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DOI: 10.15199/40.2024.3.2

Refractory metals as alloying additives for metallic materials formed via powder metallurgy techniques

Metale wysokotopliwe jako dodatki stopowe materiałów metalicznych kształtowanych metodami metalurgii proszków

Methods for the fabrication of metallic sinters via powder metallurgy techniques have been widely discussed in materials engineering for many years. Depending on the final purpose of the finished products, it is primarily important to ensure their appropriate mechanical properties. Numerous works on this topic are devoted mainly to the modification of conventional metallic materials, and one of the promising research directions is the addition of refractory metals to metal alloys. Thanks to the advantageous impact on thermal stability, mechanical properties, and corrosion resistance, the proposed solutions fit perfectly into the trends of searching for new, functional engineering materials. This work presents a review of scientific reports on the modification of metal alloys with the addition of refractory metals published over the last 15 years. First, a brief characterization of refractory metals along with a description of the basics of processing metallic materials using powder metallurgy are presented. In the following part of the article, the research results on the influence of the addition of high-melting metals on the mechanical properties and corrosion resistance of heavy and light metal alloys are discussed. The conclusion consists of data on the global metal alloys market, taking into account its current state and forecasted changes for the next few years.

Keywords: metal alloys, refractory metals, powder metallurgy, sintering, materials engineering

Metody spieków metalicznych technikami metalurgii proszków są szeroko omawiane w inżynierii materiałowej od wielu lat. Niezależnie od przewidywanego przeznaczenia gotowych wyrobów istotne jest przede wszystkim zapewnienie produktom odpowiednich własności mechanicznych. Liczne prace poświęcone tej tematyce skupiają się głównie na modyfikacji konwencjonalnych materiałów metalicznych, a jednym z obiecujących kierunków badań jest wzbogacanie stopów metali dodatkiem metali wysokotopliwych. Dzięki korzystnemu wpływowi na stabilność termiczną, własności mechaniczne i odporność na korozję proponowane rozwiązania doskonale wpisują się w poszukiwania nowych, funkcjonalnych materiałów inżynierskich. Praca stanowi przegląd doniesień naukowych opublikowanych w ciągu ostatnich 15 lat, traktujących o modyfikacji stopów metali dodatkiem metali wysokotopliwych. W pierwszej kolejności przedstawiono krótką charakterystykę metali wysokotopliwych wraz z omówieniem podstaw przetwarzania materiałów metalicznych z wykorzystaniem metalurgii proszków. W dalszej części artykułu przeprowadzono analizę wyników badań nad wpływem dodatku metali wysokotopliwych na własności mechaniczne oraz odporność korozyjną stopów metali ciężkich i lekkich. W podsumowaniu przybliżono dane dotyczące stanu globalnego rynku stopów metali wraz z uwzględnieniem zmian prognozowanych na najbliższe lata.

Słowa kluczowe: stopy metali, metale wysokotopliwe, metalurgia proszków, spiekanie, inżynieria materiałowa

Received / Otrzymano: 15.02.2024. Accepted / Przyjęto: 1.03.2024

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1. Introduction

Various methods of modifying metal alloys (MAs) and their processing have been discussed in the scientific literature for many years, and the growing need for materials with exceptional mechanical properties or resistance to extremely high temperatures has contributed to the search for new solutions in this field. These efforts initiated much research on the addition of refractory metals (RMs) to commercially available MAs, and also on the production of novel RM-based alloys. Hitherto, literature reports have been mainly focused on the modification of heavy metal alloys (HMAs) with RMs. Many studies on this matter mention the improvement of mechanical properties [1] or the advantageous influence on density and microstructure [2]. Moreover, due to the great chemical resistance of RMs [3], there are also some reports available on the corrosion resistance properties of such materials [4]. In recent years, modifications of light metal alloys (LMAs) with RMs and the impact on their characteristics have also been mentioned.

This work is focused on the review of scientific reports devoted to the modification of MAs with the addition of RMs. The classification along with brief characteristics of RMs was presented and the methods of materials processing via powder metallurgy (PM) were shortly explained. Examples of the fabrication of powder composites based on HMAs (e.g. W, Ta, Ni, Fe, or Co) and LMAs (Ti, Al) with the addition of various RMs and their processing using PM techniques are presented. Moreover, the influence of the addition of RMs to MAs on their mechanical properties and corrosion performance was discussed. The presented review was prepared based on research articles published in the last 15 years collected using ScienceDirect, Scopus, and PubMed databases. Appropriate keywords associated with the discussed matters are presented in Fig. 1. Moreover, a visualization of the interest in the field of research on the modification of MAs with RMs is compiled in a graph in Fig. 2. Phrases "alloys modification" and "heavy alloys modification" followed by "refractory metals" were applied for the search, and data from the years 2013 to 2023 in ScienceDirect were collected.

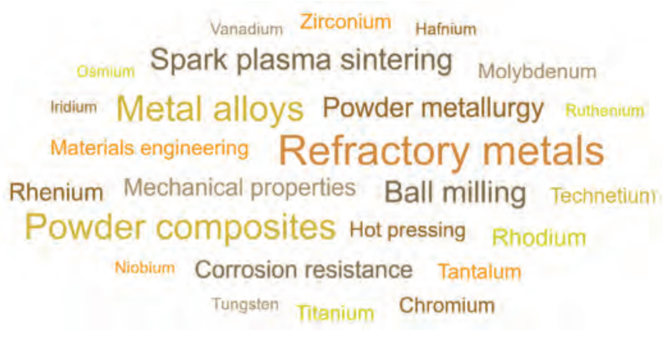

Fig. 1. Modification of MAs with the addition of RMs – keywords cloud

Rys. 1. Modyfikacja stopów metali dodatkiem metali wysokotopliwych – chmura słów kluczowych

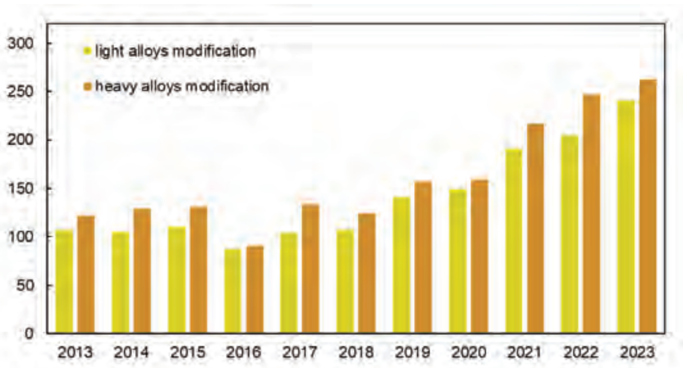

Fig. 2. The number of research reports on the modification of MAs with the addition of RMs published in the last 10 years

Rys. 2. Liczba opublikowanych w ciągu ostatnich 10 lat doniesień naukowych dotyczących modyfikacji stopów metali dodatkiem metali wysokotopliwych

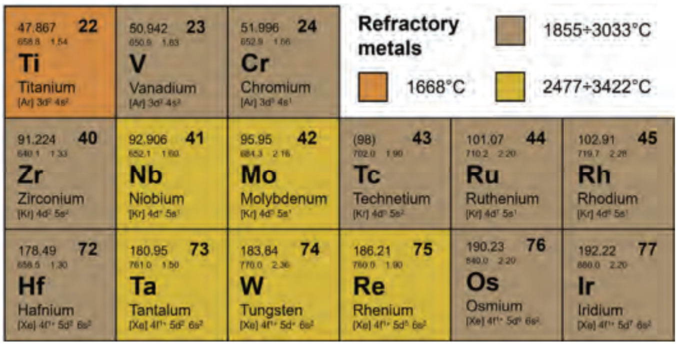

Fig. 3. A fragment of the periodic table showing the classification of RMs depending on their melting point

Rys. 3. Fragment układu okresowego przedstawiający klasyfikację metali wysokotopliwych w zależności od temperatury topnienia

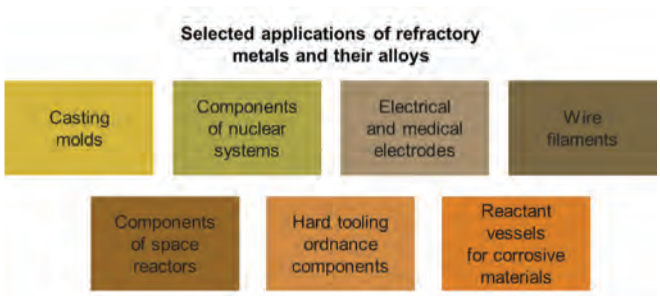

Fig. 4. Selected applications of RMs and RM-based alloys

Rys. 4. Wybrane zastosowania metali wysokotopliwych i ich stopów

2. Refractory metals – characterization

According to the most common definition, RMs include elements from the 5th (Nb and Mo) and 6th (Ta, W, Re) periods with remarkable thermal resistance. They are characterized primarily by a melting point above 2000°C [5]. However, over time, the definition has been expanded, and elements with slightly lower, though still notably high, melting temperatures, up to 1800°C, were also classified as RMs. Hence, RMs also include V, Cr, Zr, Tc, Ru, Rh, Hf, Os, and Ir. Additionally, due to its position in the periodic table, Ti is also considered an RM, even though its melting point is approx. 1600°C [6]. The classification of RMs is shown in Fig. 3.

Apart from their high melting point, RMs are characterized by high hardness and extraordinary wear resistance. These features arise from the occupation of the outer d subshell, which makes it possible for the d electrons to participate in metallic bonding. Thanks to this, RMs create highly stable bonds with the neighboring atoms and a body-centered cubic crystal structure that is resistant to deformation [7]. Selected physical properties of RMs are presented in Table 1. Additionally, most of the mentioned metals show good chemical resistance in acids, alkalis, and salt solutions (Table 2) [5], as well as high thermal and electrical conductivity [8].

Table 1. Selected physical properties of RMs
Tabela 1. Wybrane własności fizyczne metali wysokotopliwych

Metal	Melting point [°C]	Density (at 20°C) [g/cm^3]	Vickers hardness [HV]	Crystal structure (at 20°C)
Nb	2477	8.57	135	FCC
Mo	2623	10.28	156	BCC
Ta	3020	16.65	89	BCC
W	3422	19.30	350	BCC
Re	3186	21.02	250	HCP
Ti	1668	4.51	99	HCP
V	1910	6.11	64	BCC
Cr	1907	7.20	108	BCC
Zr	1855	6.51	92	HCP
Tc	2204	11.50	151	HCP
Ru	2334	12.20	234	HCP
Rh	1970	12.40	127	FCC
Hf	2227	13.07	180	HCP
Os	3033	22.50	422	HCP
Ir	2446	22.56	180	FCC

Table 2. Corrosion rate of selected RMs in acids, alkalis, and salt solutions
Tabela 2. Szybkość korozji wybranych metali wysokotopliwych w roztworach kwasów, zasad i soli

Corroding agent	Temperature [°C]	Metal loss [mm/year]			
		Mo	W	Nb	Ta
10% $HCl_{(aq)}$	20	<0.003	0.002	0	<0.001
	100	<0.025	0.005	0.005	<0.025
10% $H_2SO_{4(aq)}$	20	<0.005	<0.1	<0.1	<0.1
	100	0.17	<0.25	<0.001	0
10% $HNO_{3(aq)}$	20	18.6	<0.25	<0.013	<0.013
	100	150	<0.25	<0.076	<0.025
3% $HF_{(aq)}$	20	<0.001	<0.1	>3.0	>3.0
	100	0.18	0.15	>3.0	>3.0
10% $CH_3COOH_{(aq)}$	20	0.07	<0.05	<0.1	<0.013
	100	0.033	<0.05	<0.1	<0.013
10% $KOH_{(aq)}$	20	<0.1	<0.1	<0.2	<0.1
	100	0.054	0.01	1.2	<0.003
3% $NaCl_{(aq)}$	20	<0.1	<0.1	<0.1	<0.1
	100	<0.1	<0.1	<0.1	<0.1

Source: [5, p. 308].
Źródło: [5, s. 308].

RMs are usually processed via the consolidation of pure metal powders using different PM methods. Most commonly, they are heat-treated by sintering and then formed into wires, ingots, sheets, or foils [9, 10]. RMs are often used as alloying additives, thanks to which, due to their unique properties, they contribute to a significant improvement in the properties of MAs, even when they are added in small amounts [2]. The high thermal stability, strength, and great corrosion resistance of RMs make them suitable for hot metalworking applications. Alloys comprised of metals such as Mo, Nb, Ta, and W are widely used in space nuclear power systems. Thanks to their specific chemical and electrical properties, they can also be employed in catalytic reactions. RM alloys are exploited in lighting systems, tools, lubricants, and nuclear reaction control rods [11, 12]. A few application areas of RMs are presented in Fig. 4.

3. Powder metallurgy technology

PM includes all techniques for the fabrication of solid metal-based products from powder raw materials. PM is considered a fairly

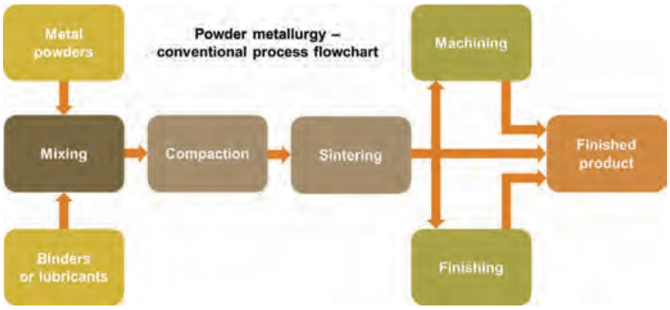

Fig. 5. Flowchart of a conventional PM process

Rys. 5. Schemat blokowy konwencjonalnego procesu metalurgii proszków

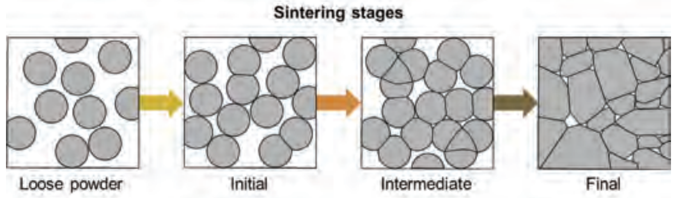

Fig. 6. Powder sintering – stages and visualization

Rys. 6. Spiekanie proszku – etapy i wizualizacja

modern metal processing technique, and its major development occurred at the beginning of the 20th century [13]. Nevertheless, the history of PM goes back much further, when for centuries all Fe-based materials were fabricated using the solid metallurgy method due to the difficulties in melting them [14].

The typical process of producing materials using PM techniques includes powder production and preparation, then consolidation using pressure along with heat treatment, and finally, the finishing processes for the obtained materials (Fig. 5) [15]. Mechanical and chemical synthesis are classified as the methods for the production of powders for the PM processes [16]. Mechanical synthesis includes milling, mixing, annealing, agglomeration or granulation. Chemical methods mainly include various reduction reactions (e.g. solid, gas, electrochemical) or decomposition reactions [13]. The preparation of materials before sintering covers mainly their shaping under pressure. The main methods for the compaction of the powders are uniaxial die compaction, cold and hot isostatic pressing, or metal injection molding [17]. Compaction steps in most cases are performed before heat treatment, however, some techniques involve pressing of powders along with their sintering. The main methods for the final consolidation of metallic materials via PM include different sintering techniques.

Sintering techniques are most often used for the fabrication and processing of MAs, especially those modified with RMs. According to the official ISO definition [18] sintering is a thermal treatment of a powder or compact, at a temperature below the melting point of the main constituent, for the purpose of increasing its strength by the metallurgical bonding of its particles. During different stages of sintering, powder particles undergo densification by the influence of atomic diffusion. In the typical approach, the loose powder is first compacted, and then necks are formed between its particles, to finally lead to the densification of the finished product (Fig. 6) [19].

According to the elementary definitions, two sintering mechanisms – solid-state and liquid-phase – can be distinguished [13]. The first one includes processes in which single components are usually sintered. It involves the bonding and densification of powder particles below their melting point. During the process, there is a decrease in free surface area and an increase in material density. Here, the employment of considerably fine powders and the application of appropriate high temperatures are required [20]. Liquid phase sintering is used for the processing of multiple component systems. In this case, the temperature should be set above the melting point of one of the consolidated materials. While one of the components turns into the liquid phase, the other one remains in solid state. Differences in capillary pressure occur and the solid particles are redistributed in the liquid phase, creating a rather homogeneous structure. This phenomenon is professionally described as particle rearrangement. In this process, more than 90% relative density can be achieved during heating [21].

In addition to conventional free sintering, many different technologies have been developed over the last few decades. These include microwave sintering (MS) [22], pulse plasma sintering (PPS) [23], or spark plasma sintering (SPS) [24], also known as field-assisted sintering technology (FAST) [25]. In the past 15 years, there has been also a growing interest in metal additive manufacturing processes, among which selective laser melting (SLM) is most commonly employed [26].

PM is commonly considered an effective method for the reduction of materials porosity [27] and the improvement of their mechanical, electrical, or thermal properties [28]. In addition, the variety of metalworking techniques via PM allows the materials obtained to be used in a wide range of practical applications – from high-performance components for the automotive or aerospace industries [29], tool materials in the manufacturing sector [30], through electronic equipment [31], to medical devices or biomaterials [32]. What is worth mentioning is that PM processes are considered to be "green" technologies. By almost completely eliminating subtractive manufacturing steps, material losses are reduced, making PM much more cost effective and energy efficient than other metalworking techniques [13].

4. Modification of heavy metal alloys

Although HMA-based materials are widely exploited for many industrial purposes, they are still eagerly discussed due to their diversity and customizability. Numerous studies dedicated to HMA modification are focused on striving to obtain materials with the best possible mechanical properties to expand their application potential. One of the directions of this pursuit is the modification of HMAs with the addition of RMs, which has a beneficial effect on several properties of the alloys.

In the study of Prasad and Annamalai [33], the influence of an addition of Re to W-Ni-Fe alloy on its properties has been investigated. Powder samples of W, Ni, Fe, and Re at different mass ratios (0÷8 wt% of Re addition) were mixed using ball milling and then sintered via the SPS technique. It was reported that the strength and hardness were improved significantly with an increasing Re ratio. The results of mechanical properties testing showed an increase in yield strength from 650 MPa to 1530 MPa and tensile strength from 930 MPa to 1560 MPa for the samples with 0 wt% and 8 wt% Re addition, respectively. The same dependence was noticed in the case of the results for micro-Vickers hardness measurements, where the values were stated at 330 Hv_{500} for the 0 wt% Re and 507 Hv_{500} for the 8 wt% Re addition.

Kiran et al. [1] presented research on mechanically alloyed W-Ni-Fe alloy with the addition of Re. First, high-energy milling of W with the addition of 1 wt% Re powders was performed. Subsequently, Ni both with Fe powders were added and mixed using ball milling so that the final composition of 89W-7Ni-3Fe-1Re was obtained. Then, powders with the same W-Ni-Fe-Re contents were conventionally milled. The prepared materials were sintered in H_2 atmosphere using the same conditions for high-energy and conventionally milled samples. It was shown that the sinters obtained from high-energy prepared alloy hold better mechanical properties (e.g. yield strength, tensile strength, elongation) in comparison with sinters from those prepared conventionally.

Jin et al. [34] presented a report on Mo diffusion to the core section in the W-7Ni-3Fe HMA. Here, commercially available W, Ni, and Fe powders were dry-mixed using a planetary ball mill for the fabrication of W-7Ni-3Fe alloy. The prepared samples were subjected to pressure-pressing and then, in order to obtain a gradient structure alloy, Mo powder plates were placed on top of W-7Ni-3Fe plates and sintered at 1480°C. It was shown that the Mo content decreases with the increasing diffuse distance and that the grain size, the volume fraction of the W phase, and the micro-hardness vary gradually due to the graded distribution of Mo.

Table 3. Selected mechanical properties of HMAs and RMs
Tabela 3. Wybrane własności mechaniczne stopów metali ciężkich i metali wysokotopliwych

Material	Sintering technique	Selected mechanical properties				Ref.
		yield strength [MPa]	tensile strength [MPa]	bending strength [MPa]	hardness [HV]	
W-1Re-7Ni-3Fe	FS	1215	1232	N/A	N/A	[1]
W-2Re-7Ni-3Fe	SPS	740	1080	N/A	355	[33]
W-4Re-7Ni-3Fe		820	1120	N/A	401	
W-6Re-7Ni-3Fe		1511	1540	N/A	486	
W-8Re-7Ni-3Fe		1530	1560	N/A	507	
W-5Ta	SPS	N/A	N/A	741.62	414.20	[35]
W-10Ta		N/A	N/A	706.27	508.65	
W-15Ta		N/A	N/A	647.59	466.58	
W-20Ta		N/A	N/A	586.81	489.68	
W-4.65Mo	FS	N/A	N/A	357	N/A	[36]
Ta-2.5W	SPS	N/A	643.63	832.29	513.50	[37]
Ta-5W		N/A	613.56	619.92	574.10	
Ta-7.5W		N/A	645.20	642.38	595.00	
Ta-10W		N/A	693.41	749.25	672.80	
Ta–10Nb	PPS	N/A	N/A	N/A	990.07	[38]
Ta–10Mo		N/A	N/A	N/A	1481.58	
Ta–10W		N/A	N/A	N/A	1136.84	

Wang et al. [35] have prepared W-Ta alloys with various weight ratios of Ta addition (5÷20 wt%). First, high-energy ball milling was used to homogenize the W and Ta powders, and then the prepared samples were sintered using the SPS technique. The influence of Ta concentration in the W matrix on the characterization and mechanical properties was investigated. It was shown that 10 wt% of Ta increases the relative density of the alloy, however the 15 wt% Ta addition causes its significant decrease. This phenomenon could be caused by the gathering of Ta in the matrix at its higher concentrations, harming the mechanical properties of materials. The highest hardness was recorded for the alloy with 10 wt% Ta (ca. 42% higher than for pure W) while the best bending strength was recorded for the samples with 5 wt% Ta addition (ca. 27% higher than for pure W).

The study on the effects of adding Mo to W on microstructure and mechanical properties was presented by Ren et al. [36]. The W and Mo powders at various contents (1÷6 wt% Mo) were milled using a high-energy planetary ball mill. Powder samples were compacted into plates using a cold isostatic pressing system and sintered at different temperatures (1000÷1300°C). It was found that alloying W with Mo reduced W grain size, and increased hardness as well as indentation toughness.

The fabrication of Ta-W alloy using PM consolidation via SPS was reported by Yu et al. [37]. Powder samples of pure Ta and Ta with different concentrations of W (2.5÷10 wt%) were prepared by ball milling and then sintered at 1600°C. It was found that with the increasing W content, the density of the alloy decreased and the grain was refined. The micro-hardness and strength of the samples increased gradually with the addition of W.

Sopata et al. [38] investigated the mechanical properties of nanocrystalline Ta alloys with Nb, Mo, and W addition at different mass ratios (5÷40 wt%). The analyzed samples were obtained by PM techniques – mechanical alloying and hot pressing using pulse plasma sintering mode. The discussed alloys showed very high hardness and stiffness, especially at 10 wt% Nb, Mo, and W addition. It was stated that in these alloys, both solid solution and grain boundary strengthening contributed to an increase in mechanical properties.

Liu et al. [39] presented research on Fe-based hard-facing alloys with varying W additions (3÷12 wt%) and its effects on microstructure and wear performance. Here, Fe-based self-shielded metal cored wire was reinforced with W powders and then applied on mild steel substrates. It was shown that the wear loss of the samples with 9 wt% W was the smallest owing mainly to the higher hardness.

Erden et al. [40] studied the impact of Mo addition on the microstructure and mechanical properties of Fe-0.55C alloys. Fe-C powders were first mixed with 1 wt% to 5 wt% Mo addition using a triaxial mixer and then sintered at 1400°C. The results showed an increase in yield and tensile strength and a reduction in strain with the increase in Mo content. The maximum yield and tensile strength were recorded for the samples with 3 wt% Mo addition.

Bai et al. [41] presented research where an Ni-based superalloy was mixed with 2.40 wt% and 4.80 wt% Ta addition using PM methods and its effect on microstructure was examined. The results revealed a significant change in the particle boundary structure of Ni alloy. It was shown that with increasing Ta content, Ni alloy morphology transforms from spheres to cuboids. It was stated that this phenomenon can lead to an improvement of the mechanical properties of the discussed Ni superalloys. A summary of the results of mechanical properties testing in the abovementioned reports is presented in Table 3.

5. Modification of light metal alloys

So far, research on the fabrication of LMA-based materials with the addition of RMs has not been particularly widespread. This is mainly due to the difficulties in the processing of such materials, related primarily to considerable differences in the melting points of LMAs and RMs. Despite this, in recent years there have been several reports devoted to research on the modification of Ti or Al alloys with the addition of RMs (e.g. Re, Mo, or Ta) and analysis of their impact on the mechanical properties or microstructure of the obtained materials.

The research conducted by Majchrowicz et al. [42] presents the results of processing Ti-Re alloys using the SLM technique. Ti-based alloys containing 0.5, 1.0, and 1.5 wt% of Re were obtained in a two-stage process. First, Ti and Re powders with a 1 : 1 wt% ratio were mixed by mechanical alloying. Afterwards, two compositions of Ti-Re alloys (2 and 4 wt%) were obtained by adding an appropriate amount of Ti powder. The effects of Re content on the microstructure, strength, and fatigue crack propagation characteristics of SLM-processed samples were investigated. It was stated that the addition of Re increases yield strength and tensile strength at the expense of reducing the ductility in comparison with a pure Ti matrix.

Ren et al. [43] have proposed research on the fabrication of Ti-based composite with 20 wt% W particles by PM. Ti and W powders were blended using a rotary V-type mixer and then consolidated by combined cold and hot isostatic pressing. The addition of W influenced its phase transformation behavior and changes in the microstructure, compared to a pure Ti matrix. The obtained composite exhibited excellent mechanical properties which could be explained by the multiple strengthening mechanisms, e.g. the occurrence of a high-hardness reinforcing phase, solid solution strengthening, or precipitation strengthening.

In the research of Wang et al. [44], Ti-Ta alloys with a lamellar microstructure were fabricated via conventional sintering. The microstructure and mechanical properties of the prepared samples were characterized. Ti powder with an addition of 15÷25 wt% Ta was ball milled and then subjected to cold isostatic pressing and pressure-free sintering at 1600°C. The increasing Ta addition contributed to an increase in tensile strength and a decrease in strain to failure. The samples with 25 wt% Ta addition exhibited the highest tensile strength. It was reported that the dominant mechanism ensuring the high strength of Ti-Ta alloys is the strengthening of the lamellar structure.

Apart from the improvement of mechanical properties by the addition of RMs to the Ti matrix for high-strength materials fabrication, there have also been reports on their biomedical applications (i.e. for orthopedic alloys fabrication). For example, research by Xu et al. [45] showed that Ti powders with 8 to 20 wt% Mo were obtained for orthopedic alloys. The effect of Mo content on corrosion and tribocorrosion of the discussed Ti-Mo alloys was investigated and it was observed that these properties improved with higher Mo content. The best results were recorded for an addition of 16 wt% Mo.

Another study by Xu et al. [46] was focused on the investigation of porous Ti-Mo composite and its microstructure, mechanical properties, and in vitro biocompatibility. Ti powder with 10 wt% Mo addition and different ratios of so-called space holder (NH_4HCO_3) was blended, then cold-pressed and consolidated using isothermal sintering at 1300°C. The influence of the space-holder concentration on the average pore size of the alloys and its impact on their mechanical properties was analyzed. The alloy with 63.4% porosity (50 wt% NH_4HCO_3 addition) exhibited the best elastic modulus and compressive yield strength. Moreover, these materials stand out with excellent in vitro biocompatibility and in vivo osteointegration making them promising candidates for implant applications.

Table 4. Selected mechanical properties of LMAs and RMs
Tabela 4. Wybrane własności mechaniczne stopów metali lekkich i metali wysokotopliwych

Material	Sintering technique	Selected mechanical properties			Ref.
		yield strength [MPa]	tensile strength [MPa]	hardness [HV]	
Ti-2Re	SLM	1112	1159	N/A	[42]
Ti-4Re		1197	1221	N/A	
Ti-15Ta	FS	942	977	N/A	[44]
Ti-20Ta		1086	1107	N/A	
Ti-25Ta		1124	1124	N/A	
Ti-10Mo	FS	N/A	N/A	355	[46]
Ti-16Mo		N/A	N/A	403	
Ti-20Mo		N/A	N/A	388	
Al5083-W	FSP	214	404	N/A	[47]

Apart from the modification of Ti and its alloys, there are a few scientific reports on Al alloys where W has been added to improve their mechanical properties. In a study by Bauri et al. [47], Al5083 with an addition of W was fabricated and its mechanical properties were compared with those of pristine Al alloy. W particles were incorporated into an Al5083 matrix by friction stir processing (FSP) which resulted in uniform dispersion of the W particles in the Al alloy matrix. Al5083 with W showed an improvement in tensile strength, while at the same time exhibiting high ductility.

Another example of the modification of Al alloy with RMs was presented by Guo et al. [48]. The deformation behavior of Al-W alloy was analyzed using isothermal compression tests at different temperatures and strain rates. Here, the dependence of the flow stress on the strain, strain rate, and deformation temperature was examined. The samples were prepared by ball milling of Al alloy and W powders and cold-pressing. It was shown that the hot processing parameters have a significant influence on the flow behavior in the hot compression of the discussed Al-W alloy – the flow stress decreases with the increasing temperature and decreasing strain rate. Selected mechanical properties of materials fabricated in the discussed works are compiled in Table 4.

6. Corrosion behavior of refractory metals and their alloys

The excellent resistance of RMs to various chemical agents has prompted the scientific community to study their behavior and applications in environments exposed to corrosion. Although the vast majority of articles are devoted to investigating the influence that RM additions have on the mechanical properties of MAs, there are more and more reports on the impact on their corrosion performance are increasingly appearing in the literature.

In the study by Zhao et al. [49], a method for Ti-Mo fabrication and research on the effect of Mo content on the corrosion resistance of Ti was reported. First, Ti-Mo was prepared by the addition of Mo in different ratios (from 1 to 5 wt%) to a Ti sponge and then processed in a vacuum smelting furnace. Corrosion behavior was tested in 10% HCl solution by microstructural characterization, electrochemical, and corrosion weight loss measurements. It was stated that the increasing Mo content enhances the corrosion resistance. The corrosion weight loss revealed that corrosion rates after 10 days of immersion were 0.19, 0.001, and 0.0007 mm/a, for Ti-1 wt% Mo, Ti-3 %wt Mo, and Ti-5 wt% Mo samples, respectively.

Another example of the influence RM additions to other metals and MAs on corrosion behavior was reported by Shankar et al. [50]. This group presented an attempt to modify the surface of commercially pure Ti coatings by adding Ta and Nb. Coatings of Ta, Nb, and Ta/Nb were obtained via the thermo-chemical decomposition method on the Ti surface and their corrosion resistance was tested in HNO_3 solution. Corrosion tests showed that Ta/Nb coated samples exhibit four times higher corrosion resistance than the uncoated Ti.

Lin et al. [51] proposed the preparation of Re coatings on Co-Cu alloy and mild steel substrates. The analysis of its corrosion performance in 3.5% NaCl solution was tested and it was shown that the Co-Cu alloy with an Re addition had a corrosion current density over 3 times lower than that of the mild steel substrate and over 2 times lower than that of the Co-Cu alloy coating. Moreover, experiments in a high-temperature oxidation environment were performed. The oxidation rate of the Co-Cu-Re alloy was the smallest compared to the steel substrates and Co-Cu alloy. It was stated that the Re had a significant influence on the corrosion performance of the tested coatings.

Apart from the research on the influence of adding RMs to MAs, there is also a high interest in the field of corrosion behavior of high entropy alloys which are most commonly RM-based. One of the reports from Patel et al. [52] research group were based on the corrosion resistance study of the TaTiVWZr and HfTaTiVZr alloys. The samples were examined in a molten eutectic salt (composed of 33 wt% NaCl, 22 wt% KCl, and 45 wt% $MgCl_2$) at high temperatures (450°C to 650°C) and results were compared with the corrosion performance of commercially available steel substrates (304 stainless steel and Inconel 718) at the same conditions. Even though it was observed that the corrosion rate of all the tested substrates increased with increasing temperature, the RM-based alloys exhibited considerable corrosion resistance in comparison with commercial steel samples. The corrosion rate was stated at 5 mm/year, 40 mm/year, 40 mm/year, and 110 mm/year for TaTiVWZr, HfTaTiVZr, Inconel 718, and stainless steel 304, respectively.

Another example of research on this matter is the ReTaWNbMo alloy presented by Yan et al. [53]. The influence of the annealing temperature of alloy samples on the microstructural evolution, mechanical properties, and corrosion resistance was examined. Samples were subjected to heat treatment at 400°C, 600°C, 800°C, and 1000°C for 12 h. Corrosion behavior was tested in 3.5% NaCl and the results showed that corrosion current density decreased as the annealing temperature rose. The best corrosion resistance was observed for the samples annealed at 1000°C. The increased annealing temperature was also advantageous for the properties of the tested alloy (e.g. yield strength, fracture strength, or compressive plasticity).

7. Summary and outlook

Although the methods for the production and modification of MA have been discussed for years, there is still an increasing demand for finding new solutions for the improvement of their mechanical and corrosive performance. This is reflected both in published scientific reports and the growing demand in the MA market. Over the last 10 years, the number of research articles on MA processing has increased from almost 4,000 to over 12,000. One of the interesting proposals for the modification of alloys is adding RMs to their matrix. Consequently, in the past decade, around 4,400 studies have been published on the exploitation of RMs as alloying additives to modify the properties of metallic materials.

According to global market reports [54], the demand for MAs is constantly growing around the world. Its projected profits are estimated at above 450 billion USD by 2030 and the compound annual growth rate (CAGR) is expected to be approximately 5.1% for the years 2022–2032. In 2021, the MA market was valued at ca. 291 billion USD, and the largest share in market revenues was held by the countries of the Asia-Pacific region (ca. 62%) and Europe (ca. 18%). The market profit in Asia-Pacific countries was estimated at CAGR of ca. 5.5% for 2030, whereas the European market is expected to grow at a CAGR of 3.8% (2030). Companies such as Alcoa Inc., ArcelorMittal, Baosteel Group, Jindal Stainless, Kobe Steel, Novelis, RUSAL, and Rio Tinto are considered key representatives in the production sector of MA and its main recipients are the automotive and construction industries. The LMA market sector deserves special attention, with an emphasis on the importance of stainless steel and Al alloys, for which the CAGR growth in 2022–2030 is estimated at 6%. According to the discussed report, LMAs are among the most often exploited alloys in the industry, and the demand for Al and Ti-based alloys is increasing mainly due to the constantly developing new technologies in the automotive and aviation industries. The need for the production of light and durable materials such as car parts or components of aircraft covers or turbines undoubtedly contributes to the increase in market profits.

PM techniques have become well-established in industrial practice over the past decades. The variety of methods for the production of MAs allows for obtaining unique properties of finished products, which broadens the spectrum of their applications. It is expected that ongoing R&D projects and partnerships between the scientific community and industry will open new opportunities for the global MA market. This will benefit the market not only by increasing production or sales, but also by improving the quality of manufactured products and developing new advanced functional materials.

Acknowledgments
This work was financially supported by the Ministry of Science and Higher Education of the Republic of Poland as part of the Implementation Doctorate Program (Grant no. RJO15/SDW/006-07).

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