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Amorphous—nanocrystalline alloys: fabrication, properties, and applications

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A B S T R A C T
Owing to their unique mechanical and functional properties, both amorphous and nanocrystalline alloys have attracted extensive research interest over the past decades. However, in spite of the tremendous efforts dedicated to both kinds of alloys, their engineering applications are still hindered today because some fundamental issues, such as low thermal stability and poor ductility, are yet to be solved. To overcome these issues, one recent strategy proposed is to combine both amorphous and nanocrystalline structures in a single alloy through the use of either an amorphous or a nanocrystalline alloy as a “template”. On the one hand, the derived amorphous—nanocrystalline alloys may inherit the unique properties from either the amorphous or the nanocrystalline “template”, such as outstanding magnetic properties, extraordinary wear/corrosion resistance, and superior hardness and strength. On the other hand, these amorphous—nanocrystalline alloys also exhibit enhanced thermal stability and ductility, which are difficult to achieve for either the amorphous or the nanocrystalline alloy template. In this review article, we would like to first discuss a number of experimental methods developed to fabricate amorphous—nanocrystalline alloys, including partial crystallization in amorphous precursors, grain boundary amorphization, and physical vapor deposition. After that, we will give an overview of the mechanical and functional properties of the amorphous—nanocrystalline alloys. Finally, we will have a discussion on the existing applications of the amorphous—nanocrystalline alloys in various areas such as renewable and green energy, catalysis, and surface protection.

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1. Introduction

An amorphous—nanocrystalline alloy is generally a dual-phase material made up of a metallic amorphous phase and nano-sized crystals. On the one hand, amorphous metals, which lack long-range translational symmetry and crystalline defects, possess large elastic strain limit, superb strength, excellent thermo-plastic formability, and good corrosion/wear resistance [1–4]. On the other hand, nanocrystalline metals, with their grain size falling into the nanometer range (<100 nm) [1], also exhibit a unique combination of enhanced mechanical, chemical, and physical properties such as high strength, superior catalytic properties, and abnormal thermal properties [2–4]. Since the advent of amorphous alloys over six decades ago [5], their development has been attracting tremendous research interest. In the first decade or so, the research on amorphous alloys was mainly focused on a few binary and ternary systems with a rather limited size [6–8]. With the development of new techniques [9,10] and theories [11–14], a large number of multicomponent systems, such as Zr–[15,16], Mg–[17], La–[18], Ti–[19], Fe–[20], Co–[21] and Ni-based [22] amorphous alloys, were developed in the 1990s, which had a good glass-forming ability (GFA) and could be cast into fully glassy rods with diameters ranging from several millimeters to centimeters.

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Compared to conventional alloys, amorphous alloys were once considered alternative structural alloys owing to their high strength and good fracture toughness [26]. However, their structural applications are much hindered even today because of their poor ductility [27]. Apart from their structural applications, amorphous alloys have various functional applications, such as electrochemical hydrogen generation [28], azo degradation for decorations, and other purposes [29].

Nanocrystalline alloys, as defined early by Gleiter [1] in 1989, are simply a metal with nano-sized grains. Since the first report of bulk nanocrystalline alloy by Birringer in 1984 [30], many methods have been developed and explored to make nanocrystalline alloys, including the ball milling method [31], full crystallization of amorphous alloys [32], ultrasonic shot peening method [33], surface mechanical attrition method [34] and electrodeposition and sputtering methods [35,36]. Compared to coarse-grained metals, nanocrystalline metals possess high strength and hardness but poor thermal stability at a high temperature [37,38] and brittleness at a low temperature [4,39].

To overcome the shortcomings and enhance the properties of nanocrystalline or amorphous alloys, one strategy proposed is to combine these two together to form amorphous–nanocrystalline alloys. Early in the 1970s, annealing-induced nanocrystallization was already observed in a number of amorphous alloys, such as Pd [40], Fe–P–C, and Fe–Si–B [40–43]. With the formation of these nanocrystals, the physical and chemical properties of the original amorphous precursors could be improved [44–46], such as the soft magnetic Fe-based amorphous–nanocrystalline alloys [47]. Aside from thermal annealing of amorphous alloys, amorphous–nanocrystalline alloys could also be obtained directly through electrodeposition and magnetic sputtering [48]. This provides a convenient route for the in-situ formation of amorphous–nanocrystalline alloys, which was already demonstrated in Al–Mo [49], Cu–Zr [50] and Mg–Cu–Y [51] obtained via magnetic sputtering or Al–Mn [52] and Ni–W [53] obtained via electrodeposition. Notably, these amorphous–nanocrystalline thin films could have many potential applications, such as for surface protection and in nano-devices [54].

Alternatively, amorphous–nanocrystalline alloys can be obtained by grain boundary (GB) amorphization in nanocrystalline alloys. In 2015, Khalajhedayati and Rupert [55] reported the formation of amorphous intergranular films in a Cu–Zr nanocrystalline alloy via thermal annealing, which was due to solute segregation in grain boundaries. As a result, the thermal stability of nanocrystalline alloys could be improved as well as their ductility and fracture toughness [56,57]. To facilitate our understanding, Fig. 1 illustrates the historic development of the techniques that were used for obtaining amorphous–nanocrystalline alloys. As seen in this figure, soon after the discovery of the first amorphous alloy by Klement et al. [5] in 1960, the first amorphous–nanocrystalline alloy was already obtained by Chen et al. [58] in 1969 through thermal annealing. After that, Ruan and Schuh [52] obtained an amorphous–nanocrystalline thin film through electrodeposition in 2009. Relatively speaking, it is a recent development to obtain amorphous–nanocrystalline alloys through GB amorphization. The first report might be due to the work of Khalajhedayati et al. in 2015 [55]. In this review article, our goal is to provide a comprehensive and up-to-date understanding of the development and properties of amorphous–nanocrystalline alloys obtained via various means, such as thermal annealing, GB segregation and amorphization, physical vapor deposition (PVD), and electrodeposition. In addition, we would like to also highlight a few important and interesting applications of amorphous–nanocrystalline alloys in recent years.

2. Fabrication methods

2.1. Controlled nanocrystallization in amorphous alloys

To form nanocrystalline amorphous alloys out of monolithic amorphous alloys, several approaches have been developed over the past decades, which include furnace or flash annealing (Joule heating [59] and micro-wave heating [60]), severe plastic deformation (high-pressure torsion [61], cold rolling [62], shot peening [63,64] and ball milling [65]), irradiation by electrons [66,67], ions [68] or pulsed laser [69] and ultrasound vibration [70]. Among these methods, annealing-induced crystallization is most attractive because of its easy control. In principle, crystallization is associated with the nucleation and growth of crystallites. Therefore, there are two basic mechanisms to form nanocrystalline amorphous alloys. As shown in Fig. 2a, the first type is associated with a good glass former, which affords relatively slow cooling. However, if it is cooled at a relatively fast cooling rate, say, 10⁵ K/s, crystallite nucleation can be bypassed, leaving a monolithic amorphous structure without quenched-in nuclei. In such a case, one can easily distinguish glass transition from crystallization on the typical DSC trace of the corresponding amorphous alloy and subsequent annealing can cause nanocrystallization [14,71,72]. In contrast, the second type is associated with a marginal glass former, in which the nucleation of crystallites can be hardly bypassed but their growth is really slow (Fig. 2b). Therefore, further growth of the quenched-in crystalline nuclei can be triggered in this type of amorphous alloy upon reheating. On the typical DSC trace of these amorphous alloys, the signal of glass transition is usually missing [73,74].

Many Zr-based amorphous alloys, such as Zr41.5Ti13.8Cu21.5Ni10Be2.5 (Vit1), are good or bulk glass formers, which can be used to make the first type of nanocrystalline amorphous alloy. In these glass-forming alloys, crystallization becomes difficult because of the presence of some local geometric short-range orders (SROs), such as icosahedral clusters, which is however not compatible with a space-filling topology and hence cannot directly lead to overall crystallization in most cases. According to Xing et al. [75] and Cang et al. [76,77], these icosahedral clusters can facilitate nanocrystallization by serving as the potential sites for heterogeneous nucleation of primary crystals. However, based on a thorough TEM study, Wang et al. [78] proposed that nanocrystalline can be also facilitated by the icosahedral clusters because of a “pinning” effect. As a crystallite grows outward from its nucleus, its growth is retarded once its boundary is pinned by the surrounding icosahedral clusters, as illustrated in Fig. 3. Once the density of the icosahedral clusters reaches 10²⁴–10²⁵ m⁻³ [79], a high density of nanocrystals can form in these bulk glass formers. According to Ref. [80], the volume fraction of the nanocrystals obtained by annealing a Zr-based amorphous alloy can be as high as 80% while the grain size is as small as 10 nm, as seen in Fig. 4a obtained from bright-field TEM. Aside from SRO-induced nanocrystallization, it was proposed [81,82] that phase separation of a type similar to spinodal decomposition could also induce the formation of high-density nanocrystals in bulk glass formers. However, it seems that the mechanistic understanding of the phase separation-induced nanocrystallization is not clear yet. To be specific, Wang et al. [83] reported the supportive evidence through the diffraction and small angle scattering on a Zr-based bulk metallic glass, whereas Kündig et al. [84] and Wang et al. [79] reported that no phase separation could be observed until the formation of icosahedral clusters through three-dimensional atom probe tomography (3DAPT).
exhibit excellent properties, such as high specific strength and good corrosion resistance. In these alloys, crystallization seems to be much easier because of the presence of quenched-in crystal nuclei [85], which in some cases manifests as a medium-range order (MRO) [86–89]. Wang et al. [85] and Bokeloh et al. [90] reported crystallization in some Al-based amorphous alloys at a temperature much lower than their crystallization temperatures, which was then attributed to the growth of the quenched-in nuclei. In the presence of a high density \(10^{22} - 10^{23} \text{ m}^{-3}\) of these pre-existing nuclei, their subsequent growth can be arrested because of the impingement of the diffusion fields that govern the crystal growth [91]. As an example, Fig. 4b obtained from dark-filed TEM shows an amorphous–nanocrystalline alloy with a high number density and small size (~16 nm) of nano-grains obtained from annealing an Al-based amorphous alloy [92].

Like Al-based amorphous alloys, some Fe-based amorphous alloys, especially useful as the precursor for the fabrication of nanocrystalline soft magnetic alloys, are also a marginal glass former that can be used to make amorphous–nanocrystalline alloys. In these Fe-based amorphous alloys, Cu-centered clusters are usually needed as the active catalytic sites for the formation of the primary bcc-Fe based nanocrystals. Hono et al. [93] first investigated the formation of nanocrystals in FINEMET (FeSiBNCu) alloy using 3DAPT. Their results showed that a high density \(10^{24} \text{ m}^{-3}\) of Cu-clusters were formed prior to crystallization, which later served as heterogeneous nucleation sites for the primary crystallization. Pradeep et al. [94] found the similar results, as illustrated in Fig. 5a. During stage III, the large atoms of Nb can be served as pinning sites to hinder the coarsening of bcc-Fe nanocrystals and stabilize the nanostructure. In a recent work [95], the authors found that the mechanism for stabilizing the nanostructure in the high Fe content alloys, which did contain large atoms, differed from that for the FINEMET alloys, because of the lack of hindrance from large atoms. The stabilization of nanostructure for these alloys stems from the soft-impingement effect between the shielding layers of the nanocrystals, as illustrated in Fig. 5b,c, which is similar to Al-based alloys [96].

### 2.2. Controlled amorphization in nanocrystalline alloys

Amorphous–nanocrystalline alloys can be also fabricated via partially transforming crystals into amorphous phases, which is known as solid-state amorphization and can be achieved through a variety of processes. These include high-energy irradiation [97], hydrogen absorption [98], annealing of diffusion couples [99], pressure-induced amorphization [100], mechanical alloying [101] and severe mechanical deformation [102]. These amorphization...
processes can be generally attributed to an increased free energy in the crystalline phase, which is higher than that of an amorphous phase \[103,104\]. The increase of the free energy can be caused by forming a nonequilibrium solid solution or by accumulating lattice defects \[105,106\]. It is interesting to note that solid-state amorphization is also possible at GBs, which results in the formation of intergranular amorphous layers \[107\]. Early in 1977, Clarke and Thomas \[108\] first observed intergranular amorphous phases in a hot-pressed ceramic. Since then, similar phenomena have been reported in several polycrystalline ceramics, such as Bi$_2$O$_3$-doped ZnO \[109\], CuO-doped TiO$_2$ \[110\] and CaO-doped Al$_2$O$_3$ \[111\]. In the 2000s, Luo et al. \[112–114\] demonstrated that intergranular amorphous films could be formed at the GBs of polycrystalline alloys, such as Ni-doped W and Ni-doped Mo. The formation of such intergranular amorphous films could be associated with GB “phase” transitions, which could result from premelting, prewetting, and multilayer adsorption \[115\]. Interestingly, experimental results showed that there is more than one type of intergranular films \[116\].

Fig. 3. Schematic drawing (left) and high-resolution TEM image (right) about the “pinning” effect of icosahedral clusters on crystallization. (Note that the TEM images are adapted from Ref. [78], reprinted with permission from Ref. [78], copyright (2011) by the American Physical Society).

Fig. 4. TEM images of Zr-based (bright-field) and Al-based (dark-field) amorphous–nanocrystalline materials: (a) Zr$_{52.5}$Al$_{10}$Ti$_5$Cu$_{17.9}$Ni$_{14.6}$ annealed under 783 K, reprinted from Ref. [80], copyright (2000) with the permission from Cambridge University Press; (b) Al$_{90}$Ni$_3$Gd$_7$ annealed under 523 K, reprinted from Ref. [92], copyright (2005) with permission from Elsevier.
In a much broader context, the concept of “complexion” was coined by Tang et al. [117] in 2006 to describe GBs with different characteristics, such as structural order and chemical composition. Later in 2007, Dillon et al. [116] discovered six distinct GB complexions in Al2O3-based ceramics (Fig. 6a). As illustrated in Fig. 6b, these GB complexions include (I) a single layer of dopants, (II) clean grain boundaries, (III) bilayers, (IV) multilayers (i.e., more than two layers), (V) intergranular film of nanoscale equilibrium thickness, and (VI) wetting films. Notably, a similar notion of “complexion” could be applied to metals [118–121]. In 2015, Khalajhedayati and Rupert [55] observed GB complexion in a nanocrystalline Cu–Zr alloy.

Since 2015, GB amorphization has been observed in a number of binary, ternary, and even multicomponent alloys, such as Ni–W [122], Cu–Zr–Hf [123] and Ni-containing high-entropy alloys (HEAs) [124]. The thickness of the intergranular amorphous films varies from 1 nm to several nanometers, as shown in Fig. 7. In these amorphous–nanocrystalline alloys, the formation of the intergranular amorphous films is mainly caused by annealing-induced solute segregation. Although GB solute segregation was first proposed by Weissmüller [125], it now becomes one of the promising routes to stabilize nanocrystalline alloys. At the fundamental level, the enhanced stability of nanocrystals could be attributed to either a reduced GB mobility due to solute drag (a kinetic mechanism) or a reduced GB energy (a thermodynamic mechanism) [37,126,127]. In 2016, Pan and Rupert [128] investigated segregation-induced GB phase transitions by using hybrid atomistic Monte Carlo/molecular dynamics simulations with Cu–Zr as the model system. They found that GBs could transition from ordered complexions (I–IV) to disordered complexions (V–VI) when the solute concentration at GBs reached a critical value. Furthermore, Schuler and Rupert [129] proposed a set of materials selection rules in 2017 to predict the formation of amorphous GB complexions. These were mainly based on two considerations, i.e., (1) encouraging the segregation of dopants to interfaces and (2) lowering the formation energy for a glassy structure. To validate their rules, a series of Cu-based binary alloys, including Cu–Zr, Cu–Hf, Cu–Nb, and Cu–Mo, were fabricated by sputtering deposition, which were subsequently heat-treated to allow for segregation and GB phase transformation. In theory, they found that the type of the GB complexion in the binary alloy can be controlled by an informed selection of the enthalpy of segregation (ΔHseg) and the enthalpy of mixing (ΔHmix). A positive ΔHseg coupled with a negative ΔHmix promotes the formation of nanoscale amorphous intergranular films, such as in Cu–Zr and Cu–Hf, whereas a positive ΔHseg coupled with a positive ΔHmix promotes ordered GB complexions, such as in Cu–Nb and Cu–Mo.

Aside from sputtering deposition and annealing, amorphous–nanocrystalline alloys could be also fabricated through other methods for solid-state amorphization, such as severe plastic deformation and irradiation. Early in 1993, Sundararaman [130] concluded that a nanocrystalline structure is desirable for solid-state amorphization reactions. In 2005, Ovid’ko and Sheinerman [131] developed a theoretical model to understand and predict irradiation-induced amorphization in nanocrystalline solids. They found that amorphization can be facilitated in nanocrystalline solids where the volume fraction of their interfacial phases became extremely large. However, because of the difficulty of sample fabrication, the experimental results are still limited, which warrants further research.

2.3. Controlled formation of nanostructured amorphous alloys through PVD

Apart from amorphization and crystallization from a solid precuror, PVD of thin films provides another route to synthesize nanostructured amorphous or amorphous–crystalline metals. As of today, a number of PVD methods are available and have been widely used for the fabrication of metallic thin films, including thermal evaporation [132,133], magnetron sputtering [134], pulsed laser deposition [135,136] and molecular beam epitaxy [137]. Among the above PVD methods, magnetron sputtering might be the most frequently used one because of its applicability to a wide range of chemical compositions. Compared to a liquid-to-solid
melting/casting routine, a typical sputtering process entails the condensation of gaseous particles into a solid state at a cooling rate as fast as \(-10^{12}\) K/s \([138]\). Aided by this, even marginal glass formers with immiscible element pairs can be synthesized into fully amorphous or crystalline–amorphous dual-phase structures via sputtering deposition \([49,50,139–143]\).

To synthesize nanostructured amorphous–crystalline metallic films, binary alloys \([49,50,139,140]\), HEAs \([141–144]\), and metallic glasses doped with nitride and nitrogen \([145]\) are promising candidate target materials. To control the chemical composition of a deposited thin film, magnetron co-sputtering \([49,139–142]\) and reactive sputtering \([143,145]\) were often utilized. Based on the prior works \([49,50,139–143,145–147]\), the atomic structure of the as-deposited films strongly depends on their chemical compositions and can be tuned systematically from a crystalline to amorphous structure or to form a mixture of the two \([49,50,140]\). Fig. 8a–c displays the atomic structures obtained from the Al–Mo \([49]\) binary system at different Mo contents. In this binary system, the initial increase in the atomic fraction of Mo (\(x_{\text{Mo}}\)) leads to the formation of local amorphous regions within an Al-rich crystalline matrix. As seen in Fig. 8d, a full amorphous alloy is obtained for \(x_{\text{Mo}} = 32\%\), whereas a full bcc crystalline alloy is obtained for \(x_{\text{Mo}} = 50\%\).

According to Inoue \([14]\), the GFA of a binary alloy can be gaged by the mixing enthalpy (\(\Delta H_{\text{mix}}\)) of the atomic pair. Usually, a good GFA corresponds to a very negative value of \(\Delta H_{\text{mix}}\) and vice versa.

**Fig. 6.** (a) High-angle annular dark-field scanning transmission electron micrographs of complexions I–III, and high-resolution transmission electron micrographs of complexions IV–VI; (b) schematic of corresponding six different GB complexions: (I) a single layer of dopants, (II) clean grain boundaries, (III) bilayers, (IV) multilayers (i.e., more than two layers), (V) intergranular film of nanoscale equilibrium thickness, and (VI) wetting films. Reprinted from Ref. [116] copyright (2007) with permission from Elsevier.
However, it can be noted that the emergence of an amorphous–
crystalline composite corresponds to a slightly negative $\Delta H_{\text{mix}}$ or
even positive $\Delta H_{\text{mix}}$. In other words, the dual-phase amorphous
crystalline structure is usually derived from a marginal glass
former. Notably, this was already exemplified by a series of binary
alloys, such as Zr–Ti ($\Delta H_{\text{mix}} = 0$ kJ/mol) [140] and Al–Mo
($\Delta H_{\text{mix}} = -5$ kJ/mol) [49]. The similar rule could be applied to
ternary systems. According to Kuan et al. [147], Mg-rich nano-
crystalline phases could be observed in the Zr–Cu–Mg amorphous
phase, which could be attributed to the positive mixing enthalpy of
Mg–Zr ($\Delta H_{\text{mix}} = +6$ kJ/mol) and the slightly negative mixing
enthalpy of Mg–Cu ($\Delta H_{\text{mix}} = -3$ kJ/mol). A similar composite
structure was also observed by Wu et al. [51] in the Mg–Cu–Y
ternary alloy. Aside from alloying, introducing nitrogen or nitride in
reactive sputtering can also facilitate the synthesis of dual-phase
amorphous–crystalline nanostructures. By increasing the concen-
tration of N$_2$ gas, it was observed that crystalline phases could
appear in the amorphous matrix in a few alloys, such as
N$_2$–TiCrAlZr [143], N$_2$–FeCoNiCrCuAlMn [144] N$_2$–ZrNiAlSi [145], and N$_2$–ZrCu [148]. According to Chang et al. [143], nitrides
can serve as the heterogeneous nucleation sites for crystallization
in reactive sputtering, therefore leading to a reduced GFA.

In contrast to marginal glass formers, which form dual-phase
amorphous–crystalline nanostructures in film deposition, good
glass formers tend to form full nanostructured amorphous films,
also termed as “nano-glass” [148–153]. Fig. 9 presents a typical
nanostructured amorphous film comprised of numerous amorph-
ous grains. In between these grains, an interface rich in free
volumes was usually conceived [154]. According to the prior works
[149,150], a high working pressure and a large sputtering power
promote an inhomogeneous distribution of atoms and hence the
formation of nano-glass, whereas a long sputtering duration causes
the coarsening of amorphous grains [152]. Interestingly, apart from
the chemical composition and GFA of a target, processing of the

Fig. 7. High-resolution transmission electron micrograph images of amorphous intergranular films in Cu–Zr samples annealed at 850 °C and 950 °C with thickness of (a) 2.6 nm, (b) 0.8 nm, (c) 4.1 nm, and (d) 2.9 nm. Reprinted from Ref. [55] copyright (2011) with permission from Springer.
target material can also affect the formation of nano-glass [149]. As reported by Chen et al. [151], powder-compressed targets can produce a more pronounced grainy amorphous structure than targets prepared by arc melting.

3. Properties

3.1. Mechanical properties

3.1.1. Hardness and strength

Early in the 1990s, several researchers already conducted mechanical characterization of Fe– [155], Al– [156–160] and Zr-based [72,161,162] dual-phase amorphous–crystalline alloys, which were fabricated either by liquid quenching or by annealing of amorphous precursors. Their results showed that most of these alloys exhibited enhanced hardness and elastic modulus with the increasing volume fraction of nanocrystals. The strength enhancement was then attributed to the hindering of shear banding with nanocrystals [155,159,163]. Similar trends were also observed in Zr– [164] and Ti-based [165] amorphous–quasi-crystalline alloys. Apart from mechanical strengthening, mechanical softening can also occur with the presence of nanocrystals. For example, Zhang et al. [166] reported that nanocrystallization in the Zr–Cu–Fe–Al bulk amorphous alloys caused the reduction in the alloy hardness. Bi et al. [167] also observed a softening behavior in an Al-based amorphous alloy after it was cold rolled and underwent

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**Fig. 8.** (a–c) High-resolution TEM micrograph with an accompanying fast Fourier transform (FFT) inset of Al–16 at.% Mo, Al–32 at.% Mo, and Al–50 at.% Mo microstructure, respectively. (b) XRD scans of the Al–Mo films as a function of Mo content. Reprinted from Ref. [49], copyright (2011) with permission from Elsevier.

**Fig. 9.** (a) Cauliflower surface morphologies of the Au46Ag6Pd2Cu27Si14Al5 alloy obtained by SEM, reprinted from Ref. [152], copyright (2011) with permission from Elsevier. (b–c) High-resolution TEM images of Au40Cu28Pd5Ag7Si20 alloy with FFT inset, the minor crystalline structures are pointed out by red arrows, reprinted from Ref. [150], copyright (2018) with permission from Elsevier.
polymorphic crystallization. These authors proposed that mechanical hardening, as found in the annealing-induced amorphous–nanocrystalline alloy, was due to solute enrichment in the residual amorphous matrix, whereas crystallization after cold-rolling led to softening because of the lack of solute partitioning.

In the literature, nanocrystalline alloys are known to be strong as a result of the Hall–Petch (HP) effect [168]. However, with further reduction in their grain size below a critical value, nanocrystalline alloys become softer and the so-called inverse HP effect comes into play [169], which could be attributed to the activation of GB mechanisms, such as GB sliding [170]. To mitigate this, GB doping was proposed to strengthen nanocrystalline alloys [171–175]. For example, Özeren et al. [172] observed that the strength of the nanocrystalline Cu alloys with Nb segregation to GBs was significantly enhanced. In addition, solute segregation could also result in the formation of nanometer thick intergranular amorphous layers [55,114,129,176]. Usually, high strength is retained in the amorphous–nanocrystalline alloys obtained via GB amorphization [176].

Dual-phase amorphous–nanocrystalline alloys can also be obtained directly from PVD or electrodeposition. In 2009, Ruan and Schuh [52] measured the hardness of the Al–Mn binary alloys with the Mn content ranging from 0 to 15.8 at%. Their results clearly showed the abrupt increase of the alloy hardness with the emergence of an amorphous phase from FCC solid solution. In 2013, Ganolka et al. [177] investigated the mechanical properties of Al–Mo alloys at different Mo contents through the tensile testing of freestanding thin films. Interestingly, their results demonstrated that incorporation of Mo into Al thin films led to substantial strengthening until the formation of a two-phase FCC/amorphous mixture. The compositional dependency of the strength of the Al–Mo thin film could be well captured by a model that combines solute strengthening with GB pinning, as seen in Fig. 10. It is also interesting to note that, with further increasing Mo content beyond 20 at%, the FCC crystals transformed to bcc, leading to a slight reduction in the tensile strength. This behavior indicated that the properties of reinforcing phase are also important to the strengthening effect of nanocrystals on the amorphous matrix. Interestingly, Zhang et al. [50] also observed GB doping in the deposited Cu–Zr film. As the Zr content increased from 0 to 8 at.% in the binary film, GB amorphization occurred, which however reduced the film strength.

3.1.2. Ductility

In 2000, Fan et al. [178] conducted a systematic study of the compressive plasticity in amorphous–nanocrystalline Zr_{60}Cu_{20}Pd_{10}Al_{10} alloys prepared by thermal annealing of the corresponding amorphous precursor. These authors found that the plastic strain to failure of the alloys initially increased with the increasing volume fraction of nanocrystals, which seemingly attained a maximum value at the volume fraction of the nanocrystals ~27%. After that, further increase in the volume fraction of nanocrystals caused the reduction in the plasticity of the alloys. A similar behavior was also observed in the Cu–Ni–Al [179] and Ti-based [165] amorphous–nanocrystalline alloys obtained by thermal annealing. Kim and Hong [180] attributed this embrittlement observed at a high concentration of nanocrystals to the solute enrichment at the amorphous–crystalline interface. According to these authors, when a certain element reached a critical value, such as the concentration of solute Ni and Y ~20 at.% in the Al–Ni–Y alloy, fracture can be easily initiated. Recently, Li et al. [181] observed the first ductile-brittle-ductile transitions in a Fe-based amorphous–nanocrystalline alloy as the volume fraction of the Fe-based nanocrystals increased from 0 to 90%. Their results indicated that the thickness of the amorphous interface played an important role in determining the compressive plasticity of the Fe-based amorphous–nanocrystalline alloy.

Apart from thermal annealing, amorphous–nanocrystalline alloys can also be obtained by solute segregation-induced GB amorphization in nanocrystalline alloys. According to Khalajedayati et al. [176], amorphous intergranular films at GBs act as dislocation sinks, which alleviate local stress concentration and improve plasticity. Compared to ordered interface or regular GBs in nanocrystalline alloys, which can easily fracture because of local stress concentration (Fig. 11a), the amorphous films can efficiently absorb dislocations (Fig. 11b), thereby suppressing crack nucleation and growth and improving the plasticity of the alloy, as seen in Fig. 11c,d [56,182]. Here, it may be worth mentioning that GB amorphization might deteriorate plasticity of nanocrystalline metallic films.

3.1.3. Fracture toughness

Some amorphous alloys could exhibit very high fracture toughness, such as those of Zr [183] and Pd [184]. However, Gilbert et al. [183] reported a great reduction of fracture toughness, from ~55 MPa√m to 1 MPa√m, after thermally induced partial or full crystallization in the Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} (Vit 1) bulk amorphous alloy. A similar phenomenon was observed in the LagsAl_{25. Cu_{10}Ni_{5}Co_{5}} bulk amorphous alloy, which underwent a significant reduction in its impact toughness by ~90% with the presence of a small atomic percentage of crystallinity [185]. Nagendra et al. [185] related the reduction of fracture toughness to the sharp rise of relaxation times of the corresponding metallic liquid, as shown in Fig. 12. These authors suggested that densification, solute redistribution, and loss of free volume upon annealing might be responsible for the fracture toughness reduction. Ketaew et al. [186] measured the fracture toughness of Zr_{44}Ti_{17}Cu_{19}Ni_{10}Be_{22.5} and Pd_{43}Cu_{29}Ni_{10}P_{20}, which contained a controlled volume fraction of nanocrystals after annealing. They found that the fracture toughness of the alloys decreased sharply by up to 50% when the volume fraction of the nanocrystals exceeded a critical value (~6%).

On the other hand, the fracture toughness of nanocrystalline alloys is generally low compared to that of their coarse-grained counterparts [187]. In 2001, Mirshams et al. [188] studied the fracture toughness of nanocrystalline Ni thin sheets. Their results showed that both thermal annealing and grain-boundary doping deteriorated the crack growth resistance of the nanocrystalline Ni. Fig. 10. Comparison of measured tensile strength of Al_{1-x}Mo thin films with strengthening theories. Models shown include solid solution strengthening (blue curve), nanocrystalline pinning strengthening (green curve), and a combination of both (black curve). Reprinted from Ref. [177], copyright (2013) with permission from Elsevier.
However, according to the molecular dynamics simulations of Pan and Rupert [56], once amorphous intergranular films formed at GBs, the fracture toughness of the nanocrystalline alloy might be improved as dislocations were absorbed at the amorphous-crystalline interface, leading to the retardation of crack nucleation and growth.

### 3.2. Functional properties

#### 3.2.1. Soft magnetic properties

Fe-based amorphous—nanocrystalline alloys exhibit a unique combination of both high-effective permeability ($\mu_\text{e}$) and saturation magnetization ($B_s$), which outperforms the variety of soft magnetic alloys [189], as shown in Fig. 13. In principle, good magnetic softness comes from low magnetic anisotropy, which is closely related to the exchange interaction of structural units [190,191]. For Fe-based amorphous—nanocrystalline alloys, their grain size is much smaller than the exchange interaction length and, thereby, the effective magnetic anisotropy will be an average over several structural units and thus reduced greatly in magnitude [192]. Meanwhile, because the $B_s$ of $\alpha$-Fe phase is much higher than that of the amorphous phase, the precipitation of $\alpha$-Fe grains also gives rise to an increase in $B_s$ of the alloy [193]. As a result, the formation of nano-sized $\alpha$-Fe grains in the Fe-based amorphous alloys increases both $\mu_\text{e}$ and $B_s$, which helps achieving high $B_s$ and high $\mu_\text{e}$ or the long-term goal for soft magnetic materials. More importantly, Fe-based amorphous—nanocrystalline alloys display very low core loss ($W$), which is only $1/5-1/3$ of that of...
Fe–Si crystalline alloys or the so-called Si-steels, as seen in Fig. 14 [194,195]. Notably, the W of the Fe<sub>75</sub>Si<sub>13</sub>B<sub>12</sub> amorphous–nanocrystalline alloys is lower than that of the Fe<sub>70</sub>Si<sub>18</sub>B<sub>12</sub> amorphous alloys (Metglas®), the latter of which is well known to be “green materials” under high maximum magnetic induction (B<sub>max</sub>) [196]. In addition, Fe-based amorphous–nanocrystalline alloys possess low coercivity (H<sub>c</sub>) and near zero magnetostriction coefficient (\(\lambda_s\)) [197], which makes them a promising “green material” for being used as the core material in various electronic devices [198].

### 3.2.2. Hydrogen storage

Mg-based amorphous–nanocrystalline alloys are a good candidate material for solid-state hydrogen storage owing to their outstanding hydrogen storage capacity, low cost, and light weight [199,200]. These dual nano-phase alloys could be easily fabricated through mechanical alloying [201,202], rapid solidification [203,204] and thermal annealing of amorphous precursors [205]. In 2005, Au [202] reported the synthesis of Mg–Ni alloys with an amorphous–nanocrystalline structure by mechanical alloying. The author found that the Mg–Ni amorphous–nanocrystalline alloys exhibited fast hydriding–dehydriding kinetics and were superior to their amorphous counterparts in hydrogen storage capacity. To be specific, the Mg 50 wt%–Ni 50 wt% amorphous–nanocrystalline alloy absorbed 5.9% hydrogen within 5 min and desorbed 5.1 wt% hydrogen within 20 min at 200 °C. As illustrated in Fig. 15, this was attributed to the unique dual nano-phase structure where the Mg matrix provides a great number of diffusion channels and interstitial sites for hydrogen migration and reaction and the Ni cluster network plays a catalytic role during the hydriding and dehydriding reaction. On the other hand, the Mg-based amorphous–nanocrystalline alloys fabricated through direct rapid solidification or subsequent devitrification of amorphous precursors also displayed promising hydrogen storage properties. For example, Kalinichenka et al. [204] studied the hydrogen storage properties of as-spun Mg–Ni–Y alloys, which consisted of Mg(Ni,Y) nanocrystals embedded in an amorphous matrix. Their results showed that these alloys can reach gravimetric hydrogen densities of up to 5.3 wt%-H with hydrogenation and dehydrogenation rates of up to 1 wt%-H/min even at the temperature of 250 °C. In 2012, Lin et al. [205] fabricated an amorphous–nanocrystalline composite by crystallizing the Mg–Ce–Ni amorphous alloy in a hydrogenation process. The composite exhibited a reversible hydrogen storage capacity of 5.3 wt% with much faster kinetics and a lower MgH<sub>2</sub> desorption activation energy than the original amorphous alloy.

### 3.2.3. Catalysis

Amorphous–nanocrystalline alloys could exhibit good catalytic properties, which lead to multiple applications, such as environmental remediation [206], petrochemical reaction [207] and energy conversion [3,208–215]. For example, Deng et al. [207] showed that the Ni–P amorphous–nanocrystalline alloy had a high-efficient catalytic performance on the decomposition of ammonium perchlorate, which could be used as an oxidizer in energetic composites. Pd-based amorphous–nanocrystalline alloys [213,214] also displayed a superior ethanol and methanol oxidation ability and could be considered a remarkable catalyst in direct alcohol fuel cells. In 2009, Pisarek et al. [215] developed a series of Ni–Al–Co amorphous–nanocrystalline alloys as active and selective catalysts of isophorone hydrogenation. Moreover, amorphous–nanocrystalline alloys also showed promising electrocatalytic activities for hydrogen and oxygen evolution reactions in alkaline water solutions [3,208–212,216]. For the hydrogen evolution reaction (HER), Mihailov et al. [216] reported that the amorphous–nanocrystalline Zr–Ni alloy possessed a better catalytic ability than the pure amorphous alloy with the same chemical composition. Apart from bulk amorphous–nanocrystalline alloys, nanoporous amorphous–nanocrystalline alloys can be fabricated by dealing with the corresponding amorphous precursor. These nanoporous alloys displayed superior electrocatalytic activities, which could be attributed to a high surface area and enhanced number of active sites [209,213]. On the one hand, nanocrystalline structures have a large number of low coordination atoms or active sites along the grain boundaries [3]. On the other hand, because of the lack of long-range translational ordering, amorphous structures are also rich in low-coordination sites and “defects” on their surface, facilitating adsorption, diffusion, and activation of reactants therein [208,210,216].

### 3.2.4. Wear resistance

In 2000, Hauert and Patscheider [217] reported that the formation of 4–7 nm sized TiC nanoparticles in the amorphous matrix of Si<sub>13</sub>N<sub>4</sub> could greatly elevate the hardness of the ceramic coatings to as high as 50 GPa. Aside from the ceramic coatings, the wear resistance of amorphous–nanocrystalline alloys obtained by annealing amorphous precursors was also investigated [218,219]. For example, Gloriant [218] found that the hardness and wear resistance of a number of amorphous alloys, including ZrAlN<sub>3</sub>Cu, PdNiCuP, LaAlNiCoCu bulk amorphous alloys, and AlNiY amorphous alloy ribbons, were significantly enhanced after annealing-induced nanocrystallization. Similar results were also reported by Wang et al. [219] who studied the tribological properties of the ZrAlTi-CuNi bulk amorphous alloy.

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**Fig. 14.** Core loss (W) of Fe<sub>75</sub>Si<sub>13</sub>B<sub>12</sub> amorphous–nanocrystalline alloys as a function of maximum magnetic induction (B<sub>max</sub>) at 50 Hz. The data of Fe<sub>70</sub>Si<sub>18</sub>B<sub>12</sub> amorphous and Fe–Si crystalline alloys are also shown for comparison, reprinted from Ref. [194], copyright (2011) with permission from Elsevier.

**Fig. 15.** Illustration of the composite structure of Mg–Ni amorphous–nanocrystalline alloy, reprinted from Ref. [202], copyright (2005) with permission from Elsevier.
Amorphous–nanocrystalline coatings could also be fabricated by several other methods, such as wire arc spraying [220], high velocity oxy fuel spraying [221], supersonic plasma spraying [222], laser cladding [223] and electrophoretic deposition [224]. In 2009, Cheng et al. [220] obtained a Fe-based amorphous–nanocrystalline coating on a stainless steel substrate by wire arc spraying. They found that the relative wear resistance of the coating is about three times higher than that of 3Cr13 martensitic stainless steel coatings. Additionally, Hong et al. [224] found that Zr-based amorphous–nanocrystalline coatings had good friction-reducing and anti-wear properties. Compared to the pristine alloy substrate, the frictional coefficient of the coated alloy decreased about 60% and the wear resistance increased by 57%.

4. Applications

4.1. Soft magnetism

The production of Fe-based amorphous–nanocrystalline ribbons is a very short process, which is of one step and low energy consumption. Because Fe-based amorphous–nanocrystalline ribbons are characterized by high Bs, high ρs, low Hc, low W, and near zero λs, they could meet the long-term target of making strong, high efficiency, energy-saving, and quiet electronic devices [198]. In practice, Fe-based amorphous–nanocrystalline ribbons can be made into magnetic cores, such as sensors, magnetic amplifiers, high-frequency (HF) transformer and inductor cores, common mode (CM) choke cores, etc. [225–227] and used in various electronic devices in our daily life, as illustrated in Fig. 16.

Fig. 17 displays the various magnetic cores made of Fe-based amorphous–nanocrystalline soft magnetic ribbons. These HF transformer cores exhibit low core loss, high efficiency, high operation flux density, and high Curie temperature (Tc), which can reduce the transformer temperature and enable the excellent thermal stability, with the serving temperature down to −20 °C to 155 °C for a prolonged time [229]. By comparison, the high core loss in Si-steel transformers leads to a high temperature rise and results in a low conversion efficiency, which affects the electromagnetic compatibility of electronic circuits and the normal resonant working condition. For ferrite transformer cores, the main challenges are their bulk size, high temperature rise, poor resistance to unbalanced current, and large leakage at a high temperature because of their low Bs, low Tc, and low permeability below 100 kHz [230]. The current transformer includes measuring current transformer and protection current transformer. The measuring current transformer is mainly used with measuring instruments to gage the current, power, and electric energy on the line under a normal working condition. The protection current transformer is matched with relay devices, which will cut off the line in case of short-circuit or overcurrent, to protect valuable equipment in the line, such as generators and transformers. The Fe-based amorphous–nanocrystalline soft magnetic materials possess high magnetic permeability, high squareness ratio, and excellent high temperature stability, which can be applied to magnetic amplifiers to improve the output adjustment accuracy and achieve high work efficiency [231]. The power loss of copper windings for the CM chokes made of Fe-based amorphous–nanocrystalline ribbons is only 50–70% to that of ferrite, and the operation temperature is much higher than that of the ferrite chokes [232,233].

Fig. 18 illustrates the practical applications of the magnetic cores made of Fe-based amorphous–nanocrystalline soft magnetic ribbons. It was reported that the deployment of Fe-based amorphous transformers in electrical grid can save almost 70% of the potential energy loss. The no-load loss of the SH15 type amorphous distribution transformer is nearly 70% lower than that of the S11 type Si-steel transformer of the same capacity and is reduced by nearly 60% compared to the S13 type Si-steel transformer [235,236]. The CM choke cores can be applied to 500 kW and 1 MW centralized photovoltaic (PV) inverters [237], as shown in Fig. 18b. The high permeability CM choke cores are suitable for the AC side electromagnetic compatibility (EMC) filtering of the high power PV inverter. The high inductance of these cores can effectively reduce the number of cores and achieve a good filtering effect. The low permeability CM choke cores are usually applied to DC side EMC filtering of a high power photovoltaic inverter. This kind of cores has good frequency characteristics, which can effectively resist unbalanced DC components and avoid burning caused by core saturation. The use of several amorphous–nanocrystalline core stacks to assemble a single choke can effectively solve the bearing current problem, which is also an effective solution to the problem of ultra-high CM noise caused by large current disturbance (peak value from tens to more than 100 amp) generated by wind power, large-range variable speed drive [238]. As shown in Fig. 18c, the Fe-based amorphous–nanocrystalline cores can be also made into direct-drive and double-fed converters covering 1 MW, 1.5 MW, 2 MW, 3 MW, etc., to be applied in wind power converters. Recently, the amorphous–nanocrystalline soft magnetic CMs have been more and more applied to an on-board charger of the battery electric vehicles and hybrid electric vehicles [238], as shown in Fig. 18d, owing to their excellent thermal stability, which can stably work over 180 °C for a long time. The wide applications of Fe-based amorphous–nanocrystalline soft magnetic materials are of great significance to the development of stronger and lighter electronic devices with a higher efficiency.

4.2. Hard magnetic materials

Early in 1995, Inoue et al. [239] found that nanostructured Fe–Nd–B alloys consisting of bcc-Fe, Fe4Nd3B2, and an intergranular amorphous phase exhibited superior hard magnetic properties, such as a remanence (Br) of 1.28 T, a coercive field (iHc) of 252 kA/m, and a maximum energy product (BH)max of 146 kJ/m3. They believed that the coexistence of the three nanoscaled ferromagnetic phases was important for the achievement of the excellent hard magnetic properties [239]. In comparison with nanocrystalline hard magnetic materials, the existence of the amorphous phase played a key role in enhancing the hard magnetic properties. On the one hand, the amorphous interphase with a thickness of 5–10 nm could act as an effective exchange magnetic coupling medium between bcc-Fe and bcc-Fe or tetragonal Fe14Nd2B phases, leading to the improved remanence [240]. On the other hand, the intergranular amorphous phase interconnected, forming a network structure that could suppress the reversion of magnetic domain walls in the central region of the otherwise soft magnetic phase, leading to the achievement of high iHc [240]. Similar notions could be also applied to the Fe–Co–Nd–Dy–B alloy. With the formation of Fe2B, Nd4Fe14B, bcc-Fe in the amorphous phase under the magnetization at a field of 1256 kA/m, the remanence, intrinsic coercive force, and (BH)max of the Fe–Co–Nd–Dy–B alloy were found to be 1.6T, 1.36T, 227 kA/m, and 110 kJ/m3, respectively [241].

4.3. Templates for porous structures

In 2017, Yu et al. [242] developed a new method to fabricate Fe-based nanoporous metallic glasses with a mean ligament size of ~75 nm and a mean pore size of ~120 nm. This was done through the selective electrochemical dissolution of the x-Fe nanocrystalline phase from a Fe–Nb–B amorphous–nanocrystalline alloy. The obtained morphology can be well controlled by controlling the
Fig. 16. Applications of amorphous–nanocrystalline soft magnetic ribbons, reprinted from Ref. [228].

Fig. 17. Various cores made of Fe-based amorphous–nanocrystalline soft magnetic ribbons, reprinted from Ref. [234].
Fig. 18. (a) Distribution transformer; (b) PV inverter; (c) wind power converter, and (d) on-board charger made of amorphous–nanocrystalline soft magnetic materials, reprinted from Ref. [238].

Fig. 19. SEM images of the nanoporous Fe–MGs fabricated from Fe82Nb6B12 amorphous–nanocrystalline alloy at three respective linear speeds of Cu wheel: (a)15 m/s, (b) 20 m/s (the cross-sectional view shown as inset), and (c)30 m/s. (d) Pore size, size distribution, and porosity as a function of the linear speed of Cu wheel. Reprinted from Ref. [242] copyright (2017) with permission from Elsevier.
cooling rate and/or the subsequent annealing of the amorphous alloy precursor as clearly demonstrated by Fig. 19. Similar results were also obtained on Fe–Si–B–P–Cu, Fe–B–P–Cu, and Fe–Cu–Zr–B amorphous–nanocrystalline alloys by Fu et al. [243,244] and Zhang et al. [245]. These authors argued that the preferential dissolution was triggered by the weak electrochemical stability of z-Fe nanocrystals. After removing z-Fe from the amorphous–nanocrystalline alloy, the obtained nanoporous structure possessed an ultra-large surface area, which was helpful in enhancing many chemical and physical properties for applications such as electrochemical catalysis, hydrogen storage, and reduction and oxidation reactions (Redox) in metal–air battery systems.

4.4. Corrosion protection

Some amorphous–nanocrystalline alloys, such as Al– [246–251], Fe– [252–257] and Ni-based [258–260] alloys, exhibit good corrosion resistance and can be used as the next generation corrosion resistant materials. For instance, by coating the surface of a magnesium alloy with the Al–Cu–Zn [248] and Al–Cr–Fe [247] amorphous–nanocrystalline film, Tan et al. [248] and Xu et al. [247] both found that the corrosion current of the coated magnesium alloy can be significantly reduced by two orders of magnitude in 0.6 M NaCl solution relative to the uncoated alloy. To protect 316L stainless steel, Ye et al. also developed a series of amorphous–nanocrystalline Cr–Al–Si–N films with remarkable anti-corrosion performance in seawater [246]. In addition, some Fe-based amorphous–nanocrystalline coatings were also developed, which contained a high concentration of chromium, such as Fe–Cr–B–Si–Nb–W [256], Fe–Cr–Si–B–Mn [254], and Fe–Co–Cr–Mo–C–B–Y [252]. These Fe-based amorphous–nanocrystalline coatings exhibited a higher corrosion potential and a lower corrosion current density than those of conventional hard chromium coatings and 316L stainless steel in NaCl solution.

The good anti-corrosion ability of the amorphous–nanocrystalline alloys can be partly attributed to the addition of refractory elements, such as Cr, Mo, and W, which is beneficial to the formation of a passive film with an improved repassivation ability [253,261,262]. In addition, the partial amorphous structure of these alloys might help to mitigate the detrimental effect of microstructural heterogeneities, which are susceptible to localized corrosion attack [261,263,264]. Sweitzer et al. [249] studied the corrosion behavior of an Al-based amorphous–nanocrystalline alloy by measuring its pitting and repassivation potentials. Their results showed that the alloy possessed good resistance to the formation of micrometer-scale pits. Interestingly, Lucente and Scully [251,265] found that the pitting and alkaline corrosion behavior of Al-based amorphous–nanocrystalline alloys were comparable or even superior to those of the fully amorphous state. Johnson et al. [266] proposed that the gradient compositional field in the amorphous matrix was able to provide highly corrosion resistant zones around solute-lean precipitates, thereby resulting in excellent corrosion resistance.

5. Summary

To summarize, we may categorize the amorphous–nanocrystalline alloys hitherto reported into three types, being in line with the different fabrication or synthesis methods:

1. The amorphous–nanocrystalline alloys obtained through the controlled nanocrystallization in amorphous alloy “templates”. Notably, many amorphous alloys are able to act as the templates or precursors to form amorphous–nanocrystalline alloys, including the good glass forming systems, such as Zr-

References


