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Breakdown of the Hume−Rothery Rules in Sub-Nanometer-Sized Ta-Containing Bimetallic Small Clusters

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The Hume−Rothery rules are empirical rules to predict the solid solubility of metals. We examined whether the rules hold for sub-nanometer-sized small particles. We prepared bimetallic cluster ions in the gas phase by a double laser ablation technique. Taking advantage of the magic compositions of the bimetallic cluster ions relating to the distinguished stabilities, the coalescence or the segregation of Ta and another element in the sub-nanometer-sized clusters was discussed. It was found that W, Nb, and Mo readily coalesce with Ta, while Ag, Al, Au, Co, Cu, Fe, Hf, Ni, Pt, Ti, and V are segregated from Ta. On the basis of these results, we concluded that the Hume−Rothery rules do not hold for sub-nanometer-sized particles.

The Hume−Rothery rules are a set of rules describing the conditions under which an element can dissolve in a bulk metal, forming an alloy.[1−3] The rules suggest that the alloy is formed, if the atomic size, electronegativity, and valency of the elements are very similar and the crystal structure of the bulk metal is shared by the two elements. Since the rules were proposed in the 1930s, they have been widely used for the bulk materials. However, it is not known if the rules are still valid for sub-nanometer-sized small particles which are composed of several atoms. In fact, the geometrical structure of small particles is typically very different from the crystal structure of the bulk, as is the electronic structure of small particles relative to the bulk. This paper considers whether the Hume−Rothery rules hold for sub-nanometer-sized small particles.

Clusters are suitable samples for such studies, as the preparation methodologies of the bimetallic ones have already been established. There are a number of studies which have been conducted on bielement clusters.[4−9] For instance, the Martin group observed mass spectra of $Au_nX_m^+$ (X = Al, In, Cs), and the size distributions were interpreted in terms of the electronic shell model.[9] However, the spatial distribution of atoms within the cluster does not need to be considered by the traditional shell model. In the present study, we prepared bimetallic clusters of Ta and another metal element in the gas phase. We examined whether the atoms in the clusters were ready to coalesce or segregate by analyzing the composition of the stable clusters.

A tantalum metal rod (99.95%) and a metal rod of another element were set downstream of the supersonic source from a solenoid pulsed valve. Each rod was irradiated with a focused laser pulse (∼10 mJ/pulse) at 532 nm: one from a Quanta Ray GCR-130 and the other from a Continuum Surelite II Nd:YAG laser for generating the plasma. The laser ablated atoms were cooled in the gas phase with He gas (>99.99995%) from the valve, forming neutral and charged clusters. The clusters were then introduced into a differentially pumped chamber, where the native or photoionized cluster ions were accelerated orthogonally by a pulsed electric field for time-of-flight mass analysis. The resolution of the mass spectrometer exceeds 1000.

Figure 1a shows a mass spectrum of Ta positive cluster ions. Evidently, a peak for Ta_4^+ is prominent compared with the other peaks assignable to Ta_n^+ ($n = 1-7$), indicating that Ta_4^+ is a “magic number”. This is consistent with results from Sumiyama’s group, who found that Ta_n^+ for $n = 4, 7, 13, 15, ...$ tend to be abundantly formed in the gas phase.[10] For $n = 7$, 13, and 15, they suggested that the magic numbers relate to the geometrical structures, but the origin of the magic number for $n = 4$ has never been discussed. It is known that cluster ions with lower ionization energies are formed with higher abundance than cluster ions with high ionization energies as a result of the competition for electrons in the cluster formation region. However, the ionization energy of Ta_4 is 5.78 eV, which is higher than the adjacent Ta clusters (Ta_3, 5.58 eV; Ta_5, 5.18 eV).[11] In addition, neutral Ta_4 is also most abundant among the small neutral Ta clusters, as confirmed by our UV photoionization experiments at 193 nm. Hence, we can assert that thermodynamic stability is the cause of the magic number. The closely packed pyramidal structure, which was determined by Metha’s group by density functional calculations, is considered to be related to thermodynamic stability.[12]

Figure 1b shows a mass spectrum of bimetallic cluster ions of tantalum and niobium: $Ta_nNb_m^+$ with various n and m formed in the gas phase. The relative abundance of $Ta_nNb_m^+$ was found to depend on n and m, exhibited as color codes in a map (see Figure 1c). In the $m = 0$ column, $n = 4$ is the brightest, indicating that Ta_4^+ was also most abundantly formed under the conditions that the bimetallic clusters were produced. In addition, there is a clear diagonal line at $n + m = 4$, indicating that $Ta_nNb_m^+$ for $n + m = 4$, with $n > 0$, were also abundantly produced in the gas phase (magic compositions). A similar experiment was performed for Ta and Al. In contrast to the Ta and Nb case, there is a parallel line to the axis at $n = 4$ (see

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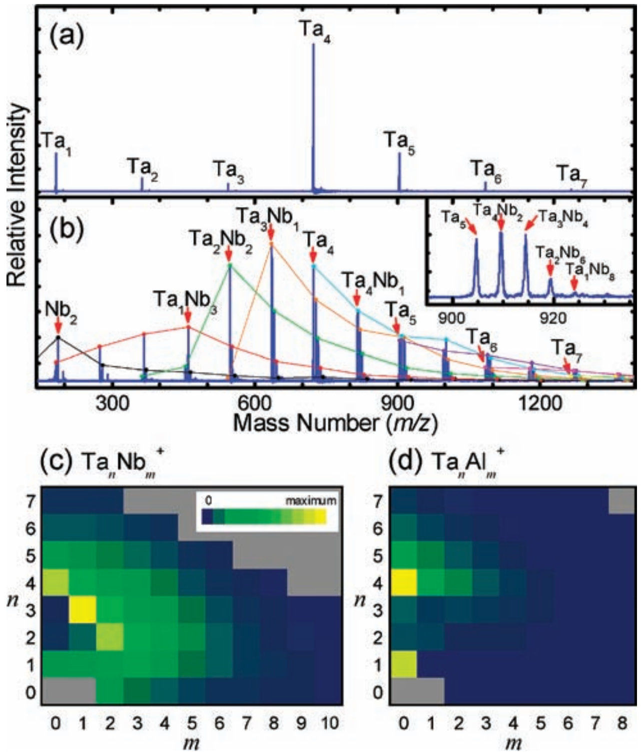

Figure 1. (a) Mass spectrum of Ta_n^+ showing that Ta_4^+ is a magic number. (b) Mass spectrum of $Ta_nNb_m^+$. Peaks of clusters involving the same number of Ta atom(s) are connected by a line of the same color (black, red, green, and orange correspond to $n = 0$, 1, 2, and 3, respectively). Inset: Peaks appearing in the mass region from 900 to 930 were assigned to $Ta_{5-k}Nb_{2k}^+$ ($k = 0-4$). (c) Relative abundance of $Ta_nNb_m^+$ exhibited as color codes. The diagonal line at $n + m = 4$ indicates that $Ta_nNb_m^+$ for $n + m = 4$ ($n > 0$) are the magic compositions. (d) Relative abundance of $Ta_nAl_m^+$ exhibited as color codes. The horizontal line at $n = 4$ indicates that $Ta_4Al_m^+$ are abundantly formed.

Figure 1d), suggesting that $Ta_nAl_m^+$ including four Ta atoms were more abundantly formed in the gas phase.

Let us discuss how atoms inside bimetallic clusters interact with each other, based on stabilities of the cluster ions. Primarily, Ta_4^+ is one of the most stable cluster ions in small single element Ta_n^+ clusters. Ta_3Nb^+, which corresponds to the cluster ion with one Ta atom in Ta_4^+ replaced by one Nb atom, was also found to be quite stable. Similar results were found for $Ta_2Nb_2^+$. Hence, the stabilities of $Ta_nNb_m^+$ do not change significantly by the replacement of the relevant atoms. This finding suggests that the Ta and Nb atoms readily coalesce in the clusters, and the stabilities of $Ta_nNb_m^+$ seem to be determined by the total number of atoms inside the cluster ions. In contrast, Ta_3Al^+ was found to be unstable. Instead, $Ta_nAl_m^+$ including four Ta atoms are more stable, as evidenced by the prominent peaks in the mass spectrum. This characteristic behavior is interpreted straightforwardly as follows: As Ta_4^+ is so thermodynamically stable that the penetration of the Al atoms into the framework of Ta_4^+ is energetically unfavorable, the Al atoms attach on the surface of Ta_4^+. This result gives strong evidence for the segregation of Ta and Al atoms in the cluster ions.

Taking advantage of the characteristic magic compositions of the Ta-containing cluster ions, we are able to discuss alloy formation in the bimetallic clusters using mass spectrometry: The diagonal and horizontal lines in the map indicate coalescence (case a) and segregation (case b), respectively. We have obtained the maps for bielement clusters of Ta with 14 different elements (Ag, Al, Au, Co, Cu, Fe, Hf, Mo, Nb, Ni, Pt, Ti, V, and W), and have classified them into case a or case b. From our investigations, all could be assigned to either case. Figure 2a exhibits the obtained results for the Darken−Gurry plot based on the Hume−Rothery rules.[12,13] For the bulk materials, elements, whose difference in radius is less than ±15% and with electronegativities within ±0.4 units, are expected to form solid solution alloys. However, the elements which form alloys with Ta in sub-nanometer-sized clusters are totally scattered in Figure 2a. For instance, Al does not form a sub-nanometer-sized alloy with Ta, although Al is adjacent to Ta in the plot. In contrast, W, which is located away from Ta in the plot, tends to form an alloy with Ta. Hence, we are able to conclude that the Hume−Rothery rules do not hold for sub-nanometer-sized small clusters. Figure 2b shows a similar plot using the molar heat of vaporization as a parameter for the vertical axis.[13] Here, W, Nb, and Mo, which readily form alloys with Ta, are very close to each other. Hence, the molar heat of vaporization may be considered a better parameter than electronegativity to categorize the elements for the alloy formation in the sub-nanometer region.

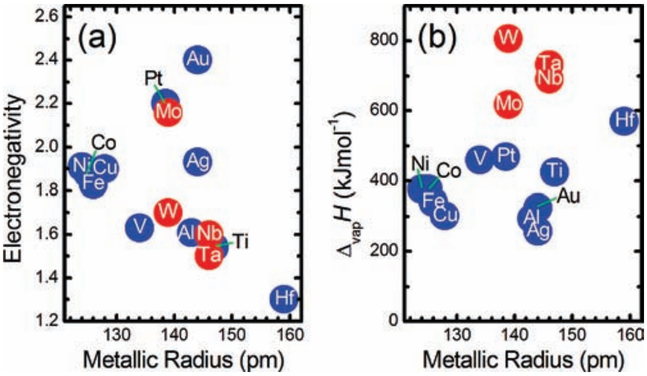

Figure 2. Elements plotted with a red circle readily form alloys with Ta in sub-nanometer-sized small clusters. (a) Elements are shown in the conventional Darken−Gurry plot using electronegativity in the Pauling scale.[13] (b) Elements are shown in the plot using the molar heat of vaporization $\Delta_{vap}H$ as a parameter for the vertical axis.

Now, the question to be answered is "why is the molar heat of vaporization more important?" The molar heat of vaporization is related to the binding energy of atoms in bulk materials. The geometrical structure of a cluster, which is composed of atoms with similar binding energies, is likely to be free from distortion. In fact, the geometrical structure of Ta_3Nb is almost perfectly pyramidal, with the Ta−Ta bond length equal to the Ta−Nb bond length (2.543 Å), while the bond length of Ta−V (2.413 Å) is much shorter than that of Ta−Ta in the Ta_3V cluster.[14] Our preliminary DFT calculations on Ta_3Au also suggests that the Ta−Au bond length is much longer than that of Ta−Ta in the Ta_3Au cluster, although the metallic radius in the bulk for Ta is very close to that of Au. The relation between the stability of the bimetallic cluster and the molar heat of vaporization or the binding energy of the component atoms needs to be more closely examined in future studies with the aid of theoretical calculations.

In summary, we prepared bimetallic cluster ions of Ta and other transition metal elements in the gas phase by a double laser ablation technique. Taking advantage of the characteristic magic compositions of the Ta-containing cluster ions appearing in the mass spectrum, we discussed the coalescence or the segregation of Ta and the other element in sub-nanometer-sized clusters. It was found that W, Nb, and Mo readily form stable alloys with Ta, while Ag, Al, Au, Co, Cu, Fe, Hf, Ni, Pt, Ti, and V are segregated from Ta. The molar heat of vaporization is considered to be a better parameter than electronegativity to categorize the elements for coalescence or segregation in the sub-nanometer region. Hence, we can conclude that the Hume−Rothery rules do not hold for sub-nanometer-sized clusters.

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