Adhesion tests for thermal spray coatings: Application range of tensile, shear and interfacial indentation methods

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Abstract

Three adhesion measurement methods for thermal spray coatings, namely tensile adhesive strength (according to EN 582), interfacial indentation and in-plane tensile tests were investigated in terms of accuracy of the results and application potential for different coating / substrate conditions. Whereas the tensile adhesive strength test is widely used in industry, the other two methods are still under development in research laboratories and therefore only few experimental data on the accuracy of the methods and on the potential in an industrial context are available. For that reason, dissimilar coating-substrate combinations covering a wide range of types of thermal spray coating-substrate systems were tested using all these methods. Ceramic (Al₂O₃) and metallic (NiCr 80-20) coatings were thermally sprayed by flame spraying with two different thickness on titanium alloy and steel substrates exhibiting each two distinct roughness levels. The distinguished coating properties include the coating toughness, shear strength, interfacial toughness, and adhesive strength. Thermally sprayed coatings do not only show an interfacial complexity, but also the integrity of the interface of substrate and coating has to be considered, as well as porosity, cracks and residual stresses. In this paper, each measurement method was found to be related to certain type of loading conditions and fracture mode. The results of the different methods are compared and the limits of applicability of the different methods are discussed.

1. Introduction

Many methods have been developed for evaluating the coating-substrate adhesion. Among them, a significant number is based on the linear elastic fracture mechanics (LEFM) approach [1-3]. However, there are no universal tests for measuring coating’s adhesion. Each method is related to a certain type of coating, loading condition, application of the coating etc. This can be explained by the variety of coatings systems which represent different types of dissimilar material interfaces that are present in many industrial applications (metal/metal, metal/ceramic, polymer/metal, polymer/ceramic, etc). The tests that work with one coating system may not necessarily work with another [4-6]. Though, there is no standard adhesion test for coating system which can suite all materials. Among the most widespread methods used are indentation tests [7, 8], shear tests [9-13], tensile adhesive strength like ASTM C633, ASTM F1147, ISO 14916, EN 582 [14-16] and double cantilever beam (DCB), where a large scatter of the results was observed and must be viewed quantitatively even the test system was very sensitive [5, 17]. The best test method often becomes the one that simulates practical stress condition [18-20]. We should also note that adhesion is not a constant in practical applications, but rather a complicated property that depends on loading conditions on coating thickness [14] and on different parameters such as grit blasting to roughen the substrate surface [21-25]. Furthermore, the residual stresses due to the mismatch in thermal and mechanical properties between coatings and substrate are of importance [26-30].

The primary objective of this study is to compare methods for the determination of coating’s adhesion and fracture properties of thermal spray coatings based on the observed failure modes. Therefore three common adhesion tests were applied to ceramic (Al₂O₃) and metallic (NiCr 80-20) thermal sprayed coatings with different thickness on substrates of titanium alloy and steel with different roughness.

2. Materials and experimental procedure

NiCr 80-20 and Al₂O₃ coatings were deposited by flame spraying on substrates St 52-3 and TiAl6V4. The substrates exhibit two different roughness produced by grit blasting (Ra 2.7 and 5.2 µm). The average coating’s thicknesses were 140 µm and 330 µm. In total 16 combinations were performed and summarized in table 1.

In order to scan the applicability of tests for a broad range of coatings, three main tests were performed: Tensile adhesive strength, tensile tests and interfacial indentation tests (figure 1).

The mechanical properties of the coatings such as hardness and Young's modulus have been determined by low-load indentation techniques [31, 32], the Young’s modulus of coatings Al₂O₃, NiCr 80-20 were measured to be 49.5 and 97.3 kN/mm², respectively. Whereas the Young's Modulus of the substrates TiAl6V4 alloy and Steel St 52-3 were determined by tensile tests as 151 and 214 kN/mm² respectively.
Table N°1: Nomenclature and combinations of materials and coating-substrate systems:

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Substrate Material</th>
<th>Coating material</th>
<th>Ra µm</th>
<th>Thickness µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 140.5.6/St</td>
<td>St 52-3 Al2O3</td>
<td>5.6</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Al 330.5.6/St</td>
<td>St 52-3 Al2O3</td>
<td>5.6</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>Al 140.2.7/St</td>
<td>St 52-3 Al2O3</td>
<td>2.7</td>
<td>140</td>
<td></td>
</tr>
<tr>
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<td>St 52-3 Al2O3</td>
<td>2.7</td>
<td>330</td>
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</tr>
<tr>
<td>M 140.5.6/St</td>
<td>St 52-3 NiCr 80-20</td>
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<td>St 52-3 NiCr 80-20</td>
<td>2.7</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>Al 140.5.6/Ti</td>
<td>TiAl6V4 Al2O3</td>
<td>5.6</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Al 330.5.6/Ti</td>
<td>TiAl6V4 Al2O3</td>
<td>5.6</td>
<td>330</td>
<td></td>
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<td>330</td>
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<td>330</td>
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<td>140</td>
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<tr>
<td>M 330.2.7/Ti</td>
<td>TiAl6V4 NiCr 80-20</td>
<td>2.7</td>
<td>330</td>
<td></td>
</tr>
</tbody>
</table>

Where Al and M are the ceramic Al2O3 and metallic NiCr 80-20 coatings, respectively, 140 and 330 are the coating thicknesses, 2.7 and 5.7 µm are the Ra values as an interfacial roughnesses, /St and /Ti are the substrates of steel and of titanium alloy respectively.

2.1 Tensile adhesive strength experiments
According to the standard test EN 582, test specimens of 25 mm diameter were joined with the cylindrical counter parts using an adhesive agent. Then they have been cured at elevated temperature (210°C). The tensile load was applied with an Universal Epprecht-Multitest tensile machine. The mean adhesive strength values were calculated from three tests performed under the same conditions. The tensile adhesive strength was calculated by:

$$\sigma_{\text{max}} = \frac{F}{A} \text{ [MPa]}$$

Where F is the maximum load at rupture, and A is the normal section of specimen. The sample geometry is shown in figure 1-a.

2.2 Tensile experiments
The geometry of the specimen is shown schematically in fig. 1-b. The specimens were loaded along their longitudinal axis. The displacement rate was 8 µm/s measured using an extensometer. The span of displacement measured was 21 mm. Videos of the specimen surface were captured during tensile testing from frontal and upper sides to gain a fundamental understanding the fracture mechanisms. The Young’s Modulus of the titanium alloy and steel substrate were measured using the extensometer. The average value found was 151, and 214 [GPa].

The energy release rate due to the crack channelling was estimated using and expression developed by Beuth [12].

$$G_c = \frac{\pi}{2} \sigma_{\text{max}}^2 h_c g(\alpha, \beta)$$

where \(\bar{E}_c = E_c/(1-\nu^2)\) is the material plane strain tensile modulus, \(g(\alpha, \beta)\) is the Dundurs parameters and \(\sigma\) is the ultimate stress of coating, \(h_c\) is the coating thickness.

Brittle coating fracture (Al2O3) and data evaluation
In our experiments, the coating’s delamination took place after first crack is produced perpendicularly to the coating/substrate interface. In this case, the coating strength is bigger than the interfacial strength (\(G_{\text{Coating}}>G_{\text{interface}}\)) (figure 2- a, c).

Therefore, the total energy release rate \(G_{\text{total}}\) is described in [7, 16] and given by:

$$G_{\text{total}} = G_c \pm G_{\text{residual}}$$

$$G_{\text{residual}} = \frac{\pi}{2} \sigma_{\text{res}}^2 h_c g(\alpha, \beta)$$

This results in a coating toughness of:

$$K_{IC} = \sqrt{\frac{E_c G_{\text{total}}}{(1-\nu^2)}}$$

Figure (1): Schematic presentation of test methods employed a) tensile adhesive test, b) tensile test with one side coating system c) interfacial indentation test.
Ductile coating fracture (NiCr 80-20) and data evaluation

The ductile coating’s fracture mode dominated by cracks fragmentation as shown in figure (2, b & c). The coating strength is smaller than the interfacial strength ($G_{\text{coating}} < G_{\text{interface}}$). The interface strength may be assessed in this case via a statistical analysis of the interfacial shear strength (IFSS) described by Y. Leterrier [10, 33].

$$\tau = 1.34 h_C \sigma_{\text{max}} \left( \frac{N}{L} \left( 1 + \varepsilon_{\text{plastic}} \right) \right)$$  \hspace{1cm} (6)

Where $h_C$ is the coating thickness, $\sigma_{\text{max}}$ is the ultimate tensile strength of coating which is similar magnitude to those occurring at the deformation of coating caused by hardness indenter [34, 35]. $N/L$ is crack density per length unite, $\varepsilon_{\text{plastic}}$ is the plastic strain. The energy release rate in relation (2) was estimated with the ultimate $\sigma_{\text{max}}$ in coating in term of the measured coating hardness $\sigma_{\text{max}} = 3.2H_v$.

$$K_{IC} = 0.015 \frac{P_C}{a_C^{3/2}} \cdot \left( \frac{E}{H} \right)^{1/2}$$  \hspace{1cm} (7)

$P_C$ and $a_C$ denote load and crack length, respectively. The square root of the ratio of the elastic modulus (E) divided by the Vickers hardness (H) at the interface is expressed by:

$$\left( \frac{E}{H} \right)^{1/2} = \frac{\left( \frac{E}{H_s} \right)^{1/2}}{1 + \left( \frac{H_s}{H_c} \right)^{1/2}} + \frac{\left( \frac{E}{H_c} \right)^{1/2}}{1 + \left( \frac{H_c}{H_s} \right)^{1/2}}$$  \hspace{1cm} (8)

Where the subscripts $i$, $s$ and $c$ stand for interface, substrate and coating, respectively.

3.1 Results of tensile adhesive strength

Coating thickness effect: the bond strength data in table 2 show that the bond strength of thermal spray coatings decreases with increasing coating thickness. This may be related to the residual stresses that produce more driving force for interface crack propagation in thicker coatings [14]. Another explication is that the adhesive used in the test could penetrate the porous thin coating more easily than a thicker one and subsequently, the adhesive may increase the adhesion of thinner coating.

Interfacial roughness effect: the bond strength of Al$_2$O$_3$ coatings on steel substrate and NiCr 80-20 coatings TiAl6V4 substrate both show a general tendency to increase with increasing Ra value. Within the experimental scatter, the interfacial roughness doesn’t show significant influence on the other combinations. As Ra is the representation of the average roughness and since it is unable to take into account the true area of contact between substrate and coating, it cannot explain accurately the impact of interface roughness on adhesion [24, 25].

As mentioned above, the bonding agent tends to penetrate the pores of the coating and modify its behaviour. This invalidates the results (as e.g. for Al$_2$O$_3$ on TiAl6V4 substrate) unless the coatings are thick and tight enough to prevent penetration. Tensile adhesive tests involve a complex mixture of tensile and shear forces which render difficult the interpretation of the results [38]. Moreover, it has been discussed extensively in the literature that this test can not be related to fracture mechanic properties like toughness, as the crack propagation is spontaneous and depends on the critical flaw size at the interface [2, 4].

Figure 2: Coating’s failure in tensile test, a & b) schematic presentation of coating delamination and failure by cracks fragmentation respectively. c) Upper view micrograph of coating failure by delamination (ceramic coating) d) Micrograph of coating failure by cracks fragmentation (metallic coating).

2.3. Interfacial indentation experiments

The approach involves a direct measurement of the length of a radial crack initiated by Vickers indentation at the interface of a coated material in a cross section (figure 1-d). The measured crack length at the interface is used to calculate the interfacial toughness using a recently developed method by Chicot, Démarecaux and Lesage [36, 37]. The interfacial toughness is expressed by:

$$K_{IC} = 0.015 \frac{P_C}{a_C^{3/2}} \cdot \left( \frac{E}{H} \right)^{1/2}$$  \hspace{1cm} (7)

$P_C$ and $a_C$ denote load and crack length, respectively. The square root of the ratio of the elastic modulus (E) divided by the Vickers hardness (H) at the interface is expressed by:

$$\left( \frac{E}{H} \right)^{1/2} = \frac{\left( \frac{E}{H_s} \right)^{1/2}}{1 + \left( \frac{H_s}{H_c} \right)^{1/2}} + \frac{\left( \frac{E}{H_c} \right)^{1/2}}{1 + \left( \frac{H_c}{H_s} \right)^{1/2}}$$  \hspace{1cm} (8)

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Table 2: The summary results of all test methods:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Test methods</th>
<th>Tensile adhesive strength</th>
<th>Tensile test</th>
<th>Interfacial indentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coatings and thickness</td>
<td>σ [MPa] and SDEV</td>
<td>σ (IFSS) [GPa]</td>
<td>$K_{IC}$ [MPa.m$^{1/2}$]</td>
</tr>
<tr>
<td>Steel</td>
<td>Al 140</td>
<td>91 ± 7</td>
<td>9.4</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Al 330</td>
<td>68 ± 9</td>
<td>16.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Al 140</td>
<td>90 ± 6</td>
<td>13.3</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Al 330</td>
<td>42 ± 8</td>
<td>6.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>M 140</td>
<td>70 ± 7</td>
<td>0.2</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>M 330</td>
<td>51 ± 4</td>
<td>0.36</td>
<td>15.3</td>
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<tr>
<td></td>
<td>M 140</td>
<td>82 ± 4</td>
<td>0.16</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>M 330</td>
<td>54 ± 14</td>
<td>0.21</td>
<td>14.8</td>
</tr>
<tr>
<td>Titanium alloy</td>
<td>Al 140</td>
<td>100 ± 4</td>
<td>13.9</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Al 330</td>
<td>78 ± 8</td>
<td>8.2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Al 140</td>
<td>105 ± 29</td>
<td>8.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Al 330</td>
<td>41 ± 19</td>
<td>8.1</td>
<td>1.0</td>
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<tr>
<td></td>
<td>M 140</td>
<td>61 ± 9</td>
<td>0.81</td>
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</tr>
<tr>
<td></td>
<td>M 330</td>
<td>91 ± 7</td>
<td>0.24</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>M 140</td>
<td>68 ± 9</td>
<td>0.25</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>M 330</td>
<td>90 ± 6</td>
<td>0.11</td>
<td>12.6</td>
</tr>
</tbody>
</table>

3.2 Results of tensile test:

Brittle coating fracture (Al$_2$O$_3$): Table 2 shows the calculated coating fracture toughness (see formula 2 and 5). An impact of interfacial roughness and coating’s thickness on the coating toughness was not observed.

Ductile coating fracture (NiCr 80-20): The adhesion in this tensile test is presented by the interfacial shear strength (IFFS) which is related to the density of coating's cracks measured in saturation stage of the cracks fragmentation. As general trend, the interfacial shear strength (IFSS) was observed to increase with increasing Ra roughness values.

The fracture toughness of ductile coatings was observed to increase with coating’s thickness increase, whereas the impact of interfacial roughness was not evidenced. The fracture toughness was calculated based on the estimated energy release rate due to crack channelling using Dundurs parameters with the pre-existing crack tip in the theoretical model of calculation (formula 2), but in our case we don’t know crack tip dimension on the coating, subsequently the results revealed a high toughness values comparing to interfacial toughness. However, the upper limit of energy release rate has been estimated.

3.3 Results of interfacial indentation:

Coating thickness effect: The interfacial toughness showed a decrease in increasing coating thickness for the TiAl6V4 substrate, on the other hand, for the steel substrate shows lower if not reverse effect of the coating thickness on the interfacial toughness. This can be explained by the presence of different residual stress states which may differ from the Titanium alloy substrate to the steel substrate [39].

Interfacial roughness effect: From table 2, it is seen for the coating with thickness 140 µm that the interfacial toughness tends to increase with Ra. In contrast, for the coating thickness of 330 µm, the interfacial toughness increases with decreasing Ra values. The crack propagation into the smooth interface is easier than into the rougher one, subsequently, the interfacial toughness should increase with Ra. Since the behaviours are opposite in the two situations, it means that the residual stress effect may be dominant.

The coating fracture toughness values obtained by tensile tests are in some case about ten times of the interfacial toughness values obtained by interfacial indentation tests. These high values were due to our calculation of the energy release rate as an upper limit.
3.4 Correlation between adhesive strength and interfacial toughness

Only interfacial indentation tests and adhesive strength test allowed to assess adhesion of metallic coating on substrates combinations. Therefore, a correlation between the measured values is discussed in the following. For the indentation test, a mechanically stable crack is introduced into the coating-substrate interface using conventional Vickers indentation. The resistance to crack propagation at the interface is then used as a measure of adhesion, by analogy with the fracture of homogeneous brittle solids, this may be characterized by a fracture resistance parameter or strength parameter. Since this fracture resistance parameter is related uniquely to the bonding across the interface, it is certainly a more fundamental measure of adhesion than the bond strength which is the result of a combination of fracture resistance and size distribution of defects. However, a general trend has been found between interfacial toughness and bond strength (figure 3). Only the full squared points were taken in consideration in this tendency because we considered that the other points (empty squared) are influenced by the penetration of the adhesive agent into the pores of the coatings. In particular, the porosity in the ceramic coating was found to be up to 7% and the adhesive resistance to tensile strength was found to be ~100 MPa. Therefore, the trend should be considered for the metallic coatings rather than for the ceramic coatings.

![Figure 3: Correlation diagram of bond strength and interfacial toughness](image)

4. Conclusion

Based on the results of this experimental study, the following general conclusions can be drawn:

1. The mechanism of coating fracture of each test method was understood and the impacts of interfacial roughness and coating’s thickness on bond strength, interfacial toughness, coating toughness have been reported. Each method employed showed a different tendency because of different loading conditions of the coating substrate systems.

2. In-plane tensile test with one side coating, the results should be developed much further with statistical models, in particular, the theory governing the development of crack patterns under axial and shear stresses in order to give quantitative results.

3. As the stress intensity and loading systems are different in interfacial indentations and in-plane tensile tests, the coating toughness values were ten times factor of the interfacial toughness values. This fact due to highly estimated energy release rate as the upper limit.

4. It was shown that the two tests, bond strength and interfacial toughness, give the same general trends for the different situations of coatings and substrates. Moreover, a correlation between the results of both tests could be drawn.

Acknowledgements

We would like to thank Ph. Schneider, B. von Gunten, G. Bürki, H. B. Mosimann and metallography-team for their help in the framework in this project, as well as, “Wissenschaft und Technologie of Armasuisse” for their financial support also A. Meier for the video image treatments.

References


