Coatings for Use at High Temperatures
Room Pacific E - Session A1-1-MoM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Dr. Sebastien Dryepondt, Oak Ridge National Laboratory, USA, **Gustavo García-Martín**, REP-Energy Solutions, Spain

10:00am **A1-1-MoM-1 Bill Sproul Award and Honorary ICMCTF Lecture: Strategies for the Development of Robust and Stable, but also Functional Ceramic Coatings*, Paul Mayrhofer*[1]**, TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

For mechanically dominated load profiles, nitrides are preferred, while oxide materials offer better protection against high-temperature corrosion. Thus, when mechanical and thermal loads are combined, the nitrides used should also have excellent temperature and oxidation resistance. How to develop such nitride materials that can withstand both high mechanical and thermal loads will be the focus of this presentation. In addition, we will also discuss the excellent supercapacitor properties of transition metal nitrides.

Using transition metal nitride coatings, we will discuss important guidelines for material development to improve strength, fracture toughness, and stability. In particular, the stability (emphasis on phase stability to composition and temperature, but also to oxidation) of nitrides is a highly interesting task. For example, while the face-centered cubic (fcc) structure of TiN_x has a relatively large homogeneity range, the fcc structure of other transition metal nitrides (such as MoN_x and TaN_x) is extremely sensitive to small chemical variations, even if only the vacancy concentration changes. We will use these model systems to explore the possibilities of alloy and structural developments.

Among the many alloying elements that have been studied for (Ti,Al)N-based coatings, tantalum is one of the most versatile, capable of simultaneously increasing strength, fracture toughness, thermal stability, and oxidation resistance. This can be further improved when alloyed with Si and reactive elements.

The concept of high entropy is also very beneficial for hard ceramic thin films. We will see that, for example, (Hf,Ta,Ti,V,Zr)N and (Al,Cr,Nb,Ta,Ti)N easily outperform their commonly used binary or ternary constituents in terms of thermal stability and thermomechanical properties. In addition, all of the highly entropic ceramic sublattice thin films studied were relatively insensitive to variations in deposition parameters-which is good because their properties are at a high level.

With superlattice coatings, we will discuss how such nanolamellar microstructures can also simultaneously improve strength and fracture toughness.

However, we will also investigate the performance of electrochemical supercapacitors, which strongly depends on chemical stability, accessible surface area, and electrical conductivity. Transition metal nitrides are also excellent candidates for this purpose, but must have a very open-pore microstructure. Glancing angle deposition enables the fabrication of such zigzag-structured electrodes based on γ-Mo_2N, combining excellent electrochemical energy storage capabilities with excellent mechanical flexibility.

The individual concepts allow the materials to be designed to meet the ever-growing demand for further coatings tailored to specific applications.

10:40am **A1-1-MoM-3 $Ti_5Si_3/TiAl_3$ Multilayer Coatings as Oxidation Protection for γ–TiAl*, Peter-Philipp Bauer,*** German Aerospace Center and Brandenburg University of Technology Cottbus, Germany*; R. Swadźba,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland*; L. Klamann,* German Aerospace Center, Germany

Titanium aluminides exhibit a high specific strength and a decent oxidation resistance up to 800 °C. This renders TiAl an excellent structural material for turbine blades. With the intention to increase the oxidation resistance at temperature above 800 °C, a large variety of different oxidation protection coatings were developed. It turned out that a combination of a diffusion inhibiting interlayer consisting of the Ti_5Si_3 phase and an oxidation resistant top layer of the $TiAl_3$ phase provided an excellent oxidation resistance. As a further development, a novel multilayer coating system of alternating Ti_5Si_3 and $TiAl_3$ layers were introduced. This design is expected to have exhibit a good oxidation resistance but also the high crack tolerance.

The coating system was produces by a continuous process using magnetron sputtering with elemental Ti, Al and Si targets. The performance of the coating was evaluated by cyclic oxidation tests in air at 900 °C for 1000 cycles (1h each) combined with thermogravimetric analysis. Scanning and transmission microscopy as well es x-ray diffraction was used to trace the oxidation and phase transformation processes.

Contrary to the expectations, the multilayer coating system showed only an insufficient oxidation protection. Although a good oxidation resistance was given during the first 100 cycles, at longer oxidation times the coating suffered under sever oxidation. In this talk, the failing mechanism as well as the lessons learned will be presented.

11:00am **A1-1-MoM-4 Max-Phase Based PVD Coatings as Protection for Lightweight Materials in High Temperature Environments*, Nadine Laska,*** *R. Anton,* German Aerospace Center, Germany*; R. Swadzba,* Lukasiewicz Research Network - Institute for Ferrous Metalurgy, Poland*; P. Nellessen,* German Aerospace Center, Germany

MAX-phases are of increasing interest as coating material for high temperature applications due to their unique combination of metallic and ceramic properties. Especially the alumina forming MAX phases of Cr_2AlC, Ti_2AlC or Ti_2AlN are promising as oxidation resistant coatings. Unfortunately, degradation of MAX phases is observed when applied on various Ti- or Ni-based alloys by interdiffusion processes between coating and alloy and the associated Al-depletion. This degradation is not present when MAX-phases are applied on the Al-rich γ-TiAl based alloys, which leads to an inward diffusion of Al from the substrate alloy into the coating and finally to a stabilization of the thermally grown alumina layer.

In the present work, the coating deposition process to get the MAX phases was DC magnetron sputtering using pure elemental targets of Ti or Cr, Al and C and in case of the Ti_2AlN MAX-phase based coating, nitrogen as reactive gas. No additional heating was applied during the sputtering process, the obtained substrate temperature was self-adjusted due to the target power. Prior to coating deposition, an Ar-plasma etching process for surface cleaning using a bias voltage of 500V and a frequency of 100 kHz was carried out for 15min. Using a threefold rotation, homogenous all-around coatings of about 10 µm were achieved with the desired stochiometric composition of the MAX-phases. The formation of the MAX-phase in the sputtered coatings was characterized during a post-annealing process at 800°C by in situ HT-XRD measurements as well as by SEM equipped with EDS and WDS, as well as by TEM with electron diffraction.

The MAX-phase coatings were tested under cyclic oxidation conditions. They provide a good oxidation protection of the γ-TiAl alloys due to the development of a protective alumina layer up to 850°C for up to 300 hrs in laboratory air. The performance of the MAX-phases is strongly depended on the substrate material and the accompanying interdiffusion processes between coating and substrate. Therefore, the Ti-Al-C based coating is more favored on TiAl alloys due to the thermodynamic stability of the Ti_2AlC MAX phase in particular in the presence of the γ-TiAl phase. In comparison, the Cr_2AlC MAX phase degrades after just 100 hrs at 850°C due to the formation of chromiumcarbides next to alumina.

11:20am **A1-1-MoM-5 Oxidation behaviors of (AlCrSiTi)N coatings on AISI 304 steel: A Combinatorial Study*, Sheng-Yu Hsu,*** *S. Chang, J. Duh,* National Tsing Hua University, Taiwan

Hard protective coatings have been widely applied in manufacturing industries to improve the performance and durability of workpiece. Scientists and engineers have dedicated to develop advanced coating materials which can be operated in harsh environments, e.g., electrochemical corrosion, high temperature oxidation. However, developing new materials has always been a crucial yet time-consuming task in materials science and engineering.

In this study, an experimental combinatorial approach via co-sputtering technique to efficiently investigate the effect of coating composition on the high temperature oxidation behaviors of (AlCrSiTi)N-coated AISI 304 steel under 700°C is demonstrated. From the elemental quantification results of 1-hour oxidized (AlCrSiTi)N, the oxygen content strongly correlates to the as-deposited coating composition, showing highest oxygen content (lowest oxidation resistance) of Ti rich composition and lowest oxygen content of Cr rich composition. TEM characterization exhibits that three oxide layers are formed after oxidation: spinel-Cr_2MnO_4 (originated from substrate diffusion), corundum-Cr_2O_3, and a thin layer of nano-crystalline mixed oxide. Except for Ti rich composition, an additional TiO_2 layer forms at the outermost layer. This study successfully demonstrates the efficiency and efficacy of developing advanced coating materials of superior high

[1] **Bill Sproul Awardee**

temperature oxidation resistance via experimental combinatorial approach.

11:40am **A1-1-MoM-6 Enhanced Pitting Resistance of Cathodic Arc Evaporated AlCrXN Coatings***, O. Hudak, F. Bohrn, P. Kutrowatz, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; E. Ntemou,* Ion Physics Group, Department of Physics and Astronomy, Uppsala University, Sweden*; D. Primetzhofer,* Ion Physics Group, Department of Physics and Astronomy, Uppsala University, Austria*; L. Shang, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl,*** Institute of Materials Science and Technology, TU Wien, Austria

With current state-of-the-art corrosion resistant coatings being far from optimized, it is of great interest to further investigate the fundamental mechanisms and underlying driving forces that dominate the degradative process.Particularly saline environments represent a technological frontier, where high-performance components suffer accelerated breakdown through a localized corrosion mechanism called-- pitting. Porosities, macroparticles, and the overall columnar growth morphology of physical vapor deposited coatings makes them particularly susceptible to inward-diffusion of corrosive media. Here, especially chloride ions play a key-role allowing for an accelerated attack at the coating substrate interface.

In a first step, this study provides a systematic approach on highlighting preferred diffusion pathways of corrosive NaCl-rich media of $Al_{0.7}Cr_{0.3}N$-based PVD thin films deposited on low alloy steel. Through an array of high-resolution techniques, such as TEM, ToF-SIMS, APT and t-EBSD, we intend to break down the possible diffusion paths from a micrometer to a nanometer scale, providing newest insights on the corrosion process. In a second step, this study showcases a doping strategy, as well as thermal treatment as viable approaches for improving the corrosion behavior of the previously discussed AlCrN system. In order to investigate the beneficial effects of the dopant, a series of $Al_{0.7}Cr_{0.3-y}X_yN$ coatings were deposited with varying alloying contents. Electrochemical tests of the as-deposited, as well as thermally treaded coatings were conducted using a three-electrode cell set up, whereupon extrapolations of Tafel-plots were used to evaluate the corrosion resistance.

Keywords: Corrosion Resistance; Pitting; Cathodic Arc Evaporation; PVD coatings; Diffusion Pathways;

12:00pm **A1-1-MoM-7 Novel Approaches for the PVD Synthesis of Advanced Aluminide Thin Films: The Example of Ruthenium-Aluminide***,* ***Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal aluminides are known for their use as high temperature materials in aerospace and gas turbine engine applications. Their best-known representatives of these intermetallics are NiAl, TiAl and FeAl. All these materials suffer from brittle behavior at room temperature and limited operating temperature of approx. 800°C. A relatively new and unknown candidate with improved properties regarding ductility, toughness and high temperature resistance is the RuAl. Thin film synthesis can enable the exploitation of their full potential for example as protective coatings at high temperature conditions. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering.Different approaches were conducted, including a multilayer thin film approach combined with a post-annealing as well as direct magnetron sputtering from a compound target to study the formation of the cubic B2 RuAl phase. Depending on the synthesis route, different microstructures and corresponding properties of the thin films were obtained, analyzed by electron microscopy and XRD techniques.

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