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Effects of metalloid content on viscosity of Fe-Si-B-P-C alloy melt

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ABSTRACT

Viscosity of $Fe_{85-x}(C1B11Si2P3)_{(15+x)/17}$ (x = 0, 2, 4, 6 and 8) alloy melts has been investigated in the temperature range of 1200–1500 °C by the oscillating cup method. An anomalous viscosity decrease for $Fe_{85-x}(C1B11Si2P3)_{(15+x)/17}$ alloy melts near 1350–1400 °C has been demonstrated in the heating process, and viscosity hysteresis in subsequent cooling process has been observed. The above phenomena are explained by the evolution of cluster in melts. The relationship between viscosity and temperature during cooling processes is well described by the Arrhenius equation. The viscosity almost increases with the increasing total metalloid content at different temperatures. The activation energy calculated by the Arrhenius equation has shown an evident minimum at x = 4, which is supposed to be close to the eutectic composition. The thermal results further confirm the eutectic composition.

1. Introduction

Viscosity of glass-forming alloy melts is an important property in the casting process by affecting the crystallization kinetics in an undercooled liquid, and the morphology and the properties of the amorphous products [1]. Moreover, viscosity is one of the most sensitive parameters to the structure at the molecular level, which can give indirect indications about the micro-heterogeneity of these alloys in the liquid state [2].

There are several reports on the viscosity of Fe-based glass-forming alloy melts [1–12]. Dahlborg et al. have measured some physical properties of several Fe-based glass-forming alloy melts (Fe-B, Fe-Co-B), such as kinematic viscosity, surface tension and magnetic susceptibility during heating and cooling processes, concluding that the alloy melts undergo a series of structural transformations ranging from the initial micro-heterogeneous state to the true solution state [3,4]. The temperature dependence of viscosity of the $Fe_{80}B_{14}Si_6$ and other glass-forming alloy melts in the temperature interval ranging from 1200 to 1600 °C under heating and cooling conditions have been studied by Bel'tyukov et al. [5,6]. An anomaly, i.e., a sharp decrease of viscosity, has been revealed during heating process, and on subsequent cooling process the hysteresis phenomenon has been observed in their experiment. For these alloys mentioned above, anomalous decrease can be observed in viscosity vs. temperature curves in heating processes. This phenomenon has been considered as a structural transformation within the certain temperature intervals in the Fe-based alloy melts, which significantly influences the properties of solidified alloys.

In recent years, amorphous and nanocrystalline energy-saving materials with high saturation magnetization (B_s) and good glass-forming ability (GFA) have become one of research focuses at home and abroad [13–18]. Among these new amorphous alloys, Fe-Si-B-P-C alloy system has attracted much attention because of excellent soft-magnetic properties and good GFA [13–16]. High Fe content $Fe_{83}C_1(Si, B, P)_{16}$ amorphous alloy with high B_s of 1.67 T, good GFA of more than 80 μm, good bending ductility and low coercivity (H_c) has been developed, making the Fe-Si-B-P-C alloy system a promising soft-magnetic material for industrial applications [16]. In addition, it is increasingly believed that the structural state of melt before quench can significantly influence the properties of alloys in the solid state [19–21]. Investigation on the behavior of structural transformation of Fe-Si-B-P-C alloy melt is thus of special importance in the further improvement of the magnetic properties and their thermotime stability. However, little attention has been paid to the characteristics of the structural state of Fe-Si-B-P-C alloy melts at high temperature. Therefore, in this paper, temperature and composition dependence of viscosity have been investigated systematically. And liquid micro-structural evolution of Fe-Si-B-P-C alloy system has been revealed from the viewpoint of cluster.

2. Experimental procedures

Multi-component alloy with nominal compositions of $Fe_{85-x}(C_1B_{11}Si_2P_3)_{(15+x)/17}$ (x = 0, 2, 4, 6 and 8) were prepared by induction melting with the mixtures of pure Fe (99.95 mass %), Si (99.99 mass %), B (99.5 mass %), pre-alloyed Fe-P (24 mass % P) and

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Fe-C (5 mass % C) ingots in Argon atmosphere. Chemical analysis was performed to check the alloy compositions.

Viscosity of Fe-Si-B-P-C alloy melts was determined by the oscillating cup method [8,22]. The samples with a weight around 140 ± 2 g were placed in a heat-resistant alundum crucible, which is contained in an graphite vessel hung by a torsional suspension chamber. After the chamber was evacuated to a pressure of 10^{-3} Pa, the samples were overheated to 150 °C above liquidus temperature of alloy at a heating rate of 10 °C/min, held for 20 min and then cooled down to the selected temperatures. To avoid the oxidation at high temperatures, all of the measurements were taken under a water-tight constant argon atmosphere. All the experiments were carried out during heating and subsequent cooling with a temperature interval of 50 °C from 1200 to 1500 °C. The cooling rate was 10 °C/min. All samples were hold for 30 min at each temperature before the measurement in order to obtain a homogeneous melt. Viscosity was measured for three times at each temperature and the mean value was used. The melting temperature and liquid temperature of the alloys were determined by differential scanning calorimetry (DSC) at a heating rate of 5 °C/min.

3. Results and discussion

The temperature dependence of the viscosity for molten $Fe_{85-x}(C_1B_{11}Si_2P_3)_{(15+x)/17}$ (x = 0, 2, 4, 6 and 8) alloys during heating and subsequent cooling processes is shown in Fig. 1. It is obvious that the viscosity of the molten alloys monotonously decreases with increasing temperature for all samples. The values in heating processes present an anomalous behavior, i.e., the viscosity exhibits a distinct decrease near 1350 °C (x = 0, 2 and 8) or near 1400 °C (x = 4 and 6) in heating processes, while the viscosity variation in cooling processes is relatively smooth. This abnormal temperature here could be called T_{dis}, the dissolution temperature [3]. In addition, another characteristic temperature T_{bra} is defined here, at which the heating and cooling curves overlap. Fig. 1 shows that T_{bra} for the alloys with x = 0, 2 and 8 and the alloys with x = 4 and 6 are 1400 °C and 1450 °C, respectively. Furthermore, the viscosity of the molten alloys in cooling processes is lower than that in heating processes at the temperature range from 1200 to 1500 °C. Note that all observations mentioned above are repeatability, i.e., the temperature dependence of the viscosity for

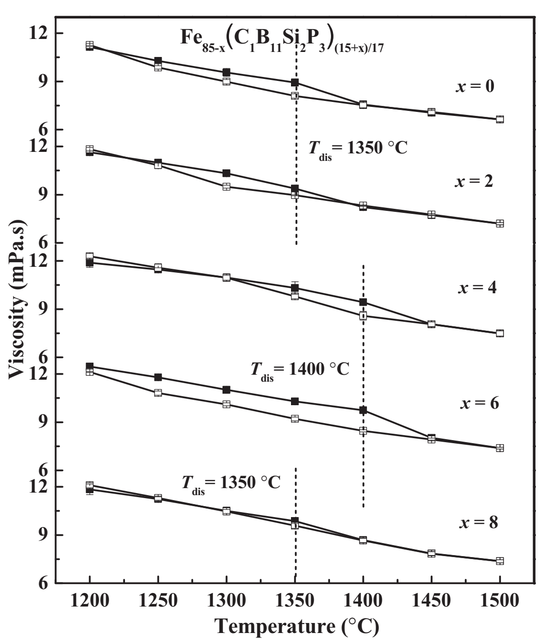

Fig. 1. Temperature dependence of viscosity for the $Fe_{85-x}(C_1B_{11}Si_2P_3)_{(15+x)/17}$ alloy melts (x = 0, 2, 4, 6 and 8) during heating (■) and subsequent cooling (□) (lines are drawn as guides to eyes).

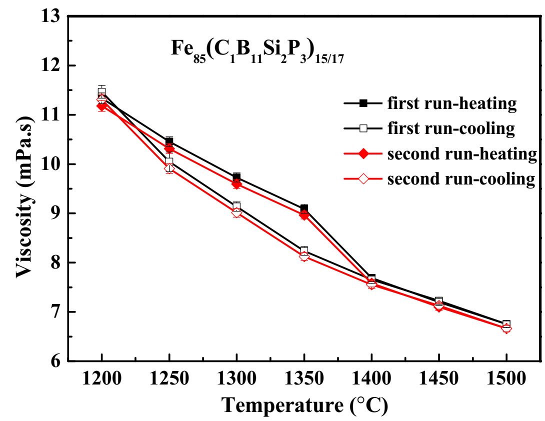

Fig. 2. Temperature dependence of viscosity for the $Fe_{85}(C_1B_{11}Si_2P_3)_{15/17}$ melt for the consecutive heating-cooling experiments: ■, first run-heating; □, first run-cooling; ◆, second run-heating; ◇, second run-cooling (lines are drawn as guides to eyes).

$Fe_{85}(C_1B_{11}Si_2P_3)_{15/17}$ melt for the two consecutive heating-cooling experiments is illustrated in Fig. 2, and the values are consistent within the experimental error. Thus, the observed phenomena are not attributed to the possible inhomogeneity of the initial alloy ingot or experimental error.

In order to explain the phenomena of viscosity anomaly and hysteresis, the evolution of clusters in the melt is briefly demonstrated by the schematic diagram in Fig. 3. It has been proved that there are a variety of clusters with different chemical components in the alloy melt based on the Fe-Si-B system [23–25]. In fact, viscosity essentially reflects the interaction between clusters in melts, and the monotonic change of viscosity versus temperature is the macroscopic reflection of the evolution of clusters in melt. Besides, the type and size of clusters is the two key factors during the evolution of clusters. Clusters with a specific type and size may maintain a thermodynamic equilibrium state at a given temperature range. When heated to a higher temperature (above T_{dis}), the melt loses its thermodynamic equilibrium, and then irreversibly transforms into a true solution state at T_{bra} at which the melt is thermodynamically stable. This transformation involves the dissociation and redistribution of clusters, such as the break-up of large clusters and the formation of flat cluster configuration, which increase the fluidity of alloy melt and thus notably decrease the viscosity at T_{dis}. However, these clusters with excellent fluidity can maintain their thermodynamic equilibrium below T_{dis} during cooling processes, resulting in the viscosity hysteresis at T_{bra}.

The phenomena of viscosity anomaly and hysteresis can also be explained by the theory of long-range density fluctuations in glass-

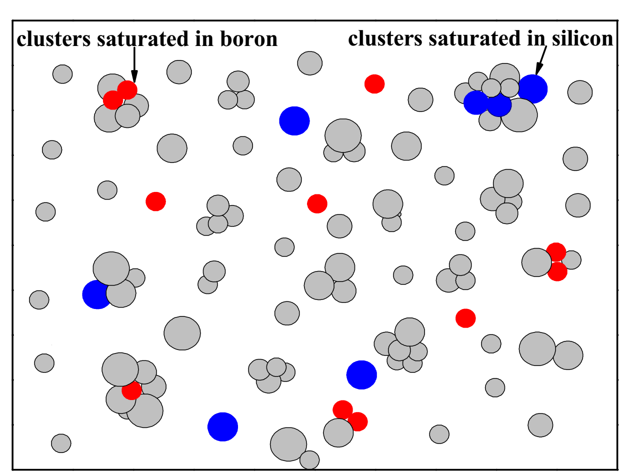

Fig. 3. The schematic diagram of the structure of Fe-Si-B-P-C alloy melt.