Understanding the role of critical elements in coatings for extreme applications

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Overview

• Fundamentals: extreme conditions and presence of critical elements in bulk and coatings

• Coatings:
  a. Fabrication techniques
  b. Hard coatings
  c. Thermal barrier coatings
  d. Coatings against corrosion

• Summary
What are "extreme conditions"

- Temperature
- Pressure
- Irradiation
- Load
- Friction
- Wear
- Corrosion
List of critical raw materials for EU

Legend
Red dots ● Critical raw materials
Blue dots ● Non-critical raw materials
Some examples of CRMs in materials under extreme conditions

- High speed machining: W, Co, Cr in bulk cemented carbide tools and in hard coatings
- Aeronautical turbines: Cr, Co, Nb in high temperature resistant Ni-based alloys, like Waspaloy and Inconel
- Construction, oil & gas, etc.: HSLA in bridges, pipelines, etc.
- Transport in general: Cr, Nb and rare earths in HSLA for lighter weight, higher strength and corrosion resistance than conventional carbon steel; CRMs in wear-resistant components, Mg in alloys
- Nuclear applications, heat exchangers, etc.: Cr and Y in ODS
An essential requirement of protective coatings is the adhesion to the substrate.
## Criteria to select the best available technology for coating fabrication


<table>
<thead>
<tr>
<th>Criteria for selecting deposition processes</th>
<th>Deposition processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVD</td>
</tr>
<tr>
<td>E-beam evaporation</td>
<td>RF Sputtering</td>
</tr>
<tr>
<td>Mechanism of production of deposition species</td>
<td>Thermal energy</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>Can be very high (up to 750000 Å/min)</td>
</tr>
<tr>
<td>Deposition species</td>
<td>Atoms &amp; ions</td>
</tr>
<tr>
<td>Uniformity for complex shaped objects</td>
<td>Poor, line of sight coverage except by gas scattering</td>
</tr>
<tr>
<td>Energy of deposited species</td>
<td>Low (~0.1-0.5 eV)</td>
</tr>
<tr>
<td>Bombardment of substrate/deposit by inert gas ions</td>
<td>Generally no</td>
</tr>
<tr>
<td>Substrate heating (by external means)</td>
<td>Yes, normally</td>
</tr>
</tbody>
</table>
Coatings for cutting tools and High Speed Machining (HSM)/ Cryogenic Machining

Machining
(e.g. milling, drilling etc.)
at very high rotational speeds
( > 15.000 rpm)

Machining (e.g. cutting) with vaporized liquid nitrogen at the contact point
Desirable properties of coating material in cutting tool technology

High thermal fatigue resistance
High hardness & hot hardness
Low thermal conductivity
High chemical stability
Low coefficient of friction
Good fracture toughness
High adhesion to substrate

CUTTING TOOL COATING PROPERTIES

Some example of hard and superhard coating

Hard coatings: $H<40$ GPa
Superhard coatings: $H>40$ GPa

<table>
<thead>
<tr>
<th>Coating</th>
<th>Material</th>
<th>$H$ (GPa)</th>
<th>Main characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single layer</td>
<td>TiN, TiC, Al$_2$O$_3$</td>
<td>21, 28, 21</td>
<td>CVD at $T$ around 1000°C on cemented carbides</td>
</tr>
<tr>
<td>Single layer</td>
<td>TiN, TiC</td>
<td>21, 28</td>
<td>PVD at $T\leq550$°C on steel substrates</td>
</tr>
<tr>
<td>Multilayer</td>
<td>TiC/TiB$_2$</td>
<td>90</td>
<td>About $10^3$ phase boundaries TiC/TiB$_2$ [2]</td>
</tr>
<tr>
<td>Single layer</td>
<td>diamond</td>
<td>90</td>
<td>High chemical affinity of C to iron</td>
</tr>
<tr>
<td>Single layer</td>
<td>TiAlN</td>
<td></td>
<td>Oxidation resistance up to 800°C [6]</td>
</tr>
<tr>
<td>Single layer</td>
<td>DLC</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Single layer</td>
<td>$\text{CN}_x$</td>
<td>50–60</td>
<td>Amorphous phase [7]</td>
</tr>
<tr>
<td>Superlattices</td>
<td>TiN/VN, TiN/NbN, etc.</td>
<td>$\sim50$</td>
<td>Substoichiometric ($x=0.2–0.35$) turbostratic structure [8,9]</td>
</tr>
<tr>
<td>Single layer</td>
<td>nc-McN/a-nitride</td>
<td>$\sim50$</td>
<td>Superlattice period 5–10 nm [10,11]</td>
</tr>
<tr>
<td>Single layer</td>
<td>nc-McN/metal</td>
<td>$\sim50$</td>
<td>Superlattice period 5–10 nm [10,11]</td>
</tr>
<tr>
<td>Single layer</td>
<td>$\text{Ti}<em>{0.4}\text{Al}</em>{0.6}\text{N}$</td>
<td>$\sim32$</td>
<td>Nanocomposite [13]</td>
</tr>
</tbody>
</table>

Examples of coatings, some of which contain CRMs, include hardcrome, cermetes (WC-Co, WC-Co-Cr), nitrides (CrN, TiNTi(C)N, TiAlN, ZrN, ZrAlN, a-CN), DLC (diamond-like carbon), oxides (Al$_2$O$_3$, TiO$_2$, etc.) and carbides (SiC, WC, VC, TiC, Cr$_3$C$_2$, BC, etc.).

HVOF sprayed cermetes (WC-Co, WC-Co-Cr) are increasingly considered as an alternative to hard chrome plating for several application, particular those where severe wear is combined with corrosion.
(Ti,Al)N hard coatings

TiN coatings are not suitable for high-speed machining due to the low temperature resistance (about 450°C).

Alloying with Al improves the hardness and the oxidation resistance and the thermal stability of the coatings, due to a dense Al₂O₃ oxide layer forming on the surface of the coating.

**TiAlN alloys have hardness ~27-31 GPa, TiN ~20-27 GPa.**

Other alloying elements are W, V, Nb, Mo, Al, Si, Cr, Zr and B, with many different chemical compositions.
Influence of alloying elements in TiN and (Ti,Al)N

- Cr and Y are known to improve oxidation and corrosion resistance.
- Addition of Zr improves the wear resistance (flank wear) of TiN based coatings. Zr stabilizes fcc TiN lattice and also forms a very thin stable oxide layer similar to Al₂O₃.
- V increases TiN hardness (at high vanadium content ductility of the coating is reduced)
- Si increases the hardness and resistance to chemical reactivity of (Ti,Al)N coatings
- B in (Ti,Al)N lattice improves the lubricated cutting performance
- Ta increases maximum milling time of approximately 20% if compared to conventional Ti–Al–N
Substrate for (Ti,Al)N coatings

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>High speed steel (AISI M2 Steel)</td>
<td>Metal machining</td>
</tr>
<tr>
<td>Alloy steel SKH 511</td>
<td>Metal machining</td>
</tr>
<tr>
<td><em>Cemented Carbides</em></td>
<td></td>
</tr>
<tr>
<td>WC–6 wt.% Co</td>
<td>Inserts for turning tools</td>
</tr>
<tr>
<td>WC–15%TiC</td>
<td>Indexable inserts</td>
</tr>
<tr>
<td>WC–5.7wt.% Co</td>
<td>Inserts for turning tools</td>
</tr>
<tr>
<td>WC–7.5wt.% Co</td>
<td>Inserts for turning tools</td>
</tr>
<tr>
<td>Hot work tool steel</td>
<td>Aluminum extrusion dies</td>
</tr>
<tr>
<td>Ti–6Al–4V alloy</td>
<td>Aluminum casting dies</td>
</tr>
<tr>
<td>Maraging hot work tool steel</td>
<td>Aluminum casting dies</td>
</tr>
</tbody>
</table>

Tipical coating thickness: 1-10 μm
Mechanical properties of (Ti,Al)N coatings vs Al concentration

Fig. 8. The hardness and Young’s Modulus as a function of the Al concentration in the (Ti$_{1-x}$Al$_x$)N films.

Hot hardness of some hard coatings

*Fig. 11. Temperature dependence of microhardness of Ti(C,N), (Ti,Al)N, TiN, and Al₂O₃*

Further improvement to the properties of hard PVD coatings is achieved by multilayer systems and superlattices (multilayers with single layer thickness of less than 10 nm (nanolaminates)) or nanocrystalline. First examples of such coatings were TiN/VN and TiN/NbN.

By a suitable combination of materials (TiN, VN, AlN, NbN, CrN, TaN, ZrN, TiCN, TiAlN), superlattices may increase hardness and improve the resistance against wear, corrosion, oxidation, toughness, etc.
Thin films, nanostructured films, multilayers and superlattices based on nitrides like **TiAlN, TiN** and **ZrN** are fabricated at ENEA, Research Centre of Brindisi.

Research project **TEMA** (TEchnologies for Production and Maintenance applied to Aeronautic Propulsion) – PON:

Hard coatings for tools in high-speed machining and cryogenic machining for aeronautical components allow increased lifetimes (about 30%).

PVD protective multilayer coatings for tribological applications, A. Rizzo, M.A. Signore, D. Valerini, EAI Energia, Ambiente e Innovazione 3/2012.
Nanocomposite superhard (H>40 GPa) coatings formed by nanometer size particles (usually MeN, MeC) embedded in amorphous or crystalline matrices are of considerable interest. These 3D architectures, also called ‘third generation ceramic coatings’, represent a new class of materials that exhibit exceptional mechanical, electronic, magnetic, and optical properties due to microstructural features which are reduced to approximately 5–10 nm.

A decrease in grain size suppresses the mobility of dislocations, and their multiplication. Nano-structure is not columnar like in PVD thicker layer.

The microstructure of nc gives rise to high H (resistance to abrasion and scratch) with relatively low Young Modulus E (high resistance to plastic deformation) providing high toughness, enhanced wear resistance, high elastic recovery, resistance against crack formation and crack propagation, high thermal stability (up to 1100 °C), and reduced thermal conductivity.
There is now growing evidence that a critical $H^3/E^2$ ratio (> 0.5 GPa) has to be satisfied for the coating to provide appropriate tribological protection. It also means that for successful tribological applications the $H^3/E^2$ and $H/E$ ratios of the used materials should be maximized. Therefore, film microstructure should be adjusted to satisfy such conditions: in this respect, PECVD and PVD metal-based nc coatings are very suitable candidates for many surface engineering and tribological solutions.
Thermal barrier coatings (TBCs) are high refractory materials applied to metallic surfaces (generally superalloys), such as gas turbine or aero-engine parts, operating at elevated temperatures. These 100 μm to 2 mm coatings serve to insulate components from large and prolonged heat loads limiting the thermal exposure of structural components, therefore extending part life by reducing oxidation and thermal fatigue.

Indeed, in the hottest part of many gas turbine engines, the coatings enable metallic materials to be used at gas temperatures above their melting points. Under such heat flux conditions, it is the thermal conductivity of the coating that dictates the temperature drop across the TBC.
A typical TBC system is composed of a metallic bond coat and a ceramic top coat. The role of the bond-coat is to protect the metal substrate from oxidation and corrosion, particularly from oxygen and corrosive elements that pass through the porous ceramic top-coat.

\[ \text{Al}_2\text{O}_3 \] usually forms in Ni Superalloys. \( \text{Al}_2\text{O}_3 \) has the lowest oxygen diffusivity.

Schematic representation of ceramic thermal barrier coatings.
Thermal Barrier Coatings (TBCs)

Figure 1. Cutaway view of Engine Alliance GP7200 aircraft engine, photograph of a turbine blade (-10 cm long) with thermal-barrier coating (TBC) from the high-pressure hot section of an engine, and a scanning electron microscope (SEM) image of a cross-section of an electron beam physical vapor deposited 7 wt% yttria-stabilized zirconia TBC. (Engine image courtesy of Engine Alliance, turbine blade photograph courtesy of YXLON, and the SEM micrograph is from Reference 4.) TGO, thermally grown oxides.

Figure 3. Progression of temperature capabilities of Ni-based superalloys and thermal-barrier coating (TBC) materials over the past 50 years. The red lines indicate progression of maximum allowable gas temperatures in engines, with the large increase gained from employing TBCs. Based on a diagram from the late Professor Tony Evans.

Thermal-barrier coatings for more efficient gas-turbine engines, David R. Clarke, Matthias Oechsner, and Nitin P. Padvure, Guest Editors, MRS BULLETIN • VOLUME 37 • OCTOBER 2012.
Properties of Top coat

- Low thermal conductivity
- Low density (high porosity)
- Must withstand the thermal expansion stresses associated with heating and cooling
- No changes of phases during heating cycles
- Must withstand prolonged high temperatures in an oxidizing atmosphere (high chemical stability)
- Compatibility with oxides formed at the substrate interface (bond coat)
Thermal Barrier Coatings (TBCs)

Fig. 1 Cross-sectional image of a YSZ thermal barrier coating deposited by electron-beam evaporation on a superalloy. During use at high temperatures, a thermally grown oxide (TGO) of Al₂O₃ forms on the metal beneath the TBC.


The main reason for TBC failure are related to stresses, due to mismatch in thermal expansion, TGO growth, bond coat creep, depletion of Al present in the bond coat, sintering and densification, delamination, cracks, etc.

Critical raw materials in TBCs

**Bond coat**
- NiAl
- MCrAlY (M=Ni, Co+Ni, Fe), Pt-modified NiCrAlY and NiCoCrAlY
- NiAlPt(Hf, Zr)
- Zr doped NiAl

**Top Coat**
- YSZ
- YCSZ
- La$_2$Zr$_2$O$_7$
- Sm$_2$Zr$_2$O$_7$
- BaZrO$_3$
- Mullite (3Al$_2$O$_3$ • 2SiO$_2$)
Substitution of YSZ (top coat)

- Mullite (3Al$_2$O$_3$•2SiO$_2$)
- La$_2$Zr$_2$O$_7$
- BaZrO$_3$
- α-Al$_2$O$_3$
- ZrO$_2$
- Al$_2$O$_3$-TiO$_2$
- Metal- Glass composites (MGCs)

Multilayers and/or graded coatings are able to increase the operating temperature and to better accommodate the thermal stresses arising from thermal expansion mismatch between bond coat and top coat and the diffusion of oxygen.

According to NACE International Institute, worldwide cost of corrosion has been estimated to be nearly $2.5 trillion per year.

Implementing corrosion prevention best practices could result in global savings of 15-35% of that cost, or $375-$875 billion.
The use of coatings is the most suitable way to protect metallic surfaces. Coatings for corrosion protection must provide an effective physical barrier which impedes the access of aggressive species to the metallic surface. They should have also the ability to inhibit the corrosion process.

The material mostly used in the past was hexavalent $\text{Cr}^{+6}$. When $\text{Cr}^{6+}$ comes into contact with most metals, it forms a passive oxide layer called a chromate conversion coating (CCC), which is resistant to most types of corrosive attack.

REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) banned hexavalent chromium because of its toxicity in almost all sectors except for the aerospace industry. Regulations restrict also the use of VOCs (volatile organic compounds) used in paints.
Corrosive environments

Classification of corrosion:

- **General corrosion**, corresponding to about 30% of failure, where the average rate of corrosion on the surface is uniform
- **Localized corrosion**, corresponding to about 70% of failures: intergranular, galvanic, pitting, transgranular.
Protective mechanisms

*Protective mechanism of anticorrosion coatings*

- **Barrier effect**: Obtained by impeding the transport of aggressive species into the surface of the substrate by application of a coating system with low permeability for liquids, gases, and ions.
- **Passivation of the substrate**: Can be obtained by a chemical conversion layer, or by addition of inhibitive pigments to the coating.
- **Sacrificial coatings**: Sacrificial coating is a type of metal coating which will undergo oxidation more than the metal surface that it protects. It is used mainly as primer.
- **Sacrificial anode**
**Primer (~75 µm)**
It is a coating first applied to a substrate because it had a singular adhesive affinity for it and/or because it provided better adhesion for a subsequent coat. May functions also as a carrier for an inhibitor.

**Secondary or intermediate layer**
The intermediate coat must serve as a tie coat between the primer and the subsequent coats. Generally, the thicker the coating the longer the life. This may involve the application of several coats.

**Top Coat (Finish coat)**
A topcoat may be required to extend the life of the preceding coats. When designed as a topcoat, the film is normally more dense and hydrophobic than the remainder of the system to reduce the rate of moisture permeation to the underlying coats. A topcoat also may be selected to confer reflectivity, reduce photodegradation, or to affect colour, among other reasons.
Coatings against corrosion

Three main classes:

- **Organic**
- **Inorganic**
- **Metallic**

**Organic coatings** include paints, resins, lacquers, and varnishes. Besides providing protection by creating a physical barrier between the metal and the environment, these coatings may also contain corrosion inhibitors or other additives.

**Inorganic coatings** include enamels, conversion coatings, hydraulic cements, ceramics and clays, glass, carbon, silicates, oxides (ZnO, SiO₂, and SiO₂–TiO₂, MgO). Conversion coatings are produced by intentionally corroding the metal surface in a controlled manner. This is done to produce an adherent corrosion product that protects the metal from further corrosion. Anodization of aluminum, one of the more commonly used conversion coating techniques, produces a protective aluminum oxide film on the aluminum metal.

**Metallic coatings** can sometimes provide cathodic protection. Metals used are then **Zn, Al, Zn-Al**. Zn performs better than Al in alkaline conditions, while Al is better in acidic conditions. If resistance to wear must be improved, Al coatings can be sprayed with alumina particles, e.g. by using cored-wires. For the protection of steel reinforcement in concrete, Zn and Ti are generally used.
Sacrificial coatings

The corrosion protection of large steel structures such as bridges, pipelines, oil tanks, towers, of structures exposed to moist atmospheres and seawater such as ships, offshore platforms, seaports is achieved by sacrificial coatings. It is achieved by cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. The metal to be protected is connected to a more easily corroded "sacrificial metal" to act as the anode.

Non critical raw materials: Zn, Al, Al-Zn. Al-Zn (antifouling)

Non sacrificial coatings

- **Cr** in chromate conversion coatings (CCCs), in primers and as corrosion inhibitor in pigments
- **NiCrAlY** materials protect against oxidation in high temperature gas environments
- **CoCrAlY** chemistries offer excellent resistance to hot corrosion (sulfidation)
- **NiCoCrAlY** provide an acceptable balance of both oxidation and sulfidation resistance
- **WC-CrNi, Cr_3C_2–NiC, WC-CoCr**
In spite of its toxicity, Cr$^{6+}$ remains an essential ingredient in the metal finishing industry for corrosion control. No substitutes perform as well as Cr$^{6+}$, particularly at high temperature. Cr$^{6+}$ An example of substitution of CCC is by highly crosslinked silane polymers.

Figure 3. Responses of Aluminum Surfaces to Corrosive Salt Spray Aluminum alloy (6005) coupons with different surface coatings were exposed to 240 h of copper-accelerated acetic-acid salt spraying. All three panels had a polyurethane powder-paint overcoat. The silane panel was pretreated with a 3/1 mixture of the bis-sulfur and bis-amino silane. The chromated panel (b) shows less scratch corrosion than the silane-treated panel (c). The self-healing character of the chromate conversion coating is responsible for this effect.

Some alternative chemical conversion coatings include phosphate permanganate, fluoride, stannate and rare earth compounds. The stannate conversion coating SCC \((\text{Me}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O})\) seems to be very promising. (Na$_2$SnO$_3$ 0.25 M; CH$_3$COONa 0.073 M; Na$_3$PO$_4$ 0.13 M; NaOH 0.05 M)

\[
\begin{align*}
\text{EIS spectrum of AZ91 Mg alloy after 3 days of immersion in Harrison's solution (aqueous solution of 0.35\% (NH}_4)_2\text{SO}_4 \text{ and 0.05\%NaCl).}
\end{align*}
\]

\[
\begin{align*}
\text{EIS spectrum after 3 days of immersion in Harrison's solution of TiO}_2\text{-stannate multilayer coating}
\end{align*}
\]

Deposition of sol gel coatings ZrO$_2$, CeO$_2$, TiO$_2$, SiO$_2$ directly on the metal substrate are considered another possible alternative to CCCs.
Self healing coatings

They possess the built-in ability to automatically repair damage to themselves. Self-healing is accomplished by incorporating microcapsules containing functional constituents (healing agent and catalyst) within a polymer matrix prior to production. These microcapsules are manufactured to release their content when mechanically ruptured, which will occur when the coating is damaged by impact or abrasion. Subsequently, the content of the microcapsules is transported to the damaged regions, where the healing agent contacts a catalyst incorporated in the polymer matrix, polymerization is initiated, and the damage is repaired.

Two main strategies:
• repairing of defects formed in the polymeric coating matrix via addition of polymerisable agents
• inhibition of corroding areas due to the presence of corrosion inhibitors

This technology is however still not mature for industrial applications.

• Several CRMs are contained in bulk and coatings for extreme applications

• Substitution of CRMs often results in lower performances

• Substitution means not only **REPLACING** but also **REDUCING** CRMs content

• Nanocomposite and multilayers generally show improved performances with respect to single layer systems
Thank you for your attention!

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