

Mechanical properties of flame sprayed free-standing coatings

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Abstract

This paper examines the mechanical properties of rod flame sprayed coatings in the system $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--ZrO}_2$. Free-standing thin coatings were tested and a new approach for their preparation was used and assessed in terms of absolute values of bending strength and their standard deviation in comparison with published values for ceramic systems. The Young's modulus shows distinct non-linear behavior. The presence of particle-, micro crack- and/or transformation toughening mechanisms can be seen by comparing mechanical properties of pure alumina- with zirconia containing coatings.

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1. Introduction

Determination of mechanical properties of thermally sprayed materials has been a widely aimed goal. A common way hereby is to spray thick layers and cut specimens from that block or cylinder [1–11]. Another frequently used strategy to obtain characteristic values for bending strength, adhesion strength, Young's modulus, fracture strain, number of survived thermal shock cycles etc. is testing the composite, i.e. coating with substrate [12–34] and the application of indentation methods [15,19,23–25,27,28,35–51]. Hereby the non-trivial interaction between substrate and coating has to be taken into account. The number of publications applying indentation method shows, that this method is very popular due to its low sample preparation complexity. The cutting and polishing procedure influences the micro crack network in an undetermined way. To minimize this impact of forces to the specimen prior testing some authors follow the strategy of spraying samples on thermally or chemically removable substrates [2–4,7,52,53]. The dimensions of the coated and later removed substrate represent the final dimensions of the free-standing coating. With this technique it is possible to produce free standing stripes with thicknesses in the range of 0.6 to several

mm [4,7,52,53] that are suitable for 3- or 4-point bending experiments. The Young's modulus of thermally sprayed materials shows typically non-linear behavior [13,33,54–56].

This paper describes a new approach of producing thin stripes of ceramic coatings for mechanical property determination and even for thermal shock experiments. The new approach is that the coating is built up on a substrate with adjusted roughness that on the one hand provides enough adhesion for coating built up but on the other hand enables the removal of the coating after the spray process with nearly no applied force. The substrate is additionally covered with a template for producing stripes of the coating in the dimensions 10 mm width and up to 100 mm length. The results of the so tested ceramic composites were compared with a compilation (Table 1) of published mechanical properties for several thermally sprayed oxide materials. There is a large scatter for mechanical properties found in literature. The big influence of spray parameters and different spray process explains most of that scatter. For oxide systems the bending strength normally lies in the range between 20 and 80 MPa; peak values for the alumina–zirconia system of 160 MPa can be found. If the values are much lower, very likely non-optimum spray parameters were applied. Most data are published for alumina- and stabilized zirconia-matrix systems. After a heat treatment the bending strength and the Young's modulus normally show strong increase due to sintering and densification. If processes appear that lead to the formation of cracks, the mechanical cohesion

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Table 1
Compiled mechanical properties of thermally sprayed oxides.

| Material (type, sample treatment, etc.) | Process | Bending strength σ [MPa] | Young's modulus [Gpa] | Fracture strain ε [%] | Fracture toughness K_{IC} [MPa m ^{1/2}] | Porosity [%] | Roughness [μ m] | Weibull modulus [–] | Type of test, comments | Ref. |
|---|---------|---------------------------------|-----------------------|-----------------------------------|---|--------------|----------------------|----------------------------|---|------|
| Al ₂ O ₃ -matrix | | | | | | | | | | |
| Al ₂ O ₃ | APS | 20 | – | – | 1.2 | – | – | – | 4-Point-bending, in situ observation of crack extension via REM | [9] |
| Al ₂ O ₃ (12 h/1550 °C) | APS | 60 | – | – | 5 | – | – | – | 4-Point-bending, in situ observation of crack extension via REM | [9] |
| Al ₂ O ₃ | RFS | ~35 | ~45 | – | – | 7.6 | – | – | 3-Point-bending of free-standing samples | [57] |
| Al ₂ O ₃ | APS | 27.2 ± 1.7 | 13 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ (4 h/1450 °C) | APS | 54.8 ± 4.1 | 95 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ | LPPS | 120 | 70 | – | – | – | – | 26 (0.3 mm) 37 (0.7 mm) | 4-Point-bending with aluminium substrate; layer thickness 0.3 and 0.7 mm | [58] |
| Al ₂ O ₃ /3 wt%TiO ₂ | APS | 35.6 ± 2.7 | 17 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ /3 wt%TiO ₂ (4 h/1450 °C) | APS | 125 ± 27 | 260 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ /13 wt%TiO ₂ (Metco 130SF) | APS | 17.6 | 14.0 | 1.7* | – | – | 4.3 (Ra) | – | 3-Point-bending of free-standing impregnated samples; indentation method (Vickers); *fracture strain very likely in % | [7] |
| Al ₂ O ₃ /13 wt%TiO ₂ (Metco 130SF, Metcoseal URS) | APS | 14.6 | 13.6 | 1.5* | – | – | 0.3 (Ra) | – | 3-Point-bending of free-standing impregnated samples; indentation method (Vickers); *fracture strain very likely in % | [7] |
| Al ₂ O ₃ /13 wt%TiO ₂ (Metco 130SF, Metcoseal ERS) | APS | 11.4 | 13.5 | 1.1* | – | – | 0.3 (Ra) | – | 3-Point-bending of free-standing impregnated samples; indentation method (Vickers); *fracture strain very likely in % | [7] |
| Al ₂ O ₃ /13 wt%TiO ₂ (Metco 130SF, Dichtol) | APS | 12.8 | 12.4 | 1.3* | – | – | 0.3 (Ra) | – | 3-Point-bending of free-standing impregnated samples; indentation method (Vickers); *fracture strain very likely in % | [7] |
| Al ₂ O ₃ /50 wt%TiO ₂ | APS | 31 | 236 | – | – | 6 | 5.28 | – | Indentation method (Vickers, Knoop); 3-point-bending of layer and substrate | [23] |
| Al ₂ O ₃ /50 wt%TiO ₂ (16 h/600 °C) | APS | 13.2 | – | – | – | 8 | – | – | indentation method (Vickers, Knoop); 3-point-bending of layer and substrate | [23] |
| Al ₂ O ₃ /30 wt%MgO | APS | 103 | 10 | 2.3* | – | 6.1 | – | – | 3-Point-bending of free-standing samples; *fracture strain very likely in % | [54] |
| Al ₂ O ₃ /22.3 wt%ZrO ₂ | APS | 32.8 ± 1.7 | 20 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ /22.3 wt%ZrO ₂ (4 h/1450 °C) | APS | 76.0 ± 4.6 | 95 | – | – | – | – | – | Ring-test | [11] |
| Al ₂ O ₃ /40 wt%ZrO ₂ | APS | 81 | 8.8 | 1.6* | – | 5.9 | – | – | 3-Point-bending of free-standing samples; *fracture strain very likely in % | [54] |
| Al ₂ O ₃ /40 wt%ZrO ₂ | APS | 163 ± 26 | 150 ± 22 | 0.13 ± 0.01 | – | 12.3 ± 0.6 | – | 6 | 3-Point-bending of free-standing samples | [1] |
| Al ₂ O ₃ /40 wt%ZrO ₂ (1 h/1400 °C) | APS | 156 ± 17 | 160 ± 41 | 0.15 ± 0.02 | – | 7.9 ± 0.4 | – | 3 | 3-Point-bending of free-standing samples | [1] |

| | | | | | | | | | |
|---|------|------------|---------------|---------|-------------------|------|----------|----|--|
| ZrO ₂ -matrix | | | | | | | | | |
| ZrO ₂ /7 wt%Y ₂ O ₃ | APS | 74 | 21.3 | 0.8* | – | 12 | – | – | 3-Point-bending of free-standing samples; *fracture strain very likely in % [54] |
| ZrO ₂ /7 wt%Y ₂ O ₃ | APS | 74 | 16 | – | – | 11.9 | – | 25 | 3-Point-bending of free-standing samples [10] |
| ZrO ₂ /7 wt%Y ₂ O ₃ (48 h/1000 °C) | APS | 123 | 31 | – | – | 10.9 | – | 18 | 3-Point-bending of free-standing samples [10] |
| ZrO ₂ /7 wt%Y ₂ O ₃ (48 h/1000 °C + 36 h/1400 °C) | APS | 314 | 45 | – | – | 8.7 | – | 20 | 3-Point-bending of free-standing samples [10] |
| ZrO ₂ /7 wt%Y ₂ O ₃ (48 h/1000 °C + 24 h/1700 °C) | APS | 10 | 4 | – | – | 12.8 | – | 5 | 3-Point-bending of free-standing samples [10] |
| ZrO ₂ /7 wt%Y ₂ O ₃ | APS | ~115 | ~55 | – | – | 11 | – | - | 4-Point-bending of free-standing samples [4] |
| ZrO ₂ /7 wt%Y ₂ O ₃ (1000 h/1250 °C) | APS | ~180 | ~105 | – | – | – | – | - | 4-Point-bending of free-standing samples [4] |
| ZrO ₂ /8 wt%Y ₂ O ₃ | APS | ~55 | ~35 | – | – | 15 | – | - | 4-Point-bending of free-standing samples [4] |
| ZrO ₂ /8 wt%Y ₂ O ₃ (1000 h/1250 °C) | APS | ~85 | ~55 | – | – | – | – | - | 4-Point-bending of free-standing samples [4] |
| ZrO ₂ /8 wt%Y ₂ O ₃ | APS | 33 ± 7 | 13 | – | KIc: 1.15 ± 0.07 | – | – | 6 | 4-Point-bending of free-standing samples, SEVNB [5] |
| | | | (tension) | | KIIc: 0.73 ± 0.10 | | | | |
| | | | (compression) | | | | | | |
| ZrO ₂ /8 wt%Y ₂ O ₃ | APS | 39.7 ± 2.7 | 9.9 ± 0.6 | – | – | – | – | – | 4-Point-bending of free-standing samples [52] |
| ZrO ₂ /8 wt%Y ₂ O ₃ (5 h/1250 °C) | APS | 91.3 ± 3.9 | 40.9 ± 4.1 | – | – | – | – | – | 4-Point-bending of free-standing samples [52] |
| ZrO ₂ /8 wt%Y ₂ O ₃ (laser treated) | APS | 10.8 ± 2.1 | 1–3 | – | – | – | – | – | 4-Point-bending of free-standing samples [52] |
| ZrO ₂ /8 wt%Y ₂ O ₃ (laser treated. 5 h/1250 °C) | APS | 19.1 ± 1.4 | 5–8 | – | – | – | – | – | 4-Point-bending of free-standing samples [52] |
| ZrO ₂ /8 wt% Y ₂ O ₃ (Amperit 827.090, tested at RT, 500 °C and 1000 °C) | APS | 4–60 | 2.5–20 | 0.2–0.4 | – | – | – | – | Free-standing samples [33] |
| ZrO ₂ /(xY ₂ O ₃ ;yCeO ₂) (0–1000 h/1000–1400 °C) | APS | 10–65 | 10–90 | – | – | – | – | – | 4-Point-bending of free-standing samples [53] |
| Ca-ZrO ₂ | APS | 25.3 ± 3.1 | 7 | – | – | – | – | – | Ring-test [11] |
| Ca-ZrO ₂ (4 h/1450 °C) | APS | 78.2 ± 9.9 | 106 | – | – | – | – | – | Ring-test [11] |
| Mg-ZrO ₂ | APS | 13.9 ± 0.2 | 3.7 | – | – | – | – | – | Ring-test [11] |
| Mg-ZrO ₂ (4 h/1450 °C) | APS | 50.1 ± 2.0 | 69 | – | – | – | – | – | ring-test [11] |
| Other oxides | | | | | | | | | |
| HA | HVOF | 41.4 ± 3.9 | – | – | – | – | 4.7 (Ra) | – | 4-Point-bending of free-standing samples [31] |
| HA | APS | 45.2 ± 5.1 | – | – | – | – | 3.1 (Ra) | – | 4-Point-bending of free-standing samples [31] |
| HA | APS | 6–14 | 0.5–3.4 | – | 0.3–1.1 | – | 6–8 (Ra) | – | Bending of layer with substrate [32] |
| | | | (tension) | | | | | | |
| | | | 3.2–5.3 | | | | | | |
| | | | (compression) | | | | | | |
| La ₂ Ce ₂ O ₇ | APS | 20.3 | 25 | – | 1.3–1.5 | – | – | – | Indentation method (Vickers, Knoop) [36] |
| MgAl ₂ O ₄ | APS | 26.7 ± 2.8 | 16 | – | – | – | – | – | Ring-test [11] |
| MgAl ₂ O ₄ (4 h/1450 °C) | APS | 64.3 ± 4.7 | 119 | – | – | – | – | – | Ring-test [11] |
| Mullite | APS | 28.6 ± 2.1 | 16 | – | – | – | – | – | Ring-test [11] |
| Mullite (4 h/1450 °C) | APS | 37.7 ± 5.6 | 46 | – | – | – | – | – | Ring-test [11] |
| ZrSiO ₄ | APS | 19.3 ± 2.1 | 6.1 | – | – | – | – | – | Ring-test [11] |
| ZrSiO ₄ (4 h/1450 °C) | APS | Fail | – | – | – | – | – | – | Ring-test [11] |

APS = atmospheric plasma spraying; RFS = rod flame spraying; LPPS = low pressure plasma spraying; HVOF = high velocity oxy-fuel flame spraying; HA = hydroxyapatite.

Table 2
Sample composition and denomination.

| Sample denomination | Al ₂ O ₃ [wt%] | TiO ₂ [wt%] | ZrO ₂ [wt%] |
|---------------------|--------------------------------------|------------------------|------------------------|
| 100:0:0 | 100 | 0 | 0 |
| 90:0:10 | 90 | 0 | 10 |
| 90:10:0 | 90 | 10 | 0 |
| 90:5:5 | 90 | 5 | 5 |
| 85:5:10 | 85 | 5 | 10 |
| 85:10:5 | 85 | 10 | 5 |
| 80:10:10 | 80 | 10 | 10 |

can completely disappear. The standard deviations given in some publications are in the range of 5–15% of the according property.

2. Materials and methods

Samples were prepared using the method of substrate with adjusted roughness; the roughness was hereby at $R_a = 2 \mu\text{m}$ and $R_z = 15 \mu\text{m}$. For a good adhesion of thermally sprayed coatings the substrate roughness should be one order of magnitude higher [59]. The thickness of the produced samples was adjusted to 0.5 mm. Seven different compositions were tested, sample composition and denomination are given in Table 2. All compositions were tested as sprayed and after heat treatment. The heat treatment with different time and temperature combinations is specified in Table 3. The treatment temperature of 1200 °C was chosen in a way that the phase change from γ - to α -Al₂O₃ should thermodynamically be completed, the different times of 10 and 100 h were chosen to evaluate the kinetics of this transformation in dependence of the composition. The highest treatment temperature of 1600 °C was taken from the maximum application temperature for pure alumina. In the style of a statistical experimental set up also the center point of this matrix was included as treatment stage. For heat treatment the samples were covered with coarse corundum. Bending strength, fracture strain and Young's modulus were calculated from 3-point-bending experiments. The rod production, spray parameters, raw materials and experimental set ups are described elsewhere [60–63].

3. Results and discussion

All data of mechanical properties are summarized in Table 4. Their discussion will follow in the next sections. Due to the non-elastic behavior the Young's moduli are given at relative strain levels of 0.2 and 0.8, the ratio of the two values indicate the degree of non-linearity. Additionally the later defined type or character of the instantaneous modulus was determined for

Table 3
Sample heat treatment.

| Temperature/time | 1200 °C | 1400 °C | 1600 °C |
|------------------|---------|---------|---------|
| 10 h | x | | x |
| 55 h | | x | |
| 100 h | x | | x |

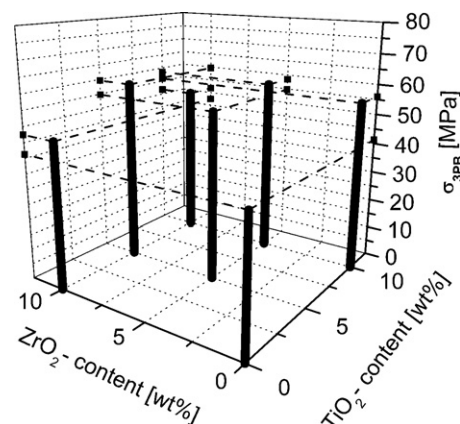


Fig. 1. Bending strength as sprayed.

every tested sample. There is no standard deviation given for the Young's moduli, their scatter lies in the range of $\pm 20\%$.

3.1. Bending strength and fracture strain

There is Ref. [57] presenting data about rod flame sprayed alumina and this value matches the current finding pretty well. Also the measured values of all other compositions lie in the range of the compiled mechanical properties and show a comparable standard deviation. Thus the presented method of preparing and testing thin free standing coatings is suitable for material characterization.

In the as sprayed state the bending strength (Fig. 1) increases starting from pure alumina with increasing amount of additions up to 15 wt% additions. This maximum in strength may correspond with the standard composition of the commercial available and widely used mixture Al₂O₃/13 wt% TiO₂. The fracture strain decreases with increasing amount of addition. Both tendencies can be explained with the increasing amount of amorphous content (see Ref. [63]) that leads to a better cohesion between both the lamellae and the columnar grown crystals within the lamellae with the secondary amorphous zones having higher influence on strength.

The heat treatment causes two different effects: sintering and growth of precipitated phases. The first process increases the bending strength and decreases the fracture strain remarkably.

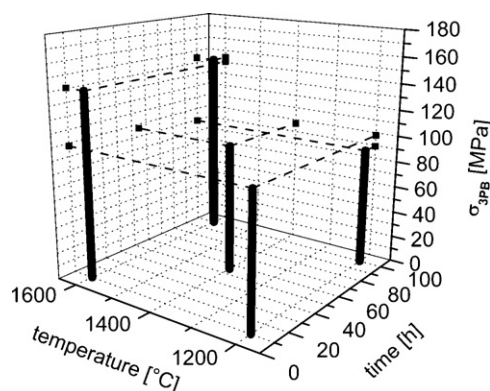


Fig. 2. Strength evolution of 100:0:0.

Table 4
Mechanical properties.

| Sample | Treatment | Bending strength σ [MPa] | Fracture strain ε [%] | Young's modulus | | Type of instantaneous modulus |
|----------|---------------|---------------------------------|-----------------------------------|-----------------|-----------------|-------------------------------|
| | | | | $E_{0.2}$ [GPa] | $E_{0.8}$ [GPa] | |
| 100:0:0 | as sprayed | 41.3 \pm 2.8 | 2.30 \pm 0.20 | 20 | 18 | 1–2 |
| | 10 h 1200 °C | 98.0 \pm 8.0 | 1.28 \pm 0.18 | 73 | 73 | 2 |
| | 100 h 1200 °C | 89.3 \pm 14.1 | 1.22 \pm 0.13 | 73 | 71 | 2 |
| | 55 h 1400 °C | 96.8 \pm 10.1 | 0.90 \pm 0.10 | 112 | 118 | 2–3 |
| | 10 h 1600 °C | 140.6 \pm 20.8 | 0.99 \pm 0.16 | 118 | 130 | 3 |
| | 100 h 1600 °C | 144.1 \pm 24.6 | 0.83 \pm 0.09 | 147 | 170 | 3 |
| 90:0:10 | as sprayed | 47.5 \pm 3.5 | 2.13 \pm 0.17 | 25 | 20 | 1 |
| | 10 h 1200 °C | 86.8 \pm 8.3 | 1.20 \pm 0.09 | 71 | 69 | 4 |
| | 100 h 1200 °C | 97.7 \pm 8.6 | 1.21 \pm 0.06 | 78 | 80 | 4 |
| | 55 h 1400 °C | 152.4 \pm 19.5 | 1.12 \pm 0.13 | 126 | 135 | 3 |
| | 10 h 1600 °C | 164.5 \pm 21.9 | 1.01 \pm 0.08 | 147 | 159 | 4 |
| | 100 h 1600 °C | – | – | – | – | – |
| 90:10:0 | as sprayed | 55.9 \pm 4.1 | 1.90 \pm 0.12 | 35 | 25 | 1 |
| | 10 h 1200 °C | 127.1 \pm 10.2 | 0.90 \pm 0.11 | 122 | 135 | 3 |
| | 100 h 1200 °C | 115.0 \pm 20.0 | 0.72 \pm 0.06 | 142 | 159 | 3 |
| | 55 h 1400 °C | 101.6 \pm 8.8 | 0.54 \pm 0.07 | 175 | 195 | 3 |
| | 10 h 1600 °C | 73.3 \pm 12.3 | 0.43 \pm 0.03 | 144 | 165 | 3 |
| | 100 h 1600 °C | 44.7 \pm 7.5 | 0.33 \pm 0.06 | 135 | 123 | 4 |
| 90:5:5 | as sprayed | 54.8 \pm 4.3 | 1.92 \pm 0.15 | 30 | 25 | 1 |
| | 10 h 1200 °C | 130.9 \pm 13.0 | 0.97 \pm 0.09 | 125 | 135 | 3 |
| | 100 h 1200 °C | 146.9 \pm 12.4 | 0.86 \pm 0.10 | 145 | 170 | 3 |
| | 55 h 1400 °C | 40.4 \pm 3.8 | 0.54 \pm 0.04 | 82 | 55 | 4 |
| | 10 h 1600 °C | 19.5 \pm 2.5 | 0.26 \pm 0.12 | 63 | 30 | 4 |
| | 100 h 1600 °C | – | – | – | – | – |
| 85:5:10 | as sprayed | 59.6 \pm 6.3 | 1.84 \pm 0.14 | 35 | 31 | 1 |
| | 10 h 1200 °C | 145.7 \pm 7.8 | 1.19 \pm 0.10 | 113 | 123 | 4 |
| | 100 h 1200 °C | 152.7 \pm 8.5 | 1.04 \pm 0.09 | 123 | 141 | 4 |
| | 55 h 1400 °C | 32.9 \pm 4.4 | 0.56 \pm 0.11 | 90 | 30 | 4 |
| | 10 h 1600 °C | – | – | – | – | – |
| | 100 h 1600 °C | – | – | – | – | – |
| 85:10:5 | as sprayed | 58.5 \pm 4.2 | 2.00 \pm 0.14 | 33 | 28 | 1 |
| | 10 h 1200 °C | 161.9 \pm 13.1 | 1.06 \pm 0.09 | 135 | 151 | 2–3 |
| | 100 h 1200 °C | 145.9 \pm 12.2 | 0.82 \pm 0.06 | 150 | 172 | 3 |
| | 55 h 1400 °C | 19.0 \pm 1.1 | 1.37 \pm 0.27 | 26 | 6 | 4 |
| | 10 h 1600 °C | 56.4 \pm 4.5 | 0.41 \pm 0.06 | 105 | 125 | 4 |
| | 100 h 1600 °C | 48.4 \pm 6.1 | 0.36 \pm 0.08 | 135 | 122 | 4 |
| 80:10:10 | as sprayed | 51.7 \pm 3.5 | 1.80 \pm 0.18 | 30 | 25 | 1 |
| | 10 h 1200 °C | 140.7 \pm 9.6 | 1.06 \pm 0.11 | 120 | 130 | 3 |
| | 100 h 1200 °C | 145.9 \pm 16.4 | 0.82 \pm 0.09 | 152 | 175 | 4 |
| | 55 h 1400 °C | 17.4 \pm 1.6 | 1.20 \pm 0.46 | 23 | 6 | 4 |
| | 10 h 1600 °C | – | – | – | – | – |
| | 100 h 1600 °C | – | – | – | – | – |

The sintering activity that depends on the diffusion of the different atomic species determines the velocity of this process. The Ti^{4+} is much more mobile than Al^{3+} or Zr^{4+} , thus in titania containing composites the sintering effects start to change the mechanical properties much faster and at lower temperatures (Figs. 2–4). Surface diffusion is the important mechanism that determines the change of properties during heat treatment [64]. The second process of precipitating phases like tetragonal or monoclinic zirconia or zirconiumtitanate has a more complex influence on the mechanical properties. This can be best seen by comparing the compositions 100:0:0 with 90:0:10. Fig. 5 shows the measured bending strength as a function of the content of monoclinic zirconia for 90:0:10. The values of pure alumina at identical heat treatment level are added to separate this effect from the influence of the sintering process. From a certain

monoclinic content there is a strong increase in bending strength due to particle and/or micro crack and/or transformation toughening mechanisms. If the monoclinic content becomes too high, the strength is decreased to zero. A similar effect causes the drop in strength in the ternary compositions. The velocity of this transformation is strongly increased by the presence of titania and some of the zirconia is bound in the form of zirconiumtitanate that lessens the detrimental effect of transformation into monoclinic zirconia.

3.2. Young's modulus

The Young's modulus in general follows the trend of the bending strength in the as sprayed as well as in the heat treated samples. Nonetheless it shows a non-linear behavior so that the

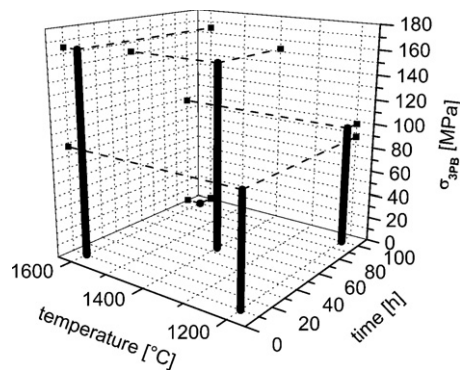


Fig. 3. Strength evolution of 90:0:10.

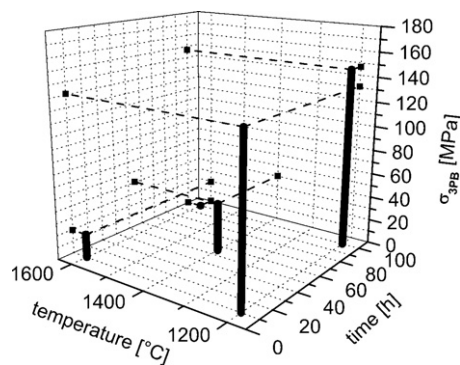


Fig. 4. Strength evolution of 90:5:5.

definition of a single number seems not appropriate. Thus the instantaneous modulus of the samples is displayed and discussed. For this the mathematical derivation of the stress–strain curve for each single measurement was calculated, the fracture strain standardized to equal 1 and then all curves were averaged. The values given in Table 4 for the Young's moduli are taken from this averaged curves; to indicate the non-linearity the value at 0.2 and 0.8 relative strain are shown. By looking at the individual instantaneous moduli four basic types can be distinct. Type one shows a more or less strong constant decrease and is representative for the as sprayed state. Two examples are shown in Figs. 6 and 7 representing the minimum (100:0:0) and the maximum (90:10:0) decrease of all tested

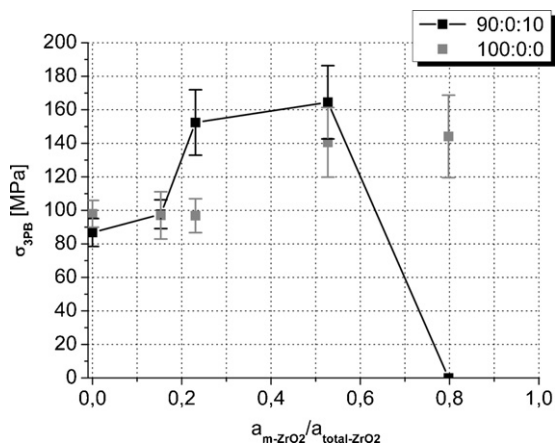


Fig. 5. Strength as a function of monoclinic zirconia content.

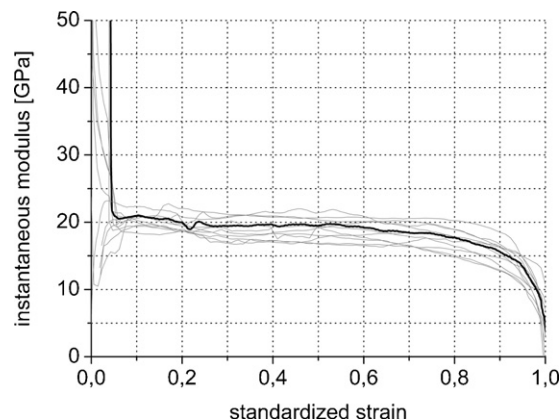


Fig. 6. Instantaneous modulus of 100:0:0 as sprayed (type 1).

compositions. After the first heat treatment stage this constant decrease changes into a plateau-like (type 2, Fig. 8) or constantly increasing type (type 3, Fig. 9). With longer temperature exposure a curved shape with a maximum develops (type 4, Fig. 10). In contrast to type 1–3 there is no such abrupt drop in the vicinity to a strain of 1. In general the decrease can be explained with growth of cracks leading to a softening of the sample. The increase might be explained with crack closure and increasing interlocking of the micro structural features. In type 4 this two mechanisms appear after each other leading to the maximum in the curve. The difference between the composi-

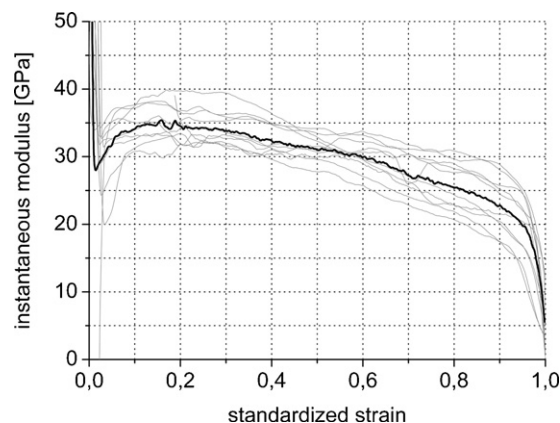


Fig. 7. Instantaneous modulus of 90:10:0 as sprayed (type 1).

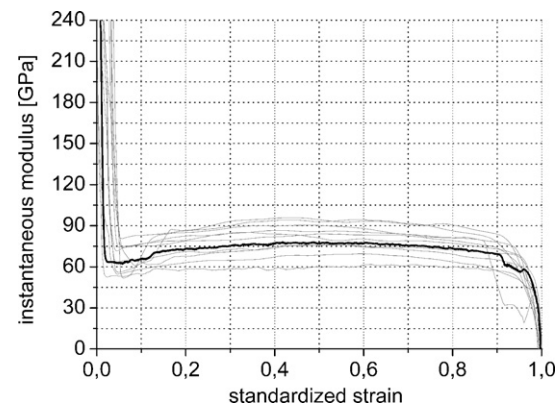


Fig. 8. Instantaneous modulus of 100:0:0 10 h 1200 °C (type 2).

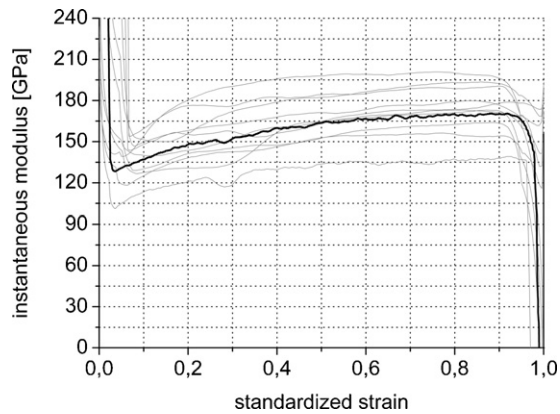


Fig. 9. Instantaneous modulus of 100:0:0 100 h 1600 °C (type 3).

tions lie in the speed they arrive at type 4. 90:0:10 and 85:5:10 reach type 4 already after the first treatment stage, 100:0:0 does not show type 4 behavior. A behavior similar to the here defined type 4 was observed by the authors of Ref. [65] in the as sprayed state and attributed to increasing splat interlocking followed by crack initiation during the experiment.

3.3. Thermal shock performance

To the best of the authors knowledge there are no published attempts of testing very thin free standing specimens in thermal shock experiments. That kind of test setup seems pointless at first view. At second view, by taking the width of the specimen and the applied method of water quenching into account it becomes clear, why significant changes in strength at certain temperature difference can occur. When the hot sample dips into the water, the part of the sample having contact with water cools down and shrinks. This causes stress in the sample. The already cooled part of the sample is under tensile, the neighboring hot part under compressive stress. This wave of tensile followed by compressive stress goes through the whole sample parallel to the immersion process. The magnitude of the strain is determined by the length of the isothermes, in case of vertical immersion this length is equal to the width of the sample. The thermal inertia is hereby very low due to very low total sample volume first reducing boiling effects and second guaranteeing immediate

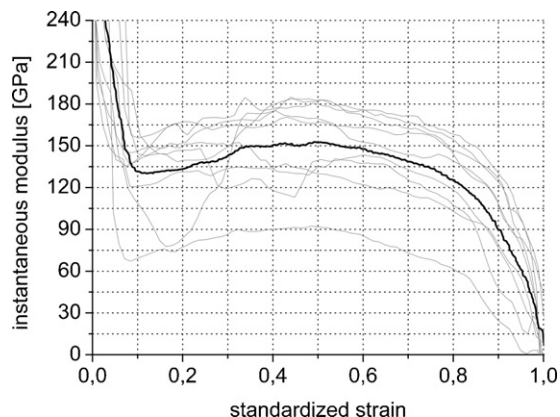


Fig. 10. Instantaneous modulus of 85:10:5 100 h 1600 °C (type 4).

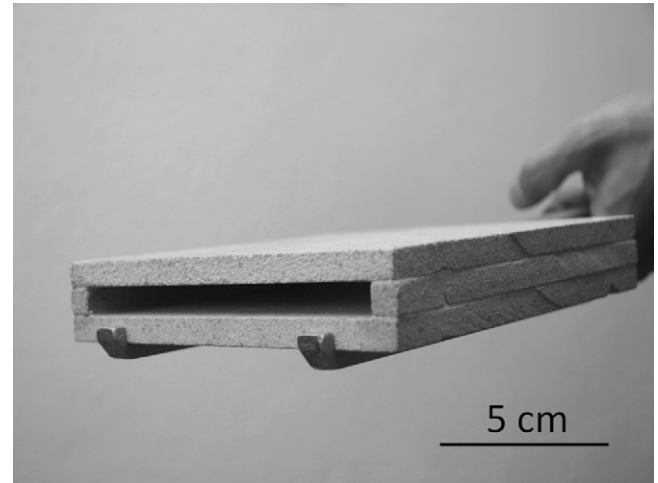


Fig. 11. Removable muffle.

temperature equalization between the sample and the cooling medium. The strain status can be assumed as planar. Four compositions were chosen for thermal shock experiments. To minimize sintering and phase change effects during heating up the samples in the thermal shock experiments all samples were previously annealed for 10 h at 1200 °C. 600 and 1000 K were chosen as ΔT for thermal shock. To minimize heat loss by radiation between removing the samples from the furnace and their contact with water a removable muffle (Fig. 11) was used. The muffle also guarantees a vertical immersion of the samples. There is significant loss in strength (Fig. 12) for samples shocked with $\Delta T = 600$ K except for 90:0:10. The higher starting strength level of 90:10:0 and 90:5:5 is caused by the increased sintering by the presence of titania. Compared to pure alumina the addition of only titania is detrimental and the addition of zirconia or zirconia plus titania beneficial for the remaining strength. After a shock with $\Delta T = 1000$ all compositions resemble at a low strength value between 10 and 15 MPa. This remaining strength might represent the contribution of the interlocking and pull-out mechanism to the complex strength in thermally sprayed materials. There seems no correlation between the type of instantaneous moduli and the loss of strength in the here tested compositions and treatment levels.

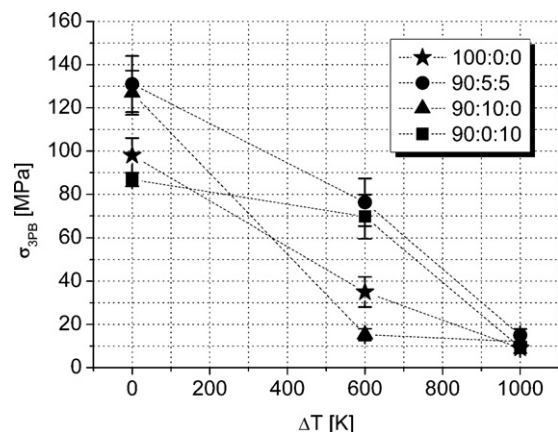


Fig. 12. Thermal shock behavior.

4. Conclusion

The here presented method of sample preparation and testing thin freestanding stripes leads to results that are comparable with published values in terms of absolute value and standard deviation. In the as sprayed state the addition of titania and zirconia to alumina increases the strength until a addition level of 15 wt%. After heat treatment the sintering causes strong increase in strength. The precipitation of second phases can influence the strength in both directions. For zirconia containing mixtures there is a critical value of the amount of monoclinic zirconia that leads to a complete loss in cohesion. The Young's moduli show distinct non-linear behavior. The increase is attributed to micro crack closure and increasing interlocking of the micro structural features and the decrease is caused by crack growth and crack recombination. It is possible to gain useful results from thermo shock experiments with thin specimens. The amount of stress is hereby determined by the width of the sample. The thermal shock resistance of thermally sprayed and annealed pure alumina is decreased by titania and increased by zirconia or zirconia plus titania additions.

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