DOE/ER/14258--T1

PROGRESS REPORT FOR PERIOD DECEMBER 2, 1992-DECEMBER 10, 1993

Metal Cluster Alloys and Oxides: Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions

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Request is hereby being made for continuation of support for the third-year period (May 1, 1994 - April 30, 1995) of the above-titled grant. Work during the last year has proceeded in accordance with the objectives stated in the original proposal and deals with elucidating the influence on reactivity of structure, charge, and electronic properties of metal alloy and metal oxide clusters. Attention is being directed to unraveling structure reactivity relationships and the physical basis for catalysis. Our discovery of a new class of molecular clusters, namely metallocarbohedrenes, or Met-Cars for short, represented a potentially major finding in cluster science. During the last year, we then developed a method for producing bulk quantities of this material (publication 375 - see below) which has prompted considerable interest on the part of the scientific community, especially in the prospect of developing a new catalytic material. Hence, we have also devoted attention to unraveling mechanisms of formation and the reactive chemistry of Met-Cars. Listed below are the titles, publication status, and abstracts for 14 publications submitted, accepted, and/or published during the past year which acknowledge support of this DOE grant. Four of these (namely 361, 362, 365, and 371) were mentioned in last year's progress report, but are re-listed since their publication status has changed during the year. The others represent new submissions and/or publications.

361. "Dehydrogenation of Gaseous Hydrogen-Containing Molecules: The Formation of Elemental and Molecular Clusters," Z. Y. Chen, G. J. Walder, and A. W. Castleman, Jr., *Phys. Rev. B*, in press.

Abstract: A general concept employing the dehydrogenation of hydrogen containing organic and inorganic compounds is shown to readily effect the production of a wide variety of elemental and binary clusters. Hydrogen containing molecules such as C_2H_4 , NH_3 , SiH_4 , or H_2O , are introduced into a laser-induced plasma source which dehydrogenates these molecules to produce nascent C, N, O, and Si atoms in the extremely energetic plasma generated from laser irradiation of the metal surface. The produced C, N, O, and Si atoms can either react with metal atoms contained in the plasma forming the

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metal carbide, nitride, silicide, and oxide clusters, or they can associate to produce pure elemental clusters such as carbon and silicon clusters. In principle, this technique can be applied to all gaseous hydrogen containing compounds. This research provides an alternative way (in some cases it could be the only feasible way) to generate these clusters. Study of the ensuing distributions provides unique insight into the cluster formation mechanisms involving this type of cluster source.

362. "Growth of Titanium Nitride: From Cluster to Microcrystal," Z. Y. Chen and A. W. Castleman, Jr., *J. Chem. Phys.* **98**, 231-235 (1993).

Abstract: Time-of-flight mass spectrometry is used to investigate $(\text{TiN})_n^+$ clusters produced by a laser-induced plasma reactor source. The mass spectral abundance patterns indicate that the clusters have cubic structures resembling subunits of the fcc lattice of solid TiN. The primary stoichiometries observed are $(\text{TiN})_n^+$ ($n=1-126$), except for $\text{Ti}_n\text{N}_{n-1}^+$ ($n=14,63$). The most stable structures of the clusters are cuboids, in some cases containing a completed terrace. Even at the very early stages of crystal growth, the gas-phase clusters prefer a cubic crystal-like atomic arrangement with a highly symmetric structure.

365. "Copper/Antimony and Copper/Bismuth Alloy Clusters: Magic Numbers and Electronic Structure," Y. Yamada, H. T. Deng, E. M. Snyder, and A. W. Castleman, Jr., *Chem. Phys. Lett.* **203**, 330-336 (1993).

Abstract: Metal alloy clusters Cu_nSb_m and Cu_nBi_m are produced by a gas aggregation source and investigated by time-of-flight mass spectrometry following ionization with a KrF excimer laser. Two types of magic numbers are observed in their cluster ions: magic numbers corresponding to jellium shell closings by counting the total valence electrons from the component metals, and other magic numbers explained by the polyhedral shape-electron counting scheme (Wade's rules). In the second type of magic numbers, Cu atoms give electrons to the skeleton of Sb or Bi to satisfy the total charge of the cluster ions, and simultaneously Cu atoms take the vacant vertex positions of the skeleton to form corresponding deltahedral structures (closo structures).

366. "Metallo-Carbohedrenes," A. W. Castleman, Jr., *1994 McGraw-Hill Yearbook of Science and Technology*, pp 263-265 (1993).

Abstract: The study of gas-phase clusters, species generally composed of weakly bound assemblies of atoms, molecules, and ions, pervades many fields of science and technology and has undergone an explosive growth since 1980. Within this broad field of research, those systems that assemble into cagelike structures have attracted particular interest. One example is hydrogen-bonded aggregates of water molecules, both pure and in varying combinations with alcohols and ammonia, that form a network structure that can encase central cations and anions (such as the cation H_3O^+ , alkali metal ions, and the anion OH^-). Another example is covalently bonded fullerenes, commonly referred to as buckyballs. In 1992, a new class of molecular clusters was discovered that form comparatively strongly bonded cagelike structures and, moreover, display a heretofore-unknown growth pattern leading to multicage assemblies. These new molecular clusters are composed of particular combinations of carbon and early transition-metal atoms; to date, they have been observed in systems composed of titanium, vanadium, hafnium, and zirconium. In view of the chemical nature of their bonding, this new class of molecular cluster materials has been termed metallo-carbohedrenes (Met-Cars for short).

371. "Gas Phase Copper Carbide Clusters," Y. Yamada and A. W. Castleman, Jr., *Chem. Phys. Lett.* **204**, 133-138 (1993).

Abstract: Copper carbide clusters are formed utilizing a gas aggregation source in which C_2H_2 is passed over a heated crucible containing copper; the abundance of the copper carbide changes depending on the concentration of the reactant in the carrier He gas. Dominant peaks are $Cu_nC_{2m}^+$ ($n=3, 5, 7, 9, 11, 13$, and 15 , $m=1, 2$) at small C_2H_2 concentrations and $Cu_{2n+1}C_{2n}^+$ ($n=1-10$) at high concentrations. These peaks reflect the electronic stability of the cluster ions resulting from fragmentation. Magic numbers at $n=5$ in $Cu_{2n+1}C_{2n}^+$ and for other clusters ($Cu_7C_8^+$, $Cu_9Cu_{10}^+$, $Cu_{11}C_8^+$, and $Cu_{20}C_{18}^+$) arise due to the geometrical stability of compact structures.

372. "Gas Phase Copper/Selenium and Silver/Selenium Clusters," Y. Yamada, H. T. Deng and A. W. Castleman, Jr., *Chem. Mater.* **5**, 1085-1088 (1993).

Abstract: Binary clusters $Cu_nSe_m^+$ and $Ag_nSe_m^+$ are produced by a gas aggregation source and investigated by time-of-flight mass spectrometry following ionization with a KrF excimer laser. Dominant species in the mass spectra are assigned as $(M_2Se)_n^+$ and $M(M_2Se)_n^+$ ($M=Cu$ or Ag), which reflect stable compositions of neutral precursors and charged clusters. In these series, magic numbers appear at $n=6$. Additionally, especially prominent peaks are observed for $M_nSe_m^+$; $(n,m)=(7,4)$, $(9,5)$, and $(11,6)$. From an investigation of the magic numbers and prominent abundances of various species, it is suggested that these binary clusters have structures related to an antiferrofluorite structure.

374. "Reactivities of $Ti_8C_{12}^+$ at Thermal Energies," B. C. Guo, K. P. Kerns and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **115**, 7415-7418 (1993).

Abstract: Reactivities of the Met-Car $Ti_8C_{12}^+$ toward various molecules have been examined at thermal energies employing a selected drift tube reactor coupled with a laser induced plasma source. It is observed that this cluster ion is quite reactive toward molecules with either large dipole moments or ones with π -bonding systems. At room temperature $Ti_8C_{12}^+$ is found to take up 8 polar molecules, but only 4 molecules with π -bonding systems. Unlike the free radical ions Ti^+ and C^+ , the Met-Car cluster ion reactions are observed to proceed mainly through association mechanisms leading to ligand attachment rather than ones that involve the breaking and forming of new chemical bonds. In addition, $Ti_8C_{12}^+$ is seen to be inert even toward oxygen, which is known to be a good free radical scavenger. The association or attachment behavior of $Ti_8C_{12}^+$ reactions is explained in terms of a closed or edgeless structure of the Met-Car and the presence of titaniums in the framework of $Ti_8C_{12}^+$. Hence, the observed reactivities of $Ti_8C_{12}^+$ provide further evidence supporting the argument that the Met-Car Ti_8C_{12} has a dodecahedral structure without dangling bonds.

375. "Production of Metallo-Carbohedrenes in the Solid State," S.F. Cartier, Z. Y. Chen, G. J. Walder, C. R. Sleppy, and A. W. Castleman, Jr., *Science* **260**, 195-196 (1993).

Abstract: Macroscopic quantities of the metallo-carbohedrenes Ti_8C_{12} and V_8C_{12} have been synthesized using an arc discharge technique. Mass spectroscopy of raw soot samples generated in both

an ac and dc arc between two metal/graphite powder composite electrodes establishes that the titanium and vanadium analogs of the metallo-carbohedrenes have been produced. An estimated yield of approximately 1% is obtained, and significantly, the Met-Cars are found to be stable in air.

378. "Metastable Dissociation of Met-Cars: Reaction Channels and Cluster Stabilities," S. Wei, B. C. Guo, J. Purnell, S. A. Buzza, and A. W. Castleman, Jr., *J. Phys. Chem.* **97**, 9559-9561 (1993).

Abstract: An investigation of the metastable unimolecular dissociation channels and decay fractions of $Ti_mC_n^+$ was made using a reflectron time-of-flight mass spectrometer, coupled with a laser vaporization source in conjunction with multiphoton ionization. The measurements of the decay fractions show that $Ti_8C_{12}^+$ is a very stable species in accordance with expectation for a closed cagelike structure and, most importantly, provide the first available data on the relative stabilities for different cluster ions involved in the formation of metallocarbohedrenes (Met-Cars). Furthermore, the results reveal that the $Ti_8C_n^+$ mainly lose carbon species for $n \geq 14$, while $Ti_mC_{12}^+$ loses only Ti for $m \geq 6$ and both Ti and C_3 for $m=4$ and 5; C_2 is never a product of decomposition for this range of Met-Car related species. The present findings are valuable in providing qualitative information for assessing theoretical calculations of structures and properties of metallocarbohedrenes and their building blocks.

384. "Dehydrogenation Reactions in $Mg^+(H_2O)_n$ Clusters," A. C. Harms, S. N. Khanna, B. Chen, and A. W. Castleman, Jr., *J. Chem. Phys.*, in press.

Abstract: Experimental observations of the effects of solvation on the dehydrogenation reaction of $Mg^+(H_2O)_n$ to produce $MgOH^+(H_2O)_{n-1}$ are presented for $n \leq 6$. The reaction is seen to occur spontaneously at room temperature for $n > 4$. Ligand switching reactions are used to show the Mg^+-OH bonds are stronger than Mg^+H_2O bonds. The results show the energy required to lose an H atom decreases with the number of water molecules attached because the magnesium changes oxidation state and this results in stronger interactions with the water ligands. Ab initio calculations are used to explain these observations.

386. "Growth Pattern of Zirconium-Carbon Clusters: Face-Centered Cubic or Multicage Structures?", S. Wei and A. W. Castleman, Jr., *J. Am. Chem. Soc.*, submitted.

Abstract: A time-of-flight mass spectrometer coupled with a laser vaporization source was utilized to study the intensity distributions of metal-carbon clusters, namely, Zr_mC_n and Ta_mC_n . A series of experiments were carefully performed to assign the mass spectrum of Zr_mC_n precisely, which is critical for considering the structures of the evolving clusters. Two distinct cluster growth patterns were observed under our experimental conditions, i.e. Zr_mC_n through a metal:carbon ratio of 2:3 while Ta_mC_n through a 1:1 ratio. These different growth mechanisms lead to two completely different cluster distributions, observed magic numbers, and cluster structures. The Ta_mC_n clusters can be well accounted for by the formation of face-centered cubic (fcc) structures. However, these fcc structures do not explain any of the cluster peaks observed in the Zr_mC_n distributions. Importantly, without any exceptions in the assignments, both the growth pattern and the magic numbers observed in the Zr_mC_n clusters are rigorously consistent with expectations for the formation of multicage structures.

388. "Probing the Structure and Dynamics of Cage-Like Clusters: From Water to Met-Cars," A. W. Castleman, Jr., *Z. Phys. D.*, in press.

Abstract: Clusters often assemble into cage-like structures, even for such diverse substances as water and metal-carbon compounds. The $(\text{H}_2\text{O})_{20}$ clathrate is stabilized by the presence of the H_3O^+ guest, while the M_8C_{12} Met-Cars arrange into cages due to the strong metal-carbon and carbon-carbon bonding. Studying these unique cluster materials further reveals the unusual nature of systems of finite size, providing new information on their formation, properties and structures.

389. "The Production of Metallocarbohedrenes by the Direct Laser Vaporization of the Carbides of Titanium and Zirconium," S. F. Cartier, B. D. May, B. J. Toleno, J. Purnell, S. Wei, and A. W. Castleman, Jr., *Chem. Phys. Lett.*, submitted.

Metallocarbohedrenes (Met-Cars) of titanium and zirconium have been produced by the direct laser vaporization of their respective pure carbides. Time-of-flight mass spectra of both ionic and neutral metallocarbohedrenes formed in the laser induced plasma are presented and compared to spectra of the same systems generated under laser vaporization/molecular beam conditions. Potential mechanisms of formation of these clusters are presented and discussed.

390. " $\text{Ti}_x\text{Zr}_y\text{C}_{12}$ and $\text{Ti}_x\text{Hf}_y\text{C}_{12}$ ($x+y=8$): Mixed Metal Metallocarbohedrenes," S. F. Cartier, B. D. May, and A. W. Castleman, Jr., *J. Chem. Phys.* submitted.

Abstract: We report the production of binary metal metallocarbohedrenes. Direct laser vaporization of mixtures of zirconium or hafnium powders with titanium carbide yield the species $\text{Ti}_x\text{Zr}_y\text{C}_{12}$ and $\text{Ti}_x\text{Hf}_y\text{C}_{12}$ ($x+y=8$). These results are discussed in the context of recent theoretical models addressing the stabilities and structures of the metallocarbohedrenes, their formation mechanism and possible implications for the synthesis of "doped" metallocarbohedrenes.

I have delivered 14 lectures reporting work from this grant: "Clusters: Getting the Magic Out of Magic Numbers," invited colloquium, Physics Department, The Pennsylvania State University, January 28, 1993; "Getting the Magic Out of Magic Numbers", invited colloquium, Department of Physics, Carnegie-Mellon University, Pittsburgh, PA, February 4, 1993; "Clusters: The Interplay of Geometric and Electronic Structure," invited seminar, Chemistry Department, University of Pittsburgh, Johnstown, February 9, 1993; "Met-Cars: A New Class of Molecular Clusters," Chemistry Department, University of Delaware, , MD, February 18, 1993; "Clusters: Getting the Magic Out of Magic Numbers," invited colloquium, Department of Physics, University of New Hampshire, Durham, NH, March 22, 1993; "The World of Clusters: Solids, Liquids and Cages," invited speaker for 28th McGregory Lecture Series, Colgate University, Hamilton, NY, April 12, 1993; "Clusters: Their

Dynamics of Ionization and Dissociation," invited seminar, Department of Chemistry, Colgate University, Hamilton, NY, April 12, 1993; "Clusters: Getting the Magic out of Magic Numbers," invited colloquium, Department of Chemistry, Northwestern University, April 23, 1993; "TiO₂ Chemistry and Preparticle Formation Mechanisms," invited talk, DuPont Chemicals, Wilmington, Delaware, May 4, 1993; "Clusters: Getting the Magic Out of Magic Numbers, invited seminar, Department of Chemistry, Lehigh University, Bethlehem, PA, May 5, 1993; "Clusters: Getting the Magic Out of Magic Numbers," invited seminar, Department of Physical Chemistry and The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Israel, May 13, 1993; "Met-Cars: A New Class of Molecular Clusters," invited seminar, Oak Ridge National Laboratory, Oak Ridge, TN, August 19, 1993; "Clusters: I. A World of Magic Numbers and Cages; II. The Interplay of Structure and Dynamics; III. Effects of 'Solvation' on Reactivity," special invited lecture series, The University of Western Ontario, Ontario, Canada, October 4-8, 1993; "Met-Cars: A New Class of Molecular Clusters," invited seminar, Auburn University, AL, November 4, 1993.

Also, during the year my students and I have made 6 other presentations at scientific conferences which report work sponsored by this grant: "Shedding Light on Magic Numbers and Reaction Dynamics of Cluster Ions," Gordon Research Conference on Structures, Energetics, and Reaction Dynamics of Gaseous Ions," Ventura, CA, March 4-5, 1993; "Reactions of Met-Cars," American Chemical Society Meeting, Denver, CO, March 28-30, 1993; "Probing the Structure and Dynamics of Cage-Like Clusters: From Water to Met-Cars," 2nd International Conference on Atomic and Nuclear Clusters '93, Santorini, Greece, June 28-July 2, 1993; "Met-Cars: Production, Properties and Reactions,," (presented by Dr. B. C. Guo) Gordon Conference on Metals and Semiconductor Clusters, Wolfboro, NH, August 9-13, 1993; "The Formation and Structure of Clusters of Transition Metal Compounds," Second Workshop for the Center for Nanoscale Systems Materials, University of Maryland, College Park, MD, October 15-17, 1993; "Gas Phase Antimony/Magnesium and Antimony/Magnesium/Oxygen Clusters," (delivered by H.-T. Deng) Fifteenth Annual East Coast ICR and Ion Molecule Chemistry Symposium, Newark, DE, October 23, 1993.

In addition to the work which is referred to in the abstracts above, we have of course conducted a number of other investigations dealing with clustering and reactions of nickel and nickel oxide clusters

and vanadium/nickel alloys and oxide clusters with NO, NO₂, and CO, and also co-interactions with H₂. Other work has been undertaken on reactions of titanium and titanium oxides with water and nitrogen oxides, and we have pursued the reactions of Met-Cars and substituted Met-Cars with a variety of small molecules involving nitrogen oxides and small hydrocarbons. The details of these findings will be presented in forthcoming publications which will be sent to you as they become available.

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