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# 中国核科技报告

# CHINA NUCLEAR SCIENCE AND TECHNOLOGY REPORT

## 铀-锆合金芯块的溶解及铀和锆在镉中的分布

## STUDY ON DIRECT DISSOLUTION OF U-10Zr ALLOY AND DISTRIBUTION OF URANIUM AND ZIRCONIUM IN LIQUID CADMIUM

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# 铀-锆合金芯块的溶解及铀和锆在镉中的分布

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## 摘　要

采用直接溶解法，研究了时间、温度、芯块表面积及搅拌与否等参数对铀-锆合金在液态镉中的溶解影响。用 JCXA-733 电子显微分析仪测定了金属镉中 U、Zr 的浓度，采用元素特征 X-射线面扫描方法分析了 U、Zr 在金属镉中的分布状态。实验结果表明，在 400℃ 和 500℃、搅拌速度约为 150 r/min 时，铀在液态镉中的溶解度分别为 0.4 g 和 2.2 g；初始 0.5 h 时，铀溶解速度分别为 0.05 g/($cm^2$ · h) 和 0.32 g/($cm^2$ · h)。U-10 Zr 合金芯块在液态镉中（液态镉与 U-10Zr 芯块质量比约为 7）直接溶解的合适条件为：溶解温度约 480℃，搅拌速度约 150 r/min，溶解时间约 4 h。U、Zr 在金属镉中分布是均匀的。

# Study on Direct Dissolution of U-10Zr Alloy and Distribution of Uranium and Zirconium in Liquid Cadmium

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## ABSTRACT

The effects of dissolution time, temperature, total surface area of U-10Zr alloy pellets and stirring on the dissolution and dissolution rate of uranium in liquid cadmium were studied. Cadmium containing U and Zr dissolved from U-10Zr alloy at 475°C and 500°C respectively was analysed with electron microanalyser. The experimental results show that at 400°C and 500°C with the stirring rate of some 150 r/min, the solubilities of uranium in liquid cadmium are 0.4% and 2.2%, respectively. At the first 30 min, the dissoultion rates of U-10Zr alloy pellets are 0.05 g/(cm$^2$ • h) and 0.32 g/(cm$^2$ • h), respectively. The suitable dissolution conditions for U-10Zr alloy pellets in liquid cadmium (the ratio of the mass of liquid cadmium to that of the pellets $\approx$7) are : temperature, about 480°C; stirring rate, about 150 r/min; dissolution time, 4 h. The distribution of uranium and zirconium in cadmium is homogeneous.

## INTRODUCTION

Electrorefining is a key step in a proposed process for recovery and purification of uranium and plutonium present in uranium-based metal fuel material discharged from a type of fast reactor known as the Integral Fast Reactor (IFR), and dissolution of U-Zr alloy in liquid cadmium is an important stage in the electrorefining step. Although the process flowsheet for IFR core and blanket has been put forward in 1980'[1,2], a few papers about dissolution of uranium in cadmium have been published[3~5], the information about the distribution of uranium and zirconium in liquid cadmium has not been searched in the literature now. In this research work, with direct dissolution of U-Zr alloy in cadmium, the effects of dissolution time, temperature, total surface area of pellets and stirring on dissolution and dissolution rate of uranium in liquid cadmium are studied, cadmium containing U and Zr dissolved from U-10Zr alloy is analysed with electron microanalyser.

## 1 EXPERIMENT

### 1.1 Materials

Analytical reagents such as KCl, $TiCl_3$, $Fe_2(SO_4)_3$, $HNO_3$, $H_2SO_4$, $NH_2SO_3H$ and standard reagent $K_2Cr_2O_7$ and chemically pure reagent metallic cadmium were used. The pellets of U-10Zr alloy were provided by the Department of Nuclear Reactor, China Institute of Atomic Energy. The density of the pellets of U-10Zr alloy is 15.92 g/cm$^3$, in which the content of Zr is 10.05%. Metallic cadmium sample for metallographic examination, which was taken out of the dissolver after the equilibrium of uranium dissolution has been reached and which contains U and Zr dissolved from U-10Zr alloy was rinsed with dilute nitric acid and polished and then washed with acetone.

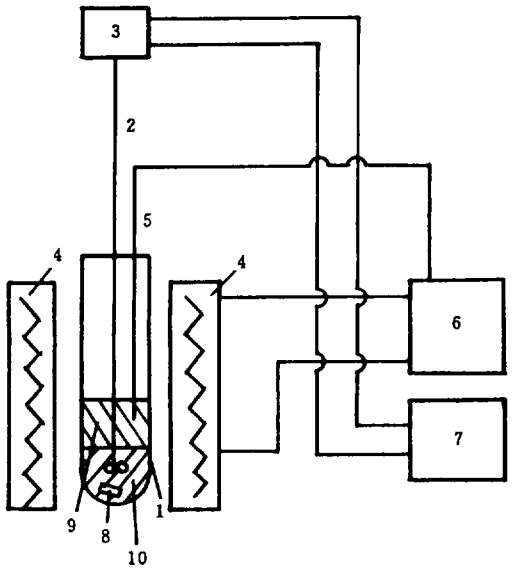


Fig. 1 Schematic diagram of the dissolution installation

1. dissolver; 2. stirring rod; 3. electrornic-stirrer; 4. infra-red heater; 5. thermocouple; 6. thermo-controller; 7. adjuster; 8. pellet of U-10Zr alloy; 9. molten salt; 10. liquid Cd.

## 1.2 Instruments

Infra red heater, DKZ-4 temperature controller, DD-60-2F adjustment device and electrostirrer, dissolver made by quartz ($\phi$30 mm×150 mm), JCXA-733 electron probe scanning electron microscope.

## 1.3 Dissolution installation and experimental procedure

### 1.3.1 Dissolution installation

The dissolution installation consists of infra red heater, dissolver, temperature controller and electro-stirrer, etc., as shown in Fig. 1. A mixture of KCl-LiCl and metallic cadmium were charged into the dissolver. Temperature check was performed in the dissolution installation.

### 1.3.2 Experimental procedure

Before use, the pellet of U-10Zr alloy (~14 g) was immersed in 50% $HNO_3$ at the boil for 2 min and then rinsed with dilute nitric acid, distilled water and acetone, respectively; and 27.5 g of KCl, 22.3 g of LiCl and 100.0 g of Cd were charged into the dissolver and heated to the temperature predetermined where both cadmium and salt melt. Then about 14 g of U-10Zr alloy pellets treated with above method were charged and dissolved in the liquid cadmium phase at stirring state. The liquid cadmium phase was covered by eutetic salt. After dissolution beginning, liquid Cd was sampled at an interval of time.

### 1.3.3 Analytical Procedures

(1) The sample containing U and Cd was dissolved in 50% $HNO_3$ at the boil. After dissolution of the sample, 1.0 ml of the solution and about 5 ml of 1 : 4 ($V/V$) $H_2SO_4$ were charged into beaker and boil away until white smoke was ended, and 10 ml of distilled water and 1 ml 1 : 4 ($V/V$) $H_2SO_4$ were charged into beaker for dissolving the residue. The content of uranium and cadmium in above solution was determined by $K_2Cr_2O_7$ titration and EDTA titration respectively.

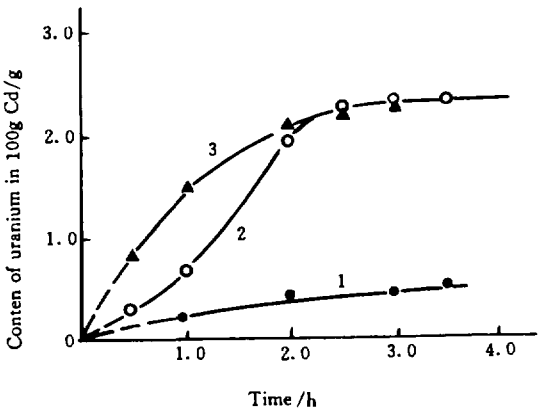


Fig. 2 Effect of time and temperature on dissolution of uranium
stirring rate: 150 r/min;
diameter of U-10Zr pellet: 10 mm;
mass of U-10Zr pellet: ~14 g;
Cd: 100 g;
1—400°C; 2—475°C; 3—500°C.

(2) The concentration of uranium and zirconium in liquid cadmium was detemined with FZAFM quantitative analysis procedure. The elements contained in the sample were determined qulitatively with QLA qulitative procedure. The distribution of uranium and zirconium in cadmium was determined with characteristic X-ray scanning microanalysis.

## 2 RESULTS AND DISCUSSION

### 2.1 Effect of dissolution time and temperature

The effect of dissolution time and temperature on direct dissolution of U-10Zr alloy is shown in Fig. 2. From Fig. 2, it can be seen that the content of uranium in liquid cadmium increases with increase of time, at 475°C or 500°C; after 3 h, the content of uranium in liquid cadmium almost is not changed, at this time, equilibrium of dissolution of uranium has been reached; the solubility of uranium in cadmium is 2.2%; the curve of dissolution of uranium at 475°C (or 500°C) rises faster than that at 400°C. The equilibrium of dissolution of uranium has not been reached yet at 400°C after 3.5 h.

### 2.2 Effect of temperature on dissolution rate

The effect of temperature on dissolution rate of uranium is shown in Fig. 3. As expected, dissolution rate of uranium at high temperature is faster than that at lower temperature. At 400°C and 500°C, at the first 30 min the dissolution rates of U-10Zr alloy pellets are 0.05 g/ ($cm^2$ • h) and 0.32 g/ ($cm^2$ • h), respectively.

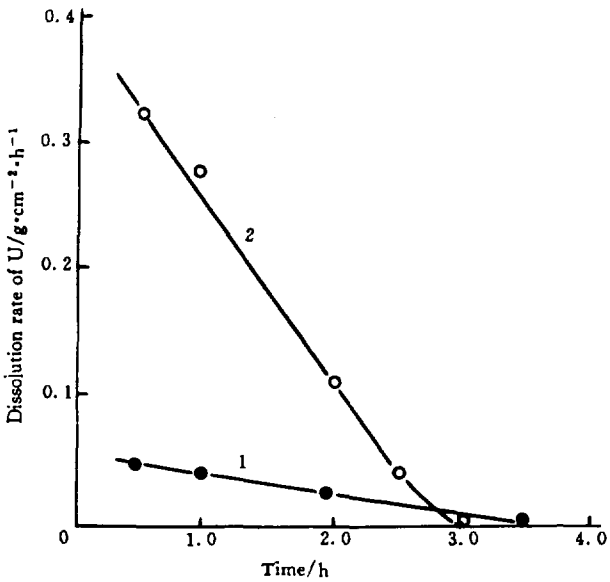


Fig. 3 Effect of temperature on dissolution rate of uranium (Experimental conditions are same as that in Fig. 2.)
1—400°C; 2—500°C.

### 2.3 Efect of area of U-10Zr alloy pellets

The experimental results are shown in Fig. 4. As expected, except for area of U-10Zr alloy pellets, all conditions are same each other, increasing total surface area of U-10Zr alloy pellets is beneficial to dis-

solution of uranium.

### 2.4 Effect of stirring

The effect of stirring on the dissolution of uraniun is shown in Fig. 5. This figure indicates that the equilibrium of dissolution of uranium is reached at 3 h, 500°C, and 150 r/min of stirring rate; but the equilibrium of dissolution of uraniun can not be reached at 5 h, 500°C and no stirring, at this time, the concentration of uranium in cadmium is 1.1 g/100 g Cd.

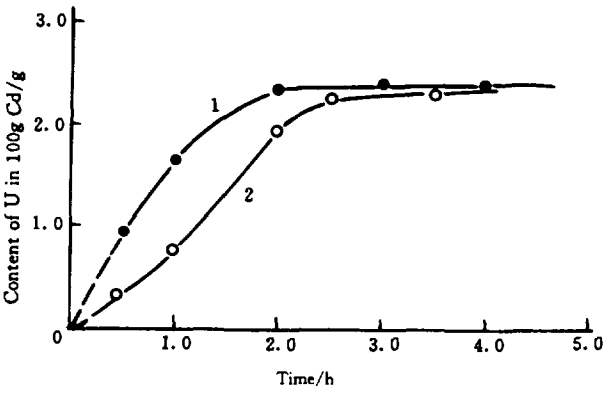


Fig. 4 Effect of total surface area of U-10Zr alloy pellet on dissolution of uranium (Temperature 475°C, others are same as that in Fig. 2.)
total surface area of U-10Zr alloy pellets:
8.0 $cm^2$——1; 5.0 $cm^2$——2.

### 2.5 Qualitative analysis results

Cadmium containing U and Zr dissolved from U-10Zr alloy was analysed with electron probe scanning electron microscope. The qualitative analysis results of samples are listed in Table 1. It is shown that besides Cd, there are U and Zr (both dissolved from U-10Zr alloy pellets) and K (as impurity in cadmium material). The bright point in Fig. 6 represents eutetoid which consists of Cd and K. Distribution of element K in Cd is non-homogeneous. The reason is not clear, which needs further investigation.

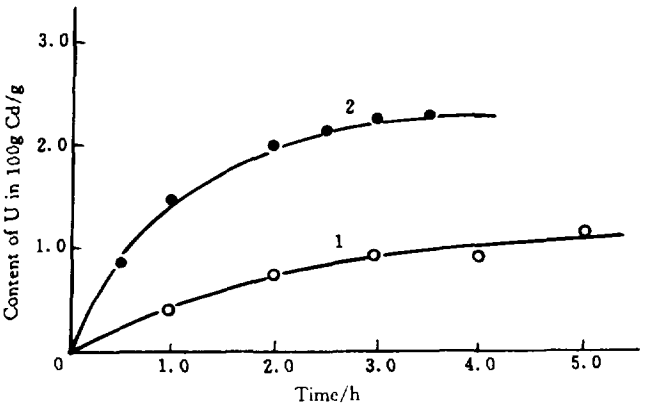


Fig. 5 Effect of stirring on dissolution of uranium (Temperature 500°C, others are same as that in Fig. 2.)
1. ——no stirring; 2. ——stirring.

### 2.6 Quantitative analysis

The contents of Zr and U in Cd were measured, and the experimental results are shown in Table 2. It indicates that the contents of Zr in Cd at 475℃ and 500℃, are equal to 0.26 g/100 g Cd, 0.27 g/100 g Cd, respectively. The content of U in Cd at 475°C and 500°C is equal to 2.2 g/100 g Cd, and the ratios of mass

of U to that of Cd in sample 1 and 2 are equal to 0.118 and 0.123, respectively.

**Table 1 Qualitative analysis results of sample 2 and material Cd**

| Item | Main element |
|---|---|
| Matrix of sampe | Cd K U Zr |
| Eutetoid | Cd K |
| Material Cd | Cd K |

**Table 2 Content of U and Zr in sample***

| Sample | Content of Zr in sample/g | Content of U in sample/g | $m_{Zr}/m_U$ |
|---|---|---|---|
| 1 | 0.26 | 2.2 | 0.118 |
| 2 | 0.27 | 2.2 | 0.123 |

* 1. Mass of Zr and U in 100 g Cd;

2. The temperatures for dissolution for sample 1 and 2 are 475℃ and 500℃, respectively.

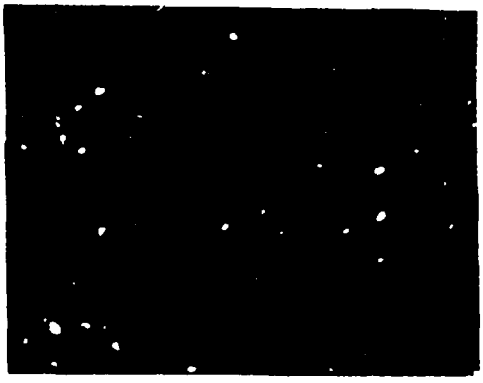

Fig. 6 Constituent diagram of micro-area of sample 2#
(amplification 2000/3.0)

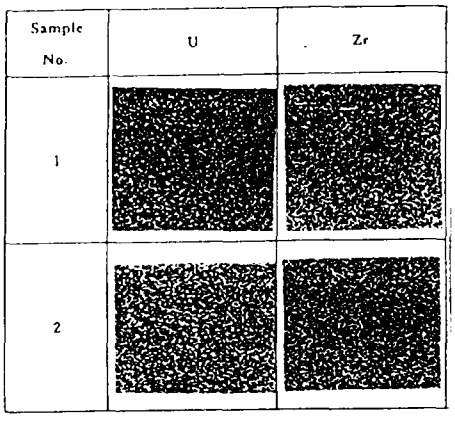


Fig. 7 X-ray scanning distribution diagram of U and Zr in cadmium (amplification 2000/3.0)
Sample. 1, temperature 475℃;
Sample. 2, temperature 500℃.

## 2.7 Charateristic X-ray scanning distribution diagram

The charateristic X-ray scanning distribution diagram of U, Zr in Cd is shown in Fig. 7. The bright point in the Fig. 7 represents U and Zr, respectively. It is

shown that the distribution of U and Zr in Cd is homogeneous.

## 3 Conclusion

(1) Increasing temperature is beneficial to dissolution of U-10Zr alloy in liquid cadmium. At 400°C and 500°C, with stirring rate of some 150 r/min, the solubilities of uranium in liquid cadmium are 0.4% and 2.2%, respectively; at the first 30 min, the dissolution rates of U-10Zr alloy pellets are 0.05 g/ ($cm^2$ • h) and 0.32 g/ ($cm^2$ • h), respectively.

(2) The suitable dissolution condition for U-10Zr alloy pellets in liquid cadmium (the ratio of the mass of liquid Cd to that of the pellets $\approx 7$): temperature, 480°C; stirring rate, 150 r/min; time, 4 h.

(3) Sample 2 contains U and Zr dissolved from U-10Zr alloy pellets and K present in original material Cd; distribution of K in Cd is non-homogeneous, distribution of Uand Zr in Cd is homogeneous.

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