APPLICATIONS BULLETIN

Characterization of thermal spray coatings by instrumented indentation and scratch testing: Part I

//// Introduction

Thermal spray coatings have been used for several decades for enhanced wear, corrosion and thermal protection in various industrial domains. These coatings are routinely used in power plant turbines, aircraft engines, on pulp rolls in the paper industry and in many other applications where extensive wear or high temperature damage occur. The most common deposition methods of thermal spray coatings are plasma spraying (water or gas stabilized), high velocity oxy-fuel (HVOF), wire arc, flame spray and detonation gun.

To achieve the best functionality of the coatings one needs to know the relationships between the mechanisms of coating formation and its mechanical properties. While the mechanisms of formation of such coatings have been rather well investigated, detailed information on mechanical properties still remains difficult to obtain because of the heterogeneity of the coating (see Fig. 1).

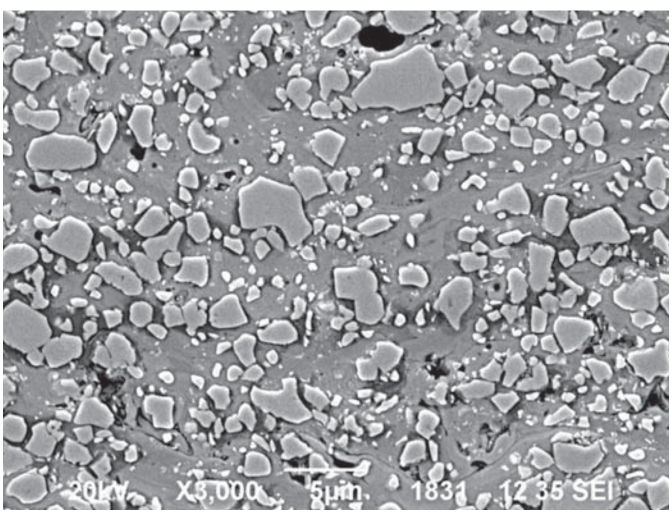

Fig. 1 – Typical microstructure of WC-17Co HVOF-sprayed coating showing WC grains and binding metal matrix (Scanning Electron Microscope image).

Until now mainly macro scale methods such as four point bending or microhardness at relatively high loads have been used for measurements of mechanical properties. Such methods measure 'composite' properties of the coating but they ignore the strongly heterogeneous structure composed usually of hard particles and a softer binding matrix. For adhesion and cohesion testing, the situation is even more complicated as one of the few standardized test is tensile testing by gluing or brazing two samples and then pulling them apart. Not only is evaluation of coating adhesion by this method quite difficult but it is also limited by the tensile strength of the glue or braze.

The research project presented here deals with new methods for testing of mechanical properties of thermal spray coatings by means of instrumented indentation and scratch testing. Part I of the work presents the results of low load indentation and scratch tests on HVOF coatings. Part II will discuss the results of both low and high load indentation and cyclic indentation on HVOF and plasma sprayed coatings. Selected results of high load indentation on HVOF coatings are also mentioned in this part of the work.

//// Thermal spray coatings: heterogeneous material

For investigation of thermal spray coatings the grain size is an important factor for determination of the indentation parameters. At very small loads of a few milinewtons the properties of the individual grains or splats can be measured whereas increasing the load larger volume is being involved which reveals a 'composite' value of mechanical properties. This composite value disregards the heterogeneity of the material and until recently mostly this type of measurement has been performed. However, to better understand the relationship between the deposition parameters and the coating functionality the properties of the material on different scales must be known. Measurement of these properties has been possible only lately using instrumented indentation and advanced automated matrix measurements. Moreover, thanks to continuous recording of force and indentation depth the instrumented indentation method makes it possible to calculate several other important characteristics of the material (in addition to hardness) such as elastic modulus and the elastic and plastic portion of the work of indentation. This allows a better understanding of the elastic-plastic behaviour of the coating which can be closely related to its wear and failure resistance.

//// Instrumented indentation on thermal spray coatings

CSM Instruments indentation machines allow measurement at different ranges:
- for properties of single splats or grains at low loads, we used the Nanoindentation tester (0 - 500 mN),
- for the 'composite' properties at higher loads, we used the Micro-Indentation tester (0.03 - 30 N).

Instrumented indentation is not limited by optical measurement of the imprint diagonal (though conventional Vickers hardness can be calculated from the residual imprint depth) and it provides other very useful information such as elastic modulus and creep properties. The basics of instrumented indentation are given elsewhere [1-3]; here we will focus on its particular application to thermal spray coatings.

//// Cohesion and adhesion tests by scratch testing

Recently there have been attempts to determine the adhesion of thermal spray coatings by using scratch tests in the same manner as in the thin film domain, i.e. scratching on the top surface of the coating with increasing load. However, due to much higher thickness and surface roughness of thermal spray coatings the method has been found to be unsatisfactory. Here we propose a method which consists of running a constant load scratch test on a cross-section of the coating. This method was first proposed by Lopez et al. [4]. The sample is cross-sectioned, embedded in resin and then polished. The scratch is done under constant load and the indenter moves from the substrate through the coating into the resin where the sample is embedded – see Fig. 2 and [4] for schematic explanation. The test is repeated at several loads and the projected area of the cone, Acn, extracted by the indenter, is calculated. Generally two types of failure are observed: the cone originates in the coating and the cone originates at the substrate-coating interface. In the first case the cohesion of the coating can be characterized while in the latter case the adhesion of the coating can be characterized.

//// Samples

The samples used in this study were sprayed from WC-17%Co, Cr_3C_2-25%NiCr and specially developed (Ti,Mo)(C,N)-39%NiCo powders. The coatings will be further referred to as WC-Co, Cr3C2-NiCr and (Ti,Mo)(C,N)-NiCo.

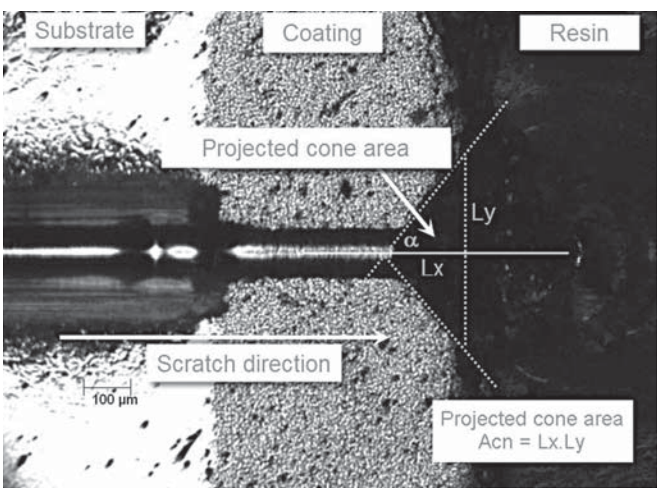

Fig. 2 – Schematics of the constant load scratch on a cross-sectioned sample.

The (Ti,Mo)(C,N)-39%NiCo powder was specially developed at the H.C. Stark GmBh (Goslar, Germany) for use in sliding applications and first tested by L-M Berger [5]. All samples were sprayed with previously optimized parameters using Praxair JP-5000 HVOF system at Skoda Research, Ltd. in Plzen, Czech Republic. The thickness of the coatings varied from 300 µm to 500 µm. All samples were sectioned, embedded in LECO resin (cat.no. 811-563-101) and metallographically polished. The microstructure (Fig. 1) of all coatings consisted of grains with dimensions of a few micrometers (WC-17Co), approx. ten micrometers (Cr3C2-NiCr) and less than three micrometers ((Ti,Mo)(C,N)-NiCo) dispersed in a metallic matrix.

//// Indentation procedure and results

Instrumented indentation was performed with a CSM Instruments Nanoindentation Tester (NHT) at four maximum loads of 2 mN, 20 mN, 100 mN and 200 mN. Experiments in Part II of this work were performed CSM Instruments Microindentation Tester (MHT) with load range of 0.05 N up to 30 N. Both instrument use the instrumented indentation method. All indentations were done on the cross-section of the coating. The loading and unloading times were each of 30 s with no pause at maximum load. The precise indent positions were preselected by using the "Visual Advanced Matrix" mode [6] which allows precise selection with the integrated optical microscope (Fig. 3). The indentations were then done automatically on these spots. The areas to indent on all tested coatings were selected so that they were as homogeneous as possible, i.e. without visible pores and grain or splat boundaries. Ten measurements were performed at each of the four selected loads to increase the statistical reliability of the results. Outlaying values caused by presence of pores and heterogeneities invisibles under the optical microscope were rejected.

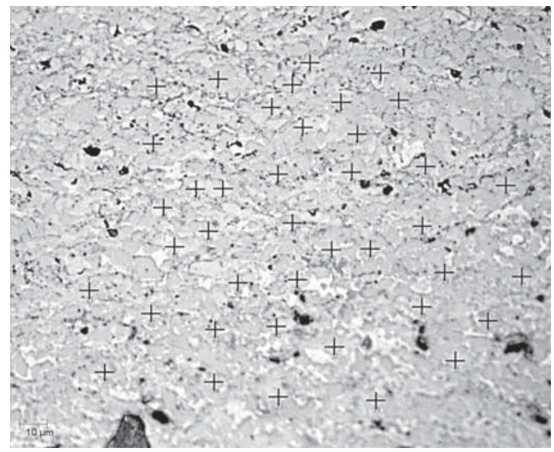
Fig. 3 – Visual Advanced Matrix mode showing the precise position of each indentation test.

The hardness results presented in Fig. 4a clearly show decrease in hardness with increase of the maximum indentation force. This trend can be explained by the volume of the material affected by the process of indentation. At small loads, the volume involved in the indentation (related to maximum indentation depth h_{max}, see Fig. 4b) corresponds to the size of individual grains or splats which are composed of carbides or hard metals. In small volumes the measurements are not influenced by pores or grain boundaries and the properties well describe homogeneous material of single grains or splats. With increasing indentation forces the volume of material influenced by indentation increases and comprises also the softer metallic matrix. This leads to the observed decrease in hardness with increasing indentation force. The anomalous behaviour of the experimental (Ti,Mo)(C,N)-NiCo coating could not be explained, although it is supposed that because of the very small size of the hard particles in this coating, the indentations at 2 mN were performed both in the particles and in the softer matrix. The increase of hardness at 20 mN load is very likely the result of pushing the hard particles into the softer matrix during the indentation which gives higher values of hardness. This interesting phenomenon will be addressed in more details in future experiments.

Simultaneously with hardness the values of elastic modulus were calculated using supposed Poisson's ratio of 0.3. The results are shown on Fig. 5. It is interesting to note that in contrast to hardness, elastic modulus remained rather constant for all coatings irrespective of the maximum indentation force.

A slight decrease in the elastic modulus was observed at higher loads (1 N to 10 N) while decrease in hardness was at such high loads less significant than at low loads.

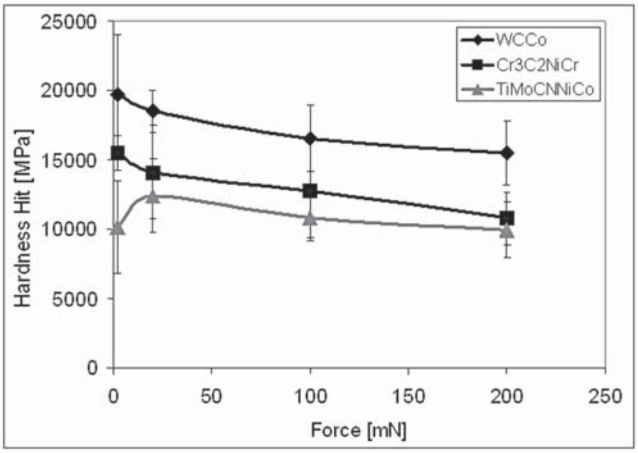

Fig. 4a – Decrease of hardness with increase of maximum indentation force for the three tested coatings.

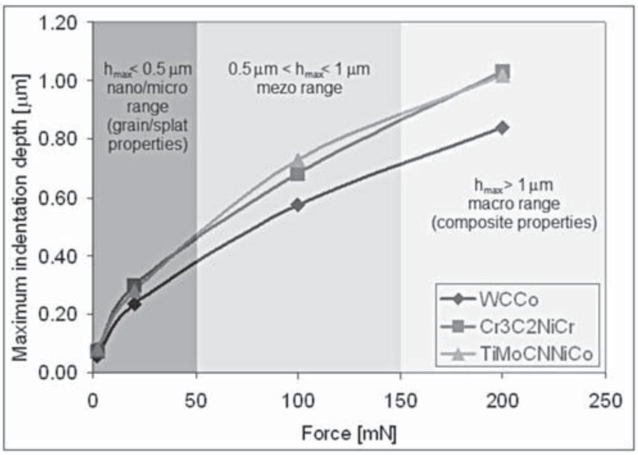

Fig. 4b – Maximum indentation depth (h_{max}) as a function of the maximum indentation force. Results from the CSM Instruments Nanoindentation Tester (NHT).

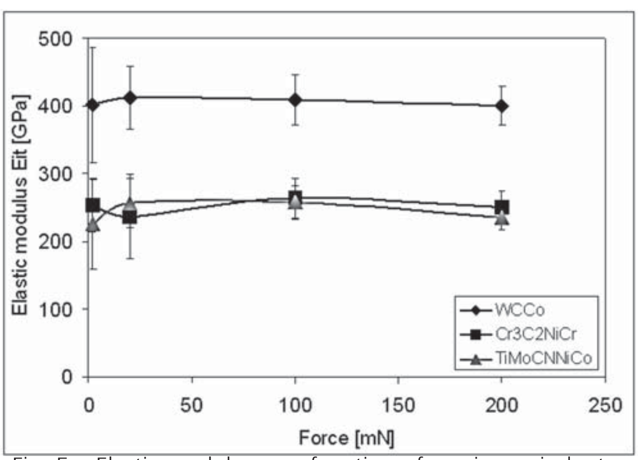

Fig. 5 – Elastic modulus as a function of maximum indentation force.

//// Work of indentation η_{IT}

A very important material property is the ratio of elastic to total work of indentation, η_{IT}. This parameter (defined by the ISO 14577 standard) characterizes well the elastic-plastic properties of the material. In the case of thermal spray coatings the value of η_{IT} changes significantly with the volume of material involved in the indentation. At small loads the deformation field extends only to the individual grains or splats as selected by the Visual Advanced Matrix mode. These measurements show very high elasticity compared to the coating as a whole: the value of η_{IT} for all three tested coatings was much higher at lower loads and progressively decreased with increasing loads – see Table 1. Indenting at low loads in the relatively homogeneous microstructure of single grains composed of carbides results in a high ratio of elastic to total work of indentation. At higher loads (above 100 mN) however, increasing contribution of plastic deformation in the metallic matrix and formation of intergranular and intersplat cracks leads to dissipation of the indentation energy which is reflected in lower fraction of elastic work of indentation. Above 1 N loads the ratio of elastic to total energy of indentation practically does not change and remains around 30 %. Interestingly, the η_{IT} value was very similar for all three tested coatings at loads above 1 N. At the lowest load, the WC-Co and Cr3C2-NiCr coatings showed similar value of η_{IT} while the (Ti,Mo)(C,N)-NiCo coating showed η_{IT} approximately 13 % lower. Since the η_{IT} value is characterizing the elastic-plastic response of the material to external load, it can be used for estimation of the ability of the material to resist wear or abrasive damage.

Force	2 mN	20 mN	100 mN	200 mN
WC-Co	48±7	34±4	30±2	29±3
Cr3C2-NiCr	50±4	38±3	31±6	30±3
(Ti,Mo)(C,N)-NiCo	37±11	34±5	28±4	28±3

Table 1 – Ratio of elastic to total work of indentation η_{IT} in percents.

//// Scratch test procedure and results

Scratch tests were performed using a CSM Instruments Revetest Scratch Tester with load range of 1 N to 200 N. The tests were performed on the cross-sectioned samples embedded in LECO resin. The scratch tests were done by CSM Instruments automatic Map by Stage procedure with constant loads of 5 N, 29 N, 52 N, 76 N and 100 N. The length of the scratch was 1.2 mm, scratching speed 2.4 mm/min and Rockwell C diamond indenter of 200 µm radius was used for all tests. Images of the cone fracture area (Fig. 6) were taken immediately after scratching using an optical microscope integrated on the Revetest instrument. The projected cone area, $A_{cn} = L_x.L_y$ (see Fig. 2) was choosen as the most characteristic factor among the L_x, L_y and cone angle values since only A_{cn} showed a monotonic relationship to the scratching load.

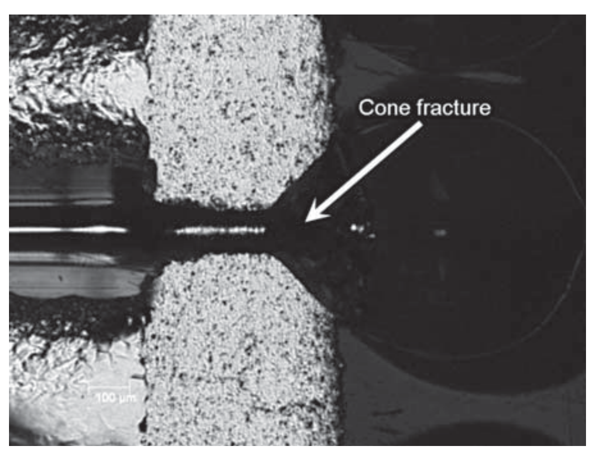

Fig. 6 – Typical example of the scratch track and cone fracture on the HVOF coating (Cr3C2-NiCr, 52N load).

The results show that the projected cone area increased with increasing scratching load. This increase was almost linear for samples WC-17Co and Cr3C2-NiCr whereas for sample (Ti,Mo)(C,N)-NiCo the increase showed a more parabolic trend (see Fig. 7). This indicates the existence of a different failure mechanism of the (Ti,Mo)(C,N)-NiCo coating at high loads compared to the Cr3C2-NiCr coating: for both these coatings the projected cone area was very similar at loads up to 50 N. At higher loads the damage in the (Ti,Mo)(C,N)-NiCo coating was larger than in the other tested coatings.

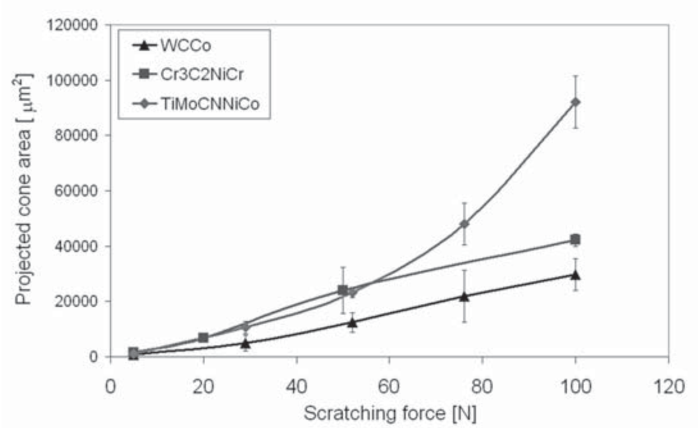

Fig. 7 – Projected cone area as a function of the constant load scratch force.

All of the cone fractures originated in the coating, thus confirming that the tests allow characterization of the cohesion of the coating. Cohesion of the coating is closely related to its wear and abrasion resistance because in both cases the failure originates in the coating. This failure is caused by application of external force via wear/abrasive particles or sliding indenter during scratch test. The obtained results correspond to already measured abrasion resistance of the tested coatings: WC-17Co showed the highest abrasion resistance followed by Cr3C2-NiCr whereas the (Ti,Mo)(C,N)-NiCo mixture showed the lowest abrasion resistance.

The presented results show that this type of constant load scratch test can be used as a fast and efficient method for characterization of cohesion and can be used for estimation of wear/abrasion resistance of thermal spray coatings.

//// Conclusions

The presented work reports on new applications of the instrumented indentation and scratch testing methods for investigation of microscopic and macroscopic properties of thermal spray coatings. The methods give a new insight into understanding the mechanical properties on micro and nano scale. The observed evolution of hardness confirms that at very low loads properties of single grains or splats are measured, while with increasing load the influence of the more soft and ductile metal matrix is observed. A new parameter was used for characterization of the coating: the ratio of elastic to total work of indentation, η_{IT}. This parameter allows characterization of elastic-plastic properties of the coating which is closely related to its resistance to failure.

The constant load scratch testing on the cross-sectioned coating is a very intuitive, fast and efficient method for characterization of cohesion and, in certain cases, adhesion of the coating. The research work now in progress is focused on developing this method to quantify the cohesion and its possible extension for adhesion determination.

The work that will be presented in Part II of this paper will complete the experiments at low loads by experiments at high loads including cyclic loading and scratching on both HVOF and plasma sprayed coatings. An overview of indentation and scratch methods available for testing of mechanical properties of thermal spray coatings will be given.

We believe that this extensive testing program will be a significant contribution to understanding the relationship between local and overall properties of these perspective materials.

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Editor Jiri Nohava, PhD

Should you require further information, please contact:

CSM Instruments
Rue de la Gare 4
CH-2034 Peseux
Switzerland

Tel: + 41 32 557 5600
Fax: +41 32 557 5610
info@csm-instruments.com
www.csm-instruments.com