Structures and Functional Properties of Amorphous Alloys

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Amorphous alloys have attracted great attention due to their distinctive properties derived from unique packing structures. Recently, significant advances have been achieved for the understanding of structural characteristics and functional applications of amorphous alloys. Herein, an overview of the state of art of structure studies, accounting for the characteristics of amorphous alloys, are presented, and recent progresses in the functional applications of amorphous alloys are highlighted. The various structural models for the short-range order, medium-range order, and long-range topological order for amorphous alloys are introduced. The functional applications in electrochemistry, mechanism, magnetism, optics, and biomedical engineering are presented in detail. The fundamental understanding of the correlations between structures and properties in amorphous alloys is discussed.

1. Introduction

Amorphous materials are ubiquitous in our daily life, such as glasses, lubricants, colloids, emulsions, and polymers. Amorphous materials feature the lack of the long-range order of the atomic or molecular arrangement and can be fabricated via rapid cooling where the liquid fails to crystallize. Their characteristics have attracted great attention in the research community, and four Nobel awards related to amorphous materials have been granted so far (N. F. Mott, P. W. Anderson, P. J. Flory, and C. K. Kao). As an important class of amorphous materials, amorphous alloys (metallic glasses) were first developed by Duwez.\(^1\) Metals tend to exit in the forms of crystals with metallic bonds. To enable the formation of metallic amorphous alloys, the nucleation and growth of crystalline phases are kinetically suppressed by rapid quenching with rates as high as \(\approx 10^6\) K s\(^{-1}\).\(^2\)–\(^3\) The fabricated amorphous metals or alloys exhibit superior mechanical, physical, and chemical properties, e.g., high strength, high elasticity, unique magnetic properties, and corrosion resistance, due to the noncrystalline structure and the lack of crystalline defects such as dislocations.\(^4\) Different from other glassy materials, amorphous alloys are formed by the simply random packing of metal atoms.\(^5\) Therefore, they can serve as the ideal model systems for studying some fundamental issues of glasses.

However, the comprehensive understanding and the realistic utilization of amorphous solids are still far from sufficient compared with the crystalline materials. This is mainly due to the disordered atomic structure, and the elusive electronic structures of amorphous materials, which are hard to be described by the classical energy band theory. On the other hand, studies show that the nonperiodic structure of amorphous alloys is not completely random but exhibits some explicit packing rules within the third-nearest neighbor.\(^6\)–\(^9\) Various structural models, such as the dense random packing model, solute-centered clusters model, quasiequivalent clusters model, fractal model, and flow units model, have been proposed to describe the local order and structural characteristics of amorphous alloys.\(^6\)–\(^11\) These models offer significant insights into the understanding of the formation mechanisms and functional properties of amorphous alloys.\(^12\)–\(^14\)

In addition to the atomic structure, the electronic structure also closely relates to the physical and chemical properties of amorphous metals. Some studies revealed the correlation between atomic bonding and deformation behaviors or glass forming ability (GFA) and demonstrated the necessity of considering the effects of the electronic structure.\(^15\)–\(^17\)

The disordered structural characteristics endow amorphous alloys many outstanding properties and application potentials.\(^4\) Therefore, numerous researches have been performed to find new compositions of amorphous alloys with good GFAs and elaborate the manufacturing methods to achieve extensive applications of amorphous alloys.\(^15\)–\(^17\),\(^4,18,19\) Inoue et al. discovered the noble-free multicomponent glass formers with very low critical cooling rates, which significantly reduce manufacturing
After these works, Zr-, Fe-, Ni-, Ti-, and Cu-based bulk amorphous alloys were also discovered. However, the bulk amorphous alloys lack tensile ductility at room temperature, and this is the intrinsic drawback of bulk amorphous alloys. This problem actually frustrated the researchers that time.

The new breakthrough in amorphous metals comes with the advances of low-dimensional materials. The amorphous metallic nanorods or films deform homogeneously due to the small-size effects suppressing catastrophic failure. The nice bending plasticity is demonstrated in the Zr-based alloy with size smaller than 1 mm. The amorphous alloy nanorods can exhibit large tensile plasticity similar to their crystalline counterparts. The Zr-based torsion bars allow for considerable improvements in actuation performance and low power consumption in micro-electromechanical systems. The amorphous CuZr alloy network can be used as transparent thermal patches, which shows high stability with temperature even under large tensile strain. Besides mechanical applications, nanoscale amorphous alloys are also promising candidates for applications in electrochemistry, magnetics, optics, and biomedical engineering. For example, the amorphous Ir nanosheets (NSs) with thickness less than 10 nm show outstanding electrocatalytic activity in acidic media. The Si-based alloy nanofibers (NFs) wrapped by reduced graphene oxide can be a stable anode with long-term cycle life. The Zr-, Mg-, and Ti-based amorphous alloys with good corrosion resistance and biocompatibility can be used as the coating layers of surgical equipment and implant stent. The amorphous alloys can also be used in microfuel cells and surface-enhanced Raman scattering (SERS) applications.

In this Review, we introduce the intrinsic structural characteristics and the recent functional applications of amorphous alloys. First, the various structural models are introduced to account for the characteristic structures of amorphous alloys. The effects of electronic structures are also introduced. Then, the realistic applications of amorphous alloys are presented in the order of electrochemistry, mechanics, magnetism, optics, and biomedical engineering, mainly involving films and nanostructures. The corresponding working principles are also represented in detail. Finally, we summarize the Review and give a short perspective.

2. Order in Disordered Materials

The internal atomic arrangements are markedly different for ideal crystal and amorphous materials. As shown in Figure 1a,
the structure of glasses exhibits no translational periodicity as opposed to crystals, and glasses are not randomly packed like gas either (see Figure 1a). Despite the absence of the long-range order, there is still obvious local order in amorphous solids. In our sketch of glasses, for example, each atom has three nearest neighbors at almost the same distance. The radial distribution function (RDF) can reveal the intrinsic differences for the three kinds of materials at the lower panel of Figure 1a. The RDFs of glasses provide crucial information on the local order within the distances of a few nearest neighbors.

2.1. Short-Range Order

Based on the analysis of RDF data, the dense random packing model (also called Bernal’s model) has been proposed. Bernal’s model describes the short-range order (SRO) regarding the nearest neighbors of monatomic metals or alloys with constituent atoms having comparable sizes. Five basic Bernal polyhedra are the basic building blocks in Bernal’s model for monatomic systems, as shown in Figure 1b. The tetrahedron accounts for the large proportion of Bernal polyhedral, and the fivefold rotational symmetry of the tetrahedron prohibits the long-range order in 3D space. Bernal’s canonical holes are thus formed and surrounded by various atomic clusters, which lead to a smaller density compared with the close-packed crystals. But this model takes all metal atoms as same rigid balls and thus fails to describe multicomponent glassy systems with different atomic sizes and pronounced chemical SRO. The solute-centered atomic clusters are then introduced as building blocks in multicomponent systems. Figure 1c shows various solute-centered atomic clusters with different coordination numbers (CNs). The solute atoms occupy these holes formed by the solvent atoms. For multicomponent systems, there are the second or third solute atoms that occupy the interstices between these clusters. Through examining the representative systems with different constituent atom sizes, Ma and coworkers demonstrated that the various polyhedra can be considered to be quasiequivalent due to the similar sizes and the minor variance in CNs for a given glass. But the average CN changes significantly with the atomic ratio between the solute and solvent atoms, R*, in binary systems (Figure 1d). Therefore, the dominant polyhedral changes with R* in binary systems. Many experimental and theoretical studies have confirmed that icosahedra are the energetically stable clusters in metal–metal-based amorphous alloys. The local order of the amorphous structure can be detected with various experimental techniques, such as X-ray and neutron diffraction, extended X-ray absorption fine structure, and nuclear magnetic resonance (NMR). The atomic structure of SRO clusters can also be determined with the coherent Angstrom beam electron diffraction technique. Although these unit clusters earlier well describe the local structure, SRO is still insufficient to completely distinguish the structural features of glasses.

2.2. Medium-Range Order

Beyond the SRO, the medium-range order (MRO) describes the connectivity and packing of these unit clusters in space. In Miracle’s model, solute-centered atomic clusters are idealized as spheres efficiently packing in fcc and hcp configurations to fill 3D space. Figure 2a shows a structure of cluster packing in a (100) plane where adjacent clusters interpenetrate each other. Miracle’s model accurately predicts the MRO for a wide range of amorphous alloys. However, the packing of the quasiequivalent clusters prefers fivefold symmetry, which is different from Miracle’s model. If the quasiequivalent clusters are regarded as hard spheres, packing is supposed to be of the icosahedral type, as shown in Figure 2b. The cavities between adjacent quasiequivalent clusters can be filled with additional solute species in multicomponent alloys. The spatial distribution of cavities is crucial for GFA, atomic diffusion, glass transition, and shear transformation in plastic flow. But these models are still insufficient to explain the excellent stability of amorphous metal–metalloid alloys.

The researches of nonequilibrium systems give some useful concepts and theories, e.g., fractal, chaos, and self-organized criticality, which can be used in the studies of amorphous alloys. For example, fractal theory is used to describe the packing of atomic clusters in a wide range of amorphous alloys. Wang and coworkers found the self-similar behavior of clusters in MRO, with the scaling relationship between the first peak position in momentum transfer q and atomic volume v. The underlying mechanisms and structural details are further identified with the percolation theory. The self-similarity of fractal disappears beyond the correlation length ξ, which resembles the characteristic length of Sierpinski gaskets in the left panel of Figure 2c. Molecular dynamics (MD) simulations confirmed the fractal network composed of local icosahedrons in Cu₄₆Zr₅₄ alloy, as shown in the right panel of Figure 2c.

It is also demonstrated that the amorphous metals are composed of the spatially and temporally “defect” regions and elastic matrix. The “defect” regions, also called flow units, exhibit loose atomic packing, low modulus and strength, small effective viscosity, high atomic mobility, and high potential energy state (Figure 2d). For bulk amorphous alloys, the average size of flow units is less than 10 nm³. Due to the instability of flow units, the atoms in flow units would dissipate energy during annealing or loading, leading to the transition of energy states of the sample. Figure 2e shows the 2D schematic of atomic motion in flow units during heating. Initially, only a few atoms in flow units are activated (pink balls). With the increase in temperature, most of the atoms in flow units are activated and β-relaxations occurs. The flow unit model implies that the mechanical properties of amorphous metals, e.g., plasticity, strength, and fracture toughness, can be improved by adjusting the activation processes of flow units.

2.3. Long-Range Topological Order

Topology is an important geometrical concept in geometry and deals with the invariant properties for objects undergoing continuous transformations. The circles, squares, and triangles are same in the topology space, as these polygons can transform to circles through continuous deformations. The SRO in amorphous materials can be easily distinguished from the crystal order due to the variation of atomic distances and the distortion of bond angles. But the SRO in amorphous materials is identical
to the crystal order from the view of topology. Some covalent amorphous solids, such as amorphous siliceous zeolite, are found to have topological order in the long range. Amorphous metallic structures, e.g., Ce$_{75}$Al$_{25}$, are also demonstrated to have the long-range topological order in MD simulations. The structures obtained with and without the fcc lattice constraint show disparity down to the atomic level. The hidden memory effect of the original fcc topology is still kept in the structure of Ce$_{75}$Al$_{25}$, as shown in the left half of Figure 3a. However, this topological order cannot be detected by the diagnostic probes of a high-resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) measurements. The XRD patterns exhibit the same peak positions, widths, and intensities for simulations and experiments (Figure 3b). Therefore, the hidden
topological order exists even in amorphous alloys without long-range translation symmetry.

3. Atomic Bonding Features

The properties of materials are related not only to the atomic structures but also to the electronic structures. For example, the metal Be with a densely packed hexagonal structure is brittle at room temperature, whereas metal Ti with the same atomic structure exhibits good ductility. The comprehensive understanding of the electronic structure is crucial for the functional applications of metallic materials. In addition, both theoretical and experimental results demonstrated the significant impact of atomic bonding on the properties of amorphous alloys, which require the fundamental understanding of electronic structures.[15–17,51,54]

Recently, the formation mechanism of amorphous alloys is revealed at the electronic level using NMR and ab initio MD simulations.[15] The isotropic Knight shifts ($K_{iso}$) and the spin–lattice relaxation times ($T_1$) of amorphous Zr$_{72}$–Co$_{28}$Al$_x$ ribbons are shown as a function of Al concentration in NMR spectra (Figure 4a). $K_{iso}$ initially decreases (region a) and then increases (region b) with Al concentration. When Al concentration is 16%, the GFA is best, and $K_{iso}$ reaches the maximum. The increase in $K_{iso}$ (region b) suggests a higher overlap between Al 3p and Co 3d states in the energy space and covalent-like bonding of Al.[55] $K_{iso}$ decreases when the Al concentration is over 16%, indicating the saturation of covalent-like bonding. At the same time, $T_1$ is only 19.8 ms for Zr$_{56}$Co$_{28}$Al$_{16}$, which is much smaller than that of amorphous ZrCuAl or ZrCuNiAlSn of ≈100 ms.[15,56] This demonstrates that the GFA of ZrCoAl amorphous alloys is closely related to the orbital hybridization effects. These effects are confirmed with the ab initio analysis (Figure 4b). The transition of covalent bonds can be represented by the Bader net charge analysis, as shown in Figure 4c. With the increase in the Bader net charge of Co, the Bader net charge of Zr decreases. However, the charge of Al initially increases and then decreases with Al concentration. The reason is the competition between the two processes, the donation of electrons from Al to Co and the acceptance of electrons from Zr to Al. Due to the directional bonds between Co–Al atomic pairs, the connective structure and the string-like atomic configurations are formed (Figure 4d). Short chains are dominant at the low Al concentration. With the increase in Al concentration, both the atomic number of the longest strings and the number of total strings increase, as shown in Figure 4e. The length maximum of strings reaches a maximum value at $x = 16$ for the atomic number of 4 and 6. This shows that the GFA results from the formation of chain-like structures with hybridized bonding. On the other hand, the orbital hybrid can lead to the decrease of Co–Al atomic distance. Figure 4f shows that the change of Co–Al bond length is consistent with the atomic number maximum of strings. These demonstrate that the properties of amorphous alloys can be evaluated and modulated with bonding characteristics.

To explore the correlation between atomic bonding and deformation properties, the work functions are calculated with the ratio of the bulk to shear modulus $K/G$ and fracture energy $G_c$ for a variety of amorphous alloys (Figure 4g).[16] The alloys in the magenta region with a low work function are more brittle and the alloys in the yellow region more ductile. In the Cu–Zr system, the calculations demonstrate that the substitutions of Cu by Al destroy Zr–Zr bond paths and promote the formation of Al–Zr bond paths (Figure 4h). The poisonings of Zr–Zr bond paths decrease the electrophilicity of the Cu–Zr lattice, and the newly formed Al–Zr bond paths reduce Poisson’s ratio and boost brittleness. The overall effect is that the new system after doping becomes more ductile. In addition, Yuan et al. found the isotropic Knight shift in $^{27}$Al NMR spectra for TM–Al alloys doped with Sn in the experiment.[15] The quantum mechanical calculations relate the isotropic shift to the directional bonding character caused by the orbital hybrid of Al 3p and TM d. Compared with the directional pd hybrid, the nondirectional s-like bonds show better mobility and absorb more energy during shear (Figure 4i). Therefore, the overlap of the s-like orbital is constant beyond the second-nearest neighbors during shear, whereas the overlap of the pd hybrid orbital dramatically drops within one atomic distance (Figure 4j). The compounds with an s-like electronic configuration exhibit a ductile property, whereas the pd hybrid orbitals promote brittleness. Besides the correlations with mechanical properties, the outer electrons are also related to the amorphous-to-amorphous transition in solvent metals upon pressure.[17] These results provide a new perspective for understanding the various properties of amorphous alloys from electronic structures.

4. Electrochemical Applications

Electrocatalysts play an important role in energy storage and conversion. It is known that noble metal-bearing catalysts can
dramatically reduce the electrolysis overpotentials and enhance the efficiencies of hydrogen and oxygen evolution reactions.\textsuperscript{[57–60]} Compared with crystalline materials, amorphous alloys have more active sites on the disordered surfaces and exhibit enhanced electrochemical performances as electrocatalysts in water splitting and as anode materials in Li-ion batteries.\textsuperscript{[29,30,61–64]} In addition, amorphous alloys have no grain boundaries and show superior corrosion resistance in acidic and alkaline electrolytes.

4.1. Catalysts

Noble metals such as Pt or Ir are the classical catalysts. Recently, the amorphous IrNiTa film with an ultralow Ir loading of 8.14 μg cm\(^{-2}\) is fabricated as a low-cost catalyst and exhibits a high intrinsic activity.\textsuperscript{[62]} The HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern of the as-deposited IrNiTa film demonstrate its amorphous nature (Figure 5a). Atomic force microscope (AFM) measurements show that the surface of the IrNiTa film is atomically flat (Figure 5b). The energy-dispersive X-ray (EDX) elemental mappings demonstrate the uniform distribution of Cu–Zr environment (left column) and the charge density distributions of the new system with a substitution of Al to Cu site (right column). Reproduced with permission.\textsuperscript{[16]} Copyright 2014, AIP Publishing. i) A sketch of the s-like and pd hybrid bonds during shear. j) The plot of the overlap of atomic orbitals with atomic shear displacement. Reproduced with permission.\textsuperscript{[15]} Copyright 2011, American Physical Society.
on molybdenum sulfides or transition metal phosphides. The excellent intrinsic activity of the IrNiTa film indicates that it is a promising catalyst for HER in acids. The outstanding catalytic performance of the IrNiTa film with a low loading of Ir can be attributed to the proper alloy system and the intrinsic amorphous structures. The disordered atomic structure provides plenty of unsaturated sites with high energy states which promote the catalytic activity of IrNiTa film.
Though noble metals or noble-bearing alloys are generally outstanding catalysts, the practical fabrications of crystalline alloys with desired nanostructures remain a big challenge. Recently, the amorphous noble monometal NSs have been fabricated by directly annealing metal acetylacetonates with alkali salt in air (Figure 5i).\(^{[29]}\) The amorphous feature is also verified by high-angle annular dark-field scanning transmission electron microscopy images with disordered atomic arrangements and diffractive halo-like patterns in SAED.\(^{[29]}\) In comparison with crystalline NSs, the RDF profiles of amorphous NSs are smoother, and the peak positions shift to larger values due to the loose packing of atoms (Figure 5j). The amorphous Ir NSs exhibit superior electrocatalytic activities under acidic media. As shown in Figure 5k, the mass activity is as high as 221.8 A g\(^{-1}\) at 1.53 V versus RHE, and the overpotential is only 255 mV at 10 mA cm\(^{-2}\) for amorphous Ir NSs. The Tafel plots of amorphous Ir NSs exhibit the smallest slope, indicating the improved kinetic behaviors of electrocatalysts (Figure 5l). The evolution process of the valance state of Ir during reactions is shown in in situ X-ray absorption fine structure measurements. The valance state of Ir remained lower than +4. The bond length Ir–C/O slightly increases from the open-circuit condition to 1.16 V and then decreases from 1.16 to 1.48 V. Moreover, the polarization curves of amorphous Ir NSs remain unchanged even after 5000 cycles, which is consistent with chronoamperometry measurements (Figure 5m). The durability tests demonstrate the excellent stability of amorphous Ir NSs. Many amorphous alloys systems, e.g., PdNiCuP, NiFe, NiFeP, and FeSiB alloys, also exhibit excellent electrocatalytic activities and superior stability.\(^{[62,64–68]}\) Based on the results of density functional theory calculations, the complex local chemical environments of atoms at the surface of amorphous alloys make the free energy distribution of active sites wider than that of crystalline materials.\(^{[64]}\) This leads to the abundant types of active sites in amorphous alloys and the superior catalytic performance. With the occurrence of dealloying during the period of catalysis, the local chemical environment and atomic coordination change. The decay of the electrochemical activity of amorphous alloys is much slow due to the abundant types of active sites, which leads to the self-stability of amorphous catalyst.

### 4.2. Anode Materials

The anode materials in lithium-ion, sodium-ion, and potassium-ion batteries can be categorized into three types: alloying type, intercalation type, and conversion type.\(^{[69]}\) Compared with intercalation and conversion type, alloying-type materials exhibit high capacity, a suitable working potential, and thus are expected to be excellent anode materials. The main challenges for alloy-based anodes are structural instability and the large volume expansion during cycles, which lead to inferior cycling capacities and the pulverization and aggregation of active materials.\(^{[70]}\) Jung et al. demonstrated that the amorphous alloy-based anodes have the potential to circumvent these drawbacks.\(^{[30]}\) The amorphous Si-based alloy NFs with reduced graphene oxide (rGO) were prepared via the complicated processes of electrospinning, annealing, and chemical reduction (Figure 6a). The rGO-wrapped amorphous Si-based alloy NFs show low capacity loss and a high initial Coulombic efficiency at 0.5 C (upper panel in Figure 6b). The capacity retention is almost 100% from the 5th cycle to 2000th cycle (570.13–569.77 mAh g\(^{-1}\)). The rGO-wrapped amorphous Si-based alloy NFs also show no decay of cycling capacities at different charge current densities (bottom panel in Figure 6b). The excellent stability in the long-term cycle and the nice rate capacity result from the characteristic amorphous structure of compositionally optimized NFs. The disorder structure leads to the homogeneous distribution of each element, which enhances the stability of the system during charge/discharge cycles. Other amorphous alloy-based materials, e.g., zinc oxysulfide, copper oxide, and tin oxide, also show improved long-term cycling stability with enhanced stable specific capacity.\(^{[71–73]}\)

Among metal-based anodes, Li metal electrodes can lead to the highest specific energy for rechargeable batteries. But its shortcomings, such as poor electrochemical reversibility and short cycle life, remain to be solved. Instead of seeking replaceable materials, Wang et al. found that the performance of Li metal electrodes can be greatly improved through changing the crystallinity of Li metal during the nucleation and growth process.\(^{[61]}\) To explore the kinetic progression of the nucleation of Li metal, the evolving nanostructure of Li metal deposits during the electrochemical process is revealed by cryogenic transmission electron microscopy (Cryo-TEM). Figure 6c–e shows the cryo-TEM images of Li metal deposits at various transient states. As the deposition time increases from 5 to 20 min, the characteristic bright diffraction spots of Li metal appear and become clearer in the corresponding fast Fourier transformed (FFT) patterns (Figure 6f–h). Note that the current density also leads to different distributions of crystalline cluster sizes.\(^{[61]}\) The disorder–order phase transition observed in Li metal suggest the multistep nature of crystallization through amorphous intermediates, which is inconsistent with the classical nucleation theory of the single-step process. Thus, the glassy Li anode enables multidimensional growth into large grains rather than dendrites during the electrochemical process. Different from dendrites, Li grains with a high density, lower porosity, and tortuosity can substantially minimize the volume expansion and maintain an effective electronic and ionic network. Therefore, the electrochemical reversibility of glassy Li is higher (Figure 4i). The favorable glassy Li metal can be made through controlling the packing density, energy transfer, and mass transfer during the nucleation process. The effective ways include reducing the current density, using the 3D substrate, appropriate electrolyte design, and interphase engineering. For high-energy rechargeable Li batteries, glassy Li metal is critical to solve the longstanding cyclability issue of Li metal. The earlier excellent performances of amorphous alloys show their promising potentials in applications of energy storage and conversion.

### 5. Mechanical Applications

Amorphous metal alloys exhibit high resistance to wear due to the amorphous nature compared with crystalline metal materials. At the same time, the thin amorphous alloys films show outstanding ductility, which endows them great potential in the applications of wearable electronics, microscanners, and the coating layer.\(^{[27,28,76–78]}\)
Figure 6. Glassy metal anode in Li-ion batteries. a) The amorphous Si-based alloy NFs were formed through annealing the Si-based alloy/polyvinylpyrrolidone (PVP) composite fibers at 700 °C in H₂/N₂ atmosphere (left in schematic). The rGO-wrapped Si-based alloy NFs with a positive charged surface were synthesized by chemical reduction processes (right in schematic). b) Charge/discharge cycling at a current density of 0.5 C (upper panel). Rate capability tests at different current densities (bottom panel). Reproduced with permission. [30] Copyright 2015, American Chemical Society. c–e) Cryo-TEM images and the f–h) corresponding FFT patterns of Li deposits at 0.5 mA cm⁻² for 5, 10, and 20 min. The bright diffraction spots from the (110) plane of Li metal are highlighted by the red arrows. i) Correlation between crystallinity of Li metal and performance. The performance of Li metal as a rechargeable Li battery anode is influenced by many factors, such as structural connection, electrochemical reversibility, and deposit density. j) Many strategies can alter the energy transfer and mass transfer barriers of Li during nucleation and growth, thus resulting in the varied crystallinity of Li metal. Reproduced with permission. [61] Copyright 2020, Nature Research.
5.1. Wearable Electronics

Stretchable electrodes are the critical modules in stretchable devices, and the key issue is the flexibility and stretchability of devices. The low-dimensional amorphous alloys have the potential to be utilized in stretchable electronics. Through electrospinning and cosputtering processes, amorphous CuZr nanotrough networks are prepared as a stretchable transparent electrode.\[28]\ The stretchable and transparent thermal patch was formed by embedding the CuZr network in PDMS (Figure 7a). The infrared images show that the temperature of the heater does not significantly change even when the heater is stretched up to 70%, as shown in Figure 7a. This patch exhibits the outstanding thermal stability under large tensile strain, demonstrating the promising potential of amorphous alloys in applications of wearable or automobile electronics. For instance, the CuZr network heater could be a portable skin patch when connected with the custom-made electronic band (Figure 7b). The thermal patch can keep the conformal contacts with the skin even when it is heated up to 50 °C and stretched up to 70%. The CuZr network heater remains stable due to the high glass transition temperature of 733 K.\[79]\ In addition, the CuZr network heater can also be used to defog the glass of automobiles or buildings. The CuZr flat films were demonstrated to exhibit enhanced thermal stability, excellent flexibility, and high reflectivity in other works.\[76,80,81]\ Recently, the CuZr amorphous alloy with well-controlled crumpled wrinkles is demonstrated to exhibit a strain limit of ≈100%, suggesting their promising potential in applications of smart skin and wearable devices.\[86]\  

5.2. Microscanners

Microscanners are the typical microelectromechanical system (MEMS) devices which have been widely used in robots, endoscopes, optical switches, and barcode scanners. The crystal Si-based microscanners are brittle and stiff due to the interior defects,\[82,83]\ which limit the scanning performance of microscanners. Compared with crystal silicon, amorphous alloys exhibit excellent mechanical properties such as low elastic modulus, high fracture toughness, and high strength, which make amorphous alloys suitable as movable elements in microscanners. Figure 7d shows the schematic illustration of the microscanner with the torsion bar made of amorphous ZrCuAlNi alloy and the micromirror coated with an amorphous alloy layer.\[27]\ The improved toughness of ZrCuAlNi torsion bars enhances the actuation performance and lowers power consumption. The practical application of ZrCuAlNi microscanner is optical coherence tomography (OCT) bioimaging, as shown in Figure 7e. The cuticle, epidermis, dermis, and sweat gland are clearly displayed in the OCT image. A large image with the size of 4 μm can be obtained by the ZrCuAlNi microscanner, and the size was around an order of magnitude larger than that acquired by the Si-based microscanner. Utilizing amorphous alloys in microscanners greatly helps the developments of low-powered MEMS devices.

5.3. Coating Films

Many efforts have been made to improve the wear and scratch hardness of materials in realistic applications, e.g., photovoltaic

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**Figure 7.** Stretchable, transparent electrodes, and microscanners. a) The schematic illustration of the fabrication of a stretchable transparent amorphous CuZr nanotrough heater and the infrared images for the heater with different strains. b) The applications of the CuZr heater in wearable and automobile electronics. c) The applications of CuZr heater as the defogger. Reproduced with permission.\[28]\ Copyright 2016, American Chemical Society. d) Schematic illustration of piezoelectric-driven microscanning mirror with the tension bar made of ZrCuNiAl amorphous alloy. e) Bioimaging of the fingertip obtained with the microscanner combined with a commercial OCT system. The tomographic image of the fingertip shows high lateral resolution. Reproduced with permission.\[27]\ Copyright 2015, Wiley-VCH.
modules, glass facades, screens, and lenses.\textsuperscript{[84,85]} Amorphous alloys exhibit superior wearing performances and can be nice coating materials. The amorphous alumina matrix doped by dispersing rigid globular polycarbosilane macromolecules is reported to be a facile and low-cost coating for different substrates.\textsuperscript{[77]} The TEM image and SAED patterns confirm the fully amorphous structure of the alumina nanocomposite (Figure 8a). In contrast to bare substrates, the wear volume of the coated sample only slightly increases with the applied load (Figure 8b). The wear resistance of coated samples is about 20–30 times larger than that of the uncoated substrate in the loading range from 1 to 3 N, as shown in Figure 8c. The durability of coating layer is well demonstrated in the cyclic loading tests in Figure 8d,e.

On the other hand, adequate amorphous metallic coating layers can enhance the strength of the microarchitecture structure. Figure 8f,g shows the scanning electron microscopy (SEM) images of the polymer microarchitectures coated with the amorphous NiB layer.\textsuperscript{[78]} The conformal coverage shows no observable defects at the junctions. The failure mechanism of microarchitectures is revealed by in situ experiments in Figure 8h–p. For 10 nm-thick NiB coating, the microarchitecture deforms homogeneously via global buckling and the coating film exhibits no cracks (Figure 8h,k,l). With the increase in coating thickness to 30 nm, ductile-to-brittle transition occurs, as shown in Figure 8i,m,n. With the increase in coating thickness to 100 nm, deformation exhibits a purely brittle behavior (Figure 8j,o,p). The amorphous coating improves the mechanical properties, damage tolerance, and wear resistance of materials and plays a significant role in realistic applications.

6. Magnetic Applications

Advanced electromagnetic devices exhibit the advantages of low energy cost, high efficiency, and miniaturization, and outstanding magnetic materials are badly needed in these devices. Compared with conventional magnetic materials, amorphous alloys exhibit nice magnetic softness and good ductility.\textsuperscript{[86,87]} Amorphous alloys usually exhibit a low saturated magnetization ($B_s$) due to the decrease of the 3d outer-shell electrons of ferromagnetic elements.\textsuperscript{[88]}

Electromagnetic interference (EMI) often occurs in the commercial and military electronic devices, which leads to electromagnetic pollution and deteriorates device performance. The
EMI shielding materials can efficiently mitigate EMI over a wide range of frequencies. Conductive polymer composites (CPCs) doped with soft magnetic constituents were demonstrated to show high EMI shielding effectiveness (SE), thermal stability, and nice flexibility. But CPC material also shows poor adhesion and severe delamination behaviors. The layer-structured amorphous alloy composites can be developed by electroless plating and exhibit good adhesion between layers. For instance, the amorphous NiCuP coating can be plated on commercial FeSiB metallic glasses, exhibiting excellent soft magnetic properties. Various composite materials (called FNMG) can be obtained via changing the plating times of NiCuP coating. Figure 9a shows the $M-H$ hysteresis loops of FeSiB and FNMG composites at room temperature. The saturation magnetizations of the layer-structured FNMG composites with NiCuP coatings are slightly lower than that of FeSiB due to the addition of nonmagnetic NiCuP coating. But the total EMI SE increases with the addition of NiCuP coating, as shown in Figure 9b.

The underlying mechanism is shown in Figure 9c. Some of the incident electromagnetic waves (EMWs) are directly reflected from the surface of NiCuP coating. The remaining waves are attenuated due to the electric loss in the NiCuP layer, the magnetic loss in the FeSiB layer, and the multiple internal reflections (green arrows) and absorption at the interface. After passing through several layers, EMWs can be completely eliminated. Figure 9d shows the EMI SE of different shielding materials. The FNMG composites exhibit both the nice EMI SE of $\approx 40$ dB rank and ultrathin thickness and are superior to other tradition metal-based shielding materials. Furthermore, the good corrosion resistance and outstanding mechanical properties enable the extensive utilization of amorphous alloys as the EMI shielding materials. In addition, Chen and coworkers reported that the ferromagnetic amorphous CoFeTaB alloy doped with nonmagnetic oxygen can be used as a magnetic semiconductor with a high Curie temperature of above 600 K. In addition, magnetism can also be used as an effective tool to probe the structure of the shear-band-affected zone in amorphous alloys. These works pave a new avenue to develop micro- and nanomagnetic devices with unique electromagnetic properties.

7. Optical Applications

Despite packing differences, amorphous alloys still exhibit some similar characteristics as metal crystals, such as the high reflection of visible light and surface plasmon resonance effect. Therefore, amorphous alloys can be exploited as color coating and SERS substrates.

7.1. Colored Films

Colorizing the surfaces of materials is widely demanded in various industrial applications. The conventional approaches, such as chemical treatment and laser irradiation, are expensive and
pollute the environment.\textsuperscript{100,101} The thin-film deposition method was developed as a flexible and environmentally friendly method to tune the color of substrates.\textsuperscript{102} For example, Al-based amorphous thin films were found to exhibit a high optical reflectivity over a wide range of wavelength.\textsuperscript{103,104} The color of stainless steel substrates can be tuned with the depositions of various amorphous ZrCuFeAlAg alloys films (Figure 10a).\textsuperscript{97} The nitrogen-free alloy films exhibit silver color, whereas the alloy films with nitrogen doping exhibit various colors with the film thickness. The nitrogen and zirconium atoms form transition-metal nitrides, and the number of free electrons in $d$ orbitals of zirconium decreases, which significantly affect the optical properties of thin films. The transmittances of alloy films can be measured with deposited structures on glass substrates. The transmittances of nitrogen-free and low-nitrogen-doped alloy films are low in the wavelength range of 550–800 nm (Figure 10b), whereas the transmittance increases greatly for the high-nitrogen-doped alloy films. The energy band gap ($E_g$) of thin films can be deduced from absorbance spectrum according to the bandgap theory. $E_g$ of thin films with different nitrogen contents is shown in Figure 10b. $E_g$ of nitrogen-free samples is very small ($\approx$0.8 eV), leading to the complete absorption of visible light. However, $E_g$ of nitrogen-doped samples is around 2.5 eV, leading to the partial transparency of films. Therefore, the nitrogen-free samples are opaque and the nitrogen-doped samples exhibit partial transparency. The schematic illustration of color changes in nitrogen-doped amorphous films is shown in Figure 10c. Visible light is mostly reflected on the surfaces of nitrogen-free or low-nitrogen-doped samples, resulting in the silver or gray color regardless of the film thickness. However, the high-nitrogen-doped samples are partially transparent. A part of visible light can penetrate into the films and then is reflected at the back film/substrate interface. The colors of these films are determined by the interference between

![Figure 10](image-url)
the reflected light from the film surface and the reflected light from the film–substrate interface. The interference effect would give different colors for films with different thicknesses. This low-cost, efficient, and ecofriendly coloring approach extends the functional applications of amorphous alloys.

### 7.2. Surface-Enhanced Raman Scattering Substrate

SERS could be used to detect the trace amounts of molecules in a variety of fields. Noble metal substrates with the uniformly distributed nanostructures are the conventional SERS substrates. For example, the uniformly arrayed amorphous PdNiP nanowire can be prepared by nanoimprinting techniques and shows a nice SERS effect. A lot of hotspots emerge on the noble metal substrates and amplify the Raman scattering signals of molecules on the surfaces. However, besides the high cost of noble metals, the nanofabrication of structured noble metal substrates is very complicated and often leads to environmental pollution. These drawbacks limit the wide applications of the SERS technique. Amorphous alloys show plenty of intrinsic nanostructures, and the fabrication of amorphous alloys is also cheap. The dispersion of a small amount of noble metal in amorphous alloys can be a good way to realize SERS effects.

The hierarchical amorphous alloys with noble Ag element can be fabricated on butterfly wing substrates. Figure 11a shows that the amorphous ZrCuAlAg alloy exhibits excellent SERS effect. The addition of only 5 at% Ag in the amorphous alloy gives rise to the SERS effect comparable with that of crystalline Ag, which demonstrates the great potential of amorphous alloys as the low-cost and efficient SERS substrates. In addition, the estimated efficiency of amorphous pure Ag is three times that of crystalline Ag, as shown in Figure 11b. The SERS effect is related to the intrinsic local structures of amorphous alloys. The atomic structure of amorphous metals is intrinsically inhomogeneous at the nanoscale including hard regions (the closely packed atomic clusters, e.g., icosahedrons) and soft regions (loosely packed sites or vacancies). The hotspots are generated among the adjacent atomic clusters, and the 3D finite-difference time-domain simulations demonstrate the electric field enhancement effects of these hotspots. When the R6G molecules are attached at the interfaces, Raman signals can be amplified by the strong local electric field (Figure 11c). These works pave the way to extend the optical applications of amorphous metals.

### 8. Biomedical Applications

The nice biomedical materials should exhibit good biocompatibility, manufacturability, and mechanical durability. Recently, Zr-, Ti-, and Au-based amorphous alloys have been successfully used as biomedical materials, such as neuroprobes, surgical tools, and load-bearing implants.

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Figure 11. Amorphous alloy nanostructures as SERS materials. a) Raman spectrum of 10^{-4} M R6G molecule absorbed on the amorphous ZrCuAlAg alloy and pure Ag films. b) Raman intensity at two peaks of 610 and 1650 cm^{-1} for the three substrates. c) The sketch view of the mechanism for SERS of amorphous alloys. Reproduced with permission. Copyright 2019, Springer GmbH.
8.1. Engineering Cellular Response

The outstanding nanoprocessability of amorphous alloys boosts the studies of engineering cellular functions at the nanolevel. The cellular morphology was measured by tracking the seeded cells on the flat and nanopatterned amorphous alloy substrates. The distinct changes in cellular morphology are shown in Figure 12a.\textsuperscript{[114]} With the increase of the nanorod size from 55 to 200 nm, fibroblasts became more circular and less elongated. For other kinds of cells, the responses were found to be different. The nanopatterns also influence the adsorption of serum protein and thus further change the focal adhesion density and Rho-A GTPase activation of fibroblasts. Therefore, the nanopatterned amorphous alloys can be used to modulate the morphologies and functions of cells.

8.2. Implantable Fiber Neuroprobes

Through using the thermal drawing technique, the long, well-ordered, and uniform amorphous alloys can be produced and the size range can span from around 40 nm to a few micrometers.\textsuperscript{[116]} The fabricated amorphous alloys exhibit the superior ability to be processed at a high viscosity and electrical conductivity in the order of $10^6$ Sm$^{-1}$, and thus the amorphous alloys can be incorporated in optoelectronic devices. For example, the optoelectronic fibers with amorphous alloys electrodes can be implanted into the pedunculopontine nucleus (PPN) of the mesencephalic locomotor region (MLR) in rats (Figure 12b), and the traces of neural recordings were detected by amorphous alloy electrodes (Figure 12c). The neural firing rates show significant differences between the resting and walking states for awake and freely moving rats. The similar phenomenon can also be observed for the firing rate at 4 weeks postimplantation (right panel of Figure 12c), demonstrating the recording potential of amorphous alloy electrodes. In addition, amorphous alloys possess high electrochemical stability and resistance to oxidation. These make amorphous alloys suitable to be used as electrode materials in fiber probes.

9. Summary and Perspective

We introduce the major structural models and the recent functional applications of amorphous alloys. These structural models relate well to the atomic arrangements and the structure characteristics of amorphous alloys, e.g., SRO and local heterogeneity, long-range disorder, and macroscopic homogeneity. The unique disordered structure endows amorphous alloys distinctive and outstanding properties, such as a high elastic limit, good wear, and corrosion resistance, which are not available in crystalline materials. The functional applications of amorphous alloys are presented in detail in this Review. The comprehensive
understanding of atomic arrangements in amorphous alloys remains a huge challenge. Although many progresses have been made to understand the structural characteristics of amorphous metals, a completely accurate model has not been proposed so far. Both significant experiments and comprehensive theories are needed to reveal the intricate nature of amorphous alloys. Meanwhile, the in-depth understanding into packing structures assists the modulation of the properties of amorphous metallic materials and promotes the practical applications of amorphous alloys.

Acknowledgements

This work was supported by National Key R&D Program of China (no. 2019YFA0308500), Beijing Natural Science Foundation (Z190010), The Strategic Priority Research Program of Chinese Academy of Sciences (grant no. XDB07030200), and National Natural Science Foundation of China (51421002, 51672307, 51991344).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

amorphous alloys, functional applications, structural characteristics

Received: July 28, 2020
Revised: October 9, 2020
Published online: November 16, 2020

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