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STUDY ON GROWTH OF HIGHLY PURE URANIUM COMPOUNDS

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**Abstract:** We developed the systems for growing highly pure uranium compounds to study their intrinsic physical properties. Uranium metal was zone refined under low contamination conditions as far as possible. Chemical analysis of the purified uranium was performed using the inductive coupled plasma emission spectrometry(ICP). The problem that emission spectra of the uranium conceal those of analyzed impurities was settled by extraction of the uranium using tri-n-butyl-phosphate(TBP). The result shows that some metallic impurities such as Pb, Mn, Cu etc. evaporated by the r.f. heating and other usual metallic impurities moved to the end of rod with molten zone. Therefore, we conclude that the zone refining technique is much effective to the removal of metallic impurities and we obtained highly purified uranium metal of 99.99% up with regard to metallic impurities. Using the purified uranium, we attempted to grow a highly pure uranium-titanium single crystal.

**Key words:** Uranium, ICP, TBP, zone refining, purification, crystal growth

## 1. INTRODUCTION

Recently, the actinide elements and their compounds are attracting such attention of many researchers. Major attention on one side arises from the nuclear fuel technology[1]. That is the treatment of nuclear wastes whose main problem is evoked by the actinide elements contained. Several solutions are proposed such as their recycling into the nuclear fuel, the annihilation through some nuclear reactions and the creation of new useful materials from them. As the actinide elements are the last elements left for human beings, the last solution may give us a possibility to realize one of our dream, namely, synthesizing new innovative materials.

Another attention on other side arises from a basic theory of the solid state physics in

connection with the so-called f-electrons. Main problem in the solid state physics is how to describe the state of electrons. Up to now, two extreme cases, namely localized and itinerant states, are successfully explained by the localized electron model and the free electron model, respectively. However, the electronic state just between these extreme states has not been explained well enough yet.

The 4f electron system such as those in the rare-earth compounds had been considered as the typical localized system until a few ten years ago, because the 4f electrons sink deeply inside other outer electron shells. However, in such the 4f electron system, many anomalous phenomena which are called as valence fluctuation state or dense Kondo state were observed. These phenomena indicate that even the 4f electron system is not the typical localized state. In the actinide compounds, their 5f electrons extend to outer electron shell compared to the 4f electrons of the rare-earth elements, and itinerant character of the 5f electron becomes stronger. Therefore, the 5f electron system is regarded as a bridge between the free and localized electron model and its investigation will lead to the comprehensive understandings of the electron state and the basic solid state physics. In this sense, the research of the actinide compounds is very important[2].

To advance in the research fields mentioned above, we need target materials with high quality because even small amounts of impurities would conceal their intrinsic properties.

Uranium and its compounds are considered to be the entrance to study of actinide elements, because of large available quantity and very weak toxicity and radioactivity compared to other actinide elements. Therefore, we initiated our study by purifying the uranium metal and then contemplated growing single crystals of its

compounds with high quality, using the highly purified uranium metal.

The purification of uranium metal was performed by two step processes. One is the zone refining method which is effective for the reduction of metallic impurities concentration, and the other is the electrotransport method which is used for the removal of interstitial impurities such as gaseous impurities[3,4]. The detailed story of purification process will be described elsewhere[5].

The ratio of resistivity at room temperature and that at the helium temperature, the so called r.r.r.( residual resistivity ratio) , is often used to check the quality of purified metal as a convenient method. However, its analysis is very complicated as many origins which scatter the electrons, such as impurities, defects, dislocation etc. contribute to it. From the standpoint that the uranium metal is a raw material for the concerned uranium compounds, the chemical analysis of each element included in the uranium as impurities is desirable. In this paper, we will present the chemical analysis of purified uranium using the inductive coupled plasma spectrometry(ICP).

Moreover, we will briefly mention our effort to grow qualified uranium compounds using the purified uranium metal.

## 2. EXPERIMENTAL

### 2.1 Development of Instruments

First of all, we determined to purify the uranium by the zone refining technique and the electrotransport method.

The uranium is chemically very active and easy to oxidize even in a high vacuum. Figure 1 shows the standard free energy,  $\Delta G^0$  for the formation of its dioxide,  $UO_2$ . [6,7&8] The oxygen partial pressure,  $P_{O_2}$ , equilibrating with  $UO_2$  at about 1400K is estimated to be from  $10^{-30}$  to  $10^{-34}$  atm. In the meantime, the reported equilibrium oxygen dissociation pressure,  $P_{VO}$  is about  $10^{-8}$  atm at 1400K, although is strongly depends on the x in  $UO_{2+x}$ .

These mentioned above indicate that the high degree of vacuum is needed to get rid of picking up oxygen in the course of the uranium treatment. However, the available technology could not realize such a high vacuum at present.

Figure 2 shows the reported vapor pressure of the uranium metal and the uranium dioxide,  $UO_2$ . [7&8] The vapor pressure of the uranium metal at its melting point is  $1.2 \times 10^{-11}$  atm, namely,  $1.5 \times 10^{-9}$  Pa. The reported vapor pressure of the  $UO_2$  at 1300K is about the same as shown in Fig. 2. Therefore, the realistic target of the vacuum will be that better than  $10^{-9}$  Pa. We set our target of the vacuum of our apparatuses to be better than  $10^{-9}$  Pa as a base pressure and to be better than  $10^{-8}$  Pa as a working pressure.

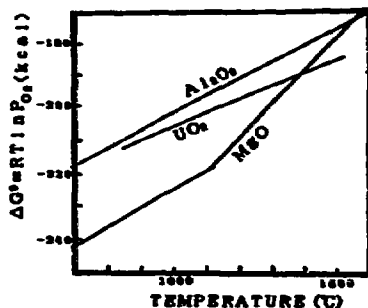


Fig. 1 Standard free energy of formation of oxides[6&7]

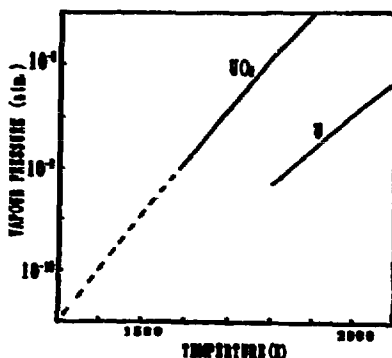


Fig. 2 Vapor pressure of uranium and uranium oxides[7&8]

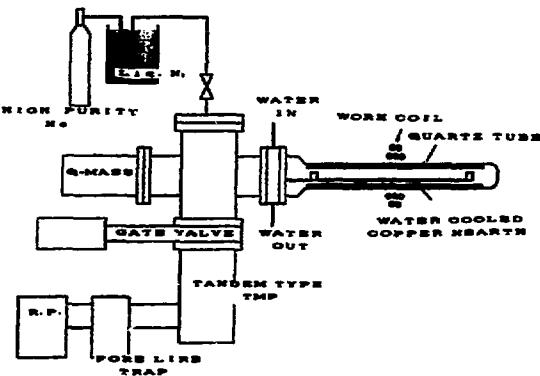


Fig. 3 Developed zone refining apparatus

Table 1 Features of developed apparatuses

S. S. E.		Horizontal zone refining	
Vacuum system	<ul style="list-style-type: none"> <li>• Ion pump</li> <li>• Ti sublimation pump with Liq. N<sub>2</sub> shroud.</li> <li>• Turbo molecular pump.</li> </ul>	Vacuum system	Tandem type turbo molecular pump.
Base pressure	~4x10 <sup>-6</sup> Pa	Base Pressure	~7x10 <sup>-6</sup> Pa
Current	DC 0A~1000A	Output power	15kW
Voltage	DC 0V~6V	Frequency	400kHz
Sample length	130mm max.	Sample length	200mm max.
		Width of molten zone	~15mm

Figure 1 also shows that alumina and magnesia crucibles are not suitable for the uranium-melting. Looking into the phase diagrams, it is found that the molten uranium is almost incompatible with any metals and refractory compounds. The experiences accumulated up to now suggest that the only water-cooled copper hearth

uncertain and the drop-off of the melted uranium will cause serious problems. So, we adopted the water-cooled copper hearth.

With regard to the heat source, there are several choices, each of which has advantages and disadvantages. The possibility of contamination with the tungsten makes us discard the electron beam melting. Also, the optical heating system appears to be difficult to stand together with the high vacuum system at present. For these reasons, we decided that the r.f. heating system is the best choice at present.

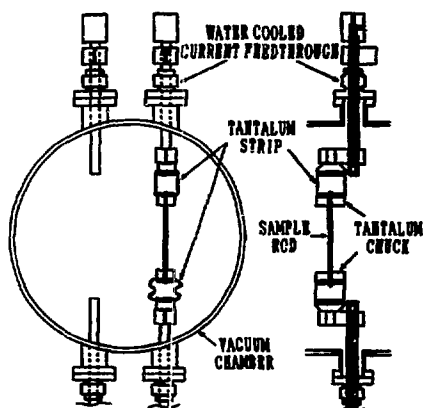


Fig. 4 Developed electrotransport instrument

Figures 3&4 depict the schema of the developed r.f. heating zone refining apparatus and the electrotransport instrument. Table 1 shows the major features of these instruments. A special copper-made hearth was developed to enable the r.f.-power to enter the uranium metal effectively through the electrically-conductive copper hearth. The hearth developed is completely compatible with the required high vacuum.

## 2.2 Purification of Uranium

The uranium metal whose content of impurities is shown in Table 2 was zone refined several times in a high vacuum or in a highly pure helium environment. In the course of the experiment, it was found that the molten part of the uranium became thermally unstable due to the interaction with the water-cooled copper hearth and the complicated interaction with the r.f.-power supply. The introduction of helium into the system stabilized the molten-part of the uranium substantially.

is compatible with the molten uranium. The floating zone technique or the adoption of the water-cooled copper hearth is the only choice for the zone refining. However, the self-sustainability of the melted part of uranium was

Table 2 Impurity content in starting uranium in mass ppm

Al 18	C 50	Fe 50	Nb 28	Ti 28
Ag 28	Ca 28	Mg 50	Ni 50	V 28
B 28	Cd 28	Mn 28	Pb 50	W 28
Be 28	Cr 28	Mo 28	Bi 50	Zn 28
Bi 28	Cu 28	Na 28	Sr 28	Zr 50

Also, it was found that the pretreatment of uranium metals and sequentially proper treatment were important for the success of the zone refining.

The uranium metal was purified as follows;

- A. Melting in an ultra high vacuum.
- B. Zone refining of several times in an ultra high vacuum.
- C. Zone refining of several times in a helium gas environment of one atmosphere.
- D. Cutting down the end side of 1/3 of uranium rod.
- E. Zone refining of several times in an ultra high vacuum.
- F. Zone refining of several times in helium gas atmosphere.
- G. Annealing.

The details of the zone refining process will be reported elsewhere[5].

The purified part of the uranium metal was then solid state electrolyzed in the electro-transport instrument for about one week just below the melting point.

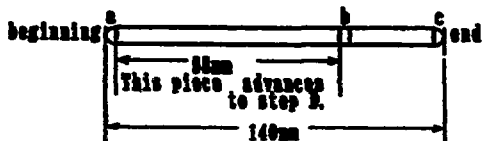
### 2.3 Analysis of Purity

We measured the electrical conductivity of the purified uranium in the temperature range of 4.2K-300K. The degree of purity of the uranium was primarily judged by the so-called r.r.r., the resistivity ratio between at 300K and at 4.2K. The chemical analysis was carried out by the ICP, inductive coupled plasma emission spectroscopy, technique.

As the ICP is not suitable for the analysis of gaseous elements such as hydrogen, nitrogen, oxygen etc. we analyzed the uranium metal purified by only zone refining process which is effective for removal of metallic impurities as said before.

Analyzed parts of the purified uranium are shown in Fig. 5 in relation to the zone refining process mentioned above. The operating conditions of ICP are shown in Table 3. The uranium metals were solved in a heated nitric acid. The acid concentration was controlled to be 8M. The standard solution of the analyzed elements was also controlled to have the same nitric acid concentration. Four kinds of the standard solution, whose concentrations of the analyzed elements are 0, 5, 10 and 15 ppm, were prepared.

•after step B



•after step E

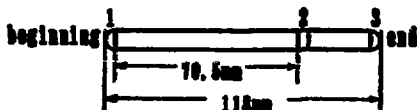


Fig.5 Analyzed positions of uranium metal rods. See text about the step C, E and G.

TABLE 3 Operating conditions of ICP

Hitachi dual monochromator-ICP/AES-PX5200	
R.F.power	1 kW
Argon gas flow rate	
Plasma	12 l/min.
Nebulizer	0.5 l/min.
Auxiliary	0.5 l/min.
Observation height above coil	15 mm
Slit width	
Spectrometer1	30μm
Spectrometer2	30μm
Grating	
Spectrometer1	3600 grooves/mm
Spectrometer2	1200 grooves/mm

To simplify the analysis, we restricted the number of analyzed elements by following conditions.

1. Elements which is difficult to be analyzed by the ICP should be excluded.
2. Elements whose chemical properties are similar each other such as the rare-earth elements should be represented by a typical element.
3. Elements which is extracted by the TBP in large amount, which will be explained later, should be excluded.

Consequently, we chose the following elements.

Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, La, Lu, Mg, Mo, Ni, Pb, Pr, Sc, Si, Sn, Ti, V, W, and Zn.

The problem in the ICP analysis of the impurities in the uranium is that many emission spectra from the uranium conceal those from the

impurity elements. Therefore, the uranium was removed by the extraction method using the TBP(Tri-n-butyl Phosphate). At first, the TBP was mixed with toluene in the ratio of 1 to 1, then the mixture was shaken with 8M nitric acid solution to make a preequilibrium state. We extracted the uranium by the TBP twice. After the extraction, any uranium in the solution could not be detected by both the ICP and the GM survey meter. The blank nitric acid solution of 8M was prepared by the same procedure as the uranium solution.

The use of the TBP causes another problem, that is, the possibility of the extraction of impurity elements. So, we examined the extraction factor of the impurity elements using the standard solution. The analyzed result of impurity was rectified by its factor.

Using the purified uranium as the starting material and the apparatuses described above, we are now trying to grow highly pure uranium compounds. One example is the growth of the  $U_2Ti$  single crystal. The  $U_2Ti$  is thought to have interesting electric properties as is the compound between so-called the 5f and the 3d elements. However, the  $U_2Ti$  is the line compound and congruent but with a solid solution phase of the  $\beta$ -Ti and the  $\gamma$ -U at 1171K. So, the conventional melting techniques are not applicable to grow its single crystal with high quality. We are now zone-heating the compound and annealing for a substantial period in a high vacuum. Results of the characterization of the obtained crystal will be reported elsewhere[9].

### 3. RESULTS AND DISCUSSION

The concentration of the impurities in the zone refined uranium metal is shown in Table 4. The result on the uranium before the zone refining is also shown as comparison. The minimum accuracy of the data is thought to be less than 1 ppm. The elements which can not be detected are not shown in Table 4.

As deduced from the zone refining of the rare-earth metals, metallic impurities usually move to the end edge of a rod with the molten zone by the zone refining processing. That is attributed to the distribution factor of impurities between the solid and the liquid phases being less than an unity. The typical elements are iron and nickel as depicted in Table 4. The elements whose concentration decrease totally by the zone refining, typical one is manganese, are thought to evaporate in the process of the zone refining in an ultra high vacuum. Behavior of copper exhibited the mixture of above two cases.

Thus, the behaviors of almost the impurities can be explained and the zone refining was confirmed to be effective for purification of the uranium metal as far as the metallic impurities are concerned.

However, the behaviors of aluminum and

calcium are strange. These two elements increased in their concentration after the zone refining. As for the calcium, we guessed that the TBP may be the origin of the contamination. Concerning the increase of aluminum concentration, we can not identify the source at present.

Adding up the concentration of the impurities except for calcium and aluminum in the most purified piece (I in Table 4), we obtained the value of 36.1 wt.ppm. Judging from this value, the total concentration of metallic impurities in the purified uranium is thought to be less than 100 mass ppm. So we think that the high purity uranium metal of 99.99 wt.% could be obtained.

It is interesting to compare the result of chemical analysis with the r.r.r.. Figure 6 is the r.r.r. of the uranium metal rod after the all zone refining processes. As stated before, the r.r.r. is influenced by the many origins. However, the influences except for impurities are thought to be almost the same in every part of the uranium rod. Further, judging from the case of the zone refining of the rare-earth metals, gaseous impurities such as oxygen, nitrogen etc. are thought to be hard to move. Therefore, we think that the r.r.r. reflects the concentration of metallic impurities to some extent. But, as the effects of substitutional metallic impurities on the electrical resistivity will be smaller compared to that of interstitial gaseous impurities, the change of the r.r.r. is smaller than that inferred from the decrease of impurities concentration. Anyway,

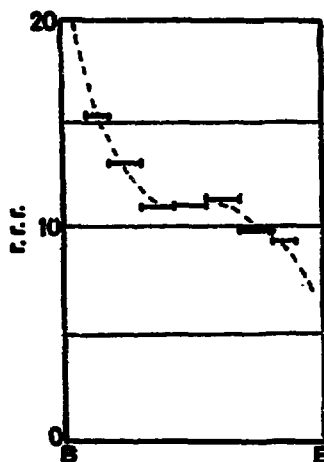


Fig. 6 The r.r.r. along uranium metal rod purified by the zone refining. The dotted line is guide for eyes. The r.r.r. of uranium metal before the zone refining is about ten.

TABLE 4 The concentration of impurities in zone refined uranium metal obtained by ICP analysis. The label a, b, c, 1,2 and 3 correspond to those in Fig. 5 .

	Al	Ca	Cr	Cu	Fe	Mn	Ni	Pb	Si	Sn	Zn
a	10	9.1	1.0	3.6	14.4	-	9.2	0.2	21.6	0	0.4
b	10	3.5	2.3	6.7	53.8	0	32.9	-	28.9	1.2	0.4
c	10	4.6	4.2	11.1	188.4	0.2	98.8	0.2	66.7	6.6	0.6
1	8	8.6	0.9	2.2	8.6	-	6.5	-	17.8	0.9	0.2
2	13	6.6	2.0	4.3	47.8	0	26.6	-	26.5	1.8	0.7
3	25	11.2	4.2	7.1	146.2	0	80.3	0.6	70.0	4.6	1.0
Before z.r.	13	4.4	2.3	17.1	53.1	6.9	33.8	9.6	34.3	2.0	2.2

although the situation of the r.r.r. is very complex, its result support the result of the ICP analysis.

#### 4. CONCLUSION

We developed instruments for the purification of the uranium metals. Using the instruments, we carried out the purification of the uranium metal. We performed the chemical analysis of the purified uranium metal using the ICP and checked the purity by the electrical resistivity measurement. The purity of the uranium is thought to be improved to be 99.99% up. We are now synthesizing the highly pure uranium compounds using the purified uranium.

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#### REFERENCES

(1) R. Kiyose edited "Aiming Fundamental Study for Nuclear Fuel Back End System", UTRCN-S-12,

Univ. Tokyo, Tokyo, (1986).

(2) H. R. Ott and Z. Fisk, Handbook of the Physics and Chemistry of the Actinides, edited

by A. J. Freeman and G. H. Lander, Vol. 5, P.85, North-Holland, Amsterdam, Amsterdam, (1987).

(3) D. Fort, B. J. Beaudry and K. A. Gschneidner, Jr., J. Less-Common Met. 134, 27 (1987).

(4) D. Fort, D. W. Jones, B. J. Beaudry and K. A. Gschneidner, Jr., J. Less-Common Met. 81, 273 (1981).

(5) A. Ochiai et. al. to be published.

(6) R. Swalin, "Thermodynamics of Solids" pp.83, John Wiley & Sons, New York, (1961).

(7) S.J. Burnett, "Properties of Refractory Materials", AERE-R-4657, AERE Harwell, Berkshire, (1969).

(8) J. Belle edited, "Uranium dioxide: Properties and Nuclear Applications", Naval Reactors, Division of Reactor Development, United States Atomic Energy Commission, Washington D.C., (1961).

(9) T. Shikama et al., to be presented at the 10th Int. Conf. on Crystal Growth, San Diego, (1992).