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Peculiarities of viscosity and solidification of the Cr–C melts in the vicinity of the eutectic composition

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A B S T R A C T

The relationship between short-range ordering of the Cr–C melts (10–17 at.% C) and their structures in the solid state has been investigated by the analysis of viscosity of these liquid alloys and their solidification at various cooling rates (20–100 °C/min). The minimum has been found in the concentration dependences of viscosity of the Cr–C melts in the vicinity of 14.5 at.% C. It has been shown that on cooling at various rates (from 20 to 100 °C/min) the Cr–C melts are crystallized by non-equilibrium mechanism with the formation of α-Cr solid solution and the α-Cr/Cr_7C_3 non-equilibrium eutectic, the latter being decomposed into equilibrium phases, α-Cr and $Cr_{23}C_6$. A τ-phase ($Cr_{23}C_6$) has been observed to form directly from liquid phase only in the Cr–C liquid alloys in the narrow concentration interval in the vicinity of the eutectic composition (13.5 to 14.5 at.% C) when the melt is cooled from the temperatures below the peritectic transformation temperatures (1612 °C).

1. Introduction

At present melt quenching at the sufficiently low rates of ~1–10^3 K/c is one of the most promising ways to obtain bulk amorphous alloys (BAA) [1–3]. Most attention is paid to production of BAA based on 3-d transition metals, especially iron [3–5]. These alloys exhibit high strength features, soft magnetic properties and high corrosion resistance. They can be extensively used as structural and functional materials [3–5]. For this group of alloys a τ-phase ($M_{23}C_6$) is the main "phase-glassformer" [3,6]. A τ-phase is observed mainly during crystallization of amorphous alloys or under highly non-equilibrium conditions [7,8]. The $M_{23}C_6$ phase is equilibrium only in a Cr–C binary system. A simple eutectic-like phase diagram is characteristic of a Cr–C binary system in the high Cr concentration area [9,10]. In this system the $Cr_{23}C_6$ carbide is formed by a peritectic reaction at 1612 °C [9]. However, high melting temperatures characteristic of Cr–C alloys and high activity of the alloys components make their investigation complicated. At present the experimental data on the structure and properties of the Cr–C alloys in solid or liquid states are few in number [11,12].

In this regard, in this paper the investigations of viscosity of the Cr–C melts in the area from 10 to 17 at.% C as well as solidification of these melts on cooling at 20–100 °C/min have been performed. On one hand, the alloys of the selected concentration area are characterized by the lowest melting temperatures. It makes it possible to increase the temperature range in order to study these alloys in the liquid state. On the other hand, the structure of these alloys contains quite a sufficient concentration of $Cr_{23}C_6$.

2. Experimental methods

The melt state was studied by viscosity as one of the most important structural-sensitive properties of the liquid phase. Kinematic viscosity, (ν), was measured by the method of damping torsional vibrations of the crucible filled with the melt. The detailed measurement and calculation techniques are described in [13]. The experiments were carried out in a crucible made of Al_2O_3 in a purified helium atmosphere. To prevent the uncontrolled effect of the oxide film a cylindrical lid made of Al_2O_3 was used as the second face surface [14]. The viscosity polytherms were obtained in heating conditions starting from the liquidus temperature to 1680 °C with subsequent cooling. The temperature is changed gradually with the step equal to 10 °C. The specimens were held under isothermal conditions for 20 min at each temperature before measurement. Then the samples were cooled up to room temperature. Replicates of the experiments on the viscosity measurements (during heating and cooling) were made using the method described above. The general root-mean-square error of the viscosity measurement does not exceed 3.5%.

The study of the crystallization processes was carried out by the differential thermal analysis (DTA), the X-ray structure analysis using a DRON-6 diffractometer (Cu-K_α radiation) and metallography as well.

The alloys were prepared by alloying the corresponding proportions of $Cr_{90}C_{10}$ and $Cr_{83}C_{17}$ ligatures in a furnace of the viscometer at 1680 °C for 1 h. The synthesis of ligatures was carried out according to the traditional metallurgical technology by alloying chromium and graphite powders in a vacuum furnace at 1730 °C for 30 min. The temperature and time of alloying the chromium and graphite powders for the ligatures synthesis were selected in accordance with prior investigations described in [15] which were made to produce ingots with the

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equilibrium phase composition and without any nonequilibrium graphite inclusions.

3. Results and discussion

Typical temperature dependences of viscosity of Cr–C melts during first heating and subsequent cooling as well as during repeated measurements are presented in Fig. 1a. It is seen that for each composition the heating and cooling polytherms coincide considering the measurement error and are reproduced in the repeated measurements. The polytherms are well described by Arrhenius dependence (Fig. 1b). The viscosity concentration dependences were calculated according to the obtained polytherms of ν at various temperatures (Fig. 2a). As seen in Fig. 2a the derived viscosity isotherms are nonmonotonic. With the carbon concentration increase a nonmonotonic viscosity change in the range of 13.5 to 15 at.% C with a minimum in the vicinity of 14.5 at.% C was found. The viscosity isotherm behavior does not change with melt temperature increasing.

As a rule, in binary systems the minimum in the concentration dependences of the viscosity is observed in the vicinity of the eutectic composition. It indicates the presence of the quasieutectic structure in the melt [16,17]. However, the minimum in the isotherms of the Cr–C melts viscosity within the investigated concentration range is located in a hypereutectic region.

The solidification processes of the Cr–C melts in the range from 10 to 17 at.% C were studied on cooling from 1680 °C at 20–100 °C/min. The melting and crystallization temperatures of each alloy were determined from the obtained heating and cooling thermograms accordingly.

The typical heating and cooling thermograms of the investigated melts are presented in Fig. 3a–c. Fig. 3a–c show that the melting of alloys agrees with the equilibrium phase diagram: it is a 2-stage process for hypoeutectic and hypereutectic compositions and a one-stage process for the eutectic alloy. However, the crystallization of these melts does not depend on the cooling rate and causes three exothermic effects. That does not correlate with the equilibrium phase diagram of this system and points to the non-equilibrium nature of the crystallization process. The equilibrium phase diagram of the Cr–C system with the points corresponding to the temperatures of the exothermic peaks determined from cooling thermograms is presented in Fig. 3d. Fig. 3d shows that the onset crystallization temperatures for hypoeutectic alloys are located near the equilibrium liquidus line in the phase diagram. For hypereutectic melts the difference between the equilibrium liquidus temperature (from equilibrium phase diagram) and the liquidus temperature determined from the cooling thermograms is increased with the increasing carbon concentration in the alloy. These points fit the metastable liquidus line which is the continuation of the line of α-Cr-based solid solution formation from the melt (a dashed line in Fig. 3d). The temperatures of the second stage of crystallization do not depend on the alloy composition and are significantly lower as compared to the equilibrium solidus. The temperature of the third effect of crystallization equals 1350 °C and does not depend on the alloy composition either. The equilibrium phase diagram shows no structural phase transformations which could correspond to third effect. At the same time according to the X-ray analysis data each Cr–C ingot obtained after DTA has the equilibrium phase composition consisted of a α-Cr solid solution and $Cr_{23}C_6$.

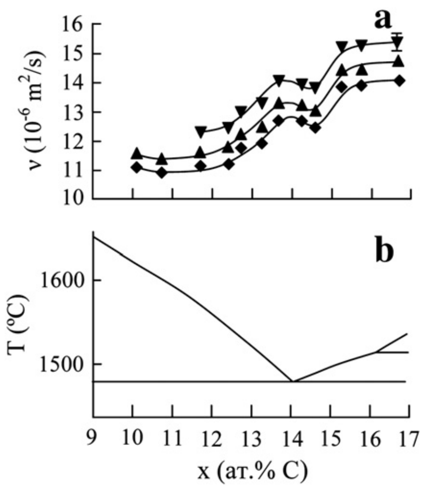

Fig. 2. The concentration dependences of viscosity of the Cr–C melts at different temperatures: ▼ — 1640 °C, ▲ — 1660, ◆ — 1680 °C (a); the equilibrium phase diagram of the Cr–C system [9] (b).

Let us consider the non-equilibrium phase diagram of the Cr–C system in the investigated concentration range (Fig. 3d, dashed lines). It can be seen that the point of the α-Cr/Cr_7C_3 nonequilibrium eutectic (i.e. the intersection point of lines of the α-Cr solid solution and the Cr_7C_3 formation from the melt) is in the vicinity of the temperature corresponding to the second stage of crystallization. Thus, the undercooling degree of the melts in given cooling conditions should be taken into consideration. On this basis we can conclude that primary crystals of the α-Cr solid solution are observed to form initially from the melt in

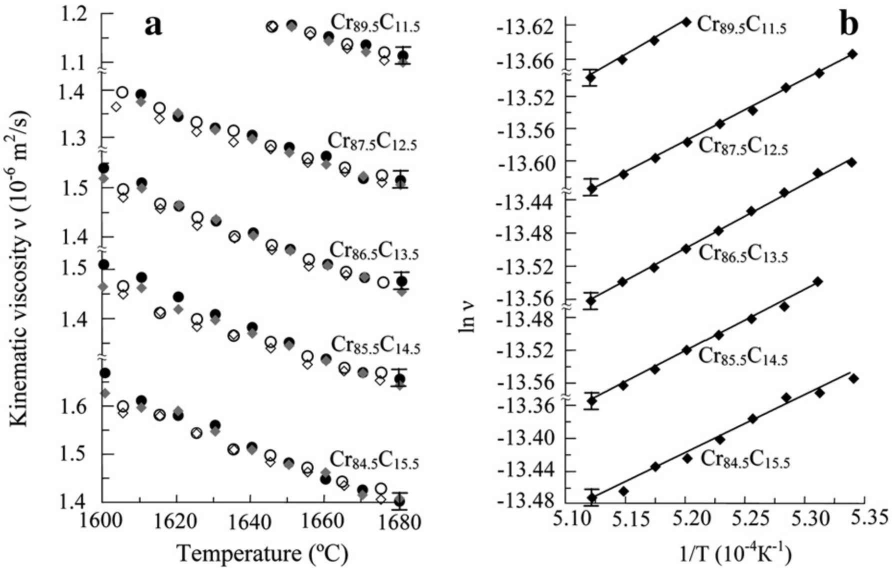

Fig. 1. The temperature dependences of viscosity of the Cr–C melts in ν(T) and lnν(1/T) coordinates (● — first heating, ○ — first cooling, ◆ — second heating, ◊ — second cooling).