Environmental Management Science Program

Project ID Number 60424

High Temperature Condensed Phase Mass Spectrometric Analysis

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June 1, 1998

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Research Objective

The purposes of this program are to design and construct a mass spectrometer for the analysis of high temperature condensed phase materials, and to use this instrument to investigate the high temperature chemistry of waste form materials. Individual mass spectrometric techniques can provide windows through which to view selected properties of materials at high temperatures, but information from several sources must be combined to obtain the larger picture. This instrument is designed to provide several types of interlaced mass spectrometric analyses from a single specimen, eliminating the uncertainties associated with combining data from several different samples analyzed in different instruments.

Research Progress and Implications

The features that are being combined in this instrument are:

1. Miniaturized sample mounting and control of sample temperature to 1300C.
2. Electron impact (EI) ionization of volatilized neutrals.
3. Surface ionization, positive and negative ions.
4. Secondary ion mass spectrometry (SIMS), positive and negative ions.
5. Ultrahigh vacuum combined with sputtering to allow surface analyses to be related to bulk composition.
6. A single mass analyzer able to sequentially analyze ions from each of the ionization modes.

These features will allow the following types of information to be obtained:

1. Atomic and molecular species vaporizing from the surface, both neutral and ionic. Neutrals will predominate in almost all systems, but the positive and negative ions which do volatize give valuable insights into the condensed phase chemistry.
2. SIMS interrogation of the surface composition, with ions sputtered from the surface analyzed by mass spectrometry. A high intensity sputter ion gun will be used to clean the surface, while a lower intensity ion gun will be used for the SIMS analysis. The ultrahigh vacuum will allow the surface to be maintained in a clean configuration until the analysis can be completed. This in turn gives information concerning the bulk composition of the material.
3. This information is obtained as a function of temperature from a single sample, so the interpretation of events will be more straight forward than merging data from different instruments.

There currently are two instruments operating in our laboratory that perform these functions; one for SIMS and surface ionization on high temperature samples, and the other for EI and surface ionization. These have provided valuable insights into the properties of materials at high temperatures, but there is uncertainty from the perspective that all analyses cannot be performed on the same sample and from the fact that neither can guarantee a clean surface.

Planned Activities

The types of research which can be conducted with this instrument are many and varied. One example which was used in the original proposal is the concept of developing ceramic and glass materials with charge centers (sometimes called color centers or F-centers) deliberately induced to greatly

reduce the migration of ionic species through the material at high temperatures. This concept originates from studies conducted on a BES Chem Sciences program in which it was shown that these charge centers, if allowed to accumulate, shut down ion migration and emission in high temperature ion emitters. Waste forms developed from this concept would have built-in mechanisms to prevent the migration of ionic species. The mass spectrometer system under development will be ideal for researching this concept.

A second example is the issue of acidic/basic conditions within the condensed state and how this relates to ion migration for different species. Rhenium is a near perfect stand-in for technetium, an important fission product requiring million year storage. Studies with rhenium indicate that keeping the condensed state acidic reduces the volatility of rhenium by forcing the +7 rhenium oxide (volatile and non-ionic) to perrhenate (also +7, but ionic and much less volatile), the migration of which can be shut down by inducing charge centers. Again, the instrument is well suited for this type of study, since it can measure volatilizing species while at the same time identifying the responsible condensed state species.

The preliminary instrument design has been completed, and many of the components ordered. The largest design effort has gone into the main chamber to ensure the compatibility of the various ionization modes with each other and with ultra high vacuum conditions. This chamber is expected to be delivered in June. The vacuum system is designed to be baked, with the main pumping coming from a 500l/sec. triode ion pump, a liquid nitrogen cryoshroud, and a titanium sublimator. The vacuum lock and the ion guns will be differentially pumped with a turbo pump. The system should easily pump into the 10's when the sample stage is cold, and should hold in the low 9's when a sample is at maximum temperature (1300° C). This will allow the surface of the hot samples to be maintained in a "clean" state so as to allow the SIMS analysis of the surface to be representative of the bulk following cleaning by sputtering.

Preliminary designs of the ion optics have been developed which look quite promising. An iterative approach is being taken in the implementation of the combined ion source. The SIMS component will be the most difficult to implement, hence the main design effort has gone into this aspect of the instrument. Surface ions are readily obtained from an implementation of SIMS, hence pose no problems. The addition of EI to the system without impacting the SIMS capability then becomes the next challenge; some alternate techniques for implementing this feature have been modeled with the ion optics program "SIMION." We have a preferred design and are examining the practicality of implementing the design into a working instrument.

The miniaturized high temperature cell has recently undergone significant improvements, with greatly improved mechanical stability as a function of temperature. The next major design effort will go into adapting this re-designed high temperature cell as the target for the instrument, so that SIMS can be conducted on the surface of the material in the cell, and so that EI can be conducted on the species volatilizing from the surface.