CHEMICAL ANALYSIS OF PURIFIED URANIUM

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Abstract - 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-butylphosphate(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 high purified uranium metal of 99.99% up with regarding to metallic impurities.

Key words Uranium, ICP. TBP. zone refining, purification

Recently, actinide elements and their compounds are attracting much attention of many researchers. Major attention on one side arise from nuclear fuel technology in connection with actual nuclear power source[1]. That is treatment of nuclear wastes which main problem is due to actinide elements contained in them. Several solutions are proposed such as reutilization of actinide elements in the waste as the nuclear fuel, transmutation of actinide elements and creation of new materials using actinide elements. Actinide elements are last elements left for humanbeing. Therefore the last solution has a possibility to realize our dream.

Another attention on other side arise from basic theory of solid state physics in connection with f-electrons. Main problem in solid state physics is how to describe the state of electrons and two extreme cases can be successfully explained by localized electron model and free electron model. However, middle case between them has not yet been explained enough. The 4f electron system such as rare earth compounds had been considered as a typical localized system several ten years ago, because the 4f electron is sinked deeply inside other electron shells. However, in such a 4f electron system, many anomalous phenomena which are called as valence fluctuation state or dense Kondo state were observed and which indicates that even 4f electron system is not a typical localized state. In actinide compounds, 5f electron expand to outer electron shell compared to the 4f electron, and itinerant character of 5f electron becomes rather strong. Therefore 5f electron system is regarded as a bridge between the free and localized electron model and its investigation leads to total comprehension of the electron state and further the basic solid state physics. In this meaning, research of actinide compounds is important[2]. Anyway, to advance above research, target material with high quarity is necessary because impurities and the like conceal its intrinsic properties.

Uranium is considered to be entrance of actinide elements because of its large available quantity and very weak toxicity and radio activity compared to other actinide elements. Moreover uranium itself and its compounds are also very attractive. Therefore, at the start we began purification of uranium metal and contemplated growing good single crystals using highly purified uranium metal.

The purification of uranium metal are performed by two step process. One is zone refining method which is effective for elimination of metallic impurities, and the other is electrotaransport method which is used for removal of interstitial impurities such as gaseous impurities[3,4]. Detail

story of purification process will be described in succeeding papers[5].

The ratio of resistivity at room temperature and residual one, so called r.r.r., is often used to check the quality of purified metal as convenient method. However its analysis is very complex as there are many scattering origin of electron which create electorical resistance, such as impurities, defects, dislocation etc.. From standpoint which uranium metal is raw material of uranium compounds, only impurities should be examined. So, chemical analysis of each element is preferable. In this paper, we shall present the chemical analysis of purified uranium using inductive coupled plasma spectrometry(ICP).

EXPERIMENTAL

As the ICP is not suitable for 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. The uranium metal was purified as follows;

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

Analyzed uranium peaces are shown in Fig. 1. Used instruments and operating conditions of ICP are shown in Table 1.

·after step B

·after step E

Fig. 1 Analyzed positions of uranium metal rods. See text about the step C, E and G.

TABLE 1 Operating conditions of ICP

Hitachi dual monochromator-ICP·AES-P·5200	
R.F.power	1 kW
Argon gas flow rate	
Plasma	12 l/min.
Nebulizar	0.5 l/min.
Auxiliary	0.5 l/min.
Observation height above coil	15 mm
Slit width	
Spectrometer1	30 μ m
Spectrometer2	30 μ m
Grating	
Spectrometer1	3600 grooves/mm
Spectrometer2	1200 grooves/mm

The uranium metals were solved in heated nitric acids. The acid concentration was controlled to 8M. The standard solution of analyzed elements was also controlled to have same nitric acid concentration. Four kind of the

standard solution were prepared, which concentration of analyzed elements are 0, 5, 10 and 15 ppm.

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

1. Elements which analysis is difficult for ICP should be excluded.
2. Elements which chemical properties are similar each other such as rare earth elements should be represented by typical element.
3. Elements which extraction by TBP, which is explained later, are large should be excluded.

Consequently, we chose following elements.

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

The problem in ICP analysis of impurities in uranium is that many emission spectra from uranium conceal those of impurity elements. So, uranium was removed by the extraction method using TBP(Tri-n-butyl Phosphate). At first, TBP was mixed with toluene in the ratio of 1 to 1, then its mixture was made to preequilibrium state by shaking with 8M nitric acid solution. We extract uranium using such TBP twice. After the extraction, any uranium in the solution can not be detected by both ICP and GM survey meter. Blank nitric acid solution of 8M was prepared by same procedure as uranium solution.

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

RESULTS AND DISCUSSION

The concentration of impurities in zone refined uranium metal is shown in Table 2. The result about uranium before zone refining is also shown. The minimum accuracy of data is thought to be less than 1 ppm. Elements which can not be detected are not shown in Table 2.

TABLE 2 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.1. (w. ppm.)

	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	21.5	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	96.8	0.2	66.7	6.5	0.8
1	8	8.6	0.9	2.2	8.6	-	5.5	-	17.8	0.9	0.2
2	13	6.6	2.0	4.3	47.8	0	28.5	-	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

As deduced from the zone refining of rare earth metal, usually metallic impurities move to end edge of rod with molten zone by the process of the zone refining. That is attributed to distribution factor of impurities being less than 1. Its typical elements are Fe, Ni as understanding from Table 2. Elements which concentration decrease totally, which typical one is Mn, is thought to evaporate in the process of the zone refining in ultra high vacuum. Behavior of Cu exhibit middle of above two cases. Therefore, behavior of almost impurities can be explained and the zone refining was confirmed to be effective for purification of the uranium metal regarding to metallic impurities. But only behavior of Al and Ca is strange. About the Ca, we imagine the contamination from TBP is origin, but about Al, its origin is not clear at present stage.

Adding up the concentration of the impurities except for Ca and Al in most purified piece (1 in Table 2), we obtained the value of 36.1 wt.ppm. Judging from this value, total concentration of metallic impurities is thought to be less than 100 wt.ppm. So we may think that high purity uranium metal of 99.99 wt.% is obtained.

It is interesting to compare the result of chemical analysis with the r.r.r.. Fig.2 is the r.r.r. of uranium metal rod after all zone refining process. As stated before, the r.r.r. is influenced by many origin. However, the influences except for impurities are thought to be almost same in every part of uranium rod. Further, judging from the case of zone refin-

ing of the rare earth metal, gaseous impurities such as oxygen, nitrogen etc. are thought to be hard to move. So, the r.r.r. is thought to reflect the concentration of metallic impurities. But, as the effect to the resistivity from substitutional metallic impurities is small compared to that of interstitial gaseous impurities, the change of r.r.r. is smaller than that inferred from that of impurities concentration. Anyway, although the situation of the r.r.r. is very complex, its result support the result of ICP analysis.

Fig. 2 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.

As the conclusion, we performed the chemical analysis of purified uranium metal using ICP. And by extraction of uranium using TBP, we obtained satisfactory result. The purity of the uranium is thought to be 99.99% up.

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