ELECTRICAL CONDUCTIVITY OF BINARY MELTS CONTAINING NbCl₅, TaCl₅ and NaCl-KCl(l:1)

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ABSTRACT

The specific electrical conductivity of the NbCl₅-NaCl-KCl (NaCl:KCl=1:1) pseudo binary system was measured because of interest in the molten salt electrolysis of niobium from its chloride melts. The phase diagrams of these systems have been determined by differential thermal analysis. The results show a trend similar to that of the NbCl₅-NaCl and NbCl₅-KCl systems. The electrical conductivity of melts increases with the increase in temperature. Two liquid phases were observed in the region rich in NbCl₅. Conductivities of pure NaCl₅ and TaCl₅ were determined between the melting point and the boiling point using a pyrex glass cell with a small cell constant.

In the same manner, the conductivity of the TaCl₅-NaCl-KCl pseudo binary system was also considered with the goal of obtaining high purity tantalum by molten salt electrolysis.

INTRODUCTION

Niobium has recently become of major interest in high technology applications such as nuclear reactors and as a superconductor catalyst. Pure tantalum metal is also important as a capacitor. Pyrochlore is the most important source of niobium because of its great abundance and low tantalum content (1-4). A recent trend of ore producing countries such as Brazil is that of exporting ferroniobium instead of the ore. Imported ferroniobium accounts for more than 60% of all niobium supplied to Japan.

As ferroniobium becomes a main source of the world's niobium supply, investigation of niobium production directly from ferroniobium is needed urgently. We have studied the chloride process and molten salt technology which are the most applicable to purification and synthesis of new materials (5,6). These studies present possible separation processes of niobium from ferroniobium which yield pure niobium chloride. It is feasible to consider producing niobium metal from niobium chloride by electrolysis in molten chloride salts.

In this paper, the specific electrical conductivity and the phase diagram of the NbCl₅-NaCl-KCl pseudo binary system were investigated. Another pseudo binary system of TaCl₅-NaCl-KCl was also considered for the production of high purity tantalum metal using chloride electrolysis.
EXPERIMENTAL

Chloride preparation

Anhydrous NbCl₅ was prepared by reacting 99.7% niobium metal powder with a small amount of carbon and dry Cl₂ gas in a chlorination apparatus at 300°C. Anhydrous TaCl₅ was prepared in the same manner using 99.5% tantalum metal. The mixture of NaCl and KCl was dehydrated by passing dry HCl gas into the NaCl-KCl(1:1) melt at 750°C. These dehydrated chlorides were transferred to conductivity cells or DTA cells in an argon filled dry box.

Conductivity Measurement

The conductivity cells (a) were made of pyrex glass or quartz with a 1 mm diameter tungsten rod welded to tungsten foil as shown in Fig. 1. The cell resistance (0.2-0.3 S⁻¹) is negligible compared to the salt bath resistance of 100-200 S⁻¹ (cell constant=100-200 cm⁻¹). Another type of pyrex glass cell (b) with a small cell constant (~2.0 cm⁻¹) was used for pure NbCl₅ and TaCl₅ because of their small specific electrical conductivities (10⁻⁶ S/cm). Electrical conductivity was measured by the AC bridge method at 1-10 kHz as shown in Fig. 2.

Differential Thermal Analysis (DTA)

DTA was used to determine the phase diagrams. The cells were made of pyrex glass or quartz with a thermocouple well at the bottom (Fig.3). The cell was sealed under vacuum. The heating rate was 10°C/min.

NbCl₅-NaCl-KCl(1:1) Pseudo Binary Phase Diagram

The phase diagram of this pseudo binary system is presented in Fig. 4. The melting points of each component (204°C for NbCl₅, 647°C for NaCl-KCl (1:1)) agree with previously reported values (204 and 645°C) (7,8). Other studies report 1:1 compounds such as NaNbCl₆ (tetragonal) and KNbCl₆ (cubic) in the NbCl₅-NaCl and NbCl₅-KCl binary systems (9-11). In the NbCl₅ rich region α, β, γ, and α'γ interphases were observed as in the NbCl₅-KCl system. In the NaCl-KCl rich region three transformations were observed as in the NbCl₅-KCl system. Unfortunately there is no structural reference to the above transformations. Two liquid phases are also observed in the NbCl₅ rich region.

Specific Electrical Conductivity of NbCl₅ and TaCl₅

The specific electrical conductivities of NbCl₅ at elevated temperatures are shown in Fig. 5. The specific electrical conductivity of pure NbCl₅ from 204°C (m.p.) to 253°C (b.p.) is 1.0x10⁻⁶ S/cm, a very low value, which is characteristic of molecular melts. The conductivity of NbCl₅ increases slightly with increasing temperature. The value of 9.4x10⁻⁷ S/cm (218°C) shows good agreement with that of Blitz (2.2x10⁻⁷ S/cm at 220°C)(11). Often the very small conductivity of NbCl₅ melt is augmented by the presence of highly
conductive impurities such as HCl. However, since the measured specific conductivities are in agreement, and the NbCl$_5$ was prepared in different ways, it is likely that the measured conductivity arises only from the dissociation of NbCl$_5$ itself.

Specific Electrical Conductivity of NbCl$_5$-NaCl-KCl Pseudo Binary System

Fig. 6 shows the temperature dependence of the conductivity for the NbCl$_5$-NaCl-KCl system. When a small amount (10mol%) of NaCl-KCl is added to pure NbCl$_5$, the conductivity rises to a very large value. It also increases rapidly with increasing temperature. This suggests that the conductivity mechanism changes from molecular NbCl$_5$ to an ionic species. From 80 to 60 mole% composition of NbCl$_5$, conductivity changes only slightly. In this composition range there are two liquid phases (Fig.4). The upper layer is pale brown, the lower is black. The conductivity of the latter liquid was measured because the electrode made contact only with the heavier black liquid. This phase corresponds to the (Na$_x$K)$_{100-x}$NbCl$_6$ eutectic melt. In the NaCl-KCl rich region, conductivity increases with the increasing concentration of ionic species.

The specific electrical conductivity isotherms for this system are shown in Fig. 7. There are three regions to the composition dependence of conductivity: I, a rapid increase region with low conductivity; II, a flat region; III, a gradually increasing region with high conductivity. Region I represents the transition from molecular to ionic conductivity. Region II corresponds to the two liquid phase of this system. Region III is influenced primarily by the contribution of the increasing concentration of the NaCl-KCl electrolyte.

The relation between log K and 1/T for NbCl$_5$-NaCl-KCl pseudo binary system is linear for almost all compositions (Fig.8). However, in the area of 90 mol% NbCl$_5$ two slopes appear which correspond to the changes of the melt structure. The activation energy of 3 kcal/mol is close to that of alkali halide melts.

The phase diagram and conductivity for the TaCl$_5$-NaCl-KCl pseudo binary system will be presented in detail. Viscosities and densities of the above systems will be also reported.

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Fig. 1 Conductance cell.

(a) For NbCl$_5$–NaCl–KCl system

(b) For NbCl$_5$

Fig. 2 Assembly for the measurement of electrical conductivity.

Fig. 3 DTA cell.
Fig. 4 Phase diagram for the NbCl₅-NaCl-KCl (1:1) pseudo binary system.

Fig. 5 Specific electrical conductivity of NbCl₅.
Fig. 6 Temperature dependence of conductivity for NbCl$_5$-NaCl-KCl(1:1) systems.
Fig. 7 Specific electrical conductivity isotherms for NbCl$_5$-NaCl-KCl(1:1) systems.

Fig. 8 Log K vs. 1/T plot for NbCl$_5$-NaCl-KCl(1:1) system.