

# REFINING OF CHROMIUM BY MEANS OF FUSED SALTS ELECTROLYSIS

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## 1. Introduction

Chromium, which is commercially produced by means of thermit process, is brittle and impure. Chromium base alloy has good resistance for generally oxidation and high strength, at high temperature, but is brittle at room temperature, so it has difficulties in working. The brittleness of chromium is owing to little impurities, especially oxygen, nitrogen and other gas components included in chromium. Recently, after the most recent research report, it was proved that chromium was to have ductility, only when it had nitrogen below 30 ppm. Therefore, ductile chromium can be produced by means of removing gas components from brittle chromium. High purity chromium is produced by Chroll's process (Chloride+Mg), (i) Chrom-alum process, (ii) Chromite process, (iii) iodide process, (iv) and fused salt electrolysis process (v).

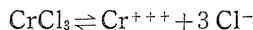
- (i)-chromium is spongy and impure,
- (ii) and (iii)-chromium has much gas contaminants as oxygen and nitrogen,
- (iv)-chromium is produced only on small scale, and
- (v)-chromium is produced by electrolysis of  $K_3CrF_6$ -NaCl fused salts.

So, the object of this investigation was for the fact that the ductile chromium was produced by electrolytic refining of fused salts ( $KCl$ - $NaCl$ - $CrCl_3$ ) with crude chromium anode. By using the fused salts, gas content such as oxygen and nitrogen could be minimized, and the produced chromium was less contaminated by the gas, so ductile.

## 2. Theoretical Consideration

### 2.1. Possibility of Electrolytic refining

For Electrolytic dissociation of  $CrCl_3$  in  $NaCl$ - $KCl$  (1 : 1) fused salts after decomposition voltage test,  $CrCl_3$  dissociates electrolytically as follows:

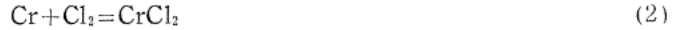


For anodic dissolution of chromium

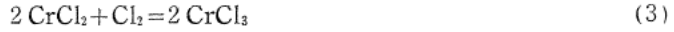


$$\Delta F^\circ = -92,660 - 22.86 T \log T + 108.2 T$$

$$\left( \Delta F = \Delta F^\circ + RT \ln \frac{(a_{CrO_2})^{2/3}}{(a_{Cr})^{2/3} (a_{Cl_2})^1} \right)$$



$$\Delta F^\circ = -92,800 - 4.85 T \log T + 42.4 T$$



$$\Delta F^\circ = -92,380 - 58.88 T \log T + 239.8 T$$

(1) and (2)-reactions both proceed, and possibility of (2) reaction is larger than (1)-reaction, but  $\text{CrCl}_2$  is changed into  $\text{CrCl}_3$  by the reaction (3), therefore  $\text{CrCl}_3$  is produced in anodic reaction.

For possibility of purification (or refining):

Crude chromium as an anode contains various impurities, which are metallic impurities and non-metallic impurities. First, as for metallic impurities, the difference of dissolution ability at anode or deposition ability at cathode for the principal metal chromium and metallic impurities is comparably shown by polarization potential at given current densities. The polarization potential is not precisely known, so we used their equilibrium potentials conveniently:

$$E^\circ = -\frac{\Delta F^\circ}{ZF}$$

$E^\circ$ : Equilibrium potential

$\Delta F$ : Free energy

$Z$ : Atomic valency

$F$ : Favadey constant

Equilibrium potentials, when the metallic impurities are laid in its chlorides, are show in Fig. 1. Fe-potential is near Cr-potential, so perfect removal of

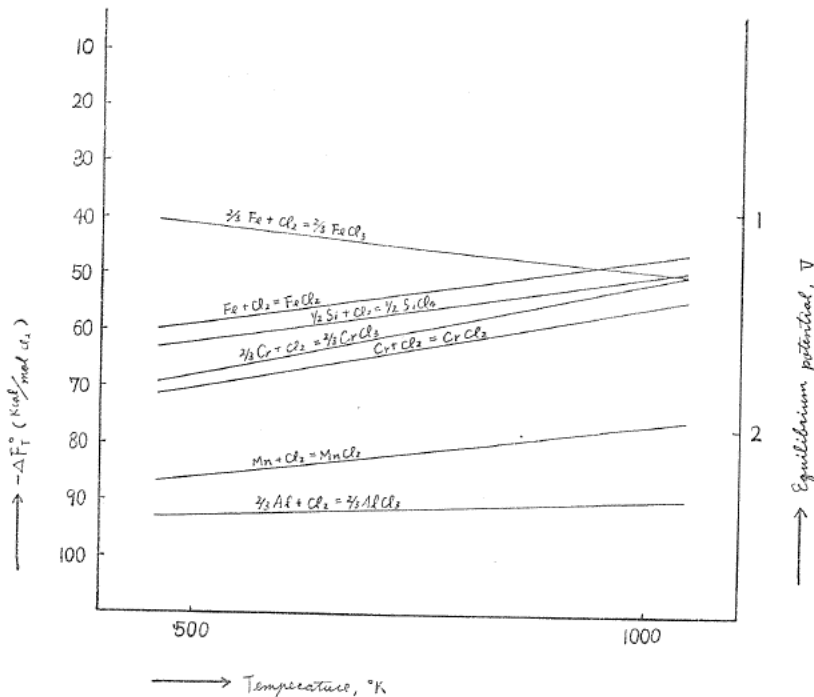


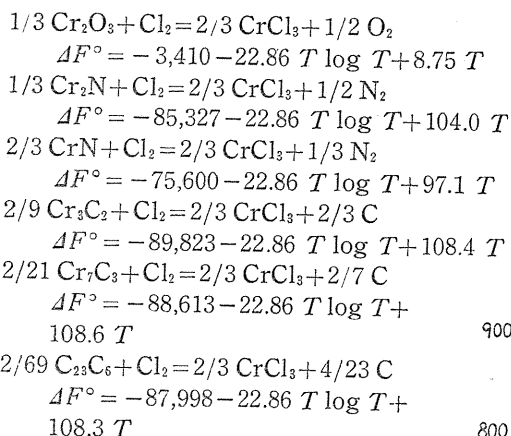
FIG. 1. Equilibrium potentials and free energy of some chlorides.

Fe is impossible. Baser metals than chromium are Mn, Al etc, and Nobler metals than chromium are Fe, Si etc. Now, if M metal is nobler and M' metal is baser 0.1 V worth than chromium, are trivalent, equilibrium concentrations of M and M' are

$$[M^{+++}]/[Cr^{+++}] \doteq \frac{1}{100} \quad [M'^{+++}]/[Cr^{+++}] \doteq 100 \quad \text{at } 1000^\circ\text{K}$$

So the metallic impurities which are noble only 0.1 V worth than chromium, dissolutes, as a iron, only one-hundredth worth of Cr into the electrolyte, but the metallic impurities which are baser only 0.1 V worth than chromium dissolutes into electrolyte 100 times of Cr and deposits at cathode, only when the metallic impurities increase 100 times worth of Cr content. The above equilibrium concentration is shown as a exponential function of  $(E_M^\circ - E_{Cr}^\circ)$ , and so the larger the difference of equilibrium potential, the better the efficiency of removing the impurity is.

For non-metallic impurities, most non-metallic impurities are compounds of chromium with oxygen or nitrogen, etc. The reactions of the impurities at anode with chlorine are as follow;



Oxide does not react at anode, but nitrides and carbides react and produce nitrogen and carbon at anode.

2.2. For fused salts

Melting point of  $CrCl_3$  is about  $1425^\circ\text{C}$ , so we let the m.p. of fused salt decrease in mixing of NaCl and KCl. Phase diagram of NaCl-KCl system is shown in Fig. 2. Pretty amount of the  $CrCl_3$  dissolutes into KCl-NaCl-fused salts at  $650^\circ \sim 800^\circ\text{C}$ . From the above consideration, by the electrolytic refining of crude chromi-

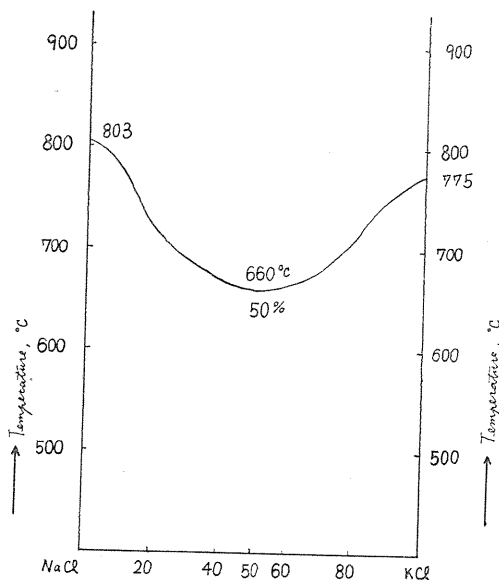


FIG. 2. NaCl-KCl diagram

um, it is possible to produce a pure ductile chromium.

### 3. Experimental and Results

#### 3.1. Experimental apparatus and materials

Experimental apparatus is shown in Fig. 3. Electrolytic cell is ceramic crucible with 50 mm inner diameter and 70 mm high. Cathode is 5 mm  $\phi$  W bar. and anode is crude chromium with silica tube for insulation.

As a crude chromium, commercial grade chromium was used, KCl and NaCl were the 1st grade reagents. And  $\text{CrCl}_3$  was produced by reaction between  $\text{Cl}_2$  and  $\text{Cr}_2\text{O}_3 + \text{C}$  mixtures at  $700^\circ\text{C}$ .

#### 3.2. Decomposition Voltage

Decomposition voltage of  $\text{CrCl}_3$  in the used KCl-NaCl  $\text{CrCl}_3$  system fused salts is inquired for the study on mechanism of electrolysis and proceeding some experiments.

Experiment conditions are; the fused salts: 5 mol%  $\text{CrCl}_3$ -47.5 mol% KCl-47.5 mol% NaCl, temperature:  $700^\circ\text{C}$ ,  $750^\circ\text{C}$ ,  $800^\circ\text{C}$ . The apparatus and connection diagrams are shown in Fig. 4 and the experimental results (voltage-current curves) are shown in Fig. 5. From experimental results, the decomposition voltages of  $\text{CrCl}_3$

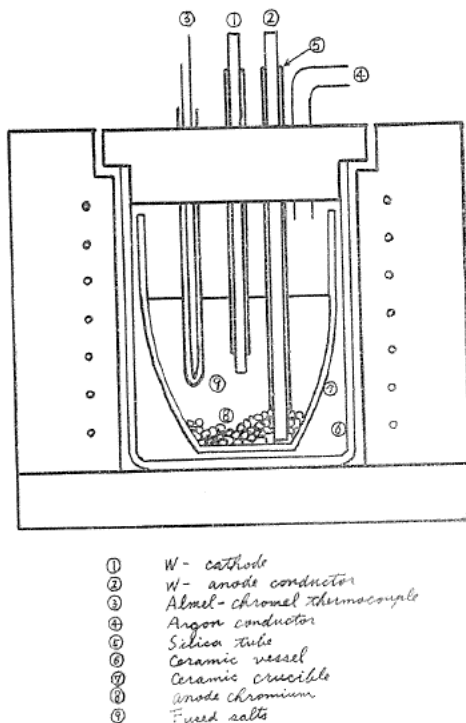


FIG. 3. Experimental apparatus of electrolytic refining.

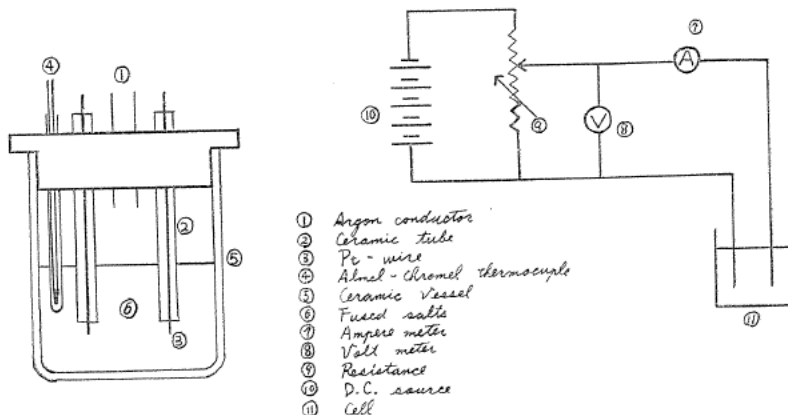


FIG. 4. Experimental apparatus for decomposition voltage.

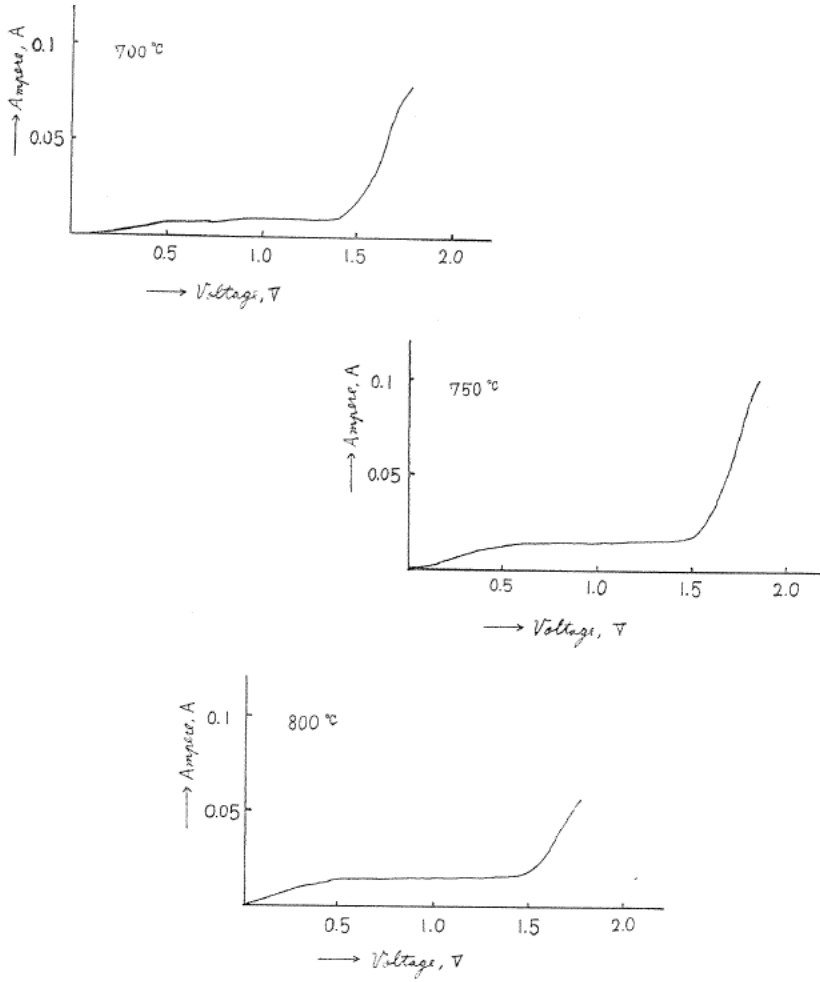


FIG. 5. Voltage-current curves for decomposition voltage.

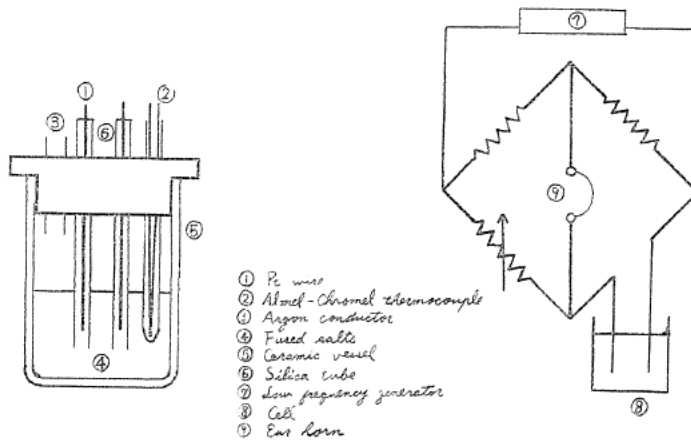


FIG. 6. Experimental apparatus of electrolytic conductivity.

in the fused salts are respectively 1.39 volt at 700°C, 1.48 volt at 750°C and 1.45 volt at 800°C.

### 3.3. Electrolytic conductivity

Experimental apparatus for electrolytic conductivity is shown in Fig. 6, and experimental conditions are the used fused salts: 5 mol%CrCl<sub>3</sub>-47.5 mol%KCl-47.5 mol%NaCl, temperature, 630°~800°C.

Experimental results are shown in Table 1. And the electric resistances for experimental electrolytic bath at the above temperatures are shown in Table 2 (The values have some range due to contact condition between crude chromium and anodic conductor.)

TABLE 1. Electrolytic Conductivity of the Fused Salts at Some Temperatures

Temp. (°C)	Electric resistance (Ω)	Specific electrolytic conductivity
800	207	2.38
775	230	2.14
750	249	1.97
725	272	1.84
700	293	1.68
673	320	1.54
650	330	1.49
635	390	1.26
630	670	0.74
629	1080	0.46

$$K(\text{S.E.C.}) = \frac{C (\text{Cell const})}{X (\text{Measured resistance})}$$

C: 492.56

TABLE 2. Electrolytic Resistances of the Fused Salts at the Electrolytic Refining Condition

Temp. (°C)	Resistance (Ω)
800	0.23-0.72
750	0.40-0.87
700	0.59-1.02
650	0.66-1.15

## 4. Electrolytic experiment

### 4.1. Experimental conditions

Electrolytic temperature, °C: 650, 700, 750, and 800.

Concentration of CrCl<sub>3</sub> in fused salts, mol%: 2.5, 5, 10, and 20.

Current density, A/cm<sup>2</sup>: 0.1, 0.25, 0.5, 1, and 2.

Distance between anode and cathode is 20 mm, and grain size of crude chromium is -24+32 mesh.

### 4.2. Experimental procedure

Put about 85 g of the mixed salts and crude chromium into the reaction crucible with close package, introducing the Ar gas. And lay the both poles in

it. Then, begin the electrolysis with flowing the D.C. After electrolysis, cool it in furnace down to room temperature, put out the crucible from the furnace. And leach the produced matter in water, wash the produced chromium with dis-water, dry and weigh the chromium.

#### 4.3. Experimental results

Table 3 shows the results for the constant concentration of  $\text{CrCl}_3$  (KCl 47.5 mol%·NaCl 47.5 mol%· $\text{CrCl}_3$  5.0 mol%) and Table 4 shows the results for some other variables with constant current density (1 A/dm<sup>2</sup>). Current efficiency-temperature curves with constant current density  $\text{CrCl}_3$  concentration current efficiency-current density curves with constant temperature and  $\text{CrCl}_3$  concentration-current efficiency- $\text{CrCl}_3$  concentration curves, and constant current density temperature are shown in Fig. 7.

The qualitative spectrographic analytical results for crude, spongy, dendritic and flaky chromiums, showed existence of Fe, Si, Al. Table 5 shows quantitative analytical results (Fe, Al, Si, N) of those chromium.

TABLE 3. Experimental Electrolytic Data in 5.0 mol%  $\text{CrCl}_3$ -47.5 mol% NaCl-47.5 mol% KCl

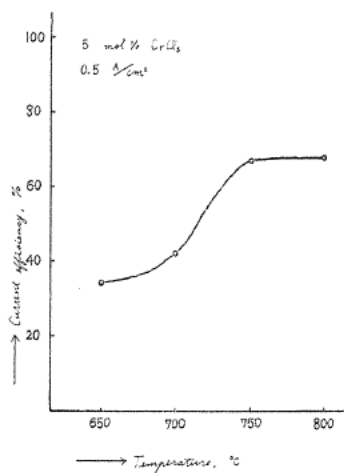
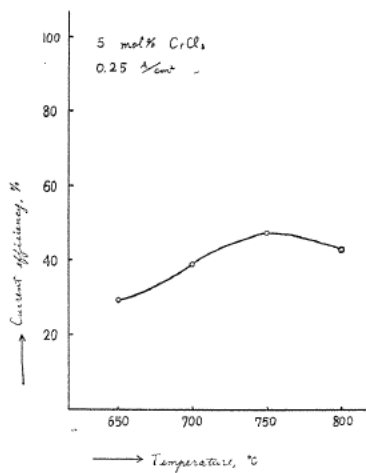
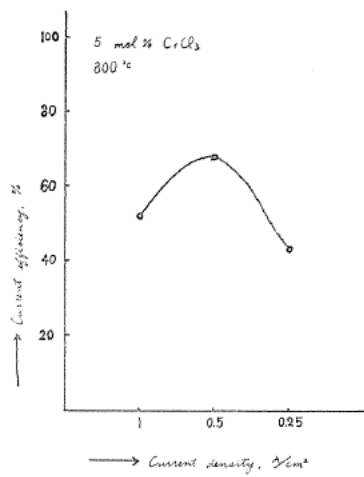
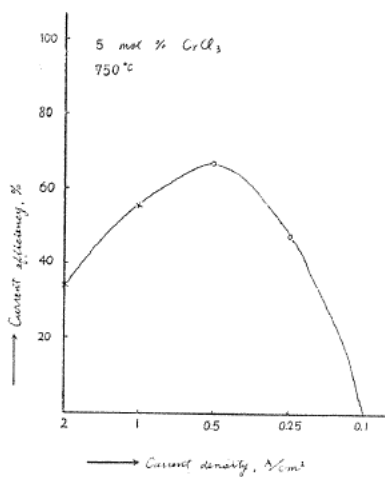
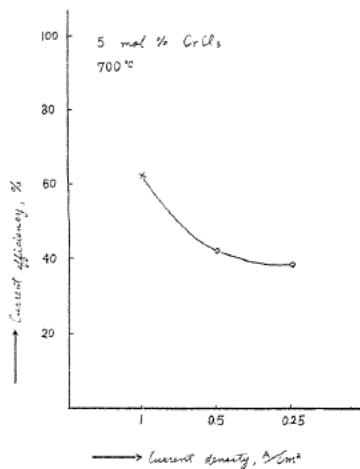
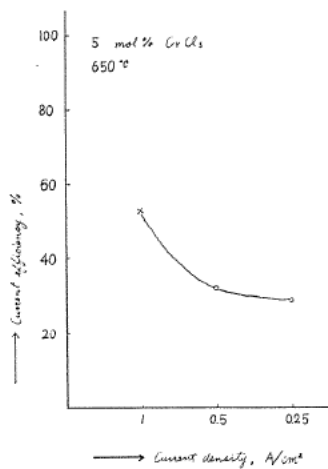
No.	Temp. (°C)	Current Density (A/dm <sup>2</sup> )	Duration (hr)	Deposit (g)	Current efficiency (%)	Deposit Conditions
1	750	2	0.51	0.512	34.1	Sponge
2	650	1	2.33	1.599	53.3	Needle or sponge
3	700	"	"	1.940	64.7	"
4	750	"	"	1.667	55.6	Dendrite or sponge
5	800	"	"	1.570	52.3	Needle or sponge
6	650	0.5	4.66	1.154	34.5	Dendrite
7	700	"	"	1.265	42.2	Dendrite or flake
8	750	"	"	2.030	67.7	"
9	800	"	"	2.044	68.1	Dendrite
10	650	0.25	9.33	0.868	28.9	"
11	700	"	"	1.161	38.7	Flake
12	750	"	"	1.432	47.8	"
13	800	"	"	0.762	43.3	Dendrite

TABLE 4. Experimental Electrolytic Data in Current Density of 1 A/cm<sup>2</sup>

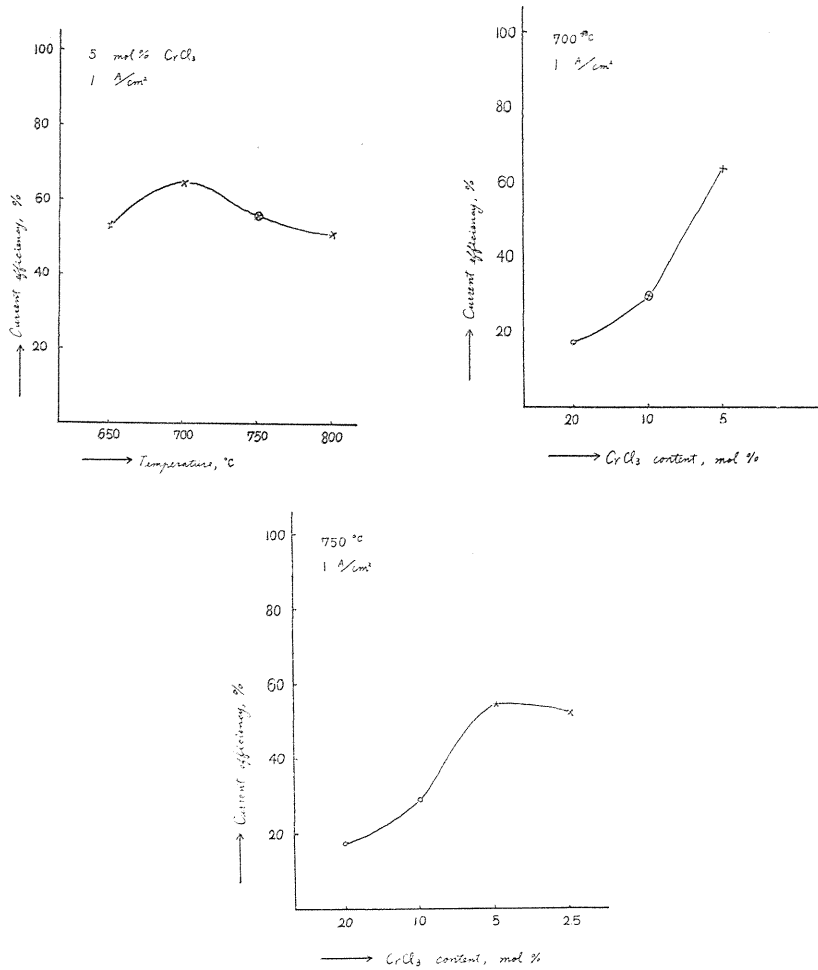
No.	Temp. (°C)	Concentration of $\text{CrCl}_3$ (mol%)	Duration (hr)	Deposit (g)	Current efficiency (%)	Deposit Conditions
14	700	10	2.33	0.875	29.2	Dendrite
15	700	20	"	0.512	17.1	"
16	750	10	"	0.881	29.4	Needle or dendrite
17	750	20	"	0.532	17.7	Dendrite
18	750	2.5	"	1.592	53.1	Needle or sponge

TABLE 5. Analytical Data of Various Produced Chromiums

Impurity → Specimen ↓	Nitrogen (ppm)	Fe (%)	Al (%)	Si (%)
Crude chromium	341	3.28	0.98	0.72
Sponge chromium	201	—	—	—
Dendritic chromium	39	Trace	Nil	Trace
Flaky chromium	14	Trace	Nil	Trace
Dendritic Cr (acid washed)	8	—	—	—







In Figures o: flaky or dendritic deposit and x: spongy or needle deposits

FIG. 7. Current efficiency at some variables.

### 5. Consideration

The condition for electrolytic production of flaky or dendritic chromium was low current density and low electrolytic temperature. This shows, owing to these conditions, the velocity of electrolytic deposit was later than (and the same as) the growing velocity of nucleus. Therefore when current density was higher and electrolytic temperature was higher, produced deposit became spongy or powder (2 A/cm<sup>2</sup>). But the good condition for deposit form has bad current efficiency, so the deposit chromium could not be obtained at 0.1 A/cm<sup>2</sup> C.D. The current density limit for electrolytic deposition of Cr was between 0.25 A/cm<sup>2</sup> and 0.1 A/cm<sup>2</sup>. Decomposition voltage was pretty good agree with the calculated value, and so electrolytic deposition of Cr occurred surely owing to the electrolysis of CrCl<sub>3</sub>, while the "Knick" (bend point) near 0.1 volt at 700°C probably shows

the decomposition of  $\text{CrCl}_2$ . Good current efficiency at higher temperature owes perhaps to the viscosity decreasing of fused salts at higher temperature.

### 6. Conclusion

1) By the electrolytic refining of crude chromium by means of fused salt electrolysis with  $\text{CrCl}_2\text{-NaCl-KCl}$ , flaky or dendritic chromium below 30 ppm of nitrogen or with trace impurities was purely produced and the refined chromium was ductile in bending test.

2) Optimum conditions were current density:  $0.5 \text{ A/cm}^2$ , temperature:  $750^\circ\text{C}$ ,  $850^\circ\text{C}$ , (in 5 mol%  $\text{CrCl}_2\text{-NaCl-KCl}$  fused salts). At these conditions current efficiency was 68%.

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