

Article

Analysis and Mechanism Study of Residual Stress during the Spontaneous Crystallisation Process of Molten Titanium-Containing Blast Furnace Slag

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Abstract: Molten titanium-containing blast furnace slag can be used to obtain cast stone materials by controlling a reasonable heat treatment system. The material acquired during this process showcases residual stress, which additionally impacts the macroscopic characteristics of the material. This article simulates the process of manufacturing microcrystalline cast stones based on the self-crystallisation ability of titanium-containing products. This research employs X-ray diffraction to precisely and conveniently assess the residual stress of microcrystalline cast stones and investigates how viscosity and the thermal expansion coefficient influence the residual stress level. The study provides a theoretical foundation for explaining titanium-containing blast furnace slag and combines characterisation methods such as XRD (X-ray diffraction), SEM (Scanning electron microscope), DTA (Differential thermal analysis), and theoretical calculations such as Factpage and Fullprop to study the effect of the TiO₂ content on the microstructure of self-crystallised mechanical characteristics of microcrystalline cast stones through residual stress. The results of the experiment indicate that as the TiO₂ content in the system increases, the glass phase is reduced, the crystallinity improves, and the main crystal phase changes from a feldspar phase to a diopside phase. Furthermore, its viscosity, thermal expansion coefficient, and residual stress decrease while its corresponding compressive strength and bending strength increase.

Keywords: residual stress; X-ray diffraction method; microcrystalline cast stone; titanium containing blast furnace slag; mechanism



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1. Introduction

In China, research into the utilisation of titanium-containing blast furnace slag resources is deepening. The TiO₂ in this slag can be used as a nucleating agent to self-crystallise titanium-containing blast furnace slag, which can then be used to produce microcrystalline glass and cast stone, representing an important way to recycle titanium-containing blast furnace slag [1]. The mechanical properties of multiphase brittle materials are largely determined by the internal microstructure characteristics and the level of residual stress generated during cooling due to the thermal and elastic mismatch between the constituent phases [2]. During the self-crystallisation process of molten titanium-containing blast furnace slag, multiple complex phases form, and their microstructure consists of one or more phases distributed within the glass matrix, which generates residual stress and substantial mechanical disparities. By studying the changes in residual stress after self-crystallisation of molten titanium-containing blast furnace slag and exploring the mechanism of stress generation, the material after self-crystallisation of titanium-containing blast furnace slag can exhibit a controllable sample structure and excellent mechanical

properties, thus greatly improving the efficiency of utilisation of titanium-containing blast furnace slag.

Residual stress refers to the internal stress that remains in equilibrium within an object despite the removal of external forces or uneven temperature fields [3]. Residual stress significantly affects the fatigue strength and shape accuracy of components. And its formation varies with the material, shape, forming, and processing of the components [4]. In production, more attention should be paid to the thermal residual stress in the crystallisation process of titanium-bearing blast furnace slag. Thermal residual stresses can be classified into three groups based on their source: (1) thermal gradient residual stresses, (2) residual stresses caused by the thermal expansion coefficient, and (3) residual stresses caused by phase transformation [5].

Currently, residual stress measurement methods are divided into mechanical and physical methods [6]. The latter are non-destructive methods. Compared to mechanical methods, measuring residual stress using physical methods is more suitable for theoretical research. The X-ray method is currently the most mature and widely used method for measuring surface residual stress. It has the following features: mature theory, high measurement accuracy, and accurate and reliable measurement results. Compared to other methods, the X-ray diffraction method has a high level of credibility when measuring stress qualitatively and quantitatively [7,8]. Due to the limited transmission depth of X-rays in the material, the depth of the measured surface layer is only 10–35 μm . Therefore, the measurement is reliant on the stress state of the material's surface, which does not alter the material's state. It is a non-destructive measurement technique that involves measuring the stress on specimens without mechanical contact. This is particularly useful in the study of different surface strengthening treatment technologies to test their impact on processes and to ensure the quality of surface machining. This strategy has significant practical implications.

Since the development of the X-ray diffraction method, numerous scholars, both domestic and international, have employed it to investigate the residual stress in materials. XIE Jun, CHENG Jinshu et al. [9] investigated the impact of CaO concentration on residual stress in glass ceramics of the CaO-Al₂O₃-SiO₂ (CAS) system via X-ray diffraction techniques. The study shows that an increase in the CaO content leads to an increase in the β -wollastonite crystal phase and higher residual stress. However, the grain size of the β -wollastonite crystal phase decreases with an increase in the CaO content, which has a negative effect on the increase in residual stress. Those two opposing factors can affect residual stress. In their study, they found that the residual stress in CAS glass ceramics initially decreases but then increases rapidly. Subsequently, XIE Jun, LONG Xinjiang et al. [10] investigated the impact of the Al₂O₃ content on residual stress in microcrystalline glass composed of CaO-Al₂O₃-SiO₂. The findings of this study revealed that an increase in the Al₂O₃ content leads to a reduction in the β -wollastonite crystal phase and a lower residual stress. The Al₂O₃ content directly effects the bending strength of CAS glass ceramics, and the maximum value of the bending strength emerges when Al₂O₃ is 7.5 wt%. H. Pinto, L. Tto et al. [11] investigated the impact of Li₂O-2SiO₂ glass ceramics incompletely crystallised on the microstructure and surface residual stress. They used X-ray diffraction to measure the residual stress. The findings suggest that in the crystals within the bulk of the samples, micro-residual stresses generated by the thermal anisotropy of the isolated individual crystallites depend on the crystallographic direction. The anisotropy of the residual stresses in these glass ceramics arise from the crystal structure of the crystalline phase formed, which may cause a crystallographic dependence of the thermal expansion coefficient and elastic constants.

The aim of this study is to analyse the residual stress of cast stone materials, which were prepared by controllable heat treatment of molten titanium-containing blast furnace slag with varying TiO₂ concentrations. The factors that affect the internal stress of cast stone obtained after self-crystallisation of titanium-containing blast furnace slag are elucidated to provide insights into improving the samples' performance. Additionally, this study aims to

provide a reasonable theoretical basis for the efficient processing and utilisation of molten blast furnace slag.

2. Principle Analysis of Residual Stress Detection Based on an X-ray Diffraction Method

The widely used classification method of residual stress was first proposed by Soviet scholars. The core basis of this classification method is that residual stresses have different effects on crystal X-ray diffraction phenomena. The first type of internal stress, which is balanced in the macroscopic size range, causes a shift in the X-ray diffraction spectrum; the second type of internal stress, which is in grain size equilibrium, causes a broadening of the X-ray spectrum; the third type of internal stress, which is balanced in the unit cell range, causes a decrease in the diffraction intensity. The first type of internal stress can be understood as the average value of internal stress in many grain regions that exists in different grains. It is commonly referred to as macroscopic stress, and in scientific and technological literature, it is commonly referred to as residual stress [12]. For polycrystalline materials, the strain that corresponds to macroscopic stress is commonly seen as the statistical outcome of lattice strain within the corresponding area. By measuring lattice strain via XRD, stress can be calculated, which is the theoretical basis for testing macroscopic stress. When a material is under external tensile stress, the spaces between different crystal planes of various crystal families are altered, as demonstrated in Figure 1. The spacing between diffraction crystal planes with normal lines parallel to the surface ($\psi = 0^\circ$) decrease, whereas the spacing between diffraction crystal planes with normal lines that are perpendicular to the surface ($\psi = 90^\circ$) increase. The greater the macroscopic stress in the material is, the greater the difference in the crystal plane spacing or diffraction angle of the same group in different orientations. Set up a coordinate system on the surface of the sample as shown in Figure 1:

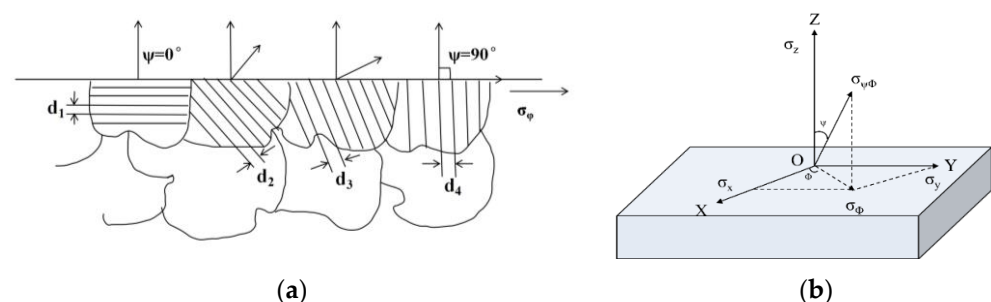


Figure 1. (a) The relationship between the ψ angle and the crystal plane spacing of the same crystal plane family; (b) sample plane coordinate map.

In Figure 1, the ψ angle is the angle between the normal of the diffraction crystal plane and the normal of the sample surface; the ϕ angle is the angle between the projection of the stress on the X axis and the X axis. When stress is applied and the angle changes from 0° to 90° , the spacing between crystal planes in a family of crystal planes changes continuously from negative to positive. This change is manifested at the macro-level as the crystal undergoes strain when subjected to stress, i.e., the diffraction peak shifts. According to the Bragg equation, the spacing between crystal planes (Δd) is related to the angle (θ). For general materials, X-rays cannot penetrate deep into the material, so this method only measures the stress on the surface of the specimen. And because the vertical component stress is 0, i.e., $\sigma_z = 0$, this stress is always a two-dimensional plane stress. In the treatment of planar stress, “ $2\theta - \sin^2\psi$ ” is often used [13]. The residual stress can be calculated by this method. Here, we briefly introduce the calculation formula of residual stress.

$$\sigma_\phi = \left[-\frac{E}{2(1+\nu)} \frac{\pi}{180} \cot\theta_0 \right] \frac{\partial 2\theta_{\psi\phi}}{\partial \sin^2\psi} \quad (1)$$

$$K = -\frac{E}{2(1+\nu)} \frac{\pi}{180} \cot\theta_0, \quad M = \frac{\partial 2\theta_{\psi\varphi}}{\partial \sin^2 \psi} \quad (2)$$

In the given equation, E represents the elastic modulus, and ν stands for Poisson's ratio. Among them, K is the stress constant, determined by the elastic modulus and Poisson's ratio; M is the slope, which is obtained through linear fitting using the least squares method based on actual experimental data.

This study focuses on simulated slag that contains titanium blast furnace slag as the research subject. The shift in the diffraction peak with higher intensity in the XRD diffraction pattern serves as the basis for stress measurement during the testing process. The experiment changes the angle (ψ) between the diffraction plane normal and the sample surface normal by rotating the sample stage. Then, the corresponding 2θ is determined by measuring the diffraction peak in the experiment. To calculate the gradient, the curve fit is performed linearly utilising the least squares method with the Originpro 2021 (9.8) software. The residual stress value can be determined by measuring the magnitude of the diffraction peak movement. We determined the material's elastic modulus to be 57.401 GPa and referenced CMAS system glass ceramics to obtain a Poisson's ratio of $\nu = 0.245$. Subsequently, residual stress was calculated using the slope and stress constant.

3. Materials and Experimental Scheme

Currently, the industry divides titanium-containing blast furnace slag into three categories based on their titanium content: low titanium slag (<10%), medium titanium slag (10%~20%), and high titanium slag (>20%). We have researched the composition of various types of titanium-bearing blast furnace slag in our previous work [14]. The following Table 1 shows the composition of three "real" (i.e., discharged from industrial blast furnaces) slags with different titanium contents.

Table 1. The composition of titanium-containing blast furnace slag (wt%).

Composition	TiO ₂	CaO	SiO ₂	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	MnO	TFe *	Others	Basicity
Slag sample 1	9.54	34.08	29.84	9.7	12.51	1.02	0.73	0.49	0.54	1.55	1.14
Slag sample 2	17.26	29.94	24.31	9.67	13.12	0.98	0.22	0.52	1.20	2.78	1.23
Slag sample 3	22.00	26.28	22.80	9.14	12.30	0.40	0.83	0.74	1.80	3.71	1.15

* TFe represents total iron.

Table 1 shows that slag with varying titanium content has a similar composition. The analysis focuses on the following points:

- (1) The blast furnace slag that contains titanium mainly consists of CaO, SiO₂, Al₂O₃, MgO, and TiO₂.
- (2) The MgO and Al₂O₃ components of the slag show very little change with variations in TiO₂ content. It is difficult to observe any significant impact on the precipitated phase of the molten titanium-containing blast furnace slag after crystallisation at the experimental scale. To ensure accurate study of the effect of TiO₂ content on residual stress of crystallised molten titanium-containing slag, it is necessary to fix the MgO and Al₂O₃ components at 10 wt% and 12 wt%, respectively. This will increase the scientific validity of the research results.
- (3) The slag has five main components. We found that, apart from changes in TiO₂ content and the stability of MgO and Al₂O₃, the basicity (CaO/SiO₂) showed a small change. As the basicity of slag with varying titanium content remains relatively constant, we have set its basicity to 1.14.
- (4) The composition of real slag is complex and variable. Apart from TiO₂, which varies with the slag, the other main components (CaO, SiO₂, Al₂O₃, MgO) are regular. To emphasise the impact of TiO₂ on the residual stress of crystallised molten titanium-bearing blast furnace slag, we typically disregard other minor components (those

that are less than 1 wt% or have a low content that does not affect the microscopic composition) to simplify the design.

Although there is a slight difference between “simulated” slag and “real” slag, the purpose of controlling changing parameters is to obtain more accurate conclusions that can guide industrial production. We adjusted the components and basicity to closely match the composition of real slag. This scientific method can be applied to various types of titanium slags.

Based on the characteristics of the above components, it can be concluded that the product, microcrystalline glass or the cast stone made from it, is generally a CaO-MgO-Al₂O₃-SiO₂ system, in which wollastonite, pyroxene, and melilite are easily precipitated. Diopside and pyroxene, both classified as metasilicate minerals, exhibit high mechanical strength [15,16], excellent wear resistance [17], and chemical stability. In industrial production, it is important to prepare products with excellent mechanical properties. The types of precipitated phases play a crucial role in determining the properties of different products due to their varying microstructures. To ensure that the “simulated” slag used in the experiment reflects the crystal phase diversity of the “real” slag, before designing the composition, we analysed the phase composition of the titanium-containing blast furnace slag after crystallisation and compared it with the “simulated” slag. Figure 2 displays the XRD diffraction patterns of “real” slag and “simulated” slag with a TiO₂ content of approximately 10 wt%. The figure illustrates that they precipitate the same phase (melilite, diopside, and perovskite) under identical process conditions. However, because the composition of the “simulated” slag is simpler than that of the “real” slag, the content of the precipitated phase is relatively stable, which also shows that the phase composition after crystallisation of the “real” slag can be stably represented by using the “simulated” slag.

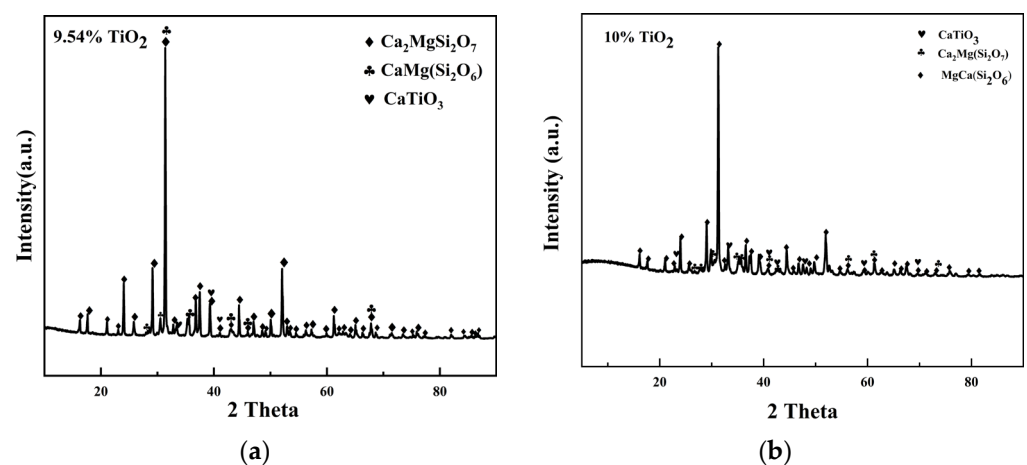


Figure 2. (a) XRD pattern of “real” slag containing about 10 wt% TiO₂; (b) XRD pattern of “simulated” slag containing 10 wt% TiO₂.

TiO₂ is a commonly used nucleating agent in the manufacture of slag glass ceramics. The presence of TiO₂ as a nucleating agent is mainly to provide a potential structure for nucleation and growth. In CaO-MgO-Al₂O₃-SiO₂ glass ceramics, the glass transition temperature and crystallisation temperature decrease with increasing TiO₂ content [18]. When the content of TiO₂ is below 5 wt%, the primary crystal phase is plagioclase. However, with an increase in TiO₂ to 10 wt%, the primary crystal phase is augite. Some researchers have found that increasing the amount of titanium slag increases the amount of TiO₂ as a nucleating agent and improves the mechanical properties of glass ceramics. Therefore, this study employs pure reagents, including calcium oxide, silicon dioxide, magnesium oxide, alumina, and titanium dioxide, to simulate the production of microcrystalline cast stones according to the slag composition. The chosen reagents were of analytical purity, with a 99% purity level. The specimens were prepared by appropriately altering the proportion of

TiO₂, as presented in Table 2, in order to investigate the influence of varying TiO₂ amounts on the residual strain in glass ceramics.

Table 2. The material ratio has been designed on the basis of the composition of the selected titanium blast furnace slag.

Group	wt (TiO ₂)/%	wt (SiO ₂)/%	wt (CaO)/%	wt (MgO)/%	wt (Al ₂ O ₃)/%	Basicity
G1	5	34.11	38.89	10	12	1.14
G2	10	31.78	36.22	10	12	1.14
G3	12.5	30.61	34.89	10	12	1.14
G4	15	29.44	33.56	10	12	1.14
G5	17.5	28.27	32.23	10	12	1.14
G6	20	27.1	30.9	10	12	1.14
G7	22.5	15.93	29.57	10	12	1.14

This experiment utilised the melting technique to produce self-crystallised products. Initially, 300 g of simulated slag material was prepared, mixed uniformly, and placed in a 450 mL corundum crucible. It was then heated in a melting furnace to 1500 °C for a duration of 2 h. Then, the molten slag was poured into two sets of moulds, one measuring 20 mm × 20 mm × 10 mm for residual stress testing, and the other measuring 65 mm × 30 mm × 20 mm for mechanical property testing. Once casting was complete, the moulds were immediately placed in a crystallisation furnace at 1017 °C for 30 min before being cooled to room temperature. A comprehensive study of various aspects of the samples obtained from the self-crystallisation of titanium-containing blast furnace slag was carried out by theoretical calculations, XRD stress analysis and phase detection, calculation of the degree of crystallisation (according to the characteristics of the amorphous peak, the crystalline phase ratio was calculated using Jade 9.0 software), scanning electron microscopy morphological analysis, and mechanical property analysis. A method for analysing the internal stress of microcrystalline cast stones from titanium-containing blast furnace slag was established, providing a control approach for the internal stress of inorganic non-metallic materials. The experimental procedure is shown in Figure 3.

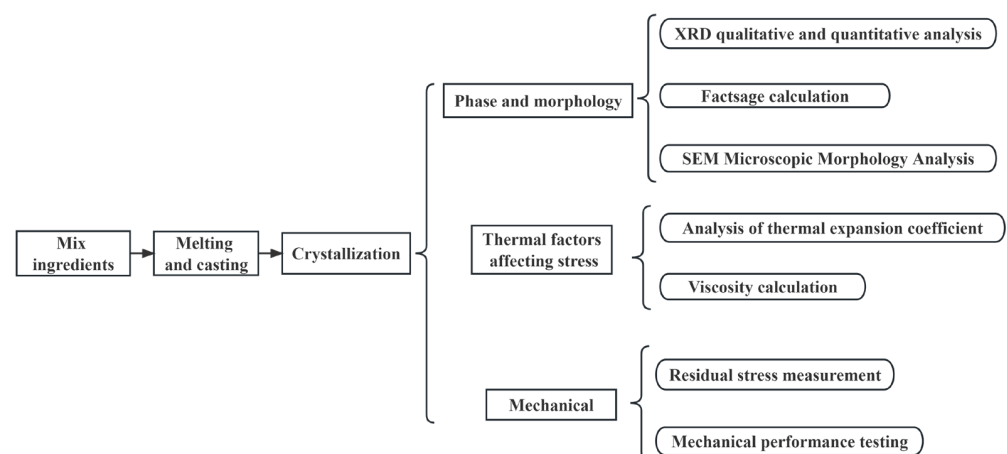


Figure 3. The process of this experimental research.

4. Results

4.1. Effect of Various TiO₂ Contents on the Crystallisation Behaviour and Microstructure of Titanium-Containing Blast Furnace Slag

Under different TiO₂ ratios, various phases were precipitated during the self-crystallisation process of titanium-containing blast furnace slag, as demonstrated in Figure 4. In this experiment, the contents of MgO and Al₂O₃ were controlled to 10 wt% and 12 wt%, respectively, based on the composition of titanium-bearing blast furnace slag, and the

self-crystallisation process of titanium-containing blast furnace slag was simulated using the phase diagram module in FactSage 7.3 software to calculate the phase diagram of the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ system in the range from 1000 °C to 1500 °C. In Figure 4, the main precipitates are melilite and perovskite when the basicity (CaO/SiO_2) is 1.14 and the TiO_2 content ranges from 5 wt% to 22.5 wt%. However, considering the changes in mass loss of calcium oxide and silicon dioxide during the melting process and their alkalinity within the range of approximately 1.14, it is possible that the precipitates may also include merwinite and clinopyroxene.

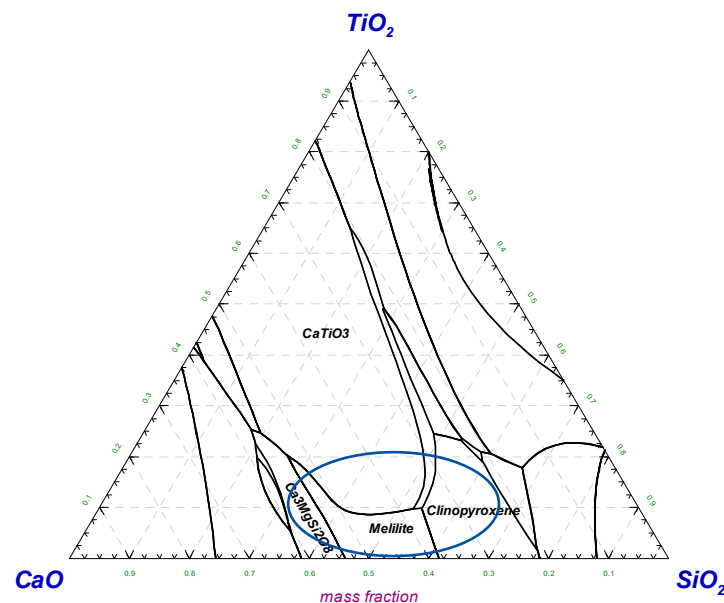


Figure 4. The phase diagram of $\text{CaO-SiO}_2\text{-TiO}_2$ with MgO and Al_2O_3 contents of 10 wt% and 12 wt% respectively. The circle indicates the phase that can precipitate in the system when the TiO_2 content is between 5 wt% and 22.5 wt%.

In order to quantitatively and qualitatively analyse the relationship between the possible precipitates in the self-crystallisation process of titanium-containing blast furnace slags with different TiO_2 contents, the possible precipitates and their contents in titanium-containing blast furnace slags with different TiO_2 contents between 800 °C and 1500 °C were calculated using the Equilib module in Factsage software. As shown in Figure 5, when the crystallisation temperature is 1017 °C, as the TiO_2 content increases from 5 wt% to 22.5 wt%, the precipitation amount of melilite decreases from 248.247 g (82.75 wt%) to 20.653 g (6.88 wt%), the precipitation amount of perovskite increases from 25.532 g (8.51 wt%) to 114.89 g (38.3 wt%), and the precipitation amount of diopside increases from 16.3554 g (5.45 wt%) to 128.276 g (42.76 wt%). As the TiO_2 content increases, melilite tends to decrease, while diopside and perovskite increase. When TiO_2 is 17.5 wt%, the precipitation amount of melilite is 112.11 g (37.37 wt%), and the precipitation amount of diopside is 95.7438 g (31.91 wt%). The main crystal phase is still melilite, but when it increases to 20 wt%, the precipitation amount of diopside is 112.006 g (37.34 wt%), which is greater than the precipitation amount of melilite and becomes the main crystal phase. Figure 5 also shows that as the TiO_2 content increases from 5 wt% to 22.5 wt%, the initial precipitation temperature ranges of the melilite, perovskite, and diopside phases are 1390 °C to 1240 °C, 1380 °C to 1440 °C, and 1090 °C to 1220 °C, respectively. Based on the above analysis, we can draw a theoretical conclusion: as the TiO_2 content increases, the main crystal phase changes from melilite to diopside, and perovskite increases. Since an increase in the TiO_2 content can lower the crystallisation temperature and the precipitation temperature of diopside is lower than that of melilite and perovskite, it is speculated that

as the TiO_2 content increases, more crystalline phases (mainly diopside) precipitate in the microcrystalline glass.

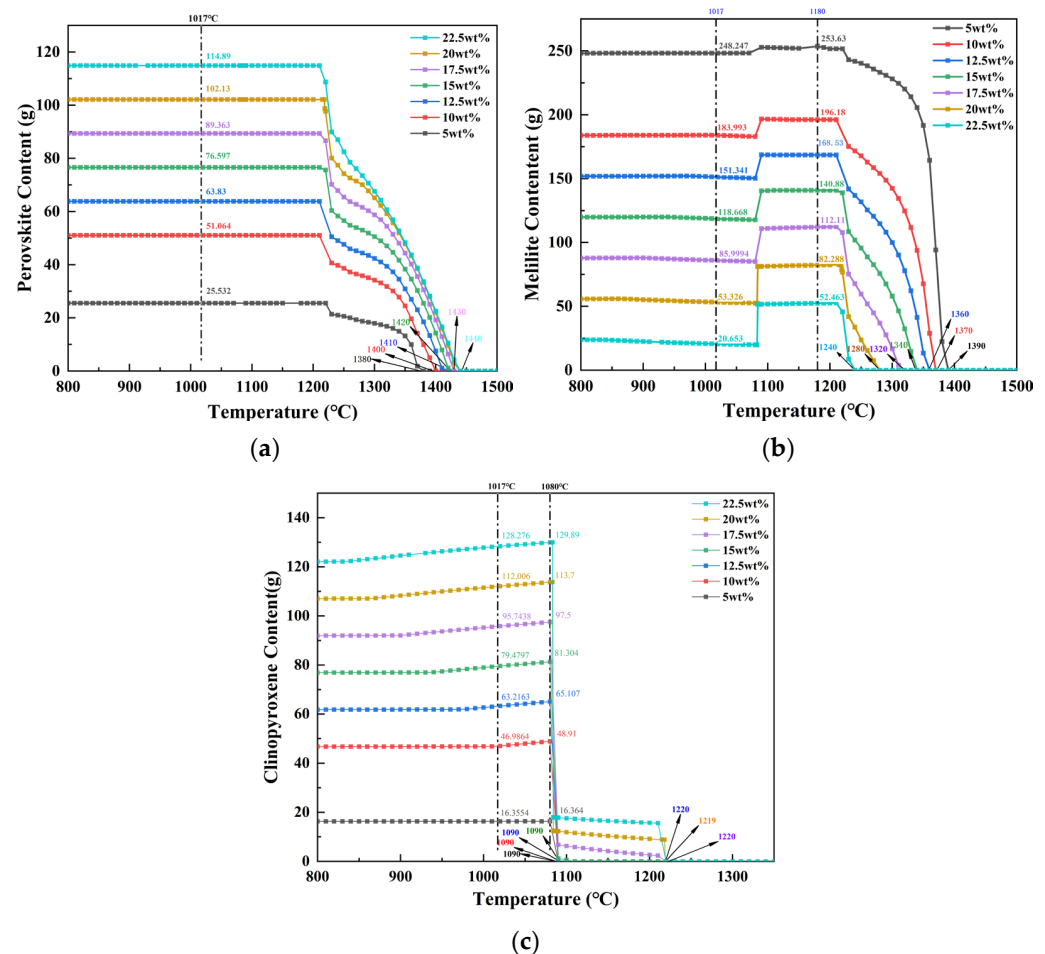


Figure 5. (a–c): Calculation of the precipitation content of melilite, diopside, and perovskite with different TiO_2 contents in the temperature range of 800 °C to 1500 °C via Factsage.

In this experiment, microcrystalline cast stone samples with 5 wt%, 10 wt%, 12.5 wt%, 15 wt%, 17.5 wt%, 20 wt%, and 22.5 wt% TiO_2 content were obtained by the melting method. The microstructure of microcrystalline cast stone samples with 10 wt% and 12.5 wt% TiO_2 content showed significant changes. As illustrated in Figure 6, the glass content of Figure 6a is notably higher than that of Figure 6b, even though only 2.5 wt% TiO_2 was added. The ratio of the glass phase to the crystal phase in the microcrystalline glass is flipped.

To confirm the earlier hypothesis, DTA (Differential thermal analysis) was employed to determine the activation energy of crystallisation for microcrystalline glass samples containing 5 wt%, 10 wt%, and 12.5 wt% TiO_2 . The analysis assessed the critical state of an abrupt increase in the crystal phase. Figure 7 displays the differential thermal analysis (DTA) curves obtained by heating water-quenched glass slag samples with different TiO_2 contents at heating rates of 10 °C/min, 15 °C/min, 20 °C/min, and 25 °C/min. The occurrence of crystallisation during the heating process is represented by a downward exothermic peak in the DTA curve. Generally, the initial temperature and peak temperature of crystallisation decrease with increasing TiO_2 content. For instance, when the TiO_2 concentration increases from 5 wt% to 12.5 wt% at a heating rate of 10 °C/min, both the initial crystallisation temperature and the peak crystallisation temperature decrease from 881.521 °C and 905.24597 °C to 861.33698 °C and 893.11798 °C, respectively. This suggests that increasing the amount of TiO_2 can minimise the overheating required for crystallisation and promote crystallisation at low temperatures. At higher heating rates, the initiation and

crystallisation temperatures of samples containing different amounts of TiO₂ shift towards higher temperatures due to thermal hysteresis.



Figure 6. (a) shows a sample with a TiO₂ content of 10 wt%; (b) shows a sample with a TiO₂ content of 12.5 wt%.

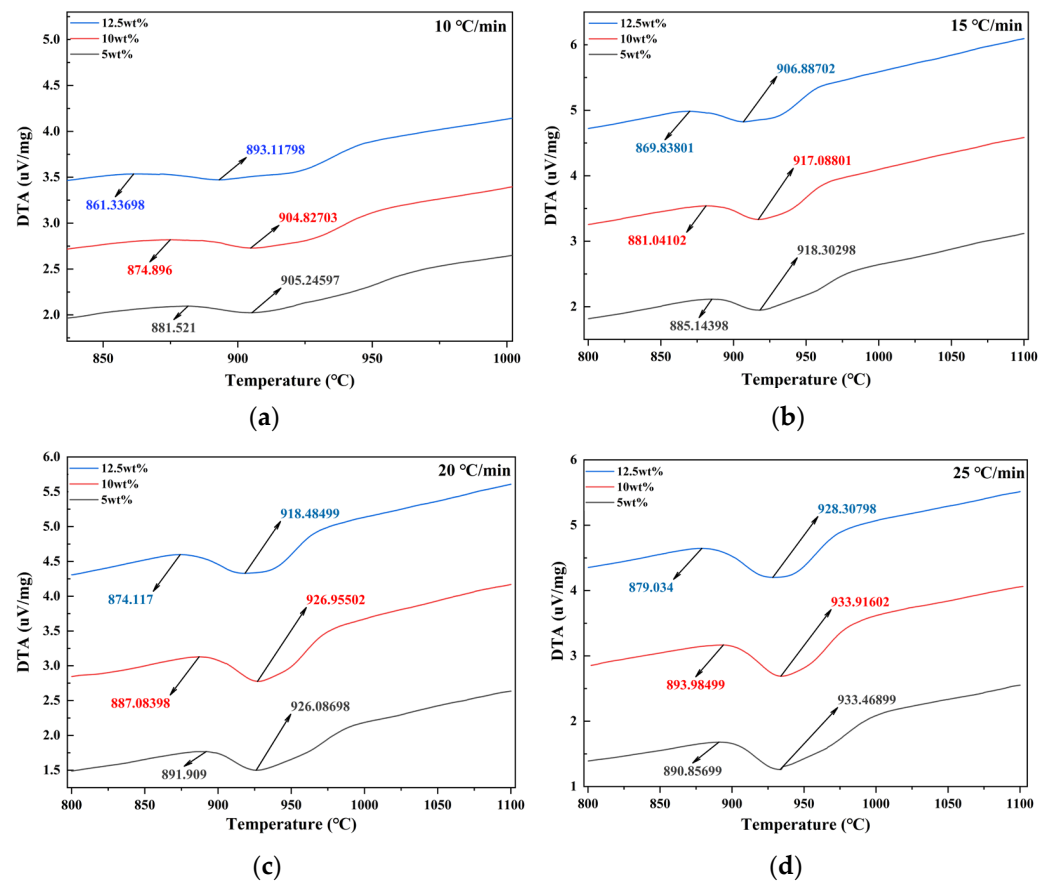


Figure 7. (a–d): DTA curves of samples with TiO₂ contents of 5 wt%, 10 wt%, and 12.5 wt% at heating rates of 10 °C/min, 15 °C/min, 20 °C/min, and 25 °C/min.

The non-isothermal crystallisation kinetics can be described using the Kissinger equation [19–22].

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{E_c}{RT_p} + \ln\left(\frac{E_c}{R}\right) - \ln v \quad (3)$$

In this equation, α denotes the heating rate (K/s), R represents the gas constant (8.314 J/(mol·K)), and E_c stands for the crystallisation activation energy (J/mol), while

ν refers to the pre-exponential factor. Figure 8 illustrates the correlation between the activation energy (E_c) and the pre-exponential factor (ν). The slope and intercept of the fitted line have been calculated separately, and the respective values are presented in Table 3.

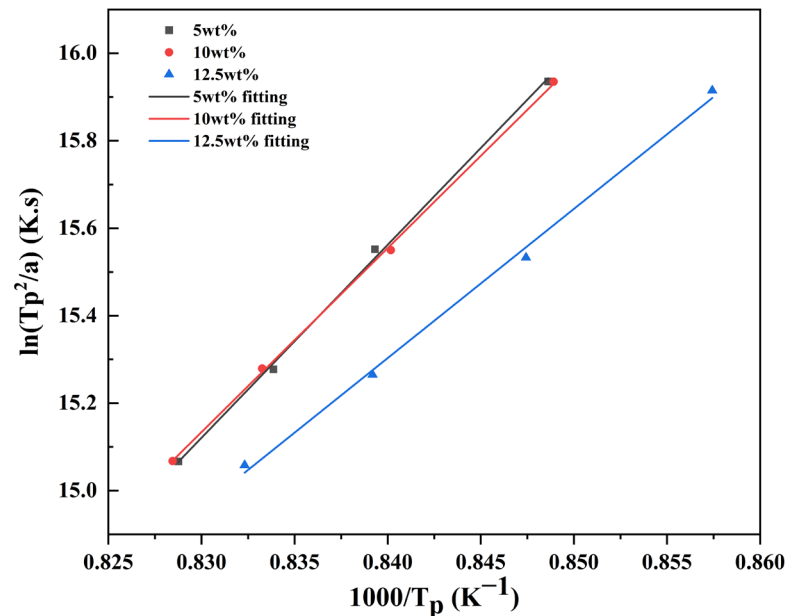


Figure 8. Relationship diagram between $\ln\left(\frac{T_p^2}{a}\right)$ and $\frac{1000}{T_p}$ of water-quenched glass slag samples.

Table 3. Crystallisation activation energy and Avrami parameter for different TiO₂ contents.

TiO ₂ (wt%)	Activation Energy E_c (kJ.mol)	Pre-Exponential Factor ν (min ⁻¹)	Avrami Parameter n
5	367.3	1.01×10^{11}	1.430057129
10	350.13	1.71×10^{10}	1.720153241
12.5	283.63	2.15×10^7	1.844855834

It can be seen that the activation energy decreases from 367.3 kJ/mol at 5 wt% to 288.63 kJ/mol at 12.5 wt%. This indicates that the increase in TiO₂ can promote crystallisation by reducing the activation energy; when the TiO₂ content is between 5 wt% and 10 wt%, the activation energy is relatively high. When it reaches 12.5 wt%, there is a significant decrease. This finding is consistent with the phenomenon that there are many glass phases inside the sample with a TiO₂ content of 10 wt% compared to the sample with a TiO₂ content of 12.5 wt% observed in Figure 6. This indicates that for this size of sample, the crystallisation driving force is insufficient when the TiO₂ content is below 10 wt%. The Avrami parameter (n) is used as an explanation for the crystallisation mechanism [23] and can be calculated from the AugisBennett equation.

$$n = 2.5 \frac{RT_p^2}{\Delta T E_c} \quad (4)$$

In this equation, ΔT represents the complete width at half height of the exothermic peak. The Avrami parameters obtained, denoted as n , are listed in the table. It can be observed that the Avrami parameter (n) of the glass sample lies between one and two, indicating that the crystal growth mode is between surface crystallisation and volume crystallisation. An increase in TiO₂ content causes a tendency towards crystal growth, ultimately improving the degree of crystallisation. Therefore, it can be deduced that adding TiO₂ enhances crystal growth, which improves crystallinity and minimises the content of the

glass phase. Crystallinity is the degree of completeness and integrity of crystallisation. The transition of a substance from amorphous to crystalline is continuous, with ideal crystals producing diffraction and ideal amorphous substances producing coherent scattering. Strong diffraction leads to high crystallinity, and distorted crystallisation can also lead to the conversion of diffraction into varying degrees of dispersion scattering. Crystalline grains with complete crystallinity are large, with high and sharp diffraction peaks, while on the contrary, the grains are small, with wide and dispersed peaks and weak diffraction ability. According to the law of conservation of X-ray scattering in fully reciprocal space, the total scattering intensity of X-rays remains conserved regardless of the intensity of the crystalline and amorphous states. The formula is as follows:

$$X_C = \frac{\sum I_c}{\sum I_c + I_a} \times 100\% \quad (5)$$

In the given formula, I_c refers to the integral intensity of crystal diffraction, and I_a refers to the intensity of amorphous diffraction. This formula can be used to calculate the relative crystallinity of a substance. Utilising the original X-ray diffraction spectrum, we calculated the relative crystallinity (in a semi-quantitative manner) of the microcrystalline cast stone (crystallised portion) formed by self-crystallisation of blast furnace slag. The results are presented in Table 4.

Table 4. Relative crystallinity of microcrystalline glass with varying TiO₂ concentrations.

TiO ₂ Content (wt%)	Relative Crystallinity (%)
5	82.36
10	84.92
12.5	90.23

The mentioned theoretical calculation error is minor, and even when there is a small content change, there can still be an ideal trend. However, there is insufficient experimental research to confirm the reliability of the theoretical analysis results. In order to verify these results, we performed X-ray diffraction on microcrystalline cast stones created through self-crystallisation at TiO₂ content levels of 5 wt%, 10 wt%, 15 wt%, and 20 wt% (taking into account crystalline portions) and refined them using FullProf 2019.9.20 software. The refined findings are presented in Figure 9. When the TiO₂ content is less than 15 wt%, the precipitated phases are melilite, perovskite, and diopside. When the TiO₂ content reaches 20 wt%, the melilite phase disappears, and the precipitated phases are perovskite and diopside. The specific content changes are shown in Figure 10. As the TiO₂ content increases from 5 wt% to 15 wt%, the melilite phase decreases from 82.71% to 28.54%, and the diopside phase increases from 13.02% to 61.15%. With a small increase in the perovskite phase, diopside replaces melilite as the main crystal phase. When the TiO₂ content is further increased to 20 wt%, the melilite phase disappears completely, in agreement with the above analysis.

Finally, to observe the microstructure and growth patterns of various phases, SEM (Scanning electron microscope) analysis was conducted on samples with titanium-containing blast furnace slag crystallised at different TiO₂ contents. This is illustrated in Figure 11. From the figure, it can be seen that the microstructure of titanium-containing blast furnace slag has undergone changes after self-crystallisation: when the TiO₂ content is 5 wt%, the main precipitated crystalline phase appears as radially elongated melilite, with partially induced crystallisation, incomplete crystallisation, and uneven crystallisation on the surface. As the TiO₂ content increases to 10 wt%, the morphology of the melilite changes from elongated to short columnar with uniform crystallisation. When the TiO₂ content increases to 15 wt%, a large amount of perovskite precipitates in addition to melilite, forming a cross-shaped and plate-like diopside precipitate. As the TiO₂ content increases to 20 wt%, the main crystalline phases precipitated are cruciform perovskite and plate-like diopside. It

can be seen that as the TiO_2 content increases, the types and shapes of precipitated crystal phases in the slag change, and perovskite and diopside gradually become more precipitated crystal phases.

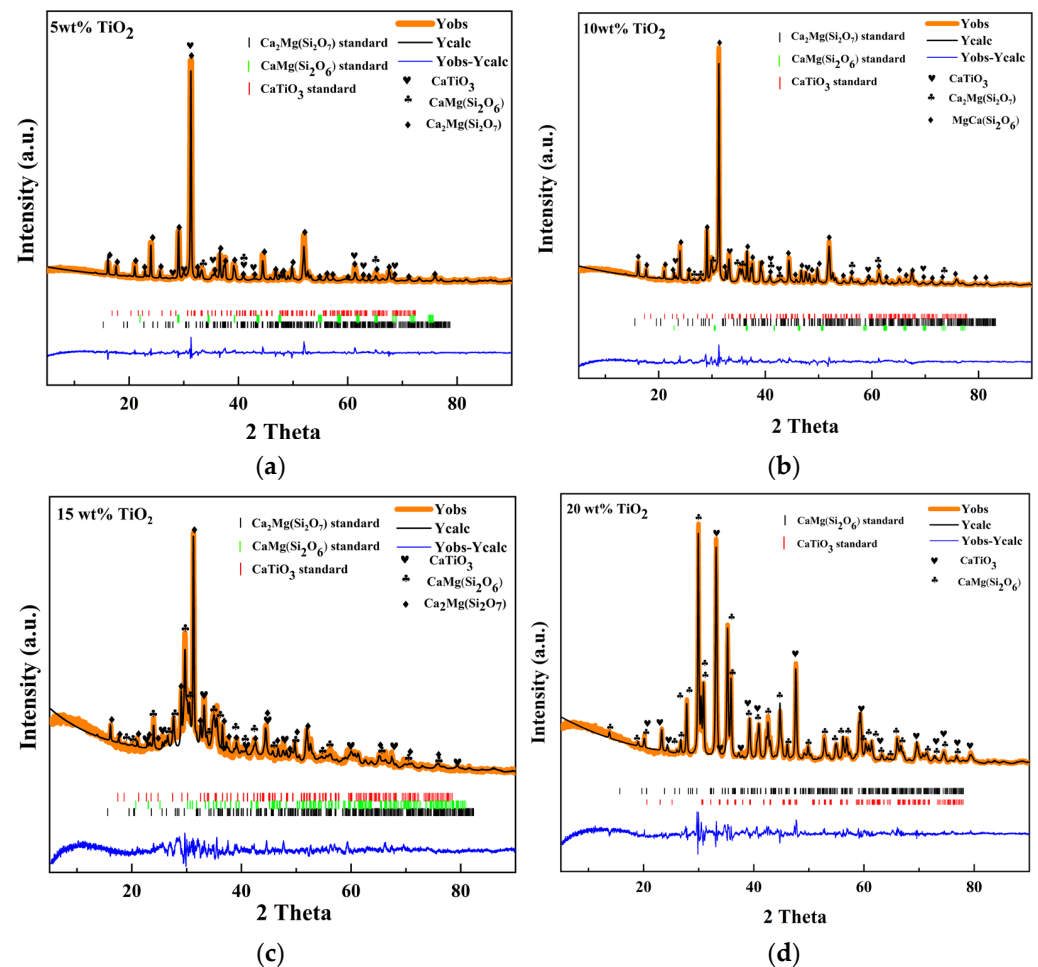


Figure 9. (a–d): Refined XRD images of titanium-bearing blast furnace slags with different TiO_2 contents after crystallisation at 1017°C .

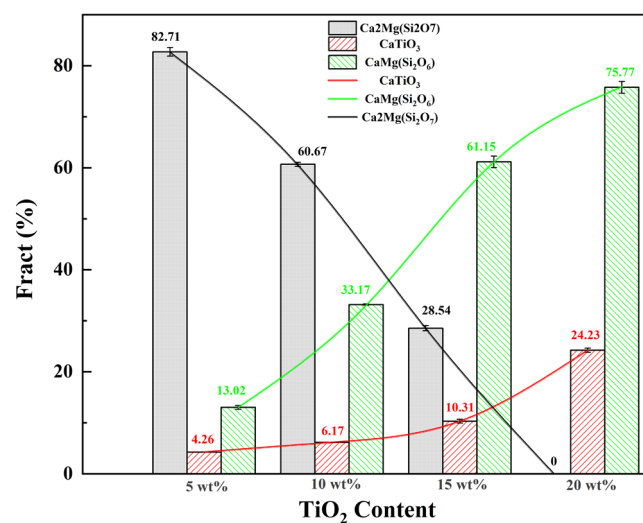


Figure 10. The change trend of the precipitated phase content at different TiO_2 contents.

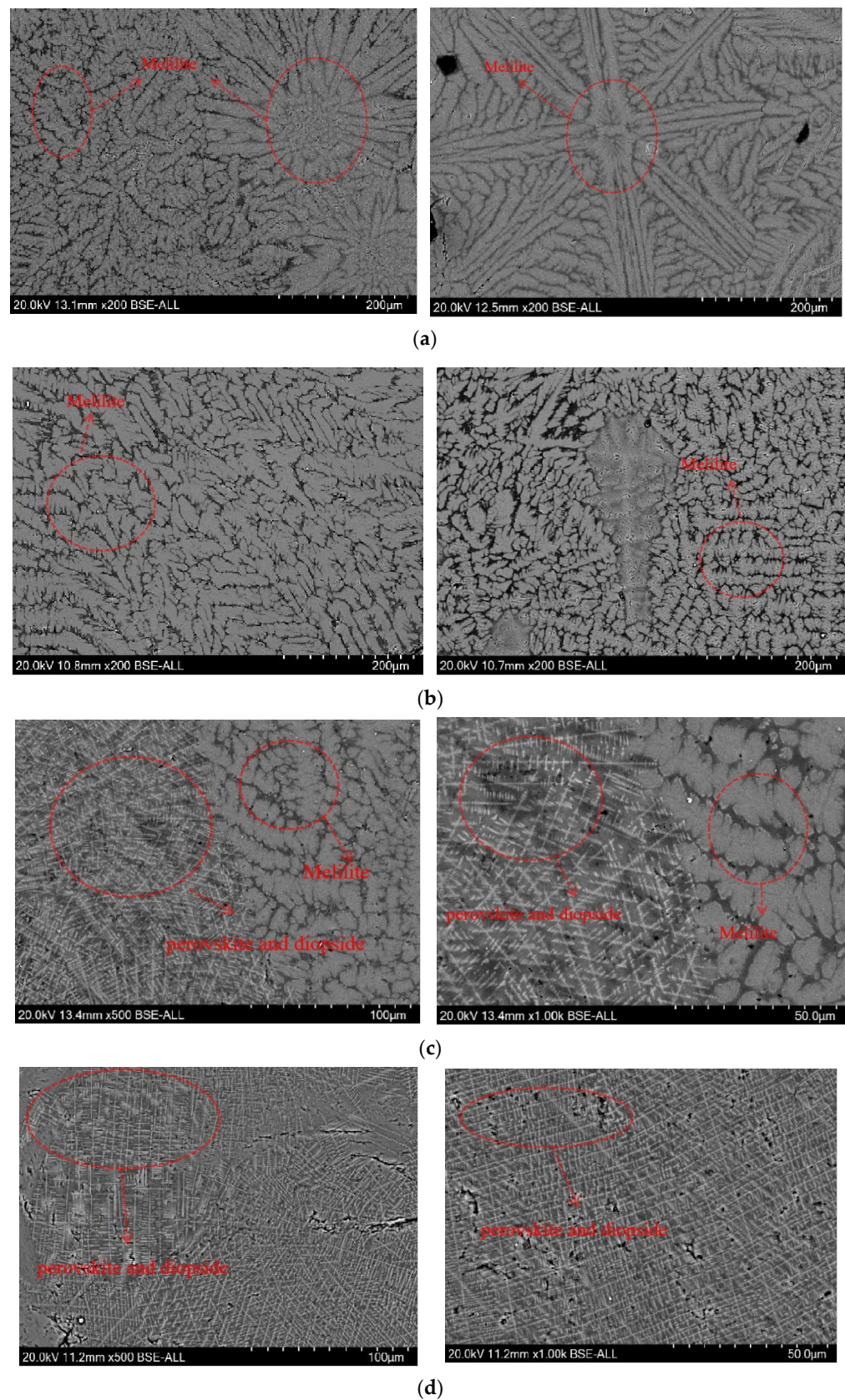


Figure 11. Scanning electron microscopy (SEM) images of specimens containing varying TiO_2 concentrations that were crystallised at 1017 °C. (a) SEM images of the sample containing 5 wt% TiO_2 ; (b) SEM images of the sample containing 10 wt% TiO_2 ; (c) SEM images of the sample containing 15 wt% TiO_2 ; (d) SEM images of the sample containing 20 wt% TiO_2 .

The SEM and XRD analysis above confirmed the previous findings that at higher levels of TiO_2 , the primary crystal converted into diopside, the activation energy for crystallisation decreased, and the microcrystalline glass had a stronger driving force for crystallisation. Consequently, there was an increase in crystallinity, with a shift from partially induced to uniform crystallisation.

4.2. Effect of Different TiO_2 Content on Residual Stress and Mechanical Properties of Titanium-Containing Blast Furnace Slag after Self-Crystallisation

The residual stress in microcrystalline glass is composed of thermal gradient, thermal expansion, and phase change residual stress. In this experiment, a unified heat treatment system is adopted, which is to keep the temperature at 1017°C for 30 min and then cool it to room temperature in the furnace, in order to study the changes in residual stress under different TiO_2 contents. The residual stress caused by the thermal gradient property during the cooling process is considered to be consistent in each group of samples and can be minimised by slow and uniform cooling. This study attributed the stress generated by the volume change during the crystallisation process (phase transformation residual stress) and the stress generated by the difference in thermal and elastic properties from high temperature cooling to room temperature (thermal mismatch residual stress) to the micro-stresses within the microcrystalline glass. The micro-stresses generated during the crystal nucleation process can be relieved by viscous flow.

After being crystallised at 1017°C , the G1–G4 samples were obtained and their $\sin^2\psi$ corresponding 2θ slope result was obtained through X-ray diffraction and linear fitting, as illustrated in Figure 12.

According to Equations (1) and (2), this sample's surface residual stress can be calculated and shown in Figure 13. The figure indicates a decreasing trend in overall residual stress size as the TiO_2 content increases. At 10 wt% TiO_2 content, stress size is 383.43 MPa, whereas at 15 wt% TiO_2 content, it drops sharply to 239.12 MPa. With a further increase to 20 wt% TiO_2 content, the residual stress decreases to 181.40 MPa. However, from the figure, we found that the residual stress initially increased. For this phenomenon, we believe that according to previous studies, as the TiO_2 content increases, the activation energy decreases, and the crystallinity increases. Therefore, when the TiO_2 content is low, very few crystalline phases in the sample are tightly enveloped by the glass phase, and the sample is considered a glassy body. As the TiO_2 content increases, when the crystal phase increases abruptly, a large number of crystal phases precipitate into the vitreous body to form defects, and the glass phase and crystal phase coexist in the sample, so the residual stress increases. As the TiO_2 content continues to increase, the crystallinity of the sample increases, the glass phase basically disappears and the residual stress in the sample is mainly influenced by the crystal phase. This is why the curve rises briefly at the beginning.

Based on the analysis of X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA), and other techniques, it can be concluded that the significant change in residual stress with the increase in the TiO_2 content in the microcrystalline glass is due to the shift in the crystallisation peak towards lower temperatures and the decrease in the crystallisation activation energy as the TiO_2 content increases. This indicates the stronger crystallisation driving force of the microcrystalline glass. The crystal undergoes a transition from one-dimensional to two-dimensional growth while the sample changes from surface crystallisation to volume crystallisation. The rise in crystallinity results in the crystal shifting from a state embedded in the glass network to a state encapsulated in the glass phase, leading to a decrease in stress caused by thermal and elastic mismatch between the glass and crystal phase due to a reduction in the glass phase. From a microstructural standpoint, it is evident that with increasing TiO_2 content, the melilite phase, which radiates locally, transforms into a uniform short columnar phase. This is followed by a significant presence of diopside and perovskite, and ultimately, diopside becomes the main crystal phase, leading to a sudden decline in residual stress.

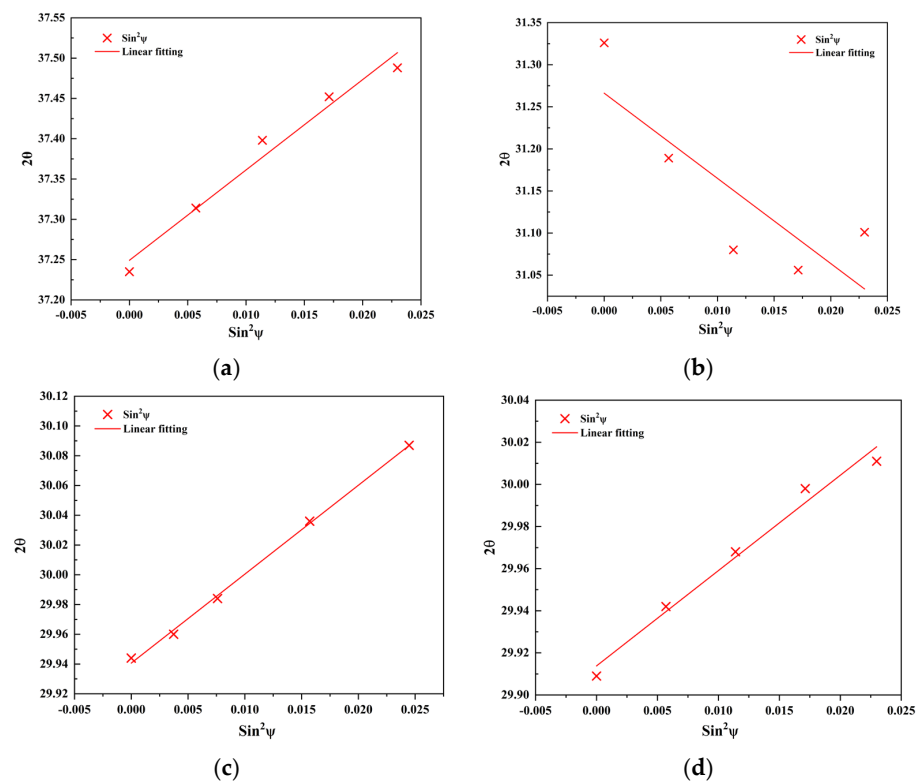


Figure 12. The 2θ – $\sin^2\psi$ relationship of samples with different TiO_2 contents after crystallisation at 1017°C . (a) Relationship diagram of 2θ – $\sin^2\psi$ for samples with 5 wt% TiO_2 content. (b) Relationship diagram of 2θ – $\sin^2\psi$ for samples with 10 wt% TiO_2 content. (c) Relationship diagram of 2θ – $\sin^2\psi$ for samples with 15 wt% TiO_2 content. (d) Relationship diagram of 2θ – $\sin^2\psi$ for samples with 20 wt% TiO_2 content.

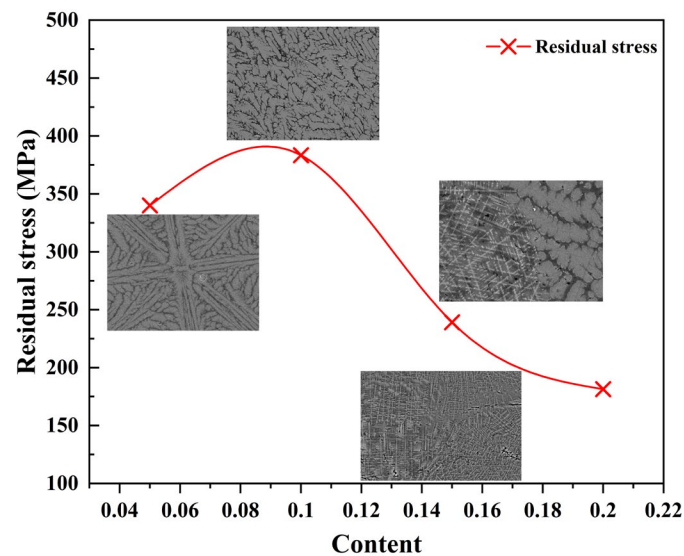


Figure 13. Relationship between TiO_2 content and residual stress.

Therefore, the relative content of the crystal phase and the glass phase as well as the type of crystal phase have a significant effect on the residual stress after self-crystallisation of titanium-bearing blast furnace slag. To investigate the dependence of residual stress on thermal and elastic factors, we first calculated the viscosity of microcrystalline glass ($65 \times 30 \times 20$ mould) with a content of 5 wt% to 22.5 wt% TiO_2 using Factsage. The results are shown in Figure 14.

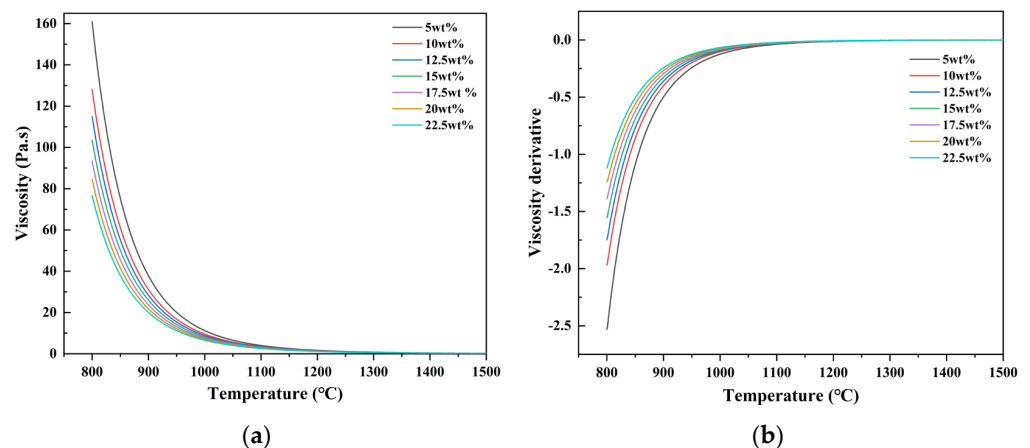


Figure 14. The viscosity and viscosity derivative trend chart for ingredients with varying TiO₂ content, as affected by temperature changes. (a) Trend chart showing viscosity changes with temperature fluctuations. (b) Trend plot illustrating the derivative of viscosity as temperature varies.

Figure 14a illustrates the relationship between viscosity and temperature. This trend is consistent for a given ingredient. The viscosity increases as the temperature decreases, while it decreases with the addition of TiO₂. Figure 14b presents a derivative plot of the viscosity curve, showing that the rate of viscosity increase intensifies when the temperature drops to a certain degree. Specifically, the rate of increase in the viscosity after 1017 °C differs significantly from the rate before this temperature. This graph illustrates that below a certain temperature, viscosity increases significantly and rapidly, causing the glass melt to transition from an approximate fluid at a higher temperature to a viscous body. When the temperature is higher than this transition temperature, the stress generated from high temperature is released through displacement due to the molecular motion inside the fluid. When the temperature falls below the transition temperature, the fluid takes on a more viscous consistency and cannot effectively release residual stress caused by thermal factors via deformation. This results in an increase in internal stress levels. As the TiO₂ content increases, the viscosity decreases. Consequently, the temperature range that permits stress to be released through deformation increases, and the temperature point at which fluid properties transition also decreases. This makes it less susceptible to stress caused by temperature gradients. Viscoelasticity refers to the combined properties of fluid viscosity and elasticity. During the heat treatment process of molten glass from liquid to solid, it exhibits the properties of solid and liquid, namely, viscosity and elasticity, under different conditions (constituents, temperature). Therefore, as the TiO₂ content decreases, the elasticity dominates, and the residual stress generated by the cooling process also decreases.

To investigate the thermal expansion properties of samples with varying TiO₂ levels, this article utilised the thermal-mechanical analysis (TMA) method. TMA measures the relationship between deformation and temperature of objects under program setting temperature and non-vibration loads. This provides the thermal expansion properties of the samples, as illustrated in Figure 15. When the TiO₂ content is 10 wt%, the average linear thermal expansion coefficient in Figure 15a at lower temperatures is 0.04884 $\mu\text{m}/^\circ\text{C}$, followed by 0.060567 $\mu\text{m}/^\circ\text{C}$ expansion until 867.24 °C. At this point, the soft melting state may undergo a sudden change from expansion to compression, which corresponds to a possible glass transition temperature (the sample is mainly composed of the glass phase). When the TiO₂ content is at 12.5 wt%, Figure 15b illustrates an abnormal occurrence during the heating process due to the relaxation effect of volume and pressure caused by the experimental application of 0.05 N force. There is a sudden change from expansion to compression at 140.65°C, and the thermal expansion coefficient changes from 0.04707 $\mu\text{m}/^\circ\text{C}$ at a lower temperature to 0.06819 $\mu\text{m}/^\circ\text{C}$. As illustrated in Figure 15c,d, the mean coefficient of thermal expansion is 0.06268 $\mu\text{m}/^\circ\text{C}$ and 0.06691 $\mu\text{m}/^\circ\text{C}$, respectively. The difference in the thermal expansion coefficient is primarily caused by the slight alteration in the crystal phase composition. When the proportion of TiO₂

risers to 22.5 wt%, diopside becomes the primary constituent of the crystal phase, leading to a significant reduction in the thermal expansion coefficient to $0.05402 \mu\text{m}/^\circ\text{C}$. The test results can explain the influence of the thermal expansion coefficient on the residual stress of the sample. As a sample close to pure glass (which cannot be obtained in the actual experimental process), the influence of the difference in the thermal expansion coefficient between the crystal phase and the glass phase is avoided as much as possible in the system. As a result, the thermal expansion coefficient is low. As the TiO_2 content increases, the coexistence of melilite, diopside, perovskite, and the glass phase occurs in the system, the thermal expansion coefficient of the sample fluctuates greatly due to the mismatch of the multiphase, and the average thermal expansion coefficient is larger than the average thermal expansion coefficient of the sample with a single glass phase, resulting in significant thermal stress. When the TiO_2 content rises to 22.5 wt%, the sample is predominantly composed of diopside and has high crystallinity. This system exhibits the lowest coefficient of thermal expansion, resulting in minimal thermal stress induced by temperature changes.

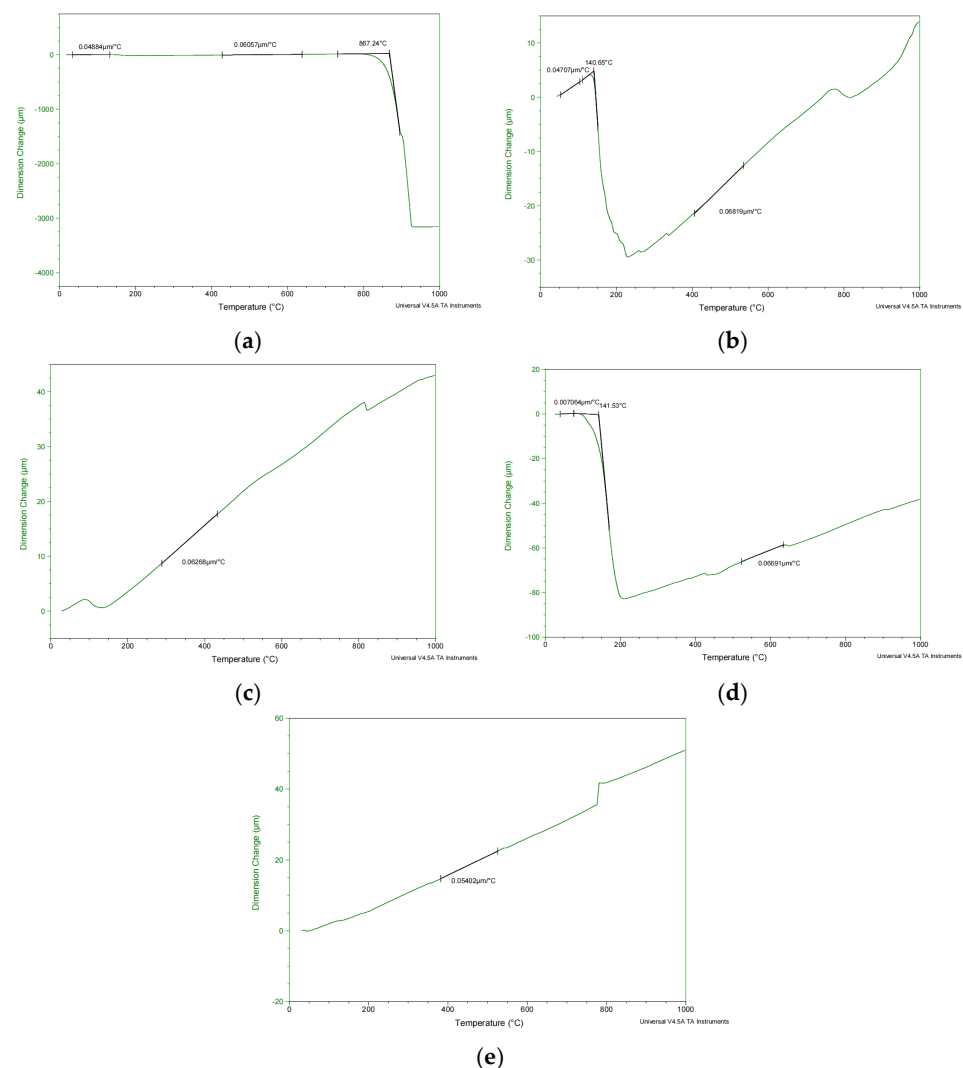


Figure 15. Trend chart displaying changes in sample size as the temperature increases with varying TiO_2 content. (a) The size variation trend of samples with a content of 10 wt% TiO_2 as temperature increases. (b) The size variation trend of samples with a content of 12.5 wt% TiO_2 as temperature increases. (c) The size variation trend of samples with a content of 15 wt% TiO_2 as temperature increases. (d) The size variation trend of samples with a content of 17.5 wt% TiO_2 as temperature increases. (e) The size variation trend of samples with a content of 22.5 wt% TiO_2 as temperature increases.

The compressive and bending strength tests were performed on samples with varying TiO_2 contents, and the findings are illustrated in Figure 16. The figure indicates that, in general, the compressive and bending strength of the sample exhibited an upward trend with increasing TiO_2 content. This is due to the decrease in glass phase content of the sample, precipitation of the primary crystalline phase of diopside, an increase in crystallinity, and a decrease in internal stress. Additionally, the glass state exhibits lower strength than the crystalline object, thus enhancing the overall strength of the sample.

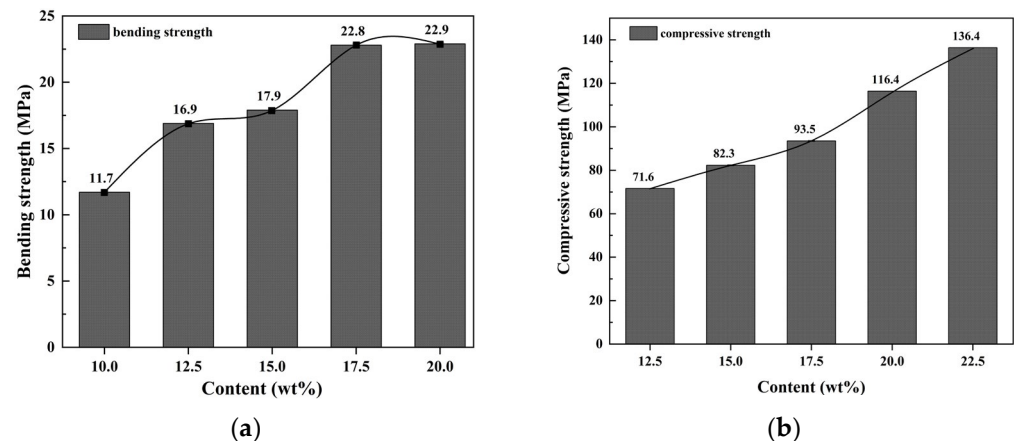


Figure 16. (a) The variation trend of the bending strength with the change in the TiO_2 content. (b) The compressive strength trend varies with the alteration in the TiO_2 content.

5. Conclusions

- (1) With increasing TiO_2 content, titanium-containing blast furnace slag has a significant driving force for crystallisation, which changes from surface crystallisation to bulk crystallisation. The ratio of the crystalline phase to the glass phase increases, and the residual stress caused by viscoelastic and thermal expansion factors between the two phases decreases. The main crystalline phase gradually changes from melilite to diopside, and the appearance of diopside plays a role in reducing residual stress and improving mechanical properties.
- (2) As the TiO_2 content increases, the residual stress decreases from 383.43 MPa to 181.40 MPa. This decrease in residual stress leads to improved mechanical properties, specifically an increase in compressive strength from 71.6 MPa to 136.4 MPa and an increase in flexural strength from 11.7 MPa to 22.9 MPa.
- (3) This experiment revealed a pattern of residual stress reduction: (a) single-phase samples have lower residual stress, and the residual stress varies with the type of phase. For example, samples with diopside as the only phase have the lowest residual stress. (b) Viscosity has a significant effect on residual stress, and as viscosity decreases the sample tends to have lower residual stress. (c) The more complex the phase in the sample, the more the residual stress is determined by multiple factors, and the residual stress is greater due to the mismatch between heat and elasticity.

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Data Availability Statement: The data are contained within the article. The graphs and tables in the article are the real data we present and can be opened. If you need the original data, you can contact the corresponding author.

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