

Full Survey Chemical Analysis of Plasma Resistant Ceramic Coatings

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CHALLENGES AND REQUIREMENTS

In the semiconductor industry in general and particularly in liquid crystal display (LCD) manufacturing, several processes involve plasma etch and plasma clean. The high-speed plasma stream can be extremely corrosive to manufacturing compartments and the surfaces that are exposed to the plasma resulting in formations of residual particles. Consequently, particles formed in chambers can contaminate substrates that are being processed, thus contributing to device defects. To minimize particle formations, plasma resistant ceramic coatings are required on various components exposed to plasma including the plasma etcher, the plasma cleaner, or the

plasma propulsion system, such as the chamber walls, bases, gas distribution plates, rings, view ports, lids, nozzles, shower heads, substrate holding frames, electrostatic chucks, face plates, and selectivity modulation devices, among others.

Plasma resistant ceramic coatings under development or currently in active use, are typically multi-layered structures that provide plasma erosion resistance, rigidity, conformability to substrate and thermal shock resistance. Rare earth oxide, alumina, carbides, and nitrides based ceramic materials are currently used and/or under further developments. Coating precursors include ceramic powders, sintered ceramic solids, metal and metal alloy targets, and metal halides, depending on the component substrate materials, coating technique and application environment.

Table 1. Some important characteristics of plasma resistant ceramic coatings

Component Base Materials (Substrate)	Coating Composition	Coating Precursors	Coating Technique	Critical Impurities	Impurity Testing Needs
Aluminum Alloy 6061, Stainless Steel 316L	Rare earth oxides: Y_2O_3 , $Y_3Al_5O_{12}$, $Y_4Al_2O_9$, $Er_3Al_5O_{12}$, $Gd_3Al_5O_{12}$, $Y_2O_3 - ZrO_2$ Fluorides: YF_3 , YOF	Ceramic powders such as Y_2O_3 , Al_2O_3 , YF_3 , ZrO_2 , SiO_2 , Er_2O_3 , Gd_2O_3 , Nd_2O_3 , etc.	Air Atmosphere Plasma Spray (APPS) Low Pressure Plasma Spray (LPPS)	B, Na, Mg, Al, Si, S, P, Ca, transition metals, rare earth impurities, etc.	Ceramic powders and coatings
		Sintered ceramic solid sputtering target such as Y_2O_3 , Al_2O_3 , YF_3 , ZrO_2 , SiO_2 , Er_2O_3 , Gd_2O_3 , Nd_2O_3 , and garnets and solid solutions including $Y_3Al_5O_{12}$, $Y_4Al_2O_9$, $Er_3Al_5O_{12}$, $Gd_3Al_5O_{12}$, $Y_2O_3 - ZrO_2$, etc.	Ion-Assisted Deposition (IAD) Plasma Spray Physical Vapor Deposition (PSPVD)	B, Na, Mg, Al, Si, S, P, Ca, transition metals, rare earth impurities, etc.	Ceramic solid pieces and coatings
		Metal and metal alloy sputtering target such as Y, Al, Al/Er alloys, etc.	Plasma Spray Chemical Vapor Deposition (PSCVD)	B, Na, Mg, Al, Si, P, S, Ca, transition metals, refractory metals such as Nb, Mo, Ta, W, etc.	Metal and alloys, and ceramic coatings
Graphite	Pyrolytic Carbon	Methane, propane, etc.	Chemical Vapor Deposition (CVD)	B, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, transition metals, etc.	Gaseous/liquid precursors and ceramic coatings
	CVD-SiC	Silanes, chlorosilanes, methane, H_2 , etc.			
	CVD-TiC	$TiCl_3$, methane, H_2 , etc.			
	CVD-ZrC	$ZrCl_4$, methane, H_2 , etc.			
	CVD-TaC	$TaCl_5$, methane, H_2 , etc.			
SiC	CVD-SiC	Silanes, chlorosilanes, methane, H_2 , etc.	Chemical Vapor Deposition (CVD)	B, N, O, Na, Mg, Al, P, S, Cl, Ca, transition metals, etc.	Gaseous/liquid precursors and ceramic coatings
Si	CVD-SiC	Silanes, chlorosilanes, methane, H_2 , etc.	Chemical Vapor Deposition (CVD)	B, N, O, Na, Mg, Al, P, S, Cl, Ca, transition metals, etc.	Gaseous/liquid precursors and ceramic coatings

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MULTILAYERED CERAMIC COATING STRUCTURES

Ceramic coating structures are designed for different plasmas, conformality to substrate, vacuum sealability and reducing thermal expansion mismatching with the substrate. The common strategy is to deposit multilayered structures, with each layer thickness ranging from micrometers to 100s micrometers. The chemical composition of layers, their morphology (amorphous, crystalline or nanocrystalline), their residual stress, and the layer thicknesses all need to be carefully controlled.^{3,4} Often heat treatment is applied after depositions to establish composition gradients through layer interfaces via thermal diffusion. In multiple layers each layer might have the same basic chemical composition or might have different chemical compositions. Some important characteristics of common plasma resistant ceramic coatings are shown in Table 1.

IMPURITIES IN CERAMIC COATINGS

Foreign elements can be incorporated into ceramic coatings from a variety of sources. Most frequently these are the precursors, the processing tools and environmental impurities. Their types, concentrations and distributions can be vastly different and dependent on the coating processes used. For example, yttria ceramic coatings can be made by plasma spray of high purity yttria powders, by ion-assisted deposition of sintered yttria solids or by ion-assisted deposition of high purity yttrium metal target in the presence of O₂ plasma². While high purity (99.999%+) yttria powders are typically synthesized from thermal decomposition of yttrium carbonates and hydroxides, high purity (99.995%+) yttrium metal is often made by thermal metal reduction of yttrium fluorides with Ca and/or Mg metal followed by vacuum distillation in Ta or W crucibles^{5,6}. In the latter case, not only the overall impurity level will be higher (total less than 50 ug/g in yttrium metals, as compared to total less than 10 ug/g in yttria powder), but impurity type, concentration and distribution in the resultant yttria coating is completely different. Table 1 lists some key impurities of concern in each coating technology.

When a ceramic coating is made by plasma spray of fused or sintered ceramic powders, each molten ceramic droplet splats onto the solid surface, forming a disc-like or fine spherical structure that rapidly solidifies.¹ The feature scale of each splat has a thickness in the micrometer range and a length that varies across the range from several to above 100 micrometers. Splats overlap one another as the deposit builds up to the required thickness. Rogue inclusions of metal oxides are often the main source of contamination. When a CVD or PVD process is employed, a smooth surface can be achieved, and the contamination mechanism also changes. Debris falling off from precursor delivery line as well as atmospheric species are the main contributors of contamination.

FULL SURVEY CHEMICAL ANALYSIS OF CERAMIC COATINGS

High resolution Glow Discharge Mass Spectrometry (GDMS) is recognized as one of the most versatile direct sampling techniques for survey chemical analysis of solids. The glow-discharge plasma source combined with high-resolution mass analyzer is suitable to evaluate mass fractions in solids directly and with very high sensitivity. The most important analytical characteristics of GDMS are summarized in Table 2. Among others, these are the key features of GDMS as the analytical technique of choice for full survey chemical analysis of ceramic coatings:

1. Direct sampling allows analyzing samples as is, thus reducing the risk of contaminating samples during sample preparation and recovery issues with solution sampling techniques (ref).²
2. Ion-Beam Ratio based quantification of 70+ elements from sub- $\mu\text{g/g}$ levels to minors and majors. This is particularly important given that solid certified reference standards are not readily available for these types of matrices.
3. A large sampling volume to ensure representative sampling. Typical analysis in flat sampling geometry is conducted using eight- or ten-mm diameter orifices and results acquired from tens of microns of sputtering depths. This allows sampling 100s of microfeatures of the ceramic coatings.
4. Flat sampling is allowing to acquire data depth specifically, thus allowing to construct depth profiling distributions maps of specific impurities.

Table 2. GDMS analytical features pertinent to impurity analysis of ceramic coatings

Performance Criteria	Values	Remark
Glow Discharge Source	Reduced pressure mode with cryo-cooling	VG9000 and Nu [®] Astrum GDMS
Sampling Volume	ϕ : 8 - 10 mm x 10s μm depth	Indium mask will cover a fraction of sampling area
Mass Resolution (MR)	400 to 4000	Typical resolution 4,000
Elemental Coverage	Virtually the entire periodic table	Non-metal impurities C, O, N possible under special conditions
Limit of Detection	sub - $\mu\text{g/g}$ to $\mu\text{g/g}$ level	
Quantification	Ion beam ratio (IBR) quantification with non-specific relative sensitivity factor (RSF)	Matrix metal ion signal used for IBR calculation and normalized accordingly
Dynamic Conc. Range	sub $\mu\text{g/g}$ — 100s $\mu\text{g/g}$	
Spatial Information	Mostly bulk	

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SAMPLING OF CERAMIC COATINGS

Generally, samples in direct current glow discharge ion sources are either serve as a cathode or they are in some way part of the cathode in the two-electrode system. Electrically non-conductive ceramic coatings are most efficiently analyzed using explicitly designed sampling orifices constructed from high purity metals.

Here we demonstrate that by applying a high purity indium (purity $\geq 99.99999\%$) sheet in the form of a mask with sampling slits is a very effective way for survey chemical analysis of ceramic coatings and for acquiring spatial distribution information of impurities in these samples. Figure 1 describes this sampling technique, the surface texture before analysis and sputter atomized spots after measurements and cross-sections of the atomized crater profile.

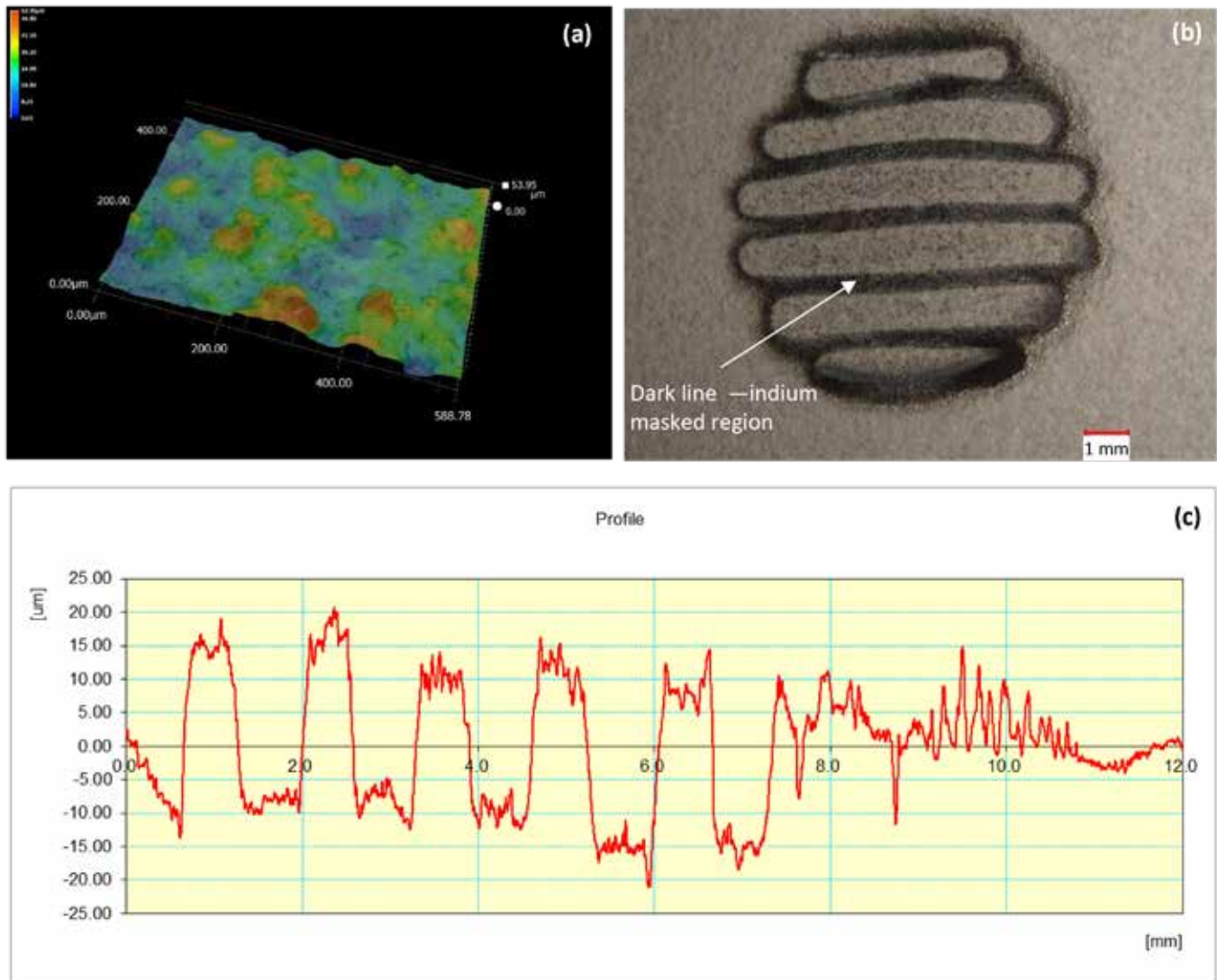


Figure 1. (a) 3D illustrations of a typical plasma resistant ceramic coating roughness; (b) plasma atomized spots using indium mask with six sampling openings. Darker lines around the atomized spots are indium deposits on the surface from the mask; (c) plasma atomized crater cross-section profile. Sampling orifice diameter $\sim \phi 10$ mm; average sputtering depth ~ 20 μm .

By using the Indium mask technique with multiple sampling openings, stable sputtering can be achieved. There are several examples illustrated on Figure 2. These show that high ion signal intensities of major elements ($1e9$ counts per second, cps) with

low intensity variations (within 10% RSD) during data acquisitions can be readily achieved on a broad variety of ceramic coatings, such as Y_2O_3 , Y_2O_3 -stabilized ZrO_2 , Y_2O_3 with Al_2O_3 , and YF_3 .

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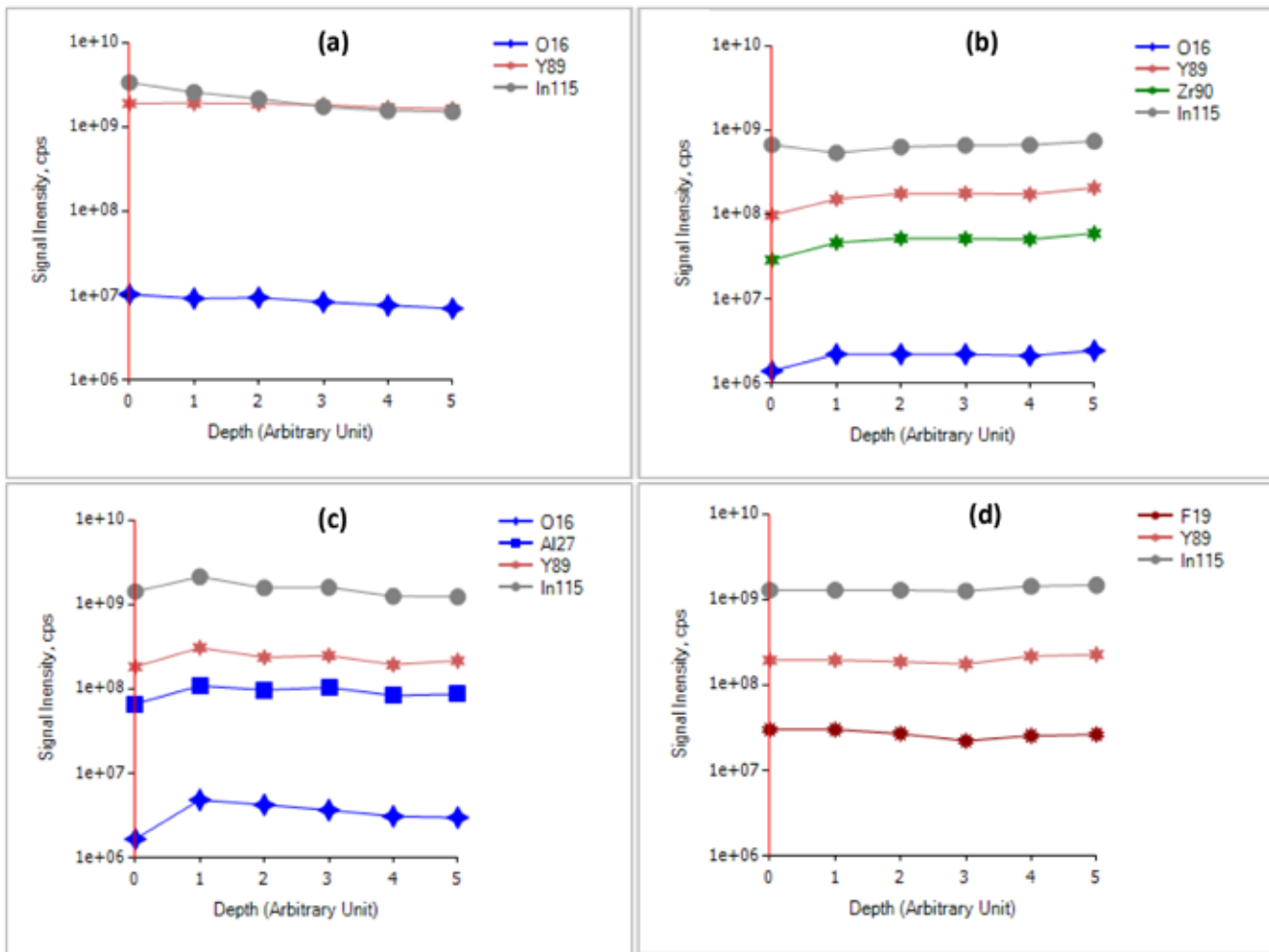


Figure 2. GDMS sputtering signal intensity of matrix elements of plasma-resistant ceramic coatings: (a) Y_2O_3 ; (b) Y_2O_3 -stabilized ZrO_2 ; (c) Y_2O_3 : Al_2O_3 ; and (d) YF_3 . The coating substrate is aluminum. For all coatings, a steady, strong matrix metal ion (e.g., Y, Al, Zr) signal (RSD < 10%) is achieved after pre-sputtering for 5 min, similar to analysis of metal samples. Glow discharge parameters: NU Astrum flat cell assembly, U: 800-1000 V; I: 2.0 mA, Argon discharge gas $\geq 99.9999\%$ purity, Indium mask purity $\geq 99.99999\%$; Sampling orifice diameter: 10 mm; Number of sampling windows: 6.

Full Survey Chemical Analysis of Plasma Resistant Ceramic Coatings

Typical surveying result using the above method for selected impurities in ceramic coating materials are listed in Table 3.

Table 3: Typical reporting limits of selected impurities by the above method of analysis on plasma-resistant ceramic coatings

Mass fractions in Key Impurities*	Mass fractions in µg/g **			
	Y ₂ O ₃	Y ₂ O ₃ : Al ₂ O ₃ (YAG)	YF ₃	ZrO ₂ : Y ₂ O ₃ (YSZ)
Na	< 0.1	< 0.1	< 0.05	< 0.05
Mg	< 0.1	< 0.1	< 0.05	< 0.05
Al	< 0.1	< 0.1	< 0.05	< 0.05
Si	< 0.1	< 0.1	< 0.05	< 0.05
P	< 0.5	< 0.5	< 0.05	< 0.05
S	< 0.5	< 0.5	< 0.05	< 0.05
K	< 0.5	< 0.5	<5	<1
Ca	< 0.5	< 0.5	< 0.5	< 0.1
Ti	<0.1	<0.1	<0.01	<0.05
V	<0.05	<0.05	<0.01	<0.05
Cr	<0.5	<0.1	<0.1	<0.05
Mn	<0.1	<0.1	<0.05	<0.05
Fe	<0.1	<0.1	<0.05	<0.05
Co	<0.05	<0.05	<0.05	<0.05
Ni	<0.1	<0.1	<0.05	<0.05
Cu	<0.5	<0.5	<1	<1
Zn	<0.5	<0.1	<1	<1
Nb	<0.1	<0.05	<0.1	<5
Mo	<0.1	<0.1	<0.1	<0.5
Ta	<100	<100	<100	<10
W	<0.05	<0.05	<0.1	<0.5

* This table doesn't reflect all elements that this method can cover.
 ** These reporting limits do not reflect the method limits of detection.

SUMMARY

This application note demonstrates that the direct sampling GDMS test method based on flat sampling and using indium mask with sampling windows can be effectively used for trace analysis of plasma resistant ceramic coatings, such as Y₂O₃, YF₃, Y₂O₃/Al₂O₃, Y-Stabilized Zirconia, and many others. Stable atomization can be achieved with this method and representative data can be acquired for full survey chemical analysis of complex ceramic coatings. High matrix ion signals (up to 1E9 cps), can be maintained through the data acquisition, with signal intensity variation of 10% RSD or better, which is comparable to analysis of metal samples. Determinations of analytes at sub-ug/g can be readily achieved for most elements. The precision was evaluated using a Y-stabilized zirconia reference material. For most of trace elements of interest, a precision of 10-40% RSD can be achieved at trace levels.

PRECISION

Table 4 shows the statistics of some key impurities for GDMS analysis of a Y-Stabilized Zirconia ceramic reference material (Kurt J. Lesker® EUDF YSZ Target – ZrO₂/Y₂O₃, 92/8 mol%). Most trace elements can achieve precision of 10-40%.

Table 4: Precision of GDMS analysis of Y-Stabilized Zirconia ceramic reference materials (Kurt J. Lesker EUDF YSZ Target – ZrO₂/Y₂O₃, 92/8 mol%)

Impurities*	LoD (µg/g)	Replicates					Average (n=5)	RSD% (n=5)
		1	2	3	4	5		
B	0.5	4.3	4.0	3.7	1.5	2.5	3.0	42%
Na	0.5	2.3	2.6	3.1	5.4	5.5	3.8	41%
Mg	0.5	3.6	3.7	4.2	5.5	7.0	4.3	31%
Al	0.5	51	58	66	86	74	67	20%
Si	0.5	63	73	73	87	120	74	13%
P	0.5	2.0	2.7	2.5	3.3	3.7	3.0	16%
S	0.5	250	230	220	250	250	240	6%
K	10	<10	<10	<10	<10	<10	-	-
Ca	5	10	11	12	10	18	12.2	27%
Ti	0.5	7	8	9	8	11	8.6	18%
V	0.5	<0.5	0.5	0.5	<0.5	1.0	0.7	43%
Cr	0.5	<0.5	0.5	0.5	0.66	1.8	0.56	17%
Mn	0.5	5.1	7.7	6.0	3.8	3.5	5.0	38%
Fe	0.5	34	56	43	38	58	46	23%
Co	1	<1	<1	<1	<1	<1	-	-
Ni	0.5	0.62	0.88	<0.4	1.1	1.4	1.0	33%
Cu	0.5	<0.5	0.67	<0.5	2.8	1.6	1.7	63%
Zn	0.5	1.1	0.7	2.2	4.1	4.8	2.6	70%
Nb	5	9.9	6.7	5	74	<5	7.2	35%
Mo	1	8.2	12	10	5.6	9.4	9.0	26%
Ta	10	<10	<10	<10	<10	<10	-	-
W	1	9.0	12	7.6	6.0	11	10	23%

* Highlighted values failed the Grubb's test and were rejected accordingly.

FOOTNOTES

- 1 Kitamura et al. "Structural, Mechanical and Erosion Properties of Yttrium Oxide Coatings by Axial Suspension Plasma Spraying for Electronic Applications", Journal of Thermal Spraying Technology, 2011, 20(1-2), 170-184.
- 2 For solution-based analytical techniques, HF acid is commonly needed to stabilize and recover Si and refractory elements such as Nb, Ta and W. Unfortunately, HF can cause the rapid precipitation of YF₃, CaF₂, and co-precipitation of other rare earth impurities.
- 3 J.Y. Sun et al., "Ion Assisted Deposition Top Coat of Rare-Earth Oxide", US Patent 9,869,013 B2. Jan 16, 2018.
- 4 J.Y. Sun et al., "Coating Architecture for Plasma Sprayed Chamber Components", US Patent Application 2018/0366302 A1. Dec 20, 2018.
- 5 H.J. Nolting, et al. "Preparation and properties of high purity yttrium metal. J. Inorganic Nuclear Chem., 1960, 14, 208-216;
- 6 A.H. Daane, et al. "Preparation of yttrium and some heavy rare earth metals." J. Electrochem. Soc., 1953, 100(10) 442-444;