

Recovery of Zirconium and Removal of Uranium from Alloy Waste by Chloride Volatilization Method

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The chloride volatilization method for the recovery of zirconium and removal of uranium from zirconium containing metallic wastes formed in spent fuel reprocessing was studied using the simulated alloy waste, i.e. the mixture of Zr foil and $\text{UO}_2/\text{U}_3\text{O}_8$ powder. When the simulated waste was heated to react with chlorine gas at 350 – 1000 °C, the zirconium metal changed to volatile ZrCl_4 showing high volatility ratio (V_{Zr}) of 99%. The amount of volatilized uranium increases at higher temperatures causing lowering of decontamination factor (DF) of uranium. This is thought to be caused by the chlorination of UO_2 with ZrCl_4 vapor. The highest DF value of 12.5 was obtained when the reaction temperature was 350°C. Addition of 10 vol.% oxygen gas into chlorine gas was effective for suppressing the volatilization of uranium, while the volatilization ratio of zirconium was decreased to 68% with the addition of 20 vol.% oxygen. In the case of the mixture of Zr foil and U_3O_8 , the V value of uranium showed minimum (44%) at 400°C with chlorine gas giving the highest DF value 24.3. When the 10 vol.% oxygen was added to chlorine gas, the V value of zirconium decreased to 82% at 600°C, but almost all the uranium volatilized ($V_{\text{U}}=99\%$), which may be caused by the formation of volatile uranium chlorides under oxidative atmosphere.

Keywords: Zirconium, Uranium, Chloride, Volatilization

Introduction

UO_2 fuels are widely used in the commercial nuclear plant (Light Water Reactor). Usually, the spent fuels are sent to the reprocessing step for the recovery of some useful components such as Pu after use. When the spent fuels are treated by Purex Process, a large amount of alloy scraps (Zircalloy-2 or -4), which are insoluble in nitric acid and contaminated by uranium and other trans-uranium elements, are produced at the nitric acid dissolution step. The disposal for these alloy wastes is suspended at present. The alloy wastes are the mixtures of zirconium metal part and oxide part containing UO_2 . In the zirconium industry[1], the ore has been mixed with carbon and reacted with chlorine to produce ZrCl_4 . Then it is reduced to zirconium sponge by Mg metal. For the nuclear alloy waste, the chloride volatilization method was thought to be applicable, i.e. zirconium is chlorinated, volatilized and recovered as ZrCl_4 , while uranium oxide is not. It would be a potential resource of zirconium after the removal of radioactive elements. In this paper, the recovery of zirconium and the removal of uranium from the simulated alloy waste containing zirconium foil and uranium oxide was studied by chloride volatilization method.

Experimental

Materials used

Uranium dioxide was prepared by heating U_3O_8 in H_2 at 1000°C for 4h. Zirconium foil of 0.1 mm thickness was purchased from Niraco Co. Ltd., and used after linsing ultrasonically by acetone. Nitrogen of 99.99% and

chlorine of 99.9% gases were obtained from Nihon Sanso Co. Ltd., and Hashimoto Chemical Ind., respectively.

Chlorination experiment

A weighed mixture of Zr foil (10x77x0.1mm, ~0.5g) and $\text{UO}_2/\text{U}_3\text{O}_8$ powder (~0.1mg) was placed on a quartz boat followed by setting the boat in a quartz reaction tube. After the reaction system was evacuated, it was refilled by nitrogen gas to ambient pressure. Subsequently, the reaction tube was heated by an IR Au-coated image furnace, ULVAC Type MR-H500, to the intended temperature. Then, the chlorine gas was introduced to the reaction part and flowed over the sample for an intended time. After the reaction, the power of the furnace was switched off. When the furnace was cooled down to room temperature, the flow of chlorine gas was ceased. The reaction temperature was changed from 350 to 1000°C. The reaction time was 1 hour. The flow of gases was controlled by a float flow-meter (Kusano Type 1/16-160). The flow rate of chlorine was 50 ml/min. The flow rates of oxygen gas added to chlorine gas were 5 (10 vol.% O_2) and 10 ml/min (20 vol.% O_2).

Analysis

After the chlorination experiments, the amounts of zirconium and uranium in the residue and condensate were analysed by ICP spectrometry using a Hitachi AES-P5200 spectrometer. The volatility ratio (V) and decontamination factor (DF) were obtained by the following equations:

$$V(\%) = 100(M_i - M_r) / M_i \quad (1)$$

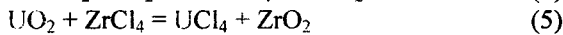
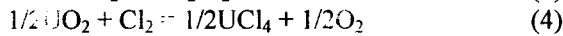
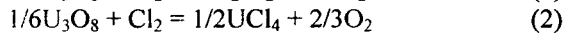
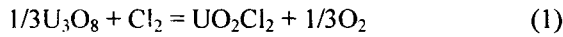
$$DF = U_i / U_v, \quad (2)$$

where M_i and M_r are the amounts of M ($M=U, Zr$) in the initial sample and residue, respectively and U_i and U_v the weight concentrations of uranium in the initial mixture and condensate, respectively.

Results and Discussion

Thermodynamical consideration

When Cl_2 gas is used for chlorination of the mixture of zirconium metal and uranium oxide, it is important to take into account the possible chlorination reactions by using the ΔG° values of the chlorination reactions[2]. They are shown by the following equations per mole of Cl_2 gas arranged in the order of magnitude from the higher ΔG° value at 300 K:



The thermodynamic states of the formed chlorides are not written in the above equations since they change in the temperature range from 300 to 2000 K. The variation of the ΔG° values with temperature is depicted in Fig. 1. The kinks in the figure show the transitions. From curve (6) of the figure, it is possible that zirconium metal is most easily chlorinated to $ZrCl_4$ by

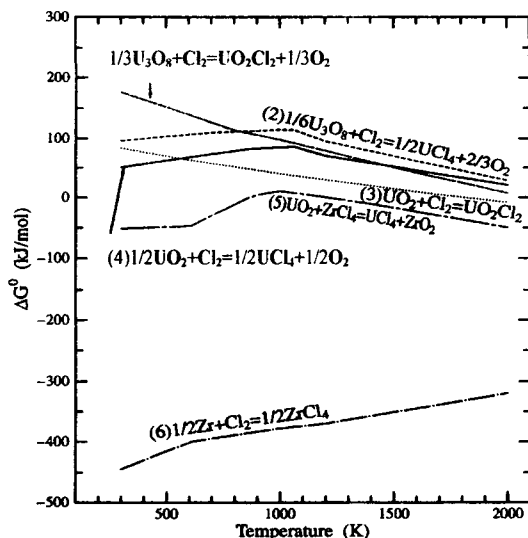


Fig. 1 Free energy change for chlorination reactions of zirconium and uranium oxides at elevated temperatures.

heating with Cl_2 in the whole temperature range. thought Chlorination of uranium oxides (curves (1), (2), (3) and (4)) will not proceed since the ΔG° values for them are positive. However, uranium dioxide seems to be chlorinated by the produced $ZrCl_4$ forming UCl_4 (curve (5)). UCl_4 shows a significant vapor pressure at temperatures higher than $331^\circ C$, it is very important for the decontamination of volatilized $ZrCl_4$ to suppress the reaction (5).

Chlorination of Zr+ UO_2 mixture

Chlorination at high temperature

In our previous paper[3], when the uranium ore was reacted with chlorine gas in the presence of activated carbon, it was found that the volatilization of uranium from the ore was suppressed by the addition of oxygen to chlorine gas. When the mixture of Zr foil and UO_2 powder was reacted with chlorine at $1000^\circ C$, effect of oxygen addition to the chlorine gas was examined. The volatility ratios of zirconium(V_{Zr}), uranium(V_U) and decontamination factor(DF) are shown in Fig. 2 as a function of oxygen amount added. When no oxygen was added to the chlorine gas, the values of V_{Zr} and V_U were 100 and 96%, respectively, giving the DF value 1. Namely, no separation effect was observed at high temperature without the addition of oxygen.

The V_{Zr} value was decreased gradually with increasing oxygen amount added between 0 and 10 vol.% O_2 , then rapidly between 10 and 20 vol.% O_2 . On the other hand, the V_U value decreased monotonically with increasing temperature. The DF value was increased from 1 of no oxygen addition to 3.8 of 20 vol.% O_2 . But the low V_{Zr} value, such as 46% of 20 vol.% O_2 is not favorable from the production standpoint of view.

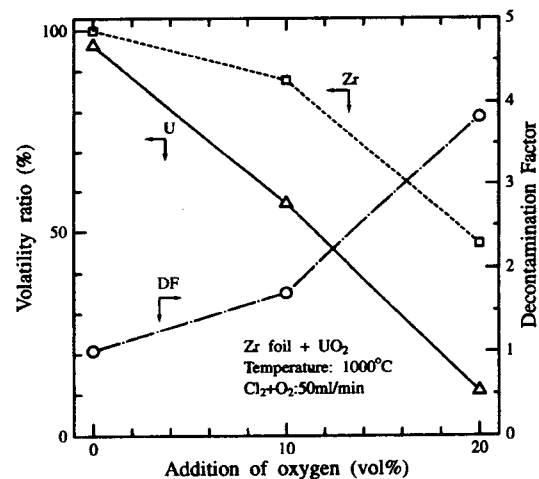


Fig. 2 Change of the volatility ratios of zirconium and uranium, and the decontamination factor of Zr foil + UO_2 sample as a function of amount of oxygen added.

Next, the effect of chlorination temperature on the volatility ratios and the decontamination factor was studied. A mixture of Zr foil and UO_2 powder was reacted with the mixture gas of chlorine and oxygen at temperatures ranging from 600 to 1000°C. The values of V_{Zr} , V_{U} and DF are shown in Fig. 3 as a function of temperature.

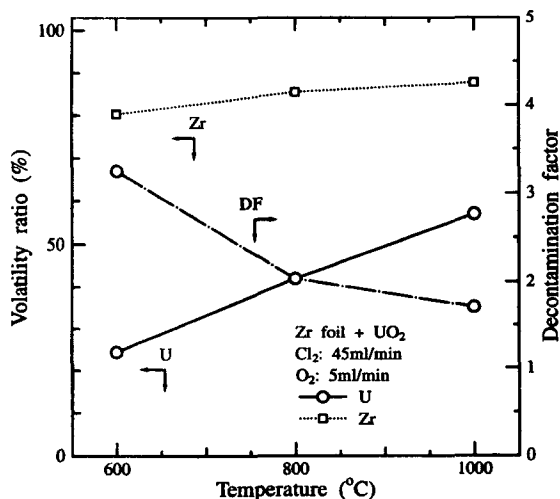


Fig. 3 Volatility ratios of zirconium and uranium, and decontamination factor for Zr foil + UO_2 sample as a function of temperature in the presence of oxygen (10 vol.% O_2).

From the result, it is seen that the value of V_{Zr} was slightly increased from 80 to 85% with increasing temperature from 600 to 1000°C. On the other hand, the value of V_{U} was gradually increased from 25 to 56% in the same temperature range, resulting in the decrease of DF value. Though the mixed gas of chlorine and oxygen was used, the DF values were still low by the high temperature chlorination.

Chlorination at low temperature

Next, chlorination of Zr foil and UO_2 powder with chlorine gas at low temperature was examined. For the mixture of Zr foil and UO_2 powder reacted with chlorine gas at temperatures ranging from 350 to 500°C, the values of V_{Zr} , V_{U} and DF are shown in Fig. 4 as a function of temperature. It is seen that the value of V_{Zr} attains to almost 99% at all temperatures examined. The value of V_{U} was low at 350°C, while it increased to around 50% at temperatures higher than 350°C. At 350°C, the DF value was highest (DF=12.5), while they were around 10 at 400 and 500°C. From these result, it is recommended that the low chlorination temperature of 350°C suppressing the vaporization of uranium is used. For the mixture of Zr foil and UO_2 powder heated with chlorine gas at 400°C, the effect of oxygen

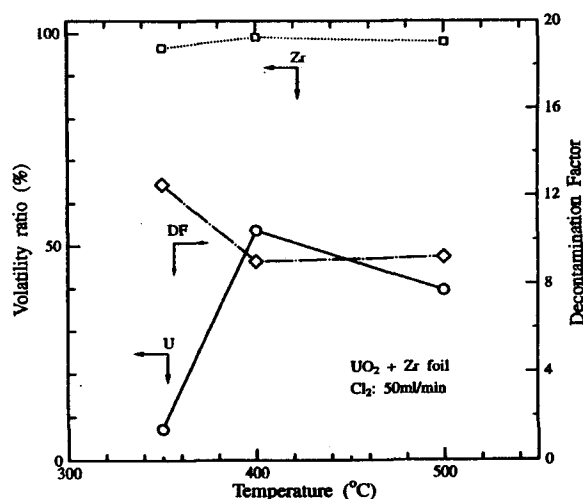


Fig. 4 Volatility ratio and decontamination factor for the chlorination of Zr foil + UO_2 sample as a function of temperature.

addition to the chlorine gas was examined. The V_{Zr} , V_{U} and DF values are shown in Fig. 5 as a function of oxygen amount added. When no oxygen was added to the chlorine gas, the values of V_{Zr} , V_{U} and DF were 99%, 54% and 8.7, respectively. By the addition of 10 vol.% O_2 to chlorine gas, Both the V_{Zr} and V_{U} values were decreased. The highest DF value of 12.5 was obtained at 400°C which was 8 times higher than that obtained at 1000°C (Fig. 2). In the case of chlorination of Zr + UO_2 mixture, it is suggested that chlorination at low temperature is useful for the recovery of zirconium with high DF value compared with that of high temperature chlorination.

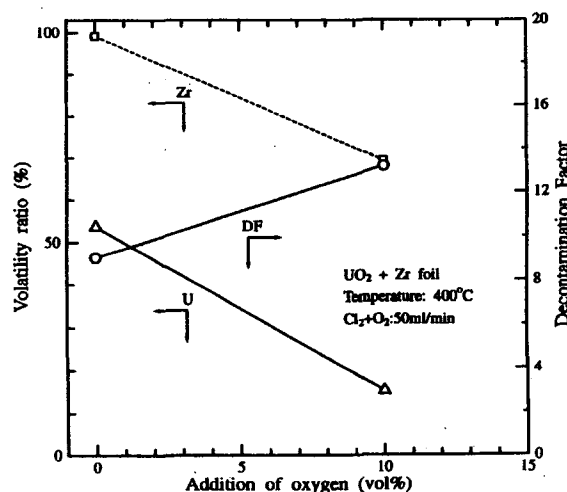


Fig. 5 Volatility ratios of zirconium and uranium, and decontamination factor for Zr foil + UO_2 sample as a function of the amount of oxygen added.

Chlorination of Zr + U₃O₈ mixture

Effect of reaction temperature

If UO₂ attached to the surface of Zircaloy cladding is oxidized under a certain condition, U₃O₈ is formed. A mixture of Zr foil and U₃O₈ powder was reacted with the mixture gas of chlorine and oxygen at temperatures ranging from 350 to 600°C. The values of V_{Zr}, V_U and DF are shown in Fig. 6 as a function of temperature. It is seen that the values of V_{Zr} are close to 100% at temperatures between 350 to 600°C. The value of V_U was low at 350°C, while it increased to around 25% at 400°C, and then decreased to less than 10% at 500 and 600°C. This behavior of volatilization of uranium could be ascribed to the the formation of higher uranium chloride, such as UCl₅ and UCl₆ which are more volatile than UCl₄. At 400°C, the highest DF value of 24.3 was obtained. From these results, it seems that low temperature is needed for suppressing the vaporization of uranium during the chlorination of the mixture of zirconium metal and uranium oxide. The higher DF values are expected if the chlorination temperature lower than 350 °C is adopted. However, such a low temperature chlorination is not favorable from the production standpoint of view, since the vapor pressure of ZrCl₄ lowers at temperatures lower than 331°C, the sublimation point of ZrCl₄.

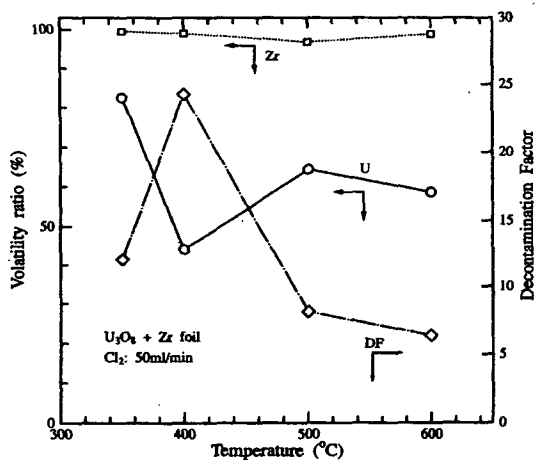


Fig. 6 Volatility ratios of zirconium and uranium, and decontamination factor for Zr foil + U₃O₈ sample as a function of temperature.

Effect of oxygen addition to the chlorine gas

For the mixture of Zr foil and U₃O₈ powder heated with chlorine at 600°C, the effect of oxygen addition to the chlorine gas was studied. The V_{Zr}, V_U and DF values are shown in Fig. 7 as a function of oxygen amount

added. When no oxygen was added to the chlorine gas, the values of V_{Zr}, V_U and DF were 99%, 59% and 6.3, respectively. By the addition of 10 vol.%O₂ to the chlorine gas, the V_{Zr} value was decreased from 99 to 85%. However, the V_U value was increased from 59 to 100%: Uranium volatilized completely from the sample. This behavior could be ascribed to the oxidation of uranium to higher oxidation state in the oxidative condition, resulting in formation of volatile uranium chlorides, such as UCl₅ and UCl₆. In the case of chlorination of Zr + U₃O₈ mixture, it is suggested that chlorination at low temperature is useful for the recovery of zirconium with high DF value. However, the addition of oxygen was unfavorable since the volatilization of uranium was enhanced under oxidative condition.

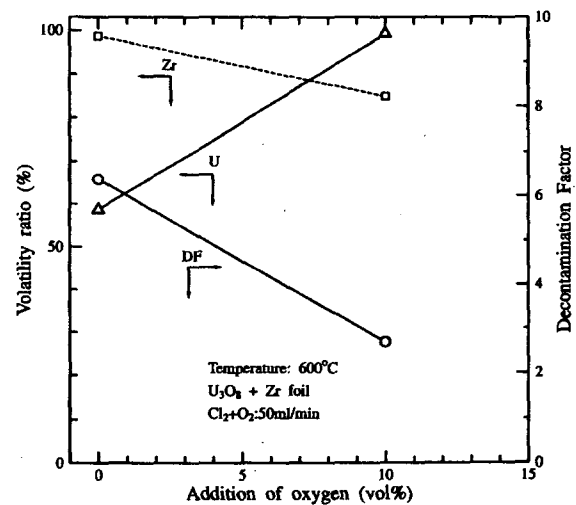


Fig. 7 Volatility ratios of zirconium and uranium, and decontamination factor for Zr foil + U₃O₈ sample as a function of the amount of oxygen added

Conclusion

Zirconium was recovered almost completely from the mixture of Zr foil and UO₂/U₃O₈ powder by chloride volatilization method using chlorine. To obtain high DF values, low temperature chlorination was found to be effective as well as the addition of oxygen to chlorine except for the case of Zr and U₃O₈ mixture where the volatilization of uranium was enhanced by the addition of oxygen.

References

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