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Plasma Quench Investigations: Tungsten-Oxide Quenchants

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Abstract

THE negative-ion forming properties of high-temperature, gas-phase tungsten oxides in the free-jet expansion of an argon plasma have been investigated. Gas-phase tungsten-oxide vapors (mainly W_3O_9 for the temperature range of this experiment) are produced by sublimating WO_3 powder in a resistively heated oven. WO_3^-, $W_2O_6^-$ and $W_3O_9^-$ have been mass spectrometrically identified. Measurement of their ion signal intensity as a function of W_3O_9 flux from the oven indicates they are good electron attachers.

Contents

The negative-ion forming properties of tungsten oxides in a plasma were investigated in the McDonnell Douglas Research Laboratories Plasma Chemistry Facility. Figure 1 shows the experimental system for mixing the tungsten-oxide vapors with an argon plasma. An electrodeless rf induction argon plasma is supersonically expanded in a free jet where it mixes with the tungsten-oxide vapors generated from WO_3 powder in a tantalum oven. The centerline of the flow is sampled through an orifice in the extractor nozzle and analyzed with a quadrupole mass spectrometer, while the electron density in the expanding plasma is measured with a Ka-band microwave interferometer. The negative-ion data presented herein were obtained for a generator power of 54 kW and an argon mass flow of 1.53×10^{-1} g·s^{-1}. For the conditions of this experiment, the electron density at the location of the interferometer was about 1.8×10^{12} cm^{-3} with the density at the oven location approximately 4.8×10^{12} cm^{-3}. The conditions behind the shock wave which forms in front of the oven are estimated to be[1]: $M=1.65$, $T=2360$ K, $p=12$ kPa (90 Torr), and the stream velocity $v=1.33\times10^5$ cm·s^{-1}. During tungsten-oxide vapor generation, the oven is heated to a maximum of 1500 K; therefore, the shock temperature is dominant in determining the gas temperature in the vicinity of the oven.

Two oven configurations were used in these experiments. The first was a resistively heated oven used to generate tungsten-oxide vapor; the second an identical, unheated oven used for SF_6 injection. The tungsten-oxygen system forms a complex mixture of gaseous oxides containing $(WO_3)_n$, where $n=1$, 2, 3, and 4 together with W_3O_8. Measurements[2-4] and equilibrium calculations[5] show that W_3O_9 is the major tungsten-oxide species above solid WO_2 or WO_3 in the temperature range of interest for these experiments (~1200-1500 K). Tungsten-oxide vapors are generated by sublimating WO_3 powder in a tantalum oven. The tungsten-oxide vapor flux emanating from the oven is a function of the vapor pressure of the oxide in the oven and the oven orifice diameter. The equilibrium vapor pressure of W_3O_9, W_2O_6 and W_4O_{12} as a function of temperature for the W-WO_2 and the WO_3-$W_{20}O_{58}$ systems has been determined experimentally by Battles.[2] The vapor pressure of the oxide species in the oven (predominately W_3O_9), and therefore the oven flux, depends on the composition of the solid sample in the oven. The original WO_3 powder in the oven was yellow; however, after repeated heating, the character of the sample remaining in the oven changed. Two residue samples were subjected to x-ray diffraction analysis; a bluish-purple residue was identified as $W_{18}O_{49}$ and a chocolate-brown residue as WO_2. In general, negative-ion measurements were made under conditions where it was reasonable to assume that the sample was either fresh WO_3 or had been heated sufficiently to assure reduction of WO_3 to WO_2. Under either of these conditions, the vapor pressure of the gaseous oxides at a given temperature was obtained from the appropriate vapor pressure-temperature relationship.[2]

Tungsten-oxide negative-ion species WO_3^-, $W_2O_6^-$, and $W_3O_9^-$ were detected and identified mass spectrometrically with WO_3^- being the dominant negative ion found under the conditions of the experiments reported herein. Figure 2 shows four sets of measurements of WO_3^- signal intensity as a function of W_3O_9 oven flux for the same plasma conditions. The data of curve 1 were obtained from a fresh charge of WO_3. The W_3O_9 flux was obtained from the vapor pressure curve for W_3O_9 from the WO_3-$W_{20}O_{58}$ system. After seven heating and cooling cylces of the same sample during which the WO_3^- signal intensity was measured, the data of curve 2 were obtained. As a result of the repetitive heating and cooling, the solid residue in the oven was reduced to WO_2. Therefore, the data of curve 2 were plotted against W_3O_9 vapor pressure from the W-WO_2 system. A new oven was charged with fresh WO_3 powder and heated to 1400-1550 K in five separate heat-cool cycles for a total of 10 h to reduce the WO_3 to WO_2. The data shown in curves 3 and 4 were then obtained from the WO_2 sample in the oven. The slope of the initial portion of all four curves of Fig. 2 is nearly the same, indicating that the WO_3^- was formed by the same process in each case. The most probable reaction, as previously suggested,[5] is

$$e+W_3O_9\rightarrow WO_3^-+W_2O_6 \tag{1}$$

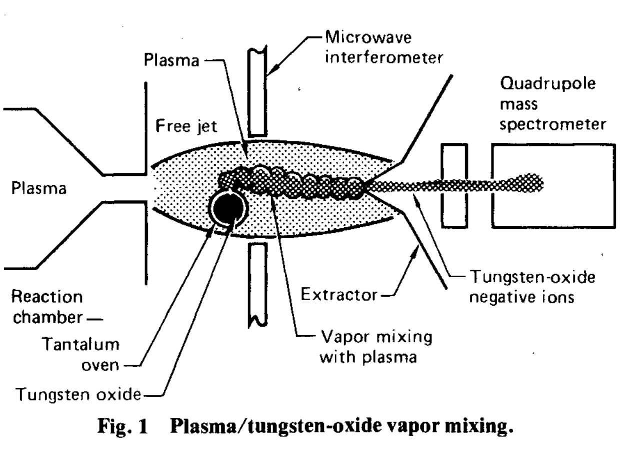

Fig. 1 Plasma/tungsten-oxide vapor mixing.

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Index categories: Thermochemistry and Chemical Kinetics; Atmospheric and Space Sciences.

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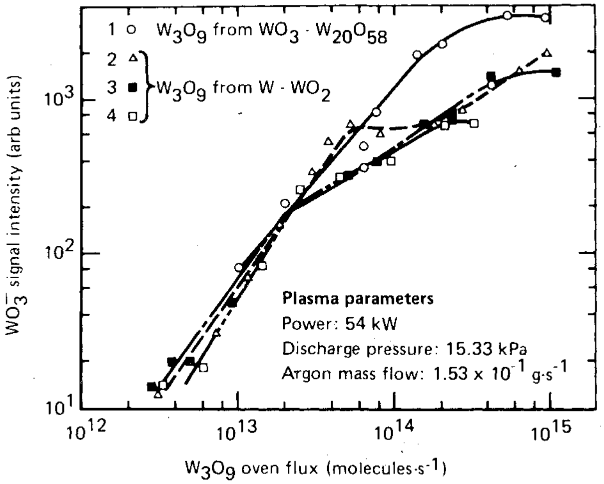

Fig. 2 WO_3^- vs W_3O_9 oven flux.

For W_3O_9 flux greater than 2.5×10^{13} molecules·s^{-1} ($T\sim1385$ K), the slope of curves 2, 3, and 4 changes, reflecting a change in the ion-formation mechanism. The W_3O_9 vapor in these three sets of measurements was obtained from solid WO_2 in the oven. The curve labeled 1, which does not change slope as the others do, was obtained from WO_3. The vapor pressure data[2] show that for the W-WO_2 system, W_2O_6 vapor is present, whereas it is not present for the WO_3-$W_{20}O_{58}$ system. Considering the W-WO_2 system at 1385 K (the point where the three curves of Fig. 2 change slope), the vapor pressure of W_2O_6 is comparable to that of W_3O_9 at about 1345 K ($\sim3.3\times10^{12}$ molecules·s^{-1}). Therefore, a competing process for the formation of WO_3^- is

$$e+W_2O_6\rightarrow WO_3^-+WO_3 \qquad (2)$$

Since W_2O_6 vapor is not present in the WO_3 system, the process described by reaction (2) would not occur, and thus, the slope of the data curve (curve 1 of Fig. 2) would not change.

The electron removal effectiveness of tungsten-oxide was compared with that of SF_6 by mixing SF_6 with the argon plasma through a modified tantalum oven. The plasma conditions were maintained the same as for the tungsten-oxide measurements except the oven was not resistively heated. With the plasma flowing around the oven, the oven temperature increased to 815 K. Figure 3 shows a set of data obtained using the SF_6 injection technique. At low SF_6 flux, SF_5^- and SF_6^- are the dominant negative ions. As the SF_6 flux increases, F^- increases while SF_5^- and SF_6^- decrease. The electron attachment cross section for the formation of SF_6^- is sharply peaked around zero electron energy and that for SF_5^- peaks at a few tenths of an electron volt. As the SF_6 flux increases, SF_6 mixes with the argon plasma farther from the oven surface, and thus, reacts with electrons in the plasma having higher energies. In this region, the formation of F^- is favored, and the intensity of SF_6^- and SF_5^- decreases. Comparison of the initial slope of WO_3^- from W_3O_9 in Fig. 2 with that of F^- from SF_6 in Fig. 3 gives a measure of the quench effectiveness (electron removal) of W_3O_9 compared with that of SF_6 under the same conditions. This comparison indicates that on the basis of unit flux of the parent neutral, the production of WO_3^- from W_3O_9 is approximately 60% that of F^- from SF_6.

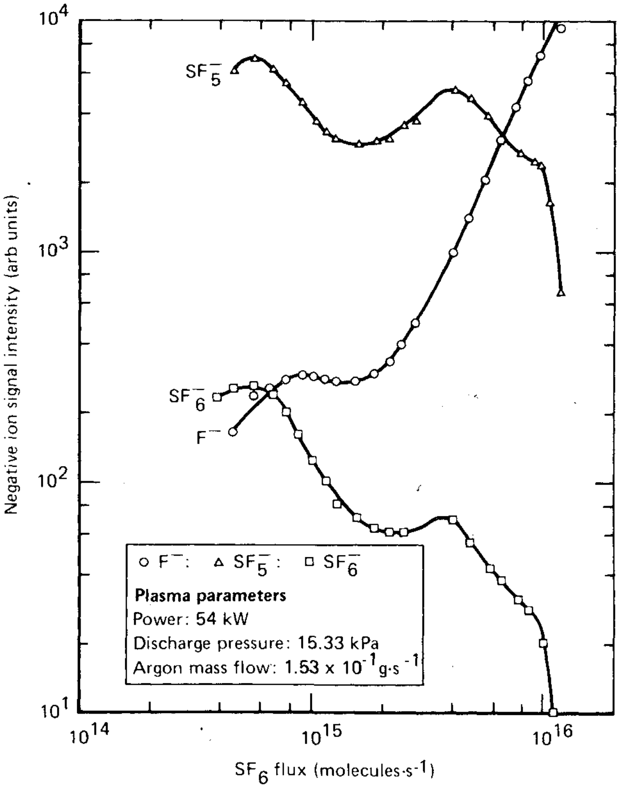

Fig. 3 Negative ions from SF_6 vs SF_6 flux.

Acknowledgments

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