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Metal dicarbides as intermediate species in thermal ion formation mechanisms☆

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ABSTRACT

Lanthanide elements (lanthanum to lutetium) and actinide elements (uranium and plutonium) adsorbed onto resin beads and mounted on rhenium filaments were studied as thermal ionization sources. Temperatures at which these ion sources gave maximum intensities were measured for each of these elements. The temperature trends correlate with the dissociation energies of the corresponding metal dicarbide compounds. The metal dicarbide functions as a carrier to take the lanthanide and actinide elements to higher temperatures than would be attainable otherwise. This results in release of the atomic species at a higher temperature where ionization probability is significantly increased.

1. Introduction

The actinide elements uranium and plutonium, adsorbed onto resin beads and analyzed by thermal ionization mass spectrometry (TIMS), have been useful for a number of ultra-trace analysis applications [1–6]. A better understanding of the chemical and physical processes on the filament will advance and could also expand these applications. The lanthanides are a family of elements that can be analyzed by this method as well, and offer a better modeling opportunity than the actinides without the introduction of radioactivity. Hence the lanthanides, as well as uranium and plutonium, were studied. These elements are highly electropositive metals. The 3+ oxidation state predominates for all of the lanthanides both in solution and in the solid state. Minor oxidation states can result when the electronic structure is an empty, half-full, or full electron shell [7]. Cerium is the only species with a 4+ oxidation state that forms due to losing its lone 4f electron resulting in an empty 4f electron shell, which helps stabilize this state. Europium, and to a lesser extent, samarium, are stable in the 2+ oxidation state because a half-filled 4f electron shell helps stabilize this state [7]. Ytterbium, and to a lesser extent, thulium, also have stable 2+ oxidation states due to the stability offered by a full 4f shell. These deviations from the 3+ oxidation state are more stable in the solid state than in solution.

The lanthanide elements demonstrate a series of regular trends for properties like atomic volume, melting temperatures, vapor pressures, and a variety of other properties of various compounds due to gradual filling of the chemically inert 4f shell [8]. All of these trends have outliers corresponding to the empty, half-full and full 4f shell [7,9]. These systematic properties are important in understanding the thermal ionization behavior of the lanthanides.

Melting temperature, ionization potential, and vapor pressure are all important properties in understanding thermal ionization of any element. As shown in Figs. 1 and 2, melting temperatures and ionization potentials increase across the lanthanide series with deviations noted for the melting temperatures of europium and ytterbium and for ionization potentials for gadolinium and lutetium. There is a rough correlation between the data in Fig. 1 (melting temperatures) and Fig. 2 (ionization potentials), with the deviations shifted up one element for ionization potentials (europium to gadolinium and ytterbium to lutetium) because the metal melting temperatures are for neutral species and ionization potentials pertain to singly charged positive ions. Another example is the vapor pressure data shown in Fig. 3, although the trends are much different than for melting temperatures and ionization potentials.

Considerable work has been conducted reacting lanthanide and actinide elements with graphite in Knudsen cell mass spectrom-

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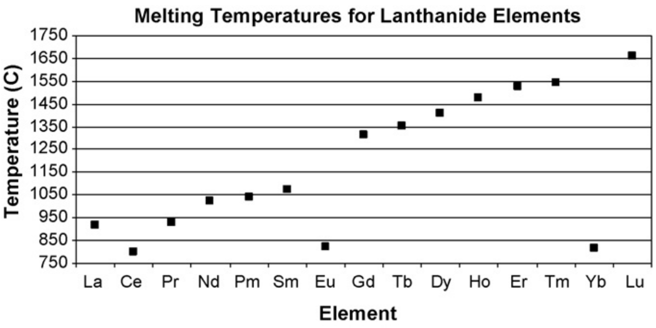

Fig. 1. Melting temperature of lanthanide metals [20].

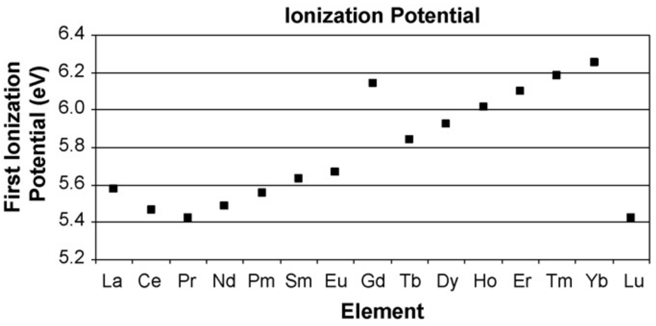

Fig. 2. First ionization potentials for the lanthanides [20].

eters [10–19] to produce a carbide compound. These can be a sesquicarbide or dicarbide, or even higher order compounds [13], with the form dictated by the reaction temperature [20]. These Knudsen cell studies are of particular relevance to the current study in several ways. First, the metals reacted with carbon to form carbides and did not emanate from the Knudsen cells at the normal volatilization temperatures of the respective metals. This demonstrates that the metals totally reacted at temperatures below the volatilization temperatures. Second, at temperatures elevated well above normal volatilization temperatures of the metals, the neutral metal atoms were observed in much greater abundance than the various carbide species [10]. This indicates that the carbides readily decompose back to the atomic species at highly elevated temperatures. Consequently, these Knudsen cell studies are consistent with formation of the metal carbide at lower temperatures, followed by decomposition to the atomic vapor species at much higher temperatures.

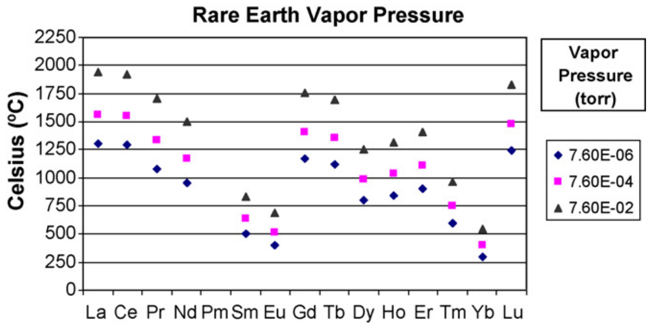

Fig. 3. Lanthanide vapor pressure data for given temperatures [20].

2. Resin bead ion source

The resin bead ion source method has been in use for over 30 years because it produces stable ion beams for TIMS from a small amount of the element of interest [1–6]. Samples can range into the sub-picogram size [3,6]. The technique involves adsorption of the analyte of interest onto a single ion exchange resin bead. Both anion and cation resin beads can be used depending upon the species to be adsorbed from solution. Anion beads are commonly used for actinides like plutonium because they readily form nitrate anion complexes in solution. The bead containing the sample is attached to a thermal ionization filament for TIMS and analyzed by heating in the mass spectrometer to produce thermal ions. This concentrates ion emission from a small area at the ion optic center of the lens where ion transmission is greatest. Samples loaded from a solution spread the sample over a much larger area, and consequently the ions are not transmitted as efficiently due to many of the ions originating from areas with lower ion transmission.

While the resin bead method is known to produce and to transmit ion beams with high efficiency, the chemistry and physics are not well understood. Smith et al. demonstrated that there is little migration across the filament with the main concentration of uranium loaded onto the bead remaining near the original location [4]. They suggested that ionization occurred at the interface of the carbon residue of the bead and the filament; however, the specific ionization mechanism was not addressed. Kelley and Robertson presented data for plutonium ion emission from a solution dried onto a single filament [6]. The temperature of ion emission versus intensity was also reported, with the mechanism for ion production from plutonium (or uranium) carbide being put forth as the most likely [6]. The implication from these two studies is that actinide carbides may be formed in the resin bead system. A better understanding of the mechanisms involved in thermal ion production could lead to improved ionization for elements difficult to ionize and thus guide research towards superior analytical techniques.

3. Experimental materials and methods

3.1. Sample preparation

The stable lanthanides from lanthanum through lutetium were included in this study. Promethium was excluded from the study because it is difficult to obtain and highly radioactive. The lanthanides, except for neodymium and ytterbium, were obtained as 1000 part-per-million (ppm) concentration standards prepared in 3 M nitric acid (Fisher Scientific). Neodymium and ytterbium oxides were dissolved in 8 M nitric acid to make the 1000 ppm solutions and diluted to 10 and 0.1 ppm solutions. Uranium was obtained as a 1000 ppm concentration standard prepared in 3 M nitric acid (Fisher Scientific). All of the initial solutions were diluted with 8 M nitric acid (Baker Ultrex, 18 $M\Omega$ water) to concentrations of 10 and 0.1 ppm. The plutonium was prepared from NBS Standard Reference Material 996 by dissolution in 1 M hydrochloric acid and converted to 8 M nitric acid. 10 μl of the 0.1 ppm concentration (1 ng mass equivalent) was initially placed on a Teflon disc, and one anion exchange bead (Bio-Rad, AG 1 × 4 anionic bead 100–200 mesh) was placed in the solution under a microscope. When this did not produce adequate signal during the analysis, a higher mass loading of 100 ng was used.

The solution and resin bead were allowed to equilibrate for 24 h; after which the bead was removed from the solution and placed on a rhenium filament. The bead was held in place with a small amount of rubber cement (about half the volume of the bead). The samples were then pyrolyzed under vacuum and treated with benzene. Pyrolysis occurred over a temperature range up to 1300 °C.

Once this maximum temperature was reached, the pressure in the pyrolysis chamber was increased from 5E−6 Torr to 5E−5 Torr with benzene vapor. This was held for 5 min, at which point the sample was ready for TIMS analysis.

The mass spectrometer used for this study has been described previously [21]. Briefly, the instrument is computer controlled for filament heating and allows for the measurement of thermal ions emitted from the filament. It can scan over desired mass ranges, collecting positive and negative data for thermal ions. Only positive thermal ions were measured.

The filament supply was programmed to produce an identical heating profile for all samples. The filament current was ramped at 0.05 A/min, while the actual filament temperatures were measured with an optical pyrometer at each step. This enabled direct comparison of maximum ion emission temperatures without concern for whether this rate was optimized for a particular sample. The idea was to produce trends of relative data for comparison to the trends of other properties—in particular, the dissociation energies of the dicarbides. So, while the heating rate was not particularly optimized to produce the very highest ion intensity for any given element, the temperatures of maximum ion emission for each element provide a valid relative comparison.

4. Results and discussion

Reaction of lanthanide metals with carbon at elevated temperatures results in formation of lanthanide carbides as documented [10–19]. The preparation of the resin bead source presents an alternate mechanism to form these carbides. Adsorption from solution puts the lanthanides inside the polystyrene structure of the resin bead. Heating in vacuum condenses the bulk of the resin bead to the metal carbide, which is evenly interspersed throughout the carbon bead.

Temperatures corresponding to the maximum ion intensity for each element are shown in Fig. 4, with the temperatures on the left. The corresponding dissociation energies of the lanthanide dicarbides are shown on the same plot and scaled against the right axis. Overall there appears to be good correlation between the two data sets. The resulting temperatures range from 1000 °C to 2200 °C with the majority near 2000 °C. Europium, samarium, ytterbium, and thulium are at lower temperatures as predicted by their lower dicarbide dissociation energies. These lower dissociation energies in turn relate to subtle differences in the chemistry corresponding to the empty, half-full, and full 4f electronic shells.

There is not a correlation of the ionization temperatures with the melting points or ionization potentials of the lanthanides. In addition, the vapor pressures of the metals (see Fig. 3) illustrate the fact that metallic lanthanides would not persist to temperatures near 2000 °C. The lowest data points show pressures well above those maintained in the instrument during analysis (<1E−7 Torr operating pressure). Therefore, the metal cannot be present in the resin bead ion source system. The lanthanides are stabilized in a compound until reaching a higher temperature than would be possible for the free metal. When the metal atom is produced from the decomposition of the metal dicarbide, a higher percentage of atoms ionize due to the higher temperature.

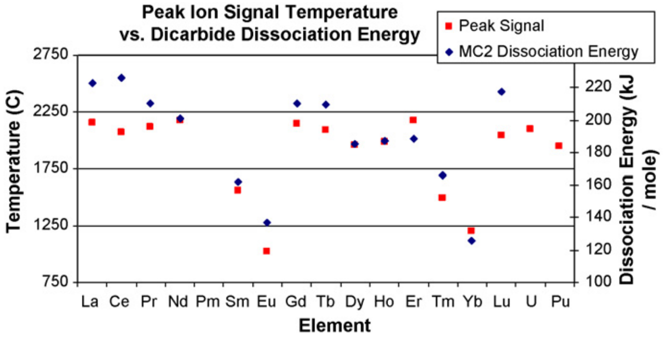

Fig. 4. Element by element, the dissociation energy of the lanthanide dicarbides [20] track the peak ion formation temperatures of the corresponding lanthanides.

During the analysis, the masses corresponding to the metal carbide, metal dicarbide, metal monoxide, and metal dioxide were monitored. No signal was observed for the oxides. There was signal present for the carbide and dicarbide, but at a fraction of the signals present for metal ions. This indicates the presence of the carbide and eliminates oxide as the stabilizing compound.

The temperature trends of the observed peak ion signal intensity were the same trends in the dissociation energies of the metal dicarbides, which leads to two conclusions: first, formation of the lanthanide dicarbide is a precursor to thermal ions; and second, the decomposition temperature where that lanthanide atom is released is far higher than the volatilization temperature of the metal. The ions are formed from the vaporization of the metal either from the hot filament surface or directly from decomposition of the carbide. This supports the concept that dissociation of the metal carbides to produce the atomic species followed by rapid volatilization is the controlling ionization mechanism.

4.1. *Application to uranium and plutonium*

Uranium and plutonium are the main elements analyzed by the resin bead method [2,3]. It is also well established that uranium and plutonium form carbides upon heating with carbon. Temperatures in excess of 2000 °C have been measured for the uranium thermal ion signal from a resin bead source. Plutonium observations show ion signal maximum at 1800–1900 °C. The temperature of the observed ion signals is well above the metal melting points (1132 °C uranium and 631 °C plutonium) [22]. No oxides were observed. The metal could not persist to the analysis temperature without volatilizing. They must be trapped in a compound like uranium and plutonium dicarbide.

Observations from the lanthanides, and uranium and plutonium, are not consistent with the metal being the specie that exists up to the analysis temperatures. The absence of oxide thermal ion signal and the presence of carbon as a reducing agent are not consistent with the oxide being the specie that exists prior to thermal ion signal production. The formation of a lanthanide, uranium, or plutonium dicarbide is consistent with the work presented above and the observations from the resin bead system.

5. Conclusion

Experimental results on lanthanide ion formation presented in this study indicate that the metal dicarbide compounds are the active intermediate species in the resin bead ion source. The carbide stabilizes the lanthanides to temperatures well in excess of volatilization temperatures of the metals. When the decomposition temperature is reached, the atomic species is volatilized from the filament as a mix of thermal ions and atomic neutrals. The ratio of atomic ions to atomic neutrals would be expected to increase as the decomposition temperature increases, accounting for the higher ionization efficiency. Another contributing factor to the high ionization efficiency is that the atomic species is more likely to ionize than a molecular species, such as the oxide. The carbon left from the polymer resin bead, as well as additional carbon from the benzene treatment of the heated sample filament, results in the dicarbide formation and suppresses the formation of oxide species. Uranium and plutonium also follow these trends.

Acknowledgements

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