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## Possible alternatives to critical elements in coatings for extreme applications

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**Abstract.** Surface functionalisation and protection have been used since a long time for improving specific properties of materials such as lubrication, water repellence, brightness, and for increasing durability of objects and tools. Among the different kinds of surface treatments used to achieve the required properties, the use of coatings is fundamental to guarantee substrate durability in harsh environments. Extreme working conditions of temperature, pressure, irradiation, wear and corrosion occur in several applications, thus very often requiring bulk material protection by means of coatings. In this study, three main classes of coatings used in extreme conditions are considered: i) hard and superhard coatings for application in machining tools, ii) coatings for high temperatures (thermal barrier coatings), and iii) coatings against corrosion. The presence of critical elements in such coatings (Cr, Y, W, Co, etc.) is analysed and the possibility to use CRMs-free substitutes is reviewed. The role of multilayers and nanocomposites in tailoring coating performances is also discussed for thermal barrier and superhard coatings.



## 1. Introduction

Profound understanding of the role of critical elements in the properties of high tech bulk and coating materials is a prerequisite to design new materials with reduced or no critical elements content. Substitution of critical raw materials (CRMs) is one of the challenges of the European Innovation Partnership (EIP) on Raw Materials, together with the improvement of the mining processes and the increase in recovery and recycling rates. The criticality of a raw material for the EU is defined basing on its supply risk and economic importance for the EU, which depend on geopolitical issues and can therefore change in a dynamic way. For this reason CRMs list is updated periodically by the EC, which released the latest list of CRMs in September 2017 [1].

**Table 1.** List of critical raw materials (CRMs) for the EU [1].

CRMs (as defined in 2017 by EC)			
Antimony	Gallium	Magnesium	Scandium
Barite	Germanium	Natural graphite	Silicon metal
Beryllium	Hafnium	Natural rubber	Tantalum
Bismuth	Helium	Niobium	Tungsten
Borate	HREEs	PGMs	Vanadium
Cobalt	Indium	Phosphate rock	
Fluorspar	LREEs	Phosphorous	

With the aim to reduce EU dependence on these raw materials, both substitution or reduction in the use of CRMs should be pursued, although even reduction represents often a challenging task. This goal becomes even more important when the considered CRM has got a high impact on environment and health. We have already examined the substitution of CRMs in bulk materials in a previous study [2], where we highlighted also the fundamental role of coatings for protection of bulk materials for application under extreme conditions in terms of wear, temperature and corrosion, and for saving critical elements. Literature is very reach of examples of high performing single layer and multilayer coatings, however, none of the papers reports about the role of critical elements in such coatings. In this study, we review on hard, thermal barrier and anticorrosion coatings, analysing CRMs content (Cr, Y, W, Co, etc.) and describing already existing or novel CRMs-free solutions.

## 2. State of the art of coatings for extreme conditions and analysis of CRMs content

### 2.1 Hard coatings for machining tools

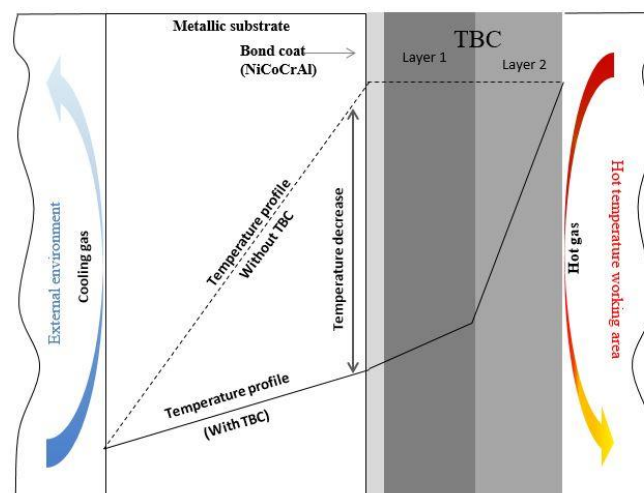
With the increasing of cutting tools speed, the demand for heat resistant materials has increased, resulting in a progressive substitution of high-speed steels with carbides and superhard materials as main tool constituents. The cemented carbides are a set of composite materials that consist of hard carbide particles in a metallic matrix. The most commonly used material is WC-Co. It is estimated that more than 60% of cemented carbides tools are coated to increase their lifetime and to allow faster machining. Examples of coatings for cutting tools include nitrides (CrN, TiN, Ti(C)N, TiAlN, ZrN, ZrAlN, a-CN), diamond-like carbon (DLC), oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, etc.) and carbides (SiC, WC, VC, TiC, Cr<sub>3</sub>C<sub>2</sub>, BC, etc.). Many of these coatings are already CRM-free, so the quest for further optimized coating composition and architecture becomes important to save the CRMs contained in the underlying bulk tools (e.g. W and Co). Apart from economic and supply reasons, another driving force for Co substitution is its toxicity, since the WC-Co mixture is considered as a possible carcinogenic material, according to the International Agency for Research on Cancer.

Among the different coating materials used on machining tools, the most widespread are represented by DLC and nitride-based coatings like monolayers and multilayers based on AlTiN, AlCrN, TiCN, as well as quaternary coatings, which are grown by Physical Vapour Deposition (PVD) or Plasma Assisted Chemical Vapour Deposition (PACVD) techniques. They currently represent one of the best solutions due to their high thermal stability, hot hardness and oxidation resistance, and they can be used to coat tools made of different materials (steel alloys, cemented carbides, Ti alloys, etc.). In TiAlN coatings, alloying with Al improves the hardness and the oxidation resistance and the thermal stability of the TiN material, thanks to a dense  $\text{Al}_2\text{O}_3$  scale forming on the surface of the coating [3]. Other alloying elements are Cr, Y, Zr, V, Si, B and Ta, where: i) Cr and Y are known for improving oxidation and corrosion resistance [4-6]; ii) Zr improves the wear resistance of TiN based coatings, stabilizes the fcc TiN lattice and forms a very thin stable oxide layer similar to  $\text{Al}_2\text{O}_3$  [3,4]; iii) V increases TiN hardness [4,7]; iv) Si increases the hardness and chemical resistance of (Ti,Al)N coatings [8]; v) B in (Ti,Al)N lattice improves the lubricated cutting performance [4]; vi) Ta improves the hardness, thermal stability and oxidation resistance, thus increasing maximum milling time with respect to conventional TiAlN [9].

High Velocity Oxygen Fuel (HVOF) sprayed WC-Co and WC-Co-Cr coatings deposited on high strength steel (HSS) are also considered as an alternative to the use of bulk WC-Co [10].

## 2.2 Thermal barrier coatings

Thermal barrier coatings (TBCs) are high refractory materials applied to metallic (generally Ni superalloys) surfaces of components such as gas turbine or aero-engine parts, which operate at elevated temperatures. These coatings are used to insulate structural components from large and prolonged heat loads, limiting the thermal exposure and therefore extending their durability by reducing oxidation and thermal fatigue. The insulating capability of TBCs enables higher operating temperatures and/or permits a reduction in the required amount of cooling air, thereby improving efficiency, reducing emission and increasing thrust/weight ratio. A typical TBC system is composed of a metallic bond coat adherent to the metallic substrate and a ceramic top coat (Fig. 2.). In these systems the main role of the superalloy substrate is to support the mechanical load. The role of the very thin bond coat (mainly NiCoCrAlY or NiAl based alloys) is to protect the metal substrate from oxidation/corrosion, particularly from oxygen and corrosive elements that penetrate the porous ceramic top coat. Bond coat also contains the source of elements to create the next thermally grown oxide (TGO) layer that provides bonding of TBC to bond coat and slows subsequent oxidation.



**Figure 1.** Schematic representation of ceramic thermal barrier coatings.

Critical elements are contained both in the bond and top coat. The most commonly used top coat is Yttria Stabilized Zirconia (YSZ), i.e.  $ZrO_2$  partially stabilised with about 6–8 wt % (3-4 to 6-8 mol %)  $Y_2O_3$ , usually deposited by Electron Beam Physical Vapour Deposition (EB-PVD) and Plasma Spray techniques. Alumina, mullite, ceria and perovskites are also used due to their high melting point and low thermal conductivity [11]. Commercial zirconia powders doped with 9.5%  $Y_2O_3$ -5.6%  $Yb_2O_3$ -5.2%  $Gd_2O_3$  Metco 206A agglomerated powder have been proposed for fabrication of thermal barrier coatings operating at temperatures up to 1500°C and they are considered as one of the best available material system for thermal protection of propulsion systems for aeronautics [12].

State of the art of bond coat is based on MCrAlY ternary system, where M stands for Fe, Co or Ni [13].

### 2.3 Coatings against corrosion

According to National Association of Corrosion Engineers (NACE), worldwide cost of corrosion has been estimated to be nearly \$2,5 trillion per year [14]. Prevention is the best practice to fight against corrosion. Coatings are essential for corrosion protection because they provide a physical barrier which impedes the access of aggressive species to the metallic substrates and/or inhibit the corrosion process. The chemical species largely used for long time against corrosion is Cr(VI), due to its ability to form a passive oxide layer (chromate conversion coating (CCC)) on the metallic substrates (e.g. Zn, Al, Mg based alloys). These layers not only provide an effective physical barrier against corrosive agents, but they have also the self-healing ability in the event of surface damage [15]. Despite its high economic importance, Cr was recently removed from the latest CRMs list of the EC, due to the decrease of its supply risk. However it is right at the edge of the criticality threshold for the EU, and it remains still a high value metal with a fundamental role in protection against oxidation. In addition, due to its toxicity, REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) identified Cr(VI) among substances of very high concern (SVHC), the use of which is restricted and must be authorised [16]. Cr(VI) use is actually allowed in aeronautic and aerospace industries, even though great concern is also increasing in these sectors.

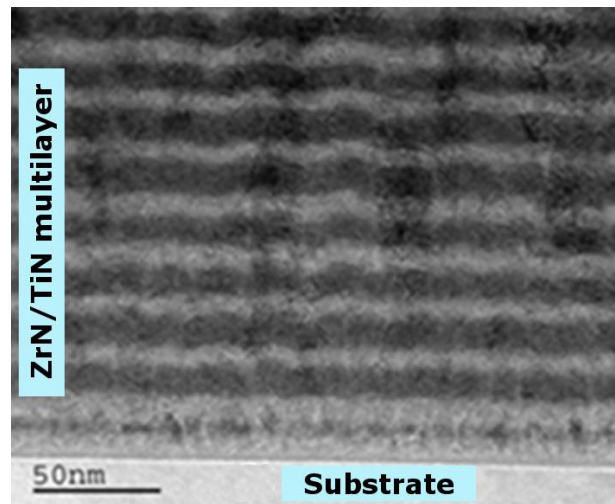
Cr is contained in several coatings: i) chromate conversion coatings and corrosion inhibitors in pigments for preventing wet/aqueous corrosion; ii) NiCrAlY materials for protection against oxidation in high temperature gas environments; iii) CoCrAlY for improving the resistance to sulfidation; iv) NiCoCrAlY to provide an acceptable balance of both oxidation and sulfidation resistance; v) thermal-sprayed WC-CrNi,  $Cr_3C_2$ -NiCr, WC-CoCr, etc. for protection against corrosion, erosion, and wear.

### 3. Beyond the state of the art: CRMs-free solutions

Concerning the coatings for cutting tools, one of the best choices is the use of CRM-free nitride-based coatings like (Ti,Al)N, TiCN, etc., deposited by PVD. Indeed, thanks to their good balance of hardness, wear resistance and high-temperature oxidation resistance, they represent an optimal improvement for protection of machining tools and mechanical components. Further enhancements in the properties of hard PVD coatings can be achieved by using graded layers, nanocomposite layers, multilayers or superlattices [17,18,19]. For example, nanocomposite superhard coatings ( $H > 40$  GPa), formed by nanometer size MeN particles (Me = metal element) embedded in amorphous or crystalline matrices, the so called “third generation ceramic coatings”, exhibit enhanced mechanical, electronic, magnetic and optical properties, thanks to their nanocrystalline structure made by nanometric (5-10 nm) features.

Superlattices are multilayers obtained by alternating several layers of different materials with nanometric thickness (up to 10 nm). An example of ZrN/TiN superlattice deposited by PVD is reported in Fig. 3. Similar multilayers were used to coat a WC-Co tool, resulting in an increased milling time of about 30% [20]. Due to their enhanced mechanical properties, such coatings may be applied to CRM-free substrates having lower performances with respect to WC-Co, so to tailor those to ones necessary for cutting tools, at least in some applications. Possible CRM-free bulk materials

candidates are composites having NiAl matrix and ceramic reinforcement ( $\text{Al}_2\text{O}_3$ ), that were recently developed by reactive sintering and successfully tested. Even though the wear resistance does not reach the performances of WC-Co composites, it exceeds the properties of current cold work tool steels without the need for heat treatment [21]. At present, these materials are relatively brittle at room temperature and therefore need further optimization, in terms of chemical composition and/or production technology, in order to achieve the necessary ductility for the application as tool materials [2].



**Figure 2.** Cross-sectional high-resolution TEM image of a ZrN/TiN multilayer [20].

Besides the proper choice of coating composition and structure, alternative solutions to get coatings with further enhanced protective characteristics may be found in the use of innovative deposition techniques, such as the HiPIMS (High Power Impulse Magnetron Sputtering) [22, 23]. This PVD technique is an evolution of the conventional sputtering technique that exploits short pulses with a very high power, giving rise to a very high plasma density and a high ionization fraction and energy of the sputtered species, together with a high rate of dissociation of the gaseous species in the deposition chamber. Compared to other standard deposition techniques like cathodic arc and conventional magnetron sputtering, the HiPIMS techniques has been reported to allow the deposition of hard coatings presenting higher density, lower content of defects and droplets, and better adhesion to the coated component. Thanks to these improved properties, nowadays HiPIMS-deposited coatings are widely available as commercial protective coatings.

Nanostructured coatings, superlattices and functionally graded coatings are also very important to tailor properties of thermal barrier coatings and reduce mismatch and thermal gradients between top coat and bond coat, which are among the reasons of coatings' failure [24-26]. In addition, they can provide a better barrier for oxygen diffusion.

The possible alternatives to YSZ top coats are constituted by Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ),  $\text{La}_2\text{Zr}_2\text{O}_7$ ,  $\text{BaZrO}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3\text{-TiO}_2$  and metal-glass composites (MGCs) [27]. Among these alternatives, some are CRM-free, but at present do not show comparable performances at high temperature with respect to YSZ. More recently, the search has been broadened by using insights from atomistic simulations and crystal chemistry, searching for new approaches for reflecting or scattering radiation and preventing it from reaching the metallic parts [28, 29]. Finally, novel compositions of high entropy alloys [30, 31] with reduced CRMs content, both metallic and oxides, could be investigated as possible bond coat and top coat, respectively.



Regarding coatings against corrosion, several alternatives to CCC have been proposed. Organosilane compounds, having the general formula  $R_nSiX_{4-n}$  (where X is the hydrolyzable group and R is an organofunctional group), are extensively investigated. These compounds show good corrosion protection properties when are deposited on different types of metal substrates: they form a barrier constituted by Si-O-Si networks [32-35]. Addition of corrosion inhibitors may further increase their corrosion resistance [36]. Highly crosslinked silane polymers made by a bis-sulfur/bis-amino (3/1) mixture showed good corrosion protection properties for many metals including aluminum alloys and galvanized steel [11].

Other already investigated alternatives to Cr are chemical conversion coatings of different nature: (i) phosphate–permanganate, fluoride and stannate for the protection of magnesium alloys [37, 38]; (ii) molybdates for zinc alloy [39] and aluminium alloy substrates [40]; (iii) permanganates, vanadates and Zr- and Ti-based coatings [40]. Some of the listed species were used as primers before the application of a top coat obtained by sol-gel or PVD techniques [41].

Recent findings showed also that compact and defect free  $TiO_2$  sol gel coatings, deposited at low temperature directly (i.e. without the need of a primer) on AA6082 substrate, showed improved corrosion resistance with respect to the uncoated alloy [42].

Almost all authors who studied these solutions agree on the fact that they limitedly represent a viable alternative to CCC, apart from some cases where less demanding corrosion conditions are present.

In a recent work, however, the corrosion resistance of a commercial processes (PreCoat A32) on Al alloys was found comparable or even better than that of the widely used conventional CCC Alodine 1200 [43].

Finally, much emphasis is given to self-healing and smart coatings with tailored functionalities for improved corrosion protection [44, 45].

#### 4. Conclusions

Among the actions aimed to decrease the EU dependence on critical raw materials, it is important to find new solutions capable to replace or reduce the content of CMRs in several technological fields, due to reasons related to economic, supply and toxicity issues, although substitution and even reduction of CRMs content is difficult especially in certain applications. In particular, in this paper the presence of critical elements in coatings against wear, high temperature and corrosion is analysed together with the possibility to reduce their content. Possible alternatives are investigated in terms of use of other CRMs-free coatings, optimization of coating structure (nanocomposite coatings and superlattices), and exploitation of advanced deposition techniques, so to obtain coatings with enhanced performances thus allowing lower CRMs content or at least saving critical elements that are present in the coated components.

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