1. Introduction and Scope

Surface phenomena such as corrosion, wear, heterogeneous catalysis, segregation, etc., have great relevance in a lot of industrial processes and products. In recent years, the surface structure and chemistry of and the surface phenomena occurring in metals, in particular segregation, oxidation, surface defects and implants, and their reactions with the human body have attracted increasing attention from many investigators. Therefore, quite a bit of scientific work has been devoted to the matter and the results contributed to deepen basic knowledge, improve industrial products and develop new industrial applications. Great attention has been paid to new coatings and processes able to functionalize the metal surface (surface engineering) so that it can play an active role towards the surrounding environment.

In addition to the more conventional characterization techniques, such as electron microscopies, X-ray diffraction (XRD), etc., advanced surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) have also been widely applied for studying various metals and their alloys.

This editorial collects both review and research papers focused on metals' surface and presents investigations in different areas of physics, chemistry, materials science and engineering. The scope is to highlight the state of the art and the latest achievements in this research field. The main topics include:

- Physical and chemical phenomena on the surface;
- Surface morphology and structure;
- Surface modifications and treatments;
- Thin coatings.

2. Contributions

The present editorial consists of two reviews [1,2] and six research papers [3–8] dealing with different metals and their properties, which were investigated by various techniques.

The review paper by Shivakoti et al. [1] describes the technique of laser surface texturing (LST) for biomedical applications. Recent developments in LST led to drastic improvements of efficient biomaterials and demonstrated the strong potential of the technique for surface modifications and successful applications of modified materials in the biomedical field. Among the methods for generating textures or patterns on a metal surface, the paper focuses the attention on texturing using laser ablation and texturing using laser interference. Various types of lasers, such as carbon dioxide, excimer, fiber laser, etc., have been used to produce texture and explore the efficacy of the process and its impact on proliferation, osteo-integration and cell adhesion. Specific applications to Ti and its alloys, zirconia, magnesium alloys, Co–Cr–Mo alloys, Cu, austenitic stainless steels and polymers are presented and critically discussed.
The second review by Bolli et al. [2] is devoted to the applications of surface-sensitive spectroscopies (XPS and AES) described by the term Electron Spectroscopy for Chemical Analysis (ESCA). The main principles of ESCA are briefly introduced and its applications for the characterization of various metals and their coatings are illustrated by numerous experimental cases, including, also, scanning photoelectron microscopy (SPM) by using synchrotron radiation. The reported examples comprise the study of defects on the surface of precious metals, the chemical distribution in Ni-based superalloys after various heat treatments, nitride coatings on stainless steel, composites of Ti6Al4V alloy reinforced by SiC fibers and graphene interface with electrodeposited metal films.

One of the research papers presents an investigation of Cr segregation in a martensitic stainless steel and its effect on fracture [3]. The examined steel is considered to be of interest for structural applications in future nuclear fusion reactors. The fracture surfaces of samples treated in two different conditions (as-quenched and quenched plus annealed) and broken in Charpy tests were examined by XPS. The dependence of Fe/Cr ratio on the test temperature revealed the segregation of Cr in microscopic zones, representing weaker spots in the steel matrix and a preferential path for moving cracks. This study evidenced how Cr segregation is playing a role not only in the intergranular mode of fracture but also in the quasi-cleavage and ductile ones. The results have been related to the formation of C–Cr associates on an atomic scale and their evolution. Another interesting finding presented in this work was obtained by small-area XPS measurements. They revealed that the Fe/Cr ratio is not constant across the surface, being lower in the inner part of the probe. Finite Element Method (FEM) simulations showed that this phenomenon is due to a slower cooling rate in the inner part of Charpy probes, with a consequently longer random walk of diffusing atoms.

The wear behavior of tempered 25Cr3Mo2NiWV steel has been described in the paper of Zhang et al. [4]. Impact wear tests were performed with a dynamic abrasive wear tester on the material previously submitted to various heat treatments for generating different mechanical properties. Both the hardness and toughness affect the wear properties of this steel; namely, the best combination of hardness and toughness corresponds to the lowest wear weight loss. Moreover, the results show that by increasing the wear time, the dominant wear mechanism changes from slight plastic deformation to micro-cutting and adhesive wear, and micro fatigue peeling finally occurs. Fatigue cracks initiate from the surface or the sub-surface and then propagate and converge to form fatigue delamination. SEM observations of cracks in the cross-section demonstrate that brittle fatigue cracks are mainly present in the steels with higher hardness, whereas the ductile fatigue ones occur in the steels with high toughness.

Erosion–corrosion problems of carbon steels, materials of interest for application in the oil and gas field, have been investigated through a bipolar electrochemistry technique by Mele et al. [5]. Steel samples were coated with high phosphorus electroless Ni (ENP) and with a thermo-sprayed coating, consisting of a Ni-based hard alloy with chromium boride dispersion, obtained with the high velocity oxy fuel (HVOF) technique. For comparison, the same experiments were carried out on uncoated steel. The paper demonstrates the suitability of this simple, contactless technique for effective discrimination of the erosion–corrosion behavior of different coatings in working conditions. Through polarization curves, visual inspection and SEM morphological analysis, the effects due to erosion–corrosion by solid particles and by fluid and those due to simple erosion were evaluated.

The modifications of surface morphology in Mo irradiated by a single laser pulse delivered by a Nd:YAG/Glass laser are reported in [6]. Mo is considered as a plasma-facing material alternative to W in the divertor armors of the International Thermonuclear Experimental Reactor (ITER). Transient high energy loads occurring in a tokamak were simulated by a high-intensity single laser pulse and the induced changes were examined by SEM observations. An erosion crater forms in the central area of the irradiated zone due to metal vaporization and the ejection of molten metal. The thermal gradient leads to radial flushing of liquid metal, giving rise to a ridge around the crater and long filaments...
along the crater walls. Moreover, in a more external area (up to a distance of about 1 mm from the laser spot center), the surface shows bubbles and long cracks. The results have been compared with similar experiments on W, where the volume of ablated metal was about 10 times lower. This strictly depends on the latent heat of fusion and latent heat of vaporization of W, which are remarkably higher than those of Mo.

The effect of hydrogen on the mechanical properties and microstructure evolution of Ti–45Al–9Nb (at.%) alloy under uniaxial tension at high temperature is investigated in [7]. The constitutive relations among stress, temperature and strain rate in the alloy were determined together with analyses of the microstructure. Due to the presence of hydride (TiAl)H_x, the elongation shows a declining trend with increasing strain rate at the same deformation temperature. Here, 0.8 at.% H softened the Ti–45Al–9Nb alloy and reduced the high-temperature plastic deformability. Microstructure examination showed that there are more residual lamellae in the hydrogenated alloy, and the extent of dynamic recrystallization is lower than that of the unhydrogenated alloy. Three types of cracks were also evidenced in the hydrogenated alloy: inter-lamellar, trans-lamellar and along-lamellar colony boundary cracks.

The last paper [8] deals with microstructural characteristics and corrosion behavior of Al–Fe alloys produced by high-frequency induction sintering from a powder mixture of pure Al and variable contents of Fe. The morphology of the produced alloys was investigated by SEM, whereas the crystalline intermetallic phases were determined by XRD. The corrosion behavior of the Al–Fe alloys was studied using the techniques of cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS). It was demonstrated that the addition of Fe into an Al matrix leads to an improvement in the hardness and corrosion resistance of the alloy.

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