Extended abstract to be included in Proceedings of NATO Advanced Study Institute on the Impact of Cluster Physics in Materials Science and Technology, Cap d'Agde, France, June 13-25, 1982.

CONF-8206159--1

Conf-8206159--1

DE83 007618

GENERATION OF BEAMS OF REFRACTORY-METAL CLUSTERS

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Interest in the physical and chemical properties of small metal clusters has recently stimulated the development of sources for the generation of molecular beams of metal clusters, since the collison-free environment of a beam has the advantage of permitting in-flight study of isolated species free of interference from surroundings. For example, spectroscopic studies utilizing tunable lasers may be performed in the molecular beam environment. The objectives of our research program are the elucidation of the physical and chemical properties of clusters of refractory metal atoms, in particular those of the catalytically active transition metals. For these purposes we have built and tested two sources suitable for generation of cluster beams of refractory metals, one for continuous beams and the other for pulsed beams.

The continuous source combines a very high temperature vaporization oven (operated up to 2000°C) with a cryogenically cooled (to−189°C) quench cell. A scaled drawing appears in Figure 1. The metal sample is usually contained in a graphite or tungsten basket suspended in a vertically mounted, resistively heated graphite tube surrounded by heat shields and a water-cooled box. Inert gas is flowed down through the graphite tube, the volatized metal vapor being entrained in the gas and carried out through an exit aperture. Measured oven operating temperatures correspond to metal vapor pressures of 0.1 to 1.0 torr. 2 to 8 mmol of metal can be placed in the source, so that steady beams can be maintained for many hours. The metal-carrier gas mixture that exits the source enters an 8.25 cm long liquid N_2-cooled copper quench cell, at the beginning of which is a manifold of 8 annular holes which directs cold quench gas downstream into the cell. The cluster beam exits the quench cell and then passes through four successive differentially pumped stages to reach a time-of-flight mass spectrometer, whose ionization region is 45.5 cm from the exit of the quench cell. In an earlier configuration, an electron impact ionization quadrupole mass spectrometer was used in the detector chamber. In a typical experiment, Ar passes through the graphite tube at a 50 sccm flow rate and N_2 is added to the quench cell at 250 sccm, which produces a quench cell pressure of 15 to 20 torr, and successive chamber pressures of 1.2×10^{-3}, 1×10^{-4}, 4×10^{-7} and 1×10^{-7} torr.

With the above arrangement continuous cluster beams of such relatively refractory metals as Al, Cr, Ni, Cu and Ag have been generated. The observed distributions of cluster ions produced by ionization of the neutral clusters by $\sim$10 eV electrons and quadrupole mass analysis are shown in Fig. 2 for Ag, Al, and Ni. These distributions can be considered only qualitative, because of the unknown relative ionization cross sections and the possible fragmentation of cluster ions. Cluster beams of Cu and Cr have also been generated with this source, but analyzed by multiphoton laser ionization and time-of-flight mass analysis. The Cu_n^+ distribution extends up to Cu_{12}^+, with the intensities of Cu^+, Cu_2^+ and Cu_3^+ being ~50 times greater than those of the higher multimers. However, with Cr only several percent of Cr_2^+ in addition to the predominant Cr^+ has been observed. A measurement of the chromium flux gave an equivalent Cr atom density of $10^8/cm^3$ in the detector region.

In addition to the continuous cluster source, a laser evaporation source similar to that of Smalley and his collaborators (1) has been developed for generating pulsed refractory metal cluster beams. In this source a 0.63 cm rod of the metal of interest is the target of a focussed beam of 249 nm photons from a pulsed (20 Hz) KrF excimer laser (~100 mj/pulse). The rod extends through a channel (at 90°) carrying a high pressure of He carrier gas, and the evaporation photons pass through a quartz window before striking the target rod. The He and the pulse of evaporated metal exit the channel through a 1.5 mm aperture. Although the source will shortly be fitted with a pulsed valve, continuous gas flow at a pressure of ~0.1 atm was maintained for the results described here. The diagnostic laser is triggered from the evaporating laser but delayed by the appropriate flight time.

With this source replacing the thermal quench continuous source in the same apparatus, a pulsed beam of Cu clusters has been generated, as indicated by multiphoton ionization-produced Cu_n^+

species with n up to 10. The intensities of Cu^+, Cu_2^+ and Cu_3^+ are each at least two orders of magnitude higher than those of the higher multimers, while the intensity of the Cu_2^+ ion itself is at least an order of magnitude higher than that measured from the continuous thermal quench source. In addition to Cu cluster ions, small yields of copper oxide ions, e.g. CuO^+, Cu_2O^+, Cu_3O^+ have been observed from both sources as well as CuO_2^+, $Cu_2O_2^+$, $Cu_3O_2^+$, $Cu_4O_2^+$ and $Cu_5O_2^+$ from the pulsed source. These oxides are believed to be due to small concentrations of oxygen in the copper target.

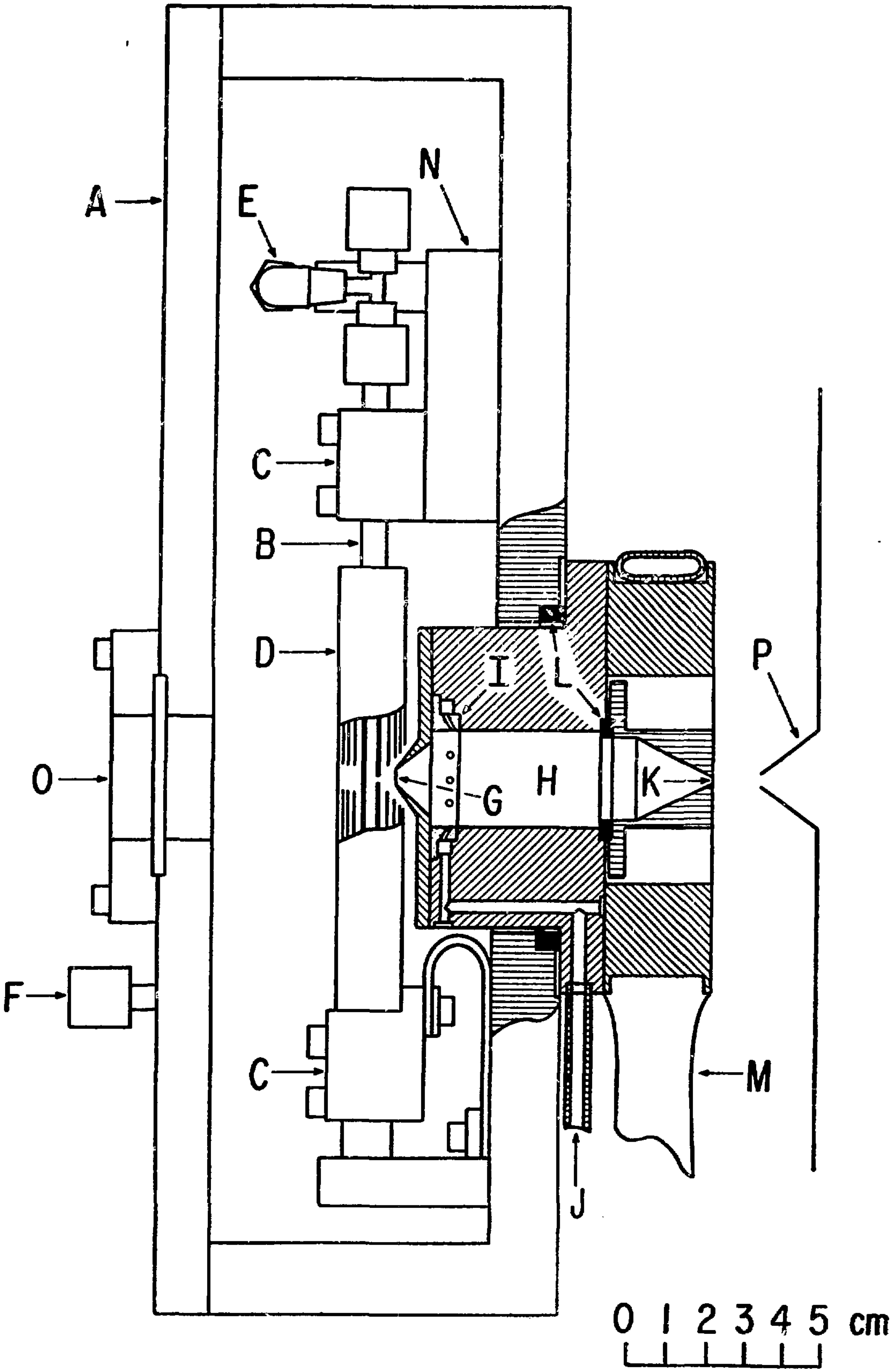
References

(1) T. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *Journal of Chemical Physics* **74**, 6511 (1981).

Figure Captions

Figure 1. Scale drawing of the continuous cluster beam source. A, copper box (water cooling now shown); B, graphite tube; C, high current clamps; D, heat shield assembly, E, nozzle gas inlet; F, box gas inlet; G, quench cell entrance aperture; H, quench cell; I, quench gas manifold; J, quench gas inlet; K, quench cell exit aperture (heater not shown); L, Teflon gaskets; M, liquid-N_2 inlet; N, Kel-F insulator; O, view port; P, skimmer separating source chamber from differential pumping chamber.

Figure 2. Cluster distributions in Ag, Al, and Ni beams as measured by low energy electron impact ionization and quadrupole mass spectrometry. The ordinates are relative intensities and n is the number of monomer units in each cluster of the distribution. Nozzle temperatures were 1295, 1465, and 1780°C for Ag, Al, and Ni, respectively, Corresponding nozzle flows (Ar) were 25, 35, and 50 sccm, and quench flows (N_2) were 300, 250, and 250 sccm.



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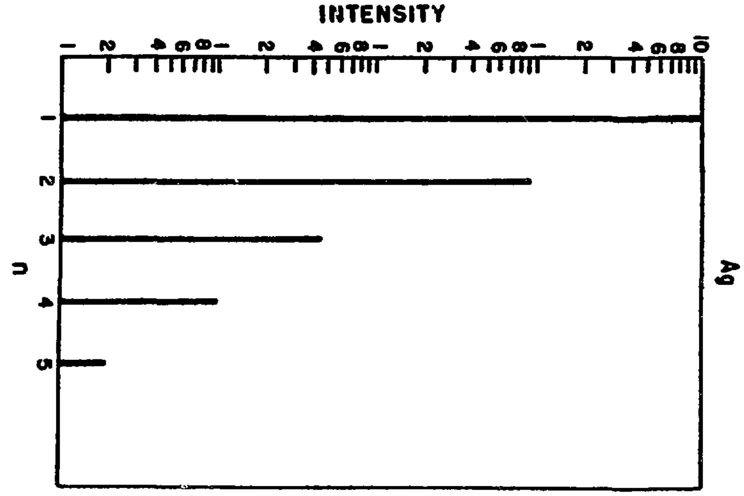
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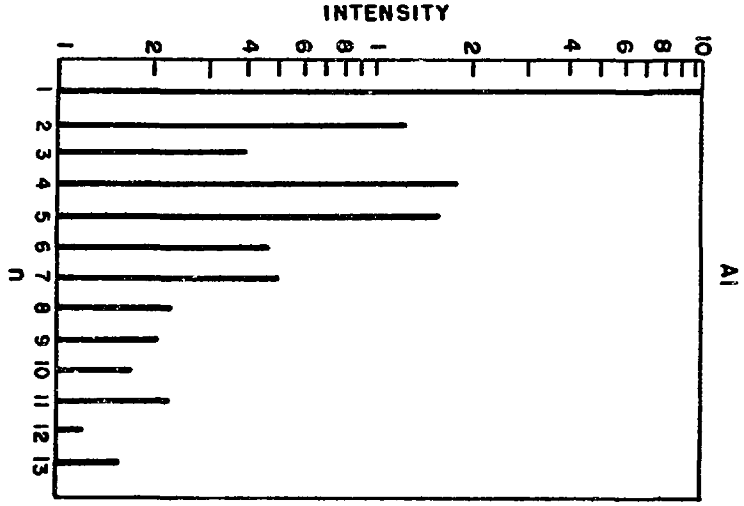
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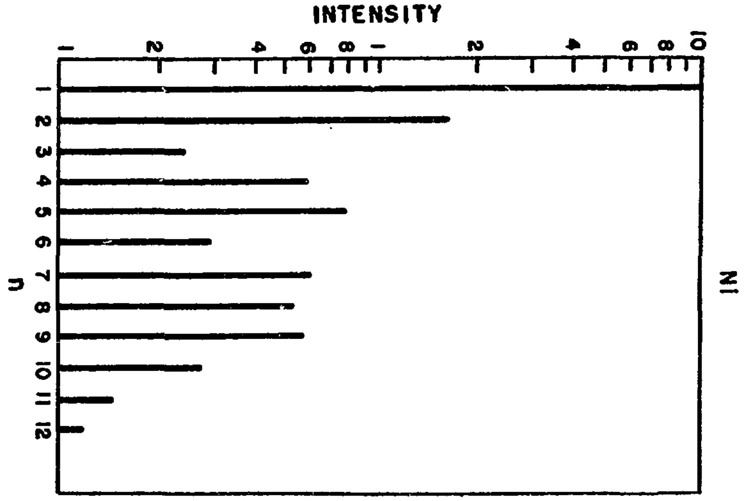
INTENSITY
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