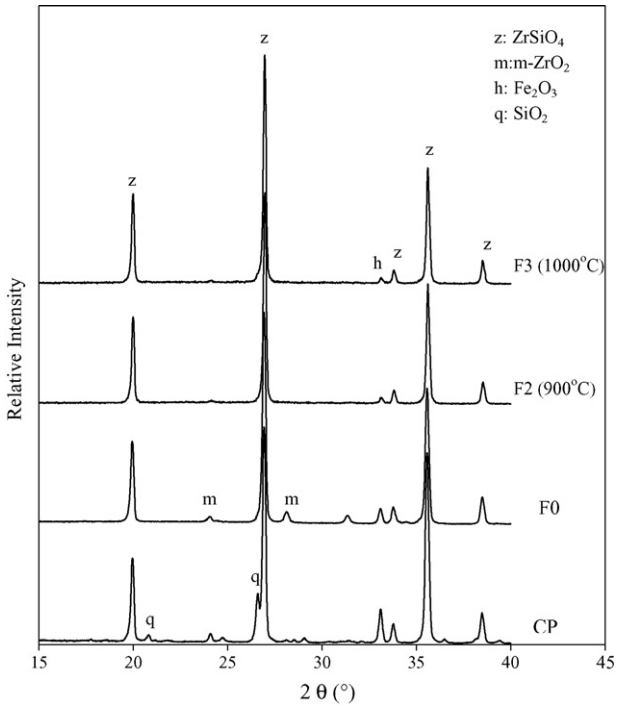

Fig. 6. XRD patterns of Fe–zircon pigments.

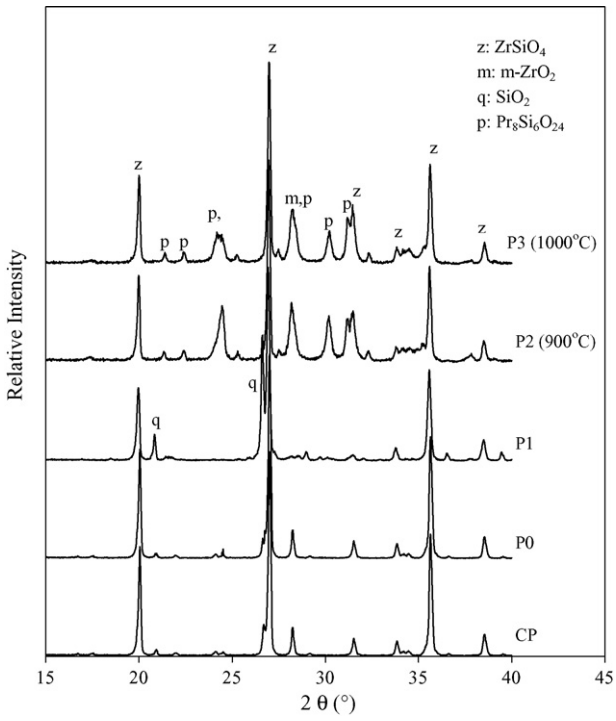

Fig. 7. XRD patterns of Pr–zircon pigments.

coordinating environment, similar to that of the Zr(IV) ion in $ZrSiO_4$.

3.2.2. Fe–zircon rose pigments

The pink colours were observed on glazes containing pigment prepared with decomposed product. Reflectance curves of glazes containing pigments are similar when compared to the commercial pigment and the pigments prepared with pure oxides. In Table 3, $L^*a^*b^*$ values of glazes containing Fe–zircon pigments prepared with decomposed products, commercial Fe–zircon pigment (CP) and pigment prepared with pure oxides (FO) are given.

Fig. 6 shows the XRD patterns of Fe-containing pink pigments produced from decomposed zircon products mixed with the excess SiO_2, $FeSO_4 7H_2O$ and mineralizer and calcined at 1000 °C. In the commercial pigment, zircon, hematite, quartz and baddeleyite phases were identified whereas main crystalline phases were zircon and hematite in the Fe–zircon pigments prepared with decomposed products. At pigments prepared with decomposed product, hematite phase was almost disappeared, probably because of the dissolution during the zircon formation from decomposed products. Although the amount of iron introduced into the zircon lattice is found to be higher, only a cream peach colour is obtained instead of a red coral, due to the lower proportion of occluded hematite.[4,8] In this respect, these results were confirmed by colour measurements which indicated that a^* values decrease with dissolution of the hematite in the zircon (Table 3).

It was also reported that Fe–zircon pigments prepared with zircon sand decomposed by NaOH/KOH waste and having pink–violet hues were obtained with 10 wt.% pigment addition into glaze.[11]

3.2.3. Pr–zircon yellow pigments

Table 3 reports the $L^*a^*b^*$ values of the Pr–zircon pigments. The yield of yellow colour is described by the value of the b^* parameter, more positive b^* values corresponding to more intense colour hues. Although pigments prepared with decomposed product are characterised by high brightness (L^* value), better yellow colour appearance with higher b^* values was obtained. In addition, reflectance curves of glazes containing pigment prepared with decomposed products closely matches with the commercial pigments (Fig. 3).

Fig. 7 reports the comparison between the XRD patterns of Pr-containing zircon pigments. In the prepared pigments, additional $Pr_8Si_6O_{24}$ and m-ZrO_2 phases were observed in comparison to the commercial pigment. Although, it is well known that praseodymium oxide is generally assumed to form a solid solution with the zircon lattice, solid solution reactions between zircon and Pr compounds were not completed and Pr compound reacted with SiO_2 to form $Pr_8Si_6O_{24}$. However, effect of this phase on the colour properties were not determined but a previous study reported that praseodymium oxide may impart a greenish yellow colour because the colouring component is not fully incorporated into the zircon lattice.[23]

4. Conclusion

In this study, zircon was decomposed with NaOH at different temperatures and decomposed product (Na_2ZrSiO_5 and Na_2ZrO_3 phases) was used as raw materials in order to produce zircon pigments. Temperature was found to be a very important factor in the decomposition of zircon with NaOH. Zircon phases were completely disappeared at 850 °C, but reformed at

875 °C. There was no absorption in glaze containing pigment prepared with decomposed product washed with water and has no colour. In contrast, blue colour was obtained in the glaze containing V-pigments prepared with decomposed product washed with H_2SO_4 solution. With Fe and Pr addition into decomposed zircon product, brilliant pink colour and yellow colour were observed. Also, colour properties of pigments prepared with the decomposed products were clearly shown to be used as a pigment by comparing colour properties of commercial pigment and pigment prepared with the pure oxides. Finally, this work has demonstrated that it is possible to obtain zircon pigments from zircon sand with an untraditional way. In particular, using intermediate products in the pigment production instead of pure zirconia would give some economical advantages.

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