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Journal of Nuclear Materials 247 (1997) 191–196

journal of nuclear materials

Identification of oxide phase and alloy phase obtained by heat treatment of calcined high level liquid waste with TiN reducing agent at 1873 K

Masayosi Uno [a,*], Hajime Kinoshita [a], Chie Miyake [a], Misato Horie [b]

[a] *Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan*
[b] *Power Reactor and Nuclear Fuel Development Corporation, O-aza Muramatsu 4-33, Tokai-Mura, Ibaraki 319-11, Japan*

Abstract

Simulated calcined HLLW was heat treated with TiN as a reducing agent at 1873 K. The treatment resulted in the melted and separated alloy phase and oxide phase. The alloy phase contains Cr–Fe–Ni alloy, Fe–Ni alloy, Cr–Ni alloy, Ru–Fe alloy, Mo and Pd metals which are dissolved by Fe and does not contain Ti. The dissolution of Fe in Ru and Mo caused the melting of alloy phase at the treatment temperature. The oxide phase contains $ZrTiO_4$, $Sr_{0.5}NdTi_2O_6$, $BaTiO_3$, $La_4Ti_9O_{24}$, $SrCeO_3$ and some neodymium–zirconium oxides phases. Some phases are those used as the host phase in the ceramic waste and the other phases are resulted from the smaller amount of Ti in the method than in ceramic waste. The formation of the complex oxides caused the melting of the oxide phase at the treatment temperature. © 1997 Elsevier Science B.V.

1. Introduction

Solidification of high level liquid waste (HLLW) has developed to the stage of commercial vitrification plants to generate vitrified high-active waste. However, basic studies in separation and/or transmutation with various processing schemes are prompted. One of such studies uses the super high temperature method by which HLLW is dry-treated in a simple process [1].

In this method, as shown in Fig. 1, HLLW is first calcined at 973 K to vaporize water and nitric acid. Further heating with a small amount of a reducing agent such as BN, AlN, Si_3N_4 or TiN above 1873 K results in separation of volatile species, Cs and Rb by vaporization, and elements with higher standard free energy of oxide formation than the reducing agents (platinum metals and other transition metals), are reduced. After melting they form the alloy phase which separates from the oxide phase of melted complex oxides of alkaline earth elements, rare earth elements, Zr, actinides and the metal element of the reducing agent (Fig. 2).

The characteristics of the method are: the separation of Cs, which may be recovered by cold trapping and be stored for attenuation or be used as a radiation source, the recovery of platinum metals and thus diminish the volume of the oxide waste. This also facilitates subsequent treatment, storage and disposal of the oxide waste which contains actinides, the key elements in high level waste management. The advantage of this method is that the above mentioned characteristics are attained by a very simple process with addition of a small amount of a reducing agent although volatile species may contaminate the process facilities.

Vaporization of all Cs from HLLW, melting and separation of both the oxide and alloy phases has been verified by the treatment of simulated calcined HLLW which contains 27 fission products (FP) and corrosion products (CP: Fe, Cr and Ni), which originate from the stainless steel walls of the vessel in the PUREX process [1–3]. The alloy phase under the oxide phase, due to the difference in density, did not adhere to the oxide phase after cooling, may be because of the difference in the thermal expansiv-

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[*] Corresponding author. Tel.: +81-6 879 7906; fax +81-6 875 5696; e-mail: uno@galaxy.nucl.eng.osaka-u.ac.jp.

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PII S0022-3115(97)00070-6

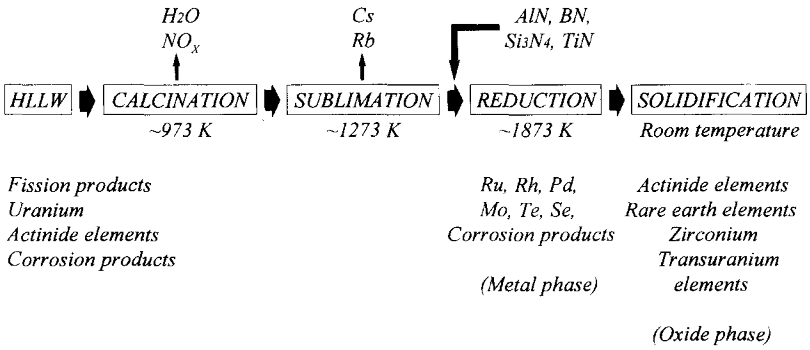

Fig. 1. The process of the super high temperature method.

ity. Previous studies on the elementary reactions in the simplified process, using a few representative elements in HLLW, have elucidated the possibility of the recovery of Re (as a surrogate for Tc), the oxide of which has a sublimation point of 523 K [5], the decrease of the melting temperature of the alloy phase by the alloying of the refractory platinum metals or Mo with CP [6] and the decrease of the melting temperature of oxide phase by the formation of complex oxides of fission products and the metal element of the reducing agent [4]. From these studies, the elementary reactions in the simplified process has been clarified and TiN has been considered to be the best reducing agent among the four because of the recovering ratio of Re, the melting temperature of the oxide phase and the chemical durability of the compounds in the oxide phase as waste.

The name of the method came form the treatment temperature above 1873 K which is higher than temperatures employed in other solidification processes involving melting of waste or separation by vaporization, such as vitrification or solidification in ceramic waste. Recently some solidification processes through melting have been proposed [7]. However, the phases obtained by such high temperature processes have scarcely been reported. In the present study, the alloy phase and oxide phase are produced by heat treatment of the simulated calcined HLLW with TiN at 1873 K, under the condition of the super high

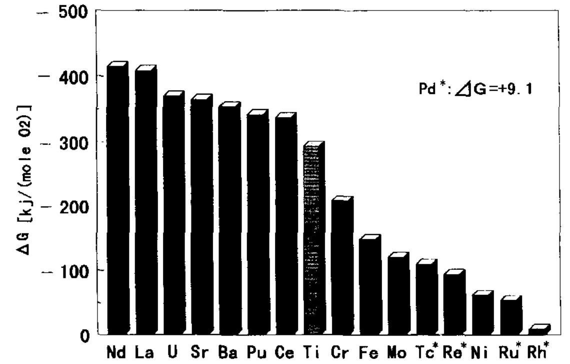

Fig. 2. Standard free energy of oxide formation; representative fission products and titanium at 1873 K, except for those marked by an asterisk, which are for the highest temperature at which data are available.

Table 1

The composition of simulated calcined HLLW

Element	Content (at.%)	Oxide	Content (mol%)
Mo	9.263	MoO_2	12.182
Ru	5.373	RuO_2	7.067
Pd	3.359	PdO	4.418
Re	1.999	ReO_2	2.629
Te	0.986	TeO_2	1.297
Rh	1.075	Rh_2O_3	0.707
Cd	0.254	CdO	0.334
Se	0.191	SeO_2	0.251
Ag	0.167	Ag_2O	0.110
Sn	0.189	SnO_2	0.248
Sb	0.040	Sb_2O_3	0.026
In	0.005	In_2O_3	0.003
Fe	25.827	Fe_2O_3	16.984
Cr	6.751	CrO	8.879
Ni	2.658	NiO	3.496
Cs	4.567	Cs_2O	3.003
Rb	1.122	Rb_2O	0.738
Ba	3.447	BaO	4.533
Sr	2.391	SrO	3.144
Ce	4.498	CeO_2	5.916
Nd	7.471	Nd_2O_3	4.913
La	2.334	La_2O_3	1.535
Pr	2.108	Pr_2O_3	1.386
Y	1.399	Y_2O_3	0.920
Sm	1.352	Sm_2O_3	0.889
Eu	0.233	Eu_2O_3	0.153
Gd	0.225	Gd_2O_3	0.148
Tb	0.005	Tb_2O_3	0.003
Dy	0.002	Dy_2O_3	0.001
Zr	10.711	ZrO_2	14.087

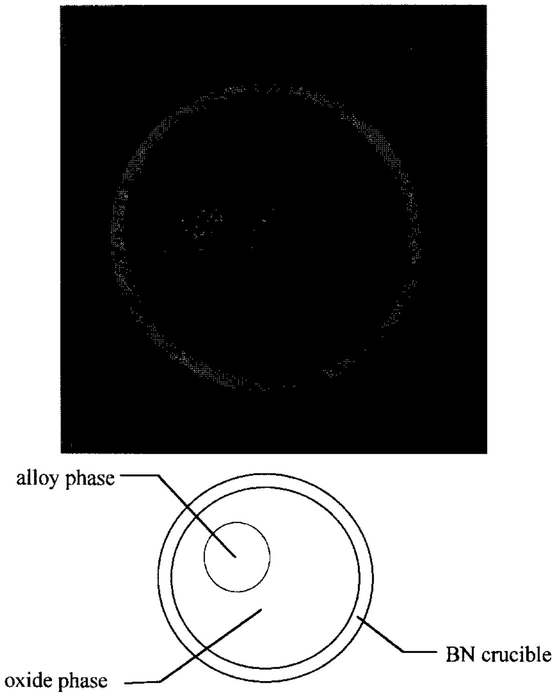

Fig. 3. The appearance of the product.

temperature method and the constituent compounds in the both phases are identified.

2. Experimental

The composition of simulated calcined HLLW is shown in Table 1. This composition is calculated based on the fuel spent for 45 Gwd/t after 5 years of cooling time. The simulated calcined HLLW is synthesized with elements containing amounts beyond 1 g/Mg-U in spent fuel and containing Re and Ce instead of Tc and Pr, respectively, and containing Fe, Cr and Ni, as CP, but no actinides.

TiN powder and the simulated calcined HLLW is mixed in the agate mortar. The composition of the reducing agent in the mixture is decided such that the reducing agent would reduce all the oxides which would come to the metallic phase (platinum metal oxides, other transition metal oxides and CP oxides). The ratio of the reducing agent to the simulated calcined HLLW is about 9:40 in weight, in other words the content of Ti in the all metal elements in the mixture is about 38 at.%.

High temperature treatment was performed in a Nagano–Keiki carbon heater furnace. A powder sample in a BN crucible was heated to 1273 K in 1 h. At this temperature the sample was maintained for 1 h and then heated to 1873 K in 1 h. After maintaining the temperature for 1 h the sample was furnace cooled under flowing argon.

Phases of the reaction products were identified by X-ray diffraction. The X-ray diffraction was performed with Cu Kα radiation on a Rigaku rad r-A diffractometer equipped with a curved graphite monochrometer. The distribution of elements in the reaction products was studied by electron probe micro analysis (EPMA) using Topkon MINI-SEM 100 and Horiba EMAX-8000 units.

3. Results and discussion

Fig. 3 shows the appearance of the products. The central region of the sample, presenting the metallic cluster, is the alloy phase which is surrounded by the dark oxide phase. The image shows that both phases melt at the temperature of the treatment, 1873 K.

The X-ray diffraction pattern for the alloy phase is shown in Fig. 4. Peaks for Cr–Fe–Ni alloy (austenitic steel), Fe–Ni alloy (taenite), Cr–Ni alloy (Cr_3Ni_2), Ru–Fe alloy (Ru_4Fe), Mo and Pd can be seen in the pattern. The results of EPMA analysis are shown in Fig. 5 together with the scanning electron micrograph (SEM). Inhomogeneous distribution of Ru, Mo and Pd and homogeneous distribution of Fe and Cr can be seen. Thus, EPMA analysis support the formation of Ru–Fe alloy and suggest the dissolution of Fe into Mo and Pd phases. It is concluded that the alloy phase contains the three CP alloys, Ru–Fe alloy, Mo and Pd metals which are dissolved by Fe. According to the binary alloy phase diagrams [8,9] Ru,

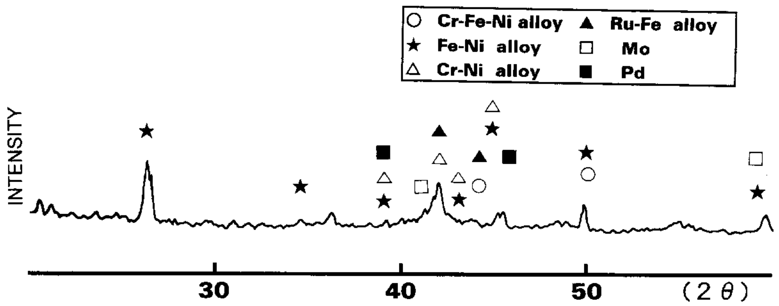

Fig. 4. X-ray diffraction pattern for the alloy phase.

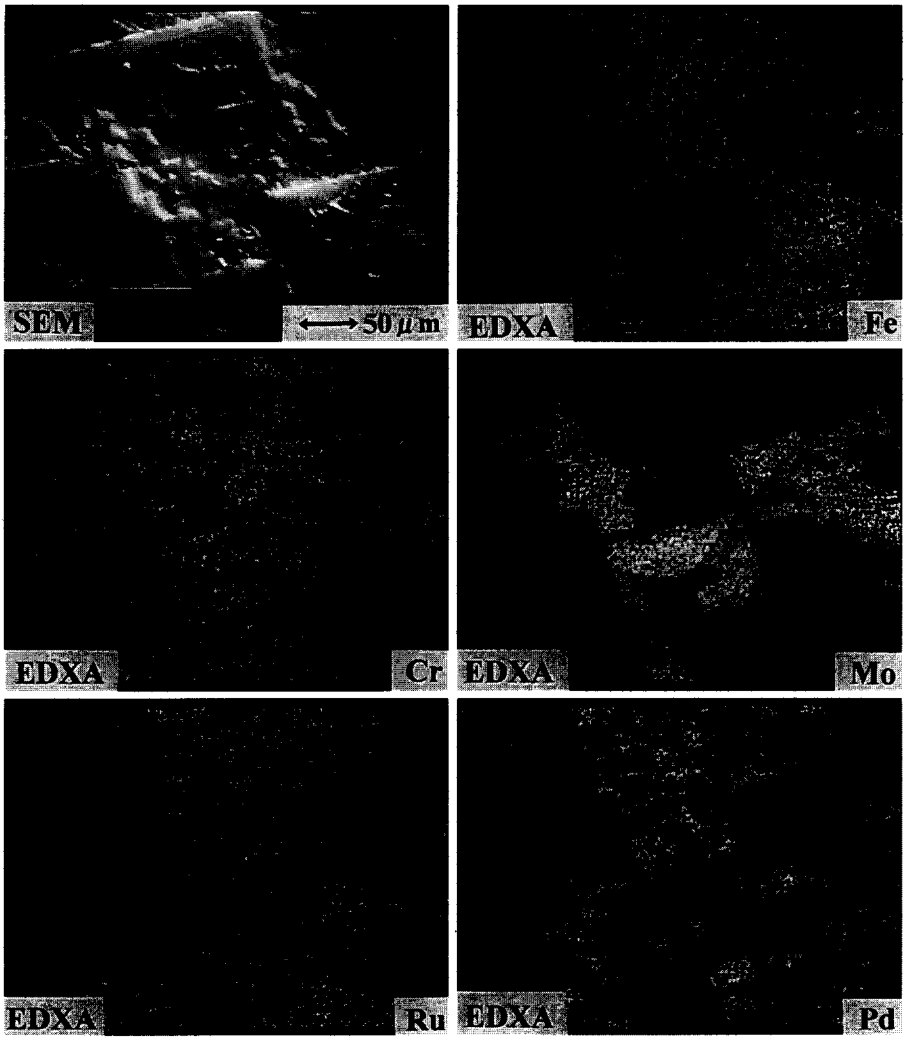

Fig. 5. Scanning electron micrograph and results of X-ray energy-dispersive analysis for the alloy phase.

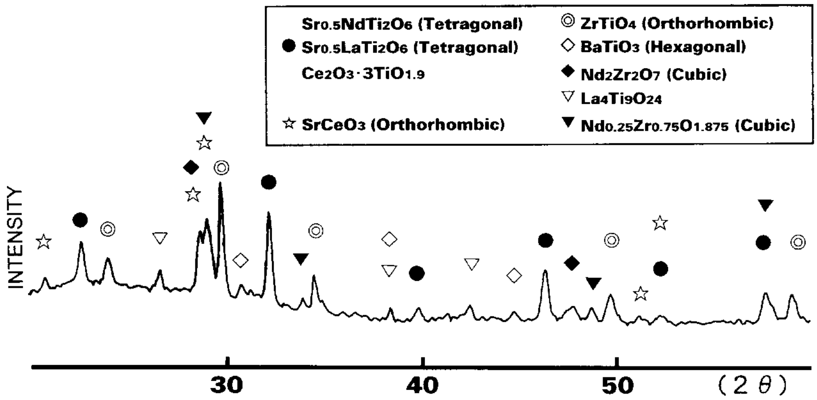

Fig. 6. X-ray diffraction pattern for the oxide phase.

which has a melting point of 2583 K, and Mo, which has the melting point of 2983 K, can melt around the temperature of the treatment by the dissolution of Fe. This dissolution of Fe to Ru and to Mo is considered to cause the melting of the alloy phase at 1873 K in the same way as the simplified system [5]. It is also seen that the metal element of the reducing agent does not exist in the alloy phase which is in agreement with the results of the simplified system [5].

Other elements, which may come to the alloy phase through the reduction by the reducing agent, were not detected by the X-ray diffraction and EPMA analysis because the composition of these elements may be too small to be detected by the present apparatus. In the simplified system, the reaction of only platinum metal oxides and rhenium oxides with TiN produced Re metal in the alloy phase, with partly sublimation of Re [6]. Se, Te and Sb and their oxides have sublimation points or boiling points below 1273 K. Some of them vaporize and some of them form alloys with platinum metals and/or Mo and some of them exist as the oxides in a simplified system. The behavior of these volatile species in the treatment will be published else where.

The X-ray diffraction pattern for the oxide phase and the results of SEM and EDXA analysis are shown in Figs. 6 and 7, respectively. As there are more than 100 compounds in the two alkaline earth elements, 10 rare earth elements-Zr–Ti–O system and compounds comprising elements which belong to the same groups but are different elements, e.g., $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$, have the same structures with slightly different lattice constants, it is difficult to identify the chemical states of all the components. However, the results of the X-ray diffraction with the support of EPMA analysis, which shows the homoge-

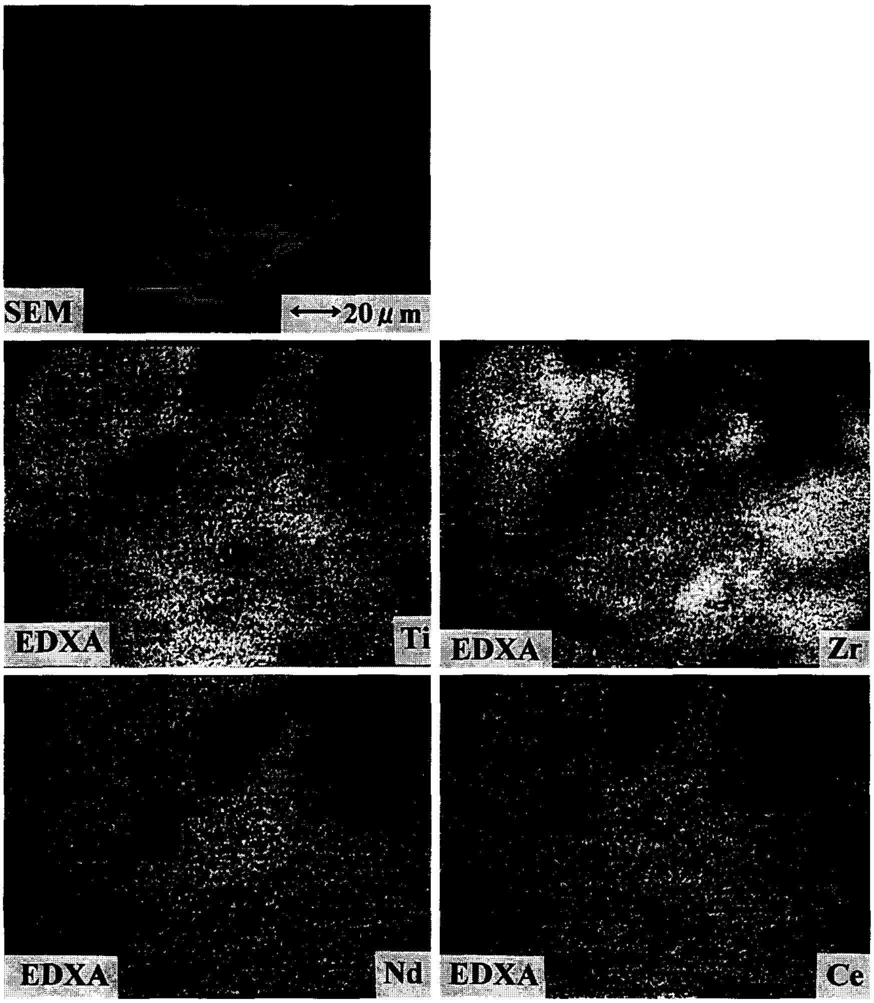

Fig. 7. Scanning electron micrograph and results of X-ray energy-dispersive analysis for the oxide phase.

neous distribution of rare earth elements (Nd, Ce) and more than two regions of different Zr or Ti concentration, enable to divide the formed phases into the following six types:

(1) the orthorhombic $ZrTiO_4$ phase, which may contain some rare earth elements,

(2) the tetragonal $Sr_{0.5}NdTi_2O_6$ phase, which may contain other alkaline earth and rare earth elements in the Sr and Nd sites, respectively,

(3) the hexagonal $BaTiO_3$ phase, which may contain other alkaline earth elements in the Ba site,

(4) the $La_4Ti_9O_{24}$ phase,

(5) the orthorhombic $SrCeO_3$ phase and

(6) some cubic neodymium–zirconium oxides which may contain other rare earth elements in the Nd site.

Thus, it is found that almost all alkaline earth and rare earth FPs form the complex oxides of Ti, except those of $SrCeO_3$ and the neodymium–zirconium oxides phase. It is seen that Zr, which is the FP with a high content in the simulated calcined HLLW, is also the host material of the complex oxides of rare earth and alkaline earth elements.

The melting points of binary titanium, zirconium, alkaline earth elements or rare earth elements oxides are beyond 2000 K. The ternary phase diagrams, however, show that Ba–Ti–O complex oxides [10] and La–Ti–O complex oxides [11] melt below 1873 K. The quaternary Sr–Ti–Zr–O phase diagram [10] also suggests that a melted quaternary phase is solidified to the $ZrTiO_4$ phase and other phases around 1700 K. Thus, it is concluded that the formation of these complex oxides contributes to the melting of the oxide phase at the temperature of treatment, 1873 K.

$BaTiO_3$ and neodymium zirconium oxides phases identified in the product are the host phases known as perovskite and pyrochlore, respectively, in ceramic waste [12,13]. The formation of $SrCeO_3$, the complex oxide of only FP elements and the formation of $ZrTiO_4$ in comparison with zirconolite, nominally $CaZrTi_2O_7$ used as the host phase in the ceramic waste may arise from the less additive to HLLW in the present study than in ceramic waste. In the super high temperature method, the amount of additive is presently fixed at the amount of the reducing agent. However, the decrease of the volume of waste with a small amount of the additive by vaporizing Cs and separation of platinum metals is also an important aspect of the method. The chemical durability of these complex oxides is now in progress.

4. Conclusions

Simulated calcined HLLW, containing 27 FP and CP elements, was heat treated with TiN as a reducing agent at 1873 K. The treatment resulted in the melted and separated alloy and oxide phase. The alloy phase contains alloys of Cr–Fe–Ni, Fe–Ni, Cr–Ni, Ru–Fe. Mo and Pd metals which are dissolved by Fe and do not contain Ti. The dissolution of Fe in Ru and Mo caused the melting of the alloy phase at the temperature of the treatment. The oxide phase contains $ZrTiO_4$, $Sr_{0.5}NdTi_2O_6$, $BaTiO_3$, $La_4Ti_9O_{24}$, $SrCeO_3$ and some neodymium–zirconium oxides phases. Some phases are those used as the host phase in the ceramic waste and the other phases result from the smaller amount of Ti in the method than in ceramic waste. The formation of the complex oxides caused the melting of the oxide phase at the temperature of the treatment.

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