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# Production Method of High Purity Copper for Semiconductor Use and Evaluation of the Quality (Report I)†

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**Abstract**

*The new refining process to remove infinitesimal sulfur (S) impurity contained in twofold electrolytic refined copper has been developed using sulfide forming method followed by zone refining.*

*Various dopant materials were examined thermodynamically and experimentally for eliminating S element in extremely small quantity and sweeping out themselves after zone refining.*

*Lanthanum element was found out to be optimal as a result of the experiment for this purpose.*

*Residual S content in copper has been reduced to less than 0.1 wt.ppm after this refining process and thus, extremely high purity copper which hardly contains not only heavy metal elements such as silver, iron, lead, tellurium, selenium, arsenic, antimony, bismuth but also S has been obtained.*

*The developed copper has been expected to be used for semiconductor application because of much higher purity than oxygen free copper available in market.*

*This paper describes the production method of high purity copper for semiconductor use together with desulfurization mechanism as a first report.*

**KEY WORDS :** (High Purity Copper) (Desulfurized Zone Refining)

## 1. Introduction

Along with the recent development in the semiconductor industry, various high purity materials come to be demanded keenly[1], and a much higher purity is required for pure copper, instead of the conventional oxygen-free copper (OFC). In the past more than two decades, gold bonding wires had been intensively used in the general internal wiring of IC and LSI, but lately attempts to replace them with copper have been proposed and studied seriously in various fields[2)~5]. In oxygen-free copper, required characteristics could not be obtained because the impurities contained in its acts as impeding factors[4),5]. Copper(Cu) contains much more infinitesimal impurities as compared with gold, and a more complicated process is needed for its metallurgical refining, and it was reported only in a laboratory scale[6)~9], and practically nothing has been disclosed about the outlook of actual mass production process. This time, the authors devised a new refining process with the purpose of control of various infinitesimal impurity elements contained in copper material, and developed a refining mechanism of various high purity copper materials based on its results, and discussed the application of these materials into semiconductor.

## 2. Manufacture of High Purity Copper

Generally, as the technique to obtain high purity copper, the electrolytic refining method and zone refining method are considered. First it is clear from **Table 1** that impurities such as silver(Ag), iron, lead, tellurium, selenium, arsenic, antimony and bismuth are mostly removed by re-electrolytic refining, and when further electrolysis is repeated, it has been known that all these heavy metal elements except sulfur(S) are removed to an undetectable limit. In this table, Ag is 0.5 wt.ppm or less, and this is because its detectable limit is higher than that of other elements, and it is judged that it has been sufficiently refined as the material. As for S, however, a residue of 0.6 wt.ppm is recognized, and it is learnt that S is hardly reduced by electrolytic refining. Accordingly, re-re-electrolytic copper was further refined in zone refining process, attempting to reduce S, but a residue of about 0.2 wt.ppm could not be removed even after 10 passes of

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zone refining process. To remove this S sufficiently, a method of adding an element which is likely to form a sulfide to the re-re-electrolytic copper, separating S compound by floatation, and removing the excess additive element by zone refining method has been developed. (This method is called the desulfurized zone refining.)

**Table 1** Chemical compositions of specimens. (wt.ppm)

| | OFC | REC | RREC | La10 |
|---|---|---|---|---|
| Ag | 8.0 | <0.5 | <0.5 | <0.5 |
| Fe | 2.1 | 0.1 | <0.1 | <0.1 |
| Pb | 0.6 | 0.2 | <0.1 | <0.1 |
| Te | 0.2 | 0.1 | <0.1 | <0.1 |
| Se | 0.8 | 0.1 | <0.1 | <0.1 |
| As | 1.7 | 0.2 | <0.1 | <0.1 |
| Sb | 2.1 | 0.2 | <0.1 | <0.1 |
| Bi | <0.1 | <0.1 | <0.1 | <0.1 |
| S | 5 | 0.7 | 0.6 | <0.1 |

OFC : Oxygen Free Copper
REC : Re-Electrolytic Copper
RREC : Re-REC
La10 : Zone Refined Copper after dooing 10ppm La.

Analytical method

| | |
|---|---|
| Ag , Fe | : ICP-AES ( Inductively coupled argon plasma atomic emission spectrometry ) |
| Pb,Te,Se,As,Sb,Bi | : Graphite furnace atomic absorption spectrometry |
| S | : Analyzer for trace sulfur |

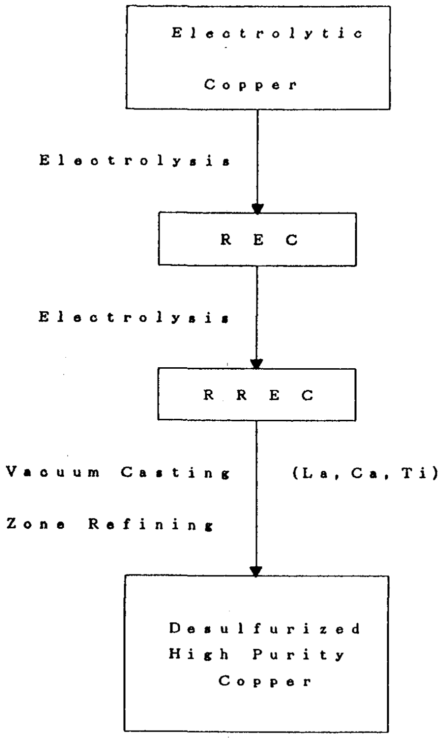
## 2.1 Manufacturing Method of Various High Purity Coppers

This new high purity copper manufacturing method is shown in a flow chart in **Table 2**. First, an electric copper used as starting material was cut into a piece measuring about 300mm×300mm×20mm and pickled. For pickling, nitric acid and purified water were mixed equally, and the piece was pickled for 10 minutes, and then it was ultrasonically cleaned in purified water, and dried in vacuum to prevent entry of impurities due to contamination from the surface. Using this electric copper as the anode, electrolytic refining was conducted, and a re-electrolytic copper-(REC) was obtained. Furthermore, using this REC as the anode, electrolytic refining was conducted again to obtain a re-re-electrolytic copper(RREC). To this RREC, a prepared base alloy containing desulfurizing by 0.1 wt.% was added, and melted in a high frequency vacuum melting furnace with output of 30 kW and frequency of 10 kHz to produce an ingot containing a desired desulfurizing element (measuring 19mm×20mm×250mm).

Using thus fabricated ingot, desulfuried zone refining was performed. The zone refining apparatus used in the present experiment was a method of induction heating by high frequency coil placed outside a transparent quartz tube in a vacuum with a carbon boat placed inside this tube, in which the position of high frequency coil was fixed and the internal carbon boat was moved (**Fig. 1**).

The high frequency oscillator used in this system had an output of 20 kW and a frequency of 250 kHz, and a high frequency coil of one turn was used in order to narrow the zone melting width. This zone refining was conducted in the conditions of moving speed of 1.5 mm/min, 3 passes and zone melting region of 30 ± 10min, in a vacuum of $1.3\times10^{-3}$ Pa.

**Table 2** Process flow chart.



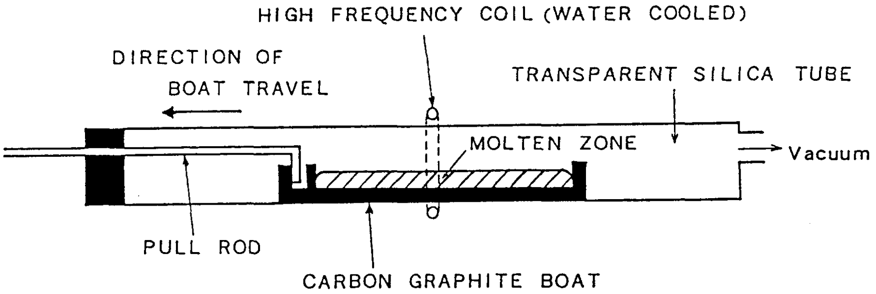


**Fig. 1** Schematic diagram of zone refining.

## 2.2 Selection of Desulfurizing Element and estimation of required amount of addition

RREC contains traces of S by about 0.6 wt.ppm. To remove this S, zone refining was attempted, but it remained even after 10 passes as stated above, and the desulfurized zone refining was tried in order to remove S from the copper more effectively.

Incidentally, the following three points were considered as the conditions required in the element used in this refining method.

(1) The standard formation free energy of sulfide must show a great negative value.
(2) The formed sulfide must be small in solubility in molten copper and be easy to separate from the molten copper by floatation.
(3) Due to economical reasons, the concentration of the added element must be within 0.1 wt.ppm in a range of over 1/2 of the copper ingot length by zone refining of three times or less.

We first selected dopants by referring to the standard formation free energy and status diagram of sulfides, and then estimated a required a mount of addition.

**Figure 2** shows the relation between the standard formation free energy and temperature of sulfides of various metals10). From this diagram, calcium(Ca), barium(Ba), lanthanum(La), and strontium are considered to be favorable as dopants because zone refining is usually done at about 1400K.

Out of them, Ca and La were selected as relatively practical desulfurizing elements. Besides: for reference, in comparison with these elements, titanium(Ti) which is small in the negative value of formation free energy of sulfide was additionally tested, too.

The next step was to check if sulfides of Ca and La could be easily separated from the molen copper by floatation. The melting point and specific gravity of CaS and LaS are shown in **Table 3**11),12),13). Successful flobtation of CaS and LaS from the molen copper partly depends on their solubility into molen copper, but from this table since CaS and LaS are solid at the temperature during zone refining and their densities are smaller than 8.96 g/cm$^3$ of copper, they were considered to separate from the molen copper by floatation. Then the quantity of additdon of Ca and La necessary for keeping the S level in copper under 0.1 wt.ppm was estimated by thermodynamic computations.

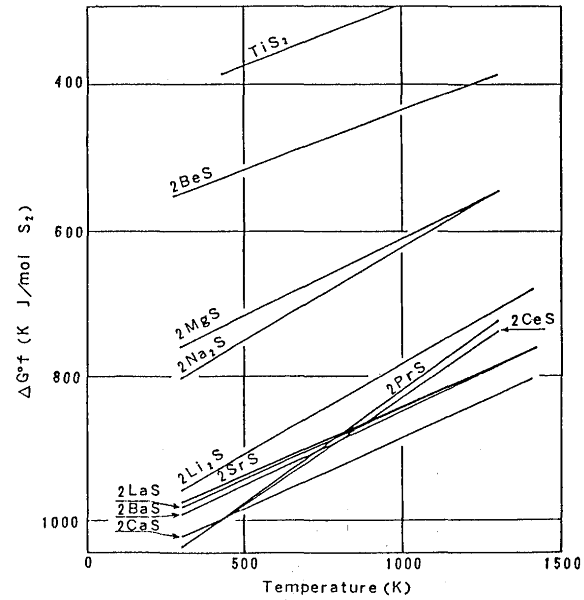


**Fig. 2** The Ellingham diagram of sulfides.

**Table 3** Physical properties of sulfide compounds.

| Compd. | m.p. (℃) | Density (g/cm³) |
|---|---|---|
| CaS | 2525 | 2.6 |
| LaS | 2200 | 5.7 |

When Ca and La are added to copper, they act not only as desulfurizing agents but also as deoxidizing agents.

Thermodynamically calculating, at 1400K, we obtain

$$2CaO_{(s)}+S_{2(g)}=2CaS_{(s)}+O_{2(g)}$$

$\Delta G^0_{1400}=174.6\text{kJ}$15)

$La_2O_{3(S)}+S_{2(g)}=2LaS_{(S)}+3/2O_{2(g)}$

$\Delta G^0_{1400}=713.6\text{kJ}$10)15)21)

Both reactions are extremely shifted to the oxide side. It was calculated by assuming that Ca or La first reacts with oxygen(O) in the molten copper and then with S. It is known that there is a solid solution of oxygen by about 4 wt.ppm in a copper ingot to which Ca or La is added before zone refining. Supposing this oxygen 0 wt.ppm, since Ca reacts with oxygen by 1:1, Ca is consumed by 10 wt.ppm when forming CaO. In the case of La, since $La_2O_3$ is formed, 3/2 of La reacts with 1 part oxygen, which means 23 wt.ppm is consumed.

The quantity of dopants Ca, La consumed as a result of formation of sulfides was calculated, assuming $a_{CaS}$, $a_{LaS}=1$. Meanwhile, suited data was not available for the activity coefficient $\gamma^\circ_{La}$ in infinite dilution of La in copper, and since the Cu-La status diagram was similar to that of Cu-Ca and it seemed an intermetallic compound was formed same as in Cu-Ca system, it was assumed to be same as the activity coefficient $\gamma^\circ_{Ca}$ in infinite dilution of Ca in copper. The thermodynamic data used in the computation is given in **Table 4**14),15),16),10).

As a result of calculation, the values of [wt.ppm Ca]×[wt.ppm S] and [wt.ppm La]×[wt.ppm S] were:

At T=1400K,

[wt.ppm Ca]×[wt.ppm S]=0.13

[wt.ppm La]×[wt.ppm S]=3.4

At T=2000K,

[wt.ppm Ca]×[wt.ppm S]=1,500

[wt.ppm La]×[wt.ppm S]=23,000

Therefore, at [wt.ppm S]=0.1 wt.ppm, it is balanced at T=1400K. The concentrations of Ca and La were respectively [wt.ppm Ca]=1.3 wt.ppm and [wt.ppm La]=34 wt.ppm, and it was also learnt that it is more advantageous for desulfurization when the temperature is lower.

To lower the S level from 1 wt.ppm to 0.1 wt.ppm, since Ca and La react with S by 1:1, Ca is consumed by 1.1 wt.ppm and La by 3.9 wt.ppm. The concentrations of Ca and La balanced with S after reaction at T=1400K are respectively 1.3 wt.ppm and 34 wt.ppm, so that the initial concentrations of Ca and La required as deoxidizing agent and desulfurizing agent are respectively

Co, Ca=12.4 wt.ppm

Co, La=60.9 wt.ppm

Next, we studied the case of removal of Ca and La remaining after reaction with O and S in copper by zone refining. Whether the impurities in a solution are easy to be removed or not by zone refining can be judged by the distribution coefficient of the impurities. That is, if the distribution coefficient is close to 1, the impurity is hardly removed by zone refining, but as it becomes smaller than 1, the zone refining comes to be more effective for removal of that impurity17). This distribution coefficient $K_e$ may be expressed in the following equation18).

$$K_e=\frac{K_0}{K_0+(1-K_0)\exp(-f\delta/D)} \qquad (1)$$

where

$K_e$ ; effective distribution coefficient

$K_o$ ; balanced distribution coefficient

$f$ ; solidification rate [cm/sec]

$\delta$ ; effective thickness of concentration boundary layer [cm]

D ; diffusion coefficient of impurity in molten matter [cm$^2$/sec]

In this equatiom, the value $\delta$ is about $10^{-3}$ cm when the molten matter is agitated firmly, and the value of D is often somewhere between $10^{-4}$ and $10^{-5}$ cm$^2$/sec. Therefore, the intrinsic factor of impurity may be considered to be $K_o$ alone. The relation of equation (1) is illustrated in

**Table 4** Standard free energies of reaction. ($\Delta G^\circ$)

| Reaction | $\Delta G^\circ$ (Joule) |
|---|---|
| $Ca\ (l) = Ca\ (wt\%)$ | $\Delta G^\circ=-33440-32.85T$ |
| $1/2S_2(g) = S\ (wt\%)$ | $\Delta G^\circ=-154802+48.32T$<br>(1388−1518K) |
| $Ca\ (l)+1/2S_2\ (g)=CaS\ (s)$ | $\Delta G^\circ=-550840+104.25T$<br>(1124−1760K) |
| $La\ (l)+1/2S_2\ (g)=LaS\ (s)$ | $\Delta G^\circ_{1400}=-409982$<br>$\Delta G^\circ_{2000}=-317107$ |

**Fig. 3**. The phase diagrams of Ca-Cu and La-Cu are shown in **Fig. 4** and **Fig. 5**[11),19)]. In these phase diagrams, the solidus line is overlapped with the perpendicular temperature axis, and since $K_o$ is considered to be smaller than 1, it is expected that zone refining be effective for removal of Ca, La.

Accordingly, the impurity distribution by zone refining at various values of $K_o$ was simulated by computer. The calculation program is shown in **Fig. 6**, and calculated results after three times of zone refining at $K_e = 0.05$ are given in **Fig. 7**.

A point of inflectional in concentration profile is noted around point 7 in the diagram, which corresponds to the position twice as much as the melting zone at the end part, and it is considered because the end of melting zone reached the final solidifying zone in one direction (the portion from point 8.4 to 10) when it suddenly contacted with the high concentration portion (around point 8.4), so that the impurity concentration in the melting zone elevated sharply, which caused to raise the concentration also in the solidifying portion of the rear side of the melting zone (around point 6.8).

From this result it is known that the impurity concentration is lowered to less than 1/100 of the initial level in about 70% area of the entire ingot when zone refining is done three times at $K_e$=9.05.

This calculation was, meanwhile, based on the follow-

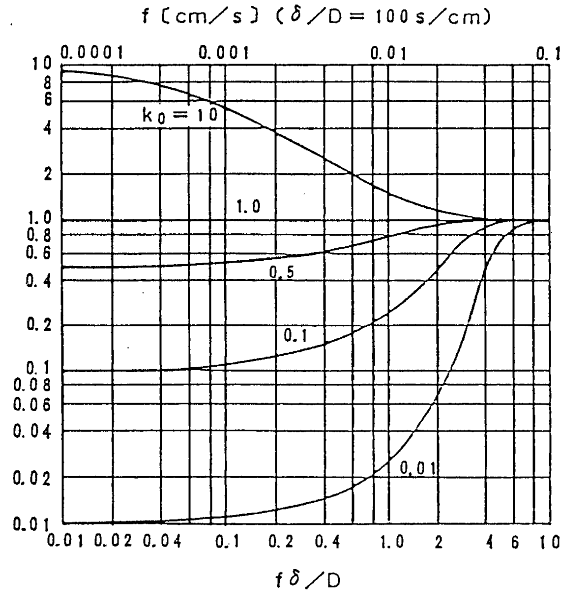


**Fig. 3** $K_e$ as a function of $f \cdot \delta$/D for various values of $K_o$.

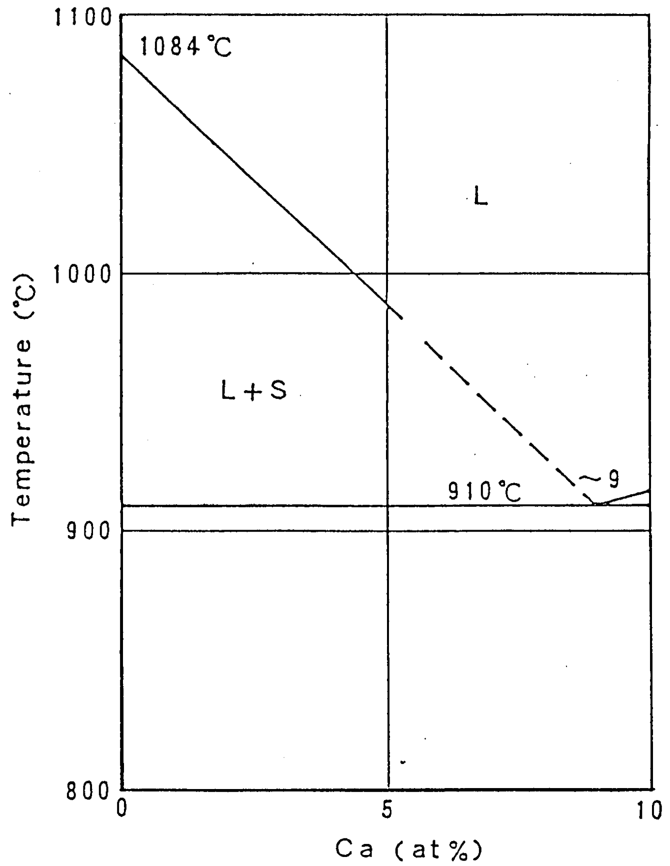


**Fig. 4** Cu-Ca phase diagram.

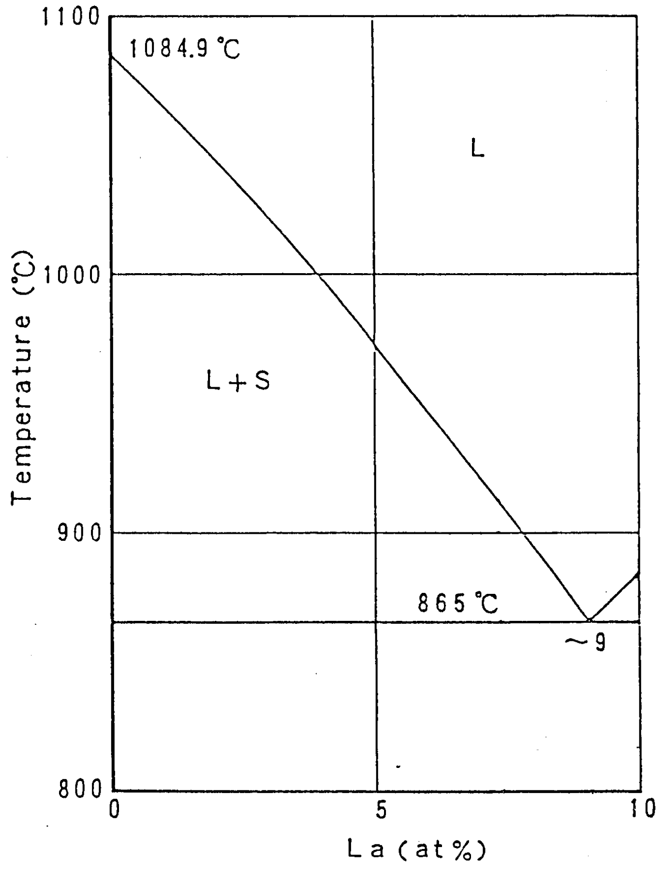


**Fig. 5** Cu-La phase diagram.

ing assumption.

(1) Composition in liquid phase is uniform.

(2) There is no diffusion in solid phase.

(3) $K_e$ is constant.

```
10 REM ************************** ZONE **************************
20 CLS
30 REM ***  CS(n,m):impurity concentration in the solid
40 REM ***       CL:impurity concentration in the liquid
50 REM ***       CO:initial concentlation/L:molten zone length
60 REM ***       NO:number of molten zone pzssages/MO:segment number
70 REM ***        K:distribution coefficient
80 REM ************************* DATA **************************
90 CO=1
100 L=160
110 NO=2
120 MO=1000
130 K=.8
140 REM ******************************************************
150 DIM CS(NO+1.MO)
160  FOR M=1 TO MO
170   CS(O.M)=CO
180  NEXT M
190 REM *****************************************************
200 FOR N=0 TO NO
210  CL=0
220     FOR M=1 TO L
230         CL=CS(N.M)+CL
240     NEXT M
250    CL=CL/L
260 REM *****************************************************
270 CSS=0
280 CSSN=0
290     FOR MM=1 TO L
300         CSS=CSS+CS(N.M)
310     NEXT MM
320  FOR M=1 TO MO-L
330         CS(N+1.M)=K*CL
340         CSS=CSS+CS(N.M+L)
350         CSSN=CSSN+CS(N+1.M)
360 CL=(CSS-CSSN)/L
370  NEXT M
380 REM *****************************************************
390     FOR I=1 TO L-1
400          G=I/L
410          MM=MO-L+I'
420              CS(N+1.MM)=K*CL*(1-G)^(K-1)
430     NEXT I
440 CSSN=0
450               FOR J=1 TO MO-1
460                   CSSN=CSSN+CS(N+1.J)
470               NEXT J
480 CS(N+1.MO)=CO*MO-CSSN
490 CST=0
500 FOR I=1 TO MO
510    CST=CS(N.I)+CST
520 NEXT I
530 PRINT CST
540 NEXT N
550 REM *****************************************************
560 REM *****************************************************
570 LINE (80.10)-(80.360)
580 LINE (80,360)-(630.360)
590 LINE (630.360)-(630.10)
600 LINE (630.10)-(80.10)
610 FOR N=0 TO NO+1
620     FOR M=1 TO MO
630          MX=80+M*11/20
640          CSY=110+(1-LOG(CS(N.M))/LOG(10))*50
650          PSET (MX.CSY)
660     NEXT M
670 NEXT N
680 END
```

**Fig. 6** Calculation program for the concentration distribution after zone refining.

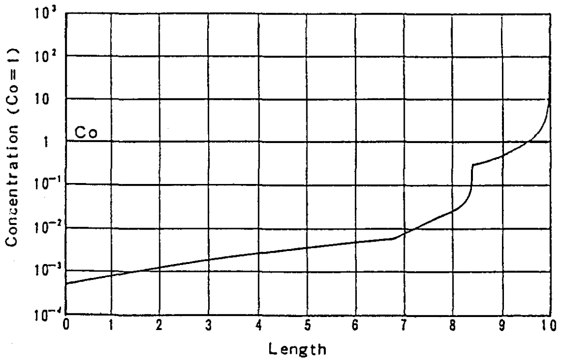


**Fig. 7** Calculated distribution of impurity along the solidified ingot. ($K_e$=0.05, Co; Initial concentration)

(4) The length of liquid phase is constant, being 16% of the entire length (according to experimental condition).

(5) Concentration of impurity is smaller than its solubility.

Incidentally, supposing $\delta$ /D = 100 sec/cm at $f = 2.5 \times 10^{-3}$ cm/sec, we obtain $K_o = 0.04$ at $K_e = 0.05$ from equation (1). If $K_o = 0.04$, the solid solution concentration at eutectic temperature of Cu-Ca, Cu-La should be 0.36 at. %, and in the phase diagrams in Fig. 4, 5 it seems that $K_e$ be smaller than 0.05 because region of solid solution is not recognized. It has been hence judged that Ca and La in Cu can be removed by three times of zone refining.

As for Ti, when its $K_o$ was determined from the solidus line and liquidus line of phase diagram, it was 0.35, and as compared with La and Ca, the zone refining effect was considered to be smaller$^{20)}$.

On the basis of the above results, the quantity of addition of dopants was determined. As for Ca, since the calculation amount necessary for desulfurization was 12.4 wt.ppm, it was decided at 3, 10 and 50 wt.ppm, and as for La which required 60.9 wt.ppm, it was set at 3, 5, 10, 50 and 200 wt.ppm.

As for Ti, since its $K_o$ is close to 1, it was considered that Ti be left over after zone refining, and relatively small doses of 3 and 10 wt.ppm were determined.

### 2.3 Desulfurization Effect by Desulfurized Zone Refining Method

In **Fig. 8(a)** to **(f)** are shown S concentration and residual profiles of dopants after desulfurized zone refining by adding La by 3, 5, 10, 50, 200 wt.ppm, Ca by 3, 10, 50 wt.ppm, and Ti, as control, by 3 and 10 wt.ppm. The sample was analyzed by dividing into 11 portions from the zone start part to end part, which were named points 0 to 10, and S was analyzed at points 0, 5, 10 and dopants, at points 0, 2, 4, 8, 10. To analyze S, a trace S analyzer was used, and La, Ca, Ti were analyzed by using an inductively coupled argon plasms atomic emission spectrometry.

First, as for La, as shown in Fig. 8(a), at a dose of 3 wt.ppm, a sharp rise of S concentration is noted after zone refining, and it is evident that it is influenced by zone refining effect, different from the case of large dose doping. In Fig. 8(b), profiles of residual La concentration after desulfurized zone refining are shown, which discloses that an extremely high concentration of La is left over in the zone end part when La is added by 50 wt.ppm or higher doses, while it is not detected at all at doses of 3 to 10 wt.ppm from the start to end of zone. It was hence estimated that, at low doses. La wholly reacts with O and S in copper to form oxides and sulfides, which were separated by floatation. Indeed, at a dose of around 3 wt.ppm, S remained by about 0.2 wt.ppm even in the parts from the start to middle of zone refining, and S was not removed completely by zone refining after desulfurization reaction, and it is considered that La was completely consumed as reaction product, and that the unreacted S remained and was partly concentrated in the end part by zone treatment. On the ther hand, at an excess dose of La over 50 wt.ppm, as mentioned earlier, La remained also in the portions other than the end by zone refining of about three passes, and in particular at the

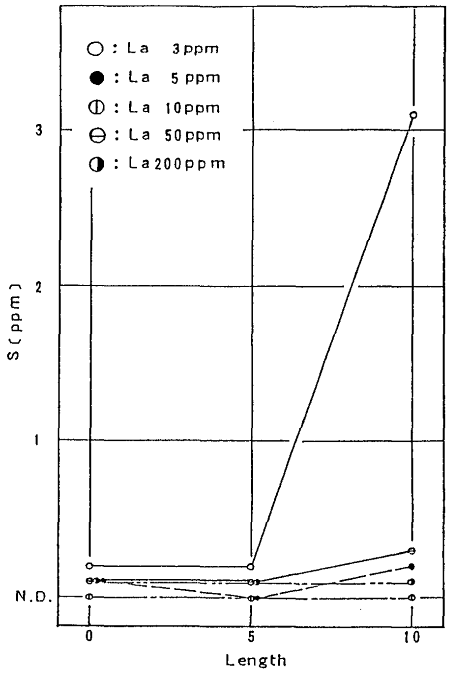


**Fig. 8 (a)** S profiles after desulfurized zone refining using La dopant.

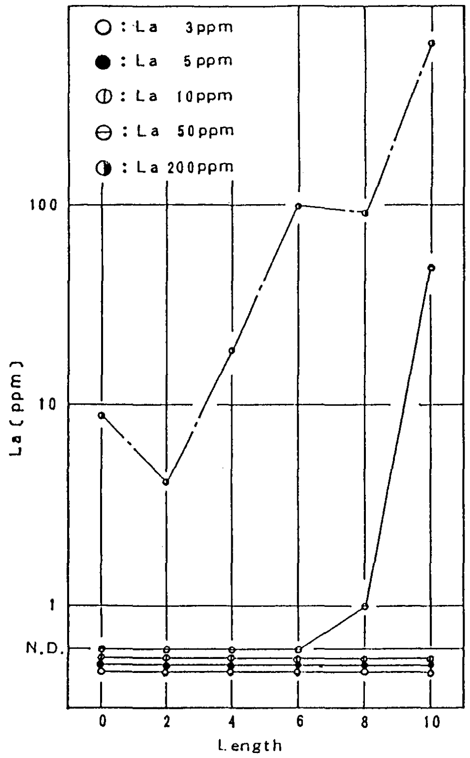


**Fig. 8 (b)** Residual La profiles after desulfurized zone refining,

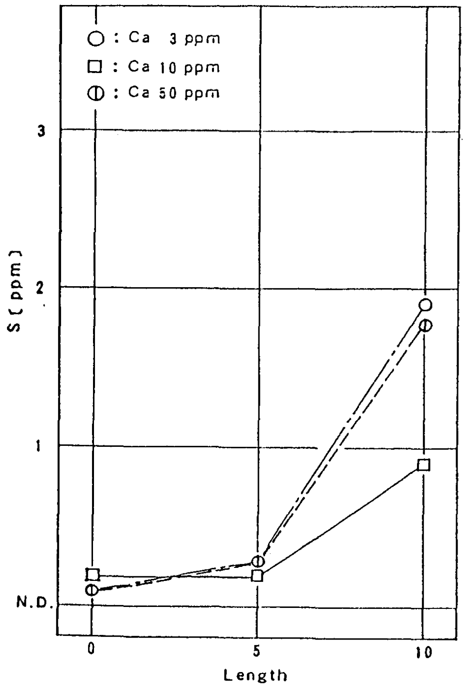


**Fig. 8 (c)** S profiles after desulfurized zone refining using Ca dopant.

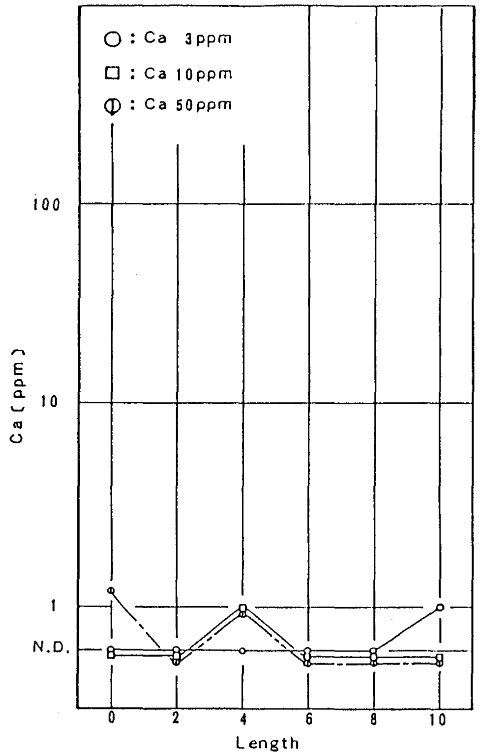


**Fig. 8 (d)** Residual Ca profiles after desulfurized zone refining.

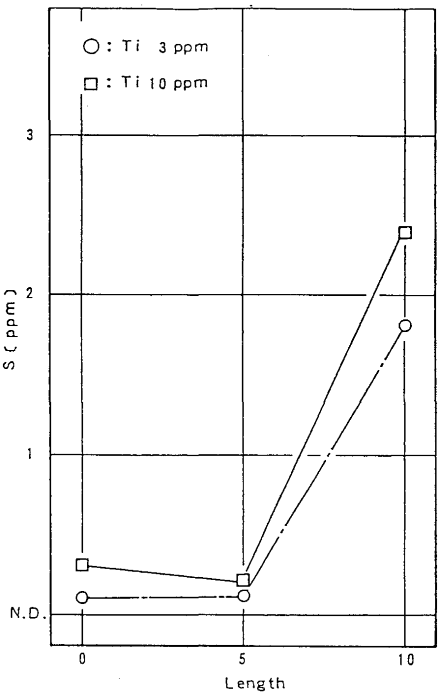


Fig. 8 (e) S profiles after desulfurized zone refining using Ti dopant.

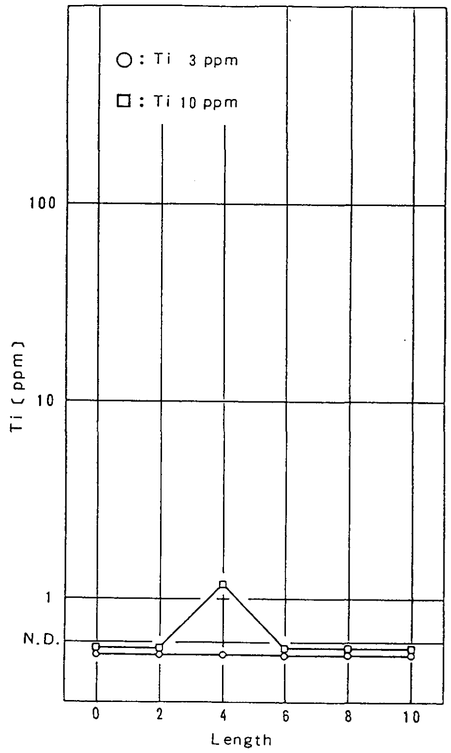


Fig. 8 (f) Residual Ti profiles after desulfurized zone refining.

higher dose of 200 wt.ppm, La was detected at high levels in all area, which was found to be unsuited to the purpose of high purity production. In this experiment, when La was added by 10 wt.ppm, neither S nor La was detected at all, and the best result was obtained. Table 1 unveils, together with the data of electrolytic coppers (REC, RREC) by conventional refining process, the analytical results in the middle part (point 5) of the La 10 wt.ppm doped material (La10) which presented an ideal result in desulfurized zone refining. According to this table, all heavy metals and S were below the detectable limit. Besides: to study the behavior of O, oxygen was analyzed for reference, and it was about 4 wt.ppm in RREC, and about 2 wt.ppm was left over after addition of La, and it seemed that sufficient deoxidation was not done. However, in the LECO analyzer used in this measurement, such trace levels of oxygen are hard to discuss and we are going to clarify the residual oxygen by further studies.

As clear from Fig. 8(c), (d) in Ca-doped materials, residual S was recognized regardless of dose, and the S refining effect was poor. Especially, Ca itself was not concentrated in either start or end part, and it is supposed that Ca was dissipated about during zone processing as stated below.

As shown in Fig. 8(e), (f) in Ti-doped materials, S remained in the end part if the dose was increased, and the residual profile of it itself was not stable, and it was judged to be unsuited as desulfurizing agent.

## 3. Discussion

In order to remove traces of S from RREC, La, Ca, Ti were added at various concentrations, and zone refining was done three times. As a result, sufficient effects were not obtained in other dopants than La.

In the case of Ca, as though a sufficient desulfurizing effect was expected thermodynamically, as shown in Fig. 8(c), a residue of S was noted, but since there was almost no residual Ca in Fig. 8(d), dissipation of Ca was estimated, but the zone refining was indeed conducted at a high vacuum of about $1.3\times10^{-3}$ Pa, and when the vapor pressure $P_{Ca}$ of Ca containing 10 wt.ppm of Ca at 100K was calculated, a high value of $P_{Ca}$=approx. $4.5\times10^{-3}$ Pa was obtained, which suggested a high possibility of evaporation of Ca during zone refining.

As a result, it is supposed that the unreacted S was left over, producing a S profile due to zone refining.

In the case of Ti, as compared with La, Ca, it was hard to form sulfide and the balanced distribution coefficient $K_0$ was closer to 1, and it was estimated that it might not be suited to desulfurized zone refining, and the behavior of S in Fig. 8(e) proved this estimation correct. The residual Ti shown in Fig. 8(f) was considerably decreased, and it was probably considered that it was removed in a form of oxides or the like.

Finally, in the case of addition of La which is considered to be most promising as dopant for eliminating sulfur, the refining mechanism was investigation. In the thermodynamic calculation, La was found to be extremely likely to be oxidized, seeing [wt.% O]$^3$ [wt.% La]$^2$=$2.7\times10^{-4}$ at T=1400K[15),19)], and after three times of zone refining by adding La at various doses, La was decreased considerably as shown in Fig. 8(b).

This rate of decrease is shown together with the dose in **Table 5**. It is considered that only the residual La is responsible for desulfurization which the majority of dose of La is consumed by oxidation, and it was attempted to analyze the phenomenon by analyzing the surface of white slag matter floating on the surface of ingot right after zone refining. **Photo 1** shows Auger electronic images of SEI, and S, O, La, Cu obtained by Auger analysis of the surface (made by Japan Electronic, model JAMP-10) after cutting out in each floating matter by performing one zone pass after adding 10 wt.ppm of La, and **Table 6** illustrates the quantitative analysis result of white part (P1) and dark part (P2) of SEI.

**Table 5** La reduced ratio after desulfurized zone refining.

| La doping amount (wt.ppm) | La reduced ratio (%) |
|---|---|
| 3 | > 67 |
| 10 | > 90 |
| 50 | > 82 |
| 200 | 26 |

**Table 6** Chemical compositions of the top surface. (La 10, 1 pass)

| Element | P1 (at %) | P2 (at %) |
|---|---|---|
| S | 1.2 | 0.8 |
| O | 25.2 | 12.0 |
| La | 73.6 | 8.5 |
| Cu | — | 78.7 |

From **Photo 1**, it is evident that La and O are present in the same position, and it is known that La is oxided.

In the S concentration in Table 6, presence of S of about 1 at % (about 0.35 wt.%) is indicated on the surface of ingot after zone, but the initial S concentration in RREC after La doping is merely about 0.6 wt.ppm, and it seems that it was enriched about 10,000 times on the ingot surface. In the estimation of the dose above, it was supposed that about 60 wt.ppm of La would be necessary, but actually a sufficient desulfurization was obtained at about 10 wt.ppm, and it was considerably lower than estimated. It suggested a possibility that the quantity of reaction with O supposed in the thermodynamic calculation be smaller than supposed (but it is necessary to study together with the precision of analysis as mentioned above), and it was estimated that sulfur was eliminated far more efficiently than expected.

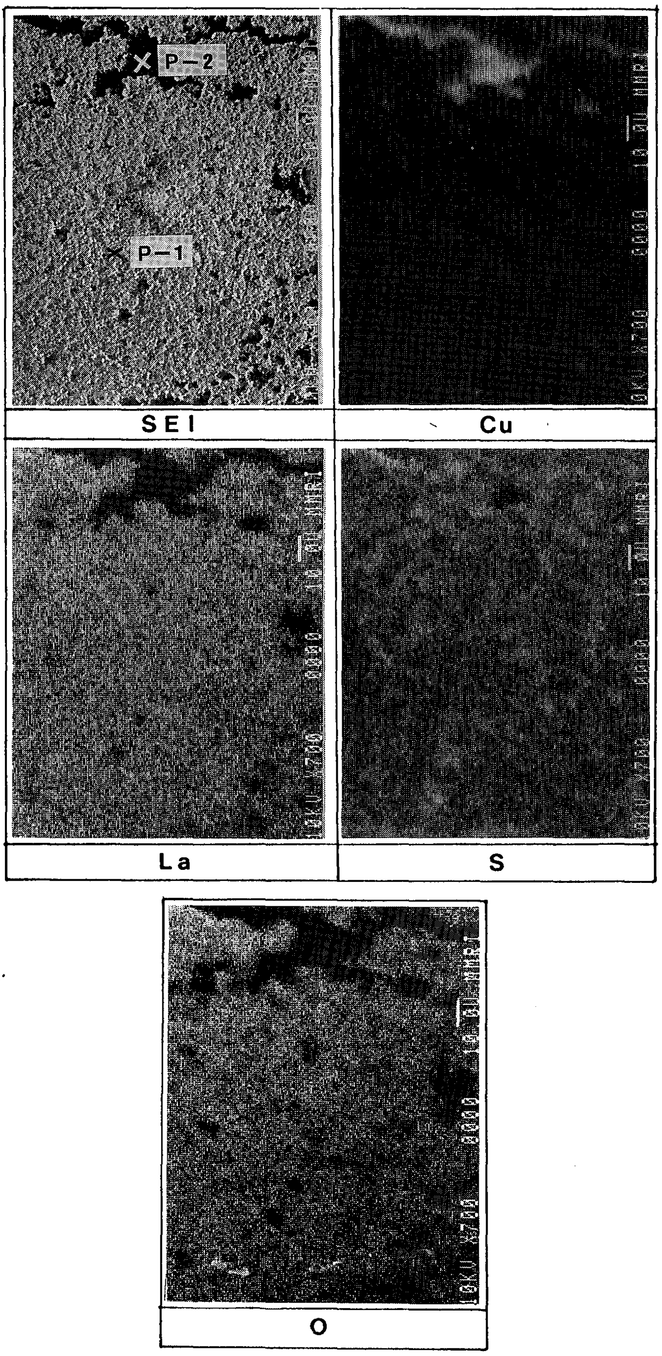


**Photo. 1** AES analysis results on the top surface after desulfurized zone refining in the case of 10 wt.ppm. La.

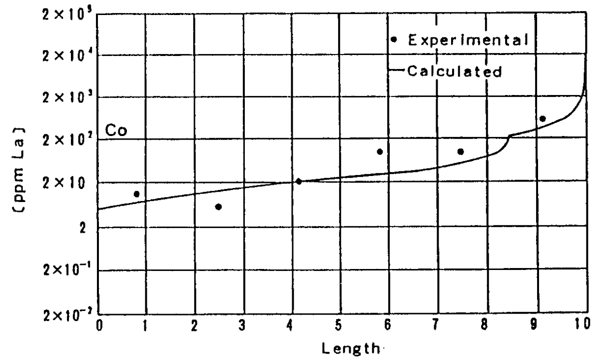


**Fig. 9** Calculated concentration curve ($K_e=0.2$) and the experimental results.

Moreover, the activity coefficient $\gamma^{\circ}{}_{La}$ of La was considerably larger than expected, and it was estimated that the level of La to be balanced with 0.1 wt.ppm of S be a considerably low concentration. As for the system, it is highly possible that desulfurization proceeds in a more complicated form such as La-S-O, and this is regarded as a subject to be studied henceforth.

On the other hand, at 50 wt.ppm, as shown in Fig. 8(b), a considerable amount of La was swept out to the end part by zone refining, which shows that the dose was excessive.

From this result, it is known that the required amount of La to be balanced with an infinitesimal S is also infinitesimal, and the effect of zone refining may be said to be removal of excess La remaining after deoxidation and desulfurization.

Hence it is enough with La of about 10 wt.ppm as the sum of the portion necessary for deoxidation (finally estimated to be 5 to 6 wt.ppm and about 4 wt.ppm necessary for desulfurization, but industrially thinking, since contents of O and S in copper are not constant, it seems proper to add in a slight excess and collect the residual La completely in the terminal part by zone refining.

Here, the refining effect of residual La at the time of zone refining was investigated with respect to the 200 wt.ppm doped material which was relatively small in the rate of decrease of La after zone refining, in **Fig. 9**, in comparison between experimental result and calculation result by simulation after three passes at $K_e=0.2$. Since the both results seem to coincide with each other very well, it was estimated that $K_0$ was about 0.2 in the condition in which the feed speed of melting zone was $25\times10^{-3}$ cm/sec. This value is considerably larger than $K_e=0.05$ estimated above, but assuming the balanced distribution coefficient $K_0=0.04$, solidification rate $f=2.5\times10^{-3}$ cm/sec, and effective distribution coefficient $K_e=0.2$, the ratio of diffusion coefficient D and boundary layer thickness $\delta$ of the melting zone, $\delta$/D, is about 600. According to Harmann Schildknecht[17)], the boundary layer thickness $\delta$ varies in a range of $10^{-1}$ to $10^{-3}$ depending on the agitation state of melting zone and solidification rate $f$, but in the indirect heating type melting using graphite as in this experiment it is estimated that the molten matter may not be agitated so much, and assuming $\delta=10^{-1}$ cm, D is $1.7\times10^{-4}$ cm$^2$/sec.

The diffusion coefficient D in liquid is usually considered to be $10^{-5}$ to $10^{-4}$ cm$^2$/sec, and this obtained value of diffusion coefficient seems to be reasonable, and hence the above $K_e$ value may be regarded as a realistic value. That is, as for the zone effect, it seems smaller than expected initially, but considering the productivity, it is supposed hard to improve the $K_e$ value greatly or increase the number of passes, and an initial concentration control is necessary to avoid excessive residual La level.

## 4. Conclusions

As a method of removing trace impurity elements in copper, the electrolytic refining method and refining method were combined, but as for traces of S of about 0.1 wt.ppm, it was difficult to refine and remove in an ordinary method.

Accordingly, a desulfurized zone refining method was devised, and as a result an extremely high purity copper could be obtained.

The obtained results can be summarized below,

(1) By repeatedly refining electrolytically an oxygen-free copper which is, so to speak, a pure copper, almost all heavy metals can be reduced to less than 0.1 wt.ppm, but S is contained by about 0.6 wt.ppm, and sufficient refining is difficult.
(2) If zone refining is repeated (10 passes) after re-re-electrolytic refining, there was a still S residue of 0.2 wt.ppm, and perfect removal was difficult.
(3) When La, Ca, Ti were added as desulfurizing elements to re-re-electrolytic copper and zone refining was conducted in three passes, considering the productivity, S could be eliminated to a level of under 0.1 wt.ppm over the entire region, when only La was added, without any effect of residual La.
(4) In the desulfurized zone refining method of La, La is bonded with O and S in copper to form compounds, which float up to be separated, while the excess La can be removed by zone refining process.
(5) In the desulfurized zone refining method of re-re-electrolytic refined copper, it is regarded proper to add La by about 10 wt.ppm.

In this method it is now possible to lower the level of S, which was difficult to control industrially in high purity copper, to an infinitesimal value by an economical method, which has made it possible to obtain a novel high purity copper. Since this material is much more higher impurity than existing materials: it finds new applications, such as copper bonding wire for use in semiconductor which is very susceptible to the effect of impurities.

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