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Research Article

Preparation and Coloration of Colored Ceramics Derived from the Vanadium-Titanium Slags

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Vanadium-titanium slag is a type of industrial solid waste from vanadium-titanium magnetite, and the resource utilization of vanadium-titanium slag is of great significance. The chemical composition of vanadium-titanium slag is similar to ceramic raw materials. Besides, the Fe, Ti, and Mn elements in vanadium-titanium slags possess strong color rendering ability. In the present study, we explored the influence of Fe, Ti, and Mn in vanadium-titanium slags on the coloration of ceramics. Besides, the crystal structures and chemical constituents of the sintered ceramics were studied by XRD, SEM, EDS, XPS, and ultraviolet-visible near-infrared spectrophotometer, and the color-rendering ability ($L^*a^*b^*$ values) of the ceramics was investigated. The results showed that the main crystal phases of the ceramics were quartz and anorthite. In addition, the color of the ceramics with the addition of vanadium-titanium slags was significantly affected by Fe and Mn ions, which decreased their L^* and a^* values. Meanwhile, Ti ion alone had no apparent coloring effect but strengthened the coloring effects of Fe and Mn ions. This work could provide the feasibility for preparation of colored ceramics based on vanadium-titanium slag, which could be used in the fields of high-value added building decoration, infrared-emission ceramic, and artwork.

1. Introduction

With the development of industrial technology and population growth, industrial wastes have become a serious social and environmental problem. These wastes cause many serious problems associated with transportation, storage, and air and environmental pollutions. Thus, recycling waste materials is urgently necessary. Some waste materials are adopted to make concrete, cement, and other building materials, and this approach reduces environmental pollution, sustainable consumption and production, and energy efficiency. Previously, numerous researchers have used industrial waste materials to produce new products. For instance, Lu et al. mixed fly ash and blast furnace slag and fluxed with borax and potash feldspar to prepare glass-ceramic glazes with low water absorption, proper stain resistance, and alkali and acid resistance [1]. Jonker and Potgieter reported that Fe-rich wastes could be used as a good flux for ceramic production and increase the strength of ceramics [2]. Sarkar et al. investigated the possibility of fabrication of vitreous ceramics in a steel-melting electric arc furnace slag [3]. They found that a certain amount of slag with other conventional raw materials could be used for sintering at a range of 1100–1150°C. Furthermore, other researchers used industrial waste materials, such as sewage sludge, fly ash, and steel slags, to produce ceramics, cement, and various building materials [4–8]. Simultaneously, vanadium-titanium slags are industrial wastes mainly concentrated in the Panxi area in south-western China. High titanium slag emissions amount to 3.6 million tons annually in the Panzhihua area and have reached nearly 70 million tons nationwide, thereby causing severe pollution. Vanadium-titanium slags are mainly composed of Fe_2O_3, TiO_2, CaO, SiO_2, and trace amounts of Al_2O_3, K_2O, and Na_2O. Chinese scholars have started studying the

Table 1: Main chemical composition of vanadium and titanium slags.

Constituent	Na_2O	MgO	Al_2O_3	SiO_2	TiO_2	V_2O_5	MnO_2	Fe_2O_3	CaO
wt. %	8.18	2.10	4.04	12.96	11.67	0.89	7.72	51.29	1.15

comprehensive use of vanadium-titanium slags since the early 1960s and have made some promising achievements. For example, Wang used titanium slags to fabricate concretes with other raw materials [9], and Sun et al. produced building bricks with titanium slags from Pangang factory and clays [10]. Besides, for the purpose of vanadium-titanium slag recycling, building bricks were prepared using vanadium-titanium slags or by extracting titanium from vanadium-titanium slags [11, 12].

Ceramic bodies are heterogeneous materials, and they mainly consist of a mixture of natural raw materials with various compositions. Currently, many previous studies mostly focus on the harmless treatment of wastes, preparation of the basic formula, and characterization of sample performances. There are few reports regarding the mechanism of ceramic coloring. Because the main ions in vanadium-titanium industrial waste slags are Fe, Mn, and Ti, vanadium-titanium industrial waste slags can replace a certain amount of clays and quartz, which are widely used to prepare ceramics. Herein, the aims of the present work are to explore the impact of Fe_2O_3, MnO_2, and TiO_2 on ceramic color performance, to study the color mechanism of ceramics after adding vanadium-titanium, and to assess the feasibility for preparation of colored ceramics, which could be used in the high-value-added building decoration field, infrared-emission field [13], and artwork.

2. Materials and Method

The basic materials were vanadium-titanium slags collected from PanGang Iron and Steel Group Co. The chemical composition of these slags is listed in Table 1. Other raw materials used to formulate the ceramic body were provided by Baita Ceramic Group Co. The mixtures were subjected to wet ball milling for 20 min and sieves using 140 mesh with a sieve margin of less than 3%.

The mixture was then filtrated, dried at 80°C for 2 h, ground, and humidified with 7.0 wt.% water. The humidified mixtures were then mold-shaped to the wafer samples with a diameter of 50 mm under 20 MPa pressure. Finally, the samples were dried at 100°C for 30 min and sintered in muffle furnace at 1100°C for 10 min.

The ceramic material colorant was characterized through the CIE1976 $L^*a^*b^*$ color system, which was established by the International Commission on Illumination in 1976. In the $L^*a^*b^*$ color system, the color is represented by three parameters, namely, L^* (lightness), a^* (color), and b^* (color). L^* shows lightness, and the L^* value ranges from 0 to 100 (black-white). a^* indicates the range from red to green, and its value ranges from +127 to −128 (red-green). b^* indicates the range from yellow to blue, and its value ranges from +127 to −128 (yellow-blue).

The phase composition of sintered ceramics was studied by X-ray diffraction (XRD, DX-1000X, Japan). The samples were scanned from 10° to 80° at a scanning speed of 2°/min. The microstructure of the samples was observed by the scanning electron microscopy (SEM, S-3400N, Japan) equipped with an energy dispersive X-ray spectrometer for elemental analysis. All samples were coated by gold for 1 min before SEM observation. The $L^*a^*b^*$ value was measured by WR-10 colorimeter. The reflectance spectrum was observed by UV-visible near-infrared spectrophotometer (UV-3600, USA) at a wavelength range of 250–1500 nm.

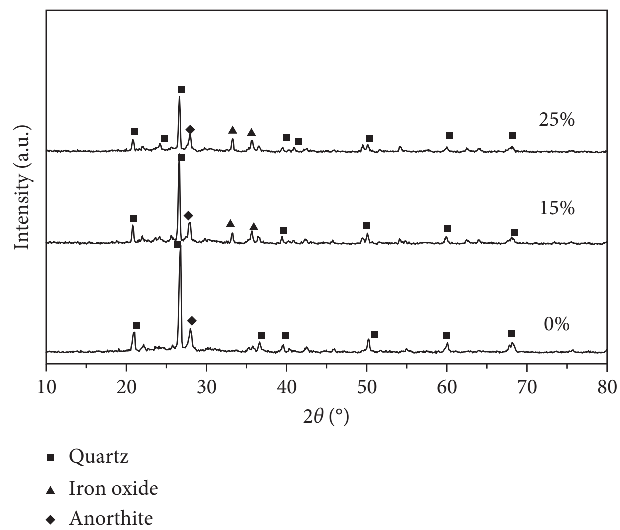


Figure 1: XRD spectra of ceramics with different amounts of vanadium and titanium industrial slags at sintering temperature of 1100°C.

3. Results and Discussion

3.1. Phase Composition. From previous researches, we can find that vanadium and titanium industrial waste slags were employed to partly replace ceramic raw materials for the preparation of ceramic bodies. Vanadium and titanium industrial waste slags exhibited the following favorable conditions: the addition amount was 15%, and the sintering temperature was 1100°C. Thus, the flexural strength of the ceramics was 31.28 MPa, and the water absorption was 7.07%. The ceramics were prepared with different amounts of vanadium-titanium slags and then sintered at 1100°C. The XRD analysis results are shown in Figure 1.

Figure 1 shows that the main crystalline phases of the sintered ceramics were quartz, anorthite, and iron oxide. Anorthite has been used in ceramics because of its high mechanical strength, dilatability, and low sintering temperature [14, 15]. The crystallization of anorthite increases the chemical stability and strength of the material and improves its physical properties including high thermal shock resistance and low thermal expansion coefficient [16–19]. The increased

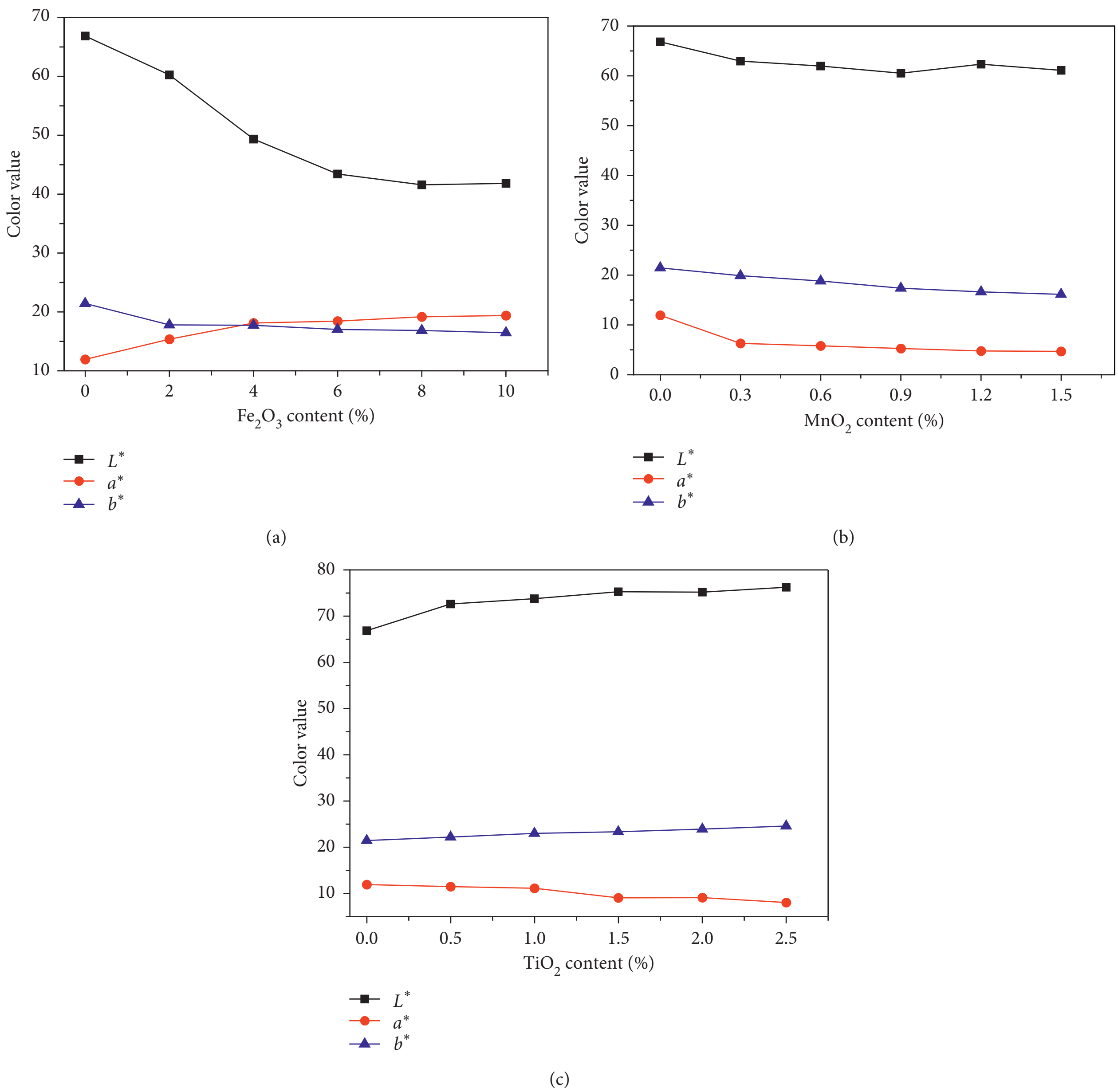


Figure 2: Effect of different colorants on the color of ceramics: (a) Fe_2O_3/addition, (b) MnO_2/addition, and (c) TiO_2/addition.

amount of the vanadium-titanium industrial waste slag resulted in the decrease of SiO_2 content and the increase of Fe_2O_3 content. The calculated area of the XRD spectra peaks indicated that when the amount of vanadium-titanium industrial waste slag increased to 15% and 25%, the iron oxide crystal phase ratios were 5.76% and 9.41%, respectively, and the composition of the raw materials decreased by 7.69% and 12.82%, respectively. The iron oxide in the ceramics was not entirely crystal and was partly in the glass phase. Similar to the network effect, the Fe^{3+} with eight ligands can damage the ceramic glass network structure by reducing the viscosity of the ceramic glass phase [20]. This effect contributes to the diffusion of atoms and ions during the sintering process and can reduce the sintering temperature, densify the ceramics, and increase the flexural strength.

3.2. Effect of Colorant on Color of Ceramics. The colorants were Fe_2O_3, MnO_2, and TiO_2 with contents of 0%–10% (wt.%), 0%–1.5% (wt.%), and 0%–2.5% (wt.%), respectively. Each colorant at various contents was added to different ceramics, and the products were sintered at 1100°C. The $L^*a^*b^*$ analysis of the ceramics is shown in Figure 2.

As shown in Figure 2(a), the lightness of the ceramics gradually decreased with the increase of the Fe_2O_3 content. When the amount of Fe_2O_3 reached 8%, the L^* value decreased gradually and then remained generally stable, whereas the a^* value increased gradually. The value of b^* decreased initially and then remained unchanged at the end. These results indicated that Fe_2O_3 could effectively reduce the lightness of materials and provide red coloring to the materials, thereby producing red ceramics. As shown in

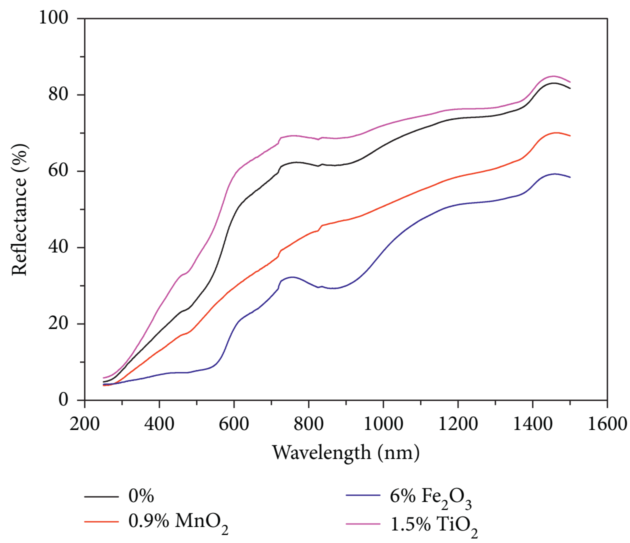


Figure 3: Reflectance spectra of ceramics with different colored oxides.

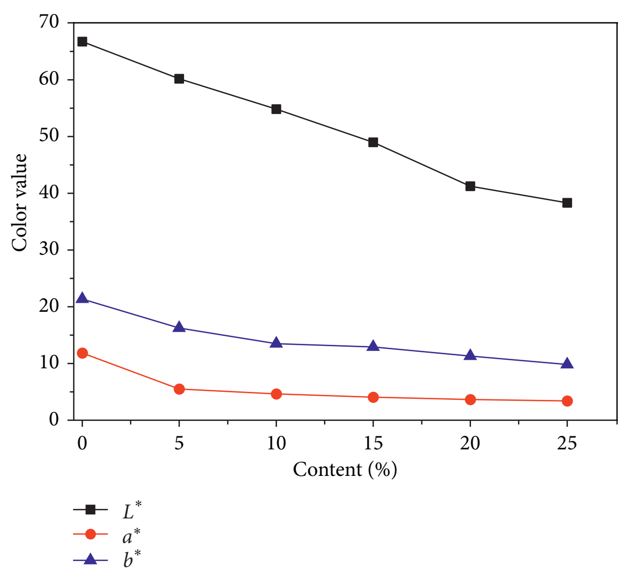


Figure 4: Effect of different vanadium-titanium slags on the color of ceramics.

Figure 2(b), when the addition of MnO_2 was minimal, it had little effect on the lightness of the ceramics. The a^* value decreased initially and kept unchanged at the end. The b^* value also decreased gradually, but the change was subtle. MnO_2 minimally reduced the redness and yellowness of the materials. Compared with Fe_2O_3 and MnO_2, TiO_2 improved the lightness, and it increased the L^* value of the materials in Figure 2(c). The a^* value increased, whereas the b^* value decreased gradually. TiO_2 improved the yellowness and reduced the redness of the materials. Therefore, the relationship among the contents of Fe_2O_3, MnO_2, TiO_2, and color parameters of the ceramics showed a monotone linear change, and single color oxide could affect the color properties of the materials.

Table 2: Color parameters of ceramics with different components.

Components	L^*	a^*	b^*
15% vanadium-titanium slags	49.08	4.15	13.03
6% Fe_2O_3	43.43	18.44	17.02
0.9% MnO_2	60.52	5.28	17.39
1.5% TiO_2	75.29	9.07	23.36

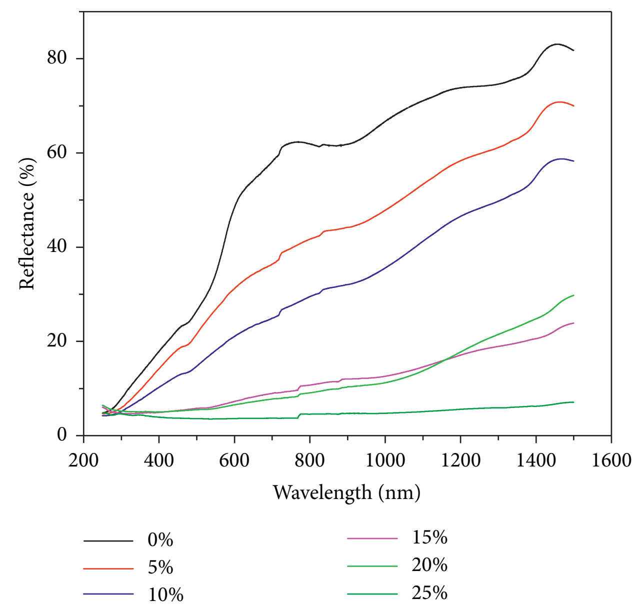


Figure 5: Reflectance spectra of ceramics with different vanadium-titanium slags.

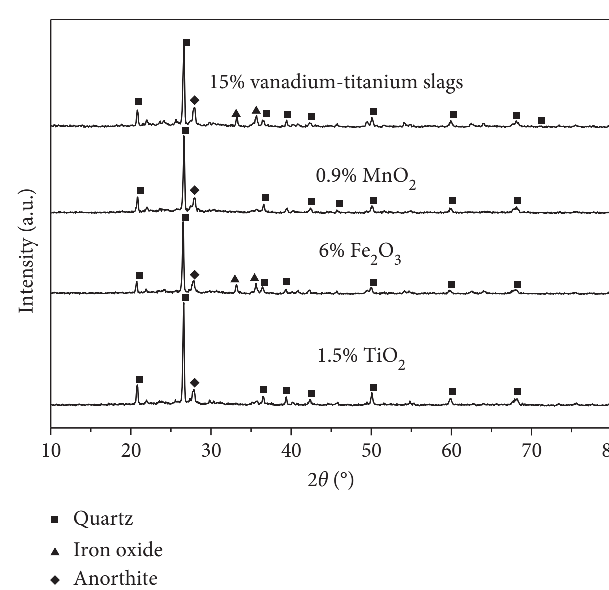
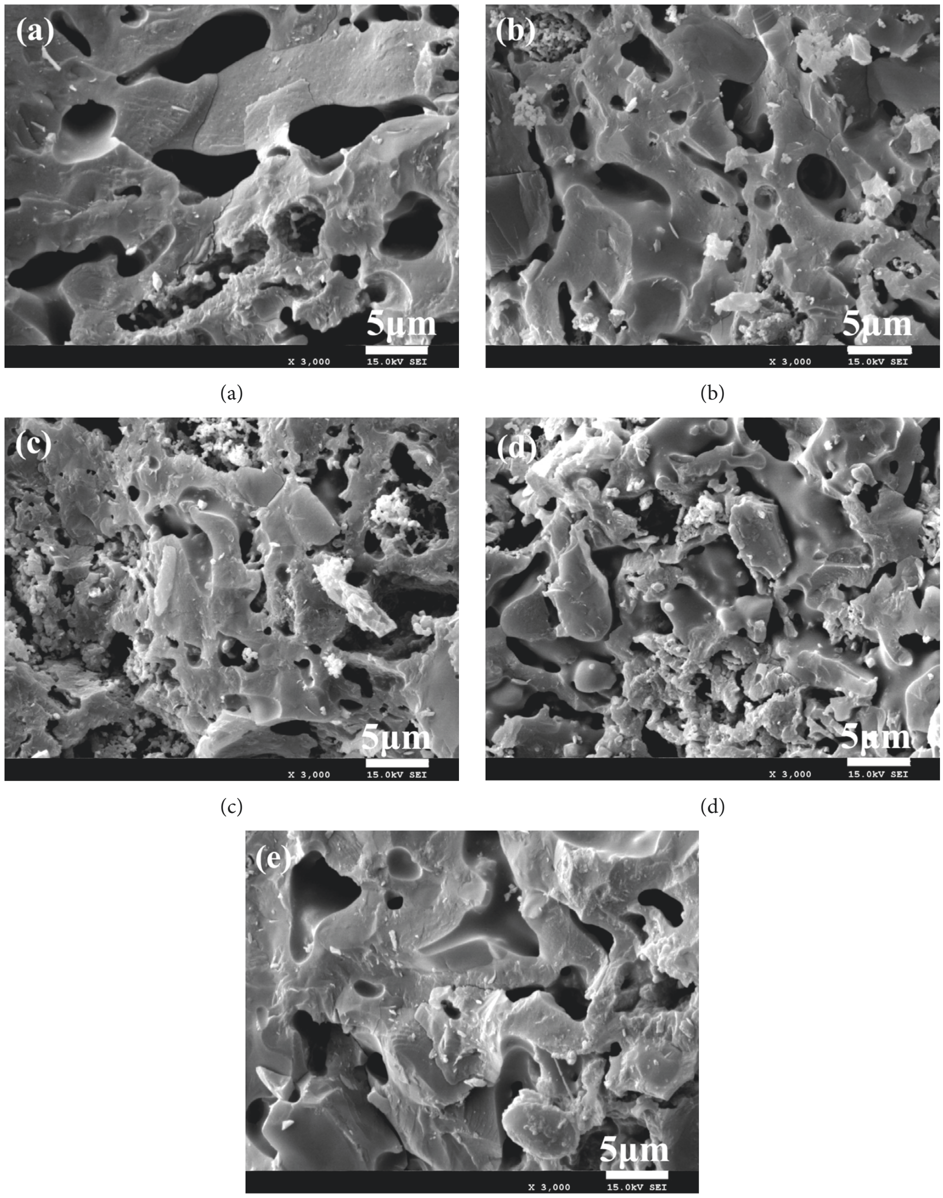


Figure 6: XRD spectra of ceramics with different additions at sintering temperature of 1100°C.

The first transition metal elements (fourth cycles) (Co, Cr, Ti, V, Mn, Fe, Ni, Cu, etc.) present generally in the form of ions in the silicate structure and have a common feature in terms of atomic structure, particularly maximum capacity of



(a) (b) (c) (d) (e)

Figure 7: Microstructures of ceramics with different additions at the sintering temperature of 1100°C: (a) no addition, (b) 15% vanadium-titanium slags, (c) 6% Fe_2O_3, (d), 1.5% TiO_2, and (e) 0.9% MnO_2.

10 electrons in 3d orbit, 1–9 electron transitions, and valence electrons jump between different energy levels (called *d*-*d* transition). Thus, the ions exhibit selective absorption in the visible region and thus render the ceramics colorful. The Fe ion has two valence states, namely, Fe^{3+} and Fe^{2+}. Fe^{2+} is easily oxidized and rare, whereas Fe^{3+} is extremely unstable at high temperatures and easily decomposes into Fe^{2+}. The coexistence of two valence states of iron oxides produces ferrous ferrite (Fe^{3+}-O-Fe^{2+}). Ferrous ferrite is a kind of Fe_3O_4 structure that renders ceramics colorful. At sintering temperature of 1100°C, the ceramics were slight red because the trivalent iron dominated.

In silicate ceramics, Ti is generally in the form of Ti^{4+}. The valence state of Ti^{4+} means that the $3d_24s_2$ of the outermost electrons of Ti is lost completely, and 3*d* orbital is completely empty. The "*d*-*d*" transition between the electrons in the *d* orbitals cannot occur. Thus, the valence state of Ti^{4+} should be colorless. However, Ti^{4+} ions strongly absorb ultraviolet light, and the absorption band can cross into the purple and blue part of visible light, subsequently rendering the materials pale brown. Ti^{4+} alone does not cause a darker color, but it can affect other transition elements and thus may strengthen and intensify the effect of the other ion colorants. In ceramic materials, Mn usually exists in the form of MnO_2, which reduces the lightness of materials.

The ceramics were prepared with colorants at varying contents and then sintered at 1100°C. The reflectance spectra of the ceramics are shown in Figure 3. The ceramics rarely

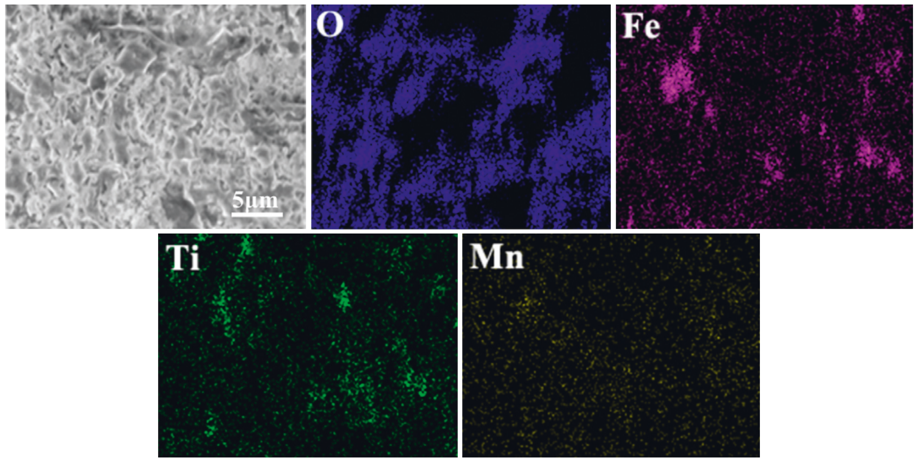


Figure 8: Element distribution of ceramics with 15% vanadium-titanium slags at the sintering temperature of 1100°C.

absorb light without colorants (Figure 3), and the ceramics were slightly yellow. No evident absorption peak was observed in the wavelength range of a single colorant, and the reflectivity increased gradually with increased wavelength. The reflectivity of ceramics with TiO_2 was higher than those of ceramics without colorants. However, the reflectivity of ceramics with Fe_2O_3 or MnO_2 decreased.

3.3. Effect of Vanadium-Titanium Slags on Color of Ceramics. The ceramics were prepared with different additions of vanadium-titanium slags and then sintered at 1100°C. The results of $L^*a^*b^*$ analysis on the ceramics are shown in Figure 4. It was found that the L^*, a^*, and b^* values all decreased with the addition of vanadium-titanium slags, in contrast to those of ceramics with different colorants, where the L^* value considerably decreased. The ceramics were purple black, which darkened gradually after the addition of vanadium-titanium slags. The color parameters of the ceramics with titanium-vanadium slags or single colorant are listed in Table 2. The color parameters of the ceramics with vanadium-titanium slags were different from those of the ceramics with a single colorant, and the L^*, a^*, and b^* values decreased. The alteration of the ceramics color with vanadium-titanium slags was attributed to the combined colors of various ions. Fe ions mainly reduced the L^* value of the material, and Mn ions mainly reduced the a^* value of the material. Ti ion alone had no evident coloring effect but strengthened the coloring effects of the Mn and Fe ions. The ion content, valence state, and sintering atmosphere cocontributed to the final color formation.

Figure 5 presents the reflectance spectra of ceramics with different amount of vanadium-titanium slags. The reflectivity of ceramics gradually decreased with the increase of vanadium-titanium slags. Moreover, the reflectivity of ceramics gradually increased with the increase of the wavelength of light, and there was no obvious absorption peak in all wavelength area, which corresponded to the color of ceramics.

3.4. Phase Composition and Microstructure. The XRD analysis of ceramics is shown in Figure 6. The main crystal phases of ceramics with different additions were quartz and anorthite and that of ceramics with vanadium-titanium slags or Fe_2O_3 was iron oxide. The microstructures of ceramics with different additions at sintering temperature of 1100°C are also depicted in Figure 7. These ceramics all displayed porous structures, and the numbers and sizes of the pores of the ceramics varied at different additions.

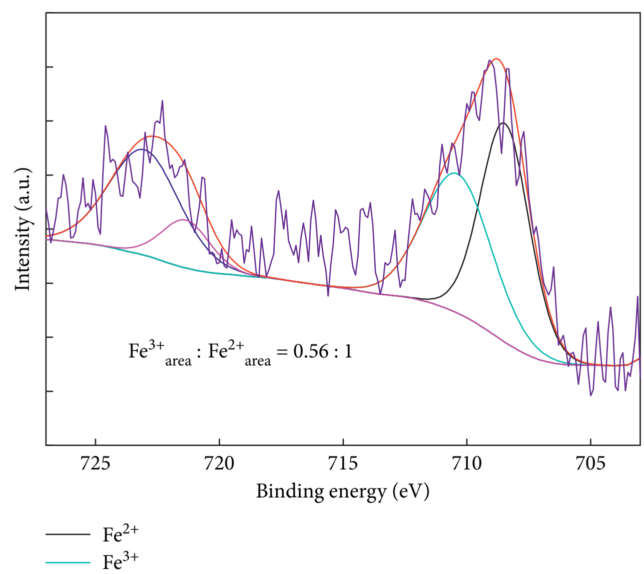


Figure 9: The XPS spectra of ceramics with 15% vanadium-titanium slags at the sintering temperature of 1100°C.

The content of SiO_2 in vanadium and titanium industrial waste slags was small, and the contents of Fe_2O_3 and Na_2O were relatively higher when vanadium-titanium slags or single oxide (such as MnO_2, Fe_2O_3, and TiO_2) were added to the ceramics. The addition reduced the content of SiO_2 in the body. Similarly, the content of SiO_2/R_2O decreased. In the sintering process, the skeleton effect of SiO_2 was partially destroyed. The aluminosilicates in clay and calcium oxide derived from the decomposition of raw materials to form anorthite. Simultaneously, iron oxide, sodium oxide, calcium oxide, and silicon dioxide formed a eutectic mixture, which produced a large number of liquid phases that promoted the sintering process.

3.5. Element Distribution. Figure 8 shows the element distribution of ceramics with 15% vanadium-titanium slags. From Figure 8, it could be seen that the elements of Fe, Ti, and Mn were distributed in the ceramics evenly, and the content of Fe was more than that of Ti and Mn. Therefore, this distribution can well describe the color of ceramics.

3.6. XPS Analysis. In order to confirm the content of Fe^{3+} and Fe^{2+}, the high-resolution XPS spectra of Fe 2p for ceramics are presented in Figure 9. And the calculated peak area ratio (Fe^{3+} area/Fe^{2+} area) of the sample has been marked in the spectra. It could be found that the content of Fe^{3+}/Fe^{2+} was 0.56. Under this condition, the valence of Mn was +4, and the valence of Ti was also +4, which was in accordance with the color of ceramics.

4. Conclusions

The vanadium-titanium industrial waste slags can partly replace ceramic raw materials for the preparation of ceramic bodies. The XRD results showed that the main crystalline phases of the ceramics with vanadium-titanium slags or single colorant were quartz and anorthite. The color of the ceramics with the addition of vanadium-titanium slags was significantly affected by various ions. The Fe and Mn ions mainly decreased the L^* and a^* values of the materials; however, Ti ions had a minimal coloring effect but affected the coloring effects of the Fe and Mn ions. The experimental results indicated that the ceramics with 15% vanadium-titanium slags could be fabricated to colored ceramics, and the color parameters were as follows: $L^* = 49.08$, $a^* = 4.15$, and $b^* = 13.03$. Our work could provide the feasibility for the preparation of colored ceramics.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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