

Short communication

Relaxation kinetics of the intrinsic compressive stress in powder aerosol deposited titania films during thermal treatment

Daniel Paulus^{*} , Kimiya Etemadieh, Ralf Moos

Department of Functional Materials, Universitätsstraße 30, Bayreuth, 95440, Germany

ARTICLE INFO

Keywords:

Aerosol deposition method
Intrinsic compressive stress
Stress relaxation
Titanium oxide

ABSTRACT

This study investigated the relaxation of intrinsic compressive stress in powder aerosol deposited films. For this purpose, titanium oxide (TiO₂) was deposited on thin YSZ substrates, and it was investigated how the stress declines with time at 150 °C and 200 °C. Based on the relaxation curves, two different processes were identified, one of which dominates at high stresses. For the high-stress-dominating process an activation energy of 0.22 eV was determined. For the other process, it was determined to be 0.11 eV. The relaxation itself was attributed by Coble creep and grain boundary sliding.

1. Introduction

The Powder Aerosol Deposition Method (PAD or ADM) is a coating process that enables the direct deposition of ceramic films. Kashu et al. were the first to report on this process [1]. Akedo later took up the method, improved it, and was the first to propose a theory on how the deposition mechanism works [2–5].

The process generally works as follows: particles are accelerated as a dry aerosol by a carrier gas through a nozzle into a vacuum chamber. There, they impact on a substrate at high speed, fragment and form a dense ceramic film on the substrate surface. Akedo described this as Room Temperature Impact Consolidation (RTIC) [4,5]. Following particles densify the previous deposited film by further impacts. Akedo called this “hammering effect”.

However, the deposition mechanism has not yet been fully understood. Akedo's theory can explain only partly why the deposition efficiency is mostly low. Linz et al. [6] used core-shell particles to show that only the outer part of the particle that comes into direct contact with the substrate is preferentially or even exclusively deposited.

These previous theories explain and clarify many film properties, such as nanocrystallinity or high intrinsic microstrain of the films after deposition. However, they cannot explain the intrinsic compressive stress that occurs in the films. This is a compressive stress in the range of 300 MPa to 3 GPa that occurs intrinsically in the films [7–10]. Please note that compressive stress should not be confused with microstrain. This intrinsic compressive stress is largely responsible for the high hardness of the films [11]. It changes slightly over the course of the film

thickness [8]. Schubert et al. [9] demonstrated that the intrinsic compressive stress depends on the carrier gas or carrier gas mixture used.

In a previous study, the authors showed that this intrinsic compressive stress relaxes almost completely after heat treatment at just a few hundred degrees Celsius [10]. This distinguishes it from the microstrain that also occurs in the films [12], which describes stress fields that arise due to defects in the crystal. In another previous study, the authors proposed the theory that intrinsic compressive stress arises during the deposition process when particles “dig” into the surface like wedges, thereby generating compressive stress. Furthermore, it was shown that intrinsic compressive stresses do not occur in materials with a special layered crystal structure [13].

The authors postulate that the relaxation of intrinsic compressive stress at such low temperatures is attributed to diffusion creep, facilitated by a high volume fraction of grain boundaries within the material. Consequently, owing to the diminutive crystallite size of approximately 15 nm, the mechanical behavior of the film material exhibits a greater resemblance to that of a nanomaterial compared to a conventional ceramic [10]. Nevertheless, the comprehensive understanding of stress relaxation remains incomplete, necessitating the development of a kinetic model. This objective will be pursued within this study.

^{*} Corresponding author.

E-mail address: functional.materials@uni-bayreuth.de (D. Paulus).

<https://doi.org/10.1016/j.ceramint.2026.07.115>

Received 23 March 2026; Received in revised form 19 June 2026; Accepted 7 July 2026

Available online 10 July 2026

0272-8842/© 2026 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

2. Material and methods

2.1. Film deposition and heat treatment

The films were deposited using a custom-built PAD device. Titania was used as film material (99.5% rutile phase, Alfa Aesar, Haverhill, MA, USA, particle size 1.0–2.0 μm). 3YSZ ceramic foils (Kerafol Keramische Folien GmbH & Co. KG, Eschenbach i. d. Opf.) with a thickness of 90 μm served as the substrate, which were previously laser-cut to a size of 10 mm $\times$ 2.5 mm. To deposit the titania, a convergent slit nozzle (with a nozzle opening of 20 mm $\times$ 0.5 mm) was utilized, with oxygen serving as carrier gas at a flow rate of 30 sl/min. The film thickness of the deposited films falls within the range of 2–5 μm .

The films were thermally post-treated in a muffle furnace (Nabertherm, Lilienthal, Germany) for a duration ranging from 15 min to 48 h at temperatures of 150 °C or 200 °C, with an additional heating phase at a rate of 5 K/min. Three samples were prepared for each heat treatment duration.

2.2. Intrinsic compressive stress determination

The intrinsic compressive film stress was determined using the curvature of the thin coated substrates. The curvature was determined with a Perthometer (Jenoptik Waveline 20) and then approximated using a second-degree polynomial. The curvature of the polynomial was used as the substrate curvature. The film stress was then determined using the Stoney equation [14] extended by Mézin [15]. Further details on the determination of curvature and film stress can be found in Ref. [10]. This method was also verified in a previous study [13]. Here the intrinsic compressive stress in these films was determined by measuring the change of the lattice parameter by synchrotron x-ray diffraction in transmission geometries.

3. Results

The stress values determined in the films after heat treatment at 150 °C and 200 °C are shown in Fig. 1. In the untreated state, the intrinsic compressive film stress is 1200 MPa. After heat treatment at 150 °C, the intrinsic compressive stress reaches a value of less than 100 MPa after 10 h. After heat treatment at 200 °C, such values are already reached after heat treatment over 3 h. This is consistent with the hypothesis from our previous study [10] that the relaxation of intrinsic compressive stress is a thermally activated process.

Based on the shape of the intrinsic compressive stress decrease over the dwell time, it can be assumed that this relaxation follows an exponential decrease according to equation (1)

$$\sigma \propto e^{-\frac{t}{\tau}} \quad (1)$$

where σ corresponds to the stress, t to the elapsed time, and τ to the proper time. Since we know the initial value, the stress before heat treatment, we can introduce it as σ_0 and use it as a proportionality factor:

$$\sigma(t) = \sigma_0 \cdot e^{-\frac{t}{\tau}} \quad (2)$$

Equation (2) can be rewritten as:

$$\ln(\sigma(t)) = \ln(\sigma_0) - \frac{1}{\tau} \cdot t \quad (3)$$

The equation now has the form of a linear equation. For the time range in which relaxation takes place, we could now plot the logarithm of $\sigma(t)$ over t . The slope can be used to determine τ . This is shown in Fig. 2. We obtain different values for τ for relaxation at different temperatures, because τ is usually temperature-dependent in thermally activated processes. In addition, it is striking that two relaxation processes exist during the heat treatment, rather than one effect that ends in a steady state. One of these processes dominates at high stresses and gets

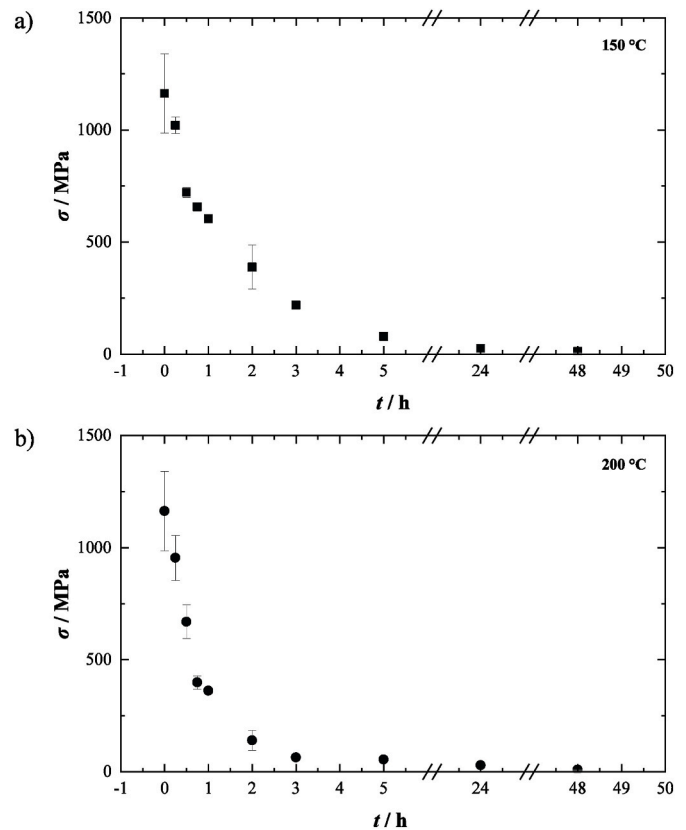


Fig. 1. Plot of the absolute value of the intrinsic compressive stress calculated according to Mézin [15] (according to convention, the compressive stress would be negative) over the heat treatment time for temperatures of 150 °C (a) and 200 °C (b).

negligible at low stresses.

This provides us with a total of four straight line slopes. These slopes enable us to determine the proper times τ for two distinct regimes and two distinct temperatures in each case. The proper times τ calculated from the reciprocal slopes and the initial stresses $\sigma_{0,i}$ derived from the intercept are summarized in Table 1.

This gives us the proper times as kinetic parameters of the processes. In addition, the intercept provides the initial stresses, which, when added together, match very well with the stresses present in the layer prior to heat treatment. This supports this model. Two temperatures do not allow us to calculate precise values, but we can estimate roughly orders of magnitude. To do this, we assume that $\tau(T)$ exhibits an Arrhenius behavior:

$$\tau(T) = \tau_0 \cdot \exp\left(\frac{E_A}{RT}\right) \quad (4)$$

This equation can also be transformed so that it follows a linear law:

$$\ln(\tau(T)) = \ln(\tau_0) + \frac{E_A}{R} \cdot \frac{1}{T} \quad (5)$$

By plotting the values according to (5), we obtain a graph as shown in Fig. 3. We can estimate the activation energy E_A from the slope of the straight lines. The intersections with the y-axis give us the logarithmic elementary time scale $\ln(\tau_0)$.

The characteristic values determined from this Arrhenius plot, as well as the activation energy E_A and τ_0 estimated from them, are listed in Table 2.

The estimated value, with an activation energy of 20.8 kJ/mol for relaxation at high stresses, is entirely reasonable. For the second process at low stress, the activation energy is about half as high and the proper

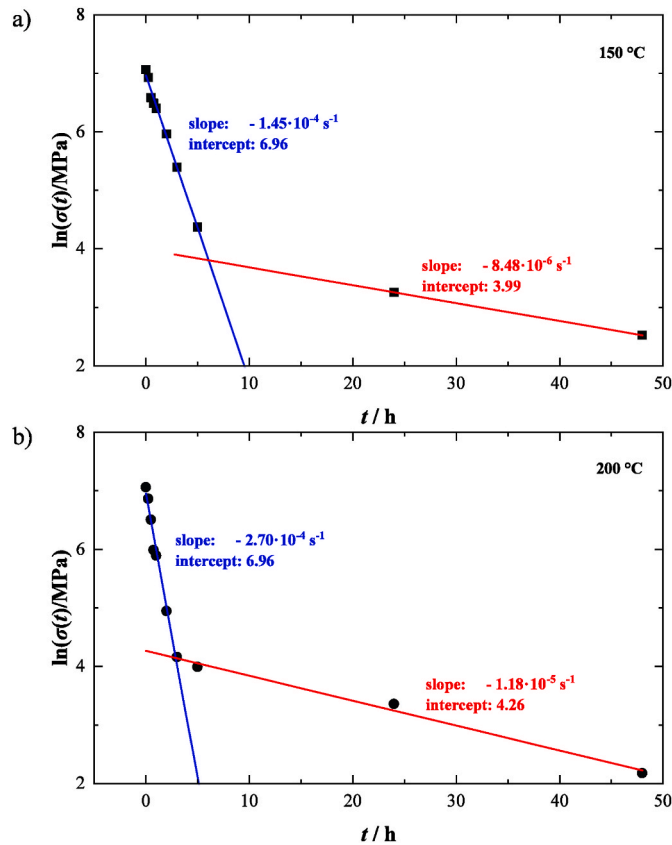


Fig. 2. Plot of the logarithmic stress after time t over the heat treatment time t for temperatures of 150 °C (a) and 200 °C (b). Linear fits assuming (acc. to (3)) of two relaxation processes are added in both diagrams.

Table 1

Linear slopes and proper times derived from them for the relaxation of the films at 150 °C and 200 °C.

Temperature	τ_1/s	$\tau_2/10^4 s$	$\sigma_{0,1}/\text{MPa}$	$\sigma_{0,2}/\text{MPa}$
150 °C	6904	11.8	1056	54
200 °C	3698	8.5	1051	71

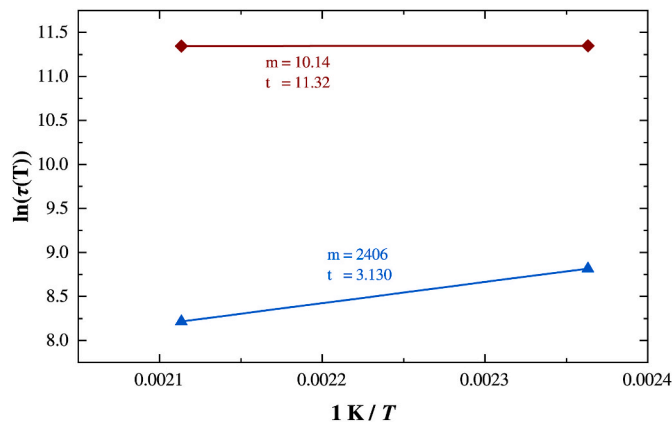


Fig. 3. Plot of the logarithmic temperature-dependent proper times $\ln(\tau(T))$ for the process at high stresses (blue squares) and the low stress range (red squares) over the reciprocal absolute temperature $1/T$. In addition, a connecting straight line with slope and y-intercept is plotted. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Activation energy E_A and the pre-exponential factor τ_0 for both relaxation processes.

	Activation energy $E_A/\text{kJ/mol}$	Activation energy E_A/eV	Elementary time scale τ_0/s
High stress process	20.8	0.22	18.8
Low stress process	11.1	0.11	5058

time is much longer. It therefore proceeds much more slowly. The activation energies, equivalent to 0.2 eV and 0.1 eV, respectively, can be attributed to diffusion processes based on their values [16].

In order to develop a better understanding of the prevailing relaxation process, it makes sense to try to identify the mechanism more precisely. From the previous study [10], we adopt the idea that this could be a creep process. We therefore apply Norton's creep law [17]:

$$\dot{\epsilon} \propto \sigma^n \quad (6)$$

Where $\dot{\epsilon}$ is the strain rate, σ the applied stress and n the stress exponent. Assuming that all stresses behave linearly elastically, we can also apply Hooke's law:

$$\sigma \propto \epsilon \quad (7)$$

By forming the time derivative, (7) can be substituted into (6) and we obtain:

$$\dot{\sigma} \propto \sigma^n \quad (8)$$

If we take the logarithms on both sides, we obtain:

$$\ln(\dot{\sigma}) \propto n \cdot \ln(\sigma) \quad (9)$$

The stress exponent n can therefore be obtained by plotting the time derivative of the stress against the stress itself. The stress exponent corresponds to the slope of the linear fit. This is shown in Fig. 4 for the test series at both temperatures in the high stress regime.

For both temperatures, the obtained stress exponent n obtained is approximately 1. For the relaxation process, this results in an overall picture of two processes with activation energies of 20.8 kJ/mol and 11.1 kJ/mol, respectively, and a stress exponent n of 1. In addition, this must be a mechanism that can take place at such low temperatures due to nanocrystallinity. At this point, it should be noted that relaxation took place at 200 °C at a homologous temperature of just 0.22. At 150 °C, the homologous temperature was only 0.2.

4. Discussion

In our previous study [10], we presented various possibilities for how stress relaxation can occur. One of the theories was that increasing the temperature lowers the yield strength of the material, thereby enabling plastic deformation. The stress then decreases until it reaches the yield strength value at the respective temperature. The other theory was that it is a creep process that causes the stress to relax. The results of this study clearly show that it is the latter.

The stress exponent n , which was determined to be 1, indicates a diffusion-driven or at least diffusion-controlled process. Higher stress exponents would indicate a process involving significant grain deformation, for example due to dislocation movements such as dislocation climbing [18]. However, such processes could also be ruled out due to the small crystallite size, which offers very little to no space for dislocations in the crystal and thus only limited freedom of movement. Furthermore, at such low temperatures, diffusion in the crystal itself is so greatly reduced that hardly any diffusion through the crystal lattice should be expected.

Therefore, diffusion creep, or rather Coble creep, which involves diffusion along grain boundaries, and grain boundary sliding are

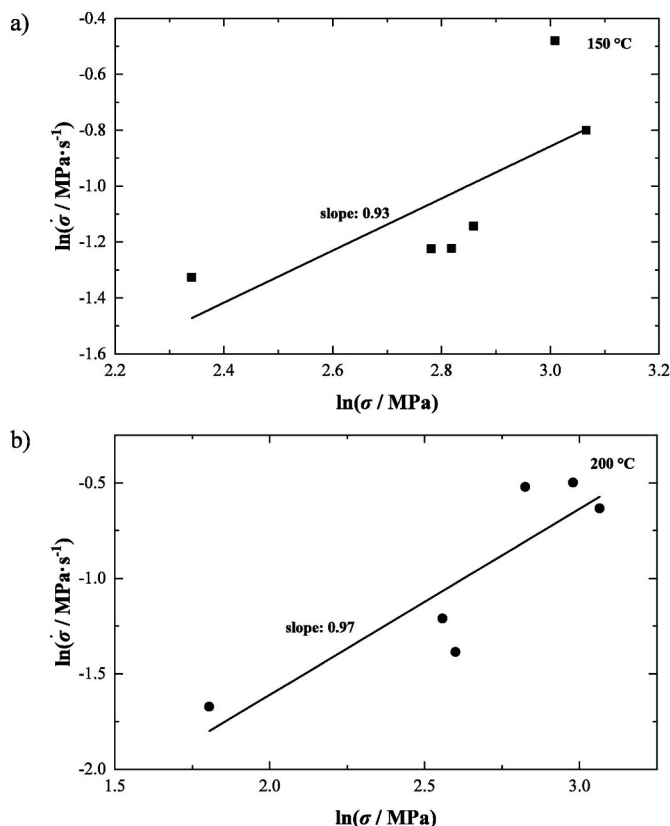


Fig. 4. Logarithmic representation of the time derivative of the intrinsic compressive stress versus the intrinsic compressive stress for heat treatment at 150 °C (a) and 200 °C (b). A linear fit is also plotted to derive the stress exponent.

probably the only possibilities, even though the latter is often associated with a stress exponent n of 2. Information about this could be provided by the activation energy of 20.8 kJ/mol. Diffusion creep usually requires a relatively high activation energy of several hundred kJ/mol [19]. However, the extremely small crystallite size of approx. 20 nm [13] and the resulting high proportion of grain boundary volume could reduce this enormously [20]. Furthermore, Hirthe et al. [19] were able to show that the activation energy for non-stoichiometric (reduced) titanium oxide is significantly lower.

We are aware that the activation energy values are about one decade lower than typical values for ceramics. This may justifiably be viewed as controversial. However, a careful analysis of the data has yielded these values. When considering these values in a controversial light, it should also be noted that the relaxation of the intrinsic film stress can be observed with the naked eye by straightening a bent substrate after heat treatment at 150 °C, a temperature at which, according to the classical understanding of ceramics, no deformation or relaxation should occur. The cause of this must therefore deviate from the standard measurable in classical ceramics.

The low temperature, combined with the small crystallite size, makes it most likely that a mixture of grain boundary sliding and grain adjustment through diffusion, as described by Lifshiz [21], occurs. Māaza et al. [22] have already shown that such low activation energies can occur in some diffusion processes. We therefore interpret the values derived here as two parallel creep processes with different thermal activation.

In the end, the data allow only for speculation as to what kinds of mechanisms are at work in the material. Even though a stress exponent of 1 does not fit classical observations of grain-boundary sliding, we nevertheless suspect this process taking place, as it is the most likely one

for a nanomaterial. In any case, further investigations are necessary to conclusively clarify the processes at work.

Finally, the question arises as to whether these findings can be generalized to other material systems. If our hypothesis is correct that stress relaxation occurs through diffusion creep in combination with grain boundary sliding, then this behavior should be applicable to most PAD films made of ceramic materials that form a microstructure with crystallite sizes in the range of 15 nm. As the melting temperature of the ceramic increases, the relaxation should proceed more slowly, as demonstrated by the sole addition of high-melting-point MgO in a previous study [10]. This behavior is not applicable to PAD films made of layered crystal structures, since these form a different microstructure during deposition, that is microcrystalline rather than nanocrystalline. Apart from that, this class of materials does not generate particularly high film stress within the material [13].

5. Summary

In this study, relaxation experiments were performed at different temperatures on TiO₂ films produced by powder aerosol deposition (PAD) that exhibit intrinsic compressive stress. It was shown that two different processes occur during relaxation, one with an activation energy of approximately 21 kJ/mol at high stresses and one at low stresses with an activation energy of approximately 11 kJ/mol. The stress exponent n was determined to be approximately 1 in both cases. The relaxation at low temperatures was attributed to Coble creep and grain boundary sliding.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used DeepL Translator and Apple writing tools in order to translate the manuscript from German to English and improve the language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

CRediT authorship contribution statement

Daniel Paulus: Conceptualization, Formal analysis, Investigation, Project administration, Supervision, Visualization, Writing – original draft. **Kimiya Etemadieh:** Formal analysis, Investigation, Methodology. **Ralf Moos:** Formal analysis, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank Dr.-Ing. Jaroslaw Kita for cutting the samples using a laser. The authors would also like to thank Kerafol Keramische Folien GmbH & Co. KG for providing the substrates.

References

- [1] S. Kashu, E. Fuchita, T. Manabe, C. Hayashi, Deposition of ultra fine particles using a gas jet, *Jpn. J. Appl. Phys.* 23 (1984) L910–L912, <https://doi.org/10.1143/JJAP.23.L910>.
- [2] J. Akeo, M. Ichiki, K. Kikuchi, R. Maeda, Jet molding system for realization of three-dimensional micro-structures, *Sensor Actuator Phys.* 69 (1998) 106–112, [https://doi.org/10.1016/S0924-4247\(98\)00059-4](https://doi.org/10.1016/S0924-4247(98)00059-4).
- [3] J. Akeo, Aerosol deposition of ceramic thick films at room temperature: densification mechanism of ceramic layers, *J. Am. Ceram. Soc.* 89 (2006) 1834–1839, <https://doi.org/10.1111/j.1551-2916.2006.01030.x>.

- [4] J. Akedo, Room temperature impact consolidation (RTIC) of fine ceramic powder by aerosol deposition method and applications to microdevices, *J. Therm. Spray Tech.* 17 (2008) 181–198, <https://doi.org/10.1007/s11666-008-9163-7>.
- [5] J. Akedo, Room temperature impact consolidation and application to ceramic coatings: aerosol deposition method, *J. Ceram. Soc. Jpn.* 128 (2020) 101–116, <https://doi.org/10.2109/jcersj2.19196>.
- [6] M. Linz, F. Bühner, D. Paulus, L. Hennerici, Y. Guo, V. Mereacre, U. Mansfeld, M. Seipenbusch, J. Kita, R. Moos, Revealing the deposition mechanism of the powder aerosol deposition method using ceramic oxide core-shell particles, *Adv. Mater.* (2023) e2308294, <https://doi.org/10.1002/adma.202308294>.
- [7] J. Adamczyk, P. Fuierer, Compressive stress in nano-crystalline titanium dioxide films by aerosol deposition, *Surf. Coating. Technol.* 350 (2018) 542–549, <https://doi.org/10.1016/j.surfcoat.2018.07.015>.
- [8] N.H. Khansur, U. Eckstein, K. Riess, A. Martin, J. Drnec, U. Deisinger, K.G. Webber, Synchrotron x-ray microdiffraction study of residual stresses in BaTiO₃ films deposited at room temperature by aerosol deposition, *Scr. Mater.* 157 (2018) 86–89, <https://doi.org/10.1016/j.scriptamat.2018.07.045>.
- [9] M. Schubert, J. Exner, R. Moos, Influence of carrier gas composition on the stress of Al₂O₃ coatings prepared by the aerosol deposition method, *Materials* 7 (2014) 5633–5642, <https://doi.org/10.3390/ma7085633>.
- [10] D. Paulus, J. Kita, R. Moos, Relaxation behavior of intrinsic compressive stress in powder aerosol co-deposited films: rethinking PAD films as nanomaterials, *Ceram. Int.* 49 (2023) 38375–38381, <https://doi.org/10.1016/j.ceramint.2023.09.065>.
- [11] F. Zhuo, U.R. Eckstein, N.H. Khansur, C. Dietz, D. Urushihara, T. Asaka, K. Kakimoto, K.G. Webber, X. Fang, J. Rödel, Temperature-induced changes of the electrical and mechanical properties of aerosol-deposited BaTiO₃ thick films for energy storage applications, *J. Am. Ceram. Soc.* 105 (2022) 4108–4121, <https://doi.org/10.1111/jace.18377>.
- [12] J. Exner, T. Nazarens, D. Hanft, J. Kita, R. Moos, What happens during thermal post-treatment of powder aerosol deposited functional ceramic films? Explanations based on an experiment-enhanced literature survey, *Adv. Mater.* 32 (2020) 1908104, <https://doi.org/10.1002/adma.201908104>.
- [13] D. Paulus, M. Linz, A.-L. Hansen, S. van Smaalen, R. Moos, A.S. Ulrich, D. Schönauer-Kamin, Structure matters: a synchrotron study reveals how crystallite structure influences the deposition mechanism for the powder aerosol deposition method, *J. Eur. Ceram. Soc.* 46 (2026) 118127, <https://doi.org/10.1016/j.jeurceramsoc.2026.118127>.
- [14] G.G. Stoney, The tension of metallic films deposited by electrolysis, *SAVE Proc.* 82 (1909) 172–175, <https://doi.org/10.1098/rspa.1909.0021>.
- [15] A. Mézin, Coating internal stress measurement through the curvature method: a geometry-based criterion delimiting the relevance of Stoney's formula, *Surf. Coating. Technol.* 200 (2006) 5259–5267, <https://doi.org/10.1016/j.surfcoat.2005.06.018>.
- [16] B.P. Uberuaga, X.-M. Bai, Defects in rutile and anatase polymorphs of TiO₂: kinetics and thermodynamics near grain boundaries, *J. Phys. Condens. Matter* 23 (2011) 435004, <https://doi.org/10.1088/0953-8984/23/43/435004>.
- [17] F.H. Norton, *The Creep of Steel at High Temperatures*, first ed., McGraw-Hill Book Company, New York, 1929.
- [18] T.G. Langdon, Grain boundary sliding revisited: developments in sliding over four decades, *J. Mater. Sci.* 41 (2006) 597–609, <https://doi.org/10.1007/s10853-006-6476-0>.
- [19] W.M. Hirthe, J.O. Brittain, High-temperature steady-state creep in rutile, *J. Am. Ceram. Soc.* 46 (1963) 411–417, <https://doi.org/10.1111/j.1151-2916.1963.tb11767.x>.
- [20] V. Gray, M. Whittaker, A discussion of non-constant creep activation energy, *J. Mater. Sci. Eng.* 6 (2017), <https://doi.org/10.4172/2169-0022.1000372>.
- [21] M. Lifshitz, On the theory of diffusion-viscous flow of polycrystalline bodies, *Soviet Phys. JETP* 14 (1963).
- [22] M. Mäaza, C. Sella, J.P. Ambroise, M. Kāabouchi, M. Milôche, F. Wehling, M. Groos, Determination of diffusion coefficient D and activation energy Q_a of nickel into titanium in Ni–Ti multilayers by grazing-angle neutron reflectometry, *J. Appl. Cryst.* 26 (1993) 334–342, <https://doi.org/10.1107/S0021889892010355>.