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Cluster-assembled metallic glasses

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Abstract

A bottom-up approach to nanofabricate metallic glasses from metal clusters as building blocks is presented. Considering metallic glasses as a subclass of cluster-assembled materials, the relation between the two lively fields of metal clusters and metallic glasses is pointed out. Deposition of selected clusters or collections of them, generated by state-of-the-art cluster beam sources, could lead to the production of a well-defined amorphous material. In contrast to rapidly quenched glasses where only the composition of the glass can be controlled, in cluster-assembled glasses, one can precisely control the structural building blocks. Comparing properties of glasses with similar compositions but differing in building blocks and therefore different in structure will facilitate the study of structure–property correlation in metallic glasses. This bottom-up method provides a novel alternative path to the synthesis of glassy alloys and will contribute to improving fundamental understanding in the field of metallic glasses. It may even permit the production of glassy materials for alloys that cannot be quenched rapidly enough to circumvent crystallization. Additionally, gaining deeper insight into the parameters governing the structure–property relation in metallic glasses can have a great impact on understanding and design of other cluster-assembled materials.

Keywords: Bottom-up approach; Metallic glasses; Metal clusters

Background

Metal clusters have been the subject of intensive investigations in the last three decades not only because they exhibit fascinating properties that largely differ from their atomic and bulk counterparts but also their size dependence and structure dependence provide unthinkable possibilities. Addition of a single atom may cause property alteration of appreciable magnitude [1-5]. Although metal clusters possess unique properties, the majority of their properties are not harvested mainly due to their high sensitivity to the surrounding environment. Metal clusters are usually produced and investigated under ultra-high vacuum conditions, which are hardly applicable outside modern research laboratories. Many innovative scientists have spelled out the desire to fabricate a new class of materials that are built from atomic clusters instead of individual atoms, in order to benefit from the unique properties of such clusters. In this respect, some examples are already realized [6-8] as so-called cluster-assembled materials (CAM).

Metallic glasses (MG) have also been studied extensively since the first amorphous metallic alloy was introduced more than half a century ago. By cooling with a high rate, Klement et al. observed the formation of glassy structure in a binary alloy $\text{Au}_{75}\text{Si}_{25}$ [9]. They also reported the instability of this material at room temperature. After discovery of bulk metallic glasses and hence the possibility to create amorphous structures with moderate cooling rates, various multicomponent alloys were found with high glass-forming ability. Many of these alloys are usable under normal conditions, and several industrial applications are currently realized [10-14]. Despite the intensive research in the field of MGs, the fundamental question about the correlation between their structure and their unique properties is yet to be answered. The major challenge to this end is rooted in the lack of a descriptive model for the structure of MGs. So far, their structures are merely considered as a collection of atoms without long-range order in contrast to crystalline materials. This definition fails to distinguish among various amorphous materials and leaves the separation to the composition of alloys.

Cluster-based models such as efficient cluster packing, cluster-plus-glass atom, and cluster resonance have already

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been suggested to describe the arrangement of atoms in metallic glasses. Many research groups have demonstrated the appropriateness of these models through theoretical simulations in combination with experimental structure analysis [15-39]. In this context, metallic glasses are considered as a subcategory of CAMs.

Here, nanofabrication of metallic glasses through the bottom-up approach incorporating size-controlled metallic clusters is proposed.

Presentation of the hypothesis

Metal clusters of various compositions and sizes can be produced by a state-of-the-art cluster beam source. Recent advances in the field of cluster science enable us to overcome the quantity gap and create a well-defined cluster films of several monolayer thickness with atomic precision within few hours. Interestingly, altering the set of the mass-selected clusters while keeping the overall composition the same would lead to the formation of a potentially different material. For example, a $\text{Cu}_{0.5}\text{Zr}_{0.5}$ film can be fabricated by deposition of CuZr dimers, Cu_2Zr_2 tetramers, or equal numbers of Cu_6Zr_7 and Cu_7Zr_6 clusters just to name some of the numerous possibilities. All these films have the same composition and, however, different structures. A schematic view of the sample preparation approach is depicted in Figure 1. The structure and local atomic structure of the film can be explored by surface X-ray diffraction and extended X-ray absorption fine structure experiments, respectively. Electron microscopy may also be employed for similar studies. Valuable insight could be gained by comparing the properties of the cluster films with known building blocks to metallic glasses with similar composition, which are created via conventional methods such as rapid quenching, melt spinning, and ball milling. The first aim at this stage would be to explore the experimental conditions under which the structural properties of the cluster film are closest to the corresponding metallic glass. This would allow correlating the properties of the MG to its structure due to the available knowledge of its building blocks.

Testing of the hypothesis

The first experiment of the kind should be performed on CuZr system based on the following reasoning. This system has been the subject of many experimental and theoretical studies in the past. Consequently, much is known about this binary system. Since only two metals are involved, generation of suitable binary clusters and their mass selection is easier compared to other multi-component systems. In addition, CuZr alloys are known to be good glass formers over a range of compositions with glass transition temperature well above the room temperature [40-42]. The fact that both elements appear

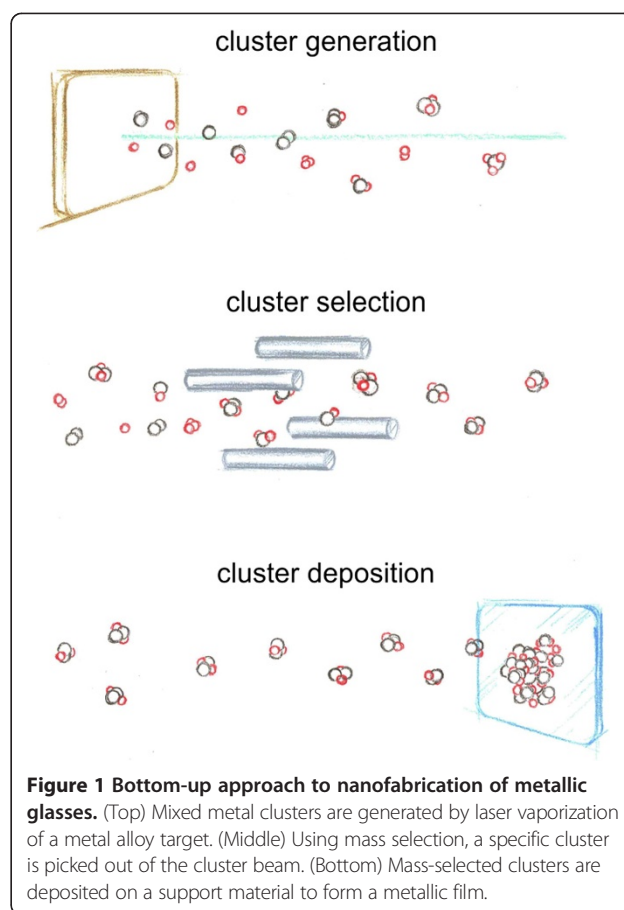
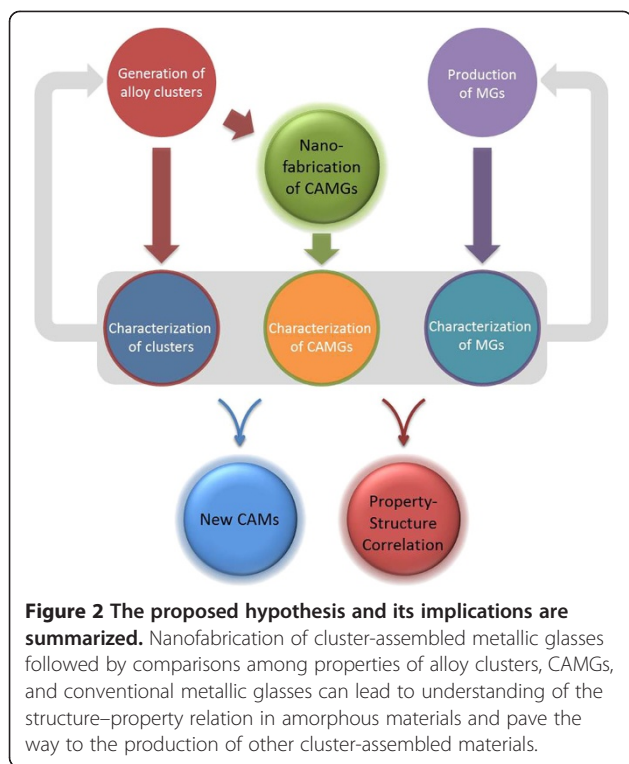


Figure 1 Bottom-up approach to nanofabrication of metallic glasses. (Top) Mixed metal clusters are generated by laser vaporization of a metal alloy target. (Middle) Using mass selection, a specific cluster is picked out of the cluster beam. (Bottom) Mass-selected clusters are deposited on a support material to form a metallic film.

in more than one stable isotope, however, counts as a drawback. This makes the mass selection and cluster isolation more challenging.

Binary metal clusters can be generated using alloy targets. Ion beam techniques employed in the production of the metal clusters facilitate the use of high-resolution size selection filters. On the basis of the recorded mass spectra, the most intense mixed cluster should be isolated and deposited on a support material, which is kept at a temperature low enough to avoid crystallization of the film during deposition. It is expected that clusters with 13 atoms (Cu_mZr_n , $n + m = 13$) form icosahedra and thus benefit from enhanced structural stability. The composition of the most abundant mixed cluster may vary for different cluster sources and with source conditions. Particular care should be taken to avoid oxidation of metal clusters prior and during deposition. To assure the latter, cluster deposition should be performed under ultra-high vacuum conditions. Finally, the sample should be handled under controlled environment (e.g., inert gas) and below room temperature (to avoid postdeposition oxidation and crystallization) throughout the analysis process. The properties of the specific metal cluster or clusters (if a combination of them is used to produce the cluster film)



can be investigated to gain knowledge on the structural building blocks. The optical, electronic, geometric, magnetic, and binding energies of metal clusters can be determined both theoretically and experimentally by state-of-the-art scientific instruments. In parallel experiments, a film of conventional metallic glass prepared through rapid quenching processes but with an identical composition as cluster film should be analyzed for comparison purposes. A constructive feedback loop between these two types of metallic glasses synthesized through bottom-up approach and conventional methods is of great importance to unravel fundamental uncertainties associated with structure-dependent properties of metallic glasses.

Implication of the hypothesis

Figure 2 presents a graphical summary of the proposed idea and its implications. Performing such a delicate experiment, i.e., nanofabricating well-defined metallic glasses comprising size-selected metal clusters as building blocks, would shed new light on the atomic structure of metallic glasses. By combining the information achieved from the experiments proposed above, it would be possible to make a link between the structure of the cluster-assembled metallic glass (CAMG) and its properties. This has been a long-standing challenge to material scientists. Lack of this knowledge has restricted the design of new metallic glasses with specific properties to the costly and inefficient method of trial and error. The properties of the MG can also be related to those of the building blocks (metal

clusters). The latter contains valuable information on CAMs, including but not limited to the stability of single clusters once in contact with other clusters and the interaction among clusters. This knowledge, on the other hand, can be very useful in designing new cluster-assembled materials.

Abbreviations

CAM: Cluster-assembled materials; CAMG: Cluster-assembled metallic glass; MG: Metallic glasses.

Competing interests

The author declares that he has no competing interests.

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References

1. Sanchez A, Abbet S, Heiz U, Schneider WD, Hakkinen H, Barnett RN, Landman U: **When gold is not noble: nanoscale gold catalysts.** *J Phys Chem A* 1999, **103**:9573–9578.
2. Heiz U, Landman U: *Nanocatalysis*. 1st edition. Heidelberg: Springer; 2007.
3. Deheer WA: **The physics of simple metal-clusters - experimental aspects and simple-models.** *Rev Mod Phys* 1993, **65**:611–676.
4. Schmidt M, Kusche R, von Issendorff B, Haberland H: **Irregular variations in the melting point of size-selected atomic clusters.** *Nature* 1998, **393**:238–240.
5. Harding D, Ford MS, Walsh TR, Mackenzie SR: **Dramatic size effects and evidence of structural isomers in the reactions of rhodium clusters, Rh-n (+/-), with nitrous oxide.** *Phys Chem Chem Phys* 2007, **9**:2130–2136.
6. Perez A, Melinon P, Dupuis V, Jensen P, Prevel B, Tuillon J, Bardotti L, Martet C, Treilleux M, Broyer M, Pellarin M, Vaille JL, Palpant B, Lerme J: **Cluster assembled materials: a novel class of nanostructured solids with original structures and properties.** *J Phys D: Appl Phys* 1997, **30**:709–721.
7. Claridge SA, Castleman AW, Khanna SN, Murray CB, Sen A, Weiss PS: **Cluster-assembled materials.** *ACS Nano* 2009, **3**:244–255.
8. Yong Y, Song B, He P: **Cluster-assembled materials based on M12N12 (M = Al, Ga) fullerene-like clusters.** *Phys Chem Chem Phys* 2011, **13**:16182–16189.
9. Klement W, Willens RH, Duwez P: **Non-crystalline structure in solidified gold-silicon alloys.** *Nature* 1960, **187**:869–870.
10. Axinte E: **Metallic glasses from "alchemy" to pure science: present and future of design, processing and applications of glassy metals.** *Mater Des* 2012, **35**:518–556.
11. Huang JC, Chu JP, Jang JSC: **Recent progress in metallic glasses in Taiwan.** *Intermetallics* 2009, **17**:973–987.
12. Inoue A, Takeuchi A: **Recent development and application products of bulk glassy alloys.** *Acta Mater* 2011, **59**:2243–2267.
13. Kumar G, Desai A, Schroers J: **Bulk metallic glass: the smaller the better.** *Adv Mater* 2011, **23**:461–476.
14. Salimon AI, Ashby MF, Brechet Y, Greer AL: **Bulk metallic glasses: what are they good for?** *Mater Sci Eng A-Struct Mater Prop Microstruct Process* 2004, **375**:385–388.
15. Almyras GA, Lekka CE, Mattern N, Evangelakis GA: **On the microstructure of the Cu(65)Zr(35) and Cu(35)Zr(65) metallic glasses.** *Scr Mater* 2010, **62**:33–36.
16. Almyras GA, Papageorgiou DG, Lekka CE, Mattern N, Eckert J, Evangelakis GA: **Atomic cluster arrangements in reverse Monte Carlo and molecular dynamics structural models of binary Cu-Zr metallic glasses.** *Intermetallics* 2011, **19**:657–661.
17. Antonowicz J, Pietnoczka A, Drobiazg T, Almyras GA, Papageorgiou DG, Evangelakis GA: **Icosahedral order in Cu-Zr amorphous alloys studied by means of X-ray absorption fine structure and molecular dynamics simulations.** *Philosophical Magazine* 2012, **92**:1865–1875.
18. Antonowicz J, Pietnoczka A, Zalewski W, Bacewicz R, Stoica M, Georgarakis K, Yavari AR: **Local atomic structure of Zr-Cu and Zr-Cu-Al amorphous alloys investigated by EXAFS method.** *J Alloys Compd* 2011, **509**:S34–S37.

19. Cheng YQ, Ma E, Sheng HW: **Atomic level structure in multicomponent bulk metallic glass.** *Phys Rev Lett* 2009, **102**:245501.
20. Delogu F: **Rotation of small clusters in sheared metallic glasses.** *Chemical Physics* 2011, **386**:101–104.
21. Fan C, Liaw PK, Liu CT: **Atomistic model of amorphous materials.** *Intermetallics* 2009, **17**:86–87.
22. Fan C, Liaw PK, Wilson TW, Dmowski W, Choo H, Liu CT, Richardson JW, Proffen T: **Structural model for bulk amorphous alloys.** *Appl Phys Lett* 2006, **89**:111905.
23. Georganakis K, Yavari AR, Louzguine-Luzgin DV, Antonowicz J, Stoica M, Li Y, Satta M, LeMoulec A, Vaughan G, Inoue A: **Atomic structure of Zr-Cu glassy alloys and detection of deviations from ideal solution behavior with Al addition by x-ray diffraction using synchrotron light in transmission.** *Appl Phys Lett* 2009, **94**:191912.
24. Hirata A, Guan P, Fujita T, Hirotsu Y, Inoue A, Yavari AR, Sakurai T, Chen M: **Direct observation of local atomic order in a metallic glass.** *Nat Mater* 2011, **10**:28–33.
25. Kaban I, Jovari P, Stoica M, Mattern N, Eckert J, Hoyer W, Beunee B: **On the atomic structure of Zr(60)Cu(20)Fe(20) metallic glass.** *J Phys Condens Matter* 2010, **22**:404208.
26. Kumar V, Fujita T, Konno K, Matsuura M, Chen MW, Inoue A, Kawazoe Y: **Atomic and electronic structure of Pd(40)Ni(40)P(20) bulk metallic glass from ab initio simulations.** *Physical Review B* 2011, **84**:134204.
27. Lagogianni AE, Almyras G, Lekka CE, Papageorgiou DG, Evangelakis GA: **Structural characteristics of Cu(x)Zr(100-x) metallic glasses by Molecular Dynamics Simulations.** *J Alloys Compd* 2009, **483**:658–661.
28. Ma D, Stoica AD, Wang XL, Lu ZP, Xu M, Kramer M: **Efficient local atomic packing in metallic glasses and its correlation with glass-forming ability.** *Physical Review B* 2009, **80**:014202.
29. Miracle DB: **A structural model for metallic glasses.** *Nat Mater* 2004, **3**:697–702.
30. Miracle DB: **The efficient cluster packing model - an atomic structural model for metallic glasses.** *Acta Mater* 2006, **54**:4317–4336.
31. Miracle DB, Egami T, Flores KM, Kelton KF: **Structural aspects of metallic glasses.** *Mrs Bulletin* 2007, **32**:629–634.
32. Miracle DB, Greer AL, Kelton KF: **Icosahedral and dense random cluster packing in metallic glass structures.** *J Non-Cryst Solids* 2008, **354**:4049–4055.
33. Miracle DB, Lord EA, Ranganathan S: **Candidate atomic cluster configurations in metallic glass structures.** *Mater Trans* 2006, **47**:1737–1742.
34. Sha ZD, Xu B, Shen L, Zhang AH, Feng YP, Li Y: **The basic polyhedral clusters, the optimum glass formers, and the composition-structure-property (glass-forming ability) correlation in Cu-Zr metallic glasses.** *J Appl Phys* 2010, **107**:063508.
35. Sheng HW, Cheng YQ, Lee PL, Shastri SD, Ma E: **Atomic packing in multicomponent aluminum-based metallic glasses.** *Acta Mater* 2008, **56**:6264–6272.
36. Wang XD, Jiang QK, Cao QP, Bednarcik J, Franz H, Jiang JZ: **Atomic structure and glass forming ability of Cu(46)Zr(46)Al(8) bulk metallic glass.** *J Appl Phys* 2008, **104**:093519.
37. Wang XD, Yin S, Cao QP, Jiang JZ, Franz H, Jin ZH: **Atomic structure of binary Cu(64.5)Zr(35.5) bulk metallic glass.** *Appl Phys Lett* 2008, **92**:011902–011902.
38. Xi XK, Li IL, Zhang B, Wang WH, Wu Y: **Correlation of atomic cluster symmetry and glass-forming ability of metallic glass.** *Phys Rev Lett* 2007, **99**:095501.
39. Yang L, Yin S, Wang XD, Cao QP, Jiang JZ, Saks K, Franz H: **Atomic structure in Zr70Ni30 metallic glass.** *J Appl Phys* 2007, **102**:083512.
40. Tang MB, Zhao DQ, Pan MX, Wang WH: **Binary Cu-Zr bulk metallic glasses.** *Chin Phys Lett* 2004, **21**:901–903.
41. Wang D, Li Y, Sun BB, Sui ML, Lu K, Ma E: **Bulk metallic glass formation in the binary Cu-Zr system.** *Appl Phys Lett* 2004, **84**:4029–4031.
42. Xu DH, Lohwongwatana B, Duan G, Johnson WL, Garland C: **Bulk metallic glass formation in binary Cu-rich alloy series - Cu100-xZrx (x=34, 36 38.2, 40 at.%) and mechanical properties of bulk Cu64Zr36 glass.** *Acta Mater* 2004, **52**:2621–2624.

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