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Proceedings Paper:

Kinoshita, H., Uno, M., Yamanaka, S. et al. (2006) Molten ceramic solidification during molten state processing of HLW. In: Van Iseghem, P., (ed.) Scientific Basis for Nuclear Waste Management XXIX. 29th International Symposium on the Scientific Basis for Nuclear Waste Management, 12-16 Sep 2005, Ghent, Belgium. , pp. 655-660. ISSN: 0272-9172. EISSN: 1946-4274.

<https://doi.org/10.1557/PROC-932-51.1>

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Molten ceramic solidification during molten state processing of HLW

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ABSTRACT

Solidification of molten ceramics during molten state processing of High-Level Waste (HLW) was studied. Simulated HLW was heated together with different reducing agents (TiN with AlN or TiO₂) either at 1673 K or 1873K for 1 to 3 hours under Ar atmosphere. Cooling rates of 5 K/min and 10 K/min did not show obvious differences in the products in the standard condition of the present study. The composition and quantity of the reducing agent had a significant effect on the melting and solidifying behaviour of the simulated HLW.

INTRODUCTION

Molten state processing of simulant HLW has been studied to develop a simple, rational and effective solidification route for immobilisation of nuclear wastes [1-4]. The process consists of 5 stages as is shown in Figure 1: (1) all the wastes are in nitric acid solution as High Level Liquid Waste (HLLW) together with corrosion products (CP) from the vessels, (2) H₂O and NO_x in HLLW first vaporize at 973 K in the calcination process, (3) Cs and Rb vaporize up to 1273 K by heating calcined HLLW and would be recovered by a cold trap, (4) further heating with a desired amount of reducing agents, typically a mixture of TiN and AlN causes reduction and melting of waste elements, and (5) the molten wastes separate into an alloy phase and an oxide phase depending on the stabilities of their oxides. Both phases are to be obtained separately after cooling.

One of the key aspects of the process is that some of the elements are reduced to the metal and excluded from the oxide phase that will be treated as a waste form. This reduction of certain elements reduces the quantity of waste. As Figure 2 shows, elements with higher standard free energy of oxide formation (platinum metals and other transition metals) than the reducing agent are reduced and form the alloy phase, whereas the others, alkaline earth elements, rare earth elements, Zr, actinides and the metal elements of the reducing agent, form the oxide phase.

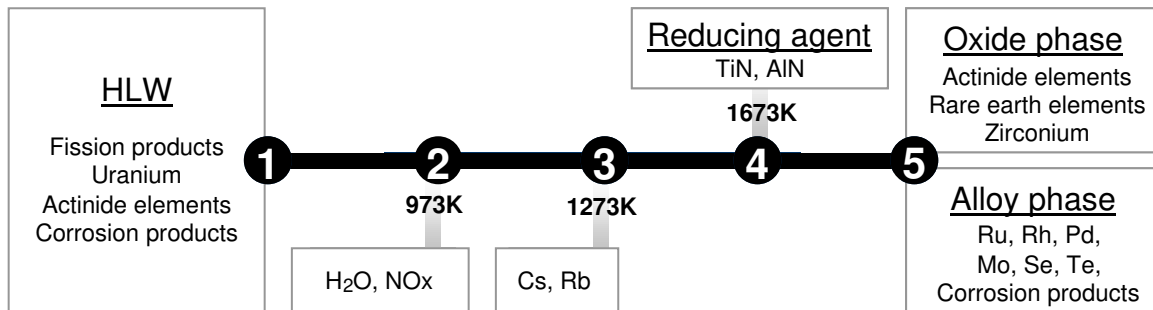


Figure 1. Processing of HLW via molten state processing.

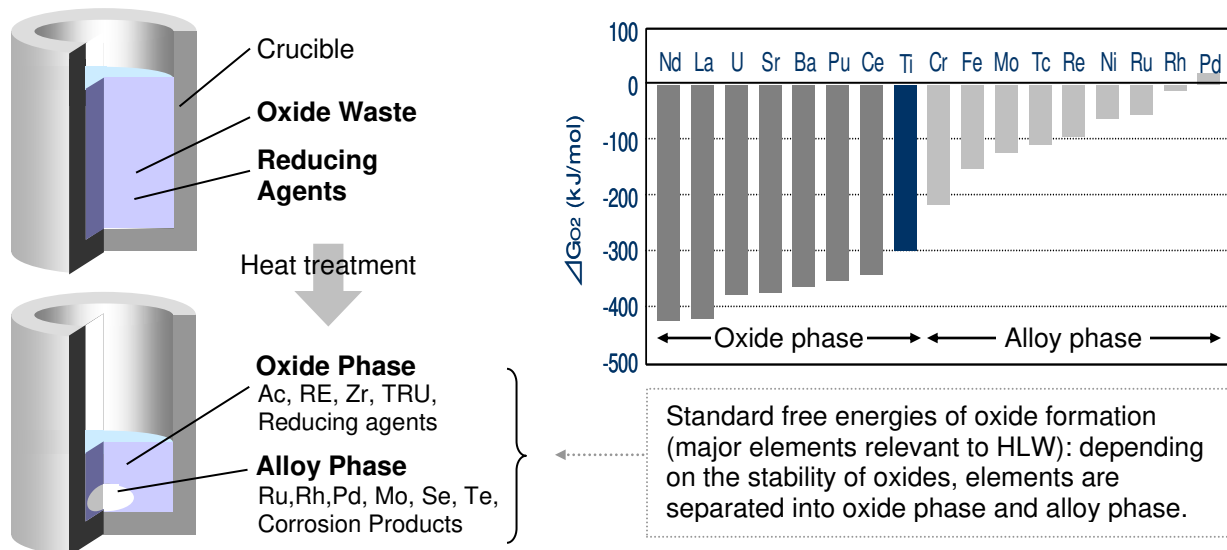


Figure 2. Schematic diagram of the separation / solidification stage (Stage 5 in Figure 1) of molten state processing for HLW.

FOCUS OF THE STUDY

The crucial point of the process is that both alloy and oxide phases are in the molten state. Our previous studies using simulated HLW revealed that the alloy phase melts up to 1673K by alloying the refractory platinum metals or Mo with corrosion products (Fe, Cr, Ni) [5]. Simultaneously the oxide phase melted at 1673 - 1873 K forming complex oxides of fission product (FP) elements and Ti and Al when a suitable mixture of TiN and AlN is added [6-9]. This route not only enables separation of the alloy and oxide phases but also shortens the process time significantly. Several hours of process time in total leads to formation of oxide phases with a sufficient chemical durability to be a waste form [9].

The present study focuses on the solidification of the molten oxide phase in the molten state processing of HLW. Differences in the obtained products from the molten state process are discussed with respect to the process temperature, cooling rate, composition and quantity of the reducing agent together with the literature data.

EXPERIMENTAL

Simulated HLW, as shown in **Table I**, contains 27 FP elements and 3 corrosion products (CP; Fe, Cr and Ni). In the standard experiment, the simulated HLW powder contained in a BN crucible with a reducing agent (TiN) was heated in an electric furnace to 1873 K. The quantity of TiN was determined to capture exactly all of oxygen from the species that will form the alloy phase. After holding at temperature for 1 - 3 h, the samples were furnace cooled at 10 K/min. The oxide phase was separated from the product using a diamond-impregnated saw, ground and polished with emery paper and diamond paste. The resulting flat surface of the selected sample was studied via SEM/EDX.

Table I. Composition of simulated HLW*

| Oxide to be reduced to metal | Content (mol%) | Oxide to remain as oxide | Content (mol%) | | |
|------------------------------|--------------------------------|--------------------------|--------------------------------|-------------------|-------|
| Alloy phase forming species | MoO ₂ | 12.182 | Volatile species | Cs ₂ O | 3.003 |
| | RuO ₂ | 7.067 | | Rb ₂ O | 0.738 |
| | PdO | 4.418 | | BaO | 4.533 |
| | ReO ₂ | 2.629 | SrO | 3.144 | |
| | TeO ₂ | 1.297 | CeO ₂ | 5.916 | |
| | Rh ₂ O ₃ | 0.707 | Nd ₂ O ₃ | 4.913 | |
| | CdO | 0.334 | La ₂ O ₃ | 1.535 | |
| | SeO ₂ | 0.251 | Pr ₂ O ₃ | 1.386 | |
| | SnO ₂ | 0.248 | Y ₂ O ₃ | 0.920 | |
| | Ag ₂ O | 0.110 | Sm ₂ O ₃ | 0.889 | |
| | Sb ₂ O ₃ | 0.026 | Eu ₂ O ₃ | 0.153 | |
| | In ₂ O ₃ | 0.003 | Gd ₂ O ₃ | 0.148 | |
| | Fe ₂ O ₃ | 16.984 | Tb ₂ O ₃ | 0.003 | |
| | CrO | 8.879 | Dy ₂ O ₃ | 0.001 | |
| | NiO | 3.496 | ZrO ₂ | 14.087 | |
| | Total | | 100.000 | | |

* Composition of simulated HLW was calculated based on spent fuel of 45 GWd/t after 5 years of cooling time. It includes elements exist more than 1g/Mg-U in spent fuel and contains Re and Ce instead of Tc and Pm, respectively, but contains no actinide species.

To further study the melting / solidification process, the following alterations to the standard condition were attempted: (1) cooling rate was changed to 5 K/min, (2) heating temperature was reduced to 1673 K and part of TiN was replaced with AlN, (3) quantity of TiN was reduced and (4) additional TiO₂ was mixed in the starting material expecting a different type of oxide phase.

RESULTS AND DISCUSSION

Figure 3 shows a photograph of the reaction product from the standard experiment heated at 1873 K under Ar atmosphere with exact amount of TiN reducing agent. Melting and solidification was successfully carried out, and alloy and oxide phases are separated. An SEM micrograph and EDX of the oxide phase are shown in Figure 4. The results suggest that Ba and Nd form complex oxides or solid solutions primarily with Ti, which is consistent with the data previously reported [6]. Although Zr is expected to form solid solutions with Nd and/or Ti [6], it was not very clear in the results of the present work.

When the cooling rate in the process was changed from 10 K/min to 5 K/min, the resultant oxide phase did not show any significant difference in its appearance. On the other hand, when the process temperature was reduced to 1673 K, the oxide phase did not melt and separation of the phases was unsuccessful even though the reduction of the elements occurred. Results from experiments with altered process conditions are shown in Table II together with previously reported data [9].

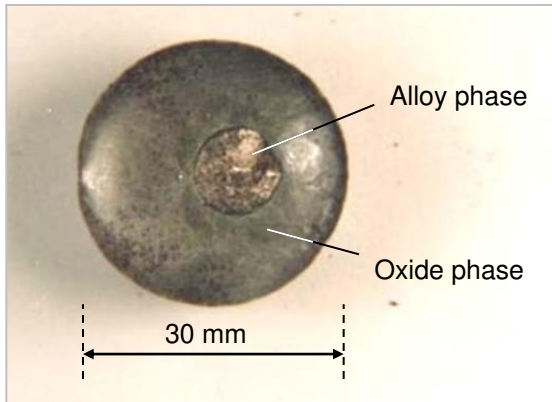


Figure 3. Reaction product from a standard molten state processing of simulated HLW: heated at 1873 K under Ar atmosphere with TiN reducing agent. Separation into two phases is clearly observed: alloy phase inside and oxide phase outside.

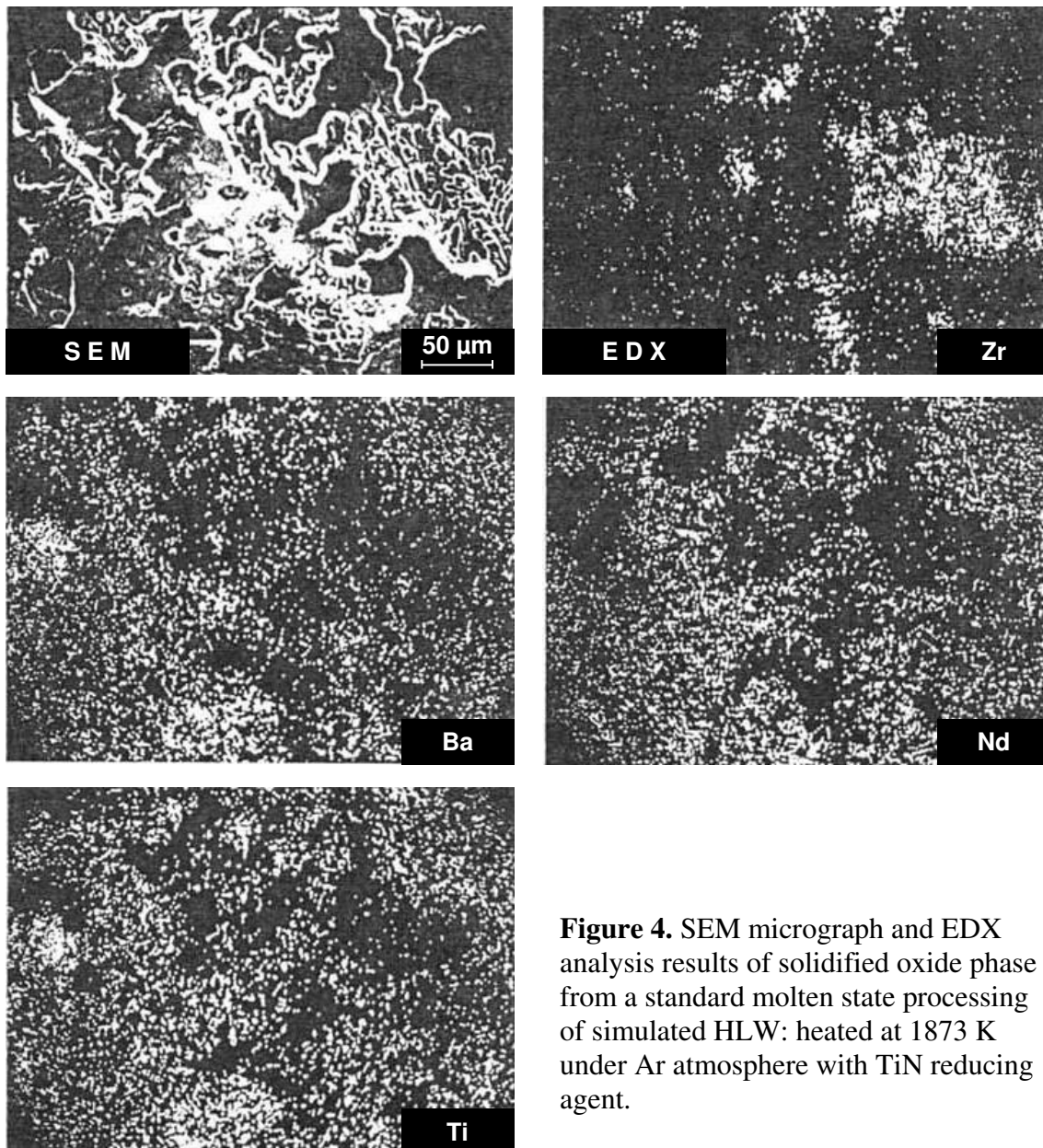


Figure 4. SEM micrograph and EDX analysis results of solidified oxide phase from a standard molten state processing of simulated HLW: heated at 1873 K under Ar atmosphere with TiN reducing agent.

Table II. Results of molten state processing with different conditions.

| Alteration | Process temperature | Additive | Molar ratio* | Result |
|---------------------------------------|---------------------|------------------------|--------------|--------------------------------|
| Part of TiN was replaced by AlN | 1673 K | TiN : AlN | 1.00 : 0.00 | Oxide phase not melted |
| | | | 0.95 : 0.05 | Oxide phase not melted [9] |
| | | | 0.90 : 0.10 | Alloy/Oxide phase obtained [9] |
| | | | 0.80 : 0.20 | Alloy/Oxide phase obtained [9] |
| Quantity of TiN was reduced | 1873 K | TiN | 1.00 | Alloy/Oxide phase obtained |
| | | | 0.90 | Single black phase obtained |
| | | | 0.80 | Single black phase obtained |
| Additional TiO ₂ was mixed | 1873 K | TiN : TiO ₂ | 1.00 : 0.20 | Alloy/Oxide phase obtained |
| | | | 1.00 : 1.00 | Oxide phase not melted |
| | | | 1.00 : 2.00 | Oxide phase not melted |

* The quantity of TiN for the standard experiment was used as the standard (1.000).

To make the melting and solidification processes successful at such low temperatures as 1673 K, it is necessary to replace some of TiN with AlN, as previously reported [9]. The replacement of TiN with AlN leads to an additional phase, $AE_5Al_8O_{17}$ (AE: Alkaline Earth) which contains La, Ti and a small amount of Zr in the solidified oxide phase [9]. When the quantity of TiN was reduced, a black single-phase product was obtained. It is difficult, at this stage, to know whether melting of the oxide phase occurred or not, as it may be a ceramic-metal composite or Cermet. This black product with a slight metallic shine is currently the subject of further study. Addition of TiO₂ appeared to have a negative effect on the melting / solidification process. It is, therefore, important to add corresponding AlN (or Al₂O₃) to make the process successful when increasing the additional TiO₂.

SUMMARY

Solidification of molten ceramics during molten state processing of HLW was studied. A standard experiment with TiN that captures exactly all of oxygen from the species that form alloy phase was successfully carried out. SEM/EDX results were consistent with that of a previous study [6]. Change in cooling rate from 10 K/min to 5 K/min did not lead to any significant difference in the solidified oxide phase. Reduction of the process temperature had a significant effect on the melting / solidification process. To make the melting and solidification processes successful at 1673 K, it is necessary to replace some of TiN with AlN. Reduction of TiN quantity had a very interesting effect on melting/solidification process. It led to the formation of a black single-phase product. Further studies in this area are currently being carried out. Addition of TiO₂ had a negative effect on melting / solidification processing. It is important to add corresponding AlN (or Al₂O₃) to make the process successful when increase additional TiO₂.

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