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Review article
Обзорная статья

Recent development in powder metallurgy of high-entropy alloys for high-temperature applications. Brief review

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Abstract. Powder metallurgy of high-entropy alloys has gained significant attention in modern applications due to its low cost and near-net-shape formability. This overview presents the state-of-the-art research on powder metallurgy of high-entropy alloys for high-temperature applications, covering basic solid state fabricating processes, phase composition, and advanced mechanical properties recently attained. The analysis showed that various methods of production and mixing of powder components, including self-propagating high-temperature synthesis, magnesium reduction, hydrogenation, mechanical alloying, plasma spheroidization, centrifugal plasma sputtering of the bar, and conventional mixing of elemental powders in high-energy mixers are used to produce powder mixtures. The most common consolidation method is spark plasma sintering, which allows obtaining compacts with high speed and preservation of fine structure. Also, for the production of long bars and billets, the extrusion of powder mixtures in shells is used. A key feature of the chemical compositions of billets produced by methods of powder metallurgy are the possibility of obtaining oxide-disperse-strengthened powder compacts, which provides additional hardening at elevated temperatures. The main elements used in the creation of high-entropy alloys for application at elevated temperatures are the refractory metals. Therefore, in order to reduce the density of new alloys, compositions with aluminum, titanium, and refractory oxides are being developed. Finally, this review identifies unresolved and critical issues in the development of approaches to obtaining high-entropy alloys using powder metallurgy methods for their practical implementation in modern industry.

Keywords: powder metallurgy, high-entropy alloys, refractory metals, mechanical alloying, plasma spheroidization, hydrogenation, extrusion, high-temperature application

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Новые достижения в области порошковой металлургии высокоэнтропийных сплавов для высокотемпературных приложений. Краткий обзор

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Аннотация. Порошковая металлургия высокоэнтропийных сплавов привлекает значительное внимание благодаря своей высокой технологичности и низкой стоимости. В этом обзоре представлены новейшие исследования в области порошковой металлургии высокоэнтропийных сплавов, разработанных для применения при высоких температурах. Рассматриваются основные процессы получения порошков и компактов из них, химический и фазовый состав, плотность, механические свойства при повышенной температуре, термостабильность. Проведённый анализ показал, что для получения порошковых смесей применяются различные методы производства и смешения порошковых компонентов, включая самораспространяющийся высокотемпературный синтез, магниотермию, гидрирование, механическое легирование, плазменную сфероидизацию, центробежное распыление прутка плазмой и традиционное смешение элементных порошков в высокоэнергетических смесителях. Наиболее распространенным способом консолидации является искровое плазменное спекание, позволяющее получать компакты с высокой скоростью и сохранением тонкой структуры. Также для производства длинномерных прутков и заготовок применяется экструзия порошковых смесей в оболочках. Ключевой особенностью химических составов заготовок, производимых методами порошковой металлургии, является возможность получения дисперсно-упрочненных оксидами порошковых компактов, что обеспечивает дополнительное упрочнение при повышенных температурах. Основными элементами, используемыми при создании высокоэнтропийных сплавов для применения в условиях повышенных температур, являются тугоплавкие металлы. Поэтому для снижения их плотности разрабатываются составы с алюминием, титаном, а также тугоплавкими оксидами. Кроме того, в этом обзоре обозначены нерешенные и критические вопросы разработки подходов к получению высокоэнтропийных сплавов методами порошковой металлургии для практического внедрения их в современную индустрию.

Ключевые слова: порошковая металлургия, высокоэнтропийные сплавы, тугоплавкие металлы, механическое легирование, плазменная сфероидизация, гидрирование, экструдирование, высокотемпературное применение

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Introduction

High-entropy alloys (HEAs) are a new generation of alloys that have been developed since 2004 [1; 2]. Despite intensive research over the past 20 years in the field of high-entropy materials, these alloys have not yet found widespread use in modern industry, although they continue to gain popularity in scientific studies each year [3; 4] due to their high physical, mechanical, and operational properties [5; 6]. High-entropy alloys are resistant to oxidation at high temperatures, which potentially broadens their technological applications, including replacing nickel-based alloys in turbine systems [7; 8]. In their review, O.N. Senkov et al. [9] explore two groups of HEAs for high-temperature applications. The first group includes HEAs based on 3*d* transition metals such as Co, Cr, Cu, Fe, Mn, Ni, and Ti. These alloys have a yield strength of over 1000 MPa at 600 °C. However, according to the authors, none of the HEAs presented possess properties superior to modern nickel-based heat-resistant alloys. The heat resistance of HEAs quickly decreases at temperatures exceeding ≈800 °C, similar to that of nickel-based heat-resistant alloys. Additionally, their ability to withstand high temperatures is limited by their melting points, which are only slightly different from those of commercial nickel-based heat-resistant alloys.

Refractory high-entropy alloys (RHEAs) represent the second group of HEAs, developed by O.N. Senkov and co-authors [10] for high-temperature applications. Since 2010, this category of alloys has attracted the interest of specialists due to their ability to maintain high static strength up to 1600 °C and potentially higher. The first RHEA was created using five refractory components (Mo, Nb, Ta, V, and W), but later alloys were made from elements of Group IV (Ti, Zr, and Hf), Group V (V, Nb, and Ta), and Group VI (Cr, Mo, and W) [10].

Refractory high-entropy alloys show promise for use in structures and products operating at high temperatures (above 1000 °C) and are considered as replacements for nickel-based heat-resistant alloys. In their recent review, W. Xiong et al. [11] demonstrated that HEAs exhibit excellent mechanical properties over a wide range of temperatures and increased resistance to high-temperature oxidation. Currently, there is a significant increase in research on RHEAs, which is also confirmed by the growing number of reviews on RHEAs developed for applications in nuclear engineering [12; 13].

Traditionally, gas-phase, liquid-phase, and solid-phase methods are used to produce HEAs [3]. Powder metallurgy methods (solid-phase methods) are considered the most rational for obtaining RHEAs for high-temperature applications [14]. Fig. 1 illustrates the process for the production of HEAs, enabling the creation of high-quality billets with geometries that meet consumer requirements. However, the analysis of recent reviews [11 – 13] in the field of HEAs for high-temperature applications indicates a lack of information on solid-phase powder metallurgy processes for HEAs since 2020.

Thus, it becomes relevant to assess the latest developments and trends in the field of HEAs for high-temperature applications. Therefore, this review examines the criteria for selecting chemical elements for the solid-phase powder metallurgy process, as well as consolidation methods, density, phase composition, mechanical properties, and future trends regarding HEAs.

Materials and methods

Using the PRISMA (*Preferred Reporting Items for Systematic Reviews and Meta-Analyses*) criteria [15], both Russian and international databases were analyzed: elibrary.ru, mdpi.com, Springer.com and sciencedirect.com.

The selected studies met the following criteria:

– mechanical properties at elevated temperatures;

– oxidation resistance;

– thermal stability.

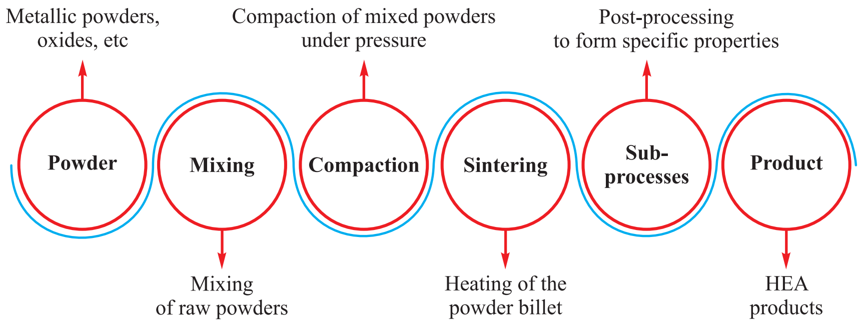

Fig. 1. Flow diagram of powder metallurgy

Рис. 1. Технологическая схема порошковой металлургии

Results and discussion

After screening for the specified criteria, thirty-nine studies related to powder metallurgy of high-entropy alloys (HEAs) for high-temperature applications were selected. The Table provides data on the studies that contain results meeting all of the aforementioned criteria.

Chemical composition

Recent studies have examined innovative oxide-dispersion strengthened (ODS) refractory high-entropy alloys (RHEAs). For example, in the study [32], 15 % Al_2O_3 was used to produce lightweight refractory alloys based on TaNbVTi. Zong L. et al. [33] used nanoscale ceramic particles of *m*-ZrO_2 to strengthen the refractory high-entropy alloy NbMoTaW, and in the study [34], they applied similar reinforcement for the WMoNbTaV alloy. Similarly, nanoscale Y_2O_3 particles were used in the study [35]. A new NbTaTiV ODS RHEA containing 0.35 wt. % Al_2O_3 was investigated in the study [25].

Strengthening HEAs with nanoscale refractory oxides can only be achieved through powder metallurgy methods. The traditional chemical compositions of HEAs, presented in the Table, replicate their compositions obtained earlier using liquid-phase methods [2; 8; 10 – 12]. Therefore, the application of powder metallurgy methods expands the technological capabilities for producing HEAs with the widest range of chemical compositions [36 – 39].

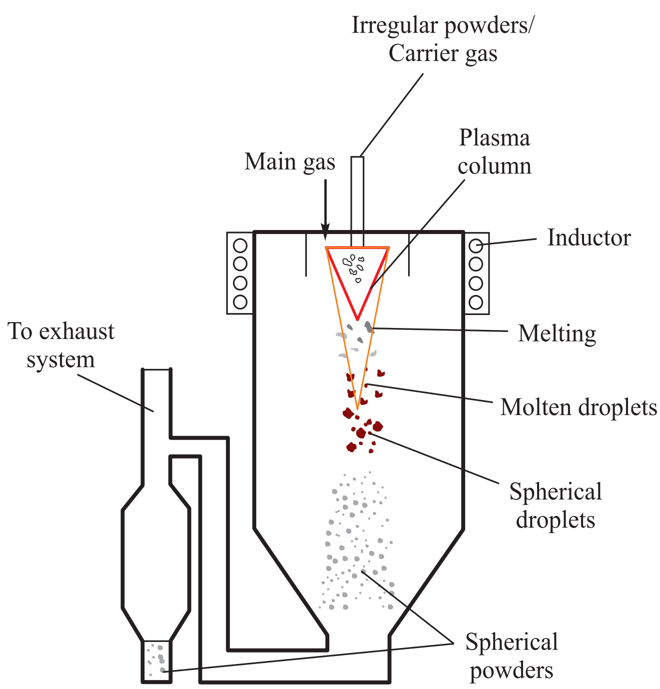

Fig. 2. Schematic diagram of plasma spheroidization system

Рис. 2. Принципиальная схема системы сфероидизации плазмы

Powder preparation

In the studies [40; 41], the approach of obtaining powder mixtures through simple mixing without additional milling was used. The most common method for producing powder is mechanical alloying in a planetary mill [42].

To expand the raw material base, in the study [43], a powder mixture was synthesized using a blend of titanium hydride and elemental powders. In the same study, Nb hydride powder and Ta hydride powder were used. The release of hydrogen during the decomposition of the hydrides helps to clean the surface of the metal powders from impurities.

For the agglomeration of fine powders, spray drying is applied. In the study [44], after spray drying, the HEA powder granules were processed in a plasma spheroidization unit (Tekna Nano-15). Induction thermal plasma (Fig. 2) was also used in the study [45] for spheroidizing WTaMoNbZr powder, which was originally irregularly shaped and obtained by grinding a hydrogenated ingot. The deoxidation during plasma processing contributed to refining the alloy.

In the study [46], pre-rolled plates with a known grain size were hydrogenated. The authors highlight the economic efficiency of the mechanical milling method and

Information on the reviewed studies

Информация об исследованиях, включенных в обзор

Author, year	Chemical composition	Powder preparation	Mechanical properties at elevated temperature
	Phase composition	Consolidation method	Oxidation resistance/thermal stability
Xiang L. et al., 2020 [16]	$TaNbVTiAl_x$ (x = 0, …, 1.0)	MA (Mechanical alloying)	Specific strength 88.37 MPa·cm^3/g, T = 900 °C; specific strength 16.03 MPa·cm^3/g, T = 1200 °C
	BCC	SPS (Spark plasma sintering)	–
Li H. et al., 2020 [17]	$Co_{25}Cr_{21}Fe_{18}Ni_{23}Mo_7Nb_3WC_2$	MA	T = 600 °C, $\sigma_{0.2}$ = 473 MPa*, σ = 741 MPa*, ε = 10.5 %; T = 900 °C, $\sigma_{0.2}$ = 142 MPa*, σ = 165 MPa*, ε = 31.0 %
	FCC + Me_6C	HP (Hot pressing)	–
Alvaredo-Olmos P. et al., 2021 [18]	$Fe_{1.5}Cr_1Al_{0.75}Mo_{0.1}Ti_{0.1}$ $Fe_{1.5}Cr_1Al_{0.75}Mo_{0.1}Ti_{0.1}Ni_{0.25}$	GA (Gas atomization)	T = 400 °C, HV = 6.1 GPa; T = 400 °C, HV = 6.5 GPa
	BCC-B2	SPS	–
Yang T. et al., 2021 [19]	CoCrFeMnNi	GA	Retention of nanostructure (55 – 160 nm) after heating to 1100 °C
	FCC	HP	–
Zhang R. et al., 2021 [20]	$Al_xCrTiMo$ (x = 0.25, …, 1.00)	MA	–
	BCC	SPS	Heat resistance at 1000 °C for 7 h
Liu Q. et al., 2021 [21]	MoNbTaTiV	MA	V = 0.5 s^{-1}, σ = 400 MPa; V = 0.0005 s^{-1}, σ = 30 MPa (T = 1300 °C in vacuum)
	BCC	SPS	–
Peng H. et al., 2022 [22]	NbMoTaWV	MA	T = 1000 °C, σ = 1978 MPa, specific strength 170.51 MPa·cm^3/g; T = 1200 °C, σ = 1433 MPa, specific strength 123.53 MPa·cm^3/g
	BCC + Tetrahedral phase	SPS	–
Gao F. et al., 2022 [23]	$TiAlV_{0.5}CrMo$	MA	–
	BCC + Laves phases	–	Retention of nanostructure at 1200 °C
Ujah C. et al., 2023 [24]	$Ti_{20}Al_{16}V_{16}Fe_{16}Ni_{16}Cr_{16}$	MA	Mechanical properties higher than Ti64 alloy
	FCC + BCC	SPS	–
Zhang X. et al., 2023 [25]	NbTaTiV + $0.35Al_2O_3$	MA	$\sigma_{0.2}$ = 690 MPa (T = 1000 °C)
	BCC + Al_2O_3	HP	–
Kuskov K.V. et al., 2023 [26]	$Co_{35}Ni_{10}Fe_{10}Cr_{10}Al_{35}$	MA + CBC	$\sigma_{0.2}$ = 1,120 MPa, T = 600 °C, specific yield strength 167.66 MPa·cm^3/g
	B2 + BCC + FCC + $L1_2$	SPS	–
Boztemur B. et al., 2023 [27]	WNbMoVTaCrAl	MA	–
	BCC + Ta_2VO_6 + (Nb,Ta)C + + $W_2C_{0.85}$ + Al_2O_3	SPS	Retention of nanostructure at 1150 °C
Das S. et al., 2023 [28]	AlCoCuFeNi	MA	–
	FCC + BCC	–	Retention of nanostructure at 900 °C
Qin M. et al., 2023 [29]	Ti–Nb–Mo–Ta–W–Ni–Zr	MA	–
	BCC + Secondary phases	SPS	Grain size <150 nm after 5 h annealing at 1300 °C
Gao F.et al., 2023 [30]	$TiAlV_{0.5}CrMo$	MA	–
	BCC1 + BCC2 + Al_2O_3	SPS	Retention of nanostructure at 1200 °C
Fu A. et al., 2023 [31]	Al – Fe – Co – Cr – Ni	GA	$\sigma_{0,2}$ = 518 MPa (T = 600 °C)
	FCC + BCC	Hot extrusion (extrusion ratio 7:1, temperature 1150 °C)	–

* Tensile test.

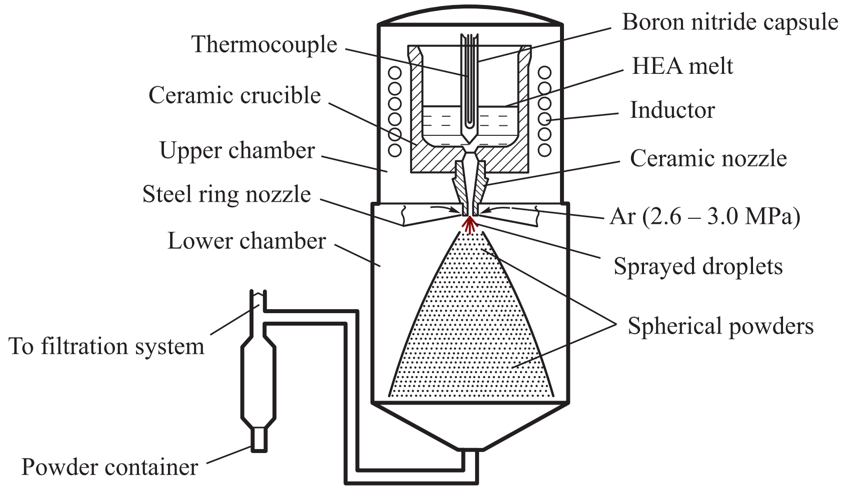

Fig. 3. Scheme of the unit for obtaining spherical powders by spraying the melt with inert gas

Рис. 3. Схема установки получения сферических порошков распылением расплава инертным газом

the clear correlation between the grain size of the plate and the resulting powders, which ranged from 6 to 102 μm.

Gas atomization (Fig. 3) is the primary method used for producing spherical powders. In the study [18], gas atomization was used to produce HEAs from 3*d* transition elements and refractory elements, while in the study [19], the same method was applied but exclusively for HEAs made from 3*d* transition elements. These powders have a homogeneous chemical composition and are suitable for various technological processes in powder metallurgy, as well as for additive manufacturing [47]. However, gas-atomized powders contain satellites, which limit their compactness. Therefore, for obtaining powders with a high degree of sphericity, the technology of centrifugal atomization of a rotating electrode is used.

In the study [48], both EIGA (*Electrode Inert Gas Atomization*, Fig. 4, *a*), and the PREP (*Plasma Rotating Electrode Process*, Fig. 4, *b*) were used to produce RHEA powders. The results demonstrated that the PREP method produced powders with high sphericity and no satellite particles, although the particle sizes were larger compared to those obtained with EIGA. The average particle sizes were 65.9 μm for PREP and 51.8 μm for EIGA.

In the study [26], self-propagating high-temperature synthesis (SHS) was used to obtain powders from mechanically activated powder, resulting in a change in the material's phase composition. This approach expands the potential for obtaining new properties in known HEA chemical compositions.

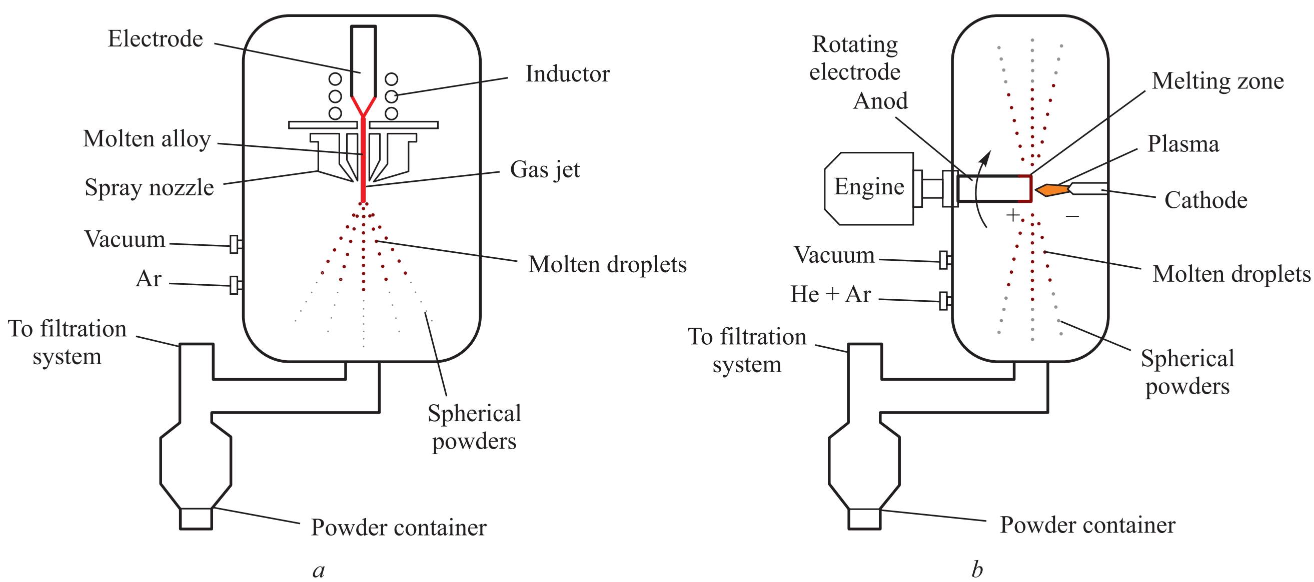

Fig. 4. Schematic diagrams of EIGA (*a*) and PREP (*b*) systems

Рис. 4. Принципиальные схемы систем EIGA (*a*) и PREP (*b*)

A combination of magnesiothermy and SHS was applied in the study [49]. The authors used a powder mixture of WO_3, Nb_2O_5, Ta_2O_3 and MoO_3 in combination with pure magnesium powder for SHS. This approach contributes to the expansion of the raw material base in the production of RHEAs.

The expansion of synthesis methods allows for obtaining powders with various chemical compositions, morphologies, and sizes. This is crucial for the next technological cycle in powder metallurgy, namely consolidation (compaction) processes.

Consolidation process

The most widely used compaction method is spark plasma sintering (SPS). In the studies [50] and [51], the maximum temperature of 1900 °C was achieved under a pressure of 50 MPa. The maximum pressure for SPS, 80 MPa, was applied in the study [52]. A key limiting factor for the pressure is the use of graphite punches in SPS.

The main advantage of the SPS method is the controllable process speed, increased sample density, and the retention of metastable structures due to high cooling rates. However, SPS has limitations in producing complex-shaped and large-sized products.

Sintering by hot pressing (HP) is a widely used technology in powder metallurgy for producing products with minimal residual porosity. The main difference between HP and SPS is in the heating and cooling rates. Additionally, HP is preferable for manufacturing large parts in industry [17; 19].

Cold isostatic pressing (CIP) and pressureless sintering are common methods in powder metallurgy. In the study [53], the maximum sintering temperature using a mixture of H_2 and Ar was 1400 °C. In the study [54], the same sintering atmosphere was used, but the maximum temperature reached 1450 °C. The data obtained on the sintering process can be adapted for high-throughput MIM (*Metal Injection Moulding*) technology [55; 56].

The method of hot extrusion is promising for producing long products with high mechanical properties. In the study [31], spherical powders in a stainless steel container were subjected to hot extrusion at a temperature of 1150 °C (extrusion ratio of 7:1). The production of long bars and wires by hot extrusion can be used both for making rod structures and for additive manufacturing processes, such as thermal spraying or wire arc additive manufacturing.

Among the reviewed studies on HEA powder metallurgy since 2020, no methods for producing billets by metal injection molding or hot isostatic pressing (HIP) were presented [57]. However, these methods enable the manufacturing of complex-shaped samples with high density and are promising for the production of parts from HEA powders. Thus, in the coming years, these methods are expected to be adapted for producing products for high-temperature applications.

Phase composition

In the reviewed studies (see Table), *X*-ray diffraction analysis of HEAs based on 3*d* transition metals primarily revealed a single-phase FCC solid solution, while for compositions based solely on refractory metals, a single-phase BCC solid solution was identified. However, for compositions containing both 3*d* transition metals and refractory metals, *X*-ray analysis detected the presence of two phases: FCC and BCC. Additionally, in some cases, the presence of carbide, oxide, sigma, and intermetallic phases was observed, which positively affect the high-temperature properties of the developed alloys.

Density

Density is a key factor for sintered samples, as it allows for assessing the effectiveness of the consolidation method.

Among the analyzed studies, the highest density was achieved for the RHEAs $(W_{35}Ta_{35}Mo_{15}Nb_{15})_{95}Ni_5$ (14.55 g/cm^3) [58] and equiatomic RHEA NbMoTaWRe (14.36 g/cm^3) [49], due to the presence of W, Ta, Nb, Mo, and Re. The lowest density, 5.98 g/cm^3, was obtained for the HEA $TiAlV_{0.5}CrMo$ [23]. Overall, chemical compositions containing Al have significantly lower densities. To further reduce the density, oxides are introduced into HEA compositions [32].

The density of powder samples is considered when calculating specific strength, which allows for comparing HEAs with different chemical compositions and densities.

It is important to note that density is also determined by the level of residual porosity, which is highest for pressureless sintering and lowest in the case of HP and SPS.

Mechanical properties at elevated temperatures

Only 20 % of the reviewed studies provide data on the properties of powder HEAs at elevated temperatures.

The authors of the study [16] found that the RHEA $TaNbVTiAl_{0.2}$ exhibits exceptional specific strength both at room temperature (207.11 MPa·cm^3/g) and at high temperatures (88.37 MPa·cm^3/g at 900 °C and 16.03 MPa·cm^3/g at 1200 °C), while maintaining acceptable ductility. Such RHEAs have the potential for use at temperatures exceeding 1200 °C. The high mechanical properties are determined by the homogeneous microstructure and solid solution strengthening.

In the study [17], a comparison of tensile test results at room temperature and at 900 °C showed that deformation increased 5.6 times, and the yield strength decreased fourfold. According to the authors, grain boundary strengthening was the dominant mechanism at elevated temperatures, where carbide particles made a significant contribution to increasing yield strength through dislocation and Orowan strengthening.

In the study [18], nanoindentation showed that increasing the temperature to 400 °C resulted in only a 10 % reduction in hardness.

In the study [21], the hot deformation characteristics of ultrafine-grained RHEA MoNbTaTiV were investigated using isothermal compression tests in the temperature range of 1100 to 1300 °C and strain rates from 0.0005 to 0.5 s^{-1}. It was found that at high temperature and low strain rate, the main deformation mechanism becomes grain boundary sliding, which is somewhat suppressed by grain growth and ultrafine precipitated phases distributed along the grain boundaries.

In the study [22], it was noted that the high strength of the NbMoTaWV alloy at elevated temperatures is primarily due to the presence of a secondary phase, which prevents grain boundary sliding. However, at elevated temperatures, the alloy became less ductile, likely due to the presence of the secondary phase, which leads to crack formation along the grain boundaries. At room temperature, the sintered NbMoTaWV demonstrated higher compressive strength and ductility compared to the corresponding cast HEA. The significant increase in strength is associated with the precipitation of the $(Ta, V)O_2$ phase and grain boundary strengthening of the BCC matrix.

In the study [25], a new super-strong RHEA NbTaTiV, oxide-dispersion strengthened with 0.35 wt. % Al_2O_3, was produced. The dual-phase material demonstrated a high yield strength (2075 MPa) and compressive ductility (15 %), maintaining high strength across a wide temperature range (25 – 1000 °C). The super-high strength of the dual-phase RHEA was mainly attributed to dispersion strengthening due to the high fraction of submicron Ti-(O, N) particles and solid solution strengthening. The alloy's performance can be significantly improved through oxide strengthening, opening new prospects for developing high-performance RHEAs.

High-temperature tests conducted in all the published studies aimed to evaluate the static strength of materials at elevated temperatures (see Table), but for practical application, an assessment of the reliability of such materials will be required. Therefore, future studies should evaluate fracture toughness, creep resistance, durability, etc.

Oxidation resistance and thermal stability

In 15 % of the reviewed studies, data on thermal stability and/or oxidation resistance were provided.

A key feature of RHEAs is the high-temperature stability of the ultrafine-grained structure, obtained through mechanical alloying followed by SPS. The high recrystallization temperature of RHEAs ensures the retention of the nanostructures formed during the preparation of powder mixtures. Therefore, RHEAs exhibit higher thermal stability compared to HEAs based on 3*d* elements.

The introduction of active elements Al and Cr into RHEA compositions promotes the formation of oxide films, which enhance heat resistance [20; 30].

Conclusions and future prospects

This review has examined new and traditional approaches used in the production of high-entropy alloys (HEAs) for high-temperature applications. The primary goal of solid-state methods for producing HEAs from refractory elements is to create cost-effective components with precise geometries and properties that are difficult or impossible to achieve using gas-phase or liquid-phase methods.

Recent research in powder metallurgy shows the use of oxides and hydrides for powder production, significantly expanding the raw material base for HEA metallurgy.

Various approaches are used to produce powder mixtures, including mechanical alloying, SHS (self-propagating high-temperature synthesis), hydride formation, metallothermy, agglomeration, spheroidization, gas atomization, and plasma atomization of a centrifugally rotating electrode.

An analysis of powder sintering methods indicates that the most commonly used method is spark plasma sintering (SPS). However, this method has known limitations regarding the shape and size of products. Therefore, the study of free sintering processes is more important for mass production. In addition, to reduce the porosity of sintered powder samples, hot isostatic pressing (HIP), which is actively used in additive manufacturing for critical products, should be applied.

The production of long bars and wires from HEAs by hot extrusion of powders can be used for making rod structures as well as for additive manufacturing processes, such as thermal spraying or wire arc additive manufacturing.

An analysis of the chemical composition of high-entropy alloys shows that HEAs based on 3*d* transition elements are suitable for temperatures up to 1000 °C, while refractory HEAs (RHEAs) are used at higher temperatures. The addition of aluminum is aimed at reducing the density of RHEAs and increasing oxidation resistance.

One of the promising methods for improving strength at high temperatures is oxide dispersion strengthening. However, in some cases, nanoparticles chemically interact with the matrix, altering the chemical composition of the dispersed particles. Therefore, the selection of strengthening nanoscale powders requires prior analysis.

The high thermal stability of RHEAs and the retention of nanoscale grains at temperatures above 1000 °C are determined by the high recrystallisation temperature.

The results of this review confirm that HEAs have potential for use in high-temperature applications. The mechanical properties of sintered RHEA samples are superior to those of samples with similar chemical compositions obtained by liquid-phase methods. However, further research and development are required to improve the oxidation resistance and mechanical properties of powder RHEAs at the desired temperatures.

A key finding from the analysis is the identification of a limited range of methods for evaluating high-temperature properties (such as compressive strength, tensile strength, and nano-hardness). This restricts consumers' ability to fully assess the feasibility of new alloys and production methods for practical applications. Therefore, it is essential to broaden the evaluation approaches to include a wider spectrum of performance characteristics, such as fracture toughness, heat resistance, wear resistance, fatigue strength, and overall durability.

Thus, future research should focus on:

– determining fatigue properties and the durability of powder products to ensure their reliability in real engineering applications;

– manufacturing large parts with complex shapes;

– reducing porosity without significantly increasing cost;

– developing low-temperature deformation methods;

– creating environmentally friendly and highly accurate production technologies.

When planning new research, it is important to focus on scalability, cost-effectiveness, and the practical application of powder synthesis and consolidation methods to enable their broader adoption in real-world engineering projects.

References / Список литературы

1. Yeh J.W., Chen S.K., Lin S.J., Gan J.Y., Chin T.S., Shun T.T., Tsau C.H., Chang S.Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Advanced Engineering Materials*. 2004;6(5):299–303. https://doi.org/10.1002/adem.200300567
2. Cantor B., Chang I.T.H., Knight P., Vincent A.J.B. Microstructural development in equiatomic multicomponent alloys. *Materials Science and Engineering: A*. 2004;375–377: 213–218. https://doi.org/10.1016/j.msea.2003.10.257
3. Murty B.S., Yeh J.W., Ranganathan S., Bhattacharjee P.P. High-Entropy Alloys. London: Elsevier; 2019:388. https://doi.org/10.1016/C2017-0-03317-7
4. Jamieson B., Peter K. High-Entropy Materials: Theory, Experiments, and Applications. Switzerland: Springer Cham; 2021:774. https://doi.org/10.1007/978-3-030-77641-1
5. Behera A. Advanced Materials. Switzerland: Springer Cham; 2022:748. https://doi.org/10.1007/978-3-030-80359-9
6. Liu F., Liaw P.K., Zhang Y. Recent progress with BCC-structured high-entropy alloys. *Metals*. 2022;12(3):501. https://doi.org/10.3390/met12030501
7. Patel P., Roy A., Sharifi N., Stoyanov P., Chromik R.R., Moreau C. Tribological performance of high-entropy coatings (HECs): A review. *Materials*. 2022;15(10):3699. https://doi.org/10.3390/ma15103699
8. Sonar T., Ivanov M., Trofimov E., Tingaev A., Suleymanova I. An overview of microstructure, mechanical properties and processing of high entropy alloys and its future perspectives in aeroengine applications. *Materials Science for Energy Technologies*. 2024;7:35–60. https://doi.org/10.1016/j.mset.2023.07.004
9. Senkov O.N., Miracle D.B., Chaput K.J., Couzinie J.-P. Development and exploration of refractory high entropy alloys – A review. *Journal of Materials Research*. 2018;33: 3092–3128. https://doi.org/10.1557/jmr.2018.153
10. Senkov O.N., Wilks G.B., Miracle D.B., Chuang C.P., Liaw P.K. Refractory high-entropy alloys. *Intermetallics*. 2010;18(9):1758–1765. https://doi.org/10.1016/j.intermet.2010.05.014
11. Xiong W., Guo A., Zhan S., Liu C., Cao S. Refractory high-entropy alloys: A focused review of preparation methods and properties. *Journal of Materials Science and Technology*. 2023;142:196–215. https://doi.org/10.1016/j.jmst.2022.08.046
12. Wang X., Huang H., Shi J., Xu H., Meng D. Recent progress of tungsten-based high-entropy alloys in nuclear fusion. *Tungsten*. 2021;3:143–160. https://doi.org/10.1007/s42864-021-00092-8
13. Shi T., Lei P., Yan X., Li J., Zhou Y., Wang Y., Su Z., Dou Y., He X., Yun D., Yang W., Lu C. Current development of bodycentered cubic high-entropy alloys for nuclear applications. *Tungsten*. 2021;3:197–217. https://doi.org/10.1007/s42864-021-00086-6
14. Karan, Pachauri P., Kumar A., Maury M. Effect of powder metallurgy on high entropy alloy materials: A review. *Materials Today: Proceedings*. 2021;47(13):4026–4033. https://doi.org/10.1016/j.matpr.2021.04.529
15. Page M.J., McKenzie J.E., Bossuyt P.M., Boutron I., Hoffmann T.C., Mulrow C.D., Tetzlaff J.M., Akl E.A., Brennan S.E., Chou R., etc. The PRISMA 2020 statement: An updated guideline for reporting systematic reviews. *BMJ*. 2021;372:n71. https://doi.org/10.1136/bmj.n71
16. Xiang L., Guo W., Liu B., Fu A., Li J., Fang Q., Liu Y. Microstructure and mechanical properties of $TaNbVTiAl_x$ refrac-

tory high-entropy alloys. *Entropy*. 2020;22(3):282. https://doi.org/10.3390/e22030282

17. Li H., Lin H., Liang X., He W., Liu B., Liu Y., Wang L. In situ development and high temperature features of CoCrFeNi-M_6C_p high entropy-alloy based hardmetal. *Metals*. 2020;10(3):408. https://doi.org/10.3390/met10030408

18. Alvaredo-Olmos P., Molina-Aldareguía J., Vaz-Romero A., Prieto E., González-Julián J., Monclús M.A. Understanding the links between the composition-processing-properties in new formulations of HEAs sintered by SPS. *Metals*. 2021;11(6):888. https://doi.org/10.3390/met11060888

19. Yang T., Cai B., Shi Y., Wang M., Zhang G. Preparation of nanostructured CoCrFeMnNi high entropy alloy by hot pressing sintering gas atomized powders. *Micron*. 2021;147:103082. https://doi.org/10.1016/j.micron.2021.103082

20. Zhang R., Meng J., Han J., etc. Oxidation resistance properties of refractory high-entropy alloys with varied Al_xCrTiMo content. *Journal of Materials Science*. 2021;56:3551–3561. https://doi.org/10.1007/s10853-020-05480-y

21. Liu Q., Wang G., Liu Y., Sui X., Chen Y., Luo S. Hot deformation behaviors of an ultrafine-grained MoNbTaTiV refractory high-entropy alloy fabricated by powder metallurgy. *Materials Science and Engineering: A*. 2021;809:140922. https://doi.org/10.1016/j.msea.2021.140922

22. Peng H., Kang Z., Long Y., Zhou L. A two-phase ultrafine-grained NbMoTaWV refractory high entropy alloy with prominent compressive properties. *Vacuum*. 2022;199:110930. https://doi.org/10.1016/j.vacuum.2022.110930

23. Gao F., Sun Y., Hu L., Shen J., Liu W., Ba M., Deng C. Microstructural evolution and thermal stability in a nanocrystalline lightweight $TiAlV_{0.5}$CrMo refractory high-entropy alloy synthesized by mechanical alloying. *Materials Characterization*. 2022;329:133179. https://doi.org/10.1016/j.matlet.2022.133179

24. Ujah C., Popoola A., Popoola O., Afolab A., Uyor U. Mechanical and oxidation characteristics of Ti20-Al16-V16-Fe16-Ni16-Cr16 high-entropy alloy developed via spark plasma sintering for high-temperature/strength applications. *Journal of Materials Engineering and Performance*. 2023;32:18–28. https://doi.org/10.1007/s11665-022-07066-y

25. Zhang X., Li T., Cao Y., Liao T., Xie Z., Fu A., Li J., Fang Q., He Z., Liu B. Oxide dispersion strengthening mediated ultrahigh strength at wide temperature range in NbTaTiV refractory high-entropy alloys. *International Journal of Refractory Metals and Hard Materials*. 2023;116:106352. https://doi.org/10.1016/j.ijrmhm.2023.106352

26. Kuskov K.V., Nepapushev A.A., Aydinyan S., Shaysultanov D.G., Stepanov N.D., Nazaretyan K., Kharatyan S., Zakharova E.V., Belov D.S., Moskovskikh D.O. Combustion synthesis and reactive spark plasma sintering of non-equiatomic CoAl-based high entropy intermetallics. *Materials*. 2023;16(4):1490. https://doi.org/10.3390/ma16041490

27. Boztemur B., Bayrak K., Gökçe H., Ayas E., Balcı-Çağıran Ö., Derin B., Ağaoğulları D. Mechanically alloyed and spark plasma sintered WNbMoVTa refractory high entropy alloys: Effects of Cr and Al on the microstructural and mechanical properties. *Journal of Alloys and Compounds*. 2023;965:171415. http://dx.doi.org/10.1016/j.jallcom.2023.171415

28. Das S., Robi P. Processing and characterizations of powder of the AlCoCuFeNi high entropy alloy. *Emergent Materials*. 2023;6:987–997. https://doi.org/10.1007/s42247-023-00466-3

29. Qin M., Shivakumar S., Luo J. Refractory high-entropy nanoalloys with exceptional high-temperature stability and enhanced sinterability. *Journal of Materials Science*. 2023;58:8548–8562. https://doi.org/10.1007/s10853-023-08535-y

30. Gao F., Sun Y., Hu L., Shen J., Liu W., Ba M., Deng C. Microstructure and strengthening mechanisms of novel lightweight $TiAlV_{0.5}$CrMo refractory high-entropy alloy fabricated by mechanical alloying and spark plasma sintering. *Journal of Alloys and Compounds*. 2023;932:167659. https://doi.org/10.1016/j.jallcom.2022.167659

31. Fu A., Cao Y., Xie Z., Wang J., Liu B. Microstructure and mechanical properties of Al-Fe-Co-Cr-Ni high entropy alloy fabricated via powder extrusion. *Journal of Alloys and Compounds*. 2023;943:169052. https://doi.org/10.1016/j.jallcom.2023.169052

32. Fu A., Cao Y., Liu Y., Xu S. Microstructure and mechanical properties of novel lightweight TaNbVTi-based refractory high entropy alloys. *Materials*. 2022;15(1):355. https://doi.org/10.3390/ma15010355

33. Zong L., Xu L., Luo C., Jiao Z., Li X., Sun W., Wei S. Mechanical properties and strengthening mechanism of the nano-sized *m*-ZrO_2 ceramic particle reinforced NbMoTaW refractory high-entropy alloy. *International Journal of Refractory Metals and Hard Materials*. 2023;113:106201. https://doi.org/10.1016/j.ijrmhm.2023.106201

34. Zong L., Xu L., Luo C., Li Z., Zhao Y., Xu Z., Zhu C., Wei S. Fabrication of nano-ZrO_2 strengthened WMoNbTaV refractory high-entropy alloy by spark plasma sintering. *Materials Science and Engineering: A*. 2022;843:143113. https://doi.org/10.1016/j.msea.2022.143113

35. Liao T., Cao Y., Guo W., Fang Q., Li J., Liu B. Microstructure and mechanical property of NbTaTiV refractory high-entropy alloy with different Y_2O_3 contents. *Rare Metals*. 2022;41:3504–3514. https://doi.org/10.1007/s12598-022-02038-6

36. Moravcikova-Gouvea L., Moravcik I., Pouchly V., Kovacova Z., Kitzmantel M., Neubauer E., Dlouhy I. Tailoring a refractory high entropy alloy by powder metallurgy process optimization. *Materials*. 2021;14(19):5796. https://doi.org/10.3390/ma14195796

37. Liu Q., Wang G., Sui X., Xu Y., Liu Y., Yang J. Ultra-fine grain Ti_xVNbMoTa refractory high-entropy alloys with superior mechanical properties fabricated by powder metallurgy. *Journal of Alloys and Compounds*. 2021;865:158592. https://doi.org/10.1016/j.jallcom.2020.158592

38. Salemi F., Karimzadeh F., Abbasi M. Evaluation of thermal and mechanical behavior of CuNiCoZnAl high-entropy alloy fabricated using mechanical alloying and spark plasma sintering. *Metallurgical and Materials Transactions A*. 2021;52:1947–1962. https://doi.org/10.1007/s11661-021-06205-9

39. Li Y., Du Z., Fu Y., Sun H., Fan J., Han Y. Microstructures and mechanical properties of novel MoTaVW refractory high-entropy alloys. *Journal of Alloys and Compounds*. 2023;968:172165. https://doi.org/10.1016/j.jallcom.2023.172165

40. Wu Y., Liaw P.K., Zhang Y. Preparation of bulk TiZrNbMoV and NbTiAlTaV high-entropy alloys by powder sintering. *Metals*. 2021;11(11):1748. https://doi.org/10.3390/met11111748
41. Shkodich N., Sedegov A., Kuskov K., Busurin S., Scheck Y., Vadchenko S., Moskovskikh D. Refractory high-entropy HfTaTiNbZr-based alloys by combined use of ball milling and spark plasma sintering: effect of milling intensity. *Metals*. 2020;10(9):1268. https://doi.org/10.3390/met10091268
42. Ivannikov A.Y., Grebennikov I.K., Klychevskikh Y.A., Mikhailova A.V., Sergienko K.V., Kaplan M.A., Lysenkov A.S., Sevostyanov M.A. Fabrication, microstructure, and physico-mechanical properties of Fe–Cr–Ni–Mo–W high-entropy alloys from elemental powders. *Metals*. 2022; 12(10):1764. https://doi.org/10.3390/met12101764
43. Sharma B., Nagano K., Saxena K.K., Fujiwara H., Ameyama K. Application of hydride process in achieving equimolar TiNbZrHfTa BCC refractory high entropy alloy. *Crystals*. 2020;10(11):1020. https://doi.org/10.3390/cryst10111020
44. Chen Y., Liu P., Dong Z., Liu H., Wang J., Guo X., Xia Y., Wang Q. Sintering, microstructure, and mechanical properties of TiTaNbZrHf high-entropy alloys prepared by cold isostatic pressing and pressure-less sintering of hydrides. *Materials*. 2023;16:1759. https://doi.org/10.3390/ma16051759
45. Liu B., Duan H., Li L., Zhou C., He J., Wu H. Microstructure and mechanical properties of ultra-hard spherical refractory high-entropy alloy powders fabricated by plasma spheroidization. *Powder Technology*. 2021;382:550–555. https://doi.org/10.1016/j.powtec.2021.01.021
46. Xia M., Chen Y., Chen K., Tong Y., Liang X., Shen B. Synthesis of WTaMoNbZr refractory high-entropy alloy powder by plasma spheroidization process for additive manufacturing. *Journal of Alloys and Compounds*. 2022;917:165501. https://doi.org/10.1016/j.jallcom.2022.165501
47. Wang H., Niu Z., Chen C., Chen H., Zhu X., Zhou F., Zhang X., Liu X., Wu Y., Jiang S. Powder production of an equimolar NbTaTiZr high-entropy alloy via hydrogen embrittlement. *Materials Characterization*. 2022;193:112265. https://doi.org/10.1016/j.matchar.2022.112265
48. Kolmakov A.G., Ivannikov A.Yu., Kaplan M.A., Kirsankin A.A., Sevost'yanov M.A. Corrosion-resistant steels in additive manufacturing. *Izvestiya. Ferrous Metallurgy*. 2021;64(9):619–650. (In Russ.). https://doi.org/10.17073/0368-0797-2021-9-619-650

    Колмаков А.Г., Иванников А.Ю., Каплан М.А., Кирсанкин А.А., Севостьянов М.А. Коррозионностойкие стали в аддитивном производстве. *Известия вузов. Черная металлургия*. 2021;64(9):619–650. https://doi.org/10.17073/0368-0797-2021-9-619-650
49. Gao S., Fu A., Xie Z., Liao T., Cao Y., Liu B. Preparation and microstructure of high-activity spherical TaNbTiZr refractory high-entropy alloy powders. *Materials*. 2023;16(2):791. https://doi.org/10.3390/ma16020791
50. Moser M., Dine S., Vrel D., Perrière L., Pirès-Brazuna R., Couque H., Bernard F. Elaboration and characterization of WMoTaNb high entropy alloy prepared by powder metallurgy processes. *Materials*. 2022;15(15):5416. https://doi.org/10.3390/ma15155416
51. Gu T., Wang LM., Hu Q., Liang X., Fu D., Chen Y., Zhao X., Sheng Y. Effect of mechanical alloying and sintering behavior on the microstructure and properties of NbMoTaWRe refractory high entropy alloy. *Metals and Materials International*. 2022;28:2571–2582. https://doi.org/10.1007/s12540-021-01165-6
52. Liu J., Zhao X., Zhang S., Sheng Y., Hu Q. Microstructure and mechanical properties of MoNbTaW refractory high-entropy alloy prepared by spark plasma sintering. *Journal of Materials Research*. 2023;38:484–496. https://doi.org/10.1557/s43578-022-00833-6
53. Maharana S., Prasad D., Seetharaman S., Sabat M. Effect of sintering parameters on phase evolution, microstructural development and mechanical behavior of Ni46Al-12Co18Cr8Fe12Mo4 high entropy alloy synthesized via mechanical alloying and spark plasma sintering. *Materials Science and Engineering: A*. 2023;886:145695. https://doi.org/10.1016/j.msea.2023.145695
54. Chen C., Chang C., Chen H. Investigation of Cr content, second phase, and sintering temperature on characteristics of WMoVTiCr refractory high entropy alloys. *International Journal of Refractory Metals and Hard Materials*. 2023;110:106034. https://doi.org/10.1016/j.ijrmhm.2022.106034
55. Zhang Y., Bian T., Shen X., Wang Z., Ye S., Feng S., Yu K., Ding C., Yu P. Sintering mechanism and microstructure evolution of a CoCrFeNiMn high entropy alloy fabricated by metal injection molding. *Journal of Alloys and Compounds*. 2021;868:158711. https://doi.org/10.1016/j.jallcom.2021.158711
56. Anwer Z., Umer M., Adeel F., Hafeez M., Yaqoob K., Luo X., Ahmad I. Microstructure and mechanical properties of hot isostatic pressed tungsten heavy alloy with FeNiCoCrMn high entropy alloy binder. *Journal of Materials Research and Technology*. 2023;22:2897–2909. https://doi.org/10.1016/j.jmrt.2022.12.078
57. Tang Z., Senkov O., Parish C., Zhang C., Zhang F., Santodonato L., Wang G., Zhao G., Yang F., Liaw P. Tensile ductility of an AlCoCrFeNi multi-phase high-entropy alloy through hot isostatic pressing (HIP) and homogenization. *Materials Science and Engineering: A*. 2015;647:229–240. https://doi.org/10.1016/j.msea.2015.08.078
58. Duan B., Yu Y., Liu X., Wang D., Wu Z. A novel non-equiatomic $(W_{35}Ta_{35}Mo_{15}Nb_{15})_{95}Ni_5$ refractory high entropy alloy with high density fabricated by powder metallurgical process. *Metals*. 2020;10(11):1436. https://doi.org/10.3390/met10111436

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