SECONDARY PHASE FORMATION AND THE MICROSTRUCTURAL EVOLUTION OF SURFACE LAYERS DURING VAPOR PHASE ALTERATION OF THE FRENCH SON 68 NUCLEAR WASTE GLASS AT 200°C

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ABSTRACT

The SON 68 inactive "R7T7" composition is the French reference glass for the LWR nuclear waste glass. Vapor phase alteration was used to accelerate the reaction progress of glass corrosion and to develop the characteristic suite of secondary, alteration phases. Extensive solid-state characterization (AEM/SEM/HRTEM) was completed on six inactive R7T7 waste glasses which were altered in the presence of saturated water vapor (200 °C) for 91, 241, 908, 1000, 1013, and 1021 days. The AEM samples were examined in cross-section (lattice-fringe imaging, microdiffraction, and quantitative thin-film EDS analysis). The glass monoliths were invariably covered with a thin altered rind. The layer became thicker with time: 0.5 µm for 22 days; 4 µm for 91 days; 6 µm for 241 days; 10 µm for 908 days; 26 µm for 1013 days; and >35 µm for 1021 days. The composite alteration layer of the SON 68 samples is at least four time less thick than that of the SRL 131 glass composition.

Six distinctive zones, based on phase chemistry and microstructure, were distinguished within the well-developed surface layers. Numerous crystalline phases such as analcime, tobermorite, apatite, and weesite were identified on the surfaces of the reacted glasses as precipitates. Two crystalline phases, Ag₂TeO₃ and (Ca,Sr)Mo₃O₉(OH)₂, were found within the inner zones of surface layers, and they must have nucleated in situ, indicating that Ag, Te, Sr, and Mo can be retained within the surface layer. The majority of the surface layer volume is composed of two morphologically and chemically different structures: one consists of well-crystallized fibrous smectite aggregates occurring along with cavities, the A-domain; and the other consists of poorly-crystallized regions containing needle-like smectite (montmorillonite) crystallites, a silica-rich amorphous matrix, and possibly ZrO₂ particles, the B-domain. The retention of rare-earths and Zr mostly occurred within B-domains and that of transition elements, such as Zn, Cr, Ni, and Mn, in A-domains. The recrystallization of poorly-crystallized B-domains into well-crystallized A-domains may influence the long-term behavior of rare-earths, Zr, and transition elements. The mechanism of surface layer formation during vapor phase alteration is discussed based on the cross-sectional AEM studies of surface layers of the SON 68 waste glasses.

INTRODUCTION

The SON 68 inactive "R7T7" composition is the French reference glass for the light water reactor (LWR) nuclear waste [1]. The objective of this study was to simulate the aqueous corrosion of the Son 68 glass over extended periods of time by using vapor phase alteration in which the surface area to solution volume ratio is high. Due to high solute concentrations, this accelerates reaction progress and the formation of a characteristic suite of secondary alteration phases. The understanding of glass corrosion and radionuclide release can be enhanced by investigating these secondary phases and the microstructural evolution of the surface layers, as glass corrosion may be influenced by mass transport through surface layers or by the effects of surface layers on the dissolution affinity. Radionuclide release can be influenced by nuclide retention in surface layers [2]. Additionally, vapor phase alteration may be an important corrosion mechanism of nuclear waste glasses in a hydrologically unsaturated geological repository [3]. The secondary reaction products formed on experimentally reacted waste glasses are often fragile, poorly crystalline, and ultrathin coatings which make sample preparation and analysis difficult [3-5]. As a result, there are
only a limited number of studies on the microstructural evolution of surface layers [6-10], and most researchers have only been able to speculate on the identity of secondary phases or the reaction mechanisms [11-13].

The vapor phase alteration experiments were done at 200 °C for 22, 56, 91, 241, 908, 1000, 1013, and 1021 days. The corresponding samples are referred to as 14D, 22D, 56D, 91D, 241D, 908D, 1000D, 1013D, and 1021D, respectively. In the present work, 91D, 241D, 908D, 1013D, and 1021D were investigated extensively by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) and analytical electron microscopy with energy dispersive X-ray spectroscopy (AEM/EDS). 22D was studied earlier by Jercinovic et al. [14]. The samples prepared by ultramicrotomy preserved the surface layers and allowed the successful description of compositional and microstructural changes in the surface layers from the outermost surface directly in contact with the leachant solution to the reaction front which migrated into the bulk glass.

EXPERIMENTAL TECHNIQUES

For the AEM analysis, very thin cross-sections of several hundred angstroms in thickness were cut perpendicular to the original sample surface. An ultramicrotomy "slicing" technique was used to obtain thin-sections for AEM observations [15]. Ultramicrotomy was completed using a Reichert-Jung Ultracut-E Microtome. The cross-sectional SEM samples were prepared by resin impregnation and by polishing cross-sections of cuts perpendicular to the original surface. Analyses by SEM/EDS were performed on the original surfaces to obtain a large-scale morphological overview of the reacted glass surface, as well as to observe the chemographic relationship of the secondary precipitated phases on the surface. SEM was done using a Hitachi S-800 with a windowless PGT EDS system operated at 20 keV. Analyses by AEM was performed using both a JEM-2000FX electron microscope with an attached Noran TN-5500 EDXS system and a JEM-2010 electron microscope with an attached Oxford Link ISIS EDS system. The microscopes were operated at 200 keV. Extensive TEM imaging included high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and EDS analysis. Quantitative EDS analyses were performed using Noran's semi-quantitative software package for metallurgical thin films. The final chemical compositions were calculated by assuming the stoichiometry of the oxides. The accuracy of the X-ray analysis was determined to be the ±5 % relative error for major elements and ±30 % for minor elements.

RESULTS AND DISCUSSION

After corrosion in saturated water vapor at 200 °C, the glass monoliths were invariably covered with a thin alteration rind. The thickness of the surface layer increased with the duration of the experiment: 0.5 μm for 22D [14], 4 μm for 91D; 6 μm for 241D; 10 μm for 908D, 26 μm for 1013D and <35 μm for 1021D, based on cross-section SEM examinations. The thickness of the surface layer developed on the reacted glasses varies substantially on a local scale. Compared to SRL nuclear waste glass under the same test conditions, the French SON 68 nuclear waste glass is apparently much more durable. For example, the reacted SRL131 glass (vapor phase altered at 150 °C) had a layer thickness of 20 μm after 180 days, and approximately 80 μm after 720 days [8]. The SRL202U glass developed a ~70 μm alteration layer after 70 days at 200 °C [16].

The surface layers were clearly visible by SEM in the backscattered electron images of the cross-sections. Six distinct zones were evident in the most well-developed surface layers (the long-term samples) and could be distinguished based on differences in contrast that are proportional to the backscattered electron density. These zones are nearly parallel to the original glass surface. The zones present a layered appearance and are identified as zones 1-6 in Fig. 1. Zone 1 is the outermost and is characterized by secondary phases formed by precipitation from the condensed water film; Zone 2 is the thin region consisting of well-crystallized and vertically oriented fibrous smectite crystals; Zone 3 is a thin ultra-fine-grained mixture of smectite crystallites, an amorphous matrix, and possible baddeleyite (ZrO₂) particles; Zones 4 and 5 account for most of the surface
layer volume and consist of mixed structures of poorly-crystallized aggregates, coarsely-crystallized smectite, and cavities; Zone 6 is the hydrated glass where smectite crystallites may have nucleated. The zoning of the surface layer is usually less well developed, and several inner zones may not be clearly differentiated in the short-term samples, such as 22D and 91D. Correspondingly, zoning of surface layers can be seen by a bright-field micrograph of an ultramicrotomed cross-section of sample 1021D (Fig. 2).

![Image of zoning of the surface layer](image1)

Fig. 1. Zoning of the surface layer (1013D, cross-sectional SEM)

![Image of zoning of the surface layer](image2)

Fig. 2. Zoning of the surface layer (1021D, cross-sectional TEM)

**Table 1. Precipitates (Zone 1) formed on the SON 68-waste glasses**

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Formula</th>
<th>22D</th>
<th>91D</th>
<th>241D</th>
<th>908D</th>
<th>1013D</th>
<th>1021D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analcime</td>
<td>Na(AlSi2O6)·H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>Ca5Si6O16(OH)2·4H2O</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca5(PO4)2(OH,Cl,F)</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weeksite</td>
<td>K2(UO2)2(Si2O5)3·4H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Na-Si phase</td>
<td>Na2SiO3·5·9H2O</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-Mo phase</td>
<td>(Ca,Sr)Mo₃O₉(OH)₂</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Ag-Te phase</td>
<td>Ag₂TeO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

Based on morphology, EDS and SAED analyses, numerous precipitated secondary phases were identified on the surfaces of the French SON 68 waste glass as Zone 1 (Table 1). In addition to tobermorite, other Ca-Si phases may be present, such as gyrolite, Ca₅Si₁₂O₃₀(OH)₄·7H₂O, afwillite, Ca₃Si₂O₄(OH)₂, and nekoite, Ca₂Si₆O₁₂(OH)₆·5H₂O. Amorphous Ca-rich silicate precipitates with a spherical morphology (10-30 µm in size) occurred on the surface of 1013D (Fig. 3B). The chemical composition is given by: SiO₂ 70.91, Al₂O₃ 3.51, Na₂O 2.05, CaO 12.05, FeO 2.40, ZrO₂ 3.06, Ce₂O₃ 0.70, and BaO 5.30 (wt. %). Additionally, two crystalline precipitates, Ca-Mo and Ag-Te phases, were found to have formed in situ within the inner zones of the surface layers. The Ca-Mo phase, as small particles (0.1-0.5 µm), has a typical formula on an 11-oxygen equivalent basis of (Ca₁.₆₉Sr₀.₃₃Ba₀.₀₁)₂₀.₀₃(Mo₂₉₈Fe³⁺₀.₀₂)₃₀.₀₀O₁₁. These two phases have not previously been reported in corrosion experiments.
Poorly-crystallized B-domains [41] (Fig. 4). These remained suspected in extensive recrystallization process. The upper part of the cross-sections in 2ID, zones 4 and 5 are homogeneously composed of the poorly-crystallized A-domains. Only crystallite occur locally in 2ID, and the interface between zones 4 and 5 is not evident. The poorly-crystallized B-domains and expelments (e.g., 102ID) are still present, however, in high external experiment (e.g., 91ID and 91D). Usually, the volume fraction of A-domains in zone 4 is higher than that of zone 5 in the low-temperature experiment. In Table 2, the transition temperature width of Zn, Fe, Zn, Fe, and Ni is compared to those of the A-domains (Table 2). The overall transition temperature width of Zn, Fe, Zn, Fe, and Ni is compared.

The microstructures shown in Figs. 3A, 3B, and 3C are consistent with the expected morphology of precipitated phases on the surface. FIG. 3. SEM micrographs showing the morphology of precipitated phases on the surface.
of earlier formed B-domains into A-domain smectites, associated with an increased cavity volume during the continued corrosion. Additionally, toward the top of Zone 4 in long-term samples such as 1013D, B-domains are very small (~100 nm). These small B-domains are even completely amorphous (high Si and Zr contents), and no smectite crystallites can be detected. This is all that remains of larger early-formed B-domains after the recrystallization of smectite crystallites (Fig. 5). These elements, especially rare-earths, are probably absorbed on the small smectite crystallites and into the silica-rich amorphous matrix during the early stages of corrosion. When the early-formed B-domains recrystallize into A-domains, most of the rare-earths in B-domains may be lost into solution. However, transition elements are incorporated into thermodynamically stable A-domain smectites. Previous workers proposed that actinides and rare-earths may be retained within the gel layer (corresponding to Zones 4 and 5 in this study) [17-19]. The recrystallization of the B-domains into the A-domain smectites is very important to understanding of the long-term behavior of rare-earths, Zr, and the transition elements.

![Fig.4. A TEM micrograph showing the typical structure of Zones 4 or 5 (908D).](image)

Zone 2 is present as a honeycomb-like layer occupying most of the surface (Fig. 3). The smectite crystals are similar to those of well-crystallized A-domains from Zones 4 and 5, close to a notronite-15Å in chemistry and structure. The smectite must have grown into the solution on the original surface of the reacted glass as evidenced by the vertically oriented fibrous texture. Thus, Zone 2 can be considered as a precipitated layer. The fibrous notronite-15Å of Zone 2 is coarsely crystalline with high concentrations of transition elements (Table 2). Zone 2 is well developed in both the short-term samples such as 22D [14] and 241D, and in the long-term samples such as 1021D. The thickness of Zone 2 increased with the duration of the experiments, for example, 0.2 µm for 22D [14], 0.4 µm for 91D, 0.6 µm for 241D, and 3 µm for 1013D (cross-section TEM results). In addition, the vertically oriented fibrous smectite layer (Zone 2) was a common structure in various waste glasses during vapor phase alteration [7-8,10,20]. However, in previous models of surface layer formation of corroded glasses proposed by Mendel [21] and by Wicks, Lodding and Molecke [22], Zone 2 was not present. The importance of the development of Zone 2 lies in the fact that this layer may act as a precipitation sink for Zn and Na from the condensed water film.

Beneath Zone 2 is the ultra-fine-grained mixture of smectite crystallites and amorphous matrices (Zone 3). This zone can be directly exposed to the solution (Fig. 3B). Structurally and chemically, Zone 3 is almost the same as the B-domains in Zones 4 and 5. However, Zone 3 has
even higher concentrations of rare-earths and Zr than those of B-domains (Table 2). The smectite crystallites are of one to three lattice fringes with a basal (001) spacing of 18 Å. The ZrO$_2$ may be present either in the amorphous silica-rich matrix or as nm-sized particles as revealed by the HRTEM micrograph (Fig. 6). The concentration of ZrO$_2$ in Zone 3 is five times higher than that of the original glass (Table 2). As the rare-earth content of Zone 3 exceeded that of a smectite stoichiometry, the excess rare-earths must have been absorbed and immobilized within the amorphous silica-rich matrix. The highly concentrated rare-earths suggest that Zone 3 may act as a filtering membrane in the processes of water diffusion and nuclide migration.

Table 2. Compositions for individual zones and zones (1021D)

<table>
<thead>
<tr>
<th></th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>A-domains</th>
<th>B-domains</th>
<th>Zone 6</th>
<th>glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>64.0</td>
<td>61.4</td>
<td>69.0</td>
<td>81.7</td>
<td>67.6</td>
<td>45.48</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>10.6</td>
<td>1.8</td>
<td>9.0</td>
<td>3.3</td>
<td>5.7</td>
<td>2.91</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.2</td>
<td>0.8</td>
<td>3.3</td>
<td>1.1</td>
<td>5.2</td>
<td>9.86</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.0</td>
<td>3.7</td>
<td>6.8</td>
<td>4.2</td>
<td>5.0</td>
<td>4.91</td>
</tr>
<tr>
<td>CaO</td>
<td>1.9</td>
<td>3.8</td>
<td>1.9</td>
<td>2.6</td>
<td>6.5</td>
<td>4.04</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>0.4</td>
<td>4.9</td>
<td>--</td>
<td>1.0</td>
<td>--</td>
<td>1.59</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>--</td>
<td>10.4</td>
<td>--</td>
<td>~1.0*</td>
<td>--</td>
<td>0.93</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>--</td>
<td>~1.0*</td>
<td>--</td>
<td>0.9</td>
<td>--</td>
<td>0.90</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.0</td>
<td>13.2</td>
<td>--</td>
<td>4.5</td>
<td>5.7</td>
<td>2.65</td>
</tr>
<tr>
<td>ZnO</td>
<td>8.3</td>
<td>--</td>
<td>4.4</td>
<td>0.8</td>
<td>2.4</td>
<td>2.50</td>
</tr>
<tr>
<td>NiO</td>
<td>~1.0*</td>
<td>--</td>
<td>3.0</td>
<td>--</td>
<td>1.8</td>
<td>0.74</td>
</tr>
<tr>
<td>MnO</td>
<td>1.6</td>
<td>--</td>
<td>~1.0*</td>
<td>--</td>
<td>~1.0*</td>
<td>0.72</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>--</td>
<td>2.7</td>
<td>--</td>
<td>2.4</td>
<td>0.51**</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated values; **More compositional data for the glass is available in reference [20]. "--" means undetected. The water contents were not included.

Fig. 5. A HRTEM micrograph showing the structure of Zone 4 (1013D). The arrow points to a B-domain which is completely amorphous.
Zone 6 is the smectite nucleation zone in the hydrated glassy matrix (0.5-1 μm in thickness). Beneath Zone 6 is the unaltered glass. This zone corresponds to the diffusion layer described by Mendel [21]. Zone 6 is characterized by amorphous material plus small smectite crystallites which are similar to the B-domains in Zones 4 and 5 (Fig. 7). The A-domain smectite is not present in this zone. The nucleation of smectite crystallites in the hydrated glass matrix is heterogeneous. Rare-earths, boron, and alkaline elements such as Na were removed from Zone 6. The concurring nucleation of smectite crystallites as a restructuring process of the hydrated glass is critical to the formation of the diffusion layer and its conversion into Zone 5.

Based on the above results, the mechanism of the surface layer formation is described as follows: At the early stage of corrosion, water diffuses into the glass and ion exchange and hydrolysis occur to form the hydrated glass. Subsequently, individual spherical centers (nm-sized), possibly nucleation centers of smectite occur in the hydrated glass matrix. The nm-sized needle-like crystallites of smectite grow in the amorphous matrix, forming Zone 6. Following smectite nucleation, the smectite crystallites continue to grow into large fibrous crystals along dissolution-created cavities, forming well-crystallized A-domains which leads to a conversion of Zone 6 to Zone 5; meanwhile, the amorphous matrix decreases in volume and appears in the form of individual spherical particles (B-domains) as seen in Zones 4 and 5. The continued nucleation and growth of smectite in B-domains finally results in the complete disappearance of the B-domains. Because Zone 2 is present in long-term, as well as short-term samples, the Zone 2 notronite-15Å must have precipitated on the original surface of the glass at a very early stage of the corrosion. The secondary phases precipitate on the surface due to solubility-limiting processes.

CONCLUSIONS

Surface layer zoning is evident during vapor phase alteration of the French SON 68 waste glass at 200 °C. Six zones were identified in the surface layers, and the thickness of the surface layers increased slowly with the duration of experiments. The surface layers on the SON 68 waste glasses were much thinner than those on SRL glasses under the same conditions, indicating a higher durability of the SON 68 waste glasses.
A number of crystalline and amorphous precipitated phases were identified on the surface of the reacted glasses, such as analcime, tobermorite, apatite, and weesite. \((\text{Ca}, \text{Sr})\text{Mo}_3\text{O}_9(\text{OH})_2\) and \(\text{Ag}_2\text{TeO}_3\) were found within the inner zones of the surface layers, indicating that Ag, Te, Sr, and Mo have been retained within the surface layers. These precipitated or in situ formed phases must be included in geochemical models used to predict long-term release of radionuclides under repository conditions. The majority of the surface layer volume (Zones 4 and 5) is composed of two morphologically and chemically different structures, the A-domain and the B-domain. A-domains have high concentrations of transition elements, such as Fe, Zn, Cr, Mn, and Ni. B-domains have high concentrations of rare-earths and Zr. The recrystallization of B-domains into A-domains (dominated by notronite-15Å) associated with the preferable dissolution of chemical components of the surface layers results in the redistribution of these elements between solids and solutions. This process is very important in determining the long-term behavior of radionuclides.

Zn and Na from the condensed water film were partly immobilized in the vertically-oriented fibrous smectite layer (Zone 2). Zone 3 contains high concentrations of rare-earth elements due to absorption; thus, Zone 3 may act as a filtering membrane during water diffusion and migration of nuclides.

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