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A short review on high-entropy alloys (HEAs)

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ABSTRACT
The demand for materials with enhanced mechanical properties at relatively low cost is increasing. In what refers to metallic materials, metal alloys represent the most representative branch. Although several conventional alloys have well-stablished phase diagrams and well-known microstructures and properties, they intrinsically have certain limitations in properties. These limitations partially led to the development of the so-called high-entropy alloys (HEAs), which represents a brand-new research field within multicomponent alloys. This paper aims at showing a short review on the state of the art of HEAs, highlighting the progress in this topic. This review starts with an introduction to HEAs and their comparison with conventional alloys. The next sections show the advances on research in terms of the existing HEAs, the combinations of elements, and the association of the processing routes with the properties obtained. The subsequent section presents a discussion about possible trends and opportunities in this promising research field. The final section refers to the conclusions.

Keywords: High-entropy alloys, Multicomponent alloys, Alloy design.

1 INTRODUCTION

A great assortment of materials has been designed by research conducted all over the world intending to provide solutions to the most varied types of applications. Notably, the main requirements a material should attend refer to its properties and cost. The performance of a material depends on its properties, which depends on its structure, which depends on its processing route. In the case of metallic materials, one or more metallic elements and/or non-metallic elements are present. Thus, they can be pure metals (only one metallic element) or metal alloys (blending of two or more elements, at least one of them being metallic).

Hence, the mechanical properties of pure metals can be highly improved by alloying each one with other metals or non-metallic elements (RAZUAN *et al*., 2013). The so-called conventional alloys are designed with a maximum of one or two main elements (SHUN *et al*., 2012).

To enhance the properties of the conventional alloys, possible solutions namely multicomponent alloys, which are defined as metal alloys containing three or more main elements, may be applied. Although they might represent the solution required in several situations, they may form intermetallic compounds (crystalline or quasi-crystalline) inside the solid solution, with complex microstructures corresponding to mechanical properties of undesirable magnitudes. These multicomponent alloys frequently include

interstitial compounds (Hagg phases). In the case of nonequilibrium conditions, some of them form metallic glasses.

To fulfill this gap, then high-entropy alloys (HEAs) were developed, in which their design is based on at least five main elements (concentrations varying between 5 and 35% in molar terms) up to 13 main elements, and other minor elements less than 5%. This denomination is due to their high entropic effects in solidification process, thus promoting simple solid solutions, in contrast with the formation of complex phases.

The universe of possible alloys is so large that the cost and time to obtain them all turn the task unfeasible (CANTOR, 2014). Thenceforth, as far as this research could reach, there are at least four main approaches applied to design an alloy: (a) molecular dynamics (MD) simulations (GAO; ALMAN, 2013) (XIE *et al*., 2013); (b) calculation phase diagrams (CALPHAD) (ZHANG *et al*., 2012) (ZHANG *et al*., 2014); (c) machine learning, which is a computational tool to statistically explore the design space (BUTLER *et al*., 2018), and (d) parametric approach, which is a method to design multi-component alloys by using a set of parameters and criteria (TAZUDDIN *et al*., 2016) (TAZUDDIN *et al*., 2017).

The first approach mentioned herein, MD simulations consist of a set of tools to predict properties of the simulated alloys. An MD box defines the boundary conditions, initial velocities and positions of each atom, pressure, temperature (ZHOU; LIU, 2022). According to the potential energy functions, Newton's equations of motion govern the path of each atom once the system reaches the thermal equilibrium. This approach stands out by the accuracy of simulated atom trajectory, which benefits the study of nucleation and development of defects in crystal lattice (CAR *et al*., 2005). In addition, deformation mechanisms can be studied under different boundary conditions, and the relationship between the deformation mechanisms and the stacking fault energy can be established. Its capacity of accuracy and predictability builds a trade-off with its high computational cost.

The second approach, CALPHAD (calculation phase diagrams), refer to geometric representations of alloys under thermal equilibrium that delimit the phase transformations in terms of pressure, temperature and composition (LI *et al*., 2020). The diagrams created is crucial for studying crystal formation and solidification. The minimization of the total Gibbs free energy is the principle applied using composition, pressure, and temperature. The success in implementing CALPHAD relies on the availability of the most adequate database, which should include at least all the binary and ternary sub-systems involved. One of the most impacting drawbacks is the lack thermodynamic databases to cover large design spaces.

The third approach, ML, refers to a computational tool to simulate possible solutions in the alloy design space using statistical techniques. The properties or even the phases can be predicted, for example, via decision trees, support vector machines (SVMs), and artificial neural networks (ANNs) (YANG *et al*., 2022). Although large databases can be handled, the quality of the training data, adequate input variables,

and the ML model impact the accuracy of prediction. Commonly, the addition of more variables improves the accuracy of the model. However, depending on the number of variables compared to the computational capacity, the computational cost can be too high to make the simulations feasible. Thus, variables with a high correlation coefficient with each other may be disregarded.

The last approach (parametric) involves the calculation of a set of parameters and the assessment of a collection of criteria that probably leads to stable solid solutions. This approach (also called first-principles calculations or ab-initio) applies quantum physical laws (including Hume-Rothery rules) to propose the parameters. In the field of HEAs a unique set of parameters and criteria is proposed in each research to obtain the specific results reported. Furthermore, each combination of elements may behave in a unique manner, implying in a particular set of parameters and criteria to be fulfilled. Therefore, there may be relative difficulty in recognizing and adopting the most adequate set to produce the required solid solution stability. In view of the difficulty in determining the most adequate set of parameters and criteria, a potential solution may be the utilization of the most relevant and all those frequently reported. The main advantages of this approach rely on the non-need of experimental data and the high predictive capacity (IKEDA *et al*., 2019). On the other hand, one of the main drawbacks refer to the high computational cost to scan the large alloy design space.

2 STATE OF THE ART ON HEAs

Some HEAs present the advantage of being used in the as-cast condition, which avoids post-processing. For example, a casting eutectic HEA with tensile strength of 1266.5 MPa and elongation of 20.3% was obtained in terms of two ingots $Ni_{30}Co_{30}Cr_{10}Fe_{10}Al_{18}W_2$ (at%). These ingots were obtained using powder purity of 99.95% via vacuum arc melting (getter Ti with Ar atmosphere), being remelted four times in a water-cooled copper mold (WU *et al*., 2019). The strategy of obtaining eutectic HEAs implies in low melting points and narrow solidification intervals.

A single-phase HEA, $Pt_2AuCuNiSn$, was obtained at low temperatures via solid-state reaction. The homogenization of the powders was conducted in an agate mortar and pressed flat pellets of 4 mm diameter were then obtained. The pellets were flushed with Ar three times before sealing the silica glass tubes (WINKLER *et al*., 2021).

Hard HEAs are also the research focus in some cases. For example, the mechanical synthesis of W and Ti carbides were conducted in an airtight mechanical reactor of a ball milling, yielding a hard metal alloy obtained via mechanochemical and spark plasma sintering (SPS), WC-5TiC-10Co. The hardness reached 1484 HV, a bending strength limit of 1924 MPa, a full density compared to the theoretical value, and a relatively fast process (13 minutes) (BURAVLEV *et al*., 2021).

Practical substitutions of commercially available products were made, as in (DA SILVA *et al*., 2021). SPS ultrafine WC-6.4Fe3.6Ni alloy was proposed in substitution of WC-Co. The increase in sintering temperature improved the microstructure and hardness, decreasing fracture toughness. 99.8% of densification was achieved using a high energy milling. The high value of densification was attributed to the wettability of milled Fe-Ni binder during heating in the SPS. Lowering the binder mean free path leaded to a decrease in fracture toughness.

In order to obtain metal alloys with high yield strength, a novel strategy was proposed: the HEA designed with multi-strength mechanisms ($Co_{21}Cr_{11}Fe_{49}Mn_4Ni_4V_2C_1Mo_3Si_5$). This includes: (a) induced martensite transformation; (b) grain refinement; (c) precipitation hardening from nanoscale precipitates; (d) addition of Mo and V. The referred alloy was designed in CALPHAD and the as-cast ingots obtained by vacuum induction melting with elements 99.9% pure. Thenceforth, these ingots were homogenized at 1200°C in Ar atmosphere for 24 hours and water quenched. They were cold rolled at room temperature, annealed, and water quenched (DO *et al*., 2022).

One of the branches on the study of HEAs is the magnetic one. The phase formation was investigated in FeCoNiMnV HEA in terms of the variation of milling time. The magnetic properties were obtained for the 48 hours-milled powder, where FCC and BCC phases coexist. In view of the results, the HEAs obtained are classified as semi-hard magnetic (ALIJANI *et al*., 2019).

A brand-new parametric study was presented for amorphous HEAs in terms of two updates: crystalline structure of alloying elements and atomic radius modification. Conventional parametric approach does not consider small compositional changes, the kinetic effects, and small number of available data points. In the case of 92TiZrHfM, TiZrHfMM, and Ti, ZrHfMMM (M=Fe, Cr, Ni, V, Nb, Al, Ag, Cu), fabricated via melt spinning, the update in atomic radii found out to be more accurate in predicting the formation of amorphous and crystalline alloys than the conventional parametric approach. Furthermore, the amorphous phase formation is highly influenced by the crystal structures of the alloying elements (HU *et al*., 2017).

In the branch of the hardest metal alloys ever made, most of them are brittle and amorphous, which reduces their possibilities of application. On the other hand, metallic diamonds (MDs), which concept relies on lattice occupation, have a BCC structure, designing and manufacturing alloys up to nine different elements. The difference of atomic radii between the involved elements may induce severe deformed configurations, modifying the symmetry of the unit cell, which may harden by solid solution. In view of this, even in a preliminary character, MDs show as-cast hardnesses from 850 to 1420 HV. When carburized, they present a hardness range from 1247 to 2507 HV (RESTIVO, T. A. G.; RESTIVO, G. M. G., 2021). Thus, through the comparison between MD and those then denominated the hardest ever known, e.g. $Fe_{49.7}Cr_{17.7}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ (1660 HV) (GUTIERREZ-NODA *et al*., 2019),

$AlCrMnMoNiZrB_{0.1}$ (1330 HV) (REN *et al*., 2011), WC-5TiC-10Co (1484 HV) (BURAVLEV *et al*., 2021), and WB_4, ReB_2, YB_{12}, and ZrB_{12} (2447 HV) (DOVALE-FARELO *et al*., 2021) it can be partially concluded that there is the possibility to design harder and tougher alloys than the currently available, also trying to aggregate adequate properties to their manufacturability.

3 DISCUSSION

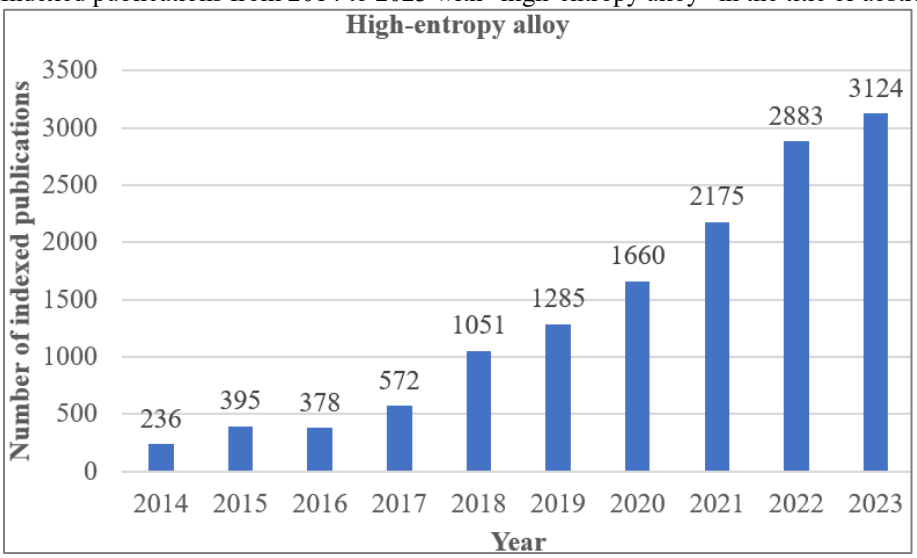
This section addresses possible trends and opportunities in HEAs' field by presenting the bibliometric research conducted and analyzing the data behavior.

In order to check the importance of the search words and capture research gaps and opportunities, some bibliometric research was conducted, which results are shown in the next six figures (Figs. 1 to 6). All plots cover the ten-year period from 2014 to 2023 and indicate the number of publications in what relates to the search word in CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, 2022) information repository. "High-entropy alloy", "Refractory high-entropy alloy", "Eutectic high-entropy alloy", "Magnetic high-entropy alloy", "High-entropy alloy coating", and "multicomponent alloy" were the searched words, which are presented in Fig. 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5, and Fig. 6, respectively.

As can be verified, Fig. 4 (magnetic high-entropy alloy) and Fig. 5 (multicomponent alloy) are the only exceptions in the trends observed in the other plots. In other words, it is worth noting that when "magnetic high-entropy alloy" is the research word, the results over the referred ten-year period tend to be stable in the last three years. When "multicomponent alloy" is the research word there was a decrease in the number of publications in the last year. However, for the other research words there is a trend to increase the number of publications, turning the research area yet more active. Based on the last two years, the highest growth rate corresponds to "eutectic high-entropy alloy", Fig. 3 (32.32%) and the lowest one is associated to "magnetic high-entropy alloy", Fig. 4 (-12.5%).

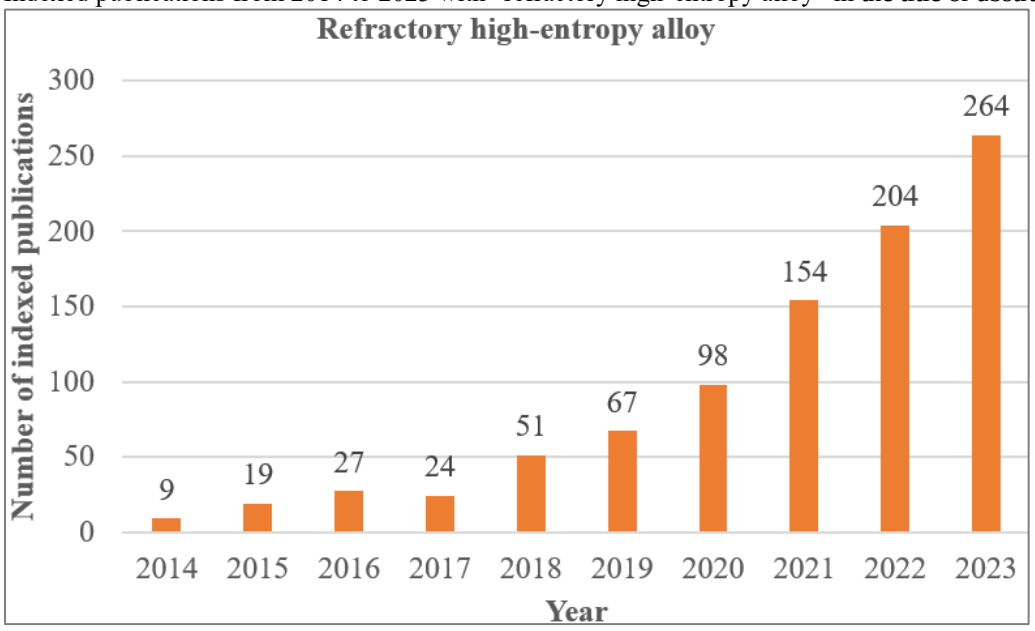
In addition, it is important to highlight that the research word "amorphous high-entropy alloy" (AHEA) returned 27 results (most of them in the first four years of the referred period), which tends to indicate non-continuity in this branch. Moreover, the research word "nano-high-entropy alloy" (NHEA) returned only 4 results (all of them in 2020 and 2023), which may point out a new trend in HEAs.

Figure 1: Indexed publications from 2014 to 2023 with “high-entropy alloy” in the title or abstract fields.



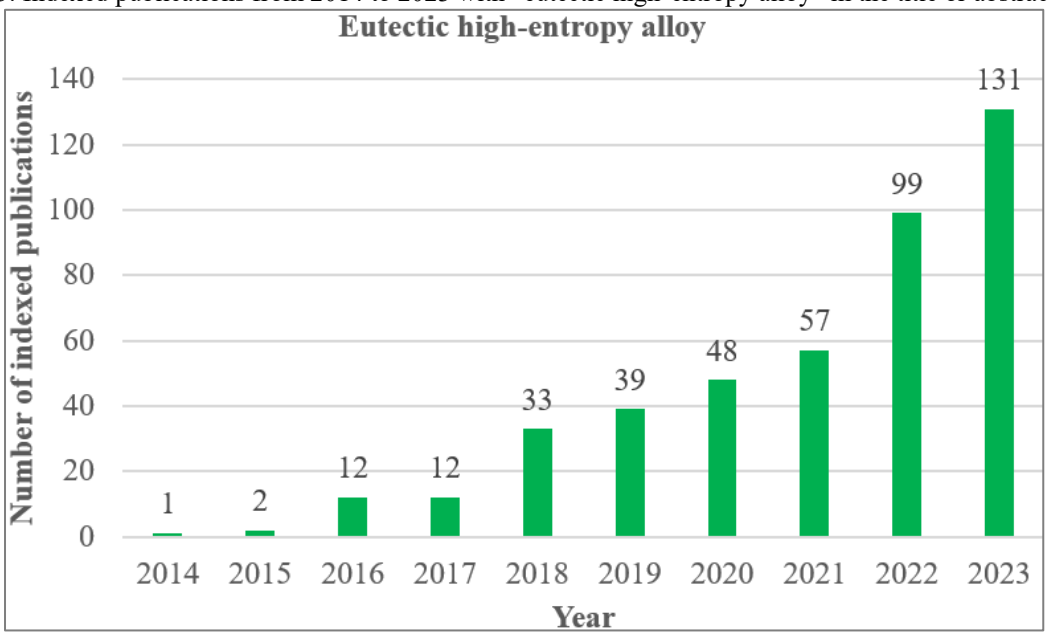
Source: CAPES, 2024.

Figure 2: Indexed publications from 2014 to 2023 with “refractory high-entropy alloy” in the title or abstract fields.



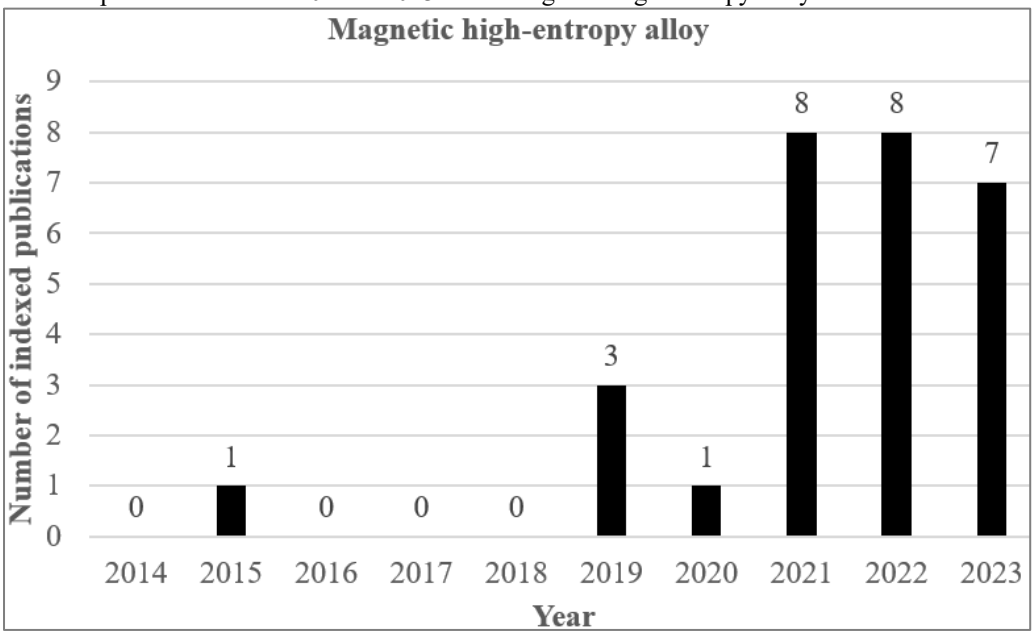
Source: CAPES, 2024.

Figure 3: Indexed publications from 2014 to 2023 with “eutectic high-entropy alloy” in the title or abstract fields.



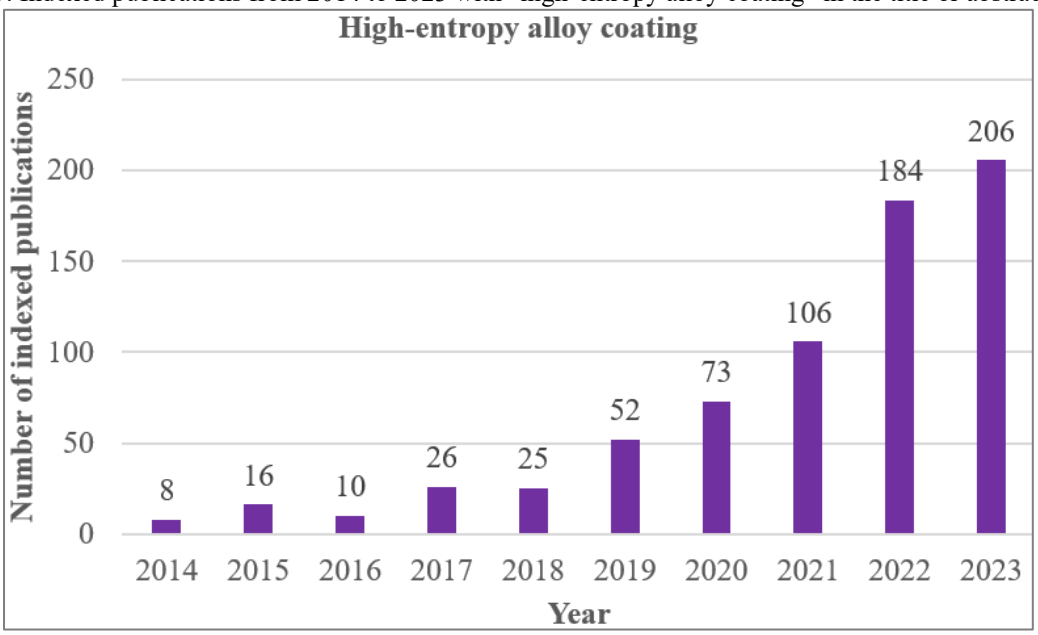
Source: CAPES, 2024.

Figure 4: Indexed publications from 2014 to 2023 with “magnetic high-entropy alloy” in the title or abstract fields.



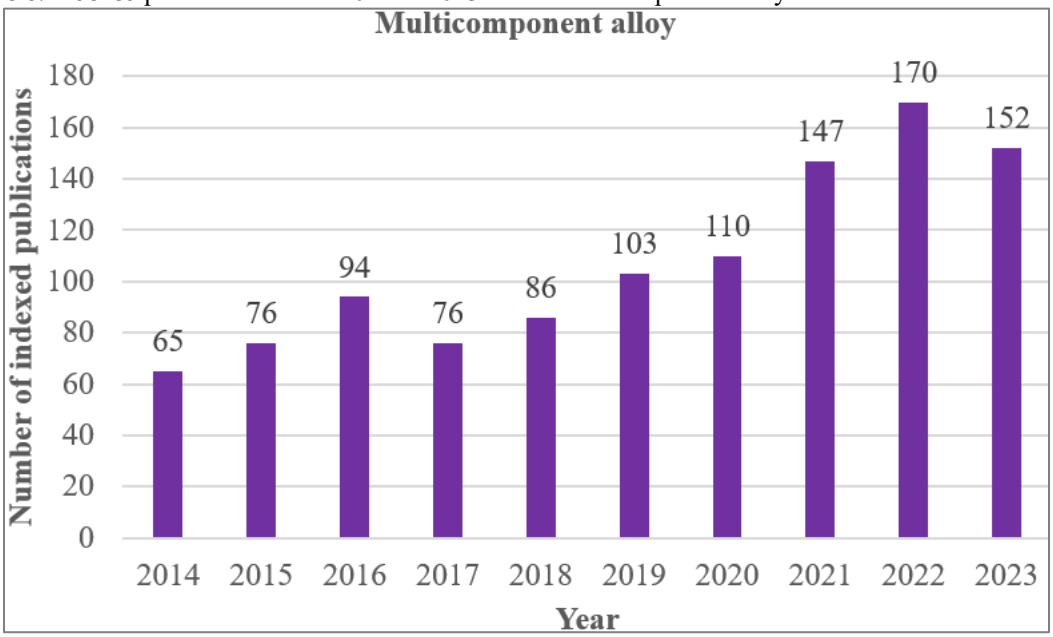
Source: CAPES, 2024.

Figure 5: Indexed publications from 2014 to 2023 with “high-entropy alloy coating” in the title or abstract fields.



Source: CAPES, 2024.

Figure 6: Indexed publications from 2014 to 2023 with “multicomponent alloy” in the title or abstract fields.



Source: CAPES, 2024.

4 CONCLUSIONS

This paper presented a short review on high-entropy alloys (HEAs). This included a succinct state of the art in this research area, as well as the progress made, trends, and opportunities. The main concept relies mainly on configurational entropy of these multicomponent alloys, the quantity of each element, and the processing route.

The definition of HEAs was presented, distinguishing HEAs from other multicomponent alloys. HEAs were compared to pure metals and to the conventional alloys too in what refers to mechanical properties.

The number of indexed publications were compared from 2014 to 2023 in terms of the most probable research words, allowing the analysis of trends, growth rates, and perspectives of each research word.

Based on this paper, although many contributions have been made to enlarge the knowledge boundaries related to HEAs, this research branch still has a great potential due to its large extent in terms of possible combinations of elements to achieve distinguished properties, and in terms of optimal methods to achieve the required properties (avoiding expensive and unnecessary experiments).

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