On the viscosity of the amorphizing Co-(Cr,Fe)-Si-B melts.

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Abstract. The study of the temperature and time viscosity dependences of the amorphizing Co₆₅.₅Fe₆.₅Si₁₈B₁₀, Co₆₅.₅Cr₆.₅Si₁₈B₁₀, Co₆₉Cr₃Si₁₈B₁₀ melts has been performed. It has been shown that the temperature and time viscosity dependences for each alloy are of the same nature. The anomaly attended by the changing of the energy activation of the viscous flow has been first determined in the viscosity polytherms under heating conditions in the vicinity of t* (t* is the characteristic temperature for each alloy, i.e. the temperature of the anomaly on the polytherm of the viscosity). This anomaly is caused by the change of the short-ordering type in the liquid phase in this temperature region as well as by the transition of its low-temperature structure into the high-temperature one. The latter being further cooled is retained up to the solidification temperatures and results in the viscosity hysteresis. It has been shown that the decrease of the alloying element concentration results in a substantial displacement of the anomaly temperature, t*, to the lower temperature region (t*=1360°C for Co₆₅.₅Fe₆.₅Si₁₈B₁₀, Co₆₅.₅Cr₆.₅Si₁₈B₁₀ and 1220°C for Co₆₉Cr₃Si₁₈B₁₀).

1. Introduction

The alloys based on the Co-Si-B system are easy amorphizing alloys and they present a new type of promising magnetically soft materials [1-3]. The alloying of these alloys by Fe or/and Cr results in increasing their glass forming ability as well as influences on the thermal stability of amorphous state of the alloys [4]. It is known that the glass forming ability of amorphizing alloys depends on a number of factors, the choice of the optimal technological parameters of the amorphous alloys production (the quenching temperature and the cooling rate of the melt in particular [5, 6]) being the most important ones. It results from the dependence of the structure formation processes on the structural state of the liquid phase and prehistory of its obtaining which are to some extent inherited at solidification [7, 8]. As is known the viscosity is one of the most structural-sensitive properties of metallic melts. Furthermore, viscosity is one of the physical melts properties which strongly influences on the choice of the quenching regimes.

In connection with this the investigations of the temperature and time viscosity dependences of the Co₆₅.₅Fe₆.₅Si₁₈B₁₀, Co₆₅.₅Cr₆.₅Si₁₈B₁₀, Co₆₉Cr₃Si₁₈B₁₀ amorphizing melts have been carried out in this work.

2. Experimental procedure

Kinematic viscosity (ν) was measured by the method of damping torsional vibrations of the crucible with the melt by an automatized viscometer [9]. All the measurements were carried out in

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purified helium atmosphere in heating conditions from the liquidus temperature to 1500ºC with further cooling, the temperature changing gradually with the step equal to 20 – 40ºC. The specimen was held under isothermal conditions for 20 minutes at each point. To prevent the uncontrolled influence of the oxide film a cylindrical lid made of Al₂O₃ was used as the second face surface. The parameters of the suspended system were recorded by the optic method using a laser and a high precision photosensor. For the confidence level of 0.95 within the interval of 1100 – 1500ºC the most probable error in determining the absolute viscosity values of the investigated melts in the unit experiment amounts to 1.5% and the total error is no more than 4%.

3. Results and discussion

In figure 1 the obtained temperature dependences of viscosity of the Co₆₅.₅Fe₆₅Si₁₈B₁₀ melt are presented. A curve fracture is observed in the viscosity polytherm in the vicinity of 1360ºC when the melt was first heated (figure 1a). When further cooling the anomaly is lack and the hysteresis occurs lower than t* (i.e. the viscosity values under cooling conditions are higher than those obtained heating conditions) (figure 1a).

When the melt was heated again (after being crystallized in the viscometer) the anomaly in the vicinity of 1380ºC was observed, too. Over t* the polytherms coincided when the melt was heated for the fist and the second times. The polytherms of cooling coincided over the range of the temperatures under investigation (figure 1).

The time dependences of the viscosity have been investigated in order to understand what happens to the melt at different temperatures. The results obtained are presented in figure 2. The investigations of the time viscosity dependences were carried out under isothermal conditions for 2 hours at different temperatures in the stepped heating and further cooling regimes. To reach the designated temperature the velocity of 50ºC/min is used. It has been found out that the viscosity values do not change with the exposure time. However, the dependences ν(τ) at cooling when t < t* are characterized by higher viscosity values than those at heating i.e. the viscosity hysteresis observed in the viscosity polytherms is manifested in the time dependences as well (figure 1).

The analogous nature of the temperature and time dependences of the viscosity is observed for the Co₆₅.₅Cr₆₅Si₁₈B₁₀, Co₆₅Cr₆₅Si₁₈B₁₀ alloys. In this case the anomaly in the viscosity polytherms under heating conditions is observed for the Co₆₅.₅Cr₆₅Si₁₈B₁₀ alloy in the vicinity of 1360ºC while the
decrease of the Cr concentration in the alloy composition results in the displacement of the anomaly temperature to the lower temperature region (t*=1220ºC for Co_{69}Cr_{3}Si_{18}B_{10} alloy) (figure 3).

The analysis of the results obtained has shown that in the range of t<t* the nature of the temperature viscosity dependences of the melt investigated is defined by the alloys state before melting, i.e. by the pre-history of their preparation. After overheating higher than the anomalies temperature all the obtained curves \( \nu(t) \) coincide.

It is known that the hysteresis of the viscosity is often observed for binary and multicomponent systems [10, 11]. According to [10] the hysteresis of structural-sensitive melts properties is caused by the irreversible changing of the melt state when the melt is heated above the defined temperatures (e.g. the dissolution of the nonequilibrium microgroups in the initial structure of the melt when it is heated above critical temperatures). In this case the heating polytherm corresponds...
to the nonequilibrium state of the liquid phase. The cooling polytherm has been found to correspond to more equilibrium one. It is necessary to note that the dissolution of the nonequilibrium microgroups occurs within the narrow temperature-time interval and in this case the characteristic maximum of viscosity in the polytherms is observed [10]. However the other causes of the hysteresis are possible to exist. As is shown in [11-13] the hysteresis can be caused by the structural transformation in the liquid phase. It appears when the melt is heated over the transformation temperature due to retaining a high-temperature structure of the liquid up to its solidification in the cooling process.

Based on the mentioned above the anomaly observed in the viscosity polytherms of the investigated melts in the vicinity of t* is believed to be caused by the change of the short-ordering type in the melts in the vicinity of these temperatures as well as by the transition of the low-temperature melt structure into the high-temperature one. The latter being further cooled is retained up to the solidification temperature and characterized by the long relaxation time. If the melt is then heated its high-temperature structure in the area lower than t* changes into the low-temperature one which appears to be equilibrium for the given temperature area.

4. Conclusions

The anomaly in the viscosity polytherms of the amorphizing Co_{65.5}Fe_{6.5}Si_{18}B_{10}, Co_{65.5}Cr_{6.5}Si_{18}B_{10}, Co_{69}Cr_{3}Si_{18}B_{10} melts in the vicinity of t* (it is a characteristic temperature for each alloy) has been first determined. It is believed to be caused by the change of the short-ordering type in the liquid phase in the vicinity of this temperature area as well as by the transition of the low-temperature melt structure into the high-temperature structure. If the melt is further cooled the high-temperature structure is retained up to the solidification temperature.

It has been shown that the substitution of the Fe atoms for the Cr atoms does not substantially influence on the nature of the temperature viscosity dependences while the decrease of the Cr concentration results in the substantial displacement of the anomaly temperature to the lower temperature region, i.e. 1360°C for Co_{65.5}Fe_{6.5}Si_{18}B_{10}, Co_{65.5}Cr_{6.5}Si_{18}B_{10} and 1220°C for Co_{69}Cr_{3}Si_{18}B_{10}.

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