Topical Review

Nanomaterials by design: a review of nanoscale metallic multilayers

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Abstract
Nanoscale metallic multilayers have been shown to have a wide range of outstanding properties, which differ to a great extent from those observed in monolithic films. Their exceptional properties are mainly associated with the large number of interfaces and the nanoscale layer thicknesses. Many studies have investigated these materials focusing on magnetic, mechanical, optical, or radiation tolerance properties. Thus, this review provides a summary of the findings in each area, including a description of the general attributes, the adopted synthesis methods and most common characterization techniques used. This information is followed by a compendium of the material properties and a brief discussion of related experimental data, as well as existing and promising applications. Other phenomena of interest, including thermal stability studies, self-propagating reactions and the progression from nano multilayers to amorphous and/or crystalline alloys, are also covered. In general, this review highlights the use of nano multilayer architectures as viable routes to overcome the challenges of designing and implementing new engineering materials at the nanoscale.

Keywords: metallic multilayers, multilayered composites, interfaces, nanolaminates, multilayer applications

(Some figures may appear in colour only in the online journal)

1. Introduction
Over the past four decades, the synthesis, characterization and applications of materials at the nanoscale has been the focus of vast amounts of research. This is in part due to the continuous progress in science and technology, which enabled the development of engineered materials with atomic-level precision [1–6]. The interest in materials synthesized at the nanoscale has remained active, since nanoscale features generally lead to unique physical and chemical properties [1, 7–11]. In the present day, the synthesis and application of thin films is one of the broadest research areas in materials research.

The term ‘thin film’ refers to a layer of material overlaying a surface [12, 13], whose purpose is property optimization and/or to provide a specific functionality to a host substrate [13]. Depending on the field, the thickness of a ‘thin film’ ranges between a few atomic layers to a micron (1 × 10⁻⁶ m) [13–15], at which point it is usually agreed that this thickness represents a coating or foil. These foils or coatings may themselves be composed of thin films, as in the case of nano multilayers, which will be discussed in further detail throughout this review. Overall, thin films have been incorporated in multiple technological and commercial areas, including, but not
limited to, diffusion barriers in integrated circuits, data storing devices, food packaging and smart textiles [13, 16–20].

Although thin films can be made from polymers, metals, ceramics or metallic alloys [11, 16, 17, 21, 22], metals are considered particularly promising materials in different technological fields, such as in catalysis and biomedicine, among others [21, 23–25]. The successful application of metallic thin films is in great part due to the fact that they can tolerate structural and chemical imperfections while still exhibiting interesting physical properties [23]. While many thin films and coatings are homogeneous in composition (homophase), some of them are prepared by alternating nanoscale layers of two (or more) different single-phase metals (heterophase) [11, 23, 26–31]. The periodic stacking of different metallic layers with individual layer thicknesses below 100 nm is commonly referred to as nanoscale metallic multilayers (NMMs), but they are often also called nanolaminates, nanolamellars, layered composites or condensates [3, 11, 23, 31–38].

To date, numerous investigations examining the properties of NMMs and relating them to microstructure and composition have been presented. However, most of the available reviews summarizing the current and previous work in the field focus on the description of their magnetic properties [1, 3, 4, 25, 39–48]. This focus can be attributed to the rapid commercialization and evolution of magnetic devices that are based on NMMs [3]. Therefore, the aim of this review is to present an overview of a wider range of applications and properties for which NMMs play a promising role, while also expanding on some new research areas. The schematic in figure 1 can be used as a guide to summarize the areas that will be covered in this review, where each quadrant represents a focus on their mechanical, optical and magnetic properties, as well as their radiation tolerance, while the outer circle outlines the use of NMMs as precursors for the development of new nanostructures. The first two sections of this review will comprise general information about NMMs and their attributes, followed in the third section by a brief description of the most common synthesis methods and characterization techniques. The fourth section will present a diverse number of NMM systems, which will be classified based on the aforementioned properties, and will depict some of the current and potential applications that have been developed based on their outstanding features. Other emerging topics of interest, such as thermal evolution in NMMs and the formation of crystalline and amorphous alloys, will also be explored. Although this manuscript will not necessarily include all multilayer systems available, it does provide a comprehensive review, which is designed to highlight a wide range of available NMM systems across multiple research fields. The aim is to present the reader with new connections and ideas that will inspire future studies and designs for the synthesis and application of novel nanomaterials.

2. Background

2.1. NMMs

The study of NMMs became popular after the discovery of the giant magnetoresistance (GMR) effect [1, 23, 25, 40, 42, 50–52]. However, the fabrication of NMMs dates back to 1923 with the synthesis of Cd/Ag films by Koepppe [10]. Further historical information covering the earlier studies of NMMs are surveyed elsewhere [10]. Soon after the discovery of GMR, the number of reports summarizing other properties increased exponentially. Since then, compositionally modulated systems have been the focus of research in the areas of mechanical [8, 53–67], optical [68–80], electrical [81] and magnetic [2, 3, 25, 29, 48, 82, 83] properties, as well as for tolerance to radiation damage [84–91], thermal conductivity [92] and thermal stability [34, 35, 38, 49, 93–96]. In NMMs, the mechanical response, the damage caused by radiation and the magnetization directions are primarily dominated by the presence of interfaces [4, 5, 8, 25, 28, 34, 38, 39, 46, 48, 54–56, 58, 61–63, 77, 97–112]. This is attributed to the fact that as the individual repeated layers become thinner, interfaces make up a significant fraction of the volume of the material [35, 58, 101, 112–114].

Most of the NMM systems that have been investigated contain two different alternated layers of metal. Such bimetallic structures are classified according to the interfaces formed between both components as coherent, semi-coherent or incoherent (non-coherent) systems [23, 115, 116]. Figure 2 presents a schematic illustration of the different interfaces that could be developed in NMMs. In coherent systems (also called superlattices), the two metal components have the same type of crystal structure and a small lattice mismatch (in general,
on the order of a few percent) [10, 32, 98, 117, 118]. In semi-coherent systems, the crystal structure of the components is the same, but the lattice mismatch is larger [108, 118]. Thus, misfit dislocations are formed in order to accommodate the mismatch. Incoherent systems, on the other hand, are formed of materials that have different crystalline structures, resulting in a larger lattice mismatch [23, 98, 118].

Interfaces within the multilayer can also be compositionally abrupt or compositionally graded over some distance in the growth direction [5, 10]. Compositionally graded means that the change in composition between the two distinct layers (material A into material B) does not occur at a sharp point, implying that atoms from material A migrated into material B through diffusion. If diffusion is not observed within the multilayers, then it is understood that an abrupt (sharp) interface exists [5]. In addition, as each of the layers deposits to form a resulting multilayer, the individual surface morphology contributes to the progression of differing levels of roughness, which affects the quality of the interfaces [5]. Further aspects of the influence of diffusion and roughness and the resulting effects on properties of interest will be discussed in section 4.

2.2. NMMs versus monolithic films

As mentioned earlier, in the text and according to extensive experimentation, simulations and theoretical studies, the enhanced properties observed in NMMs are mainly associated with the large number of interfaces, but they are also a consequence of the combined effects of the specific characteristics of the individual layers [5, 10, 25, 34, 35, 39, 95, 107, 112, 119–130]. In contrast to monolithic films, the properties of NMMs are a function of the thicknesses of the layers rather than a function of the grain size [8, 10, 11, 25, 53, 54, 56, 60, 62, 106, 115, 122, 131–136]. For instance, Ni/Cu systems with high periodicity and layer thicknesses in the range of 1.5–3 nm exhibit a different mechanical response to monolithic Ni or Cu thin films [137]. In addition, the properties further depend on the selected multilayer composition (combination of metals) and other intrinsic microstructural parameters including but not limited to roughness, texture, grain boundaries and grain morphology [4, 11, 34, 61, 81, 108, 138, 139]. For example, surface roughness contributes to the magnetic transport properties due to the scattering process that occurs at the interfaces [3, 25, 39, 82, 131, 140], while the use of a columnar grain morphology improves the thermal stability of the system and helps to better retain a multilayer configuration [93, 96].

3. Synthesis and characterization of NMMs

3.1. Methods for the synthesis of NMMs

A broad range of microstructures can be achieved in NMMs by means of various synthesis methods and parameters, which results in the ability to vary grain size, grain boundaries and grain orientations as well surface roughness within the layers. The vast number of multilayer systems reported to date were prepared via bottom-up or top-down techniques. Bottom-up methods include electrodeposition (or electroplating) [39, 48, 109, 141] as well as physical vapor deposition methods (PVD) such as electron beam evaporation (thermal evaporation), sputtering, cathodic arc deposition, pulsed laser deposition and molecular beam epitaxy (MBE) [5, 6, 17, 23, 39, 127, 142–144]. Electrodeposition is a technique in which metallic ions that are available in an electrolytic solution are reduced and then deposited onto a plating surface. This is achieved by applying an electric potential difference between a metallic substrate and a reference electrode [39]. In PVD processes, the coating is deposited in vacuum via condensation from a flux of neutral or ionized atoms of metals [12, 17]. Regardless of the chemical or physical nature of these commonly used synthesis methods, the formation of NMMs (or single-component thin films and foils) is achieved through the same phase transformations: nucleation, coalescence and growth. During nucleation, atoms or molecules condense as solid entities and grow after further accumulation. Afterwards, these species aggregate (or coalesce) until the desired material forms a continuous film, leading to growth in the thickness of the film [12, 39, 145, 146].

In earlier studies of NMMs, it was believed that controlling the individual layer thickness at the nanometer scale could only be achieved by PVD [48, 53]. Recently, top-down techniques have proved to be effective for the production of NMMs, especially via methods classified under severe plastic deformation (SPD) [84, 86, 105, 110, 134, 147–150] such as accumulative roll bonding (ARB). For comparison, figure 3 highlights three different Cu-based NMM systems fabricated by distinct methods: (a) electrodeposition, (b) magnetron sputtering and (c) ARB. Although all three systems in the figure are polycrystalline, the shape, size and orientation of the grains differ in each case, and the contrast between atomically sharp and ordered interfaces that is found in materials synthesized by PVD is evident [86, 110, 116, 150]. Irregular thicknesses and waviness are observed for the material prepared by electrodeposition (figure 3(a)), while homogeneous layers are visible in the sample prepared by sputtering (figure 3(b)). In addition to these observations, larger grains are noted in the multilayer prepared via ARB (figure 3(c)). These microstructural differences are accompanied by variations in the crystallographic texture, as well as differences in the distribution of residual stresses [82, 134, 151]. All of these distinctive characteristics lead to fluctuations in the performance of NMMs and depend on the deposition technique, as is the case of the magnetic behavior of NMMs grown by electrodeposition compared to those grown by PVD [82, 152–154]. In addition to bottom-up and top-down approaches, the flux melting technique commonly used for the synthesis of metallic alloys has recently been adopted as an alternative method for processing bulk nanolayered materials [155–157]. This was achieved by exposing the melt to an extremely high undercooling process and could be a feasible option for the synthesis of nanostructured multilayers despite the potential for solid solution formation during cooling [155–157].

A partial list of metal/metal nano multilayers classified by composition and accompanied by their respective synthesis method are shown in table 1. This information highlights
Figure 2. Schematic illustration showing the interface configurations that can be formed depending on the crystalline structure of the coupled metals in an NMM system.

the fabrication feasibility of various multilayer systems using different techniques. The selection of a particular synthesis methodology depends on several factors including: growth rates, growth morphology, residual stresses, impurities, reproducibility and microstructural imperfections, among others. As can be observed from table 1, and in agreement with other reviews [39, 142, 144], sputtering prevails as the most common synthesis technique for the growth of a wide range of NMM systems. This is partly due to the fact that almost all elements in the periodic table can be sputtered at high deposition rates, and target materials are generally commercially available or can be readily fabricated [39, 142, 144]. However, synthesis selection is also highly correlated to the end function of the NMM, which determines the requirements with regard to layer control and definition, i.e. high layer definition via PVD is required for most coatings or components for small-scale devices, while NMMs prepared by ARB are more appropriate for structural applications where bulk quantities of material are required [161, 162].

For further guidance on synthesis technique selection, reviews have been grouped for a wide variety of systems according to their respective synthesis method and mechanical [116, 130, 225, 226], magnetic [10, 39, 43, 48, 226], optical [73] and electron transport properties [226] or because of their ability to form either reactive multilayers [144] or amorphous metallic glasses (MGs) [227]. In addition, the advantages and disadvantages of several synthesis methods have been summarized in [39]. Tables and other information presented herein can be used to select the appropriate method for the fabrication of a system of interest.

3.2. Characterization of NMMs

3.2.1. Conventional characterization methods. As stated in section 2, extensive sample characterization is needed in order to correlate properties, synthesis and performance [61, 145]. This is due to the fact that the physical properties of NMMs, which determine their functionality, are sensitive to microstructure [23, 82, 134] and therefore, to their processing method. Many characterization techniques exist to study the microstructural features of multilayered materials, such as the crystal structure, preferred orientation (texture), grain size and shape, lattice defects and interfaces, among others. Additional methods are also available to measure the resulting mechanical, optical and magnetic properties, etc. These techniques offer diverse capabilities and have different requirements and levels of complexity, which range from ex situ characterization (post-deposition techniques), to the evaluation of the final performance.

For NMMs, the microstructure is usually explored by conventional x-ray diffraction (XRD) and scanning and transmission electron microscopy (SEM and TEM) [48, 62, 109, 142, 228]. XRD can quickly provide information about the crystal structure, texture and grain size without the need for special sample preparation. Various XRD techniques are also widely used to investigate additional aspects of the multilayers. Wide-angle x-ray scattering yields information on the bilayer thickness and interplanar spacings, while small-angle x-ray scattering and x-ray reflectivity experiments offer the opportunity to characterize the continuity of the interfaces between constituent layers (e.g. interface roughness, thickness and chemical intermixing) [48, 229]. SEM characterization is acquired in plane and cross-sectional view modes and is usually employed to reveal the morphology of the grains and the surface characteristics, as well as the thickness of the NMM systems. TEM characterization, which is typically performed in the cross-sectional mode, is used for the direct observation of the thickness, crystallographic orientation and formation of defects within each of the constituent layers [228]. Further crystallographic information can be obtained in TEM by collecting selected area electron diffraction patterns. In SEM, the quantitative evaluation of the crystallographic structure and the orientation of polycrystalline materials can be obtained via electron backscatter diffraction (EBSD) [28]. Since the
Table 1. Compilation of several NMM systems classified according to composition and synthesis method.

| Composition | Synthesis method(s) | References |
|-------------|---------------------|------------|
| Al/Nb       | DC magnetron sputtering | [80, 163–167] |
| Al/Ag       | DC magnetron sputtering | [168] |
| Al/Ni       | DC magnetron sputtering | [169] |
| Al/Cr       | DC sputtering | [170] |
| Al/Fe       | DC sputtering | [170] |
| Au/Ni       | DC magnetron sputtering | [64, 129] |
| Co/Au       | Vapor deposition, MBE | [43, 171] |
| Co/Ag       | Vapor deposition, MBE | [43, 171] |
| Co/Ru       | DC magnetron sputtering | [39] |
| Co/Pd       | DC magnetron sputtering | [39] |
| Co/Pt       | Vapor deposition | [39, 43] |
| Co/Cr       | DC magnetron sputtering | [172] |
| Co/Cu       | Vapor deposition/DC magnetron sputtering/jet electrodeposition/e-beam evaporation/ion beam sputtering | [2, 43, 104, 152, 153, 173–178] |
| Co/Ir       | Vapor deposition | [43] |
| Co/Mo       | Vapor deposition | [43] |
| Co/Ni       | MBE | [39, 179] |
| Cu/Zr       | DC magnetron sputtering | [8, 54, 130, 180, 181] |
| Cr/Sc       | Ion-assisted magnetron sputtering/DC magnetron sputtering | [182–184] |
| Cu/Cr       | DC magnetron sputtering | [8, 130] |
| Cu/Nb       | DC magnetron sputtering | [9, 18, 28, 36, 53, 86, 97, 102, 105, 110, 130, 136, 147, 185–190] |
| Cu/Ni       | Electrodeposition/DC magnetron sputtering/evaporation | [2, 65, 129, 191–195] |
| Cu/V        | DC magnetron sputtering | [166, 190] |
| Cu/Mo       | DC magnetron sputtering | [190, 196] |
| Cu/Ta       | ARB/DC magnetron sputtering/RF magnetron sputtering | [60, 197, 198] |
| Cu/Ru       | RF and DC magnetron sputtering | [199] |
| Cu/Pd       | DC magnetron sputtering | [191] |
| Cu/Au       | DC magnetron sputtering | [58] |
| Cu/W        | DC magnetron sputtering/ion beam sputtering | [34, 139, 200] |
| Cu/Zr       | DC magnetron sputtering | [8, 54, 130] |
| Fe/Cr       | Thermal evaporation/DC magnetron sputtering/MBE | [92, 170, 172, 201–203] |
| Fe/Co       | Thermal evaporation | [92] |
| Fe/Cu       | DC magnetron sputtering/thermal evaporation | [92, 204] |
| Fe/Pd       | Thermal evaporation | [92] |
| Fe/Ag       | Thermal evaporation | [92] |
| Fe/Hf       | Electron beam evaporation | [205] |
| Fe/Ir       | DC magnetron sputtering | [29] |
| Fe/W        | DC magnetron sputtering | [190] |
| Mg/Nb       | DC magnetron sputtering | [206] |
| Mg/Ti       | DC magnetron sputtering | [207, 208] |
| Mg/Pd       | DC magnetron | [209, 210] |
| Mo/Pt       | DC magnetron sputtering | [38, 211] |
| Mo/Y        | DC magnetron sputtering | [212] |
| Mo/V        | DC magnetron sputtering | [213] |
| Mo/Y        | DC magnetron sputtering | [70, 214] |

(continued)
thicknesses of the individual layers in NMM systems are often too thin to be characterized by EBSD, the heterophase interface character distribution method was developed to quantify the distribution of the 3D heterophase interface normal vectors using 2D EBSD images [27, 230].

By using both SEM and TEM techniques it is also possible to analyze the chemical composition using energy-dispersive x-ray spectroscopy (EDXS) [222, 228]. Microanalysis of NMMs can be achieved via electron energy-loss spectroscopy in TEM. However, the accuracy of the measurement is sensitive to the thickness of the specimen [228]. Auger electron spectroscopy (AES or AESDP) is employed to obtain depth profiles of composition and to study the possible occurrence of diffusion in the multilayers [75, 170, 231–233]. Similar to AES, x-ray photoelectron spectroscopy is another tool that can be used to quantify the elements and determine their chemical composition [234]. In addition, atom probe tomography offers high spatial resolution with respect to chemical composition in 3D, which helps to provide quantitative information on interfacial mixing, segregation and local composition [168]. As for the analysis of surface topography, scanning probe microscopy (SPM) [235] measures the 3D surface structure, providing information such as the area and volume of the particles and therefore, the roughness of the samples. SPM techniques include atomic force microscopy, scanning tunneling microscopy and more recently, magnetic force microscopy [235–237], which is used to reconstruct the magnetic structure of the surface. Profilometry, on the other hand, is able to provide information such as surface topography, thickness and the calculation of residual stresses after the deposition [36, 238].

In addition to conventional post-deposition characterisation methods, the investigation of the microstructure and properties can also be achieved with the implementation of in situ techniques. The importance of such methods relies on the fact that they provide valuable information about the sample in real time, which can be collected during deposition or when the sample is subjected to a specific set of conditions [31]. One of the most common methods is reflection high-energy electron diffraction, which is used to monitor the growth progress during material synthesis by PVD [6]. Growth stresses are another commonly studied property that may be monitored during deposition, and provide insight into the microstructure of the final NMMs [239]. In addition, in situ XRD tests have been used to study the evolution of the microstructure of NMMs upon exposure to ion irradiation [200, 240] and to determine their deformation behavior upon heating/cooling [36, 194]. Synchrotron XRD experiments have also been carried out during tensile loading to examine the gradual progression in yield behavior, and are interpreted in terms of residual stresses, as well as elastic and plastic anisotropy [136, 139, 241]. Time-resolved x-ray microdiffraction is used for the observation of selfpropagating reactions in reactive multilayers, which allows for the study of phase transformation and diffusion [31, 127, 128, 242–244]. In spite of their many advantages, in situ methods usually require access to sophisticated equipment and installations or demand a special sample size or shape preparation. Therefore, conventional ex situ characterization techniques prevail as the most common tools for correlating microstructural parameters to properties and performance.

Once extensive microstructural analysis has been carried out, and depending on the desired application, different characterization methods are available to evaluate the properties of interest. Nanoindentation tests have become one of the most widespread techniques for the mechanical testing of very small volumes of materials, a task that would be difficult or impossible with conventional mechanical testing methods due to the sample size restriction [15, 238, 245, 246]. Hardness and elastic modulus, yield strength, strain hardening, adhesive strength and fracture toughness are some of the many mechanical properties that can be evaluated using nanoindentation [122, 245, 247, 248]. In addition, tensile testing via electromechanical systems (micro tensile tests) can be used to provide a direct measure of a stress–strain curve, which serves to elucidate the onset of plastic deformation, work hardening rate, elongation to failure and fracture mode [188, 189]. If freestanding films are obtained, bulge tests can be performed, allowing for measurements of the Young’s modulus, residual

| Composition      | Synthesis method(s)                  | References |
|------------------|--------------------------------------|------------|
| Ni/Pd            | Vapor deposition                     | [43]       |
| Ni/Ag            | Evaporation/DC magnetron sputtering  | [129, 192, 200] |
| Ni/Ti            | DC magnetron sputtering              | [133, 215] |
| Ni/Pt            | DC magnetron sputtering              | [216]      |
| Nb/Ti            | Evaporation                          | [192]      |
| Nb/Ni            | Evaporation                          | [192]      |
| Ti/Al            | DC magnetron sputtering              | [217, 218] |
| Ti/Ta            | DC magnetron sputtering              | [219]      |
| V/Ti             | RF sputtering                        | [56]       |
| V/Fe             | DC magnetron sputtering              | [220, 221] |
| Zr/Nb            | Balanced magnetron sputtering/DC magnetron sputtering | [61, 62, 222, 223] |
| Cu/Ni/W          | DC magnetron sputtering              | [55]       |
| Cu/Ni/Nb         | DC magnetron sputtering              | [224]      |
stress and yield stress [18, 38, 191, 249]. Micropillar compression tests can also be an appropriate approach to characterize the deformation of NMMs and to obtain stress–strain curves in a nominally homogeneous stress state [103, 110, 200, 246, 250–252]. Synchrotron x-ray microdiffraction combined with micropillar compression experiments can provide quantitative measurements of dislocation densities in NMMs, which allows for the study of microstructural changes associated with plastic deformation [251, 252].

In the field of magnetic materials, the magnetic anisotropy can be deducted from the dynamic or static response using ferromagnetic resonance, torque magnetometry, torsion oscillating magnetometry or the magneto-optical Kerr effect [39, 131]. Correspondingly, a vast number of techniques are available for the indirect measurement of the magnetic moment, including vibrating sample magnetometry (VSM), superconducting quantum interference device (SQUID) magnetometry, fluxgate magnetometry, alternating...
A vast amount of experimental work has shown that most of the metallic elements in the periodic table have been combined in a nanoscale multilayer configuration with the aim of exploring their microstructural variations and properties. In an attempt to present a more specific classification of different NMMs, figure 5 shows a compilation of metal/metal systems grouped according to their composition, highlighting their field of application. It can be observed that many NMM systems have been incorporated into a wide range of technological and scientific areas, with an emphasis on magnetic applications. Therefore, the following sections describe some of the most significant results obtained in a broad range of fields, including a summary of early and most recent works.

4. Properties and applications of NMMs

A vast amount of experimental work has shown that most of the specific properties of a generic NMM system. Rapid transformations after the ignition of reactive multilayers has been developed to analyze the reaction propagation and the opportunity to map the plane of magnetization in materials exhibiting the presence of skyrmions. The two techniques are carried out in synchrotron facilities [236, 255]. Spin-polarized low-energy electron microscopy (SPELEM) and x-ray magnetic circular dichroism photoemission electron microscopy are high-resolution imaging techniques that are based on spatial magnetic imaging of electrons, which are either deflected or emitted from the sample [236, 256]. In particular, SPELEM is capable of quantifying the arbitrary orientation of spin states [236]. Further details about these and other magnetic imaging characterization techniques such as SEM with polarization analysis, magnetic transmission x-ray microscopy and Lorentz transmission electron microscopy, can be surveyed in [254].

For the particular case of NMMs for extreme ultraviolet (EUV) and soft x-ray (SXR) devices, the spectral reflectivity is measured to determine the functionality of the synthesized structure. Reflectivity measurements near normal incidence usually require the use of an intense and continuous light source and therefore, the characterization of such NMMs is mostly carried out using synchrotron beamlines [70, 72, 257-259]. Customized reflectometers with x-ray tubes have also been developed in order to achieve reflectivity measurements [79]. Other dedicated techniques, such as hydrogenography [207] and elastic recoil detection analysis [209, 210] have been implemented to monitor the optical changes during hydrogen absorption and desorption in metals, a phenomenon that is useful to evaluate the hydrogen storage capacity via metal hydride formation. Neutron reflectometry [260] has proved to be sensitive to local density changes induced by He implantation, which is useful to investigate the damage of materials under He irradiation. Differential scanning calorimetry (DSC) is used for the study of phase transformation and thermal stability of NMMs [168]. Nanocalorimetry, on the other hand, offers higher heating rates than the common DSC method and therefore, is used to provide deep insight into phase transformations of reactive multilayers [127, 261]. Along with nanocalorimetry, dynamic TEM with microsecond-level time resolution has been developed to analyze the reaction propagation and rapid transformations after the ignition of reactive multilayers [31, 243]. Figure 4 illustrates an overview of different techniques used to determine the microstructure, composition and the specific properties of a generic NMM system.

4.1. NMMs for enhanced mechanical properties

4.1.1. NMMs with high yield strength/hardness. The idea of developing a strong solid material by adopting an NMM configuration was first presented by Koehler in 1970 [262]. The basic principle stated that this could be achieved by preparing a composite material comprising alternated thin layers of material A and material B. The successful application of this idea was soon confirmed experimentally, with results showing that the outstanding mechanical behavior of NMMs is dominated by interfaces [8, 53–67, 111, 130], which act as sources, barriers, and preferred sites for storage and dynamic recovery of dislocations, as presented in [58, 110, 111, 114, 263].

The increased yield strength (σ), usually associated with the increase in hardness (H), is one of the most significant improvements obtained through implementing the NMM configuration. The general trend shows that higher hardness is achieved through the reduction of layer thickness (or interface spacing—h) and the strengthening effect is explained using the theories of dislocation motion. This is because dislocations are line defects that are mainly responsible for the plastic deformation of crystalline solids [114, 264, 265], and their movement is obstructed by interfaces. Various dislocation models have been developed in order to interpret the strengthening mechanisms as a function of layer thickness [30, 53, 63, 108, 111, 116, 134, 266–269]. As recently summarized in [270], the most accepted model indicates that there are three primary mechanisms to explain deformation in NMMs, and the mechanisms at play depend on the layer thicknesses. The first one is based on the Hall–Petch scaling law (σ = h⁻¹/₂), which is valid when dislocation pile-ups can be treated as a continuum, typically when h is in the micron to submicron scale. As h is reduced, the number of dislocations allowed in a pile-up will decrease until only one dislocation can be accommodated. The glide of this single dislocation bounded by the interfaces is dictated by the second mechanism, known as the confined layer slip model, and is valid for h in the range of tens of nanometers with the following scaling law: σ = (ln(h))/h. Once h is further reduced to a few nanometers, the hardness is governed by the third mechanism and is explained in terms of the interfacial barrier strength for dislocations cutting across the interface. Further details about deformation mechanisms can be found in [30, 53, 63, 108, 111, 116, 134, 266–271].

Multiple compositions of multilayer systems have been studied, showing an increase in hardness with the reduction of h. As such, table 2 presents a compilation of hardness values.
Figure 4. Illustration showing different characterization techniques commonly used to provide information about the microstructure, composition and some properties of interest of NMMs. Figures noting: (a) elemental maps obtained via EDXS; (b) diffraction pattern obtained via XRD; (c) cross-section of a multilayer system from which the grain size, morphology and orientation are observed via TEM; (d) magnetic hysteresis loops measured via VSM; (e) reflectivity measurements (and fitted profiles) obtained using synchrotron radiation and (f) engineering stress–strain plots obtained from micropillar compression tests. Generic multilayer system at the center of the figure is used as a model example to show the configuration of the stacked layers. (a) and (f) Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer, Interface Behavior, [222], Copyright © 2017, Springer Nature. (b) Reprinted from [62], Copyright (2015), with permission from Elsevier. (c) [86] John Wiley & Sons. © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Reprinted from [253], Copyright (2018), with permission from Elsevier. (e) Reproduced from [72]. CC BY 4.0.

Figure 5. Illustration showing a classification of bimetallic multilayer systems grouped according to the combined metals as well as properties that have been explored. Metal systems are color coded by the legend on the right related to the specific studies.

of systems grown upon Si substrates with repeated bilayer thicknesses. For most of these NMMs, a significant change in the elastic modulus $E$ was not observed as a function of the layer thickness (known as the supermodulus effect), and therefore, the elastic modulus values are not included. All systems in table 2 exhibit hardness values higher than those
Table 2. Hardness values of several NMM systems measured via nanoindentation.

| Composition | Nominal thicknesses (nm) | Total thickness (µm) | Hardness (GPa) | Reference |
|-------------|--------------------------|----------------------|----------------|-----------|
| Al/Nb       | 1/1                      | 1.6                  | 4.8            | [166]     |
| Ag/Nb       | 1/1                      | 1                    | 6.9            | [273]     |
| Cu/Cr       | 10/10                    | 1.6                  | 9.1            | [130]     |
| Cu/Nb       | 5/5                      | 7–11                 | 6.2            | [195]     |
| Cu/Sc       | 5/5                      | 4                    | 6.3            | [159]     |
| Cu/Sc       | 5/5                      | 8                    | 6.9            | [272]     |
| Cu/W        | 2.5/2.5                  | 1.6                  | 4.8            | [166]     |
| Cu/Sc       | 15/15                    | 1.5                  | 5.3            | [37]      |
| Cu/Zr       | 5/5                      | 1.6                  | 5.8            | [130]     |
| Mg/Ti       | 2.5/2.5                  | 1.6                  | 4.2            | [208]     |
| Mg/Nb       | 5/5                      | 5                    | 3.7            | [274]     |
| Mo/Pr       | 20/20                    | 0.43                 | 6.6            | [38, 211] |
| Ti/Al       | 10/10                    | 1                    | 6.4            | [275]     |
| Ti/Ta       | 60/60                    | 1.5                  | 11.8           | [219]     |
| Zr/Nb       | 16/16                    | 1.35                 | 5.2            | [61]      |

expected from their respective rule of mixtures. In addition, during the compilation of these results it was noted that the highest hardness values were reported for systems with the largest total thickness. For example, the Cu/Nb system with individual layer thicknesses of 20 nm and a total thickness of 1.6 µm, has a hardness of 5.4 GPa; a value that is larger than that measured for the same system with a total thickness of 1 µm (4.5 GPa). Such discrepancies could originate from the microstructural variations arising from the selected synthesis method and/or substrate contributions during the measurements. For example, as shown in table 2, Cu/V multilayers prepared via sputtering [37] yielded a hardness of 5.3 GPa, in contrast to a higher hardness of 7.25 GPa for a sample prepared by electron beam evaporation, for samples with a similar measured individual layer thickness [272]. It is important to note that for non-repeated bilayer thickness samples, a trend of higher hardness with smaller layer thickness has not been established [65]. Instead, the strengthening effect is attributed to the volume fraction of the coupled elements, which leads to an increase in the interfacial dislocation density.

In addition, a strengthening effect in NMMs has been observed as a result of structural transitions during the growth of very thin layers (usually 2.5–5 nm), which can form metastable or pseudomorphic phases. For instance, higher indentations have been reported for face-centered cubic (fcc) Cu and body-centered cubic (bcc) Nb [130] than in fcc/fcc Cu/Nb [195] samples of the same layer thickness (see table 2). The mechanical properties of other pseudomorphic phases, as well as a brief summary of available theories regarding the phase transformations at very small thicknesses, have been reviewed in the literature [271, 276]. Special attention has been given to the hexagonal close-packed (hcp) to bcc transition of Mg and Zr in NMM systems because of the possible incorporation of these compositions in aerospace and automotive applications [112, 206, 276]. Furthermore, studies exploring the effects of thermal annealing on the mechanical properties of multilayers have also been carried out, with the majority of the results showing that the increase in temperature leads to a decrease in hardness [37, 38, 211, 277]. For reference, compilations of hardness values obtained from multiple systems have been presented in [111, 116, 130, 271]. These systems, along with the ones presented in table 2, can be used as a guideline to explore the mechanical properties of other NMMs.

4.1.2. Improved ductility and wear resistance in NMMs. To date, the mechanical behavior of NMMs has mostly been determined from nanoindentation, which is a versatile tool for the estimation of mechanical properties in small volumes [116]. Nevertheless, in order to provide a comprehensive understanding of the mechanical behavior, a wide range of testing techniques are needed and should include stress–strain responses [188, 189, 278]. Therefore, microcprssion and tensile experiments have been adopted in order to provide such information [271, 278]. Micropcrssion tests can be performed in different configurations: with the compression axis parallel or normal to the surface with either a circular or squared cross section. From both tensile and compression tests, the plastic flow behavior as well as softening and hardening effects can be elucidated from the stress–strain response [188, 278, 279]. However, ductility values from tensile experiments have been shown to exhibit smaller values than those obtained via micropcrssion compression. This can be attributed to variations in sample preparation, the geometry of the system or the loading conditions of a given testing method. Overall, the number of studies presenting the deformation of NMMs remains limited, with most of the experiments performed using Cu/Nb systems [116, 188, 189, 250, 271, 278, 279], although other works have been carried out for Ag/Cu [280] multilayers and more recently for Mg/Nb [274] and Zr/Cu [159] systems. The experimental results obtained from those studies have shown that in general, the strength and ductility of materials are mutually exclusive, meaning that the ductility of multilayer systems drops with decreasing the layer thickness [199, 271, 281]. In many of these reports, the correlation factor for the flow strength (σf = H/2.7 or σf = Hr/3) has been used to compare and validate the measured data using the hardness values obtained from nanoindentation [188, 250, 278, 279] or Vickers indentation [280].

Wear studies provide further mechanical behavior insight into deformation and material loss under sliding contact [67], as well as its effects on the material’s servicability and durability [282]. Wear resistance is known to depend on hardness and therefore, a suitable approach to improved wear resistance has been achieved using systems with layers a few nanometers in thickness, for which less volume loss due to wear and deformation has been observed [67]. However, it has been seen that the
applied load, velocity, elastic properties of the constituent elements [67, 264, 282, 283] and the presence of internal stresses [264] affect the wear response. The available studies employ the ratio of hardness over modulus $H/E$ (named elastic energy) as the key parameter to describe the tribological properties of multilayers. The basic criterion indicates that the higher the magnitude of $H/E$ ratio, the better the wear resistance of the coating [67, 264, 282, 283]. Examples of multilayer structure response explored under cyclic sliding include Cu/Au [284], Cu/Ag [283] and Cu/Nb systems [67].

Other properties and behavior of interest, including creep and shear band deformation, crack propagation and toughening can be surveyed in [58, 60, 116, 177, 197, 199, 200, 250, 271, 285–287].

4.2. NMMs with superior optical properties

4.2.1. Mirrors for the EUV and SXR regions. Multilayer structures exhibiting enhanced reflectivity near normal incidence in the range of EUV and SXR (1–60 nm), are in high demand for the design and fabrication of optical elements in lithography systems, spectroscopes, microscopes and x-ray free-electron lasers [68–77]. In contrast to monolithic films, multilayered optical materials offer improved performance at near-normal incidence. This is because the small reflections that occur at each of the interfaces add coherently in phase, producing a high reflectance over a narrow range of wavelengths [288, 289]. Such wavelengths are then used to match the needs for specific practical applications, for instance, EUV lithography systems for chip fabrication typically operate in the range from 6.7 nm to 14 nm [290], while telescopes for solar astronomy work in the spectral range from 1030 nm [291–293]. Biological microscopes, on the other hand, operate in the water window region between 2.3–4.4 nm, where the contrast between carbon and water does not limit the imaging of the samples [72, 291]. As an illustrative example for the use of optical mirrors, figure 6 shows a collection of NMMs that can be used for the observation of different spectral lines emitted by the sun. As noted at the bottom part of figure 6, the imaging of single active regions is achieved in real time, providing specific information about the processes occurring in the solar atmosphere. The importance of monitoring solar activity relies on the fact that variations in solar radiation drive changes in the density and ionization in Earth’s thermosphere and ionosphere, which affects the performance of ground-based communications systems and spacecraft in low-Earth orbit [293].

The performance of multilayered mirrors has been shown to strongly depend on the composition of the multilayers, since in order to maximize the reflectance, elements with the highest possible optical contrast (absorbers) and the lowest possible absorption (spacers) have to be coupled [294]. Optical contrast indicates a material with sufficiently different values of the index of refraction and extinction coefficient, while for the spacer element, minimal absorption at the target spectral range is needed [69, 295, 296]. Depending on the application, peak reflectivity (maximum reflectance or reflection efficiency) as high as 70% and a narrow spectral band are required. The reflection efficiency influences the temporal resolution and defines the sensitivity of the instrument (meaning that acceptable clearer images/signals are achieved with shorter exposure times), while the spectral bandwidth diminishes the contribution from spectral lines that are contiguous [79]. In addition, the overall performance of these mirrors is a function of the reduced thickness of the layers, quality of the interfaces, surface characteristics of both the NMMs and the substrate, as well as by the intrinsic stresses that develop during deposition [77, 182]. The variation of any of these parameters has been shown to have either a positive or negative effect on the optical response of the multilayers. For example, by adjusting the bilayer thickness, one can tune the peak reflectivity of the multilayer and match a desired wavelength [71, 74, 75, 289]. In contrast, the existence of roughness and diffusion at the interfaces has been shown to dramatically degrade the reflectance and reduce the optical contrast [69, 71, 182, 291, 297], while residual stresses can cause deformation in the projected beam [71, 79]. These negative effects can be minimized by using super-polished substrates [69, 76, 77, 80, 214] and suitable buffer layers [79], respectively.

A compilation of successfully synthesized NMM mirrors appears in table 3, showing the experimentally measured peak reflectivity. The systems are grouped by chemical composition and are accompanied by the angle at which the maximum reflectivity was achieved, as well as the corresponding target wavelength. As shown in table 3, a maximum reflectance of 70.2% was observed in a Mo/Be system, but the health risks associated with the use of Be can restrict its usage [71, 298]. It should be noted that the peak reflectivity and target wavelengths vary from system to system, but this information is useful when comparing the performance of different mirrors and selecting possible candidates that can be suitable for several applications.

Other systems not presented in table 3, including Pd/Y [291] and La/B [307, 308], have also been studied as possible reflective mirrors, but their multilayer structure disappears due to intermixing of the components. This is caused by the poor thermal and chemical stability of the combined element system. Thermal evolution tests are required in order to ensure the functionality at operation temperature of optical mirrors used in astronomical observation and synchrotron radiation, since they are exposed to a high flux of incident photons, which can lead to degradation of the structure upon heating [71, 305, 309, 310]. As an example of sample degradation, Nechay et al. studied the effect of annealing and surface oxidation on the reflectivity of Mo/Be multilayers [310]. They observed a reduction of reflectivity as a consequence of diffusion upon annealing, but also noted that oxidation had a major impact on lowering the optical response. Similar findings were reported for a Mo/Y system when exposed to a photon flux of lesser intensity than that expected under normal operational conditions [212]. Several approaches have been adopted in order to minimize the chemical interaction and degradation of the layers. Notable examples include the reduction of diffusion and inhomogeneous crystallization during the synthesis of an Al/Zr system by doping the Al layers [311], while the stabilization of Y/La mirrors was achieved by introducing N$_2$.
4.2.1. Multilayer mirrors for hard X-ray and EUV. A number of other NMMs have been proposed theoretically as possible optical systems, promising high reflectivity in the SXR and EUV regions [69, 295, 303, 304, 312–314]. For most of these cases (including the systems in table 3), the theoretical reflectivity differs to a great extent from that measured experimentally, but such information could serve as guidelines for further exploration. Other considerations for the development of efficient, high-quality multilayer optics have been covered extensively in the literature and can be surveyed elsewhere [69, 73, 74, 79, 80, 289, 295, 296, 315].

4.2.2. Optical switches for hydrogen storage. The increasing interest in hydrogen as a cleaner and more efficient energy source has led to a fast-growing research area, which includes research of materials for its storage. The hydrogen uptake (hydrogenation) process, observed first in Y- and La-based thin films, has been considered as a feasible method to prepare devices that are able to both store and quantify the hydrogen uptake [316]. Hydrogenation depends on the metal to hydride formation, which usually leads to phase transitions, meaning that the material changes from a metal to a semiconductor [317] and therefore, the metallic film becomes transparent [318]. Under these circumstances, the optical and electronic
properties could be switched between those of the highly reactive metallic state and the semiconducting hydride states by subsequent loading and unloading of hydrogen [209, 319], allowing for real-time visualization of transmittance, reflectance and resistivity changes during hydrogen incorporation into the lattice structure [319].

The early studies of switching materials were carried out using monolithic thin films of alloys. Later on, van der Sluis et al reported that the switching effect in multilayers (kinetics of hydrogenation) was much faster than that observed in alloys of identical composition [320] and thus, NMM systems became attractive as possible optical switches. Outcomes have shown that tuning of the optical properties is possible by varying the layer thickness, while tuning the switching kinetics is attainable by varying the number of multilayers [320]. In addition, NMMs do not exhibit the disadvantageous hysteretic effects to the transmittance that monolithic thin films do, and this demonstrated reversible kinetics upon hydrogen loading and unloading ensures the reproducibility of the results during continuous operation [318].

Some of the requirements for the development of efficient multilayer optical switches include high gravimetric capacity and the ability to rapidly take up and release hydrogen (determined by the kinetic response) [321]. Since oxidation is much more favorable than hydrogenation (even at room temperature (RT)), hydrogen absorption experiments have to be carried out in ultra-high vacuum conditions and the final multilayer structure must incorporate a capping layer to prevent surface oxidation and/or to enhance the exchange of hydrogen. To date, very few NMM systems have been explored as possible switchable mirrors, including Y/Mg [318], Mg/Ti [207], Pd/Mg [209], Gd/Mg and La/Ce [320], thus leaving an opportunity for the study of other compositions.

4.3. NMMs with improved magnetic properties

4.3.1. GMR effect in NMMs and the emergence of spintronics. The discovery of the GMR effect, first observed in a trilayered Fe/Cr/Fe system [51, 52] and later in Fe/Cr multilayers [50], is perhaps the most remarkable example of how the properties of NMMs prompted a fast transition from scientific investigation to the commercialization of devices [3, 50, 322–324]. Since then, a global widespread interest in the study and application of these nanostructures has emerged, accompanied by a great number of reported studies. Therefore, we limit our discussion to present qualitative aspects about GMR with further fundamental concepts, properties, preferred compositions, synthesis methods, applications, limitations and future trends available in the literature [3, 25, 41, 48, 82, 140, 322, 324–329].

The GMR effect can be described as the change in electrical resistance in response to an applied magnetic field [3]. It is observed in NMMs composed of alternating layers of ferromagnetic (FM) and non-magnetic (NM) elements. The basic principle of this phenomenon relies on the fact that the magnetic moments of the FM layers can be aligned in parallel or antiparallel to each other by applying a magnetic field. When the magnetic moment is aligned in parallel, the scattering of the carriers is minimized, and the system achieves its lowest resistance. In contrast, if the magnetic moments of the FM layers are anti-aligned, the scattering is maximized and the resistance reaches the maximum value [330]. The accumulated experimental data indicates that the GMR depends mainly on the thickness of the NM layers (because the strength of the MR oscillates with its thickness) [3, 25, 48, 82, 140, 322, 324–328, 330], but that it is also influenced by the composition of the multilayer, the roughness, presence of defects (such as grain boundaries) and diffusion [1, 3, 140]. Depending on the application, one or multiple of these parameters may serve as determining factors for the performance of the multilayer system.

According to the literature, the systems that exhibit the greatest values of GMR include: Fe/Cr, Co/Ru, Co/Cr, Co/Cu, Co/Ag and Ni/Fe alloys, while very low GMR has been measured in Ni/Ag, Ni/Cu, Fe/Mo, Fe/Au, Co/Al and Co/Ir alloy systems [3, 48, 140, 324, 331]. Large GMR systems are attractive for the fabrication of hard disk read heads, memory chips and magnetic recording disks [1, 82, 140, 322, 324, 328, 332], but thanks to their small size, high sensitivity and low power consumption, giant magnetoelastic multilayers are also suitable for the fabrication of sensors for use in other applications including transportation systems, flexible electronics, biology and healthcare [16, 140, 323, 333]. In such cases, the composition of the stacked films is not limited to metals and/or to the assembly of periodic layers. It is now worth mentioning that the GMR effect has also been observed in systems with a reduced number of layers comprised of semiconductor materials or nanoparticles embedded in a matrix [323, 324].

### Table 3. Compilation of different multilayer systems that have been proposed for EUV and SXR optics.

| Composition | Peak reflectivity (%) | Off-normal angle of incidence (degrees) | Wavelength (nm) | Reference |
|-------------|-----------------------|----------------------------------------|----------------|-----------|
| Al/Nb       | 15                    | 40                                     | 30.0           | [80]      |
| Be/Al       | 46.0                  | –                                      | 17.1           | [298]     |
| Co/Ti       | 2.5                   | 21.5                                   | 3.1            | [296]     |
| Co/Mg       | 40.3                  | 10                                     | 30.5           | [299]     |
| Cr/Sc       | 29.6                  | 59.9                                   | 3.1            | [183]     |
| Mo/Al       | 17.3                  | 5                                      | 3.1            | [184]     |
| Mo/Be       | 33.5                  | 10                                     | 18.5           | [68]      |
| Mo/Sr       | 29.2                  | 5                                      | 19.6           | [300]     |
| Mo/Y        | 70.2                  | 5/2                                    | 11.3/11.2      | [71, 290] |
| V/Sc        | 68.7                  | –                                      | 11.3           | [301]     |
| W/Sc        | 48.3                  | 3                                      | 10.5           | [302]     |
| W/Ti        | 25.6                  | 5                                      | 11.3           | [70]      |
| Y/Nb        | 38.4                  | 5                                      | 9.5            | [214]     |
| Zr/Mg       | 55                    | 1.5                                    | 11.9           | [212]     |
| Cr/Sc/Mo    | 18.4/15.1             | 9/7                                    | 3.1            | [72]      |
|             | 3.3                   | 7                                      | 3.2            | [303]     |
|             | 8                     | 30                                     | 2.8            | [304]     |
|             | 5.2                   | 29                                     | 2.8            | [295]     |
|             | 9.4                   | 5                                      | 10.9           | [295]     |
|             | 30.6                  | 5                                      | 30.4           | [305]     |
|             | 27.4                  | 12.8                                   | 4              | [306]     |

To date, very few NMM systems have been explored as possible switchable mirrors, including Y/Mg [318], Mg/Ti [207], Pd/Mg [209], Gd/Mg and La/Ce [320], thus leaving an opportunity for the study of other compositions.
These GMR systems are known as spin valves, granular multilayers and magnetic tunnel junctions (MTJs). For reference, a comparative table showing the measured properties within different GMR systems can be surveyed in [329]. In addition, the work presented by Zheng et al. [332] summarizes the transition from NMMs to spin valves, granular multilayers and MTJs, and includes the quantification of patents and publications that have become available since 1988. Much effort, directed towards the exploration of the GMR, has also enabled the control of an electron’s motion by acting on the orientation of its spin, which led to the emergence of the field of spintronics [41, 140, 330].

4.3.2. Magnetic anisotropy in NMMs. FM materials exhibit easy or hard axis magnetization, which refers to the application of a small or large magnetic field to reach the saturation of magnetization [39]. The energy required to achieve saturation depends on the direction of the applied magnetic field relative to the crystal axes and is called magnetic anisotropy. This direction can lie in the plane of the substrate or along the surface normal to the substrate (perpendicular magnetic anisotropy (PMA)) [39, 43, 141]. If easy magnetization is achieved in the direction perpendicular to the plane of a thin film then PMA is observed. PMA results from a combination of factors: the contributions from the shape of the nanostructure (shape anisotropy), strains associated with the deposition method (magnetoelastic anisotropy) and crystalline structure of the material (magnetocrystalline anisotropy). In NMMs, the magnetic anisotropy reaches larger values due to the presence of symmetry-breaking elements, such as planar interfaces and surfaces [39]. Moreover, it has been possible to tailor the strength and occurrence of PMA by changing the thicknesses of the individual layers and by choosing appropriate materials [39, 43, 141].

A large number of systems employed in the study of magnetic anisotropy, as well as additional details about this phenomena, can be found in [131, 334]. Some of the most recent works in this area include the analysis of Co/Ni systems, which is of special interest for spintronic applications, since this composition exhibits several magnetic properties that are not attainable with other combinations of metals (e.g. high spin polarization and low intrinsic magnetic damping) [131, 179, 334]. Co/Ni multilayers are in fact suitable candidates for the fabrication of spin-transfer torque magnetic random access memories (STT-MRAM), STT oscillators and bit-patterned media [39, 43, 131, 334]. The work of Arora et al. [131] showed experimentally and theoretically how variations in the type of substrate, buffer layer and number of stacked layers, help to adjust the magnetic anisotropy of Co/Ni systems. Similar experimental findings have been obtained by other authors for the same composition [334]. Further improvements to PMA have been achieved with the synthesis of Co-based multilayers. For example, an increase in the amplitude of PMA has been possible for a Co/Au system by promoting the formation of sharper interfaces and stress relaxation upon thermal annealing [335], while the measured PMA of a Co/Pt multilayer was doubled by accommodating thin layers of Cu and forming a three-layered structure (Co/Cu/Pt) [336]. In this case, the incorporation of the Cu layer obstructed the diffusion of Co and Pt.

4.3.3. Magnetic skyrmions in multilayered systems. The study of nanoscale magnetic materials stacked in a multilayer configuration led to the discovery of magnetic skyrmions. As depicted by Jang et al. [236], naturally occurring nanoscale noncollinear spin textures (such as magnetic domain walls and magnetic vortices) are present in bulk or magnetic nanostructured materials. They originate from the competition between different energy contributions: magnetic anisotropies, dipole interactions and exchange interactions [236]. In particular, the Néel-type and Bloch-type textures are of special interest. In the Néel-type textures, the spins inside the wall rotate as cycloidal spirals within the domain wall region, while in Bloch-type textures, the spins rotate as helical spirals [236, 337]. Both topological configurations of the magnetic moments are called magnetic skyrmions [338] and have been observed in NMMs as well as in ultrathin monolithic magnetic films [236, 255, 256]. They are stabilized in most cases by the Dzyaloshinskii-Moriya interaction energy, which results from spinorbit effects in the absence of inversion symmetry. At the atomic scale, the DMI energy is defined as $E_{\text{DMI}} = \mathbf{D} (\mathbf{S}_1 \times \mathbf{S}_2)$, where $\mathbf{D}$ is the DMI vector and $\mathbf{S}_1$ and $\mathbf{S}_2$ are two coupled spins. This interaction favors a perpendicular orientation of the spins, which matches the spatial distribution of the magnetic moments [256].

The reduced size of skyrmions and the possibility of controlling their motion by applying an electrical current of small density, makes them promising candidates for several types of non-volatile magnetic memory devices [250, 236, 254, 256, 337–343]. In such applications, the information could be coded by skyrmions in a magnetic nanoribbon (similar to the one employed in racetrack memories), and the spacing between bits could be of the order of magnitude of a few nanometers (close to the diameter of the skyrmion) [254, 256, 342]. Nevertheless, before moving forward to the fabrication of devices, several issues with regards to stabilization should be addressed, e.g. RT stability without the application of an external magnetic field [237, 343]. Until now, there are some successful reports showing the stabilization of magnetic skyrmions in NMMs [237, 337, 341], but only isolated skyrmions have been observed in such systems. Examples of promising multilayer systems include: Ir/Co/Pt [255, 344, 345], Pd/Co [237], Pt/Co/Ta [346], Ir/Fe/Co/Pt [341] and Cr/Fe/Cr/Ga [340]. Similar to the properties of GMR multilayers and PMA, the thickness of the individual layers and the symmetry at the interfaces play a crucial role for the detection of magnetic skyrmions [236]. Readers interested in further exploring specific details about this topic can survey [236, 254, 256, 337, 338, 341, 342].
of interest since these forms of radiation are all capable of displacing atoms from their crystalline lattice sites [113, 240, 347]. Such interactions modify the microstructure, composition and properties, and lead to detrimental long-term performance of the materials. These deleterious effects are of special importance for structural materials employed in the design of nuclear reactors [113, 162, 347].

Several studies, including a recent and extensive review by Zhang et al. [90] have shown that the interfaces, grain boundaries and free surfaces in nanostructured materials act as sinks for radiation-induced effects [86, 91, 113, 114, 162, 260, 348, 349]. However, unlike point defect impurities, these features cannot be annihilated [84, 87, 88]. Therefore, if He is introduced into the structure of a metal (even at trace quantities), it precipitates in the form of bubbles [85, 87, 88, 348, 350, 351]. Above a critical diameter (about 10 nm), He bubbles grow to capture vacancies and develop into voids that directly affect the integrity of the material, typically causing an increase in yield strength or embrittlement [114, 271, 348]. However, below the critical diameter, the bubbles remain stable and may be relatively benign [85, 114, 347] and can lead to an increase in hardness, since bubbles act as obstacles that impede dislocation motion [89, 114, 162, 348, 352], and increase in electrical resistivity [353]. Because of the multiple effects of He, ions of this element are usually employed to evaluate the radiation damage of materials [87, 354]. Another advantage offered by He bombardment is that at sufficiently high concentrations, He bubbles are resolved under focused TEM [85, 260, 351, 355], making it possible to trace the resulting impact by direct observation.

According to multiple studies, the existence of a significant number of interfaces in NMMs has been shown to enhance the tolerance of such structures to the damage caused by radiation [85, 88, 90, 260, 350]. However, the different interfaces exhibit different sink efficiencies due to the intrinsic defects that are inherent to their internal structure, which in turn are a direct consequence of their crystallographic character (as can be seen in figure 2 with the formation of different interfaces) [86, 350]. The available literature has concluded that semi-coherent interfaces are more efficient for alleviating He bubble formation [85, 90, 114, 157, 240, 260, 350] because they consist of alternating regions of coherency separated by networks of intrinsic defects known as misfit dislocations [155]. These dislocations are high-energy regions where He bubbles preferentially migrate and aggregate [91, 260, 350, 351, 356]. As a matter of fact, it has been observed that the density of misfit dislocations controls how much He can be stabilized and trapped at the interfaces [85, 260]. Contrasting studies have proposed that coherent multilayers comprising immiscible metals could be considered as efficient materials to mitigate radiation damage [90, 178, 204, 240]. This has been correlated to several factors, including: the possible creation of sinks due to the interaction of induced defects with coherent interfaces, the promotion of defect migration due to coherency stresses, and the alignment of He bubbles along the interfaces [90, 178]. Interestingly, the work of Chen et al. [204] presented evidence for the possible effectiveness of coherent interfaces by comparing the radiation damage of coherent and incoherent Cu/Fe multilayers, which were formed with layer thicknesses below 2.5 nm and above 5 nm, respectively. In their work, the density of He bubbles in the coherent Cu/Fe system was similar to that of the monolithic Cu layers, but the bubble diameter was smaller, indicating that radiation damage could be mitigated by reducing the size of the resulting bubbles. In addition, it has been determined that the radiation damage tolerance could be related to a decrease in the thickness of the multilayers, since the diffusion distance to the nearest sink is shortened [90]. The compilation of several NMMs that have been used to explore radiation damage is shown in table 4. For comparative purposes, the maximum computed values for dpa and He concentration (by SRIM) that could be accommodated within each system are presented. The classification of radiation-tolerant NMMs summarized in [90] could be used to complement the information presented herein.

The information presented in table 4 shows that the differences in the experimental conditions directly influence the response of the materials, which is reflected in the different ranges of damage (in dpa) and He concentrations that were measured in each case. The table also shows that similar irradiation damage and He concentrations were achieved by using Ag/Ni, Cu/Co, Cu/Fe and Cu/Mo multilayers, which were tested under identical conditions of fluence, implantation energy and repeated layer thickness (5 nm). Such outcomes prove the importance of defining standard experimental protocols to perform reliable comparative studies, which lead to the proper selection of promising systems for practical applications (including the use of NMMs for the fabrication of fuel cladding materials in nuclear reactors, as shown in figure 7(a)). Radiation damage studies have also been carried out using Al/Nb multilayers. However, this is a miscible system, which has been shown to result in the formation of intermetallic precipitates along the interfaces and therefore, its usage in this type of application is not recommended [167].

In general, most radiation studies have been carried out at RT, with the exception of some works exploring the behavior of Cu/Nb systems (performed at 450 °C and 480 °C). At RT, studies performed by Li et al. [87] indicate that the implanted area (obtained by SRIM) can be partitioned into three regions. In Region I (RI), defects are a consequence of the formation of vacancies. In Region II (RII), the formation of defects stems from the synergetic contributions of He atoms and vacancies (also matching the peak concentration of He), and in Region III (RIII) defects are dominated by the implantation of He atoms. All three phenomena lead to the development of clearly distinctive zones, which in figure 7(b) appear marked as areas where bubbles were observed or areas where bubbles were not observed. However, it can be shown that the radiation damage in NMMs is a temperature-dependent phenomenon that is associated with the mobilities of vacancies and implanted atoms. When the temperature during irradiation is increased, the evolution of these distinguishable regions takes place, which implies that the microstructure of the multilayer system changes and that the resulting radiation damage becomes more evident. This effect can be observed in figure 7(c) for a Cu/Nb system. In this case, as the temperature goes from RT up to 480 °C, the shape and size of the He bubbles
Table 4. Summary of different multilayer systems explored as possible compositions for radiation tolerance applications.

| Composition       | Layer thicknesses (nm) | Implantation energy (KeV) | Fluence (ions cm$^{-2}$) | Maximum displacement per atom (dpa) | Maximum He concentration (%)/* penetration depth (nm) | Reference |
|-------------------|------------------------|---------------------------|--------------------------|-------------------------------------|-------------------------------------------------------|-----------|
| Al/Nb             | 5/50                   | 100                       | $6 \times 10^{16}$       | 5                                   | 5–6/400                                               | [167]     |
| Ag/Ni             | 1–200                  | 100                       | $6 \times 10^{20}$       | 4                                   | 4/340                                                 | [357]     |
| Ag/V              | 4/6/10/20/35/50/75      | 33                        | $1 \times 10^{17}$       | 10                                  | 10/150                                                | [352]     |
| Cu/Co             | 1–200                  | 100                       | $6 \times 10^{20}$       | 2.5                                 | 3/350                                                 | [178]     |
| Cu/Fe             | 0.75/2.5/5/25/50/100   | 100                       | $6 \times 10^{20}$       | 2.5                                 | 3/350                                                 | [204]     |
| Cu/Mo             | 5                      | 100                       | $6 \times 10^{20}$       | –                                   | 4/300                                                 | [196]     |
| Cu/Nb             | 16/58                  | 200 (450 °C)              | $2 \times 10^{17}$/$6.5 \times 10^{17}$ | 16 | 11/550                                                | [358]     |
| Cu/V              | 20                     | 200 (20 °C/450 °C/480 °C) | $2 \times 10^{21}$       | 20                                  | 15/550                                                | [359]     |
| Cu/V              | 6/25                   | 33                        | $1.5 \times 10^{17}$     | 6–9 (@150 nm)                       | –                                                     | [91]      |
| Cu/V              | 50                     | 200                       | $2 \times 10^{21}$/$7 \times 10^{22}$ | 13 | 35/650                                                | [834]     |
| Cu/V              | 2.5/5/10               | 1000                      | $6 \times 10^{16}$       | 0.2                                 | 0.004/1                                               | [353]     |
| Cu/V              | 2.5/50                 | 50                        | $6 \times 10^{20}$       | 6                                   | 5/200                                                 | [360]     |
| Fe/W              | 1/5/20/50/200          | 100                       | $6 \times 10^{16}$       | 6                                   | 4/300                                                 | [348]     |

Figure 7. Schematic illustration showing: (a) the possible use of NMMs as cladding materials for the fabrication of fuel rods for nuclear reactors; damage caused by irradiation at (b) RT and (c) at elevated temperatures. Figures serve to display the distribution of defects along the implanted areas and how defects accommodate into the three characteristic regions that develop after exposure to radiation (b), as well as microstructural changes promoted by He ions as the temperature increases (c). (b) [196] Reprinted by permission of the publisher (Taylor & Francis Ltd, http://www.tandfonline.com). (c) Reprinted from [359], Copyright (2014), with permission from Elsevier.

Increased until the regular spherical bubbles transformed into irregular faceted cavities [162]. In the same way, with the rise in temperature, the coverage of the bubbles expanded continuously, thereby affecting a greater number of layers within the multilayer system, thus leading to the degradation of the structure. In contrast to high-temperature experiments, it has been observed that for the majority of the NMM systems studied at RT, the He bubbles preferentially develop at the interfaces or in one of the metals within the multilayer. Overall, studies suggest that it is necessary to perform further experimental tests at higher temperatures (in the range of those reached or expected during normal operating conditions), in order to understand the effects of radiation damage under these working conditions.

Other irradiation studies involving heavy ions of Kr$^{++}$ [354], Ar$^+$ [361] and Cu$^{3+}$ [240], as well as protons [357],
have also been performed for the study of ion implantation in Ag/Ni, Ta/Ti and Cu/Fe systems. All of the aforementioned studies presented similar findings to when He ions are used [90], where the multilayer configuration provides sites to accommodate the implanted particles, thus stabilizing the structure upon irradiation. Notwithstanding, the nature of the particles used for irradiation led to the existence of different defects compared to those found in the Ag/Ni multilayer system. Dislocation loops were observed after the Ag/Ni multilayer was irradiated with Kr$^{+}$ ions [354], while interstitials, vacancy loops and He bubbles were formed when the system was irradiated with protons [357] and He ions [357], respectively. The development of these contrasting defects could have different effects on the properties, e.g. deformation. Thus, exploring the response of equivalent systems upon irradiation using various energetic particles could be useful to achieve a deep understanding of microstructural and property alterations. Extensive information covering further details about damage in nuclear reactors [347], the design of radiation tolerant materials [84, 86, 90], as well as defect interface interactions [114], is available to complement the results and observations summarized in this section.

5. Emerging properties and applications for NMMs

Apart from their outstanding mechanical, optical and magnetic properties, NMMs have been shown to be suitable structures to explore other phenomena and applications of interest. Figure 8 presents a schematic illustration showing additional capabilities such as reactive multilayers, model systems to achieve and explore thermal stability in nanocrystalline materials, and as precursors for the development of new nanocrystalline and amorphous systems via thermal annealing and ion beam mixing (IBM). Further details about these areas are discussed in the following sections.

5.1. Reactive multilayers

 Reactive NMMs are energetic materials that store an excess of chemical energy, which originates from the energy of elastic stresses and free energy of the interfaces [127, 128, 144]. The accumulated energy can be released in an abrupt emission of light and heat when stimulated by an external source [31]. They usually comprise pure metals such as Al and Ni, and can be prepared by multiple synthesis methods, including sputtering, evaporation, ARB and electrodeposition [31, 121, 127, 128, 144, 362, 365–368]. The release of energy in reactive multilayers can be initiated by several techniques, including mechanical loading, thermal heating, laser heating or electrostatic discharge [31, 127, 128, 144, 365–368]. The ignition starts a self-propagating reaction that is characterized by a high-temperature wavefront that propagates through the multilayer, which then transforms reactants into products [121, 127, 128, 144]. As a result of the rapid release of energy, reactive NMMs have the potential to be used in brazing, localized soldering, fabrication of igniters, flares, neutralization of biological hazards, long-term thermal batteries and possibly as car airbag initiators [31, 127, 128, 144, 365–368]. Another promising application is for facilitating the synthesis of intermetallic materials that cannot be fabricated by other methods, e.g. the metastable PtAl$_5$ [128] and Al$_6$Ni$_{12}$ [127].

The velocity of propagation (wavefront velocity or rate) and the maximum combustion temperature of reactive multilayers depend on the thickness of the constituent layers...
and varies with different modes of initiation [31, 128, 144, 365–368]. Systems with bilayer thicknesses above 1000 nm exhibit slower propagation rates than systems with thinner layers, but it has been noted that systems with bilayer thicknesses below 40 nm, where diffusion at the interface usually takes place during growth, can display a reduction of the stored chemical energy. The intermixed interfaces can also act as diffusion barriers or modify the thermal properties of the systems [127, 144, 369]. It has also been observed that the energy required to ignite the NMMs depends on the thickness of the layers and on the composition [31, 128, 144, 362, 365–369], while the total heat output can be tailored by the choice of the number of repeated bilayers [127, 144].

Comprehensive reviews that include and compare multiple reactive multilayers, and cover details about the synthesis conditions, common characterization techniques, and the influence of intermixing, individual layer thicknesses and residual stresses on the reactivity of the systems, can be surveyed elsewhere in [31, 128, 144, 244, 261]. Of these results, the Al/Ni system is by far the most studied composition and was in fact the first material in which reactive ignition was observed [127, 128, 244, 261, 366]. Both Al/Ni as well as Ni$_{91.91}$V$_{0.09}$/Al multilayers are commercially available [31, 127, 362] and are both employed in soldering applications (see figure 8(a)). Other studied reactive systems include Ag/Ni [128], Ti/Al [370], B/Ti [371] and Ru/Al [368, 372], and their fabrication has been directed towards tailoring of the ignition temperature. For example, the recent work by Pauly et al [368] showed the possible reduction of the temperature required for ignition (with respect of a bimetal Ru/Al system) by up to $150 \, ^\circ \text{C}$, and a further reduction by up to $230 \, ^\circ \text{C}$ by the use of three-layered systems comprising Ru/Al/Ni and Ru/Al/Pt. These results suggest methodologies for controlling and/or customizing the ignition temperature of reactive systems by coupling more than two metals in a multilayer structure.

5.2. Thermal stability and high-temperature properties

Thermal stability plays an important role in retaining and prolonging the functionality of materials [35, 49, 93–96, 363, 373–377]. NMMs display the same thermal stability issues observed in nanocrystalline materials because of the presence of a high density of interfaces, which result in an excess of free energy [34, 377], and makes them prone to thermal transformations when subjected to an increase in temperature [35, 93–96, 375, 376]. Different interfaces are expected to have different levels of stability depending on the initial microstructure, the thermal properties of the individual layers [94, 95], as well as on their corresponding interface energies [378, 379]. Immiscible multilayer systems (with a positive enthalpy of formation), have been shown to degrade mainly by grain boundary grooving, which often results in pinch-off of the layers, followed by the spheroidization of the discontinuous layers [96, 160, 380]. Meanwhile, miscible systems degrade by interdiffusion across the interfaces, a process that often results in the formation of solid solution or intermetallic phases [96] due to the intermixing driving force associated with their negative enthalpy of formation [96, 381–383]. Multiple studies have investigated the thermal stability of NMMs and the majority of the reports have focused on monitoring the instability mechanisms involving interdiffusion, chemical reactions, phase transformations and deterioration of the properties upon exposure to temperature. Examples of such studies include the reported deterioration of the layered structure observed in Cu/Ni [384], Cu/V [380], Cu/Ta [160, 385], Cu/W [34, 377], Co/Cu [173] and Mo/V [386] systems, the partial oxidation of Nb/Ti [387] and Zr/Nb [222, 223] multilayers (see figure 8(b)), the formation of intermetallic phases in Nb/Ni [224, 277, 388], the loss of hardness reported for Pt/Mo [38], Cu/W, Cu/Cr and Cu/Mo systems [37, 222], as well as the decay of the magnetic moment in Co/Cu [104].

More specific studies have been carried out with the aim to explore and achieve the thermal stability of NMMs by employing kinetic and thermodynamic approaches that are used for the stabilization of nanocrystalline materials. The kinetic approach attempts to retard or stop the mobility of grain boundaries by adding second-phase particles or solutes, while the thermodynamic approach promotes the reduction of the driving force for grain growth by inducing solute segregation to the grain boundaries [49, 374, 375]. Misra et al [94] observed that the realignment of triple junctions in a zig–zag pattern effectively prevented pinch–off of Cu/Nb multilayers. Such stabilization processes take place only when the initial microstructure displays a specific stacked morphology, which affects the movement of triple junctions that is driven by the imbalance in tensions between the interphase and grain boundaries [95, 96]. In addition, Ma et al [93] observed that the stabilization of the highly coherent Cu/Ag system occurred by two different effects that depended on the heating temperature: at about $200 \, ^\circ \text{C}$ the development of grooves reached an equilibrium angle, then acting as drags to inhibit the boundary migration; above $300 \, ^\circ \text{C}$, the interface energy was lowered because twins developed at the interface. In a more recent study, Riano et al [49] showed that the stabilization of the Hf/Hf-Ta system was possible by developing a bimodal multilayer structure comprising columnar and brick-like grains. The stability of the columnar grains was increased by the presence of quadrupole points that locked the grain boundaries, as well as by the presence of semi-coherent Hf interfaces, which prevented recrystallization. These research studies highlight the existence of feasible routes to achieve NMMs that are stable even at elevated temperatures, thus, presenting strategies that could stimulate new studies and applications.

5.3. Nano multilayers as precursors for the synthesis of amorphous and nanocrystalline alloys

NMMs have been shown to be useful precursors for the synthesis of MGs with different compositions, as well as for the development of nanocrystalline alloys. Amorphous metallic alloys, characterized by a dense and disordered atomic structure and the absence of grain boundaries, have resulted in several outstanding properties, including good soft-magnetic properties, high specific strength, large elastic limits and improved wear and corrosion resistance [227, 389–394]. It is important to note that the term metallic glass is often used
interchangeably to refer to all synthesized amorphous alloys. According to the literature, the term metallic glass is used to refer to non-crystalline structures that result from the rapid cooling of a liquid melt (liquid-solid transformation), while the term amorphous alloy is generally employed when dealing with non-crystalline structures resulting from solid–solid or vapor-solid transitions e.g. sputtering, SPD, etc. Readers are encouraged to survey [394–396] for a complete description of MGs and amorphous alloys prepared via different processing methods and their respective characteristics and behavior. Additional information about the properties and applications of bulk MGs and thin-film MGs can be found in [389, 391, 397, 398].

The first amorphous alloy obtained from a multilayer system was produced in 1983 by Schwarz and Johnson via medium-temperature annealing using an initial La/Au structure [391, 399, 400], but soon after, IBM proved to be a more effective route for the synthesis of MGs [227, 364, 401]. The IBM method utilizes an ion beam (typically of inert gases) to induce atomic collisions that result in the intermixing of the metallic layers. Upon the removal of the source, the resulting mixture undergoes rapid relaxation, from which only amorphous or simple structure alloys can be obtained via solid-state phase transformations [227, 401]. The use of NMMs was rapidly considered a feasible strategy for the formation of MGs, since the desired alloys could be achieved at low temperatures (less than 100 °C) [394] and because of the vast range of compositions that could be realized through tuning the total thickness of the films, relative thickness of the constituent metals and thickness of each layer [227, 391, 402]. In fact, the glass formability of different multilayers, which is based on their enthalpy of mixing and maximum possible amorphization range, has been reviewed in detail by Liu et al. [227, 401]. This work includes a list of experimental reports in which MGs have been achieved via IBM from initial NMM systems such as Al/Ni, Au/Ti, Co/Mo, Fe/W and Nb/Zr.

Other quasicrystalline and metastable binary alloys have been obtained via IBM from Cu/Zr [364], Cu/W [403], Fe/Ag [404], Fe/Pt [253], Ag/Co and Ag/Ni multilayers [405]. For all of these systems, the composition of the formed phases was tuned by changing the individual layer thicknesses, number of layers and irradiation doses [364, 403, 404]. Thermal annealing has also been used for the same purpose. For instance, magnetic L1_1 CoPt and L1_0 FePt nanocrystalline and metastable alloys have been prepared from Co/Pt [406] and Fe/Pt [402, 407–409] systems, respectively, while TiNi alloys have been obtained from Ti/Ni multilayers [133, 410]. The fast formation of ordered phases was made possible due to the existence of shorter diffusion paths between the coupled metals, which were made available by using individual layer thicknesses in the order of only a few nanometers (0.2–3 nm) [405, 408, 409, 411].

More recently, equiaxed grain nanostructured alloys have resulted after annealing Hf-Ti/Ti [374, 376], Mo-Au/Au [363], Ta-Hf/Hf [49] and NiW/NiAlW [412] systems. For these compositions, the progression from nano multilayers to nanocrystalline films is driven by different thermally activated transformations (grain boundary relaxation, grain growth, recrystallization, solute segregation), which depend on the initial microstructure and composition of the multilayers (see figures 8(c) and (d)). According to those studies, the stability of the final microstructures was achieved either due to the addition of solutes at an equilibrium composition, which effectively decreased the grain boundary energy and prevented grain growth [374, 376], or due to the occurrence of grain relaxation and phase separation [412]. It is worth mentioning that the selection of the Hf-Ti/Ti [374, 376], Mo-Au/Au [363] and Ta-Hf/Hf [49] systems was based on the thermodynamic stability maps presented by Murdoch and Schuh [413, 414], which predict the feasibility of a binary alloy having a stable nanograin configuration; while the synthesis of NiW/NiAlW [412] was chosen due to the high solubility of W in Ni, which is known to facilitate solid solution strengthening. Collectively, these studies show that NMMs could be useful for the synthesis of nanostructured and amorphous alloys, as well as model systems for studying fundamental science phenomena such as thermal processes and mechanisms that influence nanograin stability.

6. Summary and outlook

Throughout this review, a wide range of studies have demonstrated the advantages of leveraging the stacked configuration of nanoscale metallic layers in different technological areas. This is in great part due to advances in the synthesis methods, which have allowed for the preparation of stacked layers with high purity and atomic-level precision. Along with the evolution of the synthesis routes, advances in the characterization methods have led to the development of dedicated techniques, enabling extensive characterization of the microstructure, properties and performance. The resulting NMMs can lead to strong materials, which exhibit high values of hardness and resist dislocation motion. Furthermore, magnetoresistance up to an order of magnitude larger than that measured in monolithic films has been obtained with the proper combination of magnetic and non-magnetic metals. The usage of crystalline metals in NMMs has enabled the development of highly reflective mirrors (with reflectivities in the range of 70%), which have improved the resolution of optical devices such as telescopes and microscopes. Radiation-tolerant materials have been developed to take advantage of misfit dislocations in semi-coherent interfaces, which act as sinks for impurities and defects. In addition, novel phenomena and properties in NMMs, such as the formation of magnetic skyrmions or the feasible release of stored chemical energy in multilayers, are promising for magnetic data storage and micro soldering applications, respectively. Amorphous and nanocrystalline alloys have been effectively formed by inducing solid-state reactions upon the exposure of NMMs to thermal annealing or IBM. Multilayer systems have been shown to be useful as thermodynamic stability models, since thermally stable nanostructures have been obtained by selecting the appropriate compositions. These outcomes suggest the possibility to synthesize materials that can maintain and prolong their properties even when subjected to elevated temperatures.
Overall, the current review highlights the properties and behavior observed in NMMs and how specific design factors play different roles in determining a particular behavior or property. However, independent of application or function, parameters such as composition, interface type, total number of layers, surface roughness, grain morphology and residual stresses simultaneously contribute to the performance of NMMs. Therefore, in order to fully take advantage of, as well as expand and improve the properties and applications offered by multilayer systems, a comprehensive understanding of the role of each of the aforementioned parameters is imperative, as discussed throughout this manuscript.

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References

[1] Dieny B 1994 Giant magnetoresistance in spin-valve multilayers J. Magn. Magn. Mater. 136 335–59
[2] Lebbad N, Voiron J, Nguyen B and Chainet E 1996 Electrodeposition of metallic multilayers with modulated electric regimes Thin Solid Films 275 216–19
[3] Tsymbal E Y and Pettifor D G 2001 Perspectives of giant magnetoresistance Solid State Phys. 56 133–237
[4] Himpsel F J, Ortega J E, Mankey G J and Willis R F 1998 Magnetic nanostructures Adv. Phys. 47 511–97
[5] Barbee T W 1988 Multilayer structures: atomic engineering in its infancy Physics, Fabrication, and Applications of Multilayered Structures ed P Dhzee and C Weisbuch (Boston, MA: Springer) pp 17–32
[6] Shen J, Gai Z and Kirschner J 2004 Growth and magnetism of metallic thin films and multilayers by pulsed-laser deposition Surf. Sci. Rep. 52 163–218
[7] Mastorakos I N, Bellou A, Bahr D F and Zibib H M 2011 Size-dependent strength in nanolaminate metallic systems J. Mater. Res. 26 1179–87
[8] Niu J J, Zhang J Y, Liu G, Zhang P, Lei S Y, Zhang G J and Sun J 2012 Size-dependent deformation mechanisms and strain-rate sensitivity in nanostructured (Cu/X Cr, Zr) multilayer films Acta Mater. 60 3677–89
[9] Schuller I K 1980 New class of layered materials Phys. Rev. Lett. 44 1597–600
[10] Jin B Y and Keterson J B 1989 Artificial metallic superlattices Adv. Phys. 38 189–366
[11] Arzt E 1998 Overview no. 130 - Size effects in materials due to microstructural and dimensional constraints: A comparative review Acta Mater. 46 5611–26
[12] Mattos D M 2010 Substrate (“Real”) surfaces and surface modification Handbook of Physical Vapor Deposition (PVD) Processing (Amsterdam: Elsevier) pp 25–72
[13] Hora J, Hall C, Evans D and Charrault E 2018 Inorganic thin film deposition and application on organic polymer substrates Adv. Eng. Mater. 20 18
[14] Palatnik L S and Ilinski A I 1969 Mechanical properties of metallic films Sov. Phys. Usp. 11 564–85
[15] Lloyd S J, Castellero A, Giuliani F, Long Y, McLaughlin K K, Molina-Aldareguia J M, Stelmashenko N A, Vanderpere L J and Clegg W J 2005 Observations of nanoindents via cross-sectional transmission electron microscopy: a survey of deformation mechanisms Proc. R. Soc. A 461 2521–43
[16] Makarov D, Melzer M, Karnaushenko D and Schmidt O G 2016 Shapeable magnetoelectronics Appl. Phys. Rev. 3 24
[17] PalDey S and Deevi S C 2003 Single layer and multilayer wear resistant coatings of (Ti,Al)N: a review Mater. Sci. Eng. A 342 58–79
[18] Ghanem M, Goken M and Merle B 2017 Plane-strain bulge testing of thin films under compressive residual stresses Surf. Coat. Technol. 327 167–73
[19] Yan W, Page A, Nguyen-Dang T, Qu Y, Sordo F, Wei L and Sorin F 2019 Advanced multimaterial electronic and optoelectronic fibers and textiles Adv. Mater. 31 1802348
[20] Loke G, Yan W, Khudiyev T, Noel G and Fink Y 2020 Recent progress and perspectives of thermally drawn multimaterial fiber electronics Adv. Mater. 32 1904911
[21] Chen H M and Liu R-S 2011 Architecture of metallic nanostructures: synthesis strategy and specific applications J. Phys. Chem. C 115 3513–27
[22] Kowel S T, Selfridge R, Elderling C, Matloff N, Stroeve P, Higgins B G, Srinivasan M P and Coleman L B 1987 Future applications of ordered polymer thin-films Thin Solid Films 152 377–403
[23] Falco C M 1988 Growth of metallic and metal-containing superlattices Physics, Fabrication, and Applications of Multilayered Structures ed P Dzhe and C Weisbuch (Boston, MA: Springer) pp 3–15
[24] El-Sayed M A 2001 Some interesting properties of metals confined in time and nanometer space of different shapes Accounts Chem. Res. 34 257–64
[25] Gjøs M A M and Bauer G E W 1997 Perpendicular giant magnetoresistance of metallic multilayers Adv. Phys. 46 285–445
[26] Hoagland R G, Mitchell T E, Hirth J P and Kung H 2002 On the strengthening effects of interfaces in multilayered composite materialsPhys. Mag. 82 643–64
[27] Lee S B, LeDonne J E, Lim S C V, Beyerlein I J and Rollett A D 2012 The heterogeneous interface character distribution of physical vapor-deposited and accumulative roll-bonded Cu-Nb multilayer composites Acta Mater. 60 1747–61
[28] Bronkhorst C A, Mayeur J R, Beyerlein I J, Mourad H M, Hansen B L, Mara N A, Carpenter J S, McCabe R J and Sintay S D 2013 Meso-scale modeling the orientation and interface stability of Cu/Nb-Layered composites by rolling JOM 65 431–42
[29] Arias-Égido E, Laguna-Marcos A, Sanchez-Marcos J, Piquer C, Chaboy J, Avila M and Lopez J G 2018 Microstructural and magnetic characterization of Fe- and Ir-based multilayers Phys. Rev. Mater. 2 014402
[30] Subedi S, Beyerlein I J, Lesar R and Rollett A D 2018 Strength of nanoscale metallic multilayers Scr. Mater. 145 132–6
[31] Weihs T P 2014 Fabrication and characterization of reactive multilayer films and foils Metallic Films for Electronic, Optical and Magnetic Applications ed K Barmak and K Coffey (Cambridge: Woodhead) pp 160–243
[32] Falco C M 1985 Metallic multilayers and superlattices Festkörperprobleme 25 ed P Grosse (Berlin: Springer) pp 531–7
[33] Hood R Q, Falicov L M and Penn D R 1994 Effects of interfacial roughness on the magnetoresistance of
magnetic multilayered materials. Phys. Rev. B 49 368–77

[34] Cancellieri C, Moszner F, Chiotti M, Yoon S, Janczak-Rusch J and Jeurgens I P H 2016 The effect of thermal treatment on the stress state and evolving microstructure of Cu/W nano-multilayers. J. Appl. Phys. 120 195107

[35] Bobeth M, Ullrich A and Pompe W 2004 Destratification mechanisms in coherent multilayers. J. Metastable Nanocryst. Mater. 19 153–78

[36] Economy D R, Cordill M J, Payzant E A and Kennedy M S 2015 Residual stress within nanoscale metallic multilayer systems during thermal cycling. Mater. Sci. Eng. A 648 289–98

[37] Monclus M A, Karlik M, Callisti M, Frutos E, Llorca J, Polcar T and Molina-Aldareguia J M 2014 Microstructure and mechanical properties of physical vapor deposited Cu/W nanoscale multilayers: influence of layer thickness and temperature Thin Solid Films 571 275–82

[38] Bellou A, Scudiero L and Bahr D F 2010 Thermal stability and strength of Mo/Pt multilayered films. J. Mater. Sci. 45 353–62

[39] Johnson M T, Bloemen P J H, denBroeder F J A and deVries J J 1996 Magnetic anisotropy in metallic multilayers Rep. Prog. Phys. 59 1409–58

[40] Piraux L, George J M, Despres J F, Leroy C, Ferain E, Legras R, Ounadjela K and Fert A 1994 Giant magnetoresistance in magnetic multilayered nanowires Appl. Phys. Lett. 65 2484–6

[41] Felser C, Fecher G H and Balke B 2007 Spintronics: A challenge for materials science and solid-state chemistry Angew. Chem. Int. Ed. 46 668–99

[42] Dieny B, Spieros V S, Parkin S S P, Gurney B A, Wilhoit D R and Mauri D 1991 Giant magnetoresistance in soft ferromagnetic multilayers Phys. Rev. B 43 1297–300

[43] Denbroeder F J A, Hoving W and Bloemen P J H 1991 Magnetic-Anisotropy of Multilayers J. Magn. Magn. Mater. 93 562–70

[44] Bass J and Pratt W P 1999 Current-perpendicular (CPP) magnetoresistance in magnetic multilayered materials J. Magn. Magn. Mater. 200 274–89

[45] Bass J and Pratt W P 2007 Spin-diffusion lengths in metals and alloys, and spin-flipping at metal/metal interfaces: an experimentalist’s critical review J. Phys.: Condens. Matter 19 41

[46] Camley R E and Stamps R L 1993 Magnetic multilayers - spin configurations, excitations and giant magnetoresistance J. Phys.: Condens. Matter 5 3727–86

[47] Stiles M D 1999 Interlayer exchange coupling J. Magn. Magn. Mater. 200 322–37

[48] Bakonyi I and Peter L 2010 Electrodeposited multilayer films with giant magnetoresistance (GMR): progress and problems Prog. Mater. Sci. 55 107–245

[49] Riano J S and Hodge A M 2019 Exploring the thermal stability of a bimodal nanoscale multilayered system Scr. Mater. 166 19–23

[50] Baibich M N, Broto J M, Fert A, Vanderschueren D, Petroff F, Eitenne P, Creuzet G, Friederich A and Chazelas J 1988 Giant Magnetoresistance of (001)Fe/(001)Cr Magnetic Superlattices Phys. Rev. Lett. 61 2472–5

[51] Binasch G, Grunberg P, Saurenbach F and Zinn W 1989 Enhanced magnetoresistance in layered magnetic-structures with antiferromagnetic interlayer exchange Phys. Rev. B 39 4828–30

[52] Grunberg P, Schreiber R, Pang Y, Walz U, Brooks M B and Sowers H 1987 Layered magnetic-structures - evidence for antiferromagnetic coupling of Fe layers across Cr interlayers J. Appl. Phys. 61 3750–2

[53] Misra A, Hirth J P and Hoagland R G 2005 Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites Acta Mater. 53 4817–24

[54] Zhang J Y, Lei S, Niu J, Liu Y, Liu G, Zhang X and Sun J 2012 Intrinsic and extrinsic size effects on deformation in nanolayered Cu/Ze micropillars: from bulk-like to small-volume materials behavior Acta Mater. 60 4054–64

[55] Yan J W, Zhu X F, Zhang G P and Yan C 2013 Evaluation of plastic deformation ability of Cu/Ni/W metallic multilayers Thin Solid Films 527 227–31

[56] Xu J, Kamiko M, Zhou Y, Lu G, Yamamoto R, Yu L and Kojima I 2002 Structure transformations and superhardness effects in V/ Ti nanostructured multilayers Appl. Phys. Lett. 81 1189–91

[57] Muhammad I, Fayyaz H, Muhammad R and Ahmad S A 2012 Molecular dynamics study of the mechanical characteristics of Ni/Cu bilayer using nanoindentation Chin. Phys. B 21 126802

[58] Yan J W, Zhu X F, Yang B and Zhang G P 2013 Shear stress-driven refreshing capability of plastic deformation in nanolayered metals Phys. Rev. Lett. 110 155502

[59] Zhang J Y, Niu J J, Xiong X, Zhang P, Liu G, Zhang G J and Sun J 2012 Tailoring nanostructured Cu/Cr multilayer films with enhanced hardness and tunable modulus Mater. Sci. Eng. A 543 139–44

[60] Wang F, Huang P, Xu M, Lu T J and Xu K W 2011 Shear banding deformation in Cu/Ta nano-multilayers Mater. Sci. Eng. A 572 7290–40

[61] Callisti M and Polcar T 2017 Combined size and texture-dependent deformation and strengthening mechanisms in Zr/Nb nano-multilayers Acta Mater. 124 247–60

[62] Frutos E, Callisti M, Karlik M and Polcar T 2015 Length-scale-dependent mechanical behaviour of Zr/Nb multilayers as a function of individual layer thickness Mater. Sci. Eng. A 632 137–46

[63] Was G S and Foecke T 1996 Deformation and fracture in microlaminates Thin Solid Films 286 1–31

[64] Jankowski A F 1992 Measurement of lattice strain in au-ni multilayers and correlation with biaxial modulus effects J. Appl. Phys. 71 1782–9

[65] Carpenter J S, Misra A and Anderson P M 2012 Achieving maximum hardness in semi-coherent multilayer thin films with unequal layer thickness Acta Mater. 60 2625–36

[66] Fu K K, Chang L, Yang C H, Sheppard L, Wang H J, Maandal M and Ye L 2017 Plastic behaviour of high-strength lightweight Al/Ti multilayered films J. Mater. Sci. 52 13956–65

[67] Economy D R, Mara N A, Schoepfner R L, Schultz B M, Unocic R R and Kennedy M S 2016 Identifying deformation and strain hardening behaviors of nanoscale metallic multilayers through nano-wear testing Metall. Mater. Trans. A-Phys. Metall. Mater. Sci. 47A 1083–95

[68] Nii H, Niibe M, Kinoshita H and Sugie Y 1998 Fabrication of Mo/Al multilayer films for a wavelength of 18.5 nm J. Synchrotron Radiat. 5 702–4

[69] Corsi A J and Pelizzo M G 2019 Extreme ultraviolet multilayer nanostructures and their application to solar plasma observations: a review J. Nanosci. Nanotechnol. 19 532–45

[70] Montcaltom C, Sullivan B T, Ranger M, Slaughter J M, Kearney P A, Falco C M and Chaker M 1994 Mo/Y multilayer mirrors for the 8–12-Nm wavelength region Opt. Lett. 19 1173–5

[71] Montcaltom C, Bajt S, Mirkarimi P B, Spiller E, Weber F J and Folta J A 1998 Multilayer reflective coatings for extreme-ultraviolet lithography SPIE. Proc. 3331
[72] Huang Q S et al 2017 High reflectance nanoscale V/Sc multilayer for soft x-ray water window region Sci. Rep. 7 12929

[73] Barysheva M M, Pestov A E, Salashchenko N N, Toropov M N and Chkhalo N I 2012 Precision imaging multilayer optics for soft x-rays and extreme ultraviolet bands Phys. Usp. 55 681–90

[74] Spiller E 1981 Evaporated multilayer dispersion elements for soft x-rays AIP Conf. Proc. 75 124

[75] Spiller E 1988 Multilayer optics for x-rays Physics, Fabrication, and Applications of Multilayered Structures ed P Dhez and C Weisbuch (Boston, MA: Springer) pp 271–309

[76] Folta J A et al 1999 Advances in multilayer reflective coatings for extreme-ultraviolet lithography Conf. on Emerging Lithographic Technologies III, (Santa Clara, Ca: SPIE-Int Soc Optical Engineering) pp 702–9

[77] Barbey T W 1986 Multilayers for x-ray optics Opt. Eng. 25 898–915

[78] Hermann C, Kosobukin V A, Lampel G, Peretti J, Safarov V I and Bertrand P 2001 Surface-enhanced magneto-optics in metallic multilayer films Phys. Rev. B 64 11

[79] Bogachev S A, Chkhalo N I, Kuzin S V, Pariev D E, Polkownikov V N, Salashchenko N N, Shestov S V and Zuev S Y 2016 Advanced materials for multilayer mirrors for extreme ultraviolet solar astronomy Appl. Opt. 55 2126–35

[80] Kortright J B 1986 Multilayer reflectors for the extreme ultraviolet spectral region Nucl. Instrum. Methods Phys. Res. Sect. A-Acel. Spectrom. Decl. Assoc. Equip. 246 344–7

[81] Aurongzeb D, Holm T, Berg J M, Chandoulu A and Temkin H 2005 The influence of interface roughness on electrical transport in nanoscale metallic multilayers J. Appl. Phys. 98 5

[82] Rizal C, Moa B and Niraula B B 2016 Ferromagnetic multilayers: magnetoresistance, magnetic anisotropy, and beyond Magnetochemistry 2 32

[83] Diercks D, Svalov A V, Kaufman M, Vaskovskiy V O and Kurylanskaya G V 2010 Structure and electrical resistivity of sputtered Tb/Ti and Tb/Si magnetic multilayers IEEE Trans. Magn. 46 1515–18

[84] Beyerlein I J, Caro A, Demkowicz M J, Mara N A, Misra A and Uberuaga B P 2013 Radiation damage tolerant nanomaterials Mater. Today 16 443–9

[85] Demkowicz M J, Misra A and Caro A 2012 The role of interface structure in controlling high helium concentrations Cure. Opin. Solid State Mater. Sci. 16 101–8

[86] Han W Z, Demkowicz M J, Mara N A, Fu E G, Sinha S, Rollett A D, Wang Y Q, Carpenter J S, Beyerlein I J and Misra A 2013 Design of radiation tolerant materials via interface engineering Adv. Mater. 25 6975–9

[87] Li N, Demkowicz M J and Mara N A 2017 Microstructure evolution and mechanical response of nanolaminate composites irradiated with helium at elevated temperatures JOM 69 2206–13

[88] Misra A, Demkowicz M J, Zhang X and Hoagland R G 2007 The radiation damage tolerance of ultra-high strength nanolayered composites JOM 59 62–65

[89] Misra A, Zhang X, Demkowicz M J, Hoagland R G and Nastasi M 2009 Design of nano-composites for ultra-high strength and radiation damage tolerance MRS Proceedings 1188 1188-LL06-01

[90] Zhang X H et al 2018 Radiation damage in nanostructured materials Prog. Mater. Sci. 96 217–321

[91] Zhernenkov M, Gill S, Stanic V, DiMasi E, Kisslinger K, Baldwin J K, Misra A, Demkowicz M J and Ecker L 2014 Design of radiation resistant metallic multilayers for advanced nuclear systems Appl. Phys. Lett. 104 4

[92] Roldan Cuenya B et al 2008 High-energy phonon confinement in nanoscale metallic multilayers Phys. Rev. B 77 165410

[93] Ma Y J, Wei M Z, Sun C, Cao Z H and Meng X K 2017 Length scale effect on the thermal stability of nanoscale Cu/Ag multilayers Mater. Sci. Eng. A 686 142–9

[94] Misra A and Hoagland R G 2005 Effects of elevated temperature annealing on the structure and hardness of copper/niobium nanolayered films J. Mater. Res. 20 2046–54

[95] Wan H B, Shen Y, He X and Wang J 2013 Modeling of microstructure evolution in metallic multilayers with immiscible constituents JOM 65 443–9

[96] Wan H B, Shen Y, Wang J, Shen Z Q and Jin X J 2012 A predictive model for microstructure evolution in metallic multilayers with immiscible constituents Acta Mater. 60 6869–81

[97] Yu-Zhang K, Embury J D, Han K and Misra A 2008 Transmission electron microscopy investigation of the atomic structure of interfaces in nanoscale Cu-Nb multilayers Phil. Mag. 88 2559–57

[98] Medyanik S N and Shao S A 2009 Strengthening effects of coherent interfaces in nanoscale metallic bilayers Comput. Mater. Sci. 45 1129–33

[99] Xiang M Z, Liao Y, Wang K, Lu G and Chen J 2018 Shock-induced plasticity in semi-coherent 111 Cu-Ni multilayers Int. J. Plast. 103 23–38

[100] Wang Y, Zhu X Y, Liu G M and Du J 2017 Strain rate sensitivity of CuNi and Cu/Nb nanoscale multilayers Acta Metall. Sin. 53 183–91

[101] Clemens B M and Hufnagel T C 1993 Amorphous-allys formed by solid-state reaction J. Alloys Compd. 194 221–7

[102] Li N, Mara N A, Wang J, Dickerson P, Huang J Y and Misra A 2012 Ex situ and in situ measurements of the shear strength of interfaces in metallic multilayers Scr. Mater. 67 479–82

[103] Zhang J Y, Liu G, Lei S Y, Niu J J and Sun J 2012 Transition from homogenenous-like to shear-band deformation in nanolayered crystalline Cu/amorphous Cu–Zr micropillars: intrinsic vs extrinsic size effect Acta Mater. 60 7183–96

[104] Gupta M, Gupta A, Amir S M, Stahn J and Zegenhagen J 2010 Effect of Ag as a surfactant on the thermal stability in Cu/Co multilayers J. Phys.: Conf. Ser. 211 012020

[105] Beyerlein I J, Mayeur J R, Zheng S J, Mara N A, Wang J and Misra A 2014 Emergence of stable interfaces under extreme plastic deformation Proc. Natl Acad. Sci. USA 111 4386–90

[106] Abdolrahim N, Mastorakos I N and Zbib H M 2012 Precipitate strengthening in nanostructured metallic material composites Phil. Mag. Lett. 92 597–607

[107] Abdolrahim N, Zbib H M and Bahr D F 2014 Multiscale modeling and simulation of deformation in nanoscale metallic multilayer systems Int. J. Plast. 52 33–50

[108] Wang J and Misra A 2011 An overview of interface-dominated deformation mechanisms in metallic multilayers Cure. Opin. Solid State Mater. Sci. 15 20–28

[109] Ross C A 1994 Electrodeposited multilayer thin-films Annu. Rev. Mater. Sci. 24 159–88

[110] Snel J, Monclus M A, Castillo-Rodriguez M, Mara N, Beyerlein I J, Llorca J and Molina-Aldareguia J M 2017 Deformation mechanism map of Cu/Nb nanoscale metallic multilayers as a function of temperature and layer thickness JOM 69 2214–26

[111] Wang J, Zhou Q, Shao S and Misra A 2017 Strength and plasticity of nanolaminated materials Mater. Res. Lett. 5 1–19
[112] Beyerlein I J and Wang J 2019 Interface-driven mechanisms in cubic/noncubic nanolaminates at different scales MRS Bull. 44 31–39

[113] Was G S and Andresen P L 2014 Radiation damage to structural alloys in nuclear power plants: mechanisms and remediation Structural Alloys for Power Plants ed A Shrizadi and S Jackson (Cambridge: Woodhead Publishing) pp 355–420

[114] Beyerlein I J, Demkowicz M J, Misra A and Uberuaga B P 2015 Defect-interface interactions Prog. Mater. Sci. 74 125–210

[115] Zbib H M, Overman C T, Akasheh F and Bahr D 2011 Analysis of plastic deformation in nanoscale metallic multilayers with coherent and incoherent interfaces Int. J. Plast. 27 1618–39

[116] Zhou Q, Xie J Y, Wang F, Huang P, Xu K W and Lu T J 2015 The mechanical behavior of nanoscale metallic multilayers: A survey Acta Mech. Sin. 31 319–37

[117] Mastorakos I N, Zbib H M and Bahr D F 2009 Deformation mechanisms and strength in nanoscale multilayer metallic composites with coherent and incoherent interfaces Appl. Phys. Lett. 94 34

[118] Shao S A and Medyanik S N 2010 Dislocation-interface interaction in nanoscale fcc metallic bilayers Mech. Res. Commun. 37 315–19

[119] Holmstrom E, Nordstrom L, Bergqvist L, Skubic B, Hjorvarsson A, Abriskovs I A, Svedlinnd P and Eriksson O 2004 On the sharpness of the interfaces in metallic multilayers Proc. Natl Acad. Sci. USA 101 4742–5

[120] Gumbsch P and Daw M S 1991 Interface stresses and their effects on the elastic-moduli of metallic multilayers Phys. Rev. B 44 3934–8

[121] Baras F and Politano O 2011 Molecular dynamics simulations of nanometric metallic multilayers: reactivity of the Ni-Al system Phys. Rev. B 84 5

[122] Chamani M, Farrahi G H and Movahhedy M R 2016 Molecular dynamics simulation of nanoindentation of nanocrystalline Al/Ni multilayers Comput. Mater. Sci. 112 175–84

[123] Chen S D, Zhou Y K and Soh A K 2012 Molecular dynamics simulations of mechanical properties for Cu(001)/Ni(001) twist boundaries Comput. Mater. Sci. 61 239–42

[124] Lu L, Huang C, Pi W L, Xiang H G, Gao F S, Fu T and Peng X H 2018 Molecular dynamics simulation of effects of interface imperfections and modulation periods on Cu/Ta multilayers Comput. Mater. Sci. 143 63–70

[125] Wang J, Hoagland R G, Hirth J P and Misra A 2008 Atomistic modeling of the interaction of glide dislocations with “weak” interfaces Acta Mater. 56 5685–93

[126] Zhou X L and Chen C Q 2015 Molecular dynamic simulations of the mechanical properties of crystalline/crystalline and crystalline/amorphous nanolayered pillars Comput. Mater. Sci. 101 194–204

[127] Baras F, Turlo V, Politano O, Vadchenko S G, Rogachev A S and Mukasyan A S 2018 SHS in Ni/Al nanofoils: a review of experiments and molecular dynamics simulations Adv. Eng. Mater. 20 20

[128] Rogachev A S 2008 Exothermic reaction waves in multilayer nanofilms Russ. Chem. Rev. 77 21

[129] Schweitz K O, Chevallier J, Bottiger J, Matz W and Schell N 2001 Hardness in Ag/Ni, Au/Ni and Cu/Ni multilayers Phil. Mag. 81 2021–32

[130] Zhang J Y, Wu K, Zhang L Y, Wang Y Q, Liu G and Sun J 2017 Unraveling the correlation between Hall-Petch slope and peak hardness in metallic nanolaminates Int. J. Plast. 96 120–34

[131] Arora M, Hubner R, Suess D, Heinrich B and Girt E 2017 Origin of perpendicular magnetic anisotropy in Co/Ni multilayers Phys. Rev. B 96 13

[132] Chun S Y, Chayahara A and Posselt M 2004 Limitations on ultra-thin multilayers: pulsed cathodic arc and computer simulation Surf. Coat. Technol. 182 171–4

[133] Shi J, Cao Z H, Liu Y and Zhao Z P 2017 Size dependent alloying and plastic deformation behaviors of Ti/Ni nano-multilayers J. Alloys Compd. 727 691–5

[134] Misra A, Kung H and Embury J D 2004 Preface to the viewpoint set on: deformation and stability of nanoscale metallic multilayers Scr. Mater. 50 707–10

[135] Bellou A, Overman C T, Zbib H M, Bahr D F and Misra A 2011 Strength and strain hardening behavior of Cu-based bilayers and trilayers Scr. Mater. 64 641–4

[136] Polyakov M N, Lohmiller J, Gruber P A and Badawi K F 2004 Elastic constants investigation by x-ray diffraction of in situ deformed metallic multi-layers Scr. Mater. 50 723–7

[137] Hardwick D A 1987 The mechanical-properties of thin-films - a review Thin Solid Films 154 109–24

[138] Barnas J and Palasanzetas G 1997 Interface roughness effects in the giant magnetoresistance in magnetic multilayers J. Appl. Phys. 82 3950–6

[139] Goudeau P, Villain P, Girardeau T, Renault P O and Badawi K F 2004 Elastic constants investigation by x-ray diffraction of in situ deformed metallic multi-layers Scr. Mater. 50 723–7

[140] Fert A 2008 Nobel Lecture: origin, development, and future of spintronics Rev. Mod. Phys. 80 1517–30

[141] Rizal C and Niraula B B 2016 Ferromagnetic alloys: magnetoresistance, microstructure, magnetism, and beyond J. Nano Electron. Phys. 2 22

[142] Jankowski A F 1995 Metallic multilayers at the nanoscale Nanostruct. Mater. 6 179–90

[143] Shahidi S, Mozazencheli B and Ghoranneviss M 2015 A review-application of physical vapor deposition (PVD) and related methods in the textile industry Eur. Phys. J. Appl. Phys. 71 13

[144] Adams D P 2015 Reactive multilayers fabricated by vapor deposition: A critical review Thin Solid Films 576 98–128

[145] Sáenz-Trevizo A et al 2018 Functional nanostructured oxides: synthesis, properties, and applications Emerging Applications of Nanoparticles and Architecture Nanostructures ed A Barhoum and A S H Makhlof (Amsterdam: Elsevier) pp 29–69

[146] Barna P B and Radzoci C 2014 Structure formation during deposition of polycrystalline metallic thin films Metallic Films for Electronic, Optical and Magnetic Applications ed K Barmak and K Coffey (Cambridge: Woodhead Publishing) pp 67–120

[147] Carpenter J S, Vogel S C, LeDonne J E, Hammond D L, Beyerlein I J and Mara N A 2012 Bulk texture evolution of Cu-Nb nanolamellar composites during accumulative roll bonding Acta Mater. 60 1576–86

[148] Azushima A et al 2008 Severe plastic deformation (SPD) processes for metals CIRP Ann-Manuf. Technol. 57 716–35

[149] Bachmaier A and Pippin R 2013 Generation of metallic nanocomposites by severe plastic deformation Int. Mater. Rev. 58 41–62

[150] Beyerlein I J, Mara N A, Wang J, Carpenter J S, Zheng S J, Han W Z, Zhang R F, Kang K, Nizolek T and Pollock T M 2012 Structure-property-functionality of bimetal interfaces JOM 64 1192–207

[151] Knezevic M, Nizolek T, Ardeljan M, Beyerlein I J, Mara N A and Pollock T M 2014 Texture evolution in two-phase Zr/Nb lamellar composites during accumulative roll bonding Int. J. Plast. 57 16–28
[152] Rizal C, Gyawali P, Kshattry I and Pokharel R K 2012 Strain-induced magnetoresistance and magnetic anisotropy properties of Co/Cu multilayers J. Appl. Phys. 111 3

[153] Shima M, Salamanca-Riba L G, McMichael R D and Moffat T P 2001 Correlation between structural imperfections and giant magnetoresistance in electrodeposited Co/Cu multilayers J. Electrochem. Soc. 148 C518–23

[154] Ueda Y, Houga T, Zaman H and Yamada A 1999 Magnetoresistance effect of Co–Cu nanostructure prepared by electrodeposition method J. Solid State Chem. 147 274–80

[155] Zheng S, Shao S, Zhang J, Wang Y Q, Demkowicz M J, Beyerlein I J and Mara N A 2015 Adhesion of voids to bimetal interfaces with non-uniform energies Sci. Rep. 5 8

[156] Shen T D, Schwarz R B and Zhang X 2005 Bulk nanolaminate composites Acta Mater. 53 938–44

[157] Wang M, Beyerlein I J, Zhang J and Han W Z 2018 Defect-interface interactions in irradiated Cu/Ag nanocomposites Acta Mater. 160 211–23

[158] Rafaja D, Schimpf C, Klemm Y, Schreiber G, Bakonyi I and Peter L 2009 Formation of microstructural defects in electrodeposited Co/Cu multilayers Acta Mater. 57 3211–22

[159] Li J J, Lu W J, Zhang S Y and Raabe D 2017 Large strain synergetic material deformation enabled by hybrid nanolayer architectures Sci. Rep. 7 11371

[160] Zeng L F, Gao R, Fang G F, Wang X P, Xie Z M, Miao S, Hao T and Zhang T 2016 High strength and thermal stability of bulk Cu/Ta nanolamellar multilayers fabricated by cross accumulative roll bonding Acta Mater. 110 341–51

[161] Ramezani M G, Demkowicz M J, Feng G and Rutner M P 2017 Joining of physical vapor-deposited metal nanolayered composites Scr. Mater. 139 114–18

[162] Yang L X, Zheng S J, Zhou Y T, Zhang J, Wang Y Q, Jiang C B, Mara N A, Beyerlein I J and Ma X L 2017 Effects of He radiation on cation distribution and hardness of bulk nanolayered Cu-Nb composites J. Nucl. Mater. 487 311–16

[163] Kim Y, Budiman A S, Baldwin J K, Mara N A, Misra A and Han S M 2012 Microcompression study of Al-Nb nanoscale multilayer films Mater. J. Res. 27 592–9

[164] Lucadamo G, Barmak S, Hyun S, Cabral C and Lavoie C 1999 Evidence of a two-stage reaction mechanism in sputter deposited Nb Al multilayer thin-films studied by in situ synchrotron X-ray diffraction Mater. Lett. 39 268–73

[165] Polyakov M N, Coutoios-Manara E, Wang D, Chakravathanaka K, Kubel C and Hodge A M 2013 Microstructural variations in Cu/Nb and Al/Nb nanometallic multilayers Appl. Phys. Lett. 102 4

[166] Fu E G, Li N, Misra A, Hoagland R G, Wang H and Zhang X 2008 Mechanical properties of sputtered Cu/Al and Al/Nb multilayer films Mater. Sci. Eng. A 493 283–7

[167] Li N, Martin M S, Andergoul O, Misra A, Shao L, Wang H and Zhang X 2009 He ion irradiation damage in Al/Nb multilayers J. Appl. Phys. 105 8

[168] Aboufaddl H, Gallino I, Busch R and Mucklich F 2016 Atomic scale analysis of phase formation and diffusion kinetics in Ag/Al multilayer thin films J. Appl. Phys. 120 13

[169] Mingxia L, Fei M, Gengrong C, Binfeng H, Fuxing F, Fangxia Y, Lijun Y, Jun D and Kewei X 2017 Asymmetric Intermixing and the stress buildup in Ni/Al-type nanomultilayer with different characteristic scales Rare Met. Mater. Eng. 46 3222–7

[170] Cekada M, Panjan M, Cimplic D, Kovac J, Panjan P, Dolinkse J and Zalar A 2009 Analysis of the diffusion processes in Al/Cr, Al/Fe and Cr/Fe multilayers using the MRI model Vacuum 84 147–51

[171] Kingetsu T and Sakai K 1993 Perpendicular magnetic anisotropy and structures of epitaxial Co Ag and Co Au metallic superlattices J. Appl. Phys. 73 7622–6

[172] Parkin S S P, More N and Roche K P 1990 Oscillations in exchange coupling and magnetoresistance in metallic superlattice structures - Co/Ru, Co Cr and Fe/Cr Phys. Rev. Lett. 64 2304–7

[173] Bobeth M, Hecker M, Pompe W, Schneider C M, Thomas J, Ullrich A and Wetzig K 2001 Thermal stability of nanoscale Co/Cu multilayers Z. Metall. K. 92 810–19

[174] Hecker M, Pitschke W, Tietjen D and Schneider C M 2002 X-ray diffraction investigations of structural changes in Co/Cu multilayers at elevated temperatures Thin Solid Films 411 234–9

[175] Degronckel H A M, Kopinka K, Dejonge W J M, Panissod P, Schafers F, Yulin S, Feigl T and Kaiser N 2003 Chromium-scandium multilayer window mirrors for the LCLS Opt. Lett. 28 1910–3

[176] Mathon J, Villaret M, Umerski A, Muniz R B, Castro J D and Edwards D M 1997 Quantum-well theory of the exchange coupling in magnetic multilayers with application to Co/CuCo(001) Phys. Rev. B 65 11797–809

[177] Zhu X Y, Luo J T, Chen G, Zeng F and Pan F 2010 Size dependence of creep behavior in nanoscale Cu/Co multilayer thin films J. Alloys Compd. 506 434–40

[178] Chen Y, Liu Y, Fu E G, Sun C, Xu K Y, Song M, Li J, Wang Y Q, Wang H and Zhang X 2015 Unusual size-dependent strengthening mechanisms in helium ion-irradiated immiscible coherent Cu/Co nanolayers Acta Mater. 84 393–404

[179] Girod S, Gottwald M, Andrieu S, Mangin S, McCord J, Fullerton E E, Beaumont J M L, Krishnatreya B J and Kent A D 2009 Strong perpendicular magnetic anisotropy in Ni/Co(111) single crystal superlattices Appl. Phys. Lett. 94 3

[180] Zhang J Y, Lei S, Liu Y, Niu J J, Chen Y, Liu G, Zhang X and Sun J 2012 Length scale-dependent deformation behavior of nanolayered Cu/Ze micropillars Acta Mater. 60 1610–22

[181] Niu J J, Zhang P, Wang R H, Zhang J Y, Liu G, Zhang G J and Sun J 2012 Formation of multiple twins and their strengthening effect in nanocrystalline Cu/Ze multilayer films Mater. Sci. Eng. A 539 68–73

[182] Eriksson F, Johansson G A, Hertz H M, Gullikson E M, Kreissig I and Birch J 2003 14.5% near-normal incidence reflectance of Co/Sc x-ray multilayer mirrors for the water window Opt. Lett. 28 2494–6

[183] Kuhlmann T, Yulin S, Feigt I, Kaiser N, Goretik T, Kaiser U and Richter W 2002 Chromium-scandum multilayer mirrors for the nitrogen K-alpha line in the water window region Appl. Opt. 41 2048–52

[184] Schaifers F, Yulin S, Feigt I and Kaiser N 2003. At-wavelength metrology on Sc-based multilayers for the UV and water window SPIE Proc. 5188 138–45

[185] Vella J B, Mann A B, Kung H, Chien C L, Weihs T P and Cammarata R C 2004 Mechanical properties of nanostuctured amorphous metal multilayer thin films J. Mater. Res. 19 1840–8

[186] Carpenter J S, Zheng S J, Zhang R F, Vogel S C, Beyerlein I J and Mara N A 2013 Thermal stability of Cu-Nb nanolamellar composites fabricated via accumulative roll bonding Phil. Mag. 93 718–35

[187] Nizolek T J, Begley M R, McCabe R J, Avallone J T, Mara N A, Beyerlein I J and Pollock T M 2017 Strain fields induced by kink band propagation in Cu-Nb nanolaminate composites Acta Mater. 133 303–15
metallic multilayer thin films Mater. Res. Lett. 3 114–19

[225] Kong Y, Shen L M, Shen Y G and Chen Z 2016 Interfacial effect on strengthening nanoscale metallic multilayers - a combined Hall-Petch relation and atomistic simulation study Mater. Sci. Eng. A 663 29–37

[226] Schuller I K 1988 The physics of metallic superlattices: an experimental point of view Physics, Fabrication, and Applications of Multilayered Structures ed P Dhez and C Weisbuch (Boston, MA: Springer) pp 139–69

[227] Liu B X, Lai W S and Zhang Q 2000 Irradiation induced amorphization in metallic multilayers and calculation of glass-forming ability from atomistic potential in the binary metal systems Mater. Sci. Eng. R Rep. 29 1–48

[228] Genc A, Banerjee R, Thompson G B, Maher D M, Johnson A W and Fraser H L 2009 Complementary techniques for the characterization of thin film Ti/Nb multilayers Ultramicroscopy 109 1276–81

[229] Kelly D M, Fullerton E E, Santamaria J and Schuller I K 1995 A simple closed-form expression for the x-ray reflectivity from multilayers with cumulative roughness Scr. Metall. Materialia 33 1603–8

[230] Beyerlein I J et al 2013 Interface-driven microstructure development and ultra high strength of bulk nanostructured Cu-Nb multilayers fabricated by severe plastic deformation J. Mater. Res. 28 1799–812

[231] Tadayyon S M, Yoshinari O and Tanaka K 1992 Auger-electron spectroscopy and x-ray-diffraction study of interdiffusion and solid-state amorphization of Ni/Ti multilayers Jpn. J. Appl. Phys. J 31 2226–32

[232] Tanaka K, Tanaka H and Kawaguchi H 2002 Effects of hydrogenation on interlayer reactions in metallic multilayers J. Alloys Compd. 330 256–61

[233] Etienne P, Massies J, Lequien S, Cabanel R and Petroff F 1991 Molecular-beam epitaxial-growth of Cr/Fe, Ag/Fe,Ag/Cr and Ag/Co Superlattices on Mgo (001) Substrates J. Cryst. Growth 111 1003–10

[234] Yang P, Klemradt U, Tao Y, Peisl J, Peng R W, Hu A and Jiang S S 1999 Long-term stability of a quasiperiodic Ta Al multilayer: disintegration at room temperature analyzed by grazing angle x-ray scattering and photoelectron spectroscopy J. Appl. Phys. 86 267–74

[235] Karoutous V 2009 Scanning Probe Microscopy: instrumentation and Applications on Thin Films and Magnetic Multilayers J. Nanosci. Nanotechnol. 9 6783–98

[236] Jiang W J, Chen G, Liu K, Zang J D, Te Velthuis S G E and Misra A 2017 Skyrmions in magnetic multilayers Phys. Rep. 704 1–49

[237] Brandao J, Dugato D A, Seeger R L, Denardin J C, Mori T J and Czar J C 2019 Observation of magnetic skyrmions in unpatterned symmetric multilayers at room temperature and zero magnetic field Sci. Rep. 9 4144

[238] Bahr D F and Gerberich W W 1996 Plastic zone and pileup around large indentations Metall. Trans. A 27 3793–800

[239] Guo Q Y, Wan L, Yu X X, Vogel F and Thompson G B 2017 Influence of phase stability on the in situ growth stresses in Cu/Nb multilayered films Acta Mater. 132 149–61

[240] Chen Y, Li N, Bufford D C, Li J, Hattar K, Wang H and Zhang X 2016 In situ study of heavy ion irradiation response of immiscible Cu/Fe multilayers J. Nucl. Mater. 475 274–9

[241] Aydiner C C, Brown D W, Mara N A, Almer J and Misra A 2009 In situ x-ray investigation of freestanding nanoscale Cu-Nb multilayers under tensile load Appl. Phys. Lett. 94 3

[242] Liu J P et al 2017 X-ray reflectivity measurement of interdiffusion in metallic multilayers during rapid heating J. Synchrotron Radiat. 24 796–801

[243] Trenkle J C, Koerner L J, Tate M W, Walker N, Gruner S M, Weits T P and Hufnagel T C 2010 Time-resolved x-ray microdiffraction studies of phase transformations during rapidly propagating reactions in Al/Ni and Zr/Ni multilayer foils J. Appl. Phys. 107 12

[244] Trenkle J C, Koerner L J, Tate M W, Gruner S M, Weits T P and Hufnagel T C 2008 Phase transformations during rapid heating of Al/Ni multilayer foils Appl. Phys. Lett. 93 3

[245] Wheeler J M, Armstrong D E J, Heinz W and Schwaiger R 2015 High temperature nanoindentation: the state of the art and future challengesCurr. Opin. Solid State Mater. Sci. 19 354–66

[246] Akarapu S, Zbib H M and Bahr D F 2010 Analysis of heterogeneous deformation and dislocation dynamics in single crystal micropillars under compression Int. J. Plast. 26 239–57

[247] Bahr D F, Woodcock C L, Pang M, Weaver K D and Moody N R 2003 Indentation induced film fracture in hard film-soft substrate systems Int. J. Fract. 119 339–49

[248] Sebastiani M, Johanns K E, Herbert E G and Pharr G M 2015 Measurement of fracture toughness by nanoindentation methods: recent advances and future challenges Curr. Opin. Solid State Mater. Sci. 19 324–33

[249] Overman N R, Overman C T, Zbib H M and Bahr D F 2009 Yield and deformation in biaxially stressed multilayer metallic thin films J. Eng. Mater. Technol.-Trans. ASME 131 6

[250] Mara N A, Bhattacharyya D, Hirth J P, Dickerson P and Misra A 2010 Mechanism for shear banding in nanolayered composites Appl. Phys. Lett. 97 3

[251] Budiman A S, Han S M, Li N, Wei Q M, Dickerson P, Tamura N, Kunz M and Misra A 2012 Plasticity in the nanoscale Cu/Nb single-crystal multilayers as revealed by synchrotron Laue x-ray microdiffraction J. Mater. Res. 27 599–611

[252] Budiman A S, Narayanan K R, Li N, Wang J, Tamura N, Kunz M and Misra A 2015 Plasticity evolution in nanoscale Cu/Nb single-crystal multilayers as revealed by synchrotron x-ray microdiffraction Mater. Sci. Eng. A 635 6–12

[253] Marynowska A, Misuina P, Lewinska S, Dynowska E, Wawro A, Sla wheksa-Waniewska A, Botterg R, Fassbender J and Baczewski L T 2018 Modification of structural and magnetic properties in Fe/Pt (111)-oriented multilayers with ion beam irradiation Nucl. Instrum. Methods Phys. Res. B 415 136–41

[254] Chen G 2018 Magnetic skyrmions in thin films Topology in Magnetism ed J Zang et al (Berlin: Springer) pp 117–50

[255] Moreau-Luchaire C et al 2016 Additive interfacial chiral interaction in multilayers for stabilization of small individual skyrmions at room temperature Nat. Nanotechnol. 11 444–8

[256] Wiesendanger R 2016 Nanoscale magnetic skyrmions in metallic films and multilayers: a new twist for spintronics Nat. Rev. Mater. 1 11

[257] Huang Q S et al 2016 High reflectance Cr/V multilayer with B4C barrier layer for water window wavelength region Opt. Lett. 41 701–4

[258] Prascielo M, Leontowich A F G, Beyerlein K R and Bajt S 2014 Thermal stability studies of short period Sc/Cr and Sc/B4C/Sc multilayers Appl. Opt. 53 2126–35

[259] Fabian D J, Watson L M and Marshall C A W 1971 Soft x-ray spectroscopy and the electronic structure of solids Rep. Prog. Phys. 34 601

[260] Kashinath A, Wang P, Majewski J, Baldwin J K, Wang Y Q and Demkowicz M J 2013 Detection of helium bubble formation at fcc-bcc interfaces using neutron reflectometry J. Appl. Phys. 114 8
[261] Swaminathan P, Grapes M D, Woll K, Barron S C, LaVan D A and Wehrs T P 2013 Studying exothermic reactions in the Ni-Al system at rapid heating rates using a nanocalorimeter J. Appl. Phys. 113 8

[262] Kochler J S 1970 Attempt to design a strong solid Phys. Rev. B 2 547

[263] Fang Q, Tian Y, Li J, Wang Q and Wu H 2019 Interface-governed nanometric machining behaviour of Cu/Ag bilayers using molecular dynamics simulation RSC Adv. 9 1341–53

[264] Ghosh S K, Limaye P K, Swain B P, Soni N L, Agrawal R G, Dusane R O and Grover A K 2007 Tribological behaviour and residual stress of electrodeposited Ni/Cu multilayer films on stainless steel substrate Surf. Coat. Technol. 201 4609–18

[265] Wang J and Misra A 2014 Strain hardening in nanolayered thin films Curr. Opin. Solid State Mater. Sci. 18 19–28

[266] Misra A, Hirth J P and Kung H 2002 Single-dislocation-based strengthening mechanisms in nanoscale metallic multilayers Phil. Mag. A 82 2935–51

[267] Misra A and Kung H 2001 Deformation behavior of nanostructured metallic multilayers Adv. Eng. Mater. 3 9

[268] Misra A, Verdier M, Kung H, Embury J D and Hirth J P 1999 Deformation mechanism maps for polycrystalline metallic multilayers Scr. Mater. 41 973–9

[269] Misra A, Verdier M, Lu Y C, Kung H, Mitchell T E, Nastasi N and Embury J D 1998 Structure and mechanical properties of Cu-X (X = Nb,Cr,Ni) nanolayered composites Scr. Mater. 39 555–60

[270] Cui Y, Li N and Misra A 2019 An overview of interface-dominated deformation mechanisms in metallic nanocomposites elucidated using in situ straining in a TEM J. Mater. Res. 34 1469–78

[271] Zhou Q, Ren Y, Du Y, Hua D P and Han W C 2018 Cracking and toughening mechanisms in nanoscale metallic multilayer films: a brief review Appl. Sci. 8 33

[272] Wen S P, Zong R L, Zeng F, Gao Y and Pan F 2007 Evaluating modulus and hardness enhancement in evaporated Cu/W multilayers Acta Mater. 55 345–51

[273] Wei M Z, Shi J, Ma Y J, Cao Z H and Meng X K 2016 The ultra-high enhancement of hardness and elastic modulus in Ag/Nb multilayers Mater. Sci. Eng. A 651 155–9

[274] Pathak S, Velisavljevic N, Baldwin J K, Jain M, Zheng S J, Mara N A and Beyerlein I J 2017 Strong, ductile, and thermally stable bcc-Mg Nanolaminates Sci. Rep. 7 9

[275] Fu K K, An X H, Chang L, Sheppard L, Yang C H, Wang H J and Ye L 2017 Ultra-high specific strength and deformation behavior of nanostructured Ti/Al multilayers J. Phys. D: Appl. Phys. 50 7

[276] Ardeljan M, Knezevic M, Jain M, Pathak S, Kumar A, Li N, Mara N A, Baldwin J K and Beyerlein I J 2018 Room temperature deformation mechanisms of MgNb nanolayered composites J. Mater. Res. 33 23

[277] Scheppeper R L, Abdolrahim N, Salehinia I, Zbib H M and Bahr D F 2014 Elevated temperature dependence of hardness in tri-metallic nano-scale metallic multilayer systems Thin Solid Films 571 247–52

[278] Mara N A, Bhattacharyya D, Dickerson P, Hoagland R G and Misra A 2008 Deformability of ultrahigh strength 5 nm Cu/Nb nanolayered composites Appl. Phys. Lett. 92 3 217–22

[279] Mara N A, Bhattacharyya D, Dickerson P, Hoagland R G and Misra A 2010 Ultrahigh strength and ductility of Cu-Nb nanolayered composites Ductility of Bulk Nanostructured Materials 633 4 647–53

[280] Huang H B and Spaepen F 2000 Tensile testing of free-standing Cu, Ag and Al thin films and Ag/Cu multilayers Acta Mater. 48 3261–9

[281] Zhang J Y, Zhang X, Wang R H, Lei S Y, Zhang P, Niu J J, Liu G, Zhang G J and Sun J 2011 Length-scale-dependent deformation and fracture behavior of Cu/X (X=Nb, Zr) multilayers: the constraining effects of the ductile phase on the brittle phase Acta Mater. 59 7368–79

[282] Gao N, Wang C T, Wood R J K and Langdon T G 2012 Tribological properties of ultratine-grained materials processed by severe plastic deformation J. Mater. Sci. 47 4779–97

[283] Madhavan R, Bellon P and Averback R S 2018 Wear resistance of Cu/Ag multilayers: a microscopic study ACS Appl. Mater. Interfaces 10 15288–97

[284] Luo Z P, Zhang G F and Schwaiger R 2015 Microstructural vortex formation during cyclic sliding of Cu/Au multilayers Scr. Mater. 107 67–70

[285] Ma Y, Peng G J, Feng Y H and Zhang T H 2017 Nanoidentation investigation on creep behavior of amorphous Cu-Zr-Al/nano crystalline Cu nanolaminates J. Non-Cryst. Solids 465 8–16

[286] Mu J-W, Sun S-C, Jiang Z-H, Lian J-S and Jiang Q 2013 Dislocation-mediated creep process in nanocrystalline Cu Chin. Phys. B 22 037703

[287] Stoudt M R, Ricker R E and Cammarata R C 2001 The influence of a multilayered metallic coating on fatigue crack nucleation Int. J. Fatigue. 33 5215–523

[288] Voronov D L, Anderson E H, Gullikson E M, Salmassi F, Warwick T, Yashchuk V V and Padmore H A 2012 Ultra-high efficiency multilayer blazed gratings through deposition kinetic control Opt. Lett. 37 1628–30

[289] Windt D L 2015 EUV multilayer coatings for solar imaging and spectroscopy SPIE. Proc. 9604

[290] Svechnikov M V et al 2018 Influence of barrier interlayers on the performance of Mo/Be multilayer mirrors for next-generation EUV lithography Opt. Express 26 33718–31

[291] Xu D C et al 2015 Enhancement of soft x-ray reflectivity and interface stability in nitridated Pu/Y multilayer mirrors Opt. Express 23 33018–26

[292] Walker A B C, Lindblom J F, Oneal R H, Hoover R B and Barbee T W 1990 Astronomical observations with normal incidence multilayer optics - recent results and future-prospects Phys. Scr. 41 1053–62

[293] Lemen J R et al 2012 The atmospheric imaging assembly (AIA) on the solar dynamics observatory (SDO) Sol. Phys. 275 17–40

[294] Makhontkin I A, Zoethout E, van de Kruis R, Yakunin S N, Louis E, Yakunin A M, Banine V, Mullender S and Bijkker F 2013 Short period Lu/B and La/NB multilayer mirrors for similar to 6.8 nm wavelength Opt. Express 21 29894–904

[295] Montcalm C, Kearney P A, Slaughter J M, Sullivan B T, Chaker M, Pepin H and Falco C M 1996 Survey of T-, B-, and Y-based soft x-ray extreme ultraviolet multilayer mirrors for the 2- to 12-nm wavelength region Appl. Opt. 35 5134–47

[296] Sarkar P, Biswas A, De R, Rao K D, Ghosh S, Modi M H, John S, Barshilia H C, Bhattacharyya D and Sahoo N K 2017 Performance of Co/Ti multilayers in a water window soft x-ray regime Appl. Opt. 56 7525–32

[297] Falco C M and Slaughter J M 1993 Characterization of metallic multilayers for x-ray optics J. Magn. Magn. Mater. 126 3–7

[298] Chikalho N I, Parv D E, Polkovnikov V N, Salashchenko N N, Shaposhnikov A, Strooula I L, Svechnikov M V, Vainer Y A and Zuev S Y 2017 Be/Al-based multilayer mirrors with improved reflection and spectral selectivity for solar astronomy above 17 nm wavelength Thin Solid Films 631 106–11
[299] Zhu J T, Zhou S K, Li H C, Huang Q S, Wang Z S, Le Guen K, Hu M H, Andre J M and Jonnard P 2010 Comparison of Mg-based multilayers for solar He II radiation at 30.4 nm wavelength Appl. Opt. 49 3922–5

[300] Nii H, Miyagawa M, Matsuoy Sugi Y, Nii M and Kinoshita H 2002 Control of roughness in Mo/Al multilayer film fabricated by DC magnetron sputtering Jpn. J. Appl. Phys. 41 5338–41

[301] Skulina K M, Alford C S, Bionta R M, Makowiecki D M, Guillikon E M, Souli F, Kortright J B and Underwood J H 1995 Molybdenum beryllium multilayer mirrors for normal incidence in the extreme-ultraviolet Appl. Opt. 34 3727–30

[302] Sac-Lao B and Montcalm C 2001 Molybdenum-strontium multilayer mirrors for the 8–12-nm extreme-ultraviolet wavelength region Opt. Lett. 26 468–70

[303] Kozhevnkov I V et al 1994 Synthesis and measurement of normal incidence x-ray multilayer mirrors optimized for a photon energy of 390 eV NaCl. Instrum. Methods Phys. Res. Sect. A 345 594–603

[304] Mertins H C, Schaefer F, Grimmer H, Demens D, Boni P and Hörtscher M 1998 W/C, W/Ti,Ni/Ti, and Ni/V multilayers for the soft-x-ray range: experimental investigation with synchrotron radiation Appl. Opt. 37 1873–82

[305] Li H C, Zhu J T, Zhou S K, Wang Z S, Chen H, Jonnard P, Le Guen K and Andre J M 2013 Zr/Mg multilayer mirror for extreme ultraviolet application and its thermal stability Appl. Phys. Lett. 102 111103

[306] Hatano T, Ejima T and Tsuru T 2017 Cr/Sc/Mo multilayer for condenser optics in water microscopes J. Electron Spectros. Relat. Phenom. 220 14–16

[307] Kuznetsova D S, Yakshin A E, Sturm J M, van de Kruis R W E, Louis E and Bijkker F 2015 High-reflectance La/B-based multilayer mirror for 6.6 nm wavelength Opt. Lett. 40 5778–81

[308] Kuznetsova D S, Yakshin A E, Sturm J M, van de Kruis R W E and Bijkker F 2016 Structure of high-reflectance La/B-based multilayer mirrors with partial La nitridation AIP Adv. 6 115117

[309] Zhu J T, Zhou S K, Li H C, Wang Z S, Jonnard P, Le Guen K, Hu M H, Andre J M, Zhou H J and Huo T L 2011 Thermal stability of Mg/Co multilayer with B4C, Mo or Zr diffusion barrier layers Opt. Express 19 21849–54

[310] Nechay A N et al 2018 Study of oxidation processes in Mo/Be multilayers AIP Adv. 8 12

[311] Zhong Q et al 2012 Al/Zr multilayer mirror and its thermal stability for EUV application J. Phys.: Conf. Ser. 425 152010

[312] Singh M and Braat J J M 2000 Design of multilayer extreme-ultraviolet mirrors for enhanced reflectivity Appl. Opt. 39 2189–97

[313] Chkhlo N I and Salashchenko N N 2013 Next generation nanolithography based on Ru/Be and Rh/Sr multilayer optics AIP Adv. 3 9

[314] Windt D L, Donguy S, Seely J, Kjornrattanawanich B, Guillikon E M, Walton C C, Golub L and DeLuca E 2003 EUV multilayers for solar physics SPIE. Proc. 5168

[315] Stearns D G, Rosen R S and Vernon S P 1993 Multilayer mirror technology for soft-x-ray projection lithography Appl. Opt. 32 6952–60

[316] Jain J P, Vijay Y K, Malhotra L K and Uppadhyay K S 1988 Hydrogen storage in thin-film metal hydride - a review Int. J. Hydrog. Energy 13 15–23

[317] Huiberts J N, Griessen R, Rector J H, Wijngaarden R J, Dekker J P, deGroot D G and Koenman N J 1996 Yttrium and lanthanum hydride films with switchable optical properties Nature 380 231–4

[318] Giebels I A M E, Isidorsson J, Kooij E S, Remhof A, Koenman N J, Rector J H, van Gogh A T M and Griessen R 2002 Highly reflecting Y/Mg–Hx multilayered switchable mirrors J. Alloys Compd. 330–332 575–81

[319] Aruna I, Malhotra L K and Mehta B R 2006 Switchable Metal Hydride Films Handbook on the Physics and Chemistry of Rare Earths ed K A Gschneidner et al (Amsterdam: Elsevier) pp 83–279

[320] van der Sluis P 1998 Optical switches of gadolinium-magnesium multilayers Appl. Phys. Lett. 73 1826–8

[321] Vermeulen P, Wondergem H J, Graat P C J, Borsa D M, Schreuders H, Dam B, Griessen R and Notten P H L 2008 In situ electrochemical XRD study of (de)hydrogenation of MgyTi100−y thin films J. Mater. Chem. 18 3680–7

[322] Prinz G A 1998 Device physics – magnetoelectronics Science 282 1660–3

[323] Zheng C et al 2019 Magnetoresistive sensor development roadmap (non-recording applications) IEEE Trans. Magn. 55 80

[324] Tian Y F and Yan S S 2013 Giant magnetoresistance: history, development and beyond Sci. China-Phys. Mech. Astron. 56 2–14

[325] Thomson T 2014 Magnetic properties of metallic thin films Metallic Films for Electronic, Optical and Magnetic Applications ed K Barmak and K Barmak and K Coffey (Cambridge: Woodhead Publishing) pp 454–546

[326] Barthelemy A et al 2002 Magnetoresistance and spin electronics J. Magn. Magn. Mater. 242 68–76

[327] Heremans J J 1993 Solid-State Magnetic-Field Sensors and Applications J. Phys. D: Appl. Phys. 26 1149–68

[328] Inokata K 1998 Giant magnetoresistance and its sensor applications J. Electroceram. 2 283–93

[329] Daughton J M 1999 GMR applications J. Magn. Magn. Mater. 192 334–42

[330] Wolf S A, Awschalom D B, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chichielkanova A Y and Treger D M 2001 Spintronics: A spin-based electronics vision for the future Science 294 1488–95

[331] Parkin S, Jiang X, Kaiser C, Panchula A, Roche K and Samant M 2003 Magnetically engineered spintronic sensors and memory Proc. IEEE 91 661–80

[332] Prinz G A 1999 Magnetoelectronics applications J. Magn. Magn. Mater. 200 57–68

[333] Ennen I, Kappe D, Rempel T, Glesne C and Hutton A 2016 Giant magnetoresistance: basic concepts, microstructure, magnetic interactions and applications Sensors 16 24

[334] Andreu S et al 2018 CoNi multilayers for spintronics: high spin polarization and tunable magnetic anisotropy Phys. Rev. Mater. 2 064410

[335] Rizal C, Moa B, Wingert J and Shpyrko O G 2015 Magnetic anisotropy and magnetoresistance properties of Co/Au Multilayers IEEE Trans. Magn. 51 1

[336] Bandiera S, Sousa R C, Rodmacq B and Dinesy B 2012 Enhancement of perpendicular magnetic anisotropy through reduction of Co-Pt interdiffusion in (Co/Pt) multilayers Appl. Phys. Lett. 100 4

[337] Fert A, Reyren N and Cros V 2017 Magnetic skyrmions: advances in physics and potential applications Nat. Rev. Mater. 2 15

[338] Kovalev A A and Sandhoefner S 2018 Skyrmions and antiskyrmions in quasi-two-dimensional magnets Front. Phys. 6 8

[339] Parkin S and Yang S H 2015 Memory on the racetrack Nat. Nanotechnol. 10 195–8

[340] Chesnokov Y M, Vasilev A L, Prutskov G V, Pashaev E M, Subbotin I A, Kravtsov E A and Ustinov V V 2017
Microstructure of periodic metallic multilayer systems Thin Solid Films 632 79–87

[341] Soumyanarayan A et al 2017 Tunable room-temperature magnetic skyrmions in Ir/Fe/Co/Pt multilayers Nat. Mater. 16 898

[342] Ferri A, Gus V and Sampaio J 2013 Skyrmions on the track Nano. Technol. 8 152–6

[343] Lin S Z, Reichhardt C and Saxena A 2013 Manipulation of skyrmions in nanodisks with a current pulse and skyrmion rectifier Appl. Phys. Lett. 102 5

[344] Legrand W, Maccariello D, Reyren N, Garcia K, Moutafis C, Moreau-Luchaire C, Coffin S, Bouzehouane K, Cros V and Fert A 2017 Room-temperature current-induced generation and motion of sub-100 nm skyrmions Nano. Lett. 17 2703–12

[345] Maccariello D, Legrand W, Reyren N, Garcia K, Bouzehouane K, Collin S, Cros V and Fert A 2018 Electrical detection of single magnetic skyrmions in metallic multilayers at room temperature Nat. Nanotechnol. 13 233–7

[346] Woo S et al 2016 Observation of room-temperature magnetic skyrmions and their current-driven dynamics in ultrathin metallic ferromagnets Nat. Mater. 15 501–6

[347] Zinkle S J and Was G S 2013 Materials challenges in nuclear energy Acta. Mater. 61 735–58

[348] Li N, Fu E G, Wang H, Carter J J, Shao L, Maloy S A, Misra A and Zhang X 2009 He ion irradiation damage in Fe/W nanolayer films J. Nucl. Mater. 389 233–8

[349] Zeng L F, Fan P, Zhang L F, Gao R, Xie Z M, Fang Q F, Wang X F, Yuan D Q, Zhang T and Liu C S 2018 He irradiation effects in bulk Cu/V nanolayered composites fabricated by cross accumulative roll bonding J. Nucl. Mater. 508 554–60

[350] Chen D, Li N, Yuryev D, Wen J, Baldwin K, Demkowicz M J and Wang Y Q 2017 Imaging the in-plane distribution of helium precipitates at a Cu/V interface Mater. Res. Lett. 5 335–42

[351] Kashinath A, Misra A and Demkowicz M J 2013 Stable storage of helium in nanoscale platelets at semicoherent interfaces Phys. Rev. Lett. 110 5

[352] Wei Q M, Li N, Ma R, Nastasi M and Misra A 2011 Suppression of irradiation hardening in nanoscale V/Ag multilayers Acta. Mater. 59 6331–40

[353] Wang P P, Xu C, Fu E G, Du J L, Gao Y, Wang X J and Qiu Y H 2018 The study on the electrical resistivity of Cu/V multilayer films subjected to helium (He) ion irradiation Appl. Surf. Sci. 440 396–402

[354] Yu K Y, Sun C, Chen Y, Liu Y, Wang H, Kirk M A, Li M and Zhang X 2013 Superior tolerance of Ag/Ni multilayers against Kr ion irradiation: an in situ study Phil. Mag. 93 3547–62

[355] Li N, Yu K Y, Lee J, Wang H and Zhang X 2010 Size dependent strengthening mechanisms in sputtered Fe/W multilayers J. Appl. Phys. 107 10

[356] Chen Y, Liu Y, Sun C, Yu K Y, Song M, Wang H and Zhang X 2012 Microstructure and strengthening mechanisms in Cu/Fe multilayers Acta. Mater. 60 6312–21

[357] Yu K Y, Liu Y, Fu E G, Wang Y Q, Myers M T, Wang H, Shao L and Zhang X 2013 Comparisons of radiation damage in He ion and proton irradiated immiscible Ag/Al nanolayers J. Nucl. Mater. 440 310–18

[358] Zhang J Y, Zeng F L, Wu K, Wang Y Q, Liang X Q, Liu G, Zhang G J and Sun J 2016 Size-dependent plastic deformation characteristics in He-irradiated nanostructured Cu/Mo multilayers: competition between dislocation-boundary and dislocation-bubble interactions Mater. Sci. Eng. A 673 530–40

[359] Han W Z, Mara N A, Wang Y Q, Misra A and Demkowicz M J 2014 He implantation of bulk Cu-Nb nanocomposites fabricated by accumulated roll bonding J. Nucl. Mater. 452 570–60

[360] Fu E G, Carter J, Swadener G, Misra A, Shao L, Wang H and Zhang X 2009 Size dependent enhancement of helium ion irradiation tolerance in sputtered Cu/V nanolaminates J. Nucl. Mater. 385 620–22

[361] Milosavljevic M, Persudo D, Milinovic V, Stojanovic Z, Zalar A, Kovac J and Jeynes C 2010 Ion irradiation stability of multilayered AlN/TiN nanocomposites J. Phys. D: Appl. Phys. 43 6

[362] Braeuer J, Besser J, Tomoscheit E, Klimm D, Anbumani S, Wiemer M and Gessner T 2012 Investigation of different nano scale energetic material systems for reactive wafer bonding ECS Trans. 50 241

[363] Babena J A, Sebastian Riano J, Chellali M R, Boll T and Hodge A M 2018 Thermally activated microstructural evolution of sputtered nanostructured Mo–Al Materialia 4 157–65

[364] Wang T L, Huang W T, Wang W C and Liu B X 2010 Ion beam mixing to study the metallic glass formation of the Cu-Zr system Mater. Lett. 64 96–98

[365] Manukyan K, Pauls J, Shuck C, Rouvimov S, Mukasyan A, Nazaretyan K, Chhatly H and Kharatyan S 2018 Kinetics and mechanism of ignition in reactive Al/Ni nanostructured materials J. Phys. Chem. C 122 27082–92

[366] Schnabel V, Sologubenko A S, Danzi S, Kurtuldu G and Spolenak R 2017 Controlling diffusion in Ni/Al reactive multilayers by Nb-alloying Appl. Phys. Lett. 111 5

[367] Maj L, Morigel J, Mars K, Tarasek A and Godlewksa E 2018 Shear strength of reactive resistance welded Ti6Al4V parts with the use of Ni(V)/Al multilayers Metall. Mater. Trans. A-Phys. Metall. Mater. Sci. 49A 5423–7

[368] Pauly C, Woll K, Gallino I, Stuber M, Leiste H, Busch R and Mucklich F 2018 Ignition in ternary Ru/Al-based reactive multilayers-Effects of chemistry and stacking sequence J. Appl. Phys. 124 9

[369] Ramos A S, Cavaleiro A J, Vieira M T, Morigel J and Safran G 2014 Thermal stability of nanoscale metallic multilayers Thin Solid Films 571 268–74

[370] Sen S, Lake M, Wilden J and Schaaf P 2017 Synthesis and characterization of Ti/Al reactive multilayer films with various molar ratios Thin Solid Films 631 99–105

[371] Zhang Y X, Wang Y, Ai M T, Jiang H C, Yan Y C, Zhao X H, Wang L, Zhang W L and Li Y R 2018 Reactive B/Ti nano-multilayers with superior performance in plasma generation ACS Appl. Mater. Interfaces 10 21582–9

[372] Woll K, Bergamaschi A, Avchachov K, Djurabekova E, Gier S, Pauly C, Leibenguth P, Wagner C, Nordlund K and Mucklich F 2016 Ru/Al multilayers integrate maximum energy density and ductility for reactive materials Sci. Rep. 6 10

[373] Lewis A C, Josell D and Weins T P 2003 Stability in thin film multilayers and microlaminals: the role of free energy, structure, and orientation at interfaces and grain boundaries Scr. Mater. 48 1079–85

[374] Riano J S and Hodge A M 2018 Exploring the microstructural evolution of Hi-Ti: from nanometalllic multilayers to nanostructures Scr. Mater. 142 55–60

[375] Andriesvski R A 2014 Review of thermal stability of nanomaterials J. Mater. Sci. 49 1449–60

[376] Polyakov M N, Chookajorn T, Mecklenburg M, Schuh C A and Hodge A M 2016 Sputtered Hi-Ti nanostructures: A segregation and high-temperature stability study Acta Mater. 108 8–16

[377] Moszner F, Cancellieri C, Chiodi M, Yoon S, Ariosa D, Janczak-Rusz J and Jeurgens L P H 2016 Thermal stability of Cu/W nano-multilayers Acta Mater. 107 345–53
