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Multilayer and high-entropy alloy-based protective coatings for solving the issue of critical raw materials in the aerospace industry

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Abstract. Aerospace is an actively developing industry that continuously requires the implementation of modern technologies. The rapid growth in new vehicle production demands much support. Hence, the problem of resources with complicated supply and distribution is always of current interest. These critical raw materials (CRMs) are involved in almost all areas of aerospace manufacturing and service. An efficient and profitable solution to the problem of critical materials can be found in protective coatings, especially in such advanced concepts as multilayer and high-entropy alloy (HEA)-based coatings. In this paper, we study both ways of manufacturing effective coatings. We have shown that multilayer CrN/MoN coatings with exceptional toughness and hardness could find promising applications in the aerospace industry. The developed strategy for the novel materials screening based on the prediction of their properties has been demonstrated on the example of the refractory HEA-based coatings. A brief state of the art of the EU critical raw materials and their place in the aerospace/defence industry has been given.

1. Introduction

The list of critical raw materials in the EU has been updated and enlarged since 2011. That was caused by the continuous development of technologies and changes in the geopolitical and economic situation in the world. CRMs are particularly crucial in designing innovations and products relevant to high-tech due to their exclusiveness and irreplaceableness. Their intelligent extraction, supply, application and distribution is a complex issue, especially when it comes to the aerospace and defence sectors [1,2], where it is sometimes challenging to find analogues and substitutions for parts with a given level of performance. The growing demands for efficiency and productivity, along with the demand for the supply of critical materials for modern aerospace technology, reflect the major challenges that need to be addressed. Consequently, critical raw material problem attracts more and more attention of scientists

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and engineers in various fields with different approaches to its solving [1,3–10]. The main solutions from both points of view are: (1) improvement of the processes of CRM extraction and production, ensuring safety and reducing the cost of mining, etc.; (2) complete or partial substitution of critical materials; (3) improvement of the existed or creating new recycling tactics [11,12].

Since the beginning of the 60s, coatings have been closely incorporated into manufacturing and widely used in all technological solutions. Accordingly, they are considered as one of the possible ways of solving the CRM problem in this paper [13]. Applying coating technology allows partial substitution of the critical raw materials by more available analogues without significant loss in quality. Obviously, the low effect on the weight of structures, good controllability of the obtained properties, and the relatively high economic benefit of the technical process give grounds for suggesting the coatings as a partial solution to the CRM problem in the aerospace sector.

2. Critical raw materials in the EU and their usage in aerospace applications

By the European Commission, the critical raw materials are defined as raw materials of high importance to the economy of the EU and whose supply is associated with high risk [14]. According to the communication from the European Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions in 2017 [15] the Critical Raw Materials List consists of 27 raw materials and groups. Platinum group metals, heavy and light rare earth elements are counted as three positions in the list. The list of critical raw materials for the EU is a subject to regular update at least every three years, and the 2017 CRMs list follows the two subsequent reports with 14 and 20 positions in 2011 [16] and 2014 [17], respectively. The evolution of the critical raw materials list and assessment since 2011 is shown in Figure 1. It should be noted that the figure does not represent the very recent update of the CRMs list in September 2020 [18]. According to the newest version, helium has been removed from the list, and four new critical raw materials have been added: bauxite, lithium, titanium, and strontium.

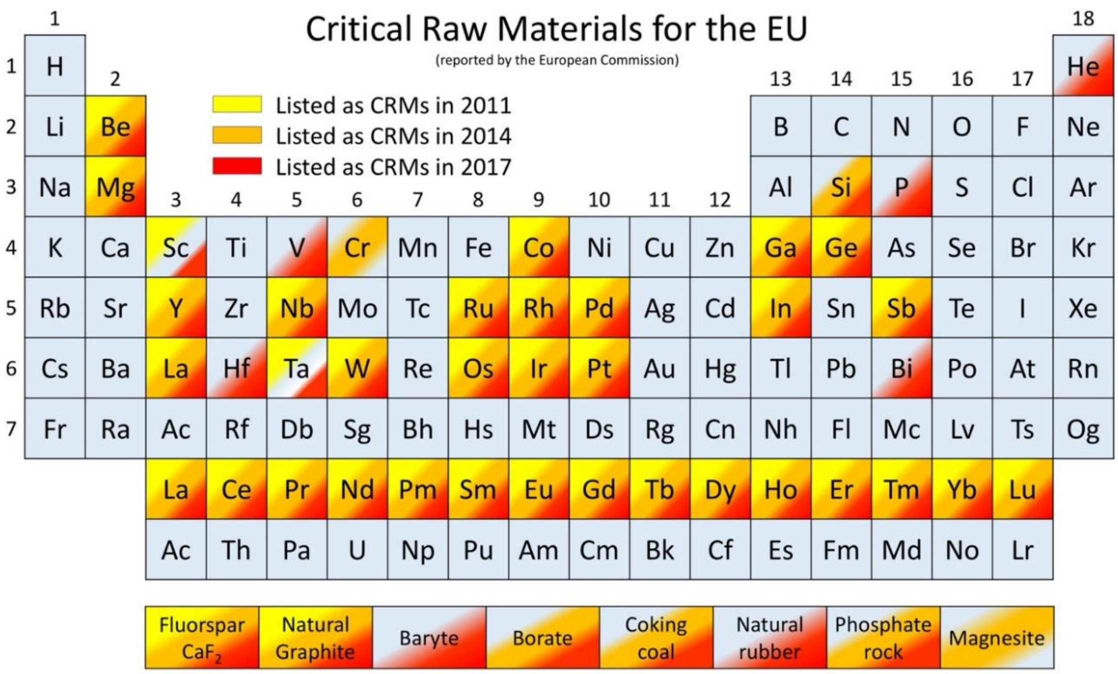


Figure 1. Critical raw materials list for 2011–2017 overlaid on the periodic table of the elements. Adapted from [3].

As reported by the European Commission, most of the materials from the CRMs list are widely used in the aerospace and defence industry (see Figure 2) [18]. They are critical in a lot of aerospace applications and manufacturing: turbines, bearings, engines, fuselages, etc.

Figure 2. Critical raw materials with applications in the aerospace/defence industry.

3. Coatings as a powerful approach to solving the CRM problem

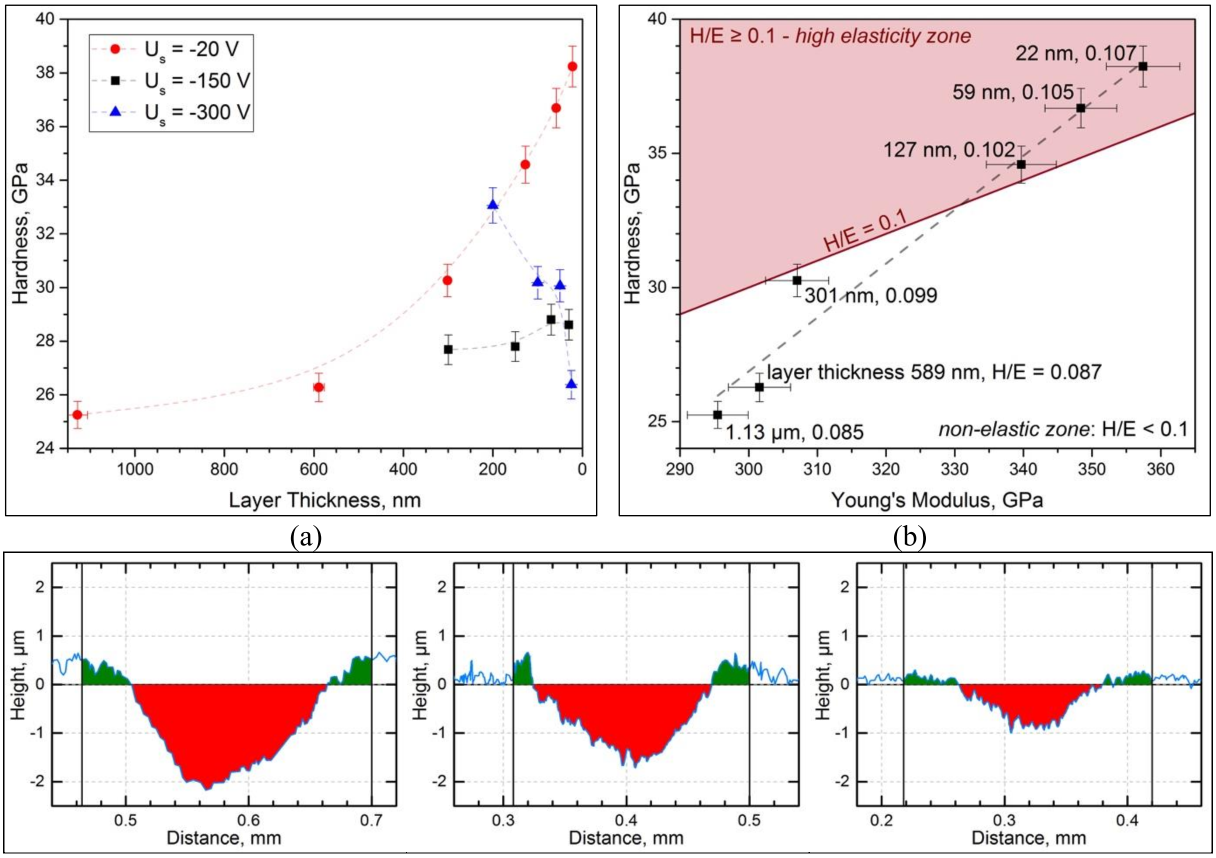
Protective coatings may significantly increase the lifetime of tools and machine parts experiencing the wear, fretting and erosion. For example, in the case of cutting tool applications, the coatings may extend the service life by 100 – 500 % at the same cutting velocities [6]. It should be noted that the result strongly depends on operational conditions and the thickness of the protective layer.

Novel concepts such as multilayer and HEA-based coatings, as well as their combination, could improve the current techniques and add new examples of implementation. Multilayer coatings demonstrate enhanced strength, hardness, wear resistance, high-temperature stability, and oxidation resistance due to Hall-Petch and superlattice effects, exceptional interfacial toughness, and by an alternation of layers with various structures and properties [19–23]. HEAs represent a new class of metallic materials, which is a topic of current interest. For their fabrication, several metal elements (usually 5 or more) are mixed in an equimolar or close to equimolar composition. They form a single- or dual-phase microstructure without intermetallic fractions [24,25]. The effect of high mixing (entropy) endows these alloys and based on them coatings with high strength, superior high-temperature stability, creep resistance, and ductility, which, as mentioned above, are extremely demanded in materials utilised in the aerospace sector [26,27].

3.1. Properties of multilayer coatings

When the "first-generation" (single-layer) coatings hit the peak of their potential and reached the plateau of their performance improvement, the multilayer coatings appeared with a considerable effect of interfaces. During the deformation, the strain energy is generated proportional to the shear modulus. The layers with different shear modulus may slow or even stop the dislocation movement. Such behaviour, in turn, results in enhanced strength, hardness and wear resistance of the material. Hard protective ceramic nitride coatings based on Ti and Al are widely used in the aerospace industry for surface modification of various rod ends, seals and bearings. Harsh serving conditions require such coatings to possess anti-galling and thermal barrier properties.

The nitride coating systems based on Cr and Mo still are not entirely studied, especially their possible applications. Such a combination of elements in multilayer architecture results in good chemical and tribological stability under extreme temperatures along with oxidation resistance. Moreover, it is possible to achieve the coherency between CrN and MoN at the specific crystallographic orientation, which may induce the "superhardness" effect (hardness values increase up to 40–45 GPa) [28]. The process of synthesising superhard CrN/MoN multilayer films by cathodic-arc physical vapour deposition (CA-PVD) and their performance characterisation were rigorously investigated and described in our recent papers [29–31]. Conducted tests (Figure 3) have shown the undeniable connection between the processing parameters and properties of the designed coatings. In particular, varying the bilayer thickness from 600 nm to 20 nm, hardness drastically increased from 26 GPa to more than 38 GPa, respectively. The durability of coatings (wear resistance) was also strongly dependent on the bilayer period and deposition parameters (such as chamber pressure and bias potential) showing the same enhancement trend with a decrease in the interfacial thicknesses.



(a) (b)

(c)

Figure 3. Tribomechanical test results of CrN/MoN hard coatings: (a) hardness measurements for samples obtained under different substrate bias voltage, (b) hardness to Young's modulus ratio (H/E) and (c) wear profiles of the samples with different bilayer thicknesses deposited at $U_S = -20$ V [29].

3.2. High-entropy alloy-based coatings

One of the main challenges of manufacturing the novel material is the uncertainty in its initial performance. Concerning HEA-based coatings, they have numerous possible composition options [24]. Thus, to assess the optimal processing-structure-properties relations, the theoretical and computational analyses are mandatory. Generally, all of the single- and dual-phase HEAs have high creep resistance, chemical inertness and ductility, which are determined as basic effects of high entropy [32]. As far as we concentrated on the mechanical and tribological properties, we consider using refractory metals, that are characterised by high melting temperature, toughness and hardness [33]. To choose the basis for further material simulations, the full list of refractory metals has been taken into account from Ti to Re excluding the Tc, Os, Rh, and Ir due to their high cost and shortage on our planet. Additionally, the covalent compounds of refractory HEA with boron, nitrogen and carbon were added to the simulation to even more improve the preconditions of calculations. The main reasons for that were the superior properties of the ceramics based on high-entropy alloys and simplicity of synthesising process of thin films via reactive sputtering technologies. The values of HEAs nitrides, borides and carbides hardness have been obtained and compared in order to suggest the best elemental combinations.

To determine values of hardness two models were separately applied: (1) Chen's theory [34] (correlated through the product of the squared Pugh's modulus ratio and the shear modulus), which is mainly applied for the all known hard compounds and (2) raw data of elastic constants of known single-crystalline materials (assessed by Density Functional Theory computations). Evaluations of the processed data were conducted using Matminer toolkit described in detail in [35].

Figure 4 highlights the obtained and normalised data regarding the simulated hardness. Note that the graph depicts values proportionally to volume per atom (vpa), which suggested as one of the most crucial parameter in predictions. Obviously, the carbides and borides exhibit the highest values up to 20 – 21.5 GPa. Increasing the fraction of elements with higher density (V, Re, Ta, W) should result in the hardness enhancement. Nevertheless, for the different types of compounds, the combinations with the highest hardness differ. For example, for borides, it is $(Ti_{10}V_{10}Cr_{35}Nb_{25}Mo_{20})B$, for nitrides – $(Nb_{15}Mo_{5}Ta_{35}Re_{10}W_{35})N$, while the composition $(Ti_{10}V_{10}Cr_{35}Nb_{25}Mo_{20})N$ has a moderate hardness value and located in the middle of the nitride graph area. That proves the necessity of further analysis of the chemical nature of certain elemental compositions and justifies the importance of calculated data.

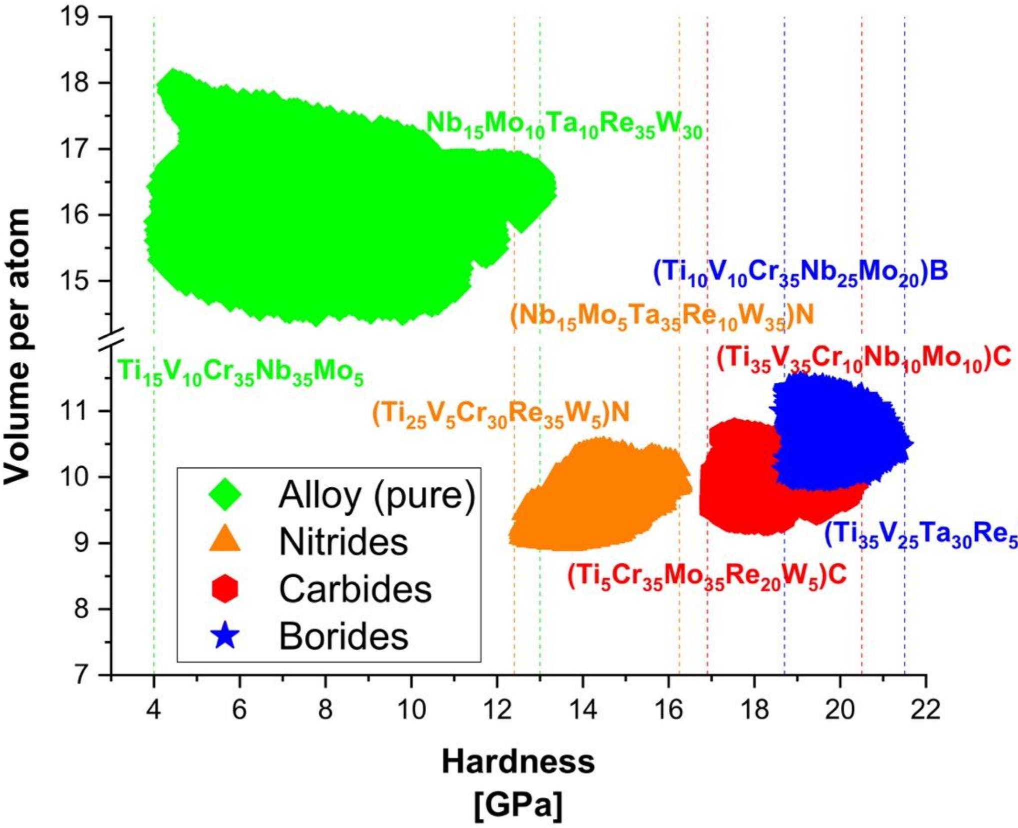


Figure 4. Graphical representation of predicted hardness of high-entropy alloys and compounds based on the refractory metals: dotted lines represent the maximum and minimum hardness.

The hardness of nitrides was in the range of 12 – 16 GPa and had the most linear trend among other graphs. Conventional HEAs of refractory metals as expected for metals showed the lowest results with a peak in 13 GPa for $Nb_{15}Mo_{10}Ta_{10}Re_{35}W_{30}$. They were also characterised by the highest dispersion in hardness values, which could be associated with more significant influence of component fraction and variety of crystalline phase shift from hexagonal-close-packed (hcp) to face-centred cubic (fcc) structure, while, for instance, borides were presented only in the hexagonal phases.

In the context of CRM problem such simulations and predictions allow to preform elemental screening prior to the experimental fabrication of alloys and coatings. This is especially important for HEAs, when the set of the alloys of at least five components with exact elemental composition is not easy and cheap to achieve for experimental purposes. The obtained properties highly depend on the elemental content, so a high number of alloys may be needed for experimental study without prior calculations.

One may notice that a high number of HEAs, including those highlighted in Fig. 4, may contain CRMs, such as refractory metals or boron (derivative of borate; 98% of the EU's supply and 42% of global production are provided by Turkey [18]). Authors believe that with the proposed approach for HEAs properties simulations and elemental screening many CRM-free or almost CRM-free HEA compositions with no compromise for excellent physical and mechanical properties may be selected for further experimental study and enhancement using additional approaches, such as multilayer architecture or deposition conditions optimisation. On the other hand, thin protective coatings require much less raw materials, but provide high wear performance and extended life time of the working parts.

Concepts of high-entropy alloys and multi-layered coatings (including HEA-based) may be considered as one of the bases for CRMs problem solution in a few directions: low waste of raw materials for thin coatings; recycled material may be used as a deposition source; enhanced wear performance and extended lifetime of products and tools; substitution of CRMs by elemental screening by simulations or machine learning. At this point the actual calculated data is getting useful.

Conclusion

In this paper, the possibilities and advantages of multilayer and HEA coating concepts as a substitution for critical raw materials in aerospace had been taken into account.

The excellent mechanical performance of CrN/MoN multilayer coatings, in particular, decent elastic recovery (H/E ~ 0.1), wear resistance and hardness (above 38 GPa), allows suggesting a great potential not only in cutting tool area but also in the aerospace industry.

The simulations showed that materials based on refractory HEAs, their carbides, borides and nitrides exhibited large variety in calculated hardness that reached from $Ti_{15}V_{10}Cr_{35}Nb_{35}Mo_{5}$ (4.1 GPa) to $(Ti_{10}V_{10}Cr_{35}Nb_{25}Mo_{20})B$ (21.3 GPa). It has been found that ceramic HEA combinations had lesser divergence in the mechanical behaviour than the metalic.Refractory HEA compounds based on the boron and carbon predicted to be with the highest values of the Vickers hardness up to 21 – 22 GPa which is 1.5 times bigger than nitride-based and about 2 times than pure HEAs. Obtained data eases the adoption of the experimental samples and give the first consistent patterns in the mechanical properties of the yet to be designed HEA-based coatings. However, to fulfil total reliability in the predicted values the real experiments are needed.

The described materials and methods could grant a beneficial result for applications in the aerospace sector, which are connected with high loads (carcasses, landing gear, shafts, etc.) and extremely high temperatures (engines, propulsion systems).

Considered approaches of multilayer and (or) high-entropy alloy-based protective coatings are proposed as one of the potential solutions for critical raw materials problem highlighting the benefit from their promising physical and mechanical properties, which results in extended lifetime of machine parts and, thus, lower CRMs waste.

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