Electrowinning of Tungsten From Fused Bath Composed of Calcium Chloride, Calcium Oxide and Tungstic Oxide

by

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텅그스텐의 熔融鹽電解

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要 約

CaCl₂, CaO 및 WO₃ 로 構成되는 熔融鹽을 黑鉛陽極과 鐵陰極으로 電解하여 순수한 金屬텅그스텐을 얻는 方法에 관하여 실험하였다.

電氣分解에 적합한 熔融浴을 選定하기 위하여 CaCl₂-CaO 系와 CaCl₂-CaWO₄ 系에 관한 二相 狀態圖를 작성하였으며 同時에 CaCl₂ 와 WO₃ 와의 高溫下에서의 化學反應을 검토하여 安定한 電解浴을 얻기 위해서는 一定量의 CaO 가 添加되어야 할 것임을 알 수 있었다.

炭素 陽極을 사용하여 WO₃ 를 W 와 CO 로 분해시킬 때의 分解電壓은 −0.1 volt 이었으며 熱力學的 計算에 의한 것은 −0.3 volt 이었다.

熔融鹽을 電氣分解한 結果 金屬텅그스텐이 100%에 가까운 電流效率로 電極에 析出되나 이는 陽極에서 二次的으로 발생하는 CO 가스에 의하여 쉽게 WC 등으로 변화하므로 순수한 텅그스텐을 얻기 위해서는 電解浴의 溫度를 1100°C 이상으로 유지하여야 된다는 것을 알게 되었다.

電解浴의 組成은 可及的 低融點과 WO₃의 分解, CaCl₂ 의 蒸發 등을 억제하기 위해서는 CaCl₂ 100分에 대하여 CaO 와 WO₃ 가 각 10 乃至 20分이 適切하였으며 CaO 와 WO₃의 몰比率은 1 이상이 요구되었다.

陰極 電流密度를 1∼5 amp/cm² 의 範圍에서 變化시켜도 電流效率에 큰 影響이 없었다.

Abstract

The electrolysis of tungstic oxide dissolved in the bath of calcium chloride and calcium oxide was studied to produce metallic tungsten using carbon as anode and iron as cathode in the temperature range of 900° to 1200°C.

The binary phase diagrams CaCl₂-CaO and CaCl₂-CaWO₄ systems were constructed to determine the suitability of bath composition and the range of temperatures for the electrolysis. As WO₃ reacted with CaCl₂ to form oxychloride in the fused salt, the addition of the proper amount of CaO was necessary to avoid the loss of WO₃. The optimum compositions of fused bath were CaCl₂ 100 parts, CaO and WO₃ each 10 to 20 parts, with the CaO, WO₃ ratio greater than unity, to keep freezing point low and to prevent the vaporization of CaCl₂. The observed decomposition voltage at which WO₃ decomposes to W and CO was −0.1 volt, whereas the calculated was −0.3 volt.

Metallic tungsten deposited at the cathode reacted easily with CO formed secondarily at the anode surface, to form WC below 1050°C, so that the cell temperature should be above 1050°C. The effects of cathode current densities on current efficiency were minor in the range of 1 to 5 amp/cm².

I. Introduction

Tungsten.has the highest melting tmperature $(3410 \pm 20°C)$ of all known metals. Unlike ordinary smelting and refining practice, therefore, the metallurgy of tungsten must employ methods of chemical decomposition and purification rather than pyro-metallurgy. Treatment of tungsten ores for the production of metallic tungsten generally involves intermediate products such as tungstic acid or ammonium para tungstate. These are then decomposed and reduced to the metallic tungsten in powder form.

For most of the tungsten products the metal powder is produced by reduction of tungstic oxide with hydrogen. As a part of tungsten metallurgy, the production method of tungsten was studied by fusion electrolysis.

The problem of obtaining metallic tungsten by electrolytic reduction has been attacked by numerous investigators. The electrolysis of aqueous solutions of tungstates did not lead to the productions of tungsten powder, but results only in plating a thin layer of tungsten on metallic cathodes[1].

Jackson, Russell and Merill[2] have obtained tungsten powder at a mercury cathode by using a 4.6N hydrofluoric acid solution, a current density of 65 to 100 amp/cm², and maintaining the bath at 95°C. Using 2 cc of mercury as cathods, only a few milligrams of tungsten were obtained in a run of several hours.

Halt and Kahrenburg[3] obtained useful results from numerous experiments on plating brass or copper cathodes with tungsten.

In the electrolysis of fused bath, Zettnow[4] obtained an impure product upon electrolysis of sodium tungstate. Key[6], in 1919, prepared tungsten electrolytically by dissolving tungstic oxide in boric acid at a temperature of.1200°C to 1400 °C and electrolyzing the fused bath thus formed. As a result, very finely divided metal was obtained. Mann and Halvorsen[6], in 1924, electroplated grey metallic tungsten on iron from a fused lithium chloride bath.

Hartmann, Ebert and Brestschneider patented a method of producing metallic tungsten electrolytically in a fused phosphate bath. Ma[8] made a success on a laboratory scale, in the direct production of tungsten metal from ore by means of electrolyzing a fused bath composed of alkali borate or alkali phosphate and tungsten ores. But the fused alkali bath for the electrolytic production of tungsten metal has the disadvantage of tungsten bronze formation when an excess of tungstic oxide is employed.

Slatin[9] invented a new method for obtaining metallic tungsten free from tungsten bronze, electrolyzing oxide of tungsten or molybdenum dissolved in a fused bath composed of calcium halide and calcium oxide. It appears, however, that basic and theoretical studies were not carried out.

The purpose of this work was to determine the feasibility of electrowinning of tungsten directly from tungsten compounds in a fused calcium oxide and calcium chloride bath. The investigation was made on the effect of electrolyte composition, temperature and current density. The phase diagrams of calcium tungstate-calcium chloride system and calcium chloride-calcium oxide system within the range of fusion electrolysis were constructed by the method of the cooling curves. Decomposition voltage was measured by means of the current-voltage measurement and compared with the theoretical value, and further the chemical reactions between bath compositions were also investigated.

II. Experimental Apparatus and Procedures

A. Experiment on Phase Diagram : Studies on phase diagrams of calcium chloride-calcium oxide and calcium chloride-calcium tungstate systems were carried out by means of the cooling

H: Heating elements (Ni-Cr wire)
B: Bath
C: Pt crucible
P: Protection tube
T: Thermocouple
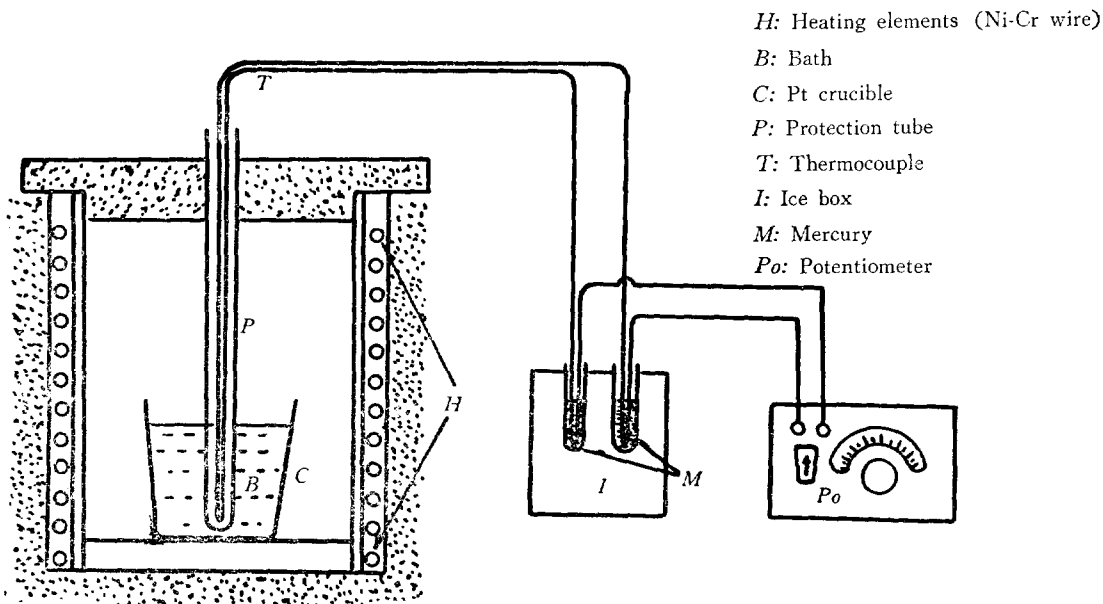I: Ice box
M: Mercury
Po: Potentiometer

Fig. 1. Apparatus for thermo-analysis.

curves within the temperature range of fusion electrolysis.

The arrangement of equipments used in this work is shown in Fig. 1. The furnace was the crucible type Ni-Cr furnace. A platinum crucible, 3.5 cm in diameter and 3.5 cm high, was placed in the center of the furnace.

The thoroughly mixed dry charge was put into the crucible. The temperature of the fused bath was measured with a chromel vs. alumel thermocouple which was protected with a platinum tube. The samples were chemically pure. Composition temperature phase diagrams were obtained by means of the cooling curves. The cooling rate was about 5°C per minute.

B. Decomposition Voltage Measurement :
The decomposition voltage was determined by the general method of the current-voltage measurement. The equipments used in this work are shown in Fig. 2. The furnace was the crucible type silicon carbide furnace with the capacity of 6 KW. Bath voltage was measured with a potentiometer. The furnace temperature was automatically controlled to maintain the predetermined temperature.

A graphite block was placed in the bottom of

the furnace, which served as a cell rest and conductor for the direct current power source. A stainless steel crucible, into which a zirconia tube was inserted so that the current may mainly

B: Lead battery
A: Ammeter
V: Potentiometer
W: Pt wire
Z: Zirconia tube
S: Stainless steel container
C: Carbon anode
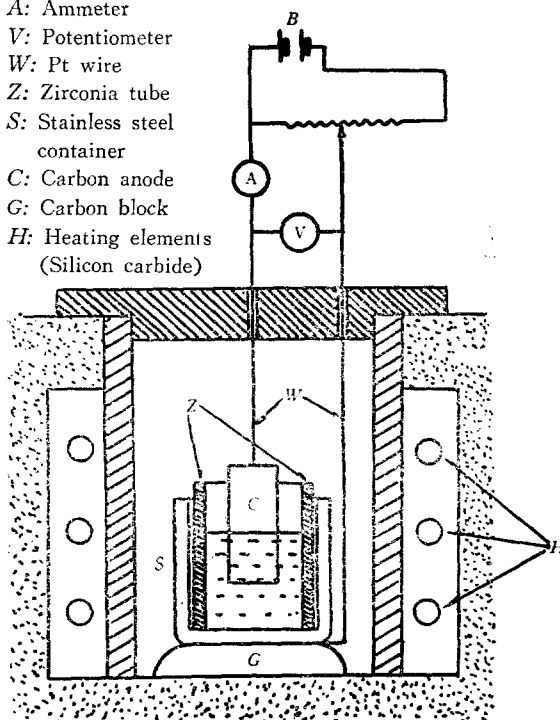G: Carbon block
H: Heating elements (Silicon carbide)

Fig. 2. Apparatus for decomposition voltage measurement.

pass through the bottom, was placed on the graphite block. In the furnace, platinum wire was inserted between the graphite block and the crucible for the electric connection. As shown in Fig. 2, the crucible served as cathode, and the anode suspended by a platinum wire was the artificial graphite electrode.

Platinum could not be used as an anode because of its anodic dissolution.

An electrolyte charge consisting of 100 grams of calcium chloride, 20 grams of calcium oxide and 10 grams of tungstic oxide was put into the crucible. After charging the electrolyte mixture, the temperature was gradually raised to 1100°C. The carbon electrode was introduced into the bath and connected, through rheostats, to the lead storage battery. The applied voltage was increased gradually and the current flowing through the cell was measured as a function of the potential difference across the electrodes.

C. Electrolysis : The arrangement of equipments is schematically depicted in Fig. 3. The electrolysis unit has basically an externally heated graphite cell with a steel cathode. The furnace was the same as that used in decomposition voltage measurement. The furnace temperature was controlled by the autometric controller. The amount of electricity that passed was measured with a copper coulometer.

A graphite block was placed on the bottom of the furnace and served as a cell rest and conductor for the direct current power source. A graphite crucible was placed on the block and functioned as cathode. After charging the electrolyte mixture of calcium chloride, calcium oxide and tungstic oxide, the temperature was gradually increased to the predetermined temperature range of 900°C to 1200°C. After stabilizing at the above temperature, the electrode was lowered into the bath, and electrolysis was started usually for 30 to 40 minutes at the current density from 1 to 5 amp/cm². After completion of electrolysis the centrally positioned cathode was removed.

The electrolyte adhering to the cathode was permitted to drain from the deposited metal for a while, then the cathode was water quenched. The electrolyte was mostly water soluble and readily dissolved from the deposited metal.

During the electrolysis, the graphite crucible was subjected to oxidation and corrosion below the bath level, as a result, some mechanical carbon contamination occurs in the metal, but is removed readily by several water washes. To avoid any possible contamination from residual electrolyte, the metal is treated with dilute or concentrated hydrochloric acid. It was then dried, weighed and analyzed by X-ray.
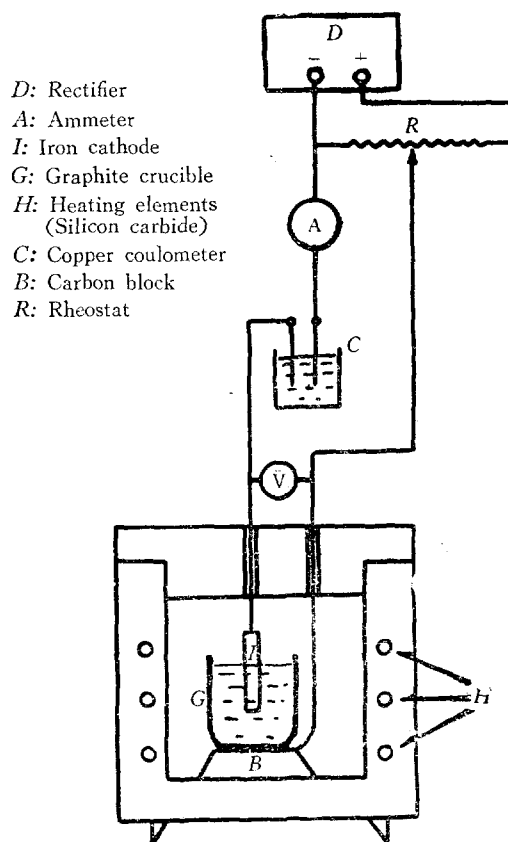

D: Rectifier
A: Ammeter
I: Iron cathode
G: Graphite crucible
H: Heating elements
   (Silicon carbide)
C: Copper coulometer
B: Carbon block
R: Rheostat

Fig. 3. Apparatus for electrolysis.

Ⅲ. Experimental Results and Discussions

A. Decomposition Voltage ;

1) Measured Decomposition Voltage :   The

voltage-current density characteristics are plotted in Fig. 4, and the decomposition voltage was found to be -0.1 volt in case of carbon anode.

2) Theoretical Decomposition Voltage: In order to calculate decomposition voltage, the following assumptions were made. (i) It is assumed that the fused bath is saturated with tungstic oxide WO_3. The exact saturation value was not determined, but this assumption was made for convenience. If the bath is saturated with tungstic oxide, dissolved tungstic oxide should be in equilibrium with solid tungstic oxide and the free energies of both sides will be equal. Therefore, the free energy of decomposition of dissolved tungstic oxide is thermodynamically equal to that of undissolved solid tungstic oxide. (ii) It is assumed that oxygen is generated at the anode during the electrolysis. In practice, oxygen reacts with carbon of the anode, liberating the mixture of CO and CO_2. But it is assumed that free oxygen is generated at the start. On the above assumptions, reaction (1) proceeds by 6 FE, where F is faraday and E is the theoretical decomposition voltage. The bath temperature is assumed as $1,100°C$ $(1373°K)$.

$$WO_3 = W + \frac{3}{2}O_2 \qquad (1)$$
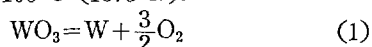
The free energy change of reaction (1) is[14]

$$\Delta G = 201,500 + 10.2\ T \log\ T - 91.7\ T \qquad (2)$$
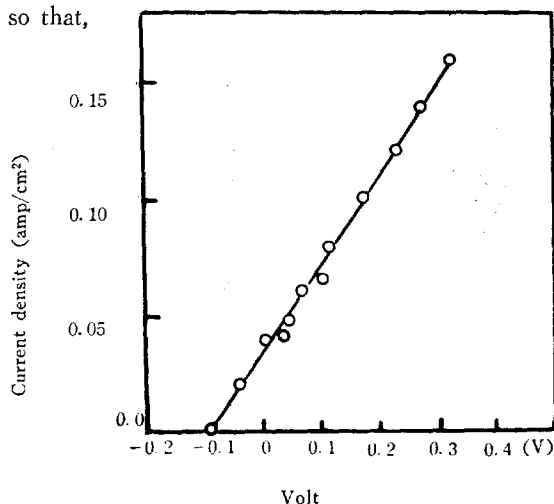
so that,

Fig. 4. Current-voltage curve.

$$E = \Delta G/6\ T = 1.455 + 7.38 \times 10^{-5}\ \log\ T - 6.63 \times 10^{-4}\ T \qquad (3)$$

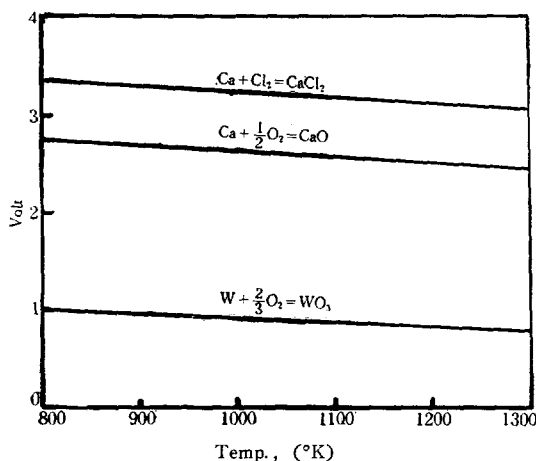Decomposition voltage at $1370°K$ $(1100°C)$ is

$$E = 0.86\ V$$

Fig. 5. Decomposition voltage.

The theoretical decomposition voltage calculated at $1370°K$ is 0.86 volt when the fused bath is saturated with WO_3. Since anode gas is in practice the mixture of CO and CO_2, the partial pressure of oxygen surrounding anode is less than unit atmosphere. If decomposition occurs under the partial pressure of oxygen Po_2, the decomposition voltage should be reduced by ΔE.

$$\Delta E = \frac{RT}{4\ F}\text{In}\frac{1}{Po_2} = \frac{0.0002}{4}T\ \log\frac{1}{Po_2} \qquad (4)$$

Po_2 is equivalent to the partial pressure of oxygen in reactions (5) and (6). When main anode gas is CO_2,

$$CO_2 = CO + \frac{1}{2}O_2 \qquad (5)$$

when main anode gas is CO,

$$2CO = 2C + O_2 \qquad (6)$$
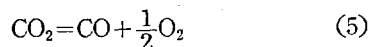
If Boudouard equilibrium, $C + CO_2 = 2CO$, is always maintained among the gases at anode, [11]

$$\log\ Pco^2/Pco_2 = 40,800/4.576\ T$$
$$+ 4.864 \log\ T - 0.301 \times 10^{-2}\ T + 0.627$$
$$\times 10^{-6}\ T^2 - 0.479 \times 10^{-10} \times T^3 - 2.926$$

Since anode gas is mostly CO at the temperature of $1100°C$, the partial pressure of oxygen,

P_{O_2}, in the reaction (6) can be calculated from the following equations;[10]

$$\Delta G = 50,800 - 4.1\ T \log T - 0.54 \times 10^{-3} T^2$$
$$+ 2.190 \times 10^{-5}\ T^{-1} + 57.58\ T$$

$$K = \frac{P_{O_2}}{P_{CO}^2}$$

Where ΔG, K, P_{O_2} and P_{CO} are the free energy change, the equilibrium constant, the partial pressure of oxygen and the partial pressure of carbon mone-oxide of the reaction (6) respectively. Setting $T = 1,373°K$ and $P_{CO} = 1$ in the above equations, the partial pressure of oxygen P_{O_2} is calculated to be 2.95×10^{-18} atm. from the following equation.

$$-\Delta G = RT\ \ln K = RT\ \ln P_{O_2}$$

Substitution of 2.95×10^{-18} in P_{O_2} of equation (4) gives

$$\Delta E = 1.2\ \text{volt}$$

The bath voltage therefore should be reduced by about 1.2volt. When the bath is saturated with WO_3 and the equilibrium among CO_2, CO and C is maintained, the theoretical decomposition voltage at $1,100°C$ is given by
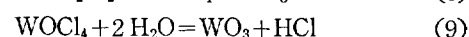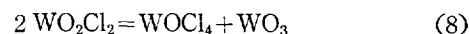
$$E = 0.9 - 1.2 = -0.3\ \text{volt}$$

3) Comparison of the Measured and the Calculated Decomposition Voltages: Compared with the calculated decomposition voltage, the measured value is 0.2 volt higher. But this difference may be allowed as a negligible error considering the fact that experimental measurements of decomposition voltages usually do not agree with theoretical values, owing to the factors such as chemical interaction of the electrodes with the electrolyte, electrode conditions in a non-standard state, temperature fluctuations, and electrode polarizations.

Fig. 5 shows the calculated decomposition voltages of components of the bath as a function of the temperature. In general, the compound having the lowest decomposition voltage is first decomposed in the mixed bath. Considering the facts mentioned above, it is evident, therefore, that the tungstic oxide is decomposed at first.

As for gases generated at the anode, no investigation was made in this experiment, but Harvey L. Slatin[9] could not detect chlorine gas in the anode gases on electrolyzing the similar fused bath.

B. Reaction of Calcium chloride and Tungstic oxide: On adding tungsten oxide to calcium chloride melt, dense white fumes were observed which were oderless. This finding coincides with Slatin's investigation[9]. Yellow powders were deposited on the wall of zirconia tube, through which the fume passed. The powders were scraped for X-ray analysis. They were found to be tungstic oxide WO_3. After fuming, the melt was cooled and dissolved in water. Calcium chloride was dissolved and the white precipitate was obtained. The precipitate was found to be calcium tungstate as a result of X-ray analysis. From these facts and reference[16] the fume can be concluded to be WO_2Cl_2 by the reaction(7). Since WO_2Cl_2 is very unstable, it is readily decomposed by the reaction(8) at temperatures above $140°C$.

$$CaCl_2 + 2\ WO_3 = CaWO_4 + WO_2Cl_2 \qquad (7)$$
$$2\ WO_2Cl_2 = WOCl_4 + WO_3 \qquad (8)$$
$$WOCl_4 + 2\ H_2O = WO_3 + HCl \qquad (9)$$

$WOCl_4$ is also very unstable and changed into WO_3 and HCl in the wet atmosphere. The tungstic oxide was deposited by the reactions (8) and (9), and the white precipitate calcium tungstate was produced by the reaction(7).

From above facts, it was concluded that it is impossible for tungstic oxide to dissolve in calcium chloride melt without loss.

C. Reaction of Calcium oxide and Tungstic oxide: Tungstic oxide is dissolved in the bath composed of calcium chloride and calcium oxide with slight fuming. This can be attributed to the following reaction.

$$CaO + WO_3 = CaWO_4$$
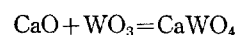
Its forming temperature was $580° \sim 950°C$ and molecular heat of formation at $25°C$ was -39.6 kcal. [13]

D. Calcium chloride-Calcium oxide system:

Phase diagram of calcium chloride-calcium oxide system is shown in Fig. 6. A peritectic is seen near 11% of CaO. This is equivalent to $4CaCl_2$. CaO (CaO 11.2%). As shown in Fig. 6, 20 to 30% of calcium oxide can be dissolved in calcium chloride at the temperature of about 1,000°C.
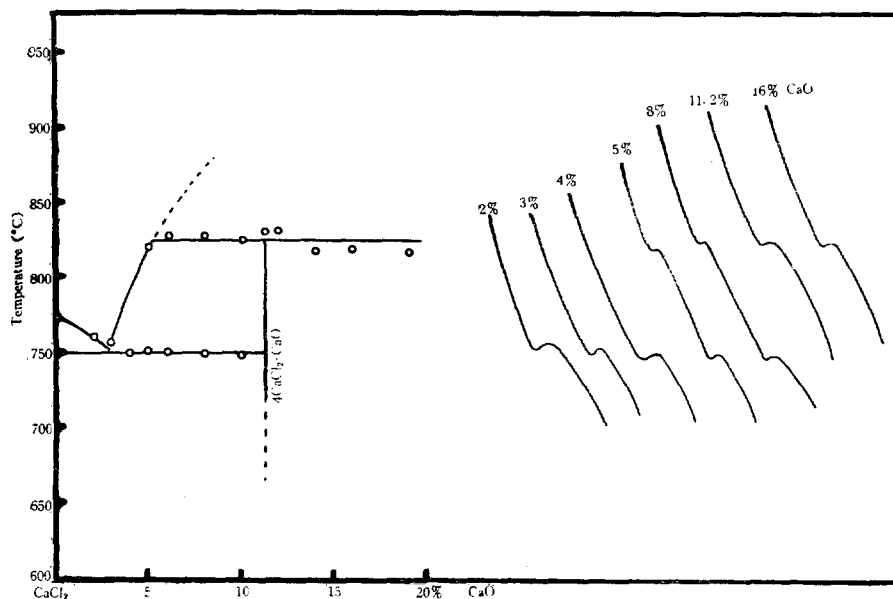
Fig. 6. Cooling curves and phase diagram of $CaCl_2$-CaO system.

E. Calcium chloride-Calcium tungstate system: Considering the mutual reactions of calcium oxide, calcium chloride and tungstic oxide, it is believed that tungstic oxide cannot exist in the stable form in the fused bath composed of calcium chloride and calcium oxide but can exist as a state of calcium tungstate. Thus the bath composition will be calcium chloride, calcium oxide and calcium tungstate eventually. Therefore, the relation between calcium chloride and calcium tungstate was investigated.

The phase diagram of calcium chloride-calcium tungstate system is shown in Fig. 7. It shows that calcium chloride and calcium tungstate can form an eutectic mixture. From the facts mentioned above, it is concluded that the molecular
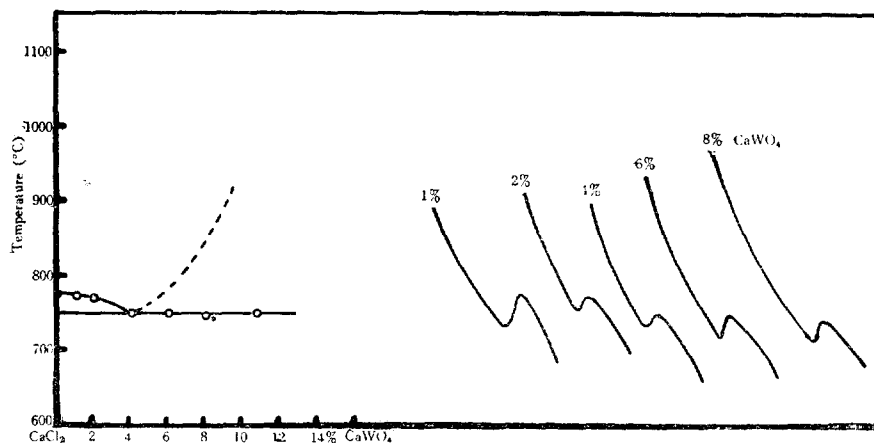
Fig. 7. Cooling curves and phase diagram of $CaCl_2$-$CaWO_4$ system.

ratio of calcium oxide to tungstic oxide in the electrolyte should be greater than 1:1 in order to prevent loss of tungstic oxide. Therefore, for the electrolytic production of tungsten, calcium tungstate instead of tungstic oxide can be supplied in the electrolyte.

F. Effect of Temperature on Electrolysis:

In determining the optimum temperature of the electrolyte for the production of tungsten from a fused salt bath containing a mixture of calcium chloride, tungstic oxide and calcium oxide, experiments were carried out at the temperatures of 900, 950, 1000, 1,050, 1,100 and 1,200°C. The results of the experiment are summarized in Table 1 and plotted in Fig. 8. As shown in Table 1 and Fig. 8, at temperatures below
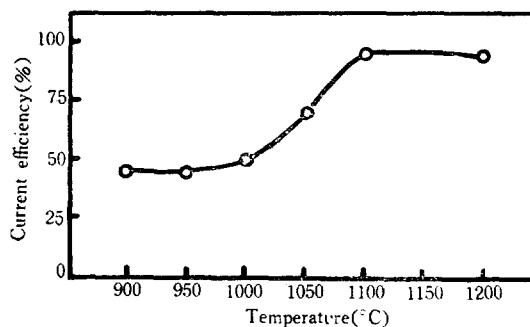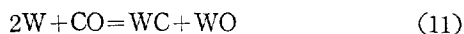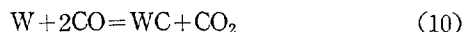

Fig 8 Effect of Temperature on Current Efficiency.

1,000°C cathode deposits were tungsten carbide with a current efficiency of below 50%. At temperatures above 1,000°C, tungsten could be obtained with the current efficiency near 100%.
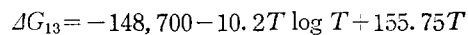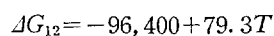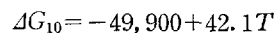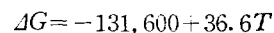
Table 1

Bath	Composition(gr.)		Bath	Cathode	Current	Cathode
CaCl$_2$	CaO	WO$_3$	Temp. (°C)	C. D. (A/cm^2)	eff. (%)	Deposits
100	10	10	900	3	45	WC
100	10	10	950	3	44	WC
100	10	10	1000	3	51	WC, minor W$_2$C
100	10	10	1050	3	70	W, minor WC&W$_2$C
100	15	10	1100	3	96	W
100	20	10	1200	3	95	W

In the course of electrolysis, tungsten deposit was obtained at the cathode and CO gas was generated at the anode. On the assumption that the following reactions (10)~(13) will take place by the reaction of CO and W, the free energy change in each reaction can be calculated.

$$W + 2CO = WC + CO_2 \qquad (10)$$
$$2W + CO = WC + WO \qquad (11)$$
$$3W + 2CO = 2WC + WO_2 \qquad (12)$$
$$4W + 3CO = 3WC + WO_3 \qquad (13)$$

ΔG_{10}, ΔG_{11}, ΔG_{12} and ΔG_{13}, the free energy changes of equations (10), (11), (12) and (13) respectively, were calculated by Hess' law using the following data. [14]

$$C + C_2 = CO_2 \qquad \Delta G = -94,200 - 0.2T$$
$$C + \frac{1}{2}O_2 = CO \qquad \Delta G = -26,700 - 20.95T$$

$$W + C = WC \qquad \Delta G = -9,100 + 0.4T$$
$$W + 3/2O_2 = WO_3 \quad \Delta G = -201,500 + 10.2T$$
$$W + O_2 = WO_2 \qquad \log T - 91.7T$$
$$\Delta G = -131,600 + 36.6T$$
$$\Delta G_{10} = -49,900 + 42.1T$$
$$\Delta G_{12} = -96,400 + 79.3T$$
$$\Delta G_{13} = -148,700 - 10.2T \log T + 155.75T$$
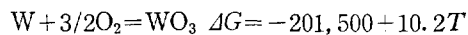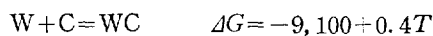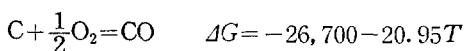
ΔG_{11} was not calculated because no data on WO was available. These are shown in Fig. 9.

If reaction (10) takes place in the bath. the free energy change at temperatures below 1,215° K (942°C) will be:

$$\Delta G_{10} < 0$$

The reaction therefore proceeds simultaneously to the right and results in the formation of WC, and the free energy change at temperatures above 1,215°K will be:

$\Delta G_{10} > 0$

The reaction will not proceed to the right and tungsten can be obtained.

In the experiment, tungsten was obtained at temperatures above around 1,050°C. The difference between the calculated temperature and the measured was about 100°C. The difference is acceptable considering errors arising from high temperature experiments and thermodynamic values calculated by Hess' law. When WC was formed, the current efficiency was only around 50%. The above fact shows that the reaction (10) cannot be a final reaction, because the current efficiency should be around 100% since one atom of tungsten can be converted into one molecule of WC. Carbon dioxide oxidizes tungsten at elevated temperatures. If carbon dioxide formed by the reaction (10) is consumed to oxidize tungsten deposited at the cathode, the reactions (11), (12) and (13) can be assumed to take place in the bath. As shown in Fig. 9, ΔG_{12} and ΔG_{13} show tendencies similar to ΔG_{10}, though they have a little different carbide form-

ation temperatures. If the reaction (12) takes place in the bath, current efficiency will be about 67% in case of the carbide formation, and if the reaction (13) takes place, the current efficiency will be about 75%. From the experimental results, however, we note that current efficiencies were only around 50%. These facts appear to justify the reaction (11). WO is the first stage oxide and may be stable at the very high temperature, [13] and is the intermediate product appearing as an adsorption layer on metallic tungsten when it is reacted by oxygen[15]. It appears that the formation of WC with the current efficiency of approximately 50% at such low temperature can be attributed to the reaction (11). The deposition of tungsten with the current efficiency near 100% at temperatures above 1,100°C can be attributed to the fact that there is no loss of tungsten due to the carbide formation and oxidation. It is necessary to maintain the bath temperature above 1,100°C to obtain high purity tungsten within the temperature range examined (900°C~1200°C).

G. Effect of Current Density on Current Efficiency: To determine optimum current density, the electrolysis was carried out at 1, 2, 3, 4 and 5 amp/cm² in the bath containing 100 parts calcium chloride, 20 parts calcium oxide and 10 parts tungstic oxide at 1,100°C. The results are
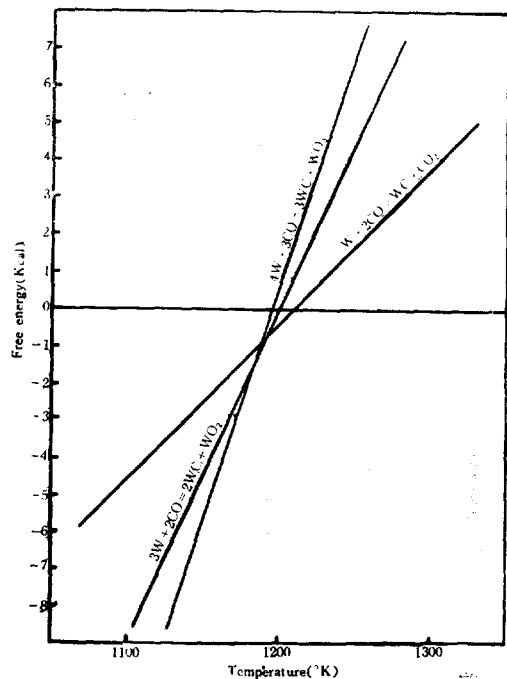

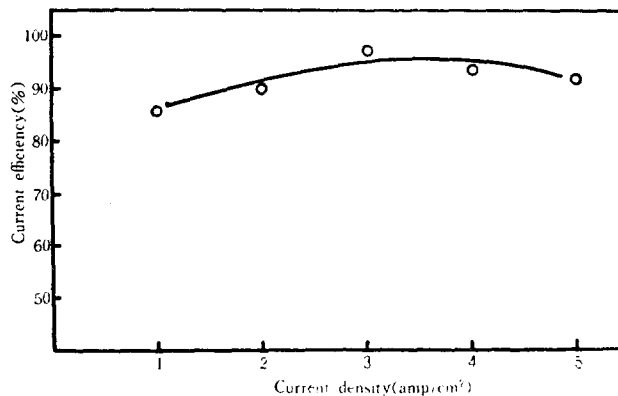Fig. 9. Free energy-temperature relation.

Fig. 10. Effect of current density on current efficiency.

plotted in Fig. 10.

From the results shown in Fig. 10, we note that the current efficiencies of more than 90% were obtained and the current density had almost no effect on the current efficiency within the range examined.

H. Effect of Bath Composition on Current Efficiency: To determine the optimum composition of the electrolyte for the production of tungsten from a fused electrolyte bath containing tungstic oxide, calcium chloride and calcium oxide, a series of experiments were conducted at $1,100°C$ and at current density of 3 amp/cm^2. The results are plotted in Fig. 11-A and Fig. 11-B.

With a bath temperature of $1,100°C$ and current density of 3 amp/cm^2, the highest current efficiency of 98% was obtained. The composition of this bath was 20 parts calcium oxide, 100 parts calcium chloride and 10 parts tungstic oxide. As to the effect of calcium oxide concentration on current efficiency, keeping the concentration of calcium chloride and tungstic oxide constant, it was found that as the calcium oxide concentration increases, the current efficiency decreases slightly. As to the effect of WO_3 concentration on current efficiency, keeping the
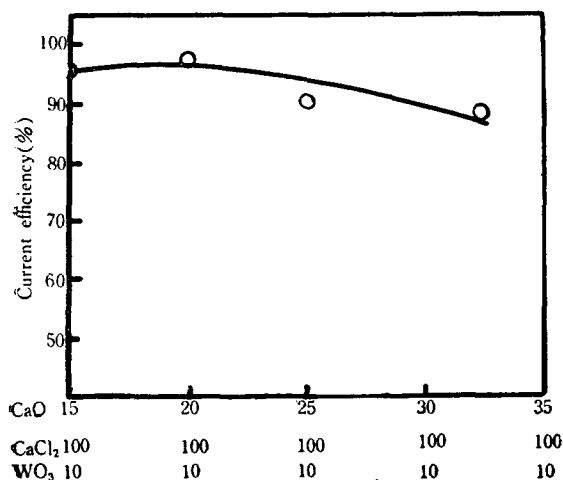

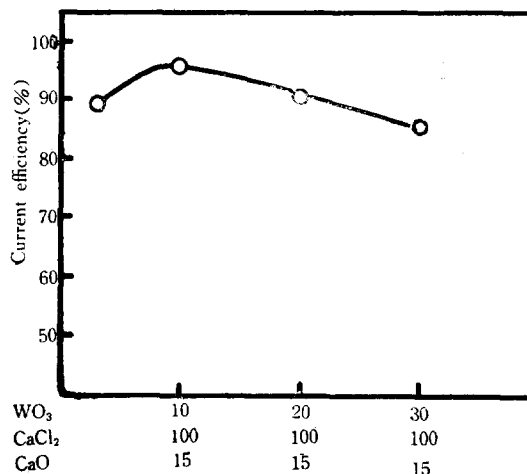| WO₃	10	20	30
CaCl₂	100	100	100
CaO	15	15	15

Fig. 11-B Effect of WO_3 concentration on current effieciency.

concentration of calcium chloride and calcium oxide constant, it was found that as the concentration of tungstic oxide in the bath is increased, the current efficiency rises, reaches the maximum and then falls again. These phenomena can be attributed to the polarization. When the percentage of calcium oxide and tungstic oxide was higher, the bath viscosity was greater. An increase in the bath viscosity increased the extent of polarization. An increase in the polarization decreased tungsten concentration at the cathode. This effect interferes tungsten ion discharge and may cause codeposition of calcium, and therefore the deposition efficiency of tungsten may decrease.

Ⅳ. Conclusion

With the view of obtaining the high purity metallic tungsten, the electrolysis of fused salt was carried out under various conditions. The tungstic oxide was dissolved in the bath of calcium chloride and calcium oxide system. The anode was artificial graphite and the cathode was platinum or iron rod.

For the deposition of metallic tungsten, the temperature dependence was particularly important by the fact that tungsten metal deposited

CaO	15	20	25	30	35
CaCl₂	100	100	100	100	100
WO₃	10	10	10	10	10

Fig. 11-A Effect of CaO concentration on current efficiency.

at cathode may be converted into tungsten carbide by the secondary reaction with carbon monoxide formed inevitably at anode surface during the electrolysis. In this connection, thermodynamic calculations have been made for the temperature of formation of metallic tungsten to compare with the observed values, and it was concluded that both the calculated and observed values coincide within the range of allowable errors.

The results of experiment are summerized as follows.

(1) The electrolysis takes place àt the expense of the tungstic oxide and carbon anode.

(2) Tungstic oxide cannot be dissolved into calcium chloride without loss because tungstic oxide is reacted upon by calcium chloride with the liberation of volatile tungsten oxychloride.

(3) Tungstic oxide reacts with calcium chloride and calcium oxide with the formation of calcium tungstate at elevated temperatures. The molecular ratio of calcium oxide to tungstic oxide in the bath must therefore be greater than 1:1 and the source of tungsten can be supplied from calcium tungstate instead of tungstic oxide in the electrolyte.

(4) On electrolysis with the carbon anode, metallic tungsten in powder form is obtained with the current efficiency near 100 percent at temperatures above 1,050°C and tungsten carbide instead of metallic tungsten is formed at temperatures below 1,050°C with the current efficiencies below 50 percent, within the temperature range of 900 to 1,200°C

(5) The optimum bath compositions for electrolysis to produce metallic tungsten are with calcium chloride to calcium oxide to tungstic oxide ratio of 100: 10-20: 10-20 by weight.

(6) The effects of cathode current density on current efficiency are not crucial factor within the range of 1 to 5 amp/cm^2 at the suitable temperatures and bath compositions.

Acknowledgements

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