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Measurement of the electrical resistance of molten lead chloride at freezing

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Abstract

The electrical resistance of molten lead chloride was measured under controlled cooling of the melt to its complete freezing. At the very beginning of the melt solidification unexpected changes in resistance were observed and their dependence on the melt temperature history was studied.

INTRODUCTION

The electrical conductance of molten salts results from the existence of mobile ions in an electric field applied to the system under consideration. From the analysis of its changes with temperature (or other parameter), an estimation of the processes taking place in molten salts can be made, in a global sense.

Molten $PbCl_2$ has been studied by various methods, but the various opinions on its structure have not been defined explicitly. According to Umetsu et al. [1] molten $PbCl_2$ behaves as an ionic liquid with small associating ability. Barta et al. [2] have explained the strong tendency of the melt towards supercooling by the formation of complexes based on $(PbCl_4)^{2-}$ and $(PbCl_6)^{4-}$. Lantratov and Moiseeva [3] have concluded from measurements of electrical conductivity that autocomplexes $Pb(PbCl_4)$ are present in the melt at temperatures below 585°C. In contrast to ref. 3, Maroni [4] has observed no Raman bands in pure $PbCl_2$ related to the complex. However, complex anions such as $(PbCl_n)^{n-2}$ $(n = 3, 4, 6)$ have been found in the system $KCl–PbCl_2$ [3–7].

This paper deals with the study of molten lead chloride by electrical resistance measurements. Our aim is to present the results of those measurements performed at temperatures close to the melting point of $PbCl_2$ and during its solidification. We assume the existence of complexes in

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the melt so in order to better understand the processes of their formation, the influence of homogenization temperature and time, and the cooling rate, on the resistance was studied in detail.

EXPERIMENTAL

The electrical resistance of molten $PbCl_2$ was measured in a special closed quartz cell having a suitably large cell constant. The cell consists of a quartz tube 12 mm in inside diameter and two carbon electrodes in narrow quartz tubes. The surface area of the electrodes equals 7 mm^2, the distance between them being maintained at 60 mm. The electrodes are connected to an external electric circuit with platinum wires. The temperature of the melt within the cell was measured with a thermocouple placed in a quartz protection tube and localized in close proximity to the electrodes. Such a configuration makes it possible to check the melt temperature along the whole length of the cell at any moment during the resistance measurements. All measurements of electrical resistance were performed in the same cell at a frequency of 10 kHz and a voltage of 1 V.

For the measurements, lead chloride and silver chloride (specially purified by zone refining) were used. The cell contained about 60 g $PbCl_2$ and its free space was filled with a protective atmosphere. The closed cell was placed in a vertical furnace and heated to the homogenization temperature; after a certain (defined) time the melt was cooled at a programmed rate. The temperature gradient along the whole measured zone was smaller than 0.5 K. The electrical resistance and the temperature were recorded simultaneously every 5 s. The measurements were taken in the temperature range 100 K above and 20 K below the freezing point, at cooling rates of 1, 2, 5 and 10 K h^{-1}. The orientation measurements were performed at rates of 20, 30 and 60 K h^{-1}.

RESULTS

The temperature dependence of the resistance of molten $PbCl_2$ (measured from 585°C to the full freezing of the melt) is shown in Fig. 1. The melt was tempered for 30 min at 585°C and then cooled at a rate of 10 K h^{-1}. It can be seen that the resistance increases very slowly (about 0.25 Ω per 10 K) as temperature decreases down to the temperature of 489°C. At this temperature a quick rise in the resistance, indicating the beginning of the freezing of the melt, is apparent. At the same moment, a step change in the temperature to the value of 496.4°C (melt undercooling being 7.4 K) takes place and the temperature then remains unchanged during the complete solidification of the melt (about 10 min). After the initial increase, the resistance decreases by about 1.7 Ω and then rises quickly to the value of 1000 Ω corresponding to the resistance of solid lead chloride. The

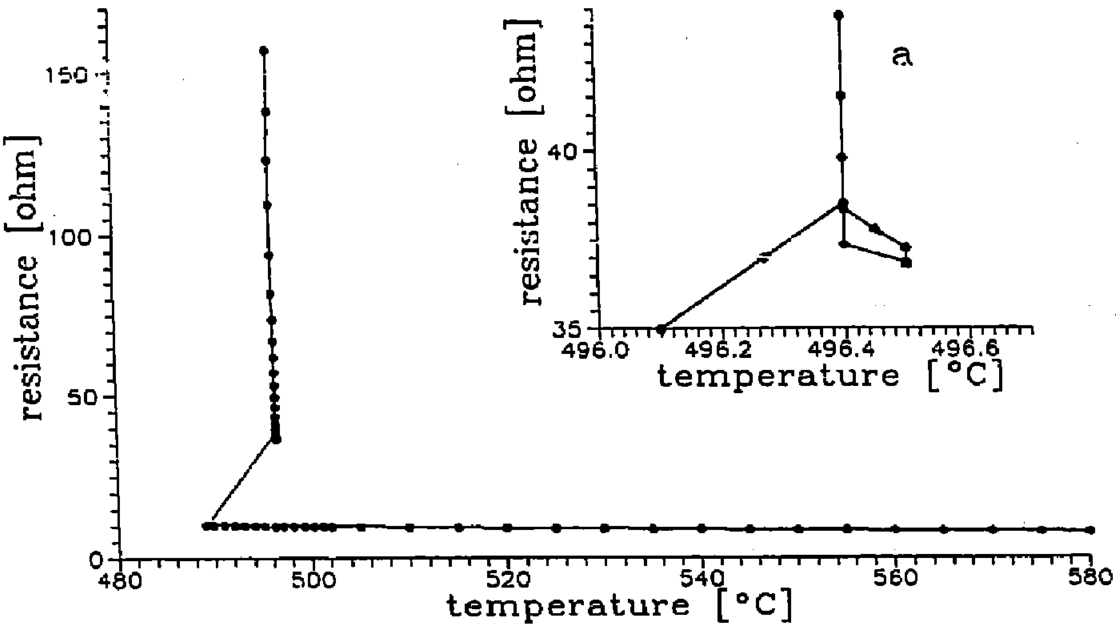

Fig. 1. The temperature dependence of the resistance of molten $PbCl_2$ at cooling rate of 10 K h^{-1}: a, the resistance changes at freezing.

dependences of resistance and temperature on time for this measurement are shown in Fig. 2.

The shapes of the resistance curves obtained give a true picture of the changes in the electrical resistance during the processes taking place during

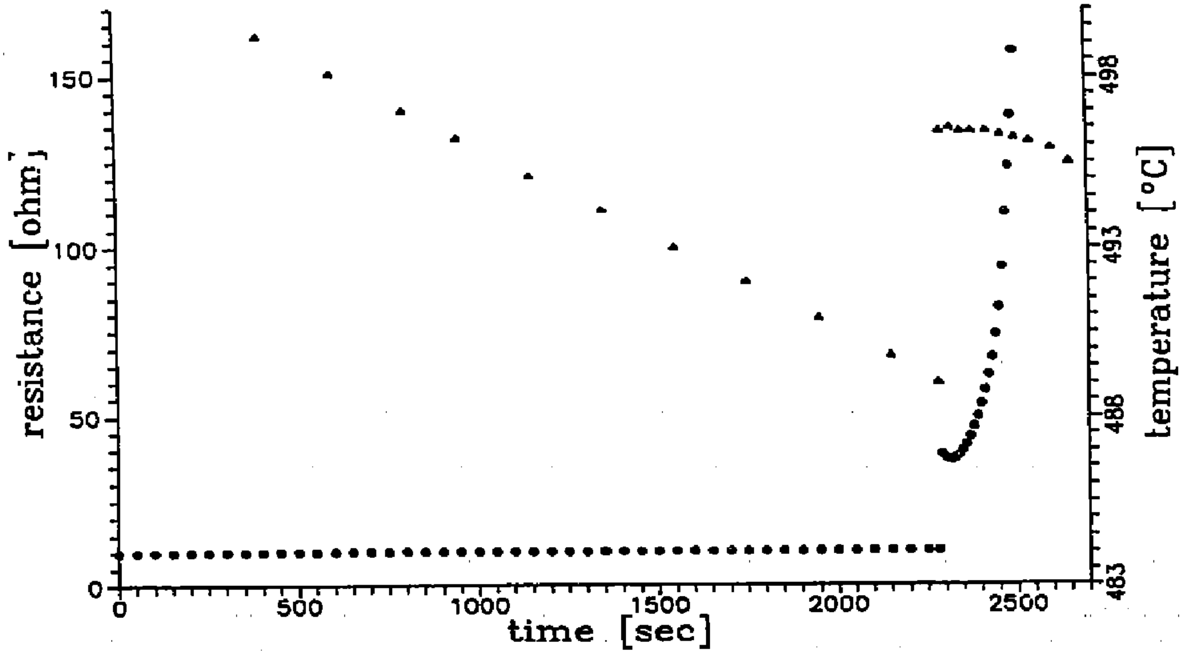

Fig. 2. Dependence of resistance R and temperature T on time at a cooling rate of 10 K h^{-1}: R, ●; T, ▲.

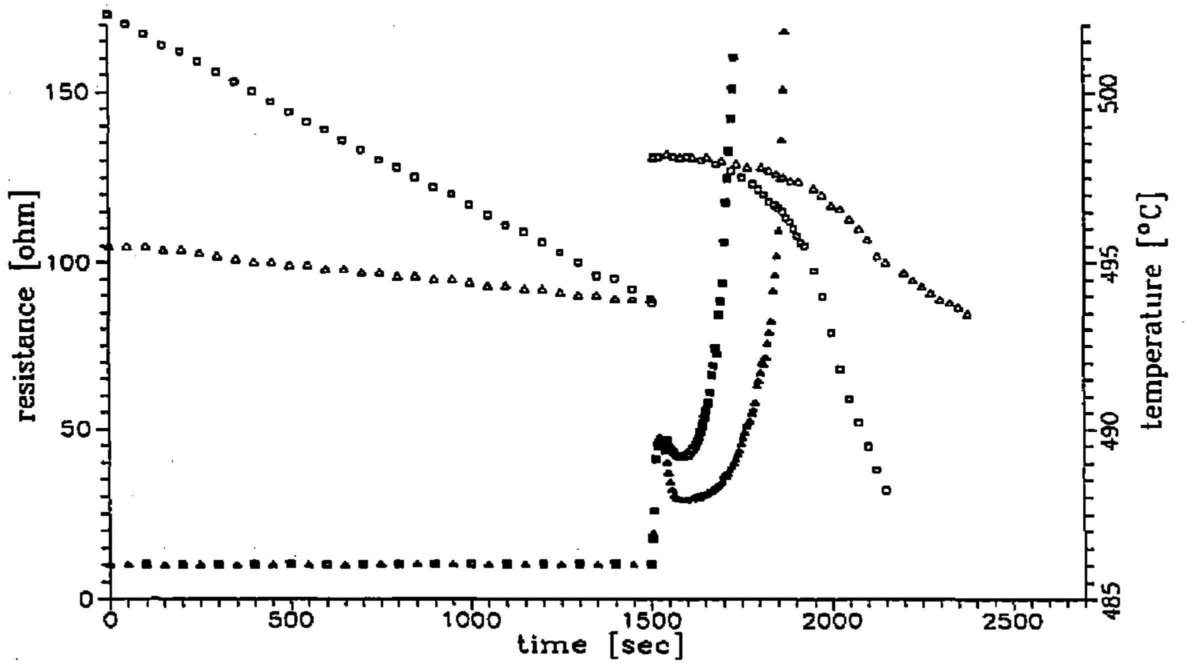

Fig. 3. Dependence of resistance R and temperature T on time at cooling rate of $10\,\mathrm{K\,h^{-1}}$ (R, ▲; T, △) and $1\,\mathrm{K\,h^{-1}}$ (R, ■; T, □).

the solidification of molten $PbCl_2$. In the case of the cooling rate studies, the melts were heated and tempered at a temperature of 510–515°C. When the cooling rates are higher than $20\,\mathrm{K\,h^{-1}}$ the melt solidifies in a very short time and only a monotonic rise in resistance can be registered. At lower cooling rates the period of solidification is longer and the resistance changes become more easily observable and can be recorded. The time dependence of the resistance and temperature at cooling rates of 1 and $10\,\mathrm{K\,h^{-1}}$ are shown in Fig. 3. In both cases the resistances increase at the beginning of freezing and they reach approximately the same maximum value. The subsequent resistance drop is several times larger at the cooling rate of $1\,\mathrm{K\,h^{-1}}$ than at the cooling rate of $10\,\mathrm{K\,h^{-1}}$; the temperature curves show the same undercooling.

The influence of the preceding homogenization temperature on the shape of the resistance curves at freezing was studied at a cooling rate of $10\,\mathrm{K\,h^{-1}}$. The most significant change in resistance occurs when the melt has been previously annealed at a temperature of 530°C for 10 min. The absolute magnitude of the resistance is also influenced by the homogenization temperature. The resistance at 500°C in the melt tempered at 600°C is always smaller than in that tempered at a temperature of 515°C.

The dependence of the magnitude of undercooling on the experimental conditions (i.e. homogenization temperature and cooling rate) was also recorded. When cooling the melt from the homogenization temperature of 515°C at rates ranging between of 1 and $10\,\mathrm{K\,h^{-1}}$ the undercooling is approximately the same in all cases (4.5 K). When the melt is cooled at

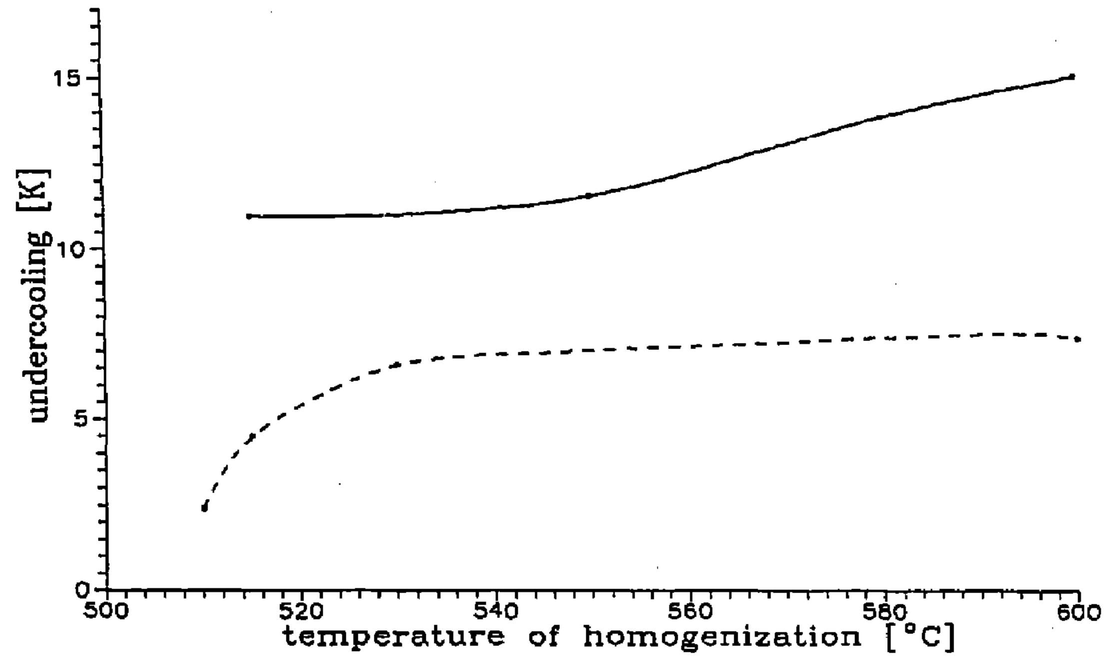

Fig. 4. The dependence of the undercooling on the homogenization temperature at cooling rate of 10 K h^{-1} (– – – –) and 60 K h^{-1} (——).

60 K h^{-1} the undercooling is 11.6 K. The dependence of the undercooling on the homogenization temperature at cooling rates of 10 and 60 K h^{-1} is shown in Fig. 4. The undercooling increases with the homogenization temperature. In the same way a larger value of undercooling is reached by cooling for a shorter period.

The shape of the resistance curve and the resistance drop during freezing depend on the magnitude of undercooling. At smaller undercooling (4.5 K), the magnitude of the resistance drop is large, in contrast to the higher undercooling (more than 10 K) when a drop in resistance is not observed.

To compare the results obtained in molten $PbCl_2$ the resistance of molten AgCl (in which no associating ability is expected) was measured. In this case the melt does not reach an undercooling and the resistance increases without any drops.

DISCUSSION AND CONCLUSIONS

Our measurements show that there are no significant changes in the resistance of molten $PbCl_2$ during cooling from 600°C down to its melting point. In all experiments performed, the melt reaches undercooling and the beginning of solidification is connected with a resistance increase and a temperature jump to freezing point. However, during the solidification a resistance drop is observed at slow cooling rates. Our results show that both the resistance and the magnitude of undercooling in freezing molten

$PbCl_2$ depend very sensitively on the melt's temperature history. This dependence of the undercooling confirms that $PbCl_2$ must exhibit some definite associating property (formation of complex anions, clusters or associates).

In the literature no reference has been found to conductivity measurements of molten salts both in close proximity to the liquidus temperature and at freezing, so our results for $PbCl_2$ can be compared only with our results for AgCl. (A long time ago Bloom [8] reported some changes in conductivity in the molten system KCl–$CdCl_2$, but these occurred 30–40 K above the liquidus line.)

Comparing the shape of the resistance curve of molten $PbCl_2$ with that of AgCl we can deduce that the resistance drop and undercooling are connected with the assumed existence of complex anions (clusters, associates). This means that the drop in resistance of molten $PbCl_2$ at freezing could be caused either by the decomposition of complex particles or by the solution of undercritical nuclei due to the melting heat released during the temperature jump. However, the explanation of the phenomenon observed at the freezing of molten $PbCl_2$ needs further experiments, especially on materials with known structures. Of course, the use of other methods would be advantageous.

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