Viscosity evaluation of hot metal containing vanadium and titanium via a novel measurement technology and the thermodynamic analysis method

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ABSTRACT

Vanadium titano-magnetite (VTM) is one of the important iron ore resources in the world. High viscosity and low fluidity are the basic characteristics of hot metal containing vanadium and titanium during the iron making process. Clarifying the influencing mechanism of the melt viscosity would be a significant issue for the high efficiency smelting of VTM. In this paper, a self-developed melt viscometer based on the principle of torsional vibration theory was employed to measure the viscosity of hot metal accurately. Simultaneously, the thermodynamic calculations and some modern detection methods were also used to investigate the precipitation behavior of high-melting-point phases in hot metal containing vanadium and titanium. The measuring results show that the viscosity of molten iron gradually increases with the increase of titanium content when the mass fraction of titanium is between 0.09 wt%-0.50 wt%. Meanwhile, the viscosity of the hot metal was affected significantly by the vanadium content. When the vanadium mass fraction was higher than 0.30 wt%, the viscosity of hot metal increased sharply, which will have a serious impact on the fluidity of the hot metal. Furthermore, it was revealed by thermodynamic calculations that an increase in titanium and vanadium content would result in the precipitation of high melting point phases such as TiC, TiN, VC, and VN in the molten iron, ultimately resulting in a decrease in its fluidity. Meanwhile, it was confirmed by SEM observation that the precipitates in the hot metal were compounds consisting of V, Ti, C, and N elements, which agrees well with the thermodynamic analysis results.

INTRODUCTION

Vanadium titano-magnetite (VTM) is a crucial mineral in the world, which contains valuable elements such as iron, vanadium and titanium, and has significant comprehensive utilization value in metallurgical industry (Chen, 2015; Tan, 2011). VTM is mainly located in South Africa, Russia, China, and Canada etc. In China, the VTM is primarily distributed in Panzhihua and Chengde regions. Generally, the hot metal produced by the VTM exhibits lower fluidity than that produced by the conventional iron minerals, due to the high content of vanadium and titanium in VTM (Zhang, 2013; Lü, 2016; Gou, 2012). Poor fluidity of hot metal in ironmaking could result in various issues such as operational difficulties and low productivity. Additionally, the steelmaking process can be also impeded by the reduced fluidity of hot metal, thereby exerting a detrimental impact on industrial production efficiency (He, 2010; Zhao, 2015; Zhang, 2015).

Normally, viscosity is defined as the shear stress needed to generate a unit shear rate, and is expressed as the ratio of shear stress to shear rate (Gu, 2018). In the 17th century, Newton's proposal of the concept of viscosity provided a theoretical basis for viscosity measurement. However, a unified standard for the measurement of viscosity has not been developed, due to the complexity of fluid research (Qu, 2015). Although there are a lot of mature devices for measuring the viscosity of fluids at room temperature or low temperature, there has been less development of equipment for measuring high-temperature melt viscosity, especially for low viscosity melt at high temperature. The primary reason for this is that the measurement of high-temperature melt viscosity is often accompanied by complex physical and chemical changes and irregular thermal disturbance, which further complicates the measurement process and reduces the accuracy (Qu, 2015; Zhang, 2015; Jia, 2010; Liu, 2015; et al).

In this study, a self-developed viscosity equipment was employed to measure the viscosity of hot metal containing vanadium and titanium. The objective is to clarify the impact of vanadium and titanium content on the fluidity of hot metal. Additionally, thermodynamic analysis and characterization methods were employed to investigate the underlying mechanisms. This study not only has important exploration value for the accurate measurement of low viscosity in molten metal, but also has important practical guidance for the improvement of industrial production efficiency.

EXPERIMENTAL

Materials

The pig iron used in the study was taken from an iron and steel plant in China, and the vanadium and titanium contents of the samples were adjusted by blending in some amounts of Ferrovanadium

and high purity titanium (99.99 %). The compositions of the pig iron and alloys were shown in Table 1.

TABLE 1-Composition of pig iron and alloy (wt%)

Elements	Pig iron	Ferrovanadium
C	4.325	0.032
Si	0.145	0.860
Mn	0.240	0.046
P	0.079	0.036
S	0.065	0.014
Ti	0.090	-
V	0.040	80.900

Methods

Before the measurement of viscosity, the sample was pre-melted using an induction furnace until the composition is uniform. Thereafter, the sample was placed in a self-developed equipment to carry out the viscosity measurement. Fig.1 shows the schematic diagram of the viscosity measurement equipment, which contains the heating system, the torsion pendulum vibration system, the photoelectric sensing system and a real-time computer recording system. After the sample was melted at 1450 °C, the viscosity measurement began through applying an external twisting force to the rotor, by which the rotor will rotate in the testing melt to do the damping motion until it stop. During this period, the damping motion of the rotor can be detected by the photoelectric sensing system and recorded by the real-time computer recording system. The viscosity value of the molten material could be obtained by analysing the curve of the damping motion.

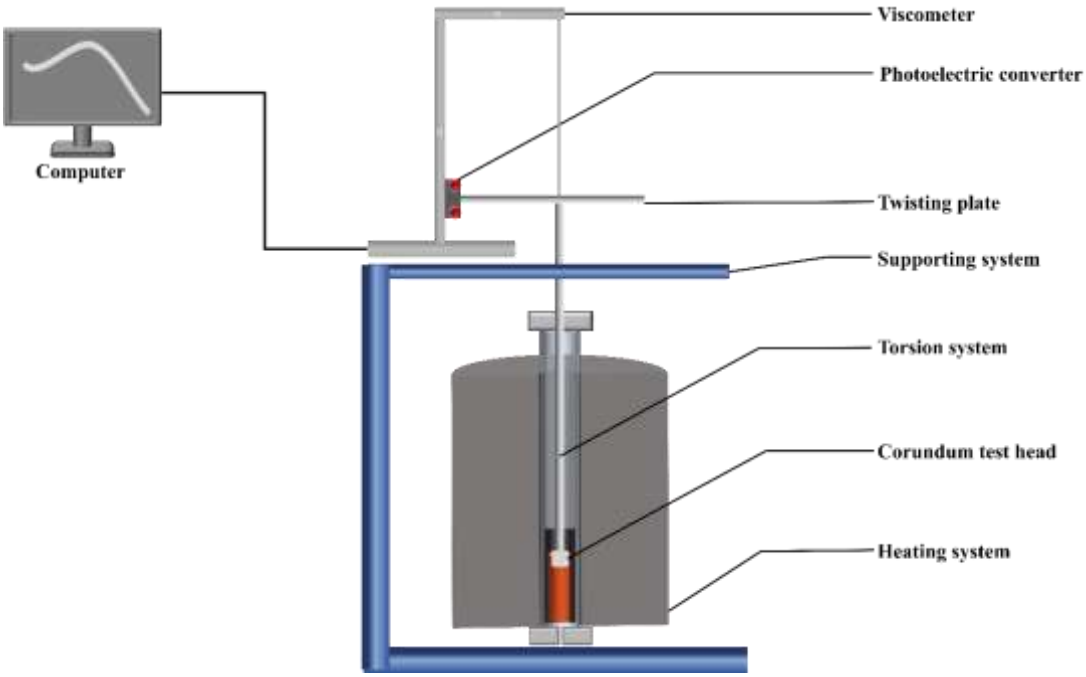

FIG 1 - Schematic diagram of the self-developed viscometer.

For the internal column torsional vibration theory, the viscosity of the liquid to be measured is positively correlated with the logarithmic decay rate (λ) of the torsional vibration system, and the relationship can be expressed by equation (1).

$$\eta = \frac{(\mathrm{DI})^{1/2}}{K}\lambda \qquad (1)$$

Where η is the viscosity of the liquid, I is the moment of inertia in the system, D is the torque per unit of twist, and K is a constant. For a definite viscosity measurement system, the D, I, and K are regarded as the fixed values.

For damped vibrations with attenuated damping, the logarithmic decay rate is defined as equation (2).

$$\lambda = \frac{lnA_n - lnA_{n+m}}{m} \qquad (2)$$

Where A_n and A_{n+m} are the amplitudes of the nth and n+mth vibrations, respectively, and m is the difference between the corresponding number of vibrations when the amplitudes are A_n and A_{n+m}.

The functional relationship between the viscosity of the tested liquid and the vibration amplitude and frequency could be obtained by combining equations (1) and (2), as shown in equation (3).

$$\eta = \frac{(DI)^{\frac{1}{2}}(lnA_n - lnA_{n+m})}{Km} \qquad (3)$$

For a definite measurement system, the D, I and K are fixed values, so the variables in the above equation include the logarithmic difference of the two amplitudes and the number of vibrations. When the amplitude difference is fixed within a specific range, the viscosity of the liquid could be inferred from the number of vibrations in that amplitude range. This relationship is expressed in equation (4), where a is a constant.

$$\eta = \frac{a}{m} \qquad (4)$$

From the equation (4), the viscosity (η) of the liquid is inversely proportional to the number of vibrations (m) within the fixed amplitude interval. To eliminate the effect of systematic error on the viscosity of the liquid, it is necessary to introduce another constant b, as shown in equation (5).

$$\eta = \frac{a}{m} + b \qquad (5)$$

Based on the above equation, the determination of the constants a and b is the only requirement to calculate the viscosity of the liquid to be measured by using equation (5).

The values of parameters a and b can be calibrated using a standard liquid with a known viscosity. In this experiment, three standard liquids with viscosities of 1, 5 and 10 mPa·s were used to calibrate the values of a and b, respectively. The damping curve of a known viscosity standard solution was measured by using the self-developed viscosity measurement equipment at room temperature, and the results are shown in Fig.2 (a)-(c). The viscosities (η) and 1/m measured by the standard liquids with known viscosities are plotted as scatter plots, and the values of a and b can be obtained by analysing the curves.

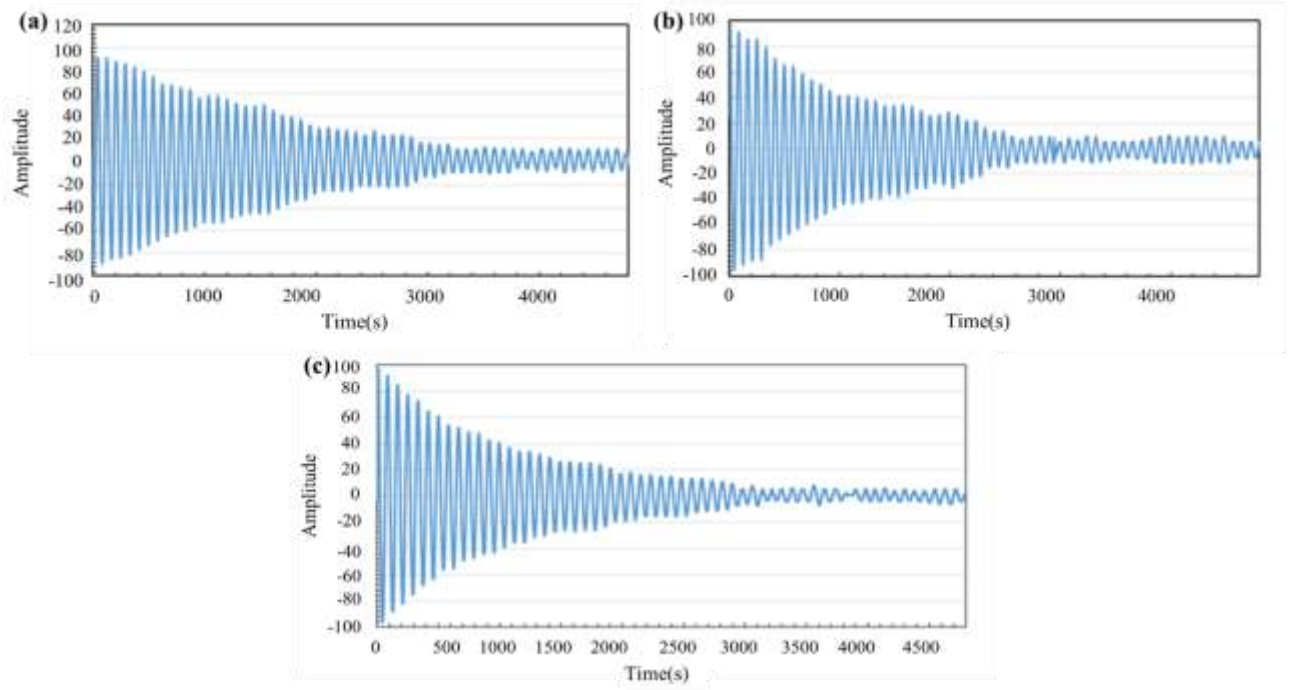

FIG 2 - Damping curves for standard fluids: (a) viscosity of 1 mPa·s; (b) viscosity of 5 mPa·s; (c) viscosity of 10 mPa·s.

Characterization

The morphology of the high melting point phase and its composition were confirmed by a scanning electron microscope equipped by the energy dispersive X-ray spectroscopy (SEM-EDS, TESCAN VEGA 3 LMH, Czech Republic).

Thermodynamic analysis

Thermodynamic calculations of the precipitation of VC, VN, TiC, and TiN compounds were performed by using FactSage 8.0 software . The database used was “F-Steel”.

RESULTS AND DISCUSSION

Effect of vanadium and titanium content on the hot metal viscosity

Fig.3 illustrates the results of the viscosity experiment. The viscosity of the hot metal shows a strong correlation with both temperature and composition. In Fig.3(a), it can be seen that the viscosity of the hot metal gradually increases with the increasing of the titanium content. The viscosity of the hot metal at 1300 °C is 24.6 mPa·s with a titanium content of 0.09 wt%. However, the viscosity increases to 124.5 mPa·s at the same temperature when the titanium content is increased to 0.40 wt%. In addition, the melting temperature of the hot metal gradually increases.

From Fig.3(c), it can be seen that the viscosity of the hot metal is also closely related to the vanadium content. As the temperature decreases, the viscosity of the hot metal gradually increases. When the vanadium content is less than 0.30 wt%, its effect on viscosity is not significant. However, when the vanadium content exceeds 0.30 wt%, the viscosity of hot metal sharply increases with the increasing of the vanadium content, and the melting temperature of the hot metal increases significantly (Fig.3(d)). Furthermore, the viscosity of the hot metal increases with vanadium content at the same temperature. Based on the above experimental results, theoretical calculations and microscopic observations will be used to further explore the mechanism of the influence of titanium and vanadium content on the viscosity of molten iron.

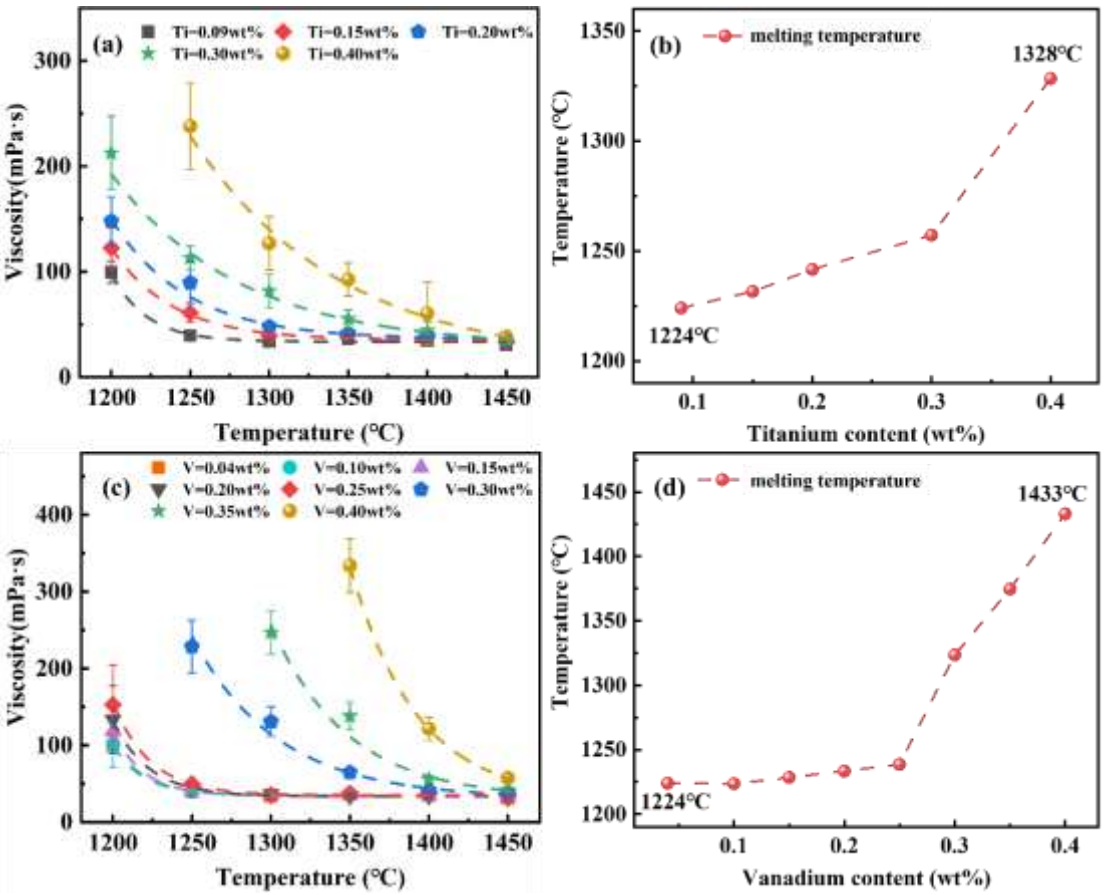

FIG 3 -Viscosity-temperature curve and melting temperature curve (Hou, 2022a).

Thermodynamic calculation

Fig.4 displays the results of thermodynamic calculations concerning the precipitation temperature and the mass of the compounds (VC, VN, TiC, and TiN) at varying titanium and vanadium contents in hot metal. Note that the content of [N] in hot metal was set as 0.05% according to our previous study (Hou, 2022a and 2022b). As depicted in Fig.4 (a) and (b), the precipitation temperatures of both TiC and TiN exhibit a gradual rise as the titanium content increases. Specifically, when the titanium content is 0.10 wt%, the precipitation temperatures for TiC and TiN are 1249 °C and 1435 °C, respectively. As the titanium content increases to 0.50 wt%, these precipitation temperatures also increase to 1392 °C and 1628 °C, respectively. In the previous study, Gao (2019) proved that as the temperature decreases, the supersaturated titanium reacts with carbon and nitrogen to produce high-melting-point phases such as TiC, TiN, and Ti (C, N). The precipitation of these high-melting-point phases leads to reduced fluidity and increased viscosity in the hot metal. This conclusion consists with the viscosity experiment results mentioned above.

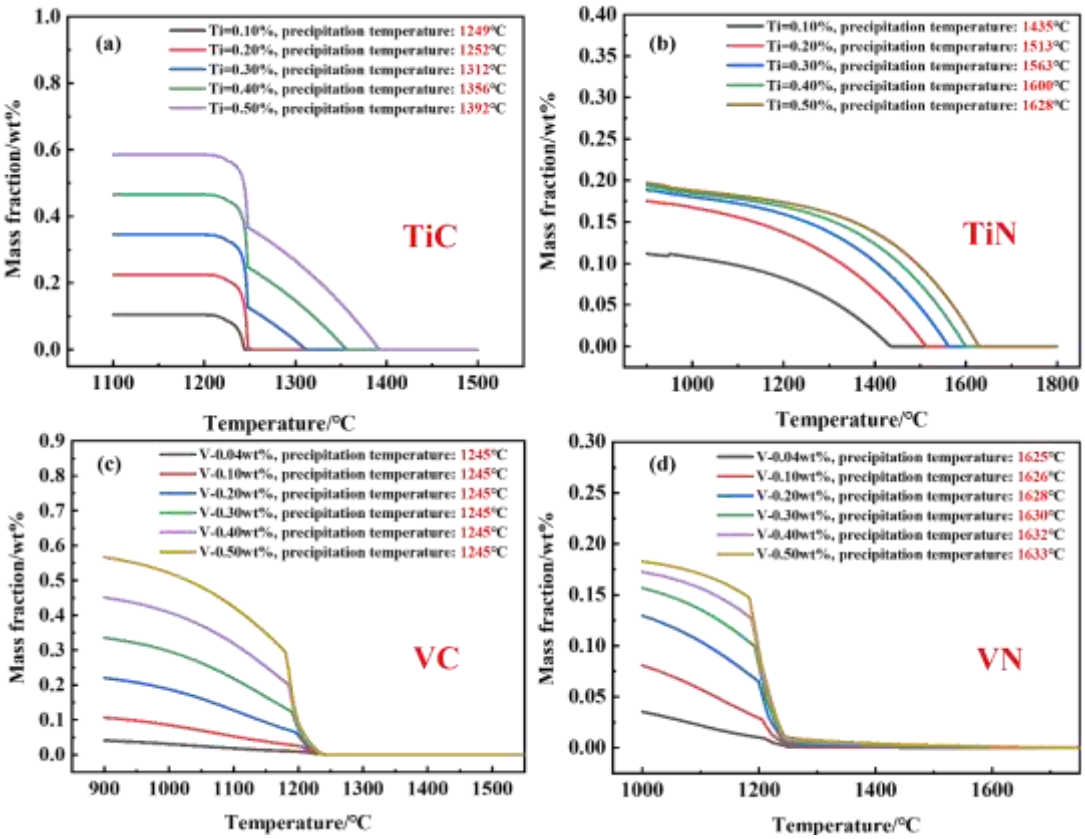

FIG 4 -Thermodynamic calculation results of precipitation for hot metal with different titanium and vanadium contents. (Hou, 2022b)

Fig.4 (c) and (d) reveal that the precipitation temperature of VC remains constant at 1245 °C regardless of the vanadium content, while the precipitation temperature of VN gradually increases as the vanadium content increases. Specifically, when the vanadium content is 0.04 wt%, the precipitation temperature of VN is 1625 °C. Increasing the vanadium content to 0.50 wt%, the precipitation temperature of VN remains at 1633 °C. This suggests that the precipitation temperature of the VN phase exceeds that of the VC phase, indicating the impact of the VN phase on viscosity in hot metal is greater than that of the VC phase. Simultaneously, the precipitation mass of VC and VN phases in the hot metal rises with increasing vanadium content, which is consistent with the viscosity results mentioned above. When the vanadium content is less than 0.30 wt%, the vanadium in the hot metal has not reached saturation due to the high solubility of vanadium in hot metal, and the precipitation amount is low. However, when the vanadium content exceeds 0.30 wt%, the vanadium in hot metal reaches supersaturation as the vanadium content increases, and a large amount of VN and VC begin to precipitate, resulting in the sharp increasing of the viscosity. In addition, the VC and VN phases continue to aggregate and grow as the temperature decreases, which will further worsen the fluidity of the melt.

Precipitation behaviour of compounds in the hot metal

The composition of the high melting point phase was analysed by SEM, and the results are shown in Fig.5. It shows that the precipitated phases in the hot metal predominantly consist of elongated and irregularly shaped crystals, possibly due to different cooling conditions across different parts of the sample. Furthermore, the EDS analyses of points 1, 2, and 4 in Fig.5 (a) and (b) demonstrate that the primary elements at these locations are C, Ti, and V, indicating that the precipitated phases at these points are primarily TiC and VC. In addition, the EDS analysis of point 3 shows that the major elements at this location are C, N, Ti, V, and Fe, indicating that Fe_3C precipitated during solidification. From Fe-C phase diagram, it was found that the precipitation temperature of Fe_3C was lower than 1150 °C when the carbon mass fraction was 4.3 %. Therefore, the precipitation of Fe_3C has small effect on the viscosity of the hot metal.

In summary, high melting point phase precipitated and existed in the form of either large particles or dispersed particles within the hot metal as hot metal cooled. With the particles continued to grow, the fluidity of the hot metal gradually decreased and its viscosity increased.

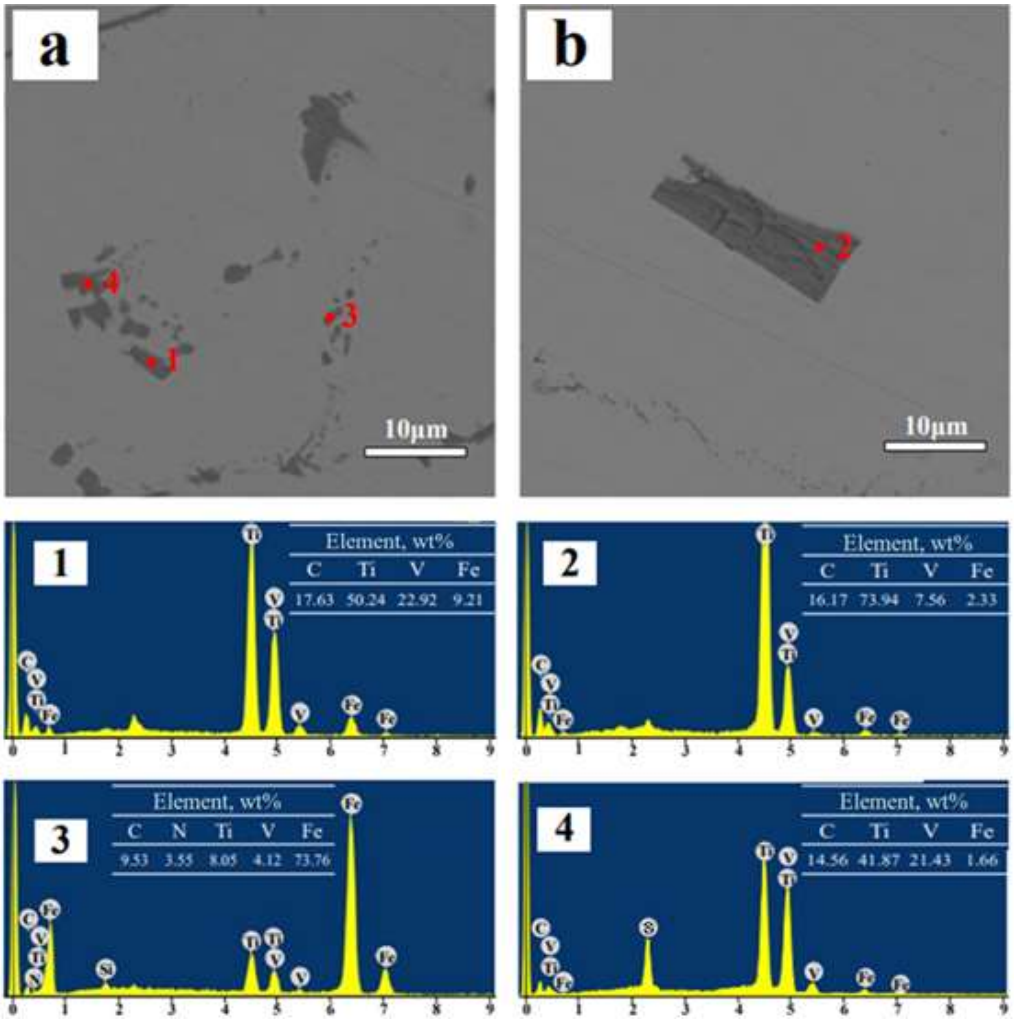

FIG 5 - SEM and EDS images of molten iron samples (Hou, 2022a).

CONCLUSIONS

The viscosity of hot metal containing titanium and vanadium was measured accurately by using a self-developed viscosity measurement equipment, and the basic conclusions were summarized as follows:

(1) With the increasing of vanadium and titanium content, the viscosity of hot metal increased gradually. When the titanium content increased from 0.09 wt% to 0.5 wt%, the viscosity of the hot metal changed from 24.6 mPa·s to 124.5 mPa·s. When the vanadium content is less than 0.30 wt%, its effect on viscosity was not significant. However, when the vanadium content exceeded 0.30 wt%, the viscosity of hot metal increased sharply.

(2) Thermodynamic calculation shows that when the titanium content in the hot metal is 0.5 wt%, the precipitation temperature of TiC is 1392 °C and that of TiN is 1628 °C; when the vanadium content in the hot metal is 0.5 wt%, the precipitation temperature of VC is 1245 °C and that of VN is 1633 °C. The high melting point phases precipitated from vanadium and titanium-containing hot metal are mainly TiN, TiC, VN, and VC, and with the decrease of temperature, the precipitation phase gradually increased, resulting in the elevation of the viscosity of the hot metal.

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