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PHYSICO-CHEMICAL PROPERTIES OF AMORPHOUS COBALT-BASED ALLOYS: A REVIEW

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Cobalt based amorphous alloys have garnered significant attention due to their unique properties and wide-ranging applications. This review article provides an extensive overview of cobalt alloys, discussing their physicGo-chemical characteristics and diverse applications in various industries. The influence of alloying elements on the properties of cobalt alloys, such as enhanced corrosion resistance and improved mechanical strength, is explored. Furthermore, the article examines the effects of heat treatment on the microstructure and magnetic properties of cobalt alloys, highlighting the importance of tailored heat treatment processes for optimizing their performance. The review also delves into emerging trends in the field, including the utilization of cobalt alloys in additive manufacturing and their potential for sustainable materials design.

Keywords: amorphous alloys, cobalt, magnetic, corrosion, annealing.

Introduction

Amorphous metal alloys (AMAs) have garnered significant attention as a distinct class of materials due to their unique atomic structure and exceptional properties. Unlike crystalline alloys, which exhibit a highly ordered arrangement of atoms, amorphous alloys possess a disordered atomic arrangement, resembling a "frozen liquid" [1]. This distinct structure imparts them with a wide range of intriguing characteristics, such as high strength, excellent corrosion resistance, enhanced soft magnetic properties, and remarkable thermal stability. Depending on the main element, amorphous metal alloys are good materials for hydrogen storage, electrochemical catalysis, the core material in various electronic devices, and corrosion protection [2, 3].

This review aims to examine the wide range of properties exhibited by amorphous alloys based on Cobalt. Through a comprehensive examination of the physic-chemical properties and applications of amorphous alloys, this review will contribute to a deeper understanding of these fascinating materials and their potential for technological advancements in various fields.

Mechanical properties

Cobalt-based alloys typically have high tensile strength, good ductility, and excellent fatigue resistance. These alloys also exhibit good thermal conductivity and can withstand thermal cycling without significant degradation. Amorphous alloys Zr–Co–Cu–Al are investigated as a source for making surgical equipment due to their ultra-high strength by authors [4]. After annealing nanoscale structural heterogeneity in $Fe_{80-x}M_xSi_9B_{11}$

amorphous alloys (M = Co and Ni; $x = 0, 2, 4$) increases with Ni substitution but decreases with higher Co content, and this variation affects the plastic deformation ability and microhardness differently for Ni and Co-doped alloys [5]. At higher annealing temperatures and thicker film thicknesses, the conduction of electron carriers becomes less restricted, leading to lower electric resistivity and sheet resistance values [6]. As the thickness increases, there is a noticeable decrease in the hardness of the material. This behavior can be attributed to various factors, such as grain size, dislocation density, and the presence of defects, which can all contribute to the overall hardness of the material [7].

Thermal Modifications

One of the important issues in the research of such alloys is the study of their transformation from an amorphous state to a crystalline state, particularly into a nanocrystalline state. During heat treatment of amorphous Co based materials, various phases such as CoB, CoSi, Co_2Si, ferromagnetic Co_2B and paramagnetic Co_5Si_2B [8] can form (Table 1). Upon the first crystallization event in the $Co_{69.5}Fe_{5.25}Si_{10}B_{15}$ alloy, cobalt-rich phases such as fcc-Co and hcp-Co emerge, while Co_2B and Co_2Si are subsequently formed during the second crystallization event [9]. The $Co_{77}Si_{11.5}B_{11.5}$ amorphous alloy experiences secondary crystallization, leading to grain coarsening. It is observed that the crystallization process initiates at the surface of the amorphous ribbons, and the altered electrochemical behavior is attributed to an increased rate of silicon diffusion, possibly resulting in the deposition and growth of a continuous and protective SiO_2 film [10]. The change in activation energy during the isothermal process suggests that small Co particles emerge in the supercooled liquid region, acting as crystallization nuclei and reducing the activation energy at the onset of crystallization [11].

The behavior of alloys during heating is significantly influenced by the presence of various elements. The introduction of Co modifies the crystallization mechanism in the $(Fe_3Co_1)_{81}Sn_7B_{12}$ alloy, initially leading to growth with an increasing nucleation rate, followed by growth with a decreasing nucleation rate until the nucleation rate reaches zero, after which the subsequent crystallization stage is governed by the growth of pre-existing nuclei [23]. The lattice constant, crystallization volume fraction, and grain size decreased as the Co content increased, while the coercivity decreased for annealed alloys compared to as-quenched alloys [24]. The incorporation of Pt into Co-based amorphous alloys destabilizes the glass structure, resulting in a reduced devitrification onset temperature and accelerated grain coarsening. Although no CoPt intermetallic compound was observed at 15 at.% Pt, the annealed alloy $Co_{63}Pt_{15}B_{10}Si_{12}$ exhibited significantly increased coercivity compared to other crystallized Co alloys [15]. The interface between the nanocrystals and the amorphous matrix of $Fe_{64}Co_{16}Zr_{10}B_{10}$ exhibits a higher concentration of Zr, while the Co concentration remains relatively consistent among the remaining amorphous matrix, nanocrystals, and the interface [25]. The introduction of Fe into the Co-based system alters the nearest-neighbor interaction, subsequently affecting the exchange interaction among the transition metal constituents [17].

$Co_{78-x}Fe_2Mn_xB_{14}Si_2Nb_4$ alloys with varying Mn content (x = 0.5% and 6.0%) demonstrate Co-rich nanocrystallites of approximately 3–5 nm after annealing, showing their potential for use in high-power electronic systems where microstructural evolution is crucial for developing low-loss components with engineered permeability [26]. Boron plays a role in inhibiting grain growth in CoFeW films, contributing to the stabilization of smaller grain sizes even at lower annealing temperatures. The findings highlight the potential of boron as a valuable addition for controlling microstructure and grain growth

[27]. The addition of a small amount of P in place of Si enhanced the thermal stability of CoFeNiSiPB ribbon [28]. The addition of Cr influences various parameters, including increasing relaxation peak temperature and activation energy while decreasing suppresses relaxation intensity and domain wall critical field. This suggests the formation of strong chemical bonds, reducing mobility and inducing stabilization effects [29]. The addition of Si stabilizes the hcp-Co phase and leads to the refinement of several solid solutions and phases, including bcc-Fe(Co), bcc-Fe(Co,Ni,Si), and fcc-Ni(Si). The presence of Si also resulted in intense microstructure refinement and the formation of an amorphous phase after prolonged milling. The segregation of Si in grain boundaries may contribute to increased structural hardening and brittleness of the particles, with the resulting nanostructure associated with dislocation concepts [30].

Table 1

Phase composition after annealing and activation energy of different multicomponent Co-based alloys

Alloys	Phases formed at crystallization onset	E_a, kJ/mol	References
$Co_{57}Fe_5Ni_{10}Si_{11}B_{17}$	hcp-Co, Co_2Si, Co_3B, $Co_{23}B_6$	–	[12]
$Co_{70}Fe_3Mn_{3.5}Mo_{1.5}Si_{11}B_{11}$	hcp-Co, fcc-Co, Co_3B	–	[13]
$Co_{66.5}Si_{15.5}B_{12}Fe_4Ni_2$	hcp -Co fcc-Co, Ni_3Fe, Ni_4B, Ni_2Si	485	[14]
$Co_{63}Pt_{15}B_{10}Si_{12}$	hcp-Co, fcc-Co, Co_2B, CoPt	–	[15]
$Co_{77}Si_{11.5}B_{11.5}$	Co_2B, Co_3B, Co_2Si	–	[10]
$Co_{69.5}Fe_{5.25}Si_{10}B_{15}$	hcp-Co, fcc-Co, Co_2B, CoO	–	[9]
$Co_{46.8}Fe_{25.27}Ta_8B_{20}$	–	445	[16]
$Co_{71}Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoCr)_2B$, $(CoCr)_3B$	153	[17]
$Co_{69}Fe_2Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoFeCr)_2B$, $(CoFeCr)_3B$	130	[17]
$Co_{67}Fe_4Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoFeCr)_2B$, $(CoFeCr)_3B$	105	[17]
$Co_{65}Fe_6Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoFeCr)_2B$	380	[17]
$Co_{63}Fe_8Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoFeCr)_2B$	331	[17]
$Co_{59}Fe_{12}Cr_7Si_8B_{14}$	hcp-Co, fcc-Co, $(CoFeCr)_2B$	155	[17]
$Co_{65}Fe_4Ni_2Si_{15}B_{14}$	Co_2Si, $Fe_{23}B_6$, NiB	461	[18]
$Co_{66}Fe_4Mo_2Si_{16}B_{12}$	hcp-Co, fcc-Co, Co_2B, Fe_2B, CoSi	–	[19]
$Co_{72}B_{19.2}Si_{4.8}Nb_4$	hcp-(Fe,Co), Fe_3B, $(Fe,Co)_{23}B_6$	–	[20]
$Co_{82}Zr_{12}V_4B_2$	fcc-Co, $Co_{23}Zr_6$, Co_5Zr	–	[21]
$Co_{70}Fe_5Si_{10}B_{15}$	hcp Co, fcc Co, $Co_{23}B_6$, Co_2Si	–	[22]
$Co_{90}Sc_{10}$	–	388	[11]

The investigation of non-isothermal crystallization kinetics not only provides insights into the relationship between annealing temperature and grain size, which can be useful for future experiments and industrial production, but also allows for a deeper understanding of the factors influencing magnetic properties by studying the nucleation mechanism and grain growth [31]. The annealing process has a profound impact on both static and dynamic magnetic properties of the material. Crystallite formation induces structural and magnetic inhomogeneity in the films, leading to significant changes in the switching behavior, overall effective anisotropy, and magnetization damping [32].

Magnetic Properties

Co-based amorphous alloys possess favorable soft magnetic properties (Table 2), characterized by high permeability and low core loss, which can be attributed to their random magnetic anisotropy [20].

Table 2

Magnetic characteristics of different multicomponent Co-based alloys

Alloys	Coercive force H_c, A/m	Saturation magnetization M_s, Am^2/kg	References
Co	0.8–72	157	[34]
$Co_{57}Fe_5Ni_{10}Si_{11}B_{17}$	200	65	[12]
$Co_{73}Fe_1Mo_1Mn_3Si_{13}B_9$	40	85	[13]
$Co_{70}Fe_3Mn_{3.5}Mo_{1.5}Si_{11}B_{11}$	180	83	[13]
$Co_{66.5}Si_{15.5}B_{12}Fe_4Ni_2$	14323	80	[14]
$Co_{46.8}Fe_{25.27}Ta_8B_{20}$	1.2	93.5	[16]
$Co_{72}B_{19.2}Si_{4.8}Nb_4$	–	54.8	[20]
$Co_{50.4}Fe_{21.6}B_{19.2}Si_{4.8}Nb_4$	–	71.3	[20]
$Co_{36}Fe_{36}B_{19.2}Si_{4.8}Nb_4$	–	96.5	[20]
$Co_{14.4}Fe_{57.6}B_{19.2}Si_{4.8}Nb_4$	–	112.5	[20]
$Co_{72}B_{19.2}Si_{4.8}Cr_4$	14.5	66.0	[35]
$Co_{64.8}Fe_{7.2}B_{19.2}Si_{4.8}Cr_4$	10	73.8	[35]
$Fe_{77.9}Si_{3.8}B_{12.35}C_{0.95}Co_5$	8.9	–	[36]
$Co_{40}Fe_{40}W_{10}B_{10}$		123	[27]
$Co_{82}Zr_{12}V_4B_2$	128 119	42.80	[21]
$Co_{82}Zr_{12}V_3B_3$	636	–	[21]

Amorphous ribbons possess significant potential for utilization in low-temperature magnetic refrigeration applications, offering opportunities for enhanced cooling capabilities and energy efficiency [33].

The Co concentration in the alloy significantly influences its microstructure and magnetic properties. For Co concentrations below 75 at.%, the film displayed an amorphous phase and exhibited soft magnetic behavior. However, with Co concentrations above 75 at.%, nanocrystals formed within the amorphous matrix, leading to a hard magnetic behavior characterized by positive remanence and antiferromagnetic exchange coupling [37]. Co addition efficiently increased the saturation magnetic flux density [36]. The emergence of magnetic anisotropy during growth is observed only in regions with high Co concentration, while regions with low Co concentration retain substrate-induced anisotropy. This highlights the significance of composition variations in determining magnetic properties and has broader implications for understanding disordered materials [38]. Co substitution enhances ferromagnetic exchange interaction and magnetic anisotropy, while Ni microalloying has a negative impact on these properties [39]. The addition of both B and Si elements an effectively improve the magnetic refrigeration capabilities [40]. The addition of Mn atoms affects the arrangement and magnetic moment of the alloy, leading to a competition between ferromagnetism and antiferromagnetism, which ultimately influences the magnetic moment of the amorphous alloy [41].

Systems demonstrated enhanced soft magnetic properties after annealing, with increased saturation magnetization and reduced coercivity values, all while preserving their amorphous phase [35]. The Co–Fe–B alloy design process resulted in the synthesis of five different amorphous compositions, each exhibiting unique magnetic properties. Among them, one composition displayed ultra-soft magnetism with low coercivity, another showed surface crystallization with higher anisotropy field compared to the amorphous samples, and a third composition exhibited nanocrystalline structure with a remarkably high saturation flux density. The surface crystallization phenomenon observed in the alloy eliminates the need for magnetic annealing to induce transverse anisotropy. This optimization strategy for alloy composition holds promise as a universal approach to fabricate alloys with exceptional properties, suitable for both high-saturation flux and low-coercivity applications [42]. CoFeSiB (Vitrovac 7600) ribbons with optimized heat treatment show promising magnetomechanical power efficiency, making them suitable for various applications, including magnetostrictive-piezoelectric-laminate-based acoustically driven antennas [43]. In $Fe_{79.5-x}Co_xSi_6B_{12}Cu_1Nb_{1.5}$ alloys ($x = 0$, 5, 10, and 15), the addition of Co atoms into the nanocrystalline grains within the amorphous matrix leads to an increase in saturation magnetization from, accompanied by a reduction in grain size after annealing [31]. The addition of an appropriate amount of Cr (up to 3 at.%) to the amorphous ribbons enhances their thermal stability, magnetic softness, and giant magnetoimpedance (GMI) value, while excessive Cr content leads to the degradation of magnetic properties due to the precipitation of Co–Fe nanocrystals in the amorphous matrix. The observed changes in magnetic properties can be attributed to modifications in magnetic anisotropy and permeability caused by Cr doping and isothermal annealing [44].

The investigation of magnetization dynamics in low-damping ferromagnetic layers, such as $Co_{40}Fe_{40}B_{20}$, reveals that surface oxidation influences their structural properties, magnetization reversal, and spin dynamics, with annealing causing partial crystallization, altering ferromagnetic resonance characteristics, and indicating the presence of inhomogeneities and two-magnon scattering [45]. Authors discovered a significant anomalous Nernst effect (ANE) signal in amorphous ferrimagnetic Co_xGd_{1-x} films with negligible magnetization, where the ANE polarity is determined by the magnetization orientation of Co sublattices, challenging conventional understanding and offering potential applications in energy-harvesting devices [46]. Amorphous magnetic alloys with perpendicular magnetic anisotropy are suitable for spintronic memory and non-reciprocal devices on-chip. Introducing oxygen into GdCo alloys enhances anisotropy energy density, resulting in stronger out-of-plane magnetization [47]. The magnetic behavior of both the as-deposited and annealed films is distinctly ferromagnetic in nature, with the as-deposited film demonstrating soft magnetic properties and the annealed films exhibiting characteristics typical of hard magnetic materials [48].

The ability of cobalt-based alloys to detect and respond to changes in temperature, strain, pressure, and magnetic fields has made them valuable in a wide range of sensor technologies, including magnetic sensors. A temperature sensor concept is presented using ferromagnetic microwire $(CoFe)_{80}(SiB)_{20}$, highlighting the correlation between temperature and the magnetic characteristics of the material [49]. A novel MEMS orthogonal fluxgate sensor, fabricated using a meander-shaped Co-based amorphous ribbon core, demonstrating high sensitivity and low noise spectral density compared to similar microfabricated fluxgate devices [50]. CoSiB-based magnetostrictive ribbon actuators, utilized in a simple RLC circuit, offer potential applications in aerospace and energy sectors for structural health monitoring, enabling detection and monitoring of cracks in critical aerospace components, oil and gas pipelines, nuclear power plants, wind turbine blades, dams, tunnels, and mines [51]. By integrating high-spin-polarization $Co_{75}Fe_{25}$ binary alloy ferromagnetic injectors and detectors in Al-based non-local spin valves, the spin signal is substantially enhanced (up to ~5 times) compared to Co, with temperature-independent current spin polarizations exceeding 60%, offering potential applications in spin accumulation sensors for next-generation hard disk drive read heads and fundamental spintronics research [52].

Chemical properties

excellent anti-corrosion performance. This makes them highly promising for applications in environments prone to corrosion, such as marine and industrial settings. [53–55]. A toxic-free $Ti_{40}Zr_{10}Co_{36}Pd_{14}$ amorphous alloy demonstrates good biocompatibility, supporting osteoblast differentiation, making it a promising candidate for biomedical applications [56]. The addition of Cr content results in a gradual improvement in corrosion resistance [44, 57].

Amorphous phases allow using amorphous alloys as positive electrode materials in a supercapacitor. The authors established that amorphous Ni–Co–Fe hydroxide electrode shows high electrochemical properties and very good long-term cycling stability, which was confirmed by retaining 94% of its capacity after 20 000 cycles. In comparison to crystalline materials, amorphous electrode cycle life is much higher [58].

A novel approach involving the incorporation of assortative strong-weak Ru–Co adsorptive atomic pairs is proposed for constructing hollow Ru–$CoMoS_x$ nanotube arrays, resulting in balanced adsorption behaviors and low reaction energy barriers. The resulting crystalline-amorphous Ru–$CoMoS_x$ heterointerface exhibits exceptional electrocatalytic activity for oxygen evolution reaction and hydrogen evolution reaction, making it promising for various water electrolysis applications and demonstrating the potential for rational design of nano-sized crystalline-amorphous heterostructures [59].

The application of AMAs as environmental catalysts has been growing steadily, highlighting their promising catalytic reactivity [60–62]. The Co−P/NF catalyst exhibited remarkable stability and durability in alkaline and seawater electrolysis, demonstrating excellent performance in both electrochemical and structural aspects for hydrogen evolution reaction [63].

AMAs exhibit excellent properties in wastewater treatment, including high efficiency and stability with reduced metal leaching [64]. The potential of using amorphous alloy based on cobalt as a catalyst for degrading organic pollutants has been explored [65]. A new Co–Mo–B amorphous alloy wire exhibits outstanding catalytic performance, degrading azo dye wastewater with 99% efficiency in just 2 minutes and maintaining 97% efficiency after 20 cycles, offering a promising solution for efficient wastewater treatment [66].

Plasma treatment of Co–B amorphous alloy nanowires enhanced their catalytic performance, modifying their electronic structure, increasing surface area, and improving reusability, providing a promising method for preserving and improving the properties of amorphous alloy nanomaterials [67].

Conclusions

Cobalt alloys have proven to be versatile materials with a wide range of applications. Through this review, it is evident that the properties of cobalt alloys can be tailored by alloying with elements such as chromium, nickel, and tungsten, resulting in enhanced mechanical strength, corrosion resistance, and magnetic behavior. The microstructural features and phase transformations of cobalt alloys can be effectively controlled through appropriate heat treatment processes, leading to improved mechanical performance. The applications of cobalt alloys in aerospace, automotive, energy, and biomedical industries show their significance in diverse technological fields.

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РЕЗЮМЕ

Марія ЛОПАЧАК, Лідія БОЙЧИШИН

ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ АМОРФНИХ СПЛАВІВ НА ОСНОВІ КОБАЛЬТУ. ОГЛЯД

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Кобальтові аморфні сплави привертають значну увагу завдяки своїм унікальним властивостям та широкому спектру застосувань. Ця стаття надає вичерпний огляд на кобальтові сплави, розглядаючи їх фізико-хімічні характеристики та застосування у різноманітних галузях промисловості. Досліджується вплив легуючих елементів та термічної обробки на властивості сплавів, таких як корозійна стійкість, механічна міцність та магнітні властивості. Розглянуто важливість варіацій складу матеріалів, зокрема вплив вмісту кобальту та додатків таких як бор, силіцій, хром, ферум, платина, манган та інших. Багато сплавів демонструють хорошу теплопровідність і можуть витримувати термоциклічні навантаження без значного зниження якостей. Окрім того, дані матеріали показують високі значення енергії активації, що залежить від складу сплавів. Наведено приклади, як мікроструктурні особливості та фазові перетворення кобальтових сплавів можна ефективно контролювати за допомогою відповідних процесів термічної обробки, що призводить до поліпшення механічної продуктивності. Сплави володіють м'якими магнітними властивостями, в тому числі мають низькі значення коерсивної сили та високу намагніченість. Під час термічної *обробки аморфних матеріалів на основі кобальту, утворюються різні фази, зокрема fcc-Co, hcp-Co CoB, CoSi,* Co_2Si*, феромагнітний* Co_2B *і парамагнітний* Co_5Si_2B*, що зумовлюють зміну поведінки сплавів. Сплави на основі кобальту володіють високою корозійною стійкістю у різних середовищах, зокрема при легуванні хромом та нагріванні знижуються потенціали та струми корозії. Аморфно-кристалічна структура дозволяє використовувати сплави як електроди з високою каталітичною активністю у реакціях виділення водню та кисню, а також при очистці вод від органічних забруднювачів. Застосування кобальтових сплавів в авіаційній, автомобільній, енергетичній та медичній промисловості свідчать про їхню значущість у різних технологічних галузях. Цей огляд статті сприяє кращому розумінню властивостей кобальтових сплавів та надає підґрунтя для подальших досліджень та розвитку у цій області.*

Ключові слова: аморфні сплави, кобальт, магнітні властивості, корозія, каталіз.

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