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V-$ZrSiO_4$ ceramic pigments obtained from chemically activated natural zircon

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Abstract

This paper presents the synthesis method of V-$ZrSiO_4$ solid solutions ($ZrV_xSi_{1-x}O_4$ and ZrV_xSiO_4, x = 0.05, 0.10, 0.15) based on products of plasma dissociated zircon which treated by ammonium hydrofluoride NH_4HF_2 aiming to explore the potential of this technology in the manufacturing of ceramic pigments. Green pigments were obtained by calcination of mixtures of fluorinated plasma dissociated zircon with vandium pentoxide at 1000 – 1500 °C. Blue pigments were obtained using mineralizer sodium fluoride NaF at 750 °C. The use of fluorinated plasma dissociated zircon led to higher yield of green and blue color of pigments. The increase of the calcination temperature of blue pigments made lower blue color yield due to formation of orange colored V-ZrO_2 solid solutions.

Keywords: Ceramic pigments, zircon, plasma activation, ammonium hydrofluoride;

1. Introduction

Ceramic pigments are an essential part of ceramic industry. They are used in coloring of ceramics goods for giving them aesthetic and decorative properties. Good coloring results are achieved by using underglaze ceramic colors, however, it requires high temperature to their applying. The number of high-temperature ceramic pigments is not so big and their palette is limited. Therefore, research of new pigments with different structures and colors is actual nowadays. One of the most perspective types of high-temperatures pigments are zircon pigments [3].

Zircon-based ceramic pigments are a modern type of pigments used in ceramic industry. They are stable at high temperatures and melted glazes due to zircon properties: its refractoriness and chemical inertness [4]. One of the major problems in the field of zircon ceramic pigments technologies is the high cost of reagents which are actually pure chemical reagents. A perspective way to solve this problem is to use the plasma dissociated zircon (PDZ) from natural mineral as a raw material [5]. PDZ is a spheroids which consists of crystalline monoclinic zirconia grains interconnected to each other by the amorphous silica glass [1]. Despite a more intense reaction between silica and zirconia with the formation of zircon, the color yield of pigments is not so high because of difficulties in solid-phase reaction of zircon colored solid solutions.

Ammonium hydrofluoride could be used for the chemical activation of PDZ. Ammonium hydrofluoride reacts with components of PDZ with their partial destruction. This partial fluorination can cause microdefects in the structure of PDZ for more intensive interactions between defective PDZ and chromophoric ions to obtain more intensively colored pigments.

This paper presents the study in the field of technology of vanadium-zircon ceramic pigments with chemical preactivation of PDZ by ammonium hydrofluoride.

2. Materials and methods

A plasma dissociated zircon, which is processed from natural zircon of Tuganskoye deposit, was used in this research. PDZ was ball milled during 24 hours until its specific surface was 7500 cm^2/g (measured on Solominsky-Hodokov instrument). NH_4HF_2 (pure grade) was used for chemical activation of PDZ at 180°C during 2 hours. The proposed mechanism of reaction is presented by the formula:

$$3xNH_4HF_2 + ZrSiO_4 \rightarrow ZrSi_{1-x}O_{4-2x} + x(NH_4)_2SiF_6 + xNH_3 + 2xH_2O$$

The sublimation of ammonium fluorosilicate was carried out by calcination at 400°C during 4 hours. Thus, the composition of mixes of PDZ with NH_4HF_2 was calculated (table 1).

Table 1. Composition of mixes for chemical activation of plasma dissociated zircon

Sample name	PDZ, wt%	NH_4HF_2, wt%	Formula
PDZ-0	100.0	0.0	$ZrSiO_4$
PDZ-1	95.5	4.5	$ZrSi_{0.95}O_{3.9}$
PDZ-2	91.4	8.6	$ZrSi_{0.90}O_{3.8}$
PDZ-3	87.7	12.3	$ZrSi_{0.85}O_{3.7}$

The mixing of components (table 2) was carried out by a precipitation of V_2O_5 from NH_4VO_3 (pure grade) with nitric acid in water suspension of fluorinated PDZ followed by drying at 90°C. The dried materials were milled using a mortar. NaF (pure grade) was used as mineralizer. It was added to a starting mixes in the amount of 5 wt% [2]. The addition of mineralizer to starting mixes and their homogenization was carried out on laboratory vibratory mill FRITSCH pulverisette 23. Isothermal calcination of mixes was carried out at 750, 1000, 1100, 1200, 1300, 1400 and 1500°C for 4 hours.

After calcinations, the pigments were milled in the mortar and washed in a sodium hydroxide solution. The XRD analyses of samples were done using a DRON-3M diffractometer with monochromatic CuK_α radiation (1.54056 Å).

Table 2. Composition of mixes for pigments

Sample name	Formula	Fluorinated PDZ, wt%	V_2O_5, wt%
PDZ-0-1	$ZrSiV_{0.05}O_4$	97.6	2.4
PDZ-0-2	$ZrSiV_{0.10}O_4$	95.3	4.7
PDZ-0-3	$ZrSiV_{0.15}O_4$	93.1	6.9
PDZ-1	$ZrSi_{0.95}V_{0.05}O_4$	97.5	2.5
PDZ-2	$ZrSi_{0.90}V_{0.10}O_4$	95.1	4.9
PDZ-3	$ZrSi_{0.85}V_{0.15}O_4$	92.7	7.3

3. Results and discussion

A phase composition of pigments consists of V-zircon and monoclinic zirconia (table 3). V-$ZrSiO_4$ formation was confirmed by the shift of zircon phase peaks on XRD patterns. The increase of calcination temperature led to higher yield of green color in materials because of the growth of vanadium solubility in zircon structure and a more crystallization degree of zircon. Brown color of pigments were formed because of formation of green V-zircon and orange V-zirconia [6].

Table 3. Color of pigments (without mineralizer)

№	Calcination temperature, °C					
	750	1100	1200	1300	1400	1500
PDZ-0-1	Light green	Light green	Light green	Light green	Green	Green
PDZ-0-2	Light green	Green	Green	Green	Green	Green
PDZ-0-3	Brownish	Brownish	Brownish	Green	Green	Green
PDZ-1	Light green	Light green	Light green	Light green	Light green	Green
PDZ-2	Brownish-green	Brownish-green	Brownish-green	Green	Green	Dark green
PDZ-3	Brownish-green	Brownish-green	Brownish-green	Brownish-green	Dark green	Dark green

The pigments had blue color in the presence of mineralizer (so-called Turkish blue). However, blue color yield reduces at higher calcination temperatures (table 4). It can be explained by the fact that the mineralizer promotes the formation of not only V-zircon, but also V-zirconia.

Table 4. Color of pigments (with mineralizer)

№	Calcination temperature, °C	
	750	1100	1200
PDZ-0-1	Light blue	Light blue	Lime
PDZ-0-2	Light blue	Blue-green	Brownish-green
PDZ-0-3	Blue	Lime	Brownish-green
PDZ-1	Light blue	Light blue	Lime
PDZ-2	Light blue	Lime	Brownish-green
PDZ-3	Blue	Lime	Brownish-green

4. Conclusion

The use of the products of fluorine-ammonium treatment for plasma-activated zircon as the raw material in the V-$ZrSiO_4$ pigments technology allows to synthesize blue and green pigments with different color characteristics depending on the degree of fluoride activation of PDZ, the amount of chromophore, the calcination temperature and the presence of mineralizer.

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