Doubly and Triply-Charged Diatomic Molybdenum Cluster Ions As Observed in Pulsed-Laser Assisted Local-Electrode Atom-Probe (LEAPTM) Tomography

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Cluster ions are rarely formed by metal atoms in atom-probe experiments, whereas they are relatively common for materials with covalent atomic bonding, e.g. Si and C (group IV), and group V elements in semiconductors [1,2]. Multiply-charged cluster ions with only two atoms are commonly assumed to be unstable due to the strong repulsive Coulomb forces, and the smallest doubly-charged clusters observed contain at least three atoms [1]. Tsong, however, reported the existence of doubly charged diatomic Mo_2^{2+} cluster ions when field-evaporating pure molybdenum at elevated temperatures (800-1000 K) in a pulsed-laser atom probe (PLAP) [2,3]. Herein, we report the formation of doubly charged diatomic Mo_2^{2+} and, for the first time, the existence of triply charged diatomic Mo_2^{3+} cluster ions.

A HastelloyTM alloy with the nominal composition Ni - 7.3 Mo - 7.2Cr - 1.6 Fe - 1.8 Al - 0.6 Ti - 0.5 Mn - 0.3 Nb - 0.3 Si - 0.03 Y (at.%) was investigated after homogenization at 1100°C for 1 h and aging at 675°C for 50 h. The alloy was field-evaporated in a LEAPTM tomograph at 9 – 13 kV specimen voltage using a 1.5 nJ laser pulse at a 250 kHz repetition rate. By varying laser pulse energy and specimen voltage at a constant field-evaporation rate, a 1.5 nJ pulse energy was measured to correspond to a 12.5% effective pulse fraction. Atom-probe tomographic (APT) analyses were performed in ultrahigh vacuum (10^{-8} Pa), and at a specimen temperature of 40 K.

Figure 1 provides a comparison of the experimentally obtained mass spectra for (a) Mo_2^{3+} and (c) Mo_2^{2+} cluster ions with (b) a simulation of the abundances of the 15 different cluster masses possible when randomly combining pairs of the seven Mo isotopes with mass numbers 92, 94, 95, 96, 97, 98, and 100 to diatomic clusters. It is evident that the experimental distributions for Mo_2^{3+} and Mo_2^{2+} match the simulated distribution very closely. At mass-to-charge state ratios 62 and 64, the much stronger lines of the corresponding Ni^+ ions obscure two of the Mo_2^{3+} lines, Fig. 1(a). A comparison reveals, however, that the unobscured 13 Mo_2^{3+} lines unambiguously match the simulated distribution, Fig. 1 (b). Therefore, we demonstrate for the first time the existence of triply-charged diatomic Mo_2^{3+} cluster ions. The stability of these cluster ions must be sufficient for a life time of at least the acceleration time in the LEAPTM tomograph, which is several nanoseconds, before the clusters possibly dissociate. Besides the diatomic Mo_2^{3+} and Mo_2^{2+} cluster ions, atomic Mo^{2+} and Mo^{3+} ions are observed with Mo^{2+} as the dominant charge state.

The existence of multiply-charged diatomic clusters may provide a crucial test case for calculations of the bonding types and bonding energies of metal clusters with a small number of atoms. The possibility of cluster ions formed from metallic elements clearly has to be taken into account for the interpretation of pulsed-laser assisted atom-probe mass spectra [4].

References

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FIG. 1. Mass spectra of (a) Mo_2^{3+} and (c) Mo_2^{2+} diatomic cluster ions, obtained by pulsed-laser assisted field-evaporation of a Ni-based superalloy, and (b) a simulation of the abundances of the 15 possible cluster masses of diatomic Mo_2 clusters. The histogram bin width in (a) and (c) is 0.02 amu.