SHORT RANGE STRUCTURE OF MOLTEN CsCl - NaCl MIXTURES OBTAINED BY XAFS ANALYSIS

Haruaki Matsuura\textsuperscript{a}, Sou Watanabe\textsuperscript{a}, Hiroshi Akatsuka\textsuperscript{a}, Tetsuo Honma\textsuperscript{b}, Norimasa Umesaki\textsuperscript{b}, Akihiko Kajinami\textsuperscript{c}, Keiichi Takase\textsuperscript{d}, Norikazu Ohtori\textsuperscript{d}, Yasuhiro Iwadate\textsuperscript{e}, Reiko Fujita\textsuperscript{f}, Ashok K. Adya\textsuperscript{g},

\textsuperscript{a}Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-10, O-okayama, Meguro-ku, Tokyo 152-8550, Japan
\textsuperscript{b}Japan Synchrotron Radiation Research Institute, Mikazuki, Hyogo 679-5198, Japan
\textsuperscript{c}Faculty of Engineering, Kobe University, 1-1, Rokkodai, Nada-ku, Kobe 657-8501, Japan
\textsuperscript{d}Graduate School of Science and Technology, Niigata University, Ikarashi-Ninocho, Niigata 950-2181, Japan
\textsuperscript{e}Graduate School of Science and Technology, Chiba University, Inage-ku, Chiba 263-8522, Japan
\textsuperscript{f}Power & Industrial Systems R&D Center, Toshiba Corporation, 4-1, Ukishima-cho, Kawasaki-ku, Kawasaki 210-0862, Japan
\textsuperscript{g}School of Contemporary Sciences, University of Abertay Dundee, Bell Street, Dundee, DD1 1HG, U. K.

ABSTRACT

The local structure of molten 2CsCl-NaCl has been investigated for the first time by XAFS measurements carried out on SPring-8 at the K-absorption edge of Cs. The nearest-neighbor Cs$^+$-Cl$^-$ distances and coordination numbers were found to be 3.26Å and 5.44 for CsCl, and 3.22 Å and 5.85 for 2CsCl-NaCl, respectively. The parameters obtained for molten CsCl are in good agreement with those derived from the previous neutron diffraction studies by using isotopic substitution on chlorine. The Cs$^+$-Cl$^-$ distance in 2CsCl-NaCl is found to be slightly shorter than that in pure CsCl, and Cs$^+$ is coordinated to ca. 6 chlorides in 2CsCl-NaCl.

INTRODUCTION

At the moment, the uranium and plutonium oxide (MOX) co-electrodeposition process is the most important technique used in Japan for the pyrochemical reprocessing of nuclear oxide fuels because of the non-proliferation policy on plutonium. By controlling chlorine and oxygen gas ratios and flowrates, the plutonium ion is oxidized and the plutonyl ion is stabilized. The redox potential of plutonyl ion is more positive than that of the uranyl ion. This is why, in principle, uranyl and plutonyl are co-
electrodeposited at the cathode as mixed oxide fuels. However, there are a lot of technical problems in using this process. Firstly, since the redox potentials of noble metals lie between those of uranyl and plutonyl, contamination of these noble metals during MOX codeposition can occur. Secondly, the difference between uranyl and plutonyl potentials can cause inhomogeneous deposition, thereby rendering the material characterisation of MOX fuel difficult. We aim to solve these problems by introducing pre- and post-electrodeposition processes and/or a pulsed electrolysis technique. However, the third problem is that the current efficiency of this process is relatively low, ca. 30% (1), Molten 2CsCl-NaCl is usually preferred as a melt bath for MOX codeposition because larger cations should stabilise uranyl and/or plutonyl ions, but the reason why this happens is still not clear. Furthermore, the physico-chemical properties and microscopic structure of the melt bath itself is still unknown and needs to be studied before attempting to investigate the complex mixture systems.

Pure molten CsCl has already been investigated by neutron diffraction isotopic substitution to extract the experimental partial structural factors. These results showed that the Cs ion is coordinated to 5.8 chlorides at 3.4Å (2). In the present study, we used the XAFS technique to investigate the coordination environment of chlorides around Cs in the presence of Na cations.

EXPERIMENTAL

EXAFS measurements

The anhydrous compounds, CsCl and 2CsCl-NaCl (AAPL, 4N), were sealed in specially designed funnel-shaped quartz cells, which are similar to those used in (3) under vacuum conditions. The quartz-sealed samples were installed into a newly designed electric furnace (Rigaku Co.) with a thermal homogeneity and stability much larger than those of the prototype used previously (4). The temperature was raised from room temperature (RT) to a value (983 K) above the melting point of pure CsCl. The furnace was kept in the best possible orientation in order to obtain the highest resolution in the EXAFS oscillations.

Transmission Extended X-ray Absorption Fine Structure (EXAFS) measurements on these samples were performed at BL01B1 and BL19B2, SPring-8 (Japan), both in the molten state and at room temperature using the Cs-K X-ray absorption edge, i.e., 35.98 keV. A white X-ray beam from a bending magnet source was monochromated by Si (311) double crystals, and purified by two Rh-coated Si mirrors to avoid any interference from high-ordered reflection X-rays. The SPring-8 storage ring was operated at 8 GeV and 100 mA for the duration of all the measurements. This helped us accumulate high resolution XAFS data even under high temperature conditions. The intensities of the incident ($I_0$) and transmitted ($I$) X-rays were measured by using ionisation chambers filled with Kr + Ar (1:3) and Kr, respectively.
Data analysis

XAFS data analyses were carried out by using the WinXAS Ver. 2.3 software (5). Background subtraction and normalisation were performed by fitting the modified Victoreen equation to the pre-edged region and linear polynomial to the post-edged region. The Cs K absorption threshold was determined from the first root in the second derivative of the near-edge region. XAFS oscillation, $\chi(k)$, was obtained after removing smoothly the atomic background using a cubic spline method. The radial structure function, FT|$\chi(k)$-$k^3$|, was obtained by Fourier transforming the $k^3$ weighted $\chi(k)$ function multiplied by a Bessel window function. The range of wave numbers used in the Fourier transformation was $2 < k (\text{Å}^{-1}) < 12$ for the solids, and $2 < k (\text{Å}^{-1}) < 8$ for the liquid melts. The curve-fitting involved the nonlinear least-square fits on the predominant Cs+-Cl$^-$ 1st neighbour correlation peak in $R$-space by using backscattering factors evaluated by FEFF 8.0 code (6). At high temperatures, the 3rd and 4th cumulants were used as fitting parameters to include the anharmonic oscillations. The most reasonable coordination number of chloride ions around a Cs ion was chosen on the basis of the inter-ionic distance and the sum of effective ionic radii (7).

RESULTS AND DISCUSSION

The extracted $\chi(k)$ EXAFS spectra and Fourier transformed structural functions of pure CsCl and 2CsCl-NaCl at room temperature and 983 K are shown in Figures 1 and 2, respectively. Similar to the observation in (8), phase shift and phase broadening in the current EXAFS spectra during melting is observed. This is reflected in the interionic distance shrinkage in the structure functions. Due to shortage of the core-hole lifetime at the X-ray absorption edge of Cs, the XAFS oscillations detected are somewhat smaller than those previously reported for molten LaCl$_3$ (3). The Cs–Cl distance, $R_{\text{Cs-Cl}}$, and the coordination number, $N_{\text{Cs-Cl}}$, corresponding to the Cs–Cl 1st coordination shell, obtained by the curve-fitting method applied on the first peak of FT|$k^3\chi(k)$| in $R$-space, are listed in Table 1. Both $R_{\text{Cs-Cl}}$ and $N_{\text{Cs-Cl}}$ decrease drastically on melting, as has previously been

![Figure 1](image_url)

Figure 1. EXAFS oscillations $\chi(k)$-$k^3$ (left), and radial structure functions (RSFs) FT|$\chi(k)$-$k^3$| (right), at 300 K and 983 K for CsCl.

138 Electrochemical Society Proceedings Volume 2004-24
suggested for several other alkali metal halides. A comparison of the present results with those from the previous neutron diffraction study (2) reveals that the structural parameters obtained for molten CsCl are quite reasonable. In the mixture with NaCl, the $R_{Cs-Cl}$ distance is found to be slightly shorter than that in pure molten CsCl. This could probably be due to a decrease in molar volume with increase in sodium chloride concentration. In the mixture, Cs$^+$ is surrounded on average by ca. 6 chlorides.

Figure 2. EXAFS oscillations $\chi(k)k^2$ (left), and radial structure functions (RSFs) $\text{FT}[\chi(k)k^2]$ (right), at 300 K and 983 K for 2CsCl-NaCl.

**CONCLUSIONS**

The XAFS technique can be one of the most useful tools to obtain the local structure around a specific element. In 2CsCl-NaCl, the Cs-Cl interionic distance is found to be shorter than that in pure CsCl, and a Cs cation is surrounded on average by ca. 6 chlorides. This is a case study in the employment of XAFS and diffraction techniques complementarily to elucidate the structure of molten salts. The experience gained through this work will be valuable for studying more complicated and difficult systems, e.g., for in-situ XAFS measurements and for studying compounds involving actinide elements.

**ACKNOWLEDGMENT**

The synchrotron radiation experiments were performed at the BL01B1 and BL19B2 in SPring-8 with the approval of the JASRI (Prop. Nos. 2003B0628-NXa-np, 2004A0548-NI-np).

**REFERENCES**

1. S. K. Vavilov, T. Kobayashi and M. Myochin, *JNC Tech. Report*, JNC TN8400 2003-030, 15 (2003).
2. J. Locke, S. Messoloras, R. J. Stewart, R. L. McGreevy and E. W. J. Mitchell, *Phil. Mag. B*, 51, 301 (1985).
3. Y. Okamoto, H. Shiwaku, T. Yaita, H. Narita, H. Tanida, *J. Mol. Struct.*, 641, 71 (2002).
4. M. Ablanov, H. Matsuura, R. Takagi, *Electrochemistry*, 67, 839 (1999).
5. T. Ressler, *J. Phys. IV*, 7, C2-C269 (1997).
6. S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, M. J. Eller, *Phys. Rev.*, B 52, 2995 (1995).
7. R. D. Shannon, Acta Cryst., A32, 751 (1976).
8. S. Watanabe, *et al.*, *Physica Scripta B*, (Proc. of XAFS12, Malmö, 2003) in press.

Table 1. The nearest-neighbour structural parameters obtained by the curve-fitting procedure.

|               | \(S_0^2=0.880\) | intrinsic loss factor |
|---------------|-----------------|-----------------------|
| **300 K**     |                 |                       |
| Cs-Cl         | \(N\)           | \(R(\text{Å})\)     | \(\sigma^2(10^{-2} \text{ Å}^2)\) | \(C_3(10^{-3} \text{ Å}^3)\) | \(C_4(10^{-3} \text{ Å}^4)\) | Res. (%) |
| 8.0 (fix)     | 3.47±0.00       | 2.65±0.00             | 0.0 (fix)                             | 0.0 (fix)                        | 5.44     |
| 6.0 (fix)     | 4.08±0.00       | 2.41±0.01             | 0.0 (fix)                             | 0.0 (fix)                        | 3.47     |
| **983 K**     |                 |                       |
| Cs-Cl         | \(N\)           | \(R(\text{Å})\)     | \(\sigma^2(10^{-2} \text{ Å}^2)\) | \(C_3(10^{-3} \text{ Å}^3)\) | \(C_4(10^{-3} \text{ Å}^4)\) | Res. (%) |
| 5.44±0.24     | 3.26±0.04       | 5.59±0.21             | 4.63±0.12                             | 1.01±0.11                         | 11.88    |

**2CsCl-NaCl**

|               | \(N\)           | \(R(\text{Å})\)     | \(\sigma^2(10^{-2} \text{ Å}^2)\) | \(C_3(10^{-3} \text{ Å}^3)\) | \(C_4(10^{-3} \text{ Å}^4)\) | Res. (%) |
|---------------|-----------------|---------------------|----------------------------------|--------------------------------|--------------------------------|----------|
| **300 K**     |                 |                     |                                  |                                |                                |          |
| Cs-Cl         | \(N\)           | \(R(\text{Å})\)     | \(\sigma^2(10^{-2} \text{ Å}^2)\) | \(C_3(10^{-3} \text{ Å}^3)\) | \(C_4(10^{-3} \text{ Å}^4)\) | Res. (%) |
| 9.32±0.01     | 3.45±0.00       | 3.00±0.00            | 0.0 (fix)                         | 0.0 (fix)                       | 3.64                           |
| Cs-(Cs+Na)    | 9.41±0.10       | 4.07±0.01            | 2.93±0.01                         | 0.0 (fix)                       | 3.00±0.00                       | 3.64     |
| **983 K**     |                 |                     |                                  |                                |                                |          |
| Cs-Cl         | \(N\)           | \(R(\text{Å})\)     | \(\sigma^2(10^{-2} \text{ Å}^2)\) | \(C_3(10^{-3} \text{ Å}^3)\) | \(C_4(10^{-3} \text{ Å}^4)\) | Res. (%) |
| 5.85±0.25     | 3.22±0.01       | 5.98±0.17            | 4.12±0.08                         | 1.18±0.04                       | 11.87                          |