The 67th IUVSTA "CERAMAX" Workshop on "High temperature amorphous and nanostructured ceramic coatings: challenges and opportunities" was held at The Cockcroft Institute, STFC Daresbury Laboratory, Daresbury, UK from 23 – 27 September 2012.

The Workshop was organized by John Colligon (IUVSTA Thin Film Division) and Peter Schaaf (IUVSTA Surface Engineering Division)

The 27 delegates attending this workshop enjoyed extensive and very fruitful discussions during the following 12 topical sessions:

1. An overview of the properties of MAX phases and their existing and potential applications
2. Coating structure: advantages of amorphous and/or nanocrystalline materials
3. Effects of energy-assistance on nucleation and growth of ceramic coatings
4. Round Table discussion on the Industrial view of high temperature coating utilisation and requirements
5. Thermodynamic considerations of phase formation and computer simulation of multi-component ceramic systems
6. Bulk MAX phases and damage resistance
7. Relation between microstructure and properties of coatings
8. High resolution TEM studies of MAX phases
9. High temperature oxide ceramics: production, analysis and applications
10. Methods for formation of high temperature ceramic coatings and modelling
11. Growth of working structures; substrate considerations, barrier layers, interface layers
12. The influence of dopants on the formation of nanograin thin film materials.

The Round Table discussion on the Industrial view of high temperature coatings showed that there are many areas where established coatings work well enough but requirements for improved coatings remain. For example the diamond-like coatings work well, but only up to 300 degrees C and problems remain with binder failure and thermal fatigue from temperature cycling. There are essentially two routes to apply a new material in an industrial environment. The first is to deposit the thin film in an industrial machine and optimize the deposition conditions to reach the properties requirements. An alternative route is to study the growth of the material at the laboratory scale. The latter route has the advantage that a wider range of materials can be studied. However, (and this was the key point and the take-home message of the oxides session) there is a need for scale-up from laboratory results to industrial production of the same material. Monitoring the energy flux and contaminant species arriving at the substrate is an important requirement for nanocomposite systems so that industrial systems can evolve from laboratory-scale discoveries. In addition, for thin film coatings, the substrate-film interface has to be optimised and energy-assist processes such as HIPIMS will be important to attain the most durable coating.

It was agreed that further research in the materials area is valuable to industry but acknowledged that a specific need for an improved product is essential before such activity can attract funds. The current established areas of application are in coatings to improve tribological properties and in the use of γ-TiAl in turbines. Vacuum systems for dry etching often require coatings which survive the aggressive gases used and there is a need for coatings on hot filaments and other components used as sensors in such vacuum systems.

The discussions on coating microstructure highlighted the tunability of nanocrystalline materials in terms of physical and functional properties by controlling the size and distribution of grains. Thermal stability of each phase of nanostructures (nanocomposite or complex nanocrystalline) and bond strength in the case of amorphous materials to sustain operation at high temperatures is always of key importance and is dictated by structure-dependent diffusion processes across the film/substrate interface and through the film bulk in relation to oxidation processes and destabilization of the film microstructure.

Analysis of samples is clearly of high importance and TEM seems to be an essential technique for MAX phase materials. Perhaps too little has been done so far on fully exploiting the potential of conventional TEM in terms of relating microstructure to micro-diffraction information and systematically assessing large areas to get 'the full picture' (rather than carrying out 'spot' analyses, which might not be representative). There is a need to look at interfaces and large interest in studying radiation damage.

HRTEM gives much needed atomic-scale information, but requires better and more in-depth analysis Laterally atomically resolved HAADF and EELS are uniquely suited techniques but the SuperSTEMs are the ideal (and maybe currently the only) instruments to deliver this info. The Daresbury national EPSRC SuperSTEM facility can offer access free at the point of use (provided a small-scale proposal is accepted) and the study of ceramics and MAX phases seem to be ideal materials to reveal these instruments' potential. EELS can give information on chemistry, sites and bonding on the atomic scale and on highly localised electronic band structure properties. Time-resolved TEM as well as in-situ techniques are currently being developed. The advanced SuperSTEM is probably the only way to make headway in demonstrating the existence and properties of the novel 2-D MXene materials which are MAX phases with the 'A' element etched out.

In all there is huge potential for TEM studies of ceramics and MAX phases. For the new MAX and MXene phases, there are a many aspects to be investigated. The main issue for the potential application of MAX phases is to find a way to decrease the deposition temperature. A possible route is to look for a new phase which can be formed at low temperature, such as 211 phases with Cr, V transition metals. The second way is fast annealing of room temperature deposited films. What we can do with HRTEM is to look for the new phases with electron diffraction and investigate the crystal structure changes during the annealing.

MXene is a two dimensional novel material, which has wide applications in future, such as its use as battery materials, or electronic devices. HRTEM is used to reveal the new structure, and it will provide more structural information of MXene materials.

Enhancement of the oxidation resistance of nanocrystalline/amorphous materials can be achieved by formation of a protective surface layer acting as a diffusion barrier for oxygen inward diffusion, hence the importance of the structure and composition of the oxide scale to ensure its high protective capability.

Radiation resistance of MAX Phases was reported for irradiation of $Ti_3SiC_2$ , $Ti_3AlC_2$ and $Cr_2AlC$ by energetic ions. Early results indicate that $Ti_3AlC_2$ is more resistant. $Ti_3SiC_2$ survives higher doses than $Ti_3AlC_2$ at higher temperatures, whereas Cr-Al exchange occurs for $Cr_2AlC$ and the material becomes amorphous.

The possibility of extraordinary performance of thin films in high-temperature applications by developing a combination of suitable nanostructured and amorphous materials in a sophisticated architecture was proposed. It was noted that certain crystal structures are associated with specific properties; for example a triagonal crystal such as W-Fe-C tends to form a glassy metal. Silicon-dicarbide and so-named “Glitter”, a proposed new allotrope of carbon, are tetragonal-containing structures with special properties.

Some predictions of such unconventional phases can be found by taking a stochastic mixture of atoms of 3 elements and allowing them to relax to a lowest energy state. In this area the use of sputtering and ion-assistance is likely to allow further excursions in microstructure and in composition not predicted in normal thermodynamic situations as already seen in the Me-Si-N systems.

The final session attempted to highlight some of the main conclusions drawn from the 4 days of discussion. The MAX phases were seen to be very versatile with some excellent properties but other materials were often already available which have similar performance in terms of a specific property, such as High Temperature Stability. However, some MAX phases appear to exhibit multiple properties, for example high temperature stability and radiation resistance. The most interesting development reported at the Workshop was the novel material where the ‘A’ material in the MAX phase had been etched out to form an open layered structure known as MXene. This may have special electronic properties and will provide a very interesting area for further study.

It was agreed that a more thorough study of the multiple properties of MAX phases is needed and that members of this workshop group have the resources and experience to lead such a programme. The proposed follow-up study should be undertaken using a standard material prepared in the laboratory of one of the workshop members. As a first follow-up step it was agreed to work with a standard $Cr_2AlC$ and to send it to the laboratories of several of the participating groups to evaluate its performance in terms of temperature stability, self-healing, wear, corrosion, resistivity, radiation performance and biocompatibility. The suggestion was that Aachen University should be asked to prepare some samples on 3 inch Si wafers, Linkoping University would be invited to analyse these to provide a documented control of initial properties and then pieces of these samples would be sent to other laboratories to be evaluated in terms of their performance under various test conditions. This is really a vital first step because, at present, all reported data is being published on samples prepared in different ways with different degrees of MAX-phase content. Such mixed data is simply confusing the issue. Current modelling work uses *ab initio* calculations which apply to ideal single crystal structures so, to test these models, single crystal samples are also required. The future modelling challenge is to include effects of point defects and more realistic practical structures. It was suggested that development of new models to predict magnetic properties of MAX phases materials, currently not understood, may help to achieve an improved understanding of general defect-containing MAX-phase materials.

A second follow-up proposal was to screen the material properties literature to identify groups of elements that promote certain properties; for example low friction. It was noted that, in the USA, a Materials Genome Initiative was already under way. On this theme some trends, showing how the relative concentrations of Si, B, C and N in a non-MAX compound influenced friction, stability and stress, were reported. It was agreed that members of this Workshop should attempt to collate data showing, for example, which elements promote low friction in a compound and, in a similar way, which elements are associated with other material properties. We could then concentrate on trying to form MAX Phases from two elements with different properties to see if the combination exhibited the combined attributes. In these surveys we need to identify applications where nanolaminated MAX-phases are unique, for example in high temperature applications with liquid metals. Delegates were reminded in the sessions of the importance of impurities in formation of nanostructured materials and we need to look at the influence of these impurities on material performance. It was suggested that data from all the new studies outlined above could be reported in a special issue of a scientific journal to provide a standardised overview of the current status of the MAX phase field.

Outside the meeting room the event was complemented by a Welcome reception on the Sunday evening, for which our thanks are due to The British Vacuum Council. There was also a talk and tour of the facilities in STFC Daresbury to see the SuperSTEM, the Accelerators and Lasers in Combined Experiments (ALICE) facility, Electron Machine for Many Applications (EMMA) and Electron Beam Test Facility (EBTF). A memorable evening was held in Ruthin Castle in Wales where we feasted in Jacobean style to the sound of some beautiful Welsh singing and dancing.

The workshop also included a presentation on IUVSTA by John Colligon.

Finally our thanks are due to Ms Sue Waller and her colleagues for excellent background support and organisation of this event.

John Colligon

October 2012

**Version 1**

## IUVSTA Workshop

| | Fee | Budget Count |
|---|---|---|
| Advance registration | £190,00 | 18 |
| Late registration | | 0 |
| Fees waived | | 9 |
| **Total participants** | | 27 |

| | Fee | Number | Servings | |
|---|---|---|---|---|
| **REVENUE** | | | | |
| Income | | | | |
| IUVSTA | | | | £5.000,00 |
| BVC | | | | £500,00 |
| Registrations | | | | £3.420,00 |
| **REVENUE TOTAL** | | | | £8.920,00 |
| **EXPENDITURE** | **Fee** | **Number** | **Servings** | |
| **Catering** | | | | |
| Refreshments | £1,80 | 27 | 12 | £583,20 |
| Water | £1,10 | 16 | 1 | £17,60 |
| Orange Juice | £1,10 | 4 | 1 | £4,40 |
| Lunch at CI | £11,00 | 27 | 4 | £1.075,20 |
| Dinner at Ruthin Castle | £50,00 | 39 | 1 | £1.950,00 |
| Reception at Doubletree Hotel | £20,00 | 35 | 1 | £700,00 |
| Reception drinks | | | | £316,30 |
| **Media Services** | | | | |
| AV services | | | | £90,00 |
| Printing | | | | £150,00 |
| **Transportation** | | | | |
| To/from hotel and Ruthin Castle | | | | £1.495,00 |
| **Other expenses** | | | | |
| 40 Folders | | | | £525,60 |
| Photography | | | | £98,70 |
| **EXPENDITURE TOTAL** | | | | £7.006,00 |
| Speakers expenses | | | | **£1.914,00** |
| **BALANCE** | | | | **£0,00** |

**Budget Code - STGA00058.01**

Speakers expenses

| | |
|---|---|
| 4 nights (348.00) accommodation for 4 invited speakers | £1.392,00 |
| | |
| 6 nights accommodation for Fanni Misjak | £522,00 |
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| | |
| Total | £1.914,00 |