Abschlussbericht DFG-Schu 729/16-2 (2009)

1. Allgemeine Angaben

1.1	DFG-Geschäftszeichen	Schu 729/16-2
1.2	Antragsteller	Prof. Dr.-Ing. Michael Schütze
1.3	Institut/Lehrstuhl	DECHEMA e.V. Karl-Winnacker-Institut Theodor-Heuss-Allee 25 D-60486 Frankfurt am Main
1.4	Aus DFG-Mitteln bezahlte wissenschaftliche Mitarbeiter/innen mit Angabe des Beschäftigungszeitraums	Dr. D. Renusch 01.09.2007 – 31.12.2008 Dr. M. Rudolphi 01.02.2009 – 31.03.2009
1.5	Thema des Projekts	The Role of Interacting Failure Mechanisms for APS-TBC Life Time
1.6	Berichtszeitraum Förderzeitraum insgesamt	01.05.2006 - 31.03.2009 01.05.2005 - 31.03.2009
1.7	Fachgebiet, Arbeitsrichtung	Werkstoffwissenschaften, Hochtemperaturkorrosion
1.8	Verwertungsfelder	Stationäre Gasturbinen, Flugtriebwerke, Dieselmotoren, generell für alle Fälle mit keramischen Schichten auf metallischen Substraten
1.9	Am Projekt beteiligte Kooperationspartner	Begleitung der Arbeiten durch Siemens Powergen, Mülheim, Alstom, Baden/CH, Rolls Royce Deutschland, Dahlewitz, MTU München, DLR Köln, FZ Jülich

Anm: Der Bericht ist in Englisch abgefaßt, da der wissenschaftliche Bearbeiter Dr. Renusch US-amerikanischer Staatsbürger ist und seine Deutschkenntnisse für die Berichterstellung noch nicht ausreichend wären.

2 Zusammenfassung

2.1 Darstellung der wesentlichen Ergebnisse und Ausblick
(Summary of the Results and outlook)

To ensure a sufficient service life time at continuous and cyclic operating temperatures the land based gas turbine and aero engines components utilize the combined advantages of both metallic and ceramic materials by applying a ceramic thermal barrier coating (TBC) of yttria stabilised zirconia (YSZ) on top of the vacuum (or low pressure) plasma sprayed protective bond coat (BC), which protects the underlying substrate material from oxidative attack. There is still a demand for reliable life time prediction models for TBC coating, that can ensure conditions and operations of 25000hr. This project has made substantial progress to meeting these demands.

Life time prediction models of high reliability and accuracy require a detailed understanding of the degradation/spallation mechanisms and measured data that probes mechanistic issues. Most of the life time models found in the literature consider that top coat spallation is caused by only one "mechanical" failure mechanism /1-6/. The approach developed in this project has divided spallation life time of the atmospheric plasma sprayed thermal barrier coating (APS-TBC) into three cases namely: Case 1 thermal fatigue failure, Case 2 thermal ageing failure and Case 3 Al depletion failure /7-9/. This classification produces a conceptual framework that separates "mechanical" and "chemical" spallation mechanisms, which can in turn be modeled separately when the appropriate measurement data is available.

To a large extent this project has achieved its aims. This was a particular challenge because the project plan in the grant proposal was for a 24 month project, however, the DFG reduced the duration to 18 months.

The modeling equations have undergone major improvements. The mechanisms for the "mechanical" spallation cases, namely Case 1 "thermal fatigue failure" and Case 2 "thermal ageing failure", are now described by one equation. Prior to this project two mechanistic equations were required to describe the spallation due to thermal fatigue and thermal ageing. This produces the following benefits:

1. The life time model has become less complicated (only for case 1 and 2).
2. The number of parameters is reduced.
3. The amount of measurement data required to make an accurate prediction is reduced.

The mechanism for the "chemical" spallation case, namely Case 3 "Al depletion failure", is now described by equations that allow the bond coat and substrate to have different diffusion coefficients. The bond coat diffusion rate may be higher because the BC is polycrystalline and grain boundary diffusion is possible. However in the case of the substrate CMSX-4, which is single crystal, grain boundary diffusion is not possible. The developed diffusion equations also satisfy the mathematical "boundary conditions" of the system (i.e. Al is not mathematically "created" or "destroyed", also referred to as mass balance), which is necessary for producing accurate life time predictions, up to 25000hr.

The most recent technical advances made by this project are the production of four prototype spallation prediction software tools, namely:

Delta-T Spallation Calculator

This prototype software tool is for the Case 1 “thermal fatigue” and Case 2 “thermal ageing” failures. It analyzes spallation data form laboratory and /or turbine engine and makes some limited spallation predictions. The software “Thermal Barrier Coating Lifetime Analysis 1.0” has replaced the “Delta-T Spallation Calculator”. Results from the “Delta-T spallation calculator” can be found in reference /9/, and will not be reproduced in this report.

Thermal Barrier Coating Lifetime Analysis 1.0

This prototype software tool is the upgraded version of the “Delta-T Spallation Calculator”. “Thermal Barrier Coating Lifetime Analysis 1.0” provides an improved analysis of spallation data and improved prediction capabilities. Results from this software will be presented below.

Bond Coat Al Simulation 1.0

This prototype software tool simulates all of the conditions for Case 3 “Al depletion failure”. Results from this software will be presented below.

Kinetics 1.0

This software is a support tool for the “Bond Coat Al Simulation 1.0” software. In order to determine the amount of Al consumed by the formation of a compact thermal grown oxide (TGO) and inward grown oxides (IGO) the growth kinetics need to be known. “Kinetics 1.0” will fit the time and temperature dependent oxidation kinetics equation to measured TGO thickness and the IGO penetration depths. The fit parameters returned by this software can be put into the “Bond Coat Al Simulation 1.0” software. This software will also analyze mass gain data. Results will be presented below.

All four software tools run in Microsoft Windows. These tools have made life time prediction easy, because all of the complicated equations are built into the software calculation engines. The user has to only be concerned with the quality of the input data and the validation of the predictions.

Finally, all of the modeling and software have been validated with a substantial amount of laboratory measurement data.

3 Arbeits- und Ergebnisbericht

3.1 Ausgangslage und Arbeitshypothesen (Former State of the Science and Working Hypothesis)

For more than one decade (from about 1989 to 2001) the influence that the oxidation behavior has on the life time of laboratory samples has been described by simply the thermally grown oxide thickness /1-3/. This critical TGO thickness approach was never very reliable. The spallation prediction models that consider the frequency of the thermal cycles proved to be far more accurate and reliable /4-7, 10-14/. It was then proposed in 2004 /8/ that in order to achieve reliable prediction for life times up to 25000hr a spallation prediction model would have to consider “Interacting Failure Mechanisms”.

Laboratory samples are usually tested under accelerated conditions (i.e. short life times <1000h) produced by testing with higher temperatures (>1050°C) and rapid cycle frequencies (hot dwell times <2 h). However, the TBCs in land based gas turbines can have life times greater than 25000h, with bond coat temperature of 900°C and service inspection intervals of up to 1000h. Consequently, when the accelerated laboratory test data is extrapolated to the turbine operational conditions the failure mechanisms could change. This was the theme of this project, which started in 2005 and the final result are below.

In this project we used a multiple mechanistic approach. Top coat spallation has been classified into three cases, namely, Case 1 "thermal fatigue failure", Case 2 "thermal ageing failure" and Case 3 "Al depletion failure", which are depicted in figure 1. Cases 1 and 2 are considered to be, more or less, oxidation induced mechanical failures, where case 3 is considered to be a type of chemical failure. This classification produces a conceptual framework that separates "mechanical" and "chemical" spallation mechanisms, which can in turn be modeled separately when the appropriate measurement data is available.

Case 1 Thermal Fatigue Failure

The sample on the left of figure 1 failed during thermal cyclic oxidation. The oxidation test was at 1100°C and during each cycle the sample experienced one hour at temperature, also during each cycle the sample was cooled to room temperature and remained at room temperature for at least 30 minutes. This type of cycle will produce the maximum thermal expansion mismatch strains ($\varepsilon_{th}=\Delta\alpha\Delta T$). The macroscopic delamination crack seen in the figure, which plays a critical role with regard to top coat spallation, lies mostly within the YSZ top coat with some of the cracking extending into the thermally grown oxide (TGO). The sample spalled after 277cy, which is 277hr at temperature. Here it is proposed that this sample failed due to a thermal cyclic fatigue mechanism. Additionally, bear in mind that the TGO thickness is about 7µm and is mostly Al_2O_3, which indicates that the bond coat is not critically depleted of Al.

Case 2 Thermal Ageing Failure

The sample in the middle of figure 1 failed after isothermal oxidation. It was tested at 1100°C for 1000hr and experienced only one cooling step. The macroscopic delamination crack seen in this photo again passes through the YSZ top coat and with a significant part of the cracking extending into the thermally grown oxide. In contrast to the case 1 sample the case 2 sample lived three times longer. The life time of cycled TBC in many cases is shorter than that of isothermally exposed specimens, which is viewed as the thermal cycling produces a thermal cyclic fatigue mechanism that can dominate the life time of the sample. The degradation of the top coat under isothermal condition is likely to be caused by sintering of the YSZ and TGO growth. The TGO in the case 2 sample is about 9µm, which is about 38% thicker than the case 1 sample. The composition of the TGO is again mostly Al_2O_3, which is again an indication that the bond coat is not critically depleted of Al.

Case 3 Al Depletion Failure

The samples of case 1 and case 2 show the crack path passing through the top coat, consequently, the mechanical properties of the YSZ and how the mechanical reliability of the top coat degrades with the respective thermal exposure are suspected to be of crucial importance. The sample on the right side of figure 1 (spallation case 3) is showing something completely different when compared to cases 1 and 2. The case 3 sample was isothermally oxidized at 1050°C for 5000hr, where it spalled after cooling. The crack face passes only through the TGO. The TGO is >30µm thick and is composed of Al_2O_3 with a large amount of

Ni (Co,Cr)-spinels. The formation of the spinels and the TGO thickness, which should be 13µm thick when calculated from the Al_2O_3 oxidation kinetics data, is a strong indication that the bond coat is critically depleted of Al. Consequently, case 3 is classified as Al depletion failure.

3.2 Beschreibung der durchgeführten Arbeiten (Description of the Work Performed)

From the preceding section it is shown that oxidation failure can have as many as three failure mechanisms. Consequently, the work plan has attempted to quantify these spallation cases. In order to meet the project aims testing equipment, samples and data from former TBC projects were used. As stated in the work plan of the project proposal section 3.2.1 the existing databases of APS-TBC measurement data were reviewed. In order to meet the project aims the samples and tests preformed in the framework of the current project were chosen to span a wider range of the exposure and TBC system parameters. For the case of bond coat and substrate Al diffusion a VPS-β-NiAl and Alloy 600 were added to the investigation. The bond coat VPS-β-NiAl and substrate Alloy 600 have Al contents of 21.0wt% and 0.18 wt%, respectively. For the cases of spallation due to Thermal Fatigue and Thermal Ageing some tests were conducted up to 1350°C. The longest exposure times were 10000hr at 950 and 1050°C. In order to explore the role that a temperature gradient across the top coat has on the spallation life time burner rig data from reference 4 is used. It should be point out that the coatings tested in this project were produced by the same work group as the samples tested in reference /4/.

3.2.1 Samples

The APS TBC systems under investigation are listed in table 1. The elemental compositions of the substrates and vacuum plasma sprayed (VPS) bond coats are listed in table 2. The TBC systems are given short names in order to expedite the text. As an example, the short name 12/56 SX is a TBC system with bond coat and substrate Al contents of 12.5 wt% and 5.6wt%, respectively. The SX and DS stand for single crystal and directionally solidified, respectively. The IN738, Alloy 600 and all of the bond coats are polycrystalline. The bond coat thickness of the 12/56 DS 150 and 12/56 DS 75 are 150µm and 75µm, respectively. The top coats are APS yttria stabilized zirconia (YSZ) with ~12% cumulative porosity and with thicknesses of 150 µm and 300µm.

Table 1. TBC Systems

Short Name	**Substrate**	**Bond Coat**
12/56 SX	CMSX-4	150µm of Abler Ni 192-8
12/56 DS 150	CM247-DS	150µm of Abler Ni 192-8
12/56 DS 75	CM247-DS	75µm of Abler Ni 192-8
12/34	IN738	150µm of Abler Ni 192-8
8/34	IN738	150µm of SC2231
12/0	Alloy 600	125µm of Abler Ni 192-8
21/56 DS	CM247-DS	150µm VPS-β-NiAl

Table 2 Elemental Compositions

Substrate or Bond Coat	**Elemental Composition (wt%)**
CMSX-4	61.7 Ni, 10 Co, 6.0 Cr, 5.6 Al, 6.0 W, 0.6 Mo, 1.0 Ti, 6.0 Ta, 3 Re, 1 Hf
CM247	61.9 Ni, 9.0 Co, 8.5 Cr, 5.6 Al, 9.0 W, 0.5 Mo, 0.7 Ti, 4.0Ta, 0.07 C, 0.7 Si
IN738	61.7 Ni, 8.5 Co, 16 Cr, 3.4 Al, 1.7 W, 2.6 Mo, 3.5 Ti, 1.7 Ta, 0.9, Nb, 0.17 C

Alloy 600	74.5 Ni, 0.05 Co, 16 Cr, 8.3 Fe, 0.18 Al,, 0.03 C, 0.29 Si, 0.27 Mn,
Abler Ni 192-8	47.25 Ni, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.25 Hf, 0.4 Si
SC2231	30 Ni, 38 Co, 27 Cr, 8.0 Al, 0.5 Y, 0.5 Si
VPS-β-NiAl	69 Ni, 8.4 Co, 1.0 Cr, 21 Al, 0.6 Y

3.2.2 Testing With Regards to Spallation Case 3 Bond Coat Depletion of Aluminium

For the prediction of spallation due to bond coat depletion of aluminium the Al depletion kinetics have to be modelled and compared to a critical Al content. This project has investigated the Al profiles from a total of 95 samples from 7 different substrate / bond coat combinations with the electron microprobe (EPMA) line scans. The systems and the number of samples per system are shown in table 3. Prior to make the line scans the samples were given isothermal oxidation treatments up to 10000hr at 1100, 1050, 1000, and 950°C.

An example of an Al profile measured with the EPMA is shown in figure 2. Three line scans are made per sample. The three line scans are averaged together. During the early stages of oxidation (i.e 24hr at 1100°C) this averaging has the effect of smoothing out the ß-phase precipitates. During the end of the TBC life time the averaging has a very minor effect, because the ß-phase precipitates have dissolved (see fig 3 1000hr 1100°C).

Seven different substrate / bond coat combinations were both measured and modelled in order to validate the model not only over a range of temperatures and times but also a range of Al concentrations. The Al concentrations for the substrates and bond coats are shown in figure 3. The range of Al content that this project has investigated has a minimum of 0.18wt% (Alloy 600 substrate) up to a maximum of 21wt% (VPS-β-NiAl bond coat). This range of Al content should cover all TBC systems used for gas turbines.

Table 3: Statistics of the number of samples investigated.

Temperatures (°C)	**1100**	**1050**	**1000**	**950**
Oldest Sample (hr)	1000	10,000	5000	10,000
Systems	**Number of Samples**	**Number of Samples**	**Number of Samples**	**Number of Samples**
12/56 SX	5	11	6	9
12/56 DS 150		6		5
12/56 DS 75		6		5
12/34	5	6		5
8/34	5			
12/0		6		8
21/56 DS		6		
Total Number of Samples Investigated	**15**	**42**	**6**	**32**

As stated above in order to determine the amount of Al consumed by the formation of a compact thermally grown oxide (TGO) and inward grown oxides (IGO) the growth kinetics need to be known. The TGO thickness has been measured from 101 cross-sectioned samples, where the thickness is measured at 20 to 30 different locations of each sample, in order to find an average thickness. The standard deviation for the measured thicknesses of each sample was about 20%. These samples were isothermally oxidized up to 10000hr at 1100, 1050, 1000, and 950°C. The systems investigated are listed in table 3.

Thirty four of the 12/56 SX samples investigated, were suffering from “cauliflower”/9,15,16/ inward grown oxidation. The penetration depths of these inward grown oxides ware measured in 20 to 30 different locations.

The time and temperature TGO and IGO kinetics were analyzed using the software “Kinetics 1.0” where the results are shown below.

3.2.3 Testing With Regards to Spallation Case 1 Thermal Fatigue And Case 2 Thermal Aging

In order to meet the project aims this project has investigated 58 spalled APS-TBC samples from four different systems namely: 12/56DS, 12/56SX, 12/34 and 8/34. The number of spalled samples investigated per TBC system is plotted in figure 4 where the minimum is 13 and the maximum is 16 with an average of 14.5. These spalled samples were produced by thermal cycling with a verity of hot dwell times and temperatures. Plotted in figure 5 for each of the four systems are the bond coat temperatures and hot dwell times of the spalled sample produced by this project. The temperature ranges from 1000 to 1350°C and the hot dwell time ranges from 1hr to 1000hr. For the 12/34 system we are using burner rig data from reference 4. It should be pointed out that the coatings tested in this project were produced by the same work group as the samples tested in reference /4/. By including this data the project we can explore the role that a temperature gradient across the top coat has on the spallation life time.

The important point in figure 4 is that the four systems were tested under different conditions (temperatures and hot dwells) where a direct comparison of all of the data is not possible with out using a life time model, or ignoring a significant number of measurement points. In the results section this data will be analyzed by using the “Thermal Barrier Coating Lifetime Analysis 1.0” prototype software.

3.2.4 Modeling Spallation Case 3 Bond Coat Depletion of Aluminium

As stated in section 2.1 the modeling equation for spallation due to bond coat depletion of Al are incorporated into the calculation engine of the “Bond Coat Al Simulation 1.0” prototype software. As stated in the project proposal one of the project aims was to model the Al diffusion so that the bond coat and substrate can have different diffusion coefficients. The bond coat diffusion rate may be higher because the BC is polycrystalline and grain boundary diffusion is possible. However, in the case of the superalloy substrate grain boundary diffusion may be limited or even not possible. This is illustrated more clearly in figure 6 and 7, for three possible diffusion situations:

1. The bond coat and substrate diffusion coefficients are equal (D_{sub}=D_{bc}).
2. The bond coat diffusion coefficient is greater than the substrate diffusion coefficient (D_{sub}=D_{sub} /5).
3. The substrate diffusion coefficient is greater than the bond coat diffusion coefficient (D_{sub}=5xD_{bc}).

From figure 6 the model predicts that these three situations will produce different Al profiles, which can make the assessment of EPMA line scan data more difficult. Moreover figure 7, the case where the bond coat diffusion coefficient is greater than the substrate diffusion coefficient (D_{sub}=D_{sub} /5), shows that a retardation of the flow of Al from the substrate into the bond coat will occur, and consequently this situation can cause an earlier Al depletion failure.

This new diffusion model, by allowing the bond coat and substrate to have different diffusion coefficients, provides a better understanding of the Al reservoir and the role that the substrate plays in the failure of TBC due to Al depletion.

The model is a solution of Fick's Second Law Eq 1.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} + Q \qquad \text{Eq. 1}$$

where C is the bond coat and substrate Al content. The z, t, T are the position beneath the TGO, time and temperature, respectively. The diffusion coefficient is only dependent on temperature Eq 2.

$$D(T) = D_o \exp\left(\frac{-E_{A-Al}}{R \cdot T}\right) \qquad \text{Eq. 2}$$

Equation 1 has been solved by separating diffusion of Al into the TGO (C_{out}) from inward diffusion of Al into the substrate (C_{in}) Eq 3-5.

$$C(Z,t,T) = C_{in}(Z,t,T) - C_{out}(Z,t,T) \qquad \text{Eq. 3}$$

Where

$$C_{in}(Z,t,T) = \frac{(C_{bc} - C_{sub})}{2}\left[erf\left(\frac{d_{bc} - z}{2\sqrt{tD}}\right) + erf\left(\frac{d_{bc} + z}{2\sqrt{tD}}\right)\right] + A \qquad \text{Eq. 4}$$

and

$$C_{out}(Z,t,T) = \frac{(C_{tgo} + C_{inox})}{B}\left[1 - erf\left(\frac{z}{2\sqrt{tD}}\right)\right] \qquad \text{Eq. 5}$$

The C_{bc} and C_{sub} are the Al content of the as sprayed bond coat and substrate, respectively. The d_{bc} and d_{sub} are the thicknesses of the as sprayed bond coat and substrate, respectively. The C_{tgo} and C_{inox} are the aluminum consumed by the TGO and IGO growth, respectively. Consequently, inward and outward diffusion can be investigated separately, which is helpful for understanding the role that the substrate and TGO play in the consumption of bond coat Al. The parameters in the above equations "A" and "B" have to be found by applying the mathematical boundary conditions. This has been done using the same approach as in the Zwischenbericht /9/. The analytical expressions for the parameters "A" and "B" are not shown here, they are programmed into the "Bond Coat Al Simulation 1.0" software. Consequently, the new model does not mathematically "create" or "destroy" aluminum. The "trick" for finding the analytical expression for "A" and "B" was to solve the problem twice once for the situation $D_{bc} \geq D_{sub}$ and again for the situation $D_{bc} < D_{sub}$.

3.2.3 Modeling Spallation Case 1 Thermal Fatigue And Case 2 Thermal Aging

As stated in section 2.1 the modeling equations for spallation due to "Thermal Fatigue" and "Thermal Aging" are incorporated into the calculate engine of the "Thermal Barrier Coating

Lifetime Analysis 1.0" prototype software. Consequently, the description of this model will be briefer. More information about this model approach can be found in the Zwischenbericht /9/. The primary exposure parameters that govern these failure cases have been identified as the exposure temperature, the thermal cycle frequency and the temperature gradient across the TBC /9/. Here it is proposed that the spallation life time of the APS-TBC under isothermal oxidation condition can be described by the following phenomenological relation.

$$t_s(\Delta T) = k_o \exp\left(\frac{E_A}{R \cdot \Delta T}\right) \qquad \text{Eq. 6}$$

The temperature dependence is described by ΔT, which is the temperature drop during cooling, because the driving force behind the TGO and top coat damage is mostly the thermal expansion mismatch stress and/or strain (i.e $\varepsilon_{th}=\Delta\alpha\Delta T$). This has been shown to be reasonable by acoustic emission data in references /7-14/. Analysis of acoustic emission data shows that most of the cracking sustained by the APS-TBC and TGO occurs during cooling, with no detectable cracking at high temperature, a small amount of cracking occurring when the TBC is cold or being reheated. The E_A and k_o in Eq.6 are constants that describe the temperature dependence of the TBC life time. For the case of spallation after thermal cycling and for hot dwell times such as 5min, 1h, 24h, 100h, and 1000h and for temperature gradients across the top coat equation 6 has to be modified.

$$t_s(\Delta T, t_{hd}, \delta T) = t_{hd}^F (k_o)^{1-F} \exp\left(\frac{(E_A)\cdot(1-F)}{R\cdot(\Delta T + G\delta T)}\right) \qquad \text{Eq. 7}$$

Where t_{hd}, , F, δT, and G are the hot dwell time, thermal fatigue exponent, temperature gradients across the top coat and thermal gradient constant, respectively. For values of F and G that are equal to zero Eq 7 reduces to Eq 6. The F represents the susceptibility that a TBC system has to thermal fatigue, which is plotted in figure 8. For F=0 the TBC top coat is impervious to thermal fatigue and the thermal cyclic life time is the same as the isothermal life time. For values of F greater than zero the TBC is susceptible to thermal fatigue and the faster it is cycled the shorter its life time. Larger values of F represent a lower resistance to thermal fatigue. The absolute value of the thermal gradient constant G is expected to be less than 1 and it is assumed that δT is less than ΔT. In Eq 7 the δT is added to ΔT because the temperature gradient across the top coat produces a strain gradient across the top coat. A portion of this strain gradient may add to the thermal expansion mismatch strain and cause accelerated thermal fatigue ageing. The G is a proportionality constant and its effect on the calculated life times is plotted in figure 8. For G=0 the TBC top coat is impervious to a temperature gradient across the top coat. Larger positive values of G represent a lower resistance to a thermal gradient and a decrease in spallation life time. Both F and G are not mathematically forbidden from having negative values, however, the physical meaning would require further investigations. As shown in figure 7 a negative value for F would cause the model to predict an increase in the spallation life time as the cycle frequency increases. A negative value for G would cause the model to predict an increase in the spallation life time when a thermal gradient is applied across the top coat.

3.3 Darstellung der erzielten Ergebnisse (Results)

Here we present the results of the laboratory measurement program in conjunction with the modeling and prototype software; Kinetics 1.0, Bond Coat Al Simulation 1.0 and Thermal Barrier Coating Lifetime Analysis 1.0.

3.3.1 Results: Kinetics 1.0 Prototype Software Tool

Prior to simulating the bond coat aluminum depletion kinetics the TGO and IGO growth kinetics have to be determined. This was the motivation for the development of the "Kinetics 1.0" software tool. This tool will fit the time and temperature kinetics equation, Eq. 8, to the measured TGO thickness and measured penetration depths of the IGO.

$$d\ (t,T) = k_o \exp\left(\frac{-E_A}{R \cdot T}\right) \cdot \left(\frac{t}{t_o}\right)^n \qquad \text{Eq. 8}$$

The T, t and R are the temperature (Kelvin), time (sec) and the Gas Constant, respectively, where t_o is equal to 1 sec. The k_o, and E_A is the rate constant and the activation energy respectively. The n is the exponent of oxidation. Eq. 8 can be used for TGO growth, IGO penetration, and mass gain.

In figure 9 is a picture of the "Kinetics 1.0" graphics user interface (GUI). In the lower left hand corner of figure 9 is a table (or spread sheet) where the measurement data can be typed in. The columns "Time (hr)" and "Temperature (°C)" are the exposure times and temperatures respectively. The column "Kinetics Data" is for TGO thickness or IGO penetration depth or mass gain data. The four buttons in figure 9 labeled "Load Data", "Save Data", "Clear Table" and "Delete 1 Point" are for managing the data table on the left. The button labeled "Analyze Data" will make a least squares fit of the measurement data to equation 8, the two plots "Analysis" and "% Errors" will be generated and the parameters "n", "ko", "E", "Average % Error" and "STD%" will be returned. The "Average % Error" and "STD%" are the percent systematic error and standard deviation respectively, of the fit compared to the measurement data.

Note: This software fits both the time and temperature dependence of the kinetics at the same time.

The software will also fit measurement data made all at one temperature. The "About" button when pressed will show a pop up screen containing the corporate identity information and license agreement. The "More Plots" button will show the screen in figure 10. The "Plots Screen" is for the purpose of plotting the results of the data analysis. The lines in the plot are color-coded black, red and green, which correspond to "Trace 1","Trace 2" and "Trace 3" respectively. The parameters for "Trace 1","Trace 2" and "Trace 3" are listed in the field below the labels. The user can edit the values of the parameter for the three traces. For example the user can plot three different temperatures over any time interval. The export buttons on the bottom of this screen when pressed will write an ASCII data file of the plotted data to the hard drive, which can be read by any commercially available software, such as, Microsoft Excel or Origin.

The measured TGO thickness from 101 oxidized samples and IGO penetration depth from 34 oxidized samples as described in section 3.2.2 where analyzed using the "Kinetics 1.0" software tool, where the results are in table 4. Additionally, mass gain data from the thermo-gravimetric analysis (TGA) of fluorinated TiAl was analyzed using the same software. The TGO and IGO growth were found to be sub-parabolic (n=0.375) and super-parabolic (n=0.601) respectively. The standard deviation between the fit and measurement data was 20% and 31% for the TGO and IGO growth respectively, which are similar to the values reported in the Zwischenbericht /9/. The parameters in table 4 will be used in the next section.

Table 4: Oxidation Fit Paramates

	TGO	IGO	TiAl (TGA)
n	0.375	0.601	0.287
ko	1.58 μm	6.76 x 10^3 μm	753 mg/cm^2
E	-44551 J/mol	-152582 J/mol	-88997 J/mol
# of Data Points	101	34	11753
Average % Error	-1.82	-405	-0.863
STD %	20	31.2	26
Exposure Temperatures	950 1000 1050 1100	950 1000 1050 1100	900 1000

3.3.2 Results: Bond Coat Al Simulation 1.0 Prototype Software Tool

In figure 11 is a picture of the "Analysis" screen of the "Bond Coat Al Simulation 1.0" software tool. The purpose of this screen is to provide calculated Al profiles that can be compared to measured EPMA aluminium profiles. The plot on the top of the screen shows the modelled Al profile produced by the growing TGO and/or IGO. The plot in the middle of the screen shows the Al profile produced by the interdiffusion of Al between the bond coat and superalloy substrate. The plot on the bottom of this screen can be compared to measured Al profiles, for the purpose of validating the modelling parameters. This plot is the mathematical difference of the two plots above it. Again the lines in these three plots are color-coded black, red and green, which correspond to "Trace 1","Trace 2" and "Trace 3" respectively. The parameters for "Trace 1","Trace 2" and "Trace 3" are listed in the field below the labels. The calculations are made for any given exposure time and temperature. By plotting 3 traces the user can simulate the Al diffusion profiles for three different temperatures or three different times and make a comparison. The results of the calculations can be exported as an ASCII file by pressing the "Export Trace 1", "Export Trace 2", and "Export Trace 3" buttons. The exported data can be compared to the measurement data from the measured EPMA aluminium profiles by using any commercially available software, such as, Microsoft Excel or Origin.

By pressing the "Depletion Kinetics" button the aluminum "Depletion Kinetics" screen will pop up as shown in figure 12. The purpose of the screen is to calculate the bond coat aluminum depletion kinetics as shown on the right side of this figure. The plot on the left side of figure 12 shows the evolution of the aluminum profiles as a function of exposure time in a type of time laps video sequence. The lines in the plots are color-coded using the same convention as above. On this screen the three traces correspond to three different temperatures. Consequently, the user can compare the Al depletion kinetics for three temperatures at the same time. The results of the calculations can be exported by pressing the "Export All" button.

The input data can be entered into the simulator by using the "System Properties" screen, figure 13, which is activated by pressing the "System Properties" button shown in the lower left had corner of figure 11. The input data are the design parameters, i.e. bond coat and substrate thicknesses, and aluminum concentrations. The oxidation parameters are the TGO and IGO growth kinetics, which were found in the previous suction by using the "Kinetics 1.0" software tool. The "TGO Al Consumption Rate" and "IGO Al Consumption Rate" are constants that convert TGO thickness and IGO penetration into concentration of consumed aluminum, and were described in equations 14 and 15 of the Zwischenbericht /9/. The bond coat and substrate diffusion coefficients are plotted in figure 14 and listed in table 5. On the left side of figure 14 are "average" diffusion coefficients for 5 different TBC systems. These values were found by making a least squares fit of the modeling equations to the EPMA line scan data where the diffusion coefficient was the only fit parameter, and under the assumption that the boat coat and substrate have the same diffusion coefficient. These values were then fit by equation 2, where the fit parameters are in table 5. Also plotted in figure 14 are literature values for the diffusion coefficients, from Evans /17/, and Nesbitt /18/, where the agreement provides confidence. In order to find the diffusion coefficient for each bond coat and substrate the same least squares fit procedure was used. However, the fit region was restricted to only the bond coat or substrate regions of the EPMA line scan data. When comparing the bond coat and substrate diffusion coefficients to the "average" diffusion coefficients a multiplication factor was found, which is listed in table 5. The diffusion coefficient for the bond coat and substrates are plotted on the right side figure 14, where it can be seen that the polycrystalline alloys (i.e. bond coats, and IN738) have slightly higher diffusion rates than the single crystal and directionally solidified alloys (i.e. CMSX4 and CM247). The diffusion coefficients for the bond coats and substrates were assumed to have the same temperature dependence because the scatter in the measurement data was a little too high to find separate energy values for each material.

Table 5: Bond Coat and Substrate Diffusion Coefficients

	D_o (m^2/s)	E_a (J/mol)	Factor	Comment
Average	0.0597	333340	1	
Bond Coats	0.101	333340	1.7	Polycrystalline
IN738	0.0500	333340	0.83	Polycrystalline
CMSX-4 **CM247**	0.017	333340	0.28	Single Crystal Directionally Solidified

3.3.2 Comparison: Measurement vs. Bond Coat Al Simulation 1.0 Prototype Software Tool

An example of the measured and simulated Al profiles are plotted in figure 15 for the 12/34 and 12/56 SX systems after oxidation at 1050°C for 5000hr, where the "Bond Coat Al Simulation 1.0" software was used. All of the parameters used for the simulation are listed in the above tables, except the substrate thickness where a value of 4000μm was used. What can be seen in figure 15 is that the bond coat Al is lower than the substrate Al and that at the interface there is a step, where this step is a little smaller for the IN738 substrate when compared to the CSMX-4 substrate. This step behavior is caused by the substrates having a lower diffusion coefficient than the bond coat. From figure 14 and table 5 the diffusion coefficients of IN738 and CMSX-4 are about 1/2 and 1/6 as large as for the bond coat, respectively. As stated in section 3.2.4 and figure 7 this situation can have a retarding effect on the Al depletion kinetics, because the flow of Al from the substrate into the bond coat is slower and the substrate Al is making a smaller contribution to the total Al reservoir.

In figure 16 is an example of the measured and simulated Al depletion kinetics for the 12/34 and 12/56 SX systems after oxidation at 1050°C. The measurement data validates the simulation up to 10000hr. The Bond Coat Al Simulation 1.0 software was again used to make the simulations. All of the parameters used for the simulation are listed in the above tables, except the "TGO Al Consumption Rate" and "IGO Al Consumption Rate" where the values from the Zwischenbericht /9/ where used, namely, 0.6298 and 0.0625, respectively. The Al depletion rate is a little higher for the IN738 system (12/34) than for the CMSX-4 system (12/56SX), because the IN738 has less Al then CMSX-4 (3.4 and 5.6 wt%, respectively). The measured and simulated Al depletion kinetics also show that with extensive IGO penetration the bond coat depletes rapidly i.e. <8000hr (figure 16). Consequently, with extensive IGO penetration the TBC will spall in less than 8000hr at 1050°C. In order to test the limits of the model and software Al depletion kinetics for the extreme systems 21/56 SX and 12/0 are plotted in figure 17. The 21/56 SX system has 21 wt% aluminum in the bond coat, and the 12/0 system has 0.18 wt% aluminum in the substrate. For the simulation the most of the parameters are in the above tables, except for the polycrystalline Alloy 600 substrate the diffusion coefficient used was the same as the for the polycrystalline IN738 in table 5. The measurement data validates the simulation up to 5000hr at 1050°C. These limiting cases were part of the project aims. Clearly, from figure 17 the 12/0 system depletes much faster than the 21/56 SX system. This is due to the 12/0 system having much less aluminum. It should also be pointed out that the 12/0 system is not used in the real gas turbines and is purely an academic system for this project and to develop a deeper understanding of Al depletion.

3.3.3 Results: Thermal Barrier Coating Lifetime Analysis 1.0 Prototype Software Tool

In figure 18 is a picture of the “Analysis” screen of the “Thermal Barrier Coating Lifetime Analysis 1.0” prototype software tool. This tool was developed for the Case 1 “thermal fatigue” and Case 2 “thermal ageing” failures. The measured spallation life times from accelerated laboratory testing are entered into the table (or spread sheet) on the lower left hand corner of the “Analysis” screen. The columns “Temperature (°C)”, “Hot Dwell (hr)”, “Lifetime (hr)” and “Gradient (°C)” are the testing temperatures, the hot dwell times, the spallation life times and the temperature gradient across the TBC, respectively for each of the spalled samples. For samples tested without a gradient a value of 0 should be used. The five buttons in figure 18 labeled “Load Data”, “Save Data”, “Clear Table”, “Delete 1 Point”, and “About” have the same functions as described above for the “Kinetics 1.0” software. When the “Analyze Data” button is pressed the laboratory data is analyzed, the results are graphically displayed in the “Arrhenius Diagram” and “NASA Accuracy Assessment” plot. From these figures the user can quickly assess the quality of the analysis. The fit parameters can be found by pressing the “Parameters” button. The “Statistics” button provides information about the laboratory data, such as; maximum, minimum, average testing temperatures; maximum, minimum, average, hot dwell times; maximum, minimum, average spallation life time; and maximum, minimum, average temperature gradient.

The prognostics screen of the “Thermal Barrier Coating Lifetime Analysis 1.0” prototype software tool is shown in figure 19. This screen uses the modeling parameters determined by the above analysis to predict the life time of the top coat. The software will calculate the life times as a function of bond coat temperature for a given input of hot dwell time and temperature gradient (top plot in figure 19). From this screen the bond coat and YSZ top coat surface temperature limits for a target life time (i.e. 15000hr or 25000hr) can be calculated (middle plot in figure 19). Finally, the gas turbine operational limits (i.e. number of turbine shutdowns vs. spallation life time) can be calculated for a given input of temperature and temperature gradient (bottom of figure 19).

Again all of the results produced by this software can be exported as an ASCII data file, which can be read by any commercially available software, such as, Microsoft Excel or Origin, by pressing the “Export” buttons on the bottom of figure 18.

3.3.2 Comparison: Measurement vs. Thermal Barrier Coating Lifetime Analysis 1.0 Prototype Software Tool

All of the spallation life time data from section 3.2.3 and figures 4 and 5 were analyzed with the "Thermal Barrier Coating Lifetime Analysis 1.0" prototype software tool. Added to the data for the 12/34 system is burner rig data from reference /4/. The fit parameters found by the software are listed in table 6. The energy parameters E_a span a relatively narrow range from 23000 to 36000 J/mol, and have positive values because the life times decrease as the bond coat temperature increases. The fatigue parameters F also span a relatively narrow range from 0.18 to 0.27 and are positive because the life times decrease as the cycle frequency increases. The gradient parameter is zero for the 12/56 SX, 12/56DS and 8/34 systems because these systems were tested without a temperature gradient. The 12/34 system has a value for the G parameter of 0.29 because this data set includes the burner rig data from reference /4/ (temperature gradient of up to 250°C). Plotted in figure 20 is the NASA accuracy assessment plot and a plot of the systematic and random errors. From the NASA plot we see the modeled and measured life times are distributed around the "Perfect Fit" line, which means that the model is tracking all of the exposure conditions, temperature, hot dwell time, temperature gradient, and life time. Additionally, the NASA plot shows that all of the measured and modeled life times are in agreement to within a factor of 3 accuracy, including the outliers. The systematic errors were less than 10% for all four TBC systems. The random errors are one standard deviation and are between 25 and 51%.

By using the prognostics function (the top plot in figure 19) the life times as a function of temperature for the 1 and 2 hour hot dwell times were calculated and plotted with the spallation life times measured in the laboratory for all four TBC systems investigated, see figure 21. From these figures it can be seen that the software works quite well for all four of the TBC systems. Plotted in figure 22 are the temperature limits for a target life time of 25000hr for the four TBC systems, these calculations were made by using the prognostics function in the middle of figure 19. The data from the 12/34 system has temperature gradient data from the burner rig from reference 4. Consequently, for this system it is possible to calculate the temperature limits for the bond coat and TBC surface for a target life time of 25000hr (left side of figure 22). For the 12/34 system if it were used in the aero engine with flight times less than 10hr the bond coat temperature should be less than 880°C with a surface temperature less than 1080°C for 25000hr of service life time. For the same system used in the power generation turbine with shut downs every 1000hr the bond coat temperature should be less than 940°C with a surface temperature less than 1140°C for 25000hr of service life time. On the right side of figure 22 are the temperature limits for all four systems calculated without temperature gradients. For 25000hr lifetime and a rapid thermal cycle (i.e. 1hr) these temperature limits fall between 900 and 960°C. For the slower cycle (1000hr) these temperature limits fall between 960 and 1000°C. By using the prognostics function, the bottom plot in figure 19, the turbine operational limits, can be calculated. These limits are plotted in figure 23, where the expected spallation life times for a given number of turbine shutdowns are shown. On the left side is the 12/34 TBC system where the calculation compares the lifetime without a temperature gradient at 950°C to the situation with a 200°C temperature gradient (bond coat 950°C, surface 1050°C). On the right side is plotted the shutdowns vs life times for all four TBC systems investigated. The lines in these plots have a negative slope because of the cycle frequency dependence of the TBC life time.

Table 6: Spallation Life Time Parameters

	12/56 SX	**12/56 DS**	**12/34**	**8/34**
Life Energy E_A (J/mol)	233903	249058	324445	357690
Life Constant k_o (hr)	5.07E-9	9.67E-10	2.81E-13	4.16E-15
Fatigue Exponent	0.18	0.23	0.27	0.23
Gradient Parameter	0	0	0.29	0

Systematic Error (%)	8.13	3.80	10.50	8.60
Random Error (%)	40.40	26.9	51.0	38.7

3.4 Ausblick auf zukünftige Arbeiten (Outlook for Future Research)

The results from this project have produced a considerable amount of insight with regard to the degradation/spallation mechanisms and the life time of the APS top coat. The TBC spallation prediction has made its first steps into a new level of technology, with the prototype software produced by this project. The outlook is to further develop this technology to incorporate LCF, HCF and TMF, cycles into the research program. Additional, this program should be extended to also include the spallation of EB-PVD TBC systems, and possibly a general ceramic coating failure model for all ceramic/metal systems.

3.5 Interdisziplinäre Weiterentwicklung

This project is regarded as a typical example of an interdisciplinary study. High temperature oxidation and Al diffusion are part of the field of solid state chemistry; acoustic emission is from the discipline of physics. Stresses, strains, fatigue, and fracture are from mechanical engineering. There is a bit of mathematics in the since that the differential equation, Fick’s Second Law Eq 1, can be solved analytically for layered systems and that numerical solutions are not always necessary. Finally, there is software engineering.

3.6 Anwendung

The prototype software produced by this project is presently in a state which is not yet sufficient for a wide practical application. However, it is the aim of future work to develop this spallation prediction software further so that it may be distributed to academic and industrial researchers.

3.7 Beteiligte Wissenschaftler

Prof. Dr. Schütze was the project-managing director, guiding theoretician and publication co-author. Dr. Renusch was the project coordinator and chief scientist. The VPS MCrAlY coating and APS top coats were sprayed by Mr. Rauwald and Prof. Dr. Vaßen of the Forschungszentrum Jülich. This project had collaborations with projects funded by BMBF-BEO (coordinated by Siemens, Rolls Royce and MTU) and AIF-FVV (coordinated by Technische Universität Darmstadt). The substrate materials, IN738, and bond coat powder, SC2231, were donated by Siemens. The substrate material, CM247, was donated by Alstom and Doncasters.

3.9 References

/1/ J.T. DeMasi, K.D. Sheffler, M. Ortiz, „Thermal Barrier Coating Life Prediction Model“, NASA Report CR 182230, (1989)

/2/ S.M. Meier, D.M. Nissley, K.D. Sheffler, „Thermal Barrier Coating Life Prediction Model“, NASA Report CR 189111, (1991)

/3/ R. Herzog, P. Majerus, S. Heckmann, R. Steinbrech, W.J. Quadakkers, F. Schubert, L. Singheiser, H. Echsler, M. Schütze, “Contribution to Life Prediction of Thermal Barrier Coatings: A Concept of Accumulated Damage”, Proceedings: Materials Week, October, 1-4, 2001, Munich, Germany

/4/ F. Traeger, M. Ahrens, R. Vaßen, D. Stöver, “A life time model for ceramic thermal barrier coatings”, Materials Science and Engineering A358 (2003) p.255-265

/5/ E. P. Busso, J. Lin, S. Sakurai, M. Nakayama, Acta mater. 49 (2001) 1515

/6/ E. P. Busso, J. Lin, S. Sakurai, Acta mater. 49 (2001) 1529

/7/ D. Renusch, M. Schütze, Die Rolle der Bondcoat-Oxidation für die Lebensdauer von Wärmedämmschichten, Abschlussbericht, Deutsche Forschungsgemeinschaft project No. DFG-Schu 729/11 (2004) (in English)

/8/ D. Renusch, H. Echsler, M. Schuetze, ”The Role That Interacting Failure Mechanisms Have on the Lifetime of APS-TBC Under Oxidizing Conditions”, Conf. Proc. 6th International Symposium on High Temperature Corrosion and Protection of Materials, 16-21 may 2004, Les Embiez, France Materials Science Forum, vol. 461-464, p. 729-736 (2004)

/9/ D. Renusch, M. Schütze, Zwischenbericht “The Role of Interacting Failure Mechanisms for APS-TBC Life Time, DFG-Schu 729/16-1 (2006)

/10/ D. Renusch, H. Echsler, M. Schütze, ”Progress in Life Time Modeling of APS-TBC Part I: Residual, Thermal and Growth Stresses Including the Role of Thermal Fatigue”, MATERIALS AT HIGH TEMPERATURES 21(2) (2004) p. 65–76

/11/ D. Renusch, H. Echsler, M. Schütze, “Progress in Life Time Modeling of APS-TBC Part II: Critical Strains, Macro-cracking, and Thermal Fatigue”, D. Renusch, H. Echsler, M. Schütze, MATERIALS AT HIGH TEMPERATURES 21(2) (2004) p. 77-89

/12/ D. Renusch, H. Echsler, M. Schütze, “New Approaches to the Understanding of Failure and Life Time Prediction of Thermal Barrier Coating Systems”, Conf. Proc. in Life Time Modeling of High Temperature Corrosion Processes Editors M. Schütze, W. J. Quadakkers, J. R. Nicholls, EFC-Publication No. 34, IoM Publication, London (2001) p. 324

/13/ D. Renusch, H. Echsler, M. Schütze, “Life Time Modeling of APS-TBC by Using Acoustic Emission Analysis”, Conf. Proc. Turbomat-Symposium June 17-19 2002 Bonn, DLR Köln (2002) p 48-52

/14/ M. Schütze, D. Renusch, H. Echsler, “The Influence of Oxidation on the Life Time Of Thermal Barrier Coatings”, Conf. Proc. NACE CORROSION 2003, San Diego CA., January 2003, Paper No. 03509, NACE, Huston 2003

/15/ H. Echsler, D. Renusch, M. Schütze, “Kinetics of the Evolution of Physical Defects in the TGO and its Vicinity for Life Time Prediction of TBC Systems”, Conf. Proc. Turbomat Symposium, June, 17-19, 2002, Bonn, DLR Köln (2002), p 152-156

/16/ H. Echsler, D. Renusch, M. Schütze, ”Bond Coat Oxidation and its Significance for the Life Expectancy of Thermal Barrier Coating Systems”, Materials Science and Technology Vol. 20, (2004) pg. 307

/17/ H. E. Evans, M. E. Taylor, “Diffusion Cells and Chemical Failure of MCrAlY Bond Coats in Thermal-Barrier Coating Systems”, Oxidation of Metals, **55** (2001) p17

/18/ J. A. Nesbitt, “Predicting Minimum Al Concentrations for Protective ScaleFormation on Ni - Base Alloys”, J. Electrochem Soc. 136 (1989) no. 5, p1511

4.0 Liste der Publikationen aus dem Projekt

4.1 Papers

A Prototype Software Tool for Life Time Assessment of Thermal Barrier Coating Systems. D. Renusch, M. Schütze, Materials Science Forum **595** (2008) 151-158.

The Role That Bond Coat Depletion of Aluminum Has on the Lifetime of APS-TBC Under Oxidizing Conditions, D. Renusch, M. Schütze, Materials and Corrosion, **59**, No. 7 (2008) 547-555.

Measuring and Modeling the TBC Damage Kinetics by Using Acoustic Emission Analysis, D. Renusch, M. Schütze, Surface & Coatings Technology **202** (2007) 740–744.

Software Tool for Life Time Assessment of TBCs, D. Renusch, M. Schütze, submitted, Proceedings of the Second Japanese-German Workshop on Thermal Barrier Coating Systems for Gas Turbines, May 27th -29th 2009, Ritsumeikan University, Kyoto, Jopan

4.2 Contribution to Conferences

Invited Talks

The Role That Interacting Failure Mechanisms Have on the Lifetime of APS-TBC Under Oxidizing Conditions, D. Renusch, Gordon Research Conference on High Temperatures Corrosion, July 24-29, 2005, Colby-Sawyer College, New London, NH, USA

Measuring and Modeling the Thermal Barrier Coatings Degradation Kinetics, D. Renusch, M. Schütze, Feb 1st 2007, Symposium Series, "Dünne Schichten - Verfahren und Anwendungen", Institute for Materials Technology, Darmstadt University of Technology, Darmstadt, Germany

Modelling the Oxidation Induced Failure of APS Thermal Barrier Coatings, D. Renusch Gordon Research Conference on High Temperatures Corrosion, July 26-31, 2009, Colby-Sawyer College, New London, NH, USA

Talks

Interacting spallation mechanisms and life time prediction of ceramic thermal barrier coatings, D. Renusch, M. Schütze, First Japanese-German Workshop on: Properties and Performance of Thermal Barrier Coating Systems and Factors Affecting it, September 13-15, 2006, Institute for Materials Technology, Darmstadt University of Technology

The Role That Bond Coat Depletion of Aluminum Has on the Lifetime of APS-TBC Under Oxidizing Conditions, D. Renusch, M. Schütze, EFC Workshop "Protective Systems for High Temperature Applications: From Theory to Industrial Implementation" 12 – 13 October 2006, Frankfurt am Main, Germany

Measuring and Modeling the Bond Coat Aluminum Depletion Kinetics, D. Renusch, M. Schütze, International Conference on Metallurgical Coatings and Thin Films 2007, April 23-27, San Diego CA. USA

Software Tool for Life Time Assessment of TBCs, D. Renusch, M. Schütze, Second Japanese-German Workshop on Thermal Barrier Coating Systems for Gas Turbines, May 27th -29th 2009, Ritsumeikan University, Kyoto, Jopan

Posters

Measuring and Modeling the TBC Damage Kinetics by Using Acoustic Emission Analysis, D. Renusch, M. Schütze, International Conference on Metallurgical Coatings and Thin Films 2007, April 23-27, San Diego CA. USA

A Prototype Software Tool for Life Time Assessment of Thermal Barrier Coating Systems. D. Renusch, M. Schütze, 7th International Symposium on High Temperature Corrosion and Protection of Materials, 18-23 of May 2008, Les Embiez, France.

Bond Coat Aluminum Depletion Kinetics, D. Renusch, M. Schorr, G. Schmidt, M. Schütze, Gordon Research Conference on High Temperatures Corrosion, July 29 - August 3, 2007, Colby-Sawyer College, New London, NH, USA

The Role of Interacting Failure Mechanisms for APS-TBC Life Time (part 1), D. Renusch, M. Schütze, 12. Karl-Winnacker-Institut Jahreskolloquium November 2004

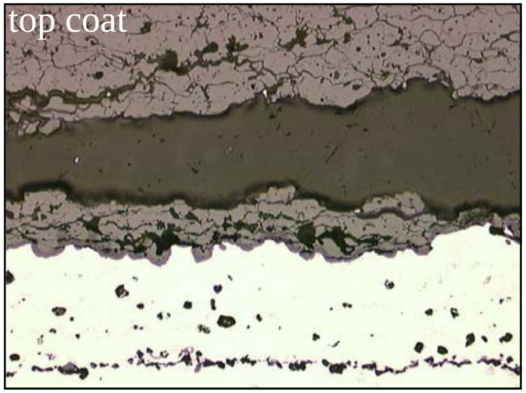
The Role of Interacting Failure Mechanisms for APS-TBC Life Time (part 2), D. Renusch, M. Schütze, 13. Karl-Winnacker-Institut Jahreskolloquium November 2005

The Role of Interacting Failure Mechanisms for APS-TBC Life Time (part 3), D. Renusch, M. Schütze, 14. Karl-Winnacker-Institut Jahreskolloquium November 2006

The Role of Interacting Failure Mechanisms for APS-TBC Life Time (part 4), D. Renusch, M. Schütze, 15. Karl-Winnacker-Institut Jahreskolloquium November 2007

The Role of Interacting Failure Mechanisms for APS-TBC Life Time (part 5), D. Renusch, M. Schütze, 16. Karl-Winnacker-Institut Jahreskolloquium November 2008

Case 1
Thermal Fatigue Failure



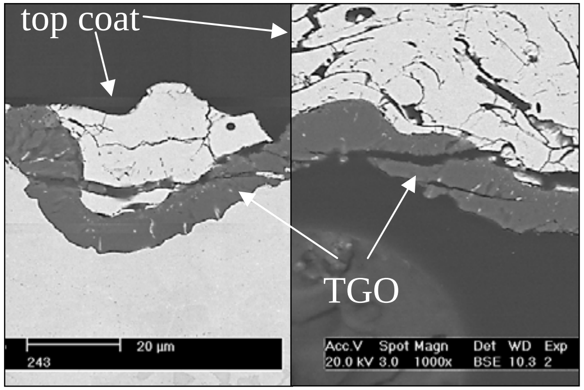
277 hrs
277 cy
At 1100°C

The crack passes through mostly the top coat.

TGO Thickness 6.7 µm

TGO is mostly Al_2O_3

Case 2
Thermal Ageing Failure



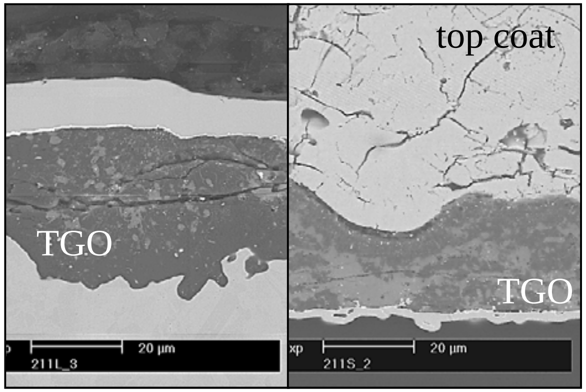
1000 hrs
1 cy
At 1100°C

The crack passes through the top coat and TGO.

TGO Thickness 9.3 µm

TGO is mostly Al_2O_3

Case 3
Al Depletion Failure



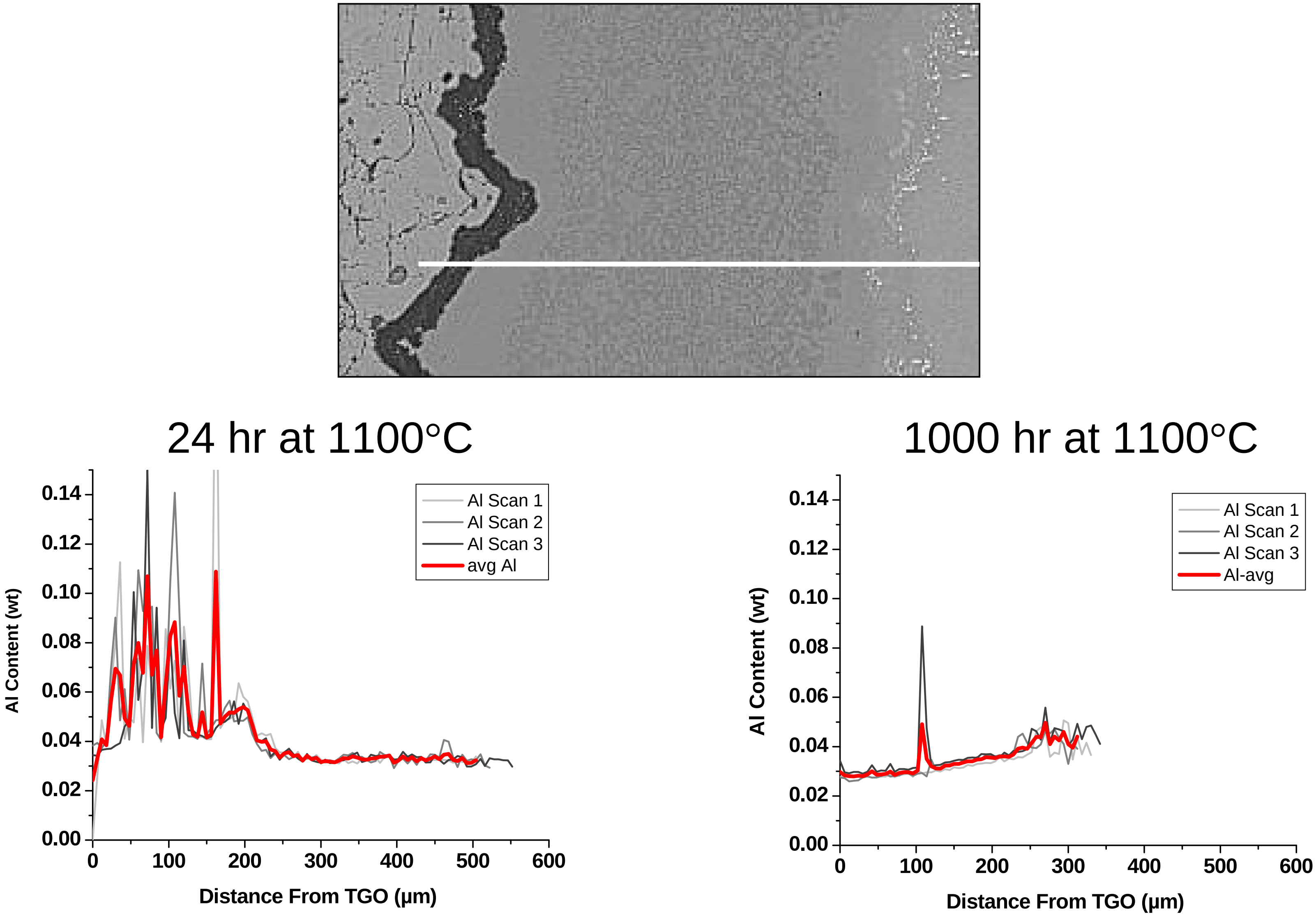
5000 hrs
1 cy
At 1050°C

The crack passes through only TGO.

TGO Thickness >30 µm
(From Al_2O_3 oxidation kinetics TGO should be 13.1 µm)

TGO contains Ni(Co,Cr)-spinels

Figure 1: Spallation Cases: Case 1) Thermal Fatigue Failure; Case 2) Thermal Ageing Failure And Case 3) Al Depletion Failure.


Electron Microprobe Line Scan

24 hr at 1100°C

1000 hr at 1100°C

Figure 2: Example of Electron Microprobe Line Scan Data from the 8/34 System.

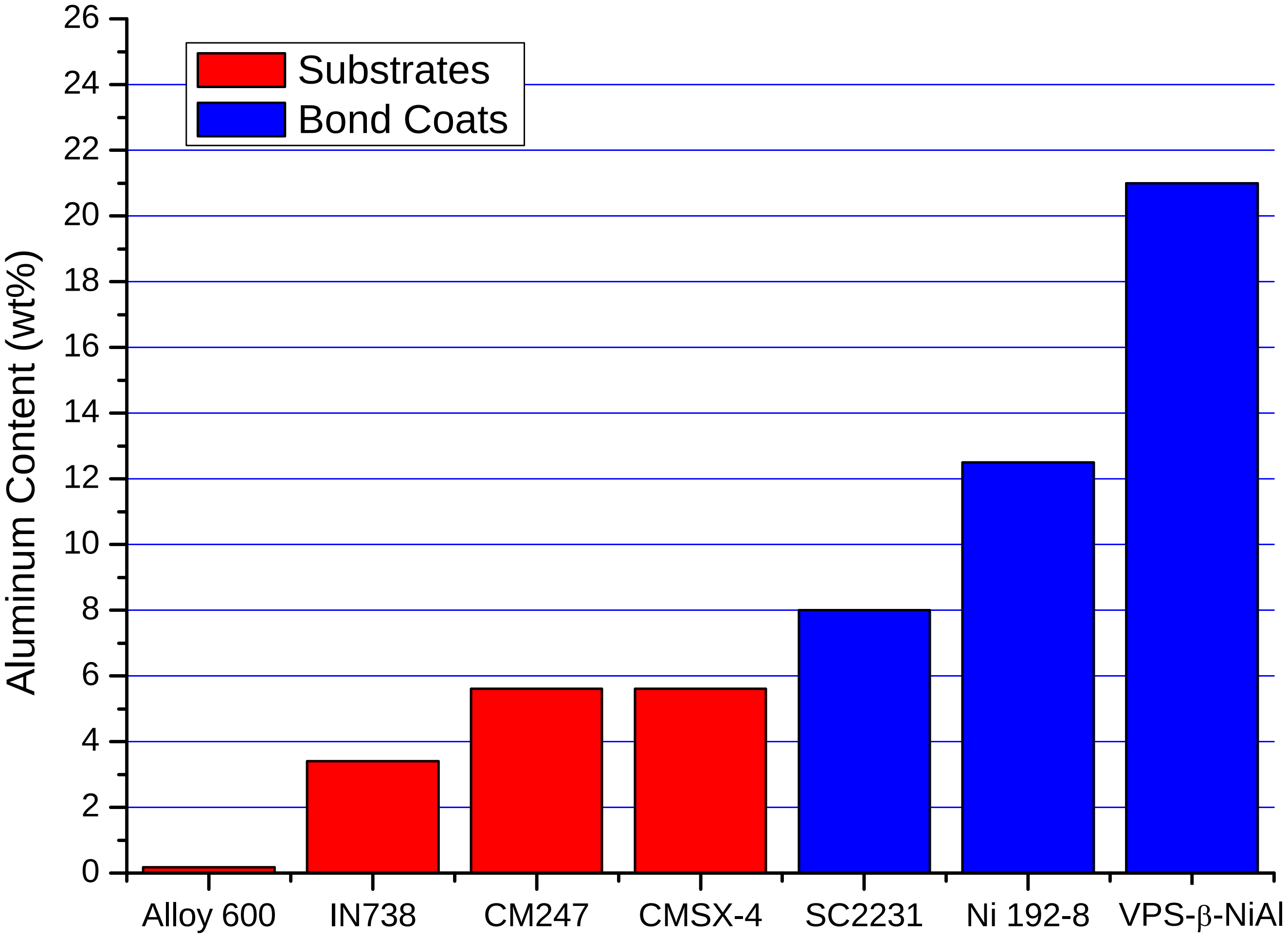


Figure 3: **Al concentrations for the substrates and bond coats investigated in this project.**

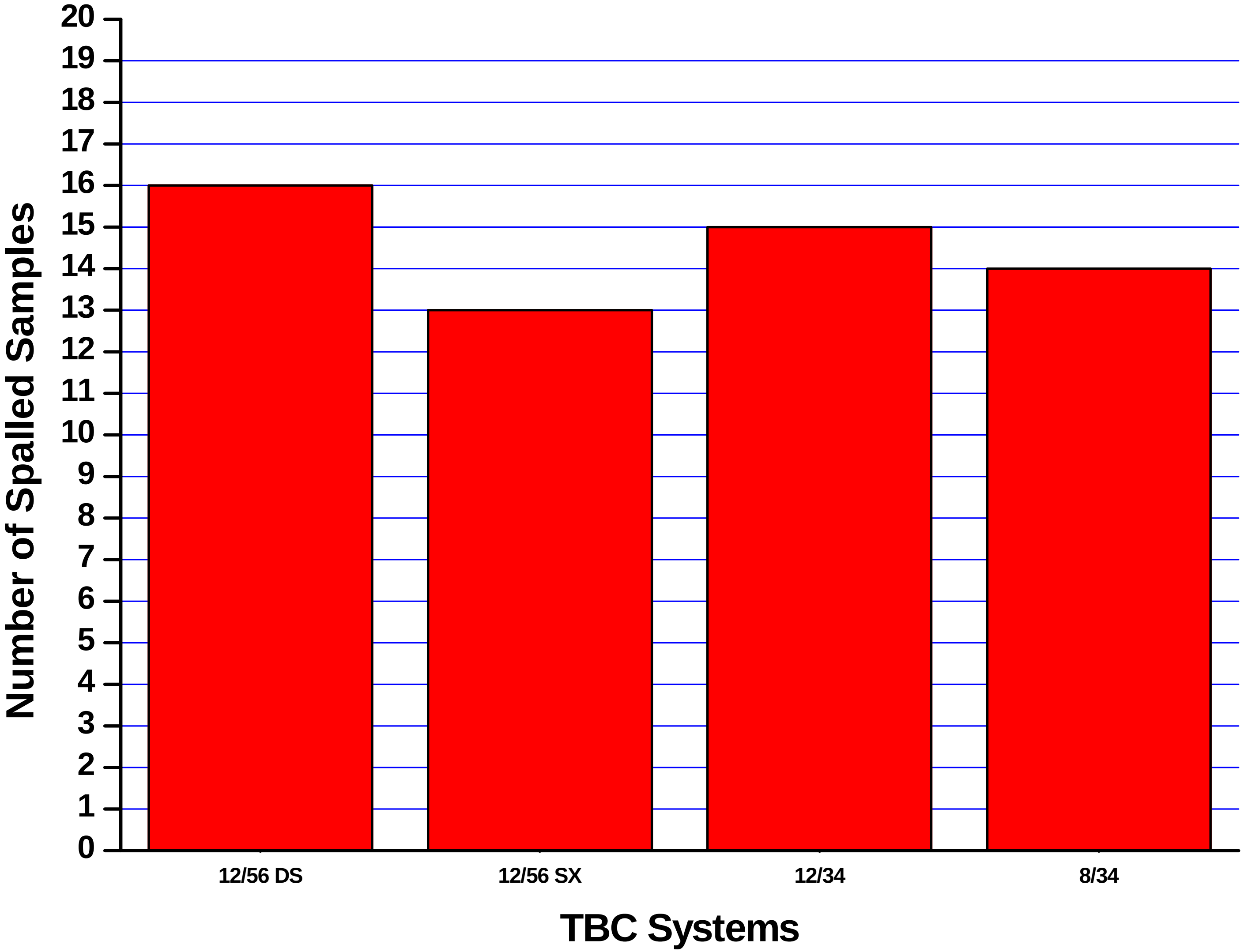


Figure 4: The number of spalled samples investigated by this project.

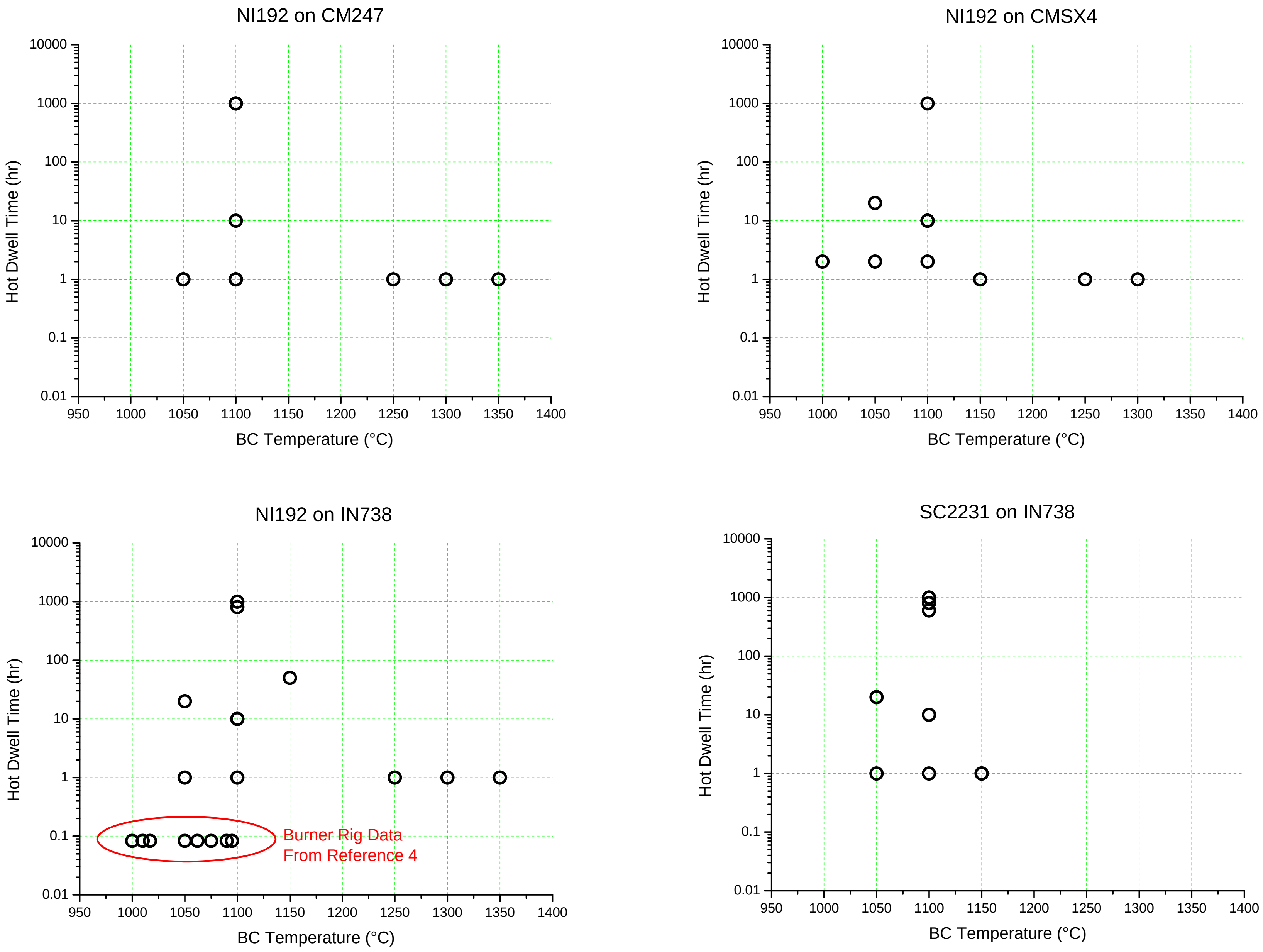


Figure 5: **The bond coat temperatures and hot dwell times of the spalled sample investigated by this project.**

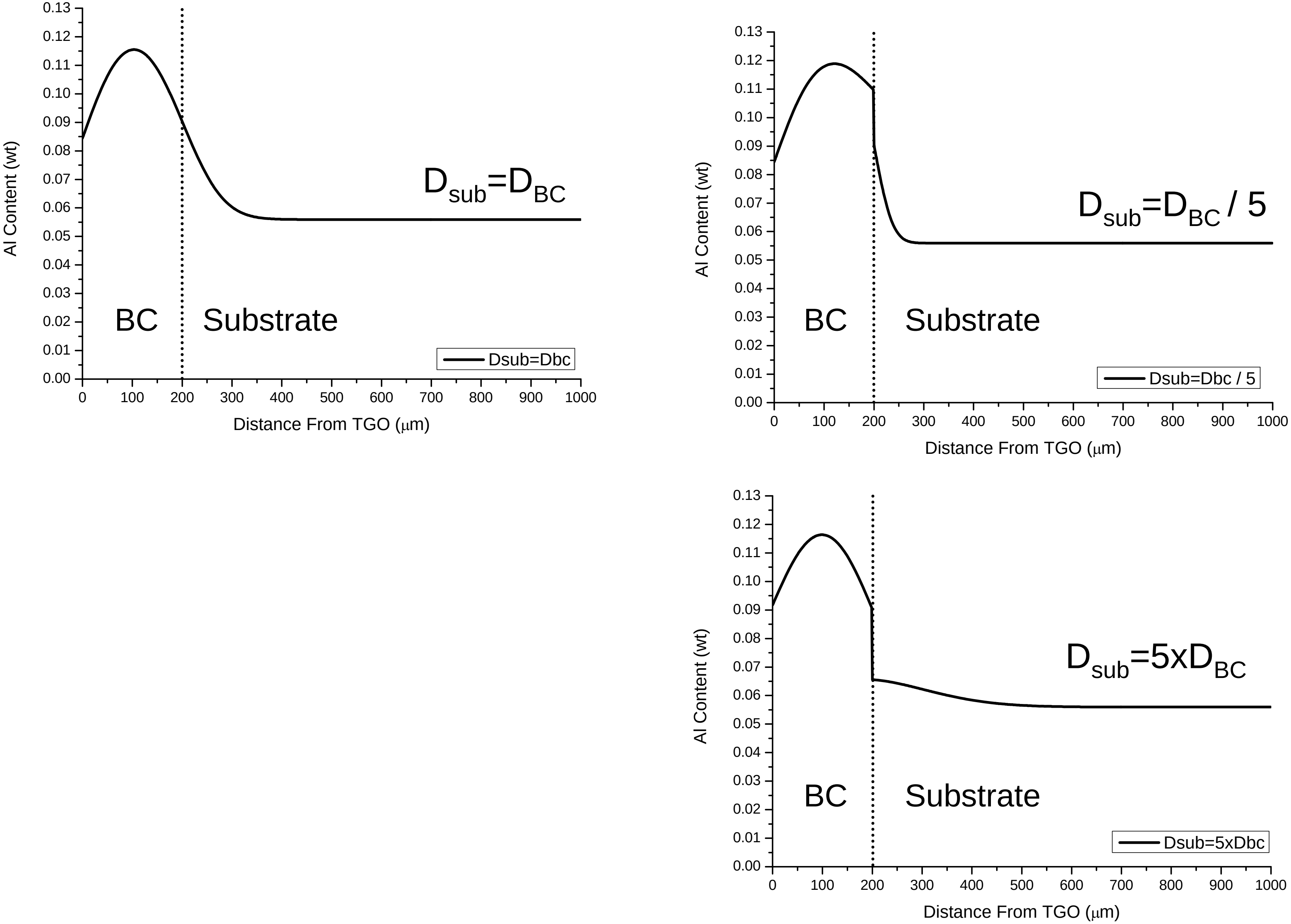


Figure 6: Al profiles for 3 possible bond coat / substrate Al diffusion situations.

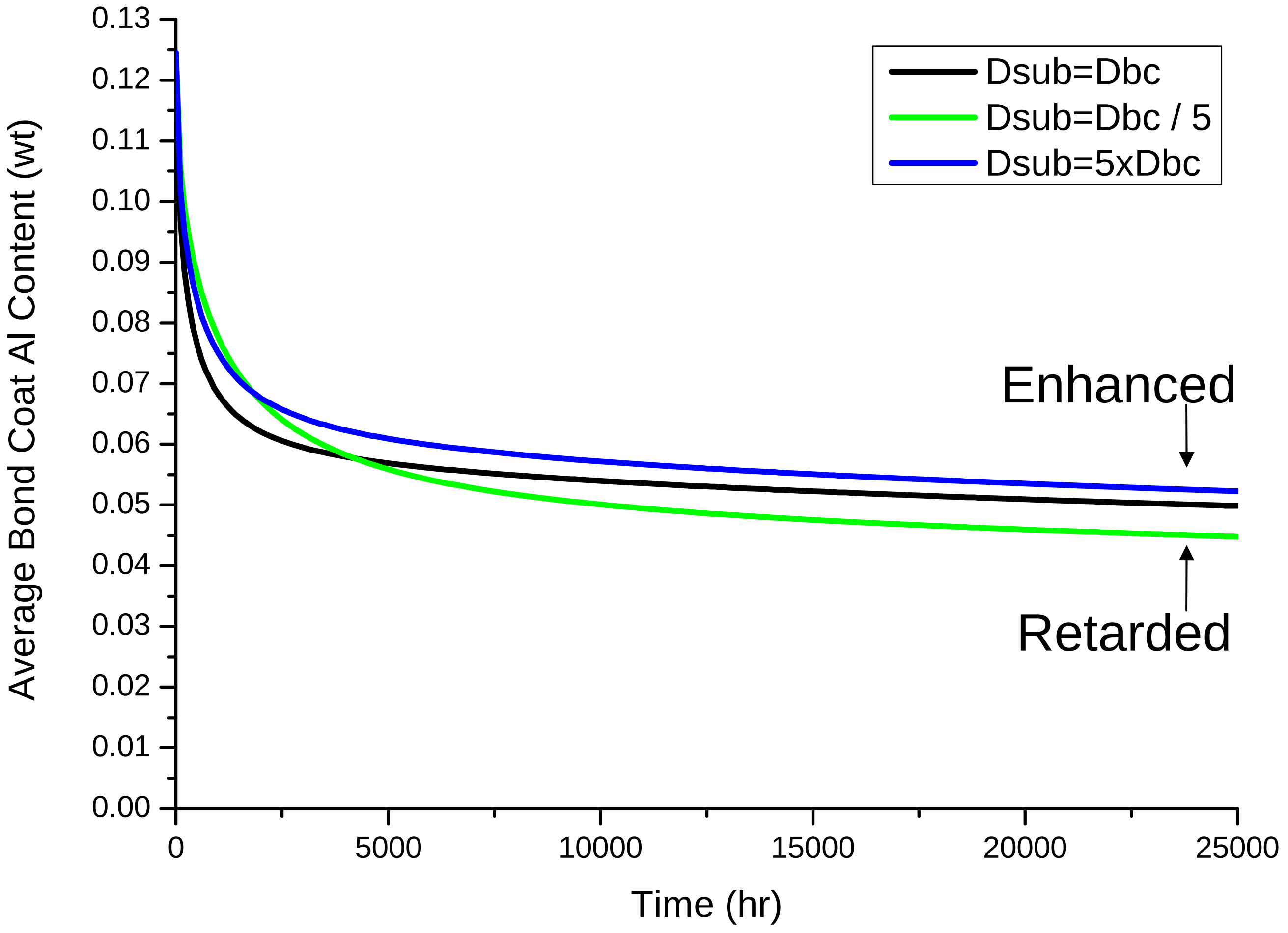


Figure 7: **Al depletion kinetics for 3 possible bond coat / substrate Al diffusion situations.**

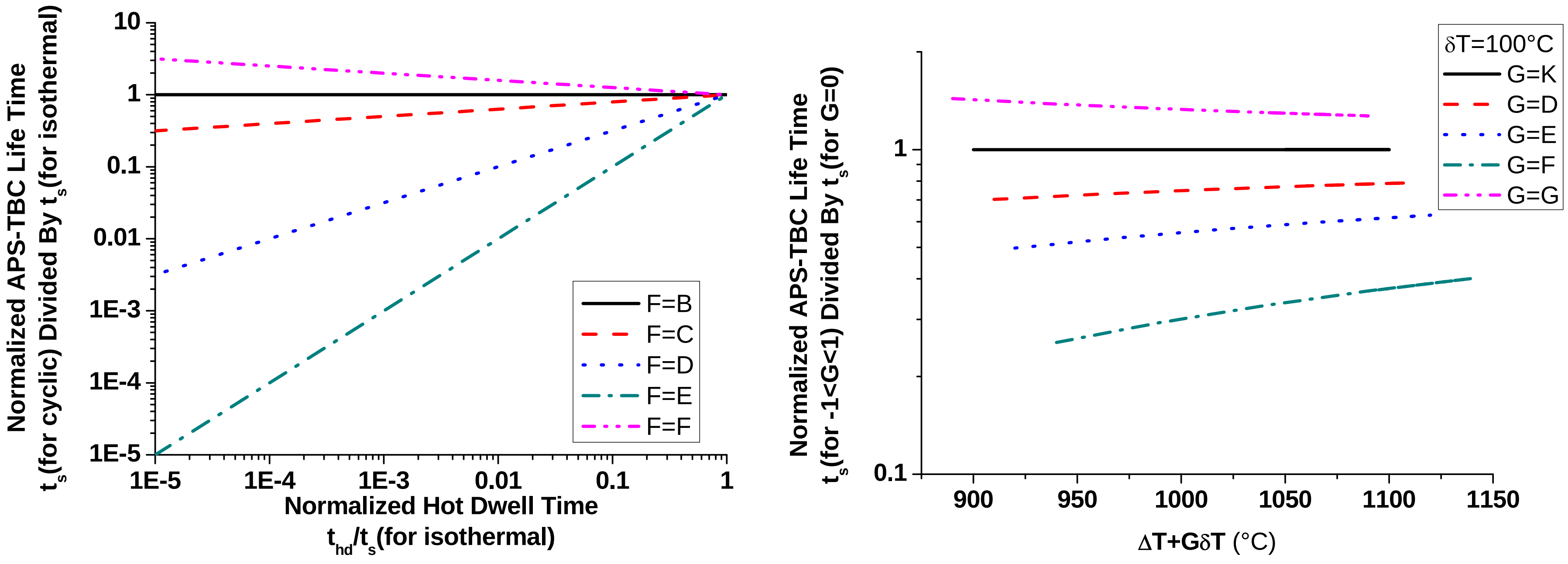
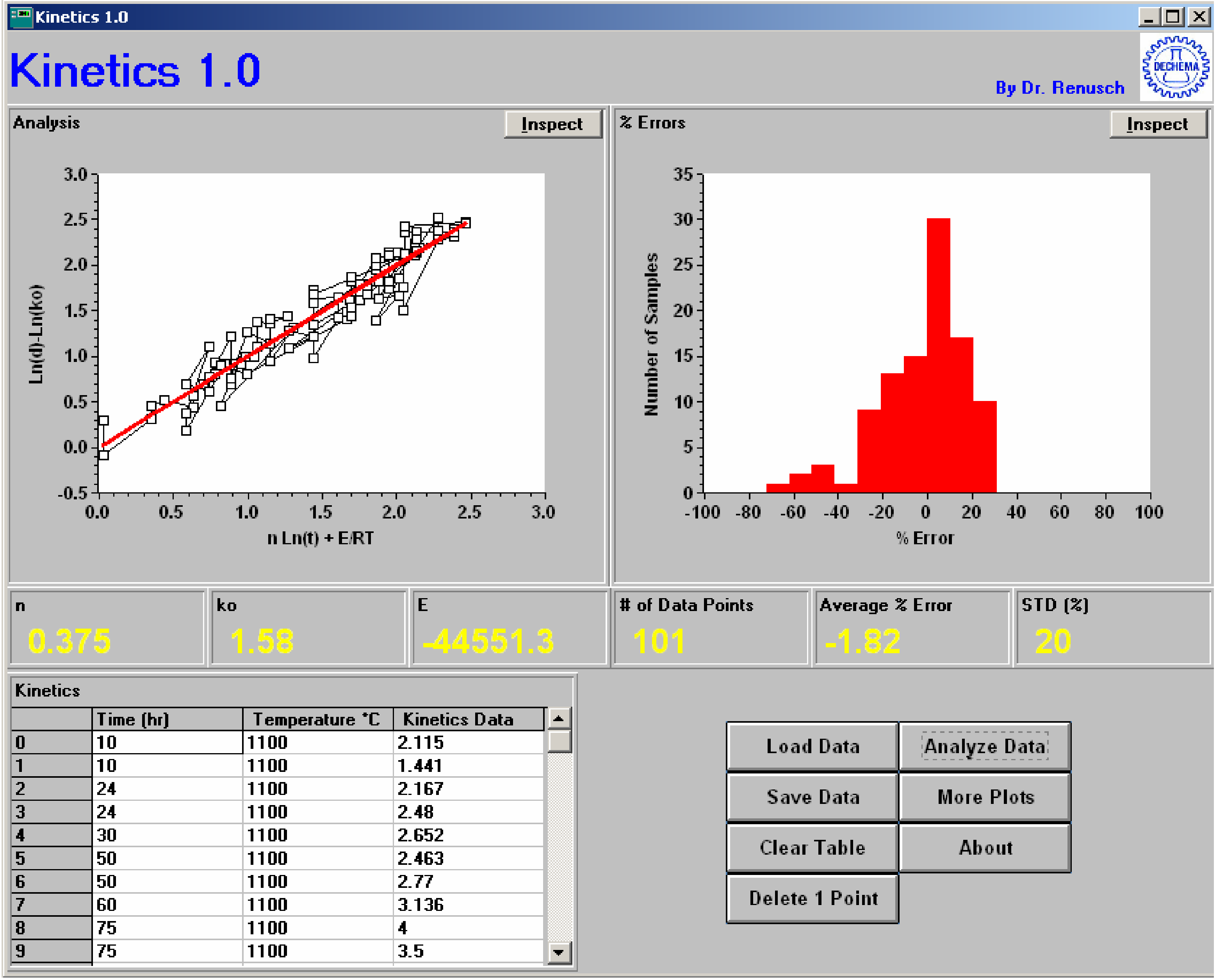


Figure 8:The change in the normalized TBC life time for different values of the thermal fatigue parameter F (left side). The change in the normalized TBC life time for different values of the modelling parameter G (right side).

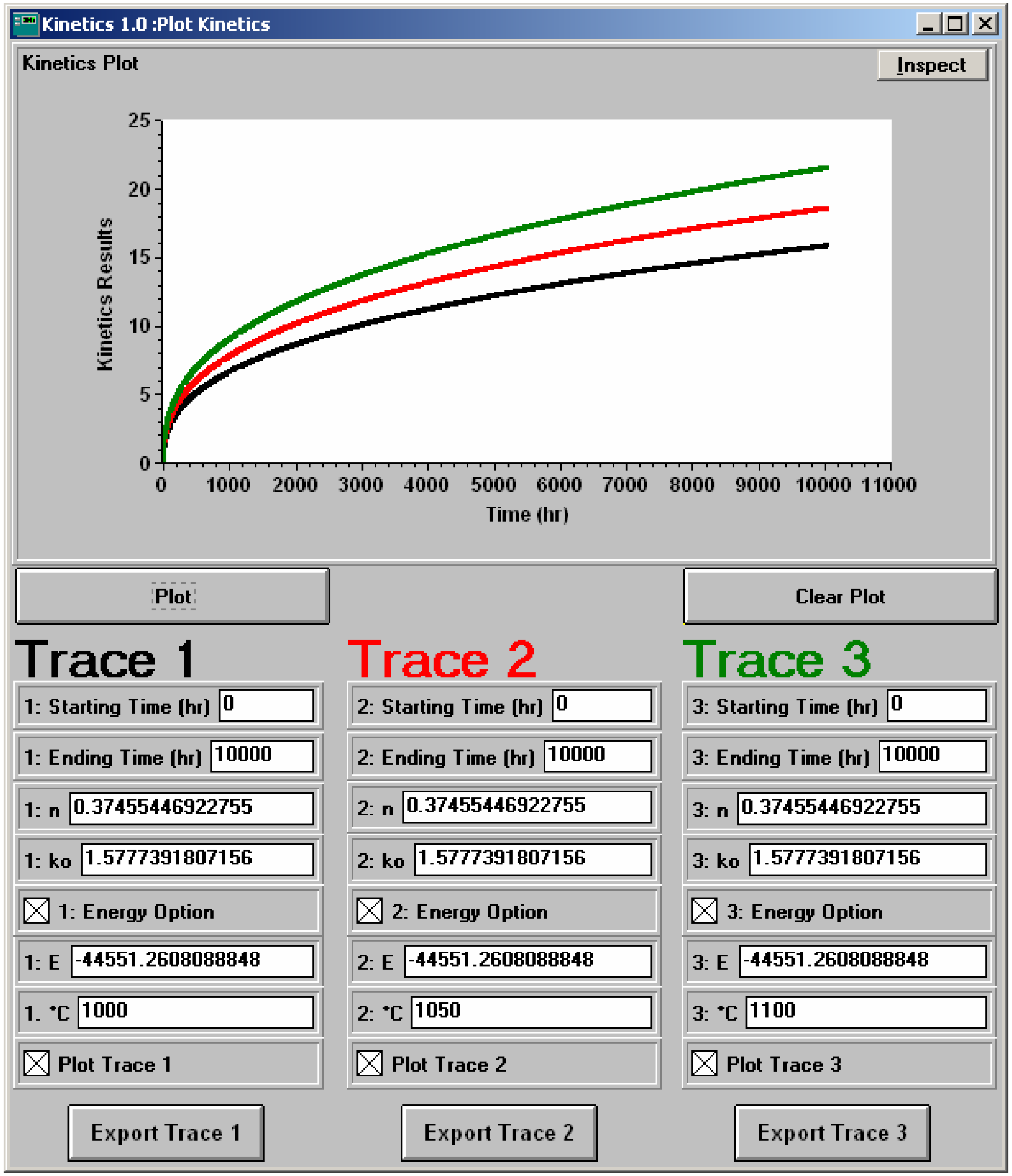


n	ko	E	# of Data Points	Average % Error	STD (%)
0.375	1.58	-44551.3	101	-1.82	20

Kinetics

	Time (hr)	Temperature °C	Kinetics Data
0	10	1100	2.115
1	10	1100	1.441
2	24	1100	2.167
3	24	1100	2.48
4	30	1100	2.652
5	50	1100	2.463
6	50	1100	2.77
7	60	1100	3.136
8	75	1100	4
9	75	1100	3.5

Figure 9: “Analysis” Screen of the Kinetics 1.0 software.



Trace 1

1: Starting Time (hr) 0
1: Ending Time (hr) 10000
1: n 0.37455446922755
1: ko 1.5777391807156
☒ 1: Energy Option
1: E -44551.2608088848
1. °C 1000
☒ Plot Trace 1

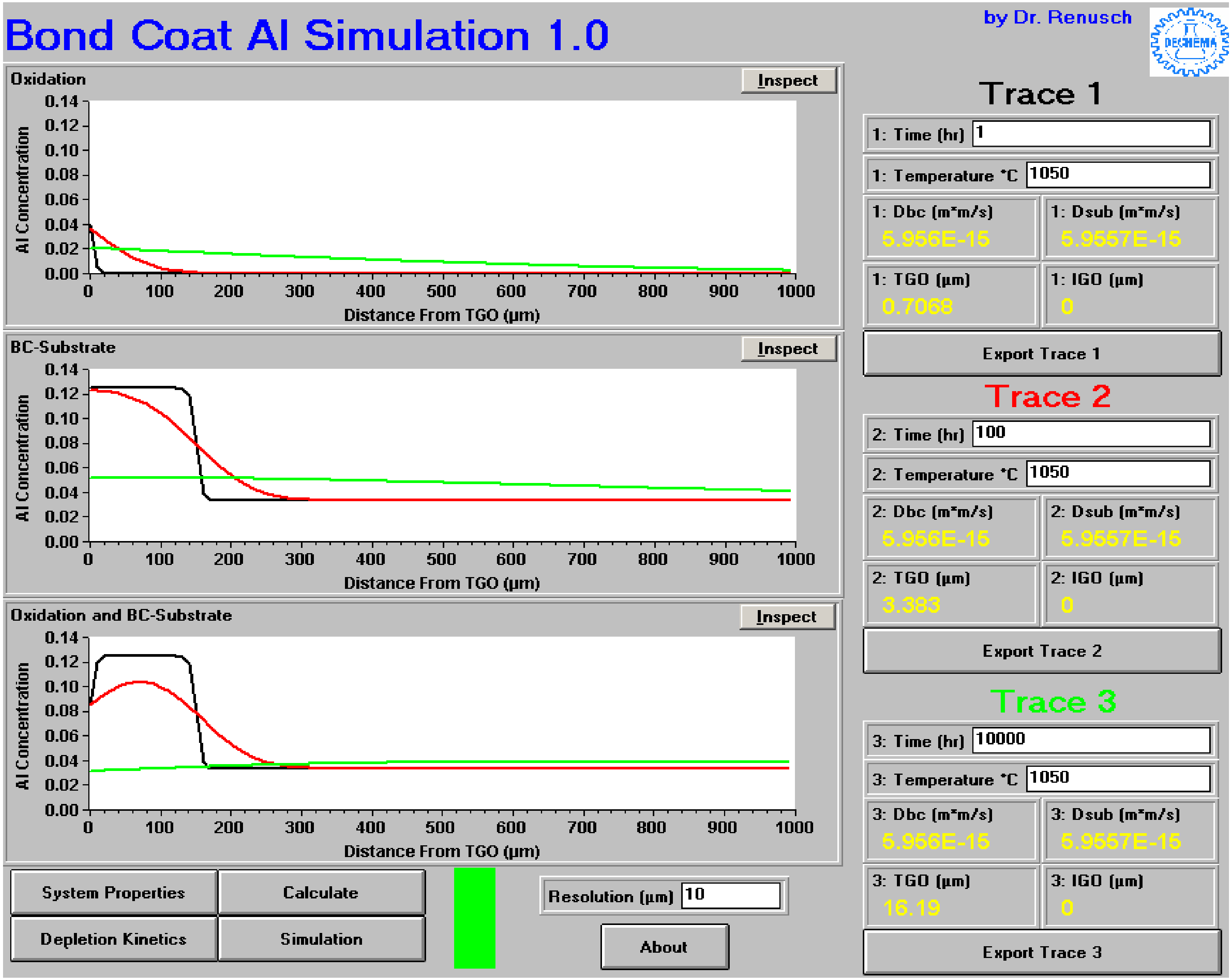
Trace 2

2: Starting Time (hr) 0
2: Ending Time (hr) 10000
2: n 0.37455446922755
2: ko 1.5777391807156
☒ 2: Energy Option
2: E -44551.2608088848
2: °C 1050
☒ Plot Trace 2

Trace 3

3: Starting Time (hr) 0
3: Ending Time (hr) 10000
3: n 0.37455446922755
3: ko 1.5777391807156
☒ 3: Energy Option
3: E -44551.2608088848
3: °C 1100
☒ Plot Trace 3

Figure 10: “Plots” Screen of the “Kinetics 1.0” software.



Trace 1

1: Time (hr) 1

1: Temperature °C 1050

1: Dbc (m*m/s) 5.956E-15

1: Dsub (m*m/s) 5.9557E-15

1: TGO (µm) 0.7068

1: IGO (µm) 0

Trace 2

2: Time (hr) 100

2: Temperature °C 1050

2: Dbc (m*m/s) 5.956E-15

2: Dsub (m*m/s) 5.9557E-15

2: TGO (µm) 3.383

2: IGO (µm) 0

Trace 3

3: Time (hr) 10000

3: Temperature °C 1050

3: Dbc (m*m/s) 5.956E-15

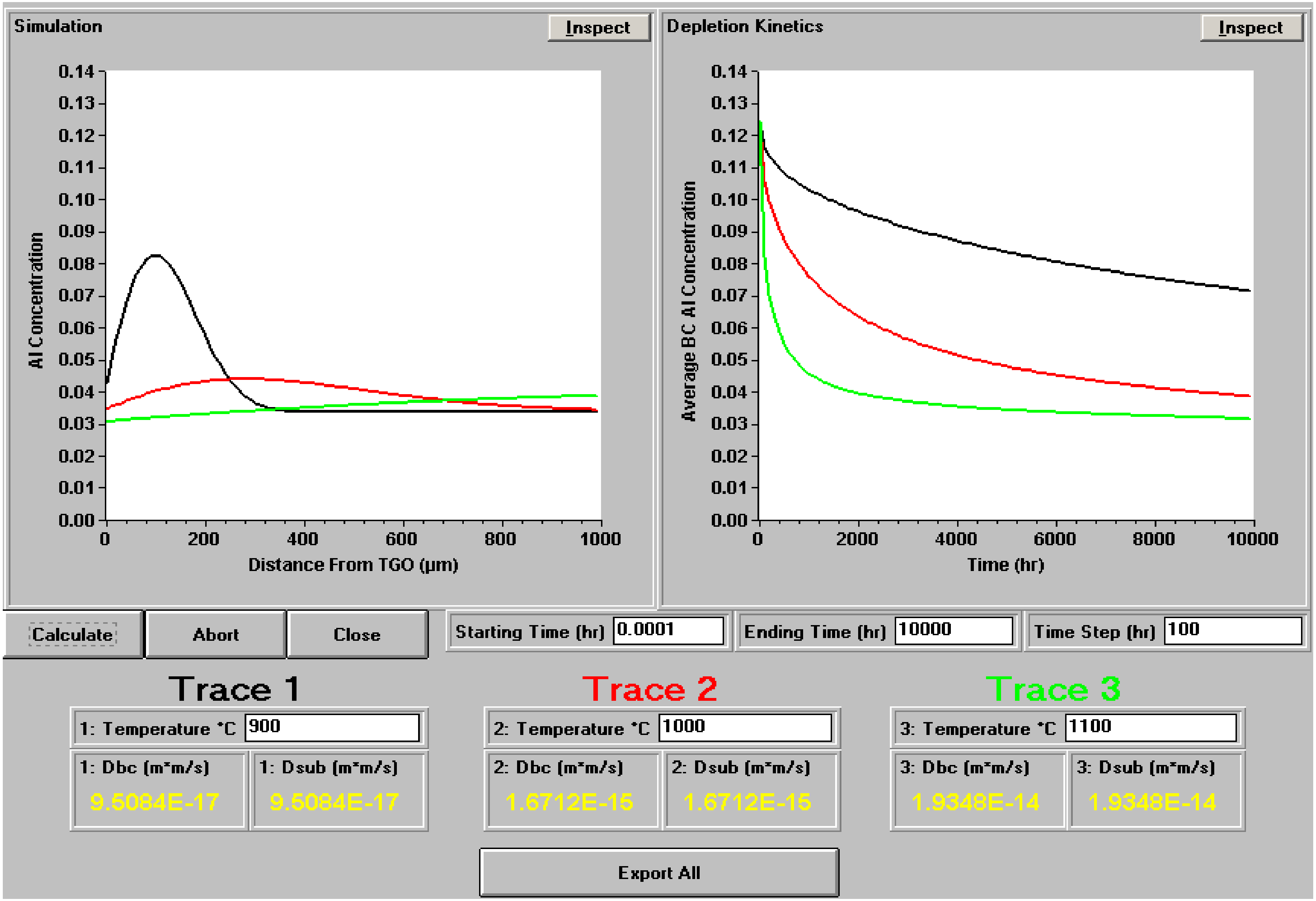
3: Dsub (m*m/s) 5.9557E-15

3: TGO (µm) 16.19

3: IGO (µm) 0

Resolution (µm) 10

Figure 11: “Analysis” Screen of the “Bond Coat Al Simulation 1.0” software.



Starting Time (hr) 0.0001

Ending Time (hr) 10000

Time Step (hr) 100

Trace 1

1: Temperature °C 900

1: Dbc (m*m/s) 9.5084E-17

1: Dsub (m*m/s) 9.5084E-17

Trace 2

2: Temperature °C 1000

2: Dbc (m*m/s) 1.6712E-15

2: Dsub (m*m/s) 1.6712E-15

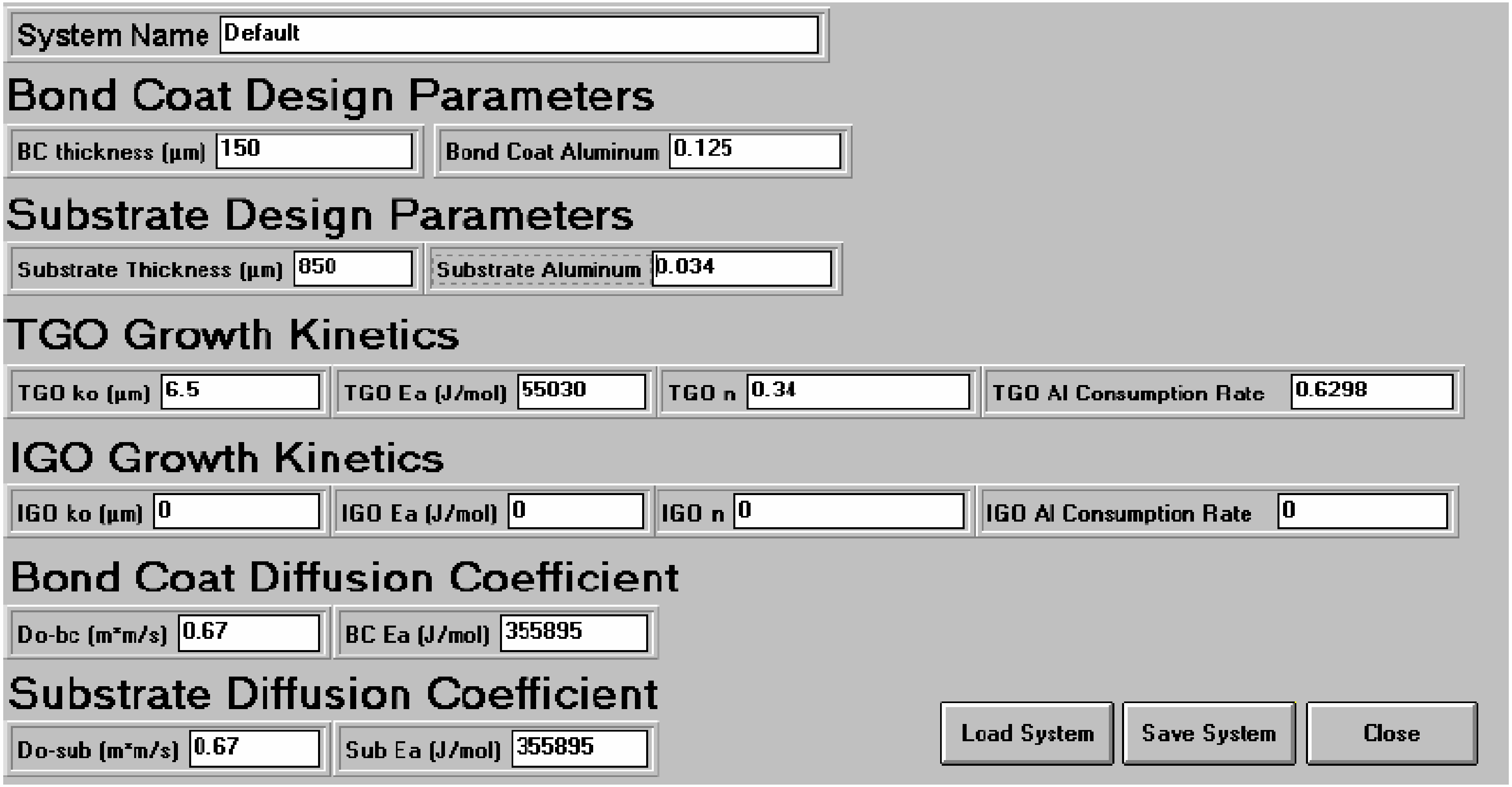
Trace 3

3: Temperature °C 1100

3: Dbc (m*m/s) 1.9348E-14

3: Dsub (m*m/s) 1.9348E-14

Figure 12: Aluminum “Depletion Kinetics” Screen of the “Bond Coat Al Simulation 1.0” software.



System Name: Default

Bond Coat Design Parameters

BC thickness (µm): 150

Bond Coat Aluminum: 0.125

Substrate Design Parameters

Substrate Thickness (µm): 850

Substrate Aluminum: 0.034

TGO Growth Kinetics

TGO ko (µm): 6.5

TGO Ea (J/mol): 55030

TGO n: 0.34

TGO Al Consumption Rate: 0.6298

IGO Growth Kinetics

IGO ko (µm): 0

IGO Ea (J/mol): 0

IGO n: 0

IGO Al Consumption Rate: 0

Bond Coat Diffusion Coefficient

Do-bc (m*m/s): 0.67

BC Ea (J/mol): 355895

Substrate Diffusion Coefficient

Do-sub (m*m/s): 0.67

Sub Ea (J/mol): 355895

Figure 13: “System Properties” Screen of the “Bond Coat Al Simulation 1.0” software.

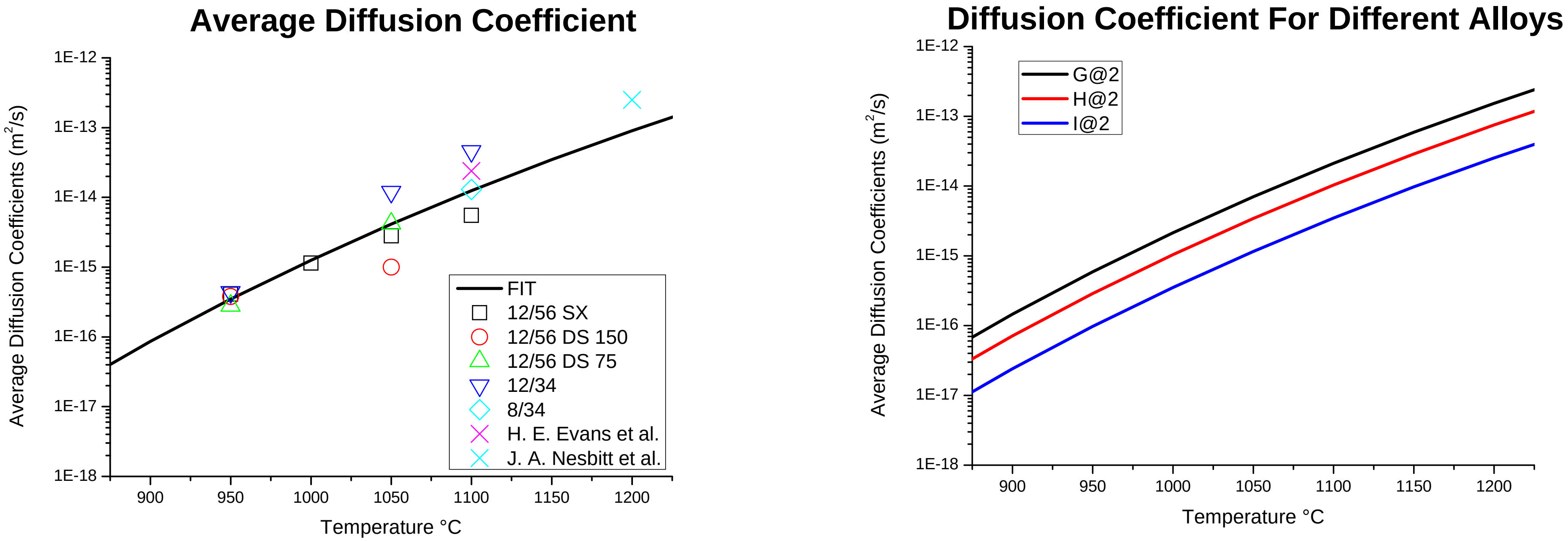


Figure 14: The binary diffusion coefficients for bond coat and substrate aluminum diffusion.

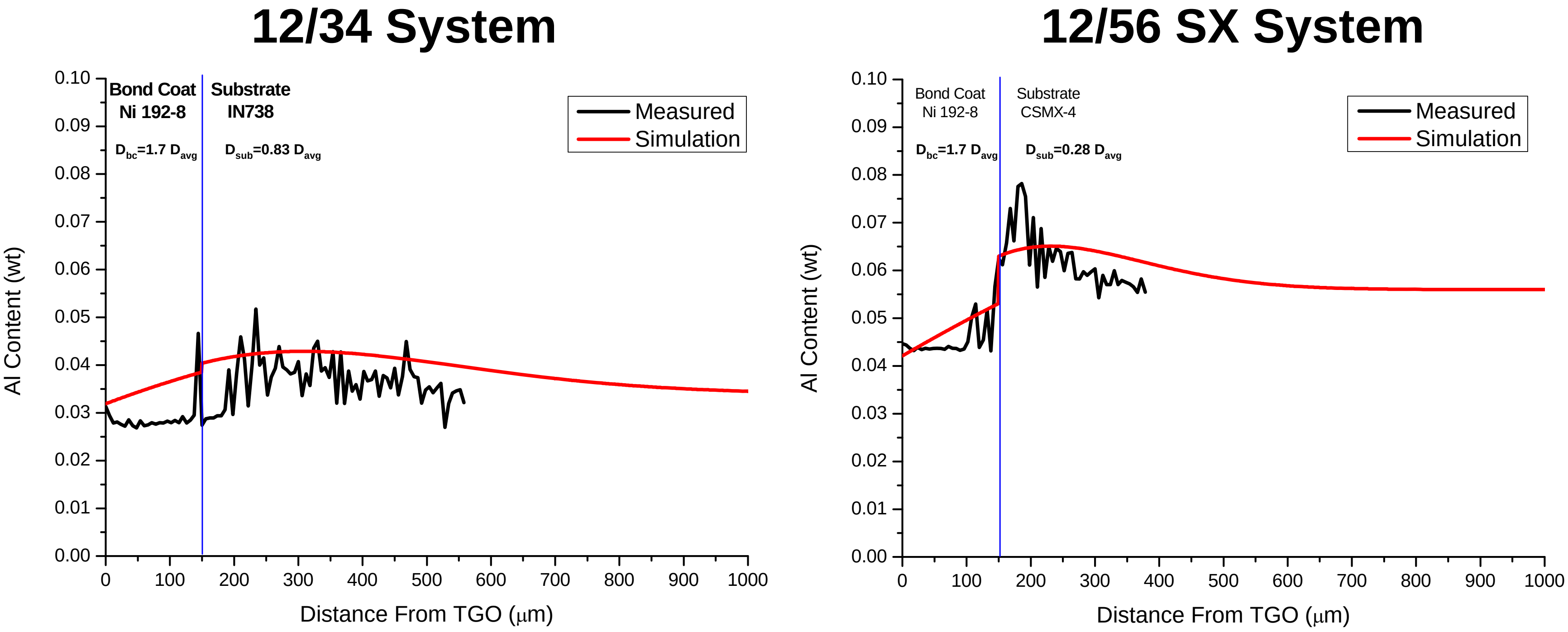
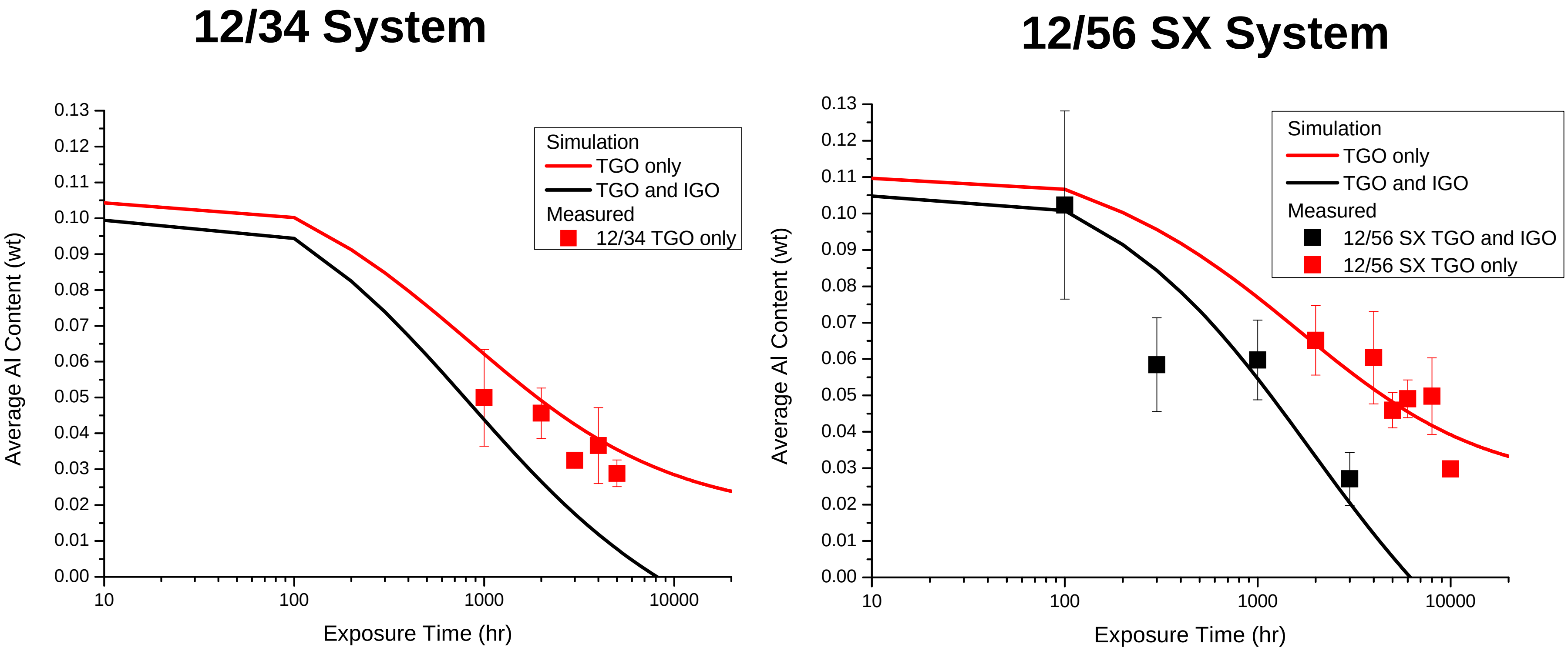
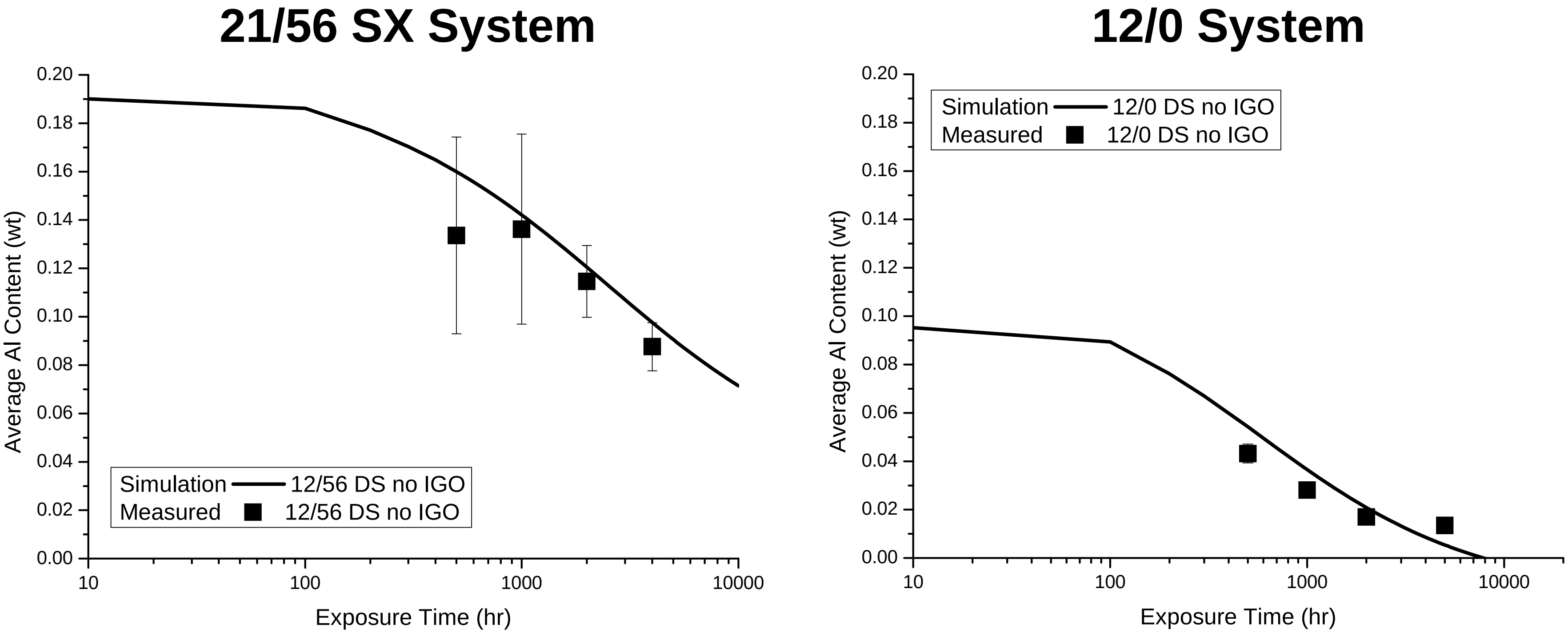


Figure 15: Measured and simulated aluminum profiles for the 12/34 and 12/56 SX system after 5000hr at 1050°C. The simulated profiles were made using the "Bond Coat Al Simulation 1.0" prototype software tool.


12/34 System

12/56 SX System

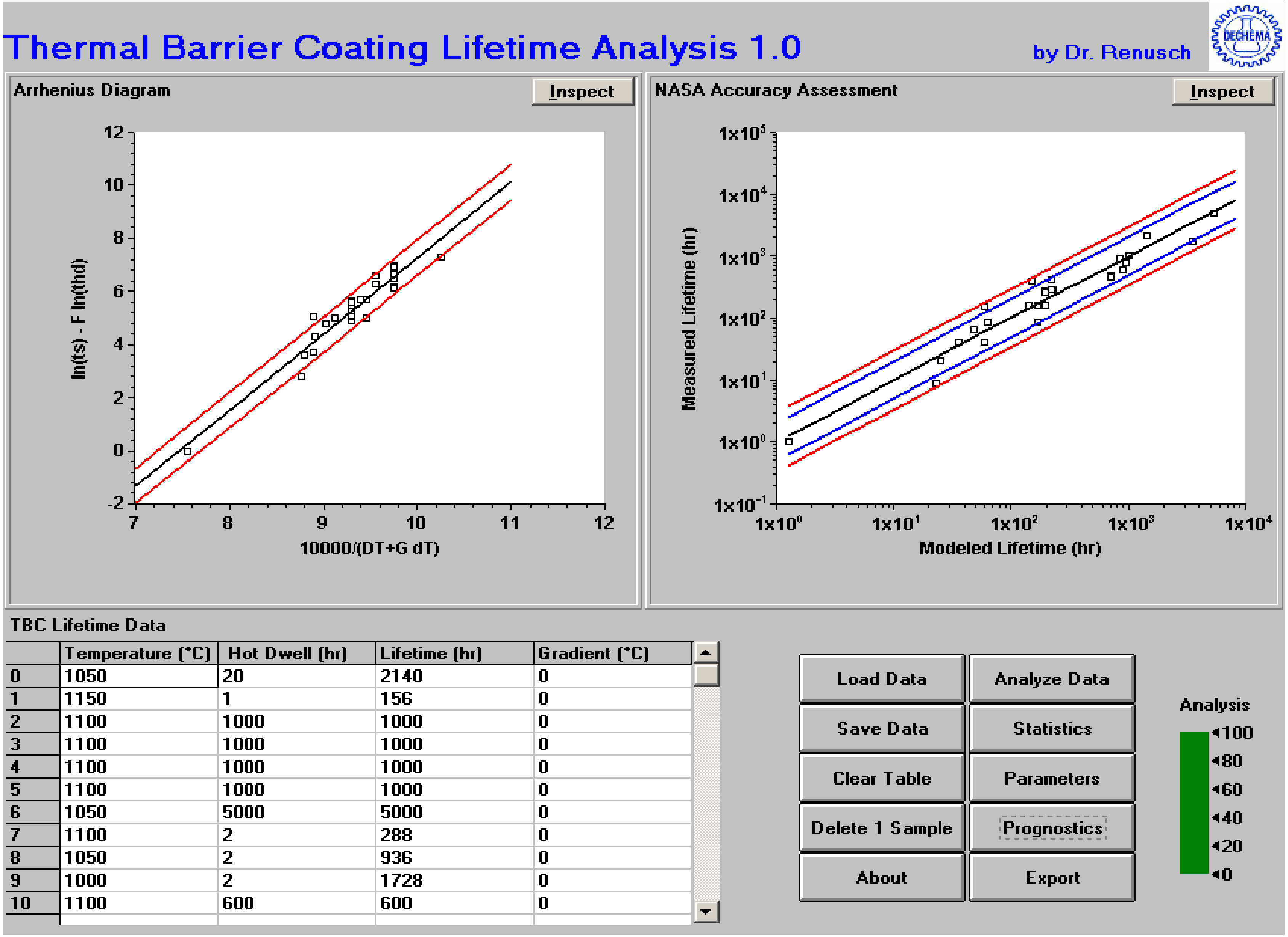
Figure 16: Measured and simulated bond coat Al depletion kinetics for exposure at 1050°C. The simulated depletion kinetics were made using the "Bond Coat Al Simulation 1.0" prototype software tool.



21/56 SX System

12/0 System

Figure 17: Measured and simulated bond coat Al depletion kinetics for exposure at 1050°C. The simulated depletion kinetics were calculated using the "Bond Coat Al Simulation 1.0" prototype software tool.



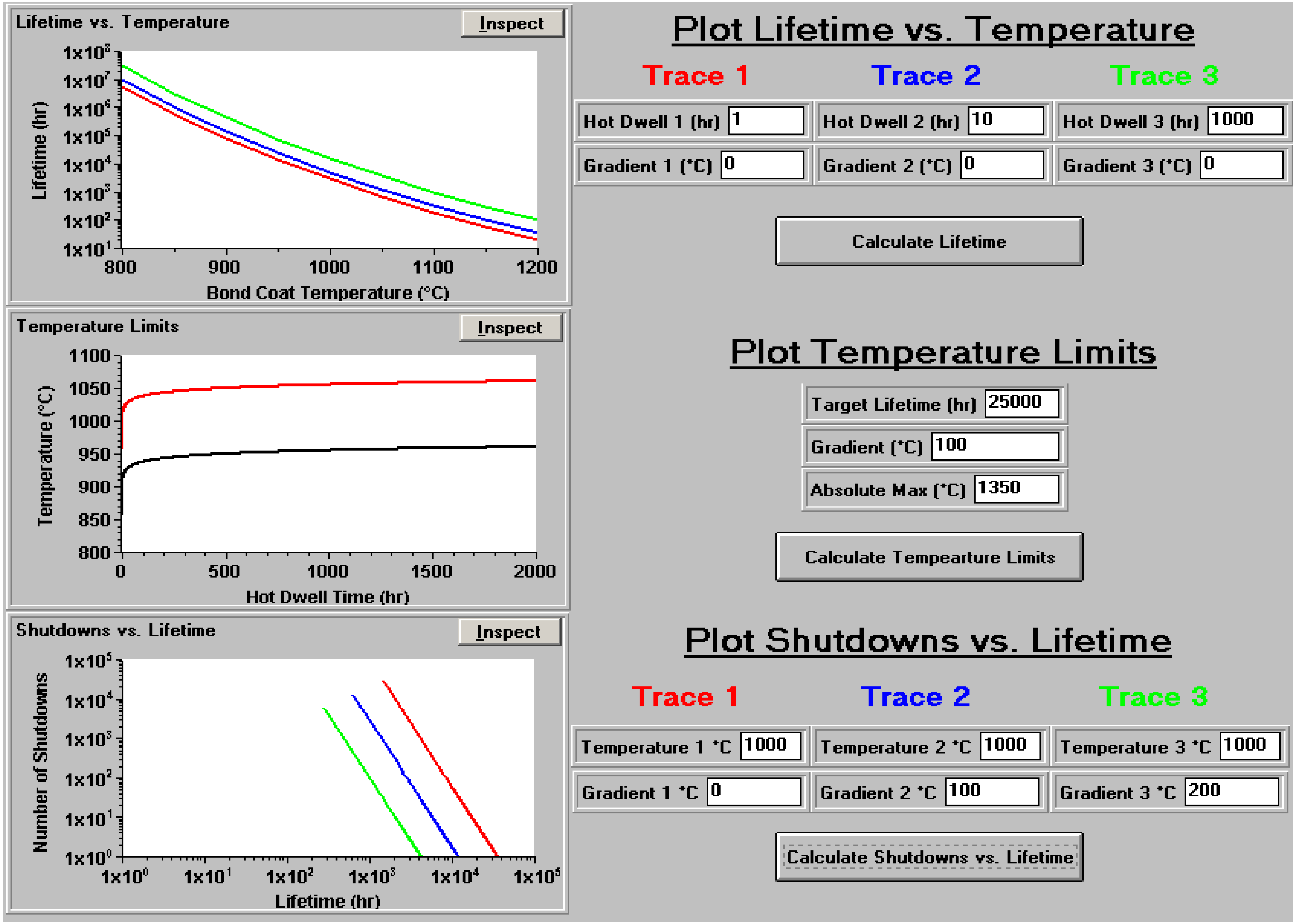
Thermal Barrier Coating Lifetime Analysis 1.0

by Dr. Renusch

TBC Lifetime Data

	Temperature (°C)	Hot Dwell (hr)	Lifetime (hr)	Gradient (°C)
0	1050	20	2140	0
1	1150	1	156	0
2	1100	1000	1000	0
3	1100	1000	1000	0
4	1100	1000	1000	0
5	1100	1000	1000	0
6	1050	5000	5000	0
7	1100	2	288	0
8	1050	2	936	0
9	1000	2	1728	0
10	1100	600	600	0

Figure 18: “Analysis” Screen of the “Thermal Barrier Coating Lifetime Analysis 1.0” software.



Plot Lifetime vs. Temperature

Trace 1		Trace 2		Trace 3	
Hot Dwell 1 (hr)	1	Hot Dwell 2 (hr)	10	Hot Dwell 3 (hr)	1000
Gradient 1 (°C)	0	Gradient 2 (°C)	0	Gradient 3 (°C)	0

Plot Temperature Limits

Target Lifetime (hr)	25000
Gradient (°C)	100
Absolute Max (°C)	1350

Plot Shutdowns vs. Lifetime

Trace 1		Trace 2		Trace 3	
Temperature 1 °C	1000	Temperature 2 °C	1000	Temperature 3 °C	1000
Gradient 1 °C	0	Gradient 2 °C	100	Gradient 3 °C	200

Figure 19: “Prognostics” Screen of the “Thermal Barrier Coating Lifetime Analysis 1.0” software.

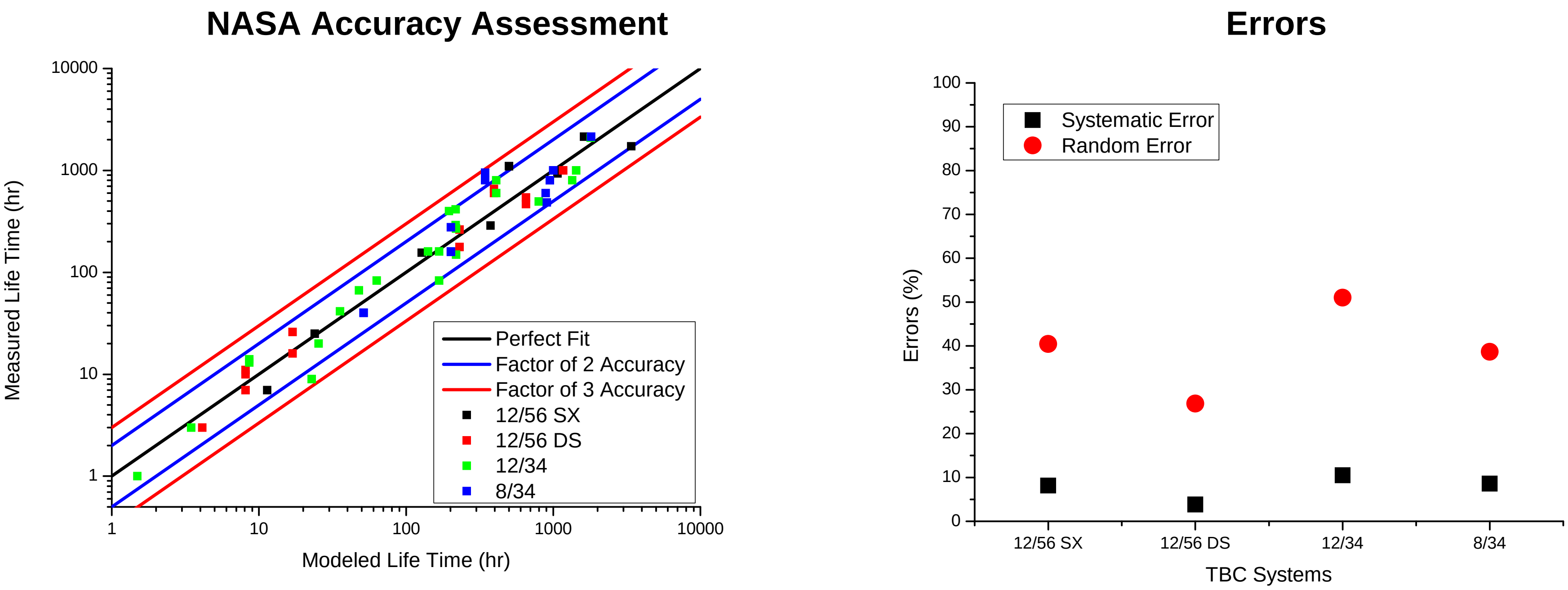


Figure 20: NASA accuracy assessment and errors plots. Calculated by the "Thermal Barrier Coating Lifetime Analysis 1.0" software.

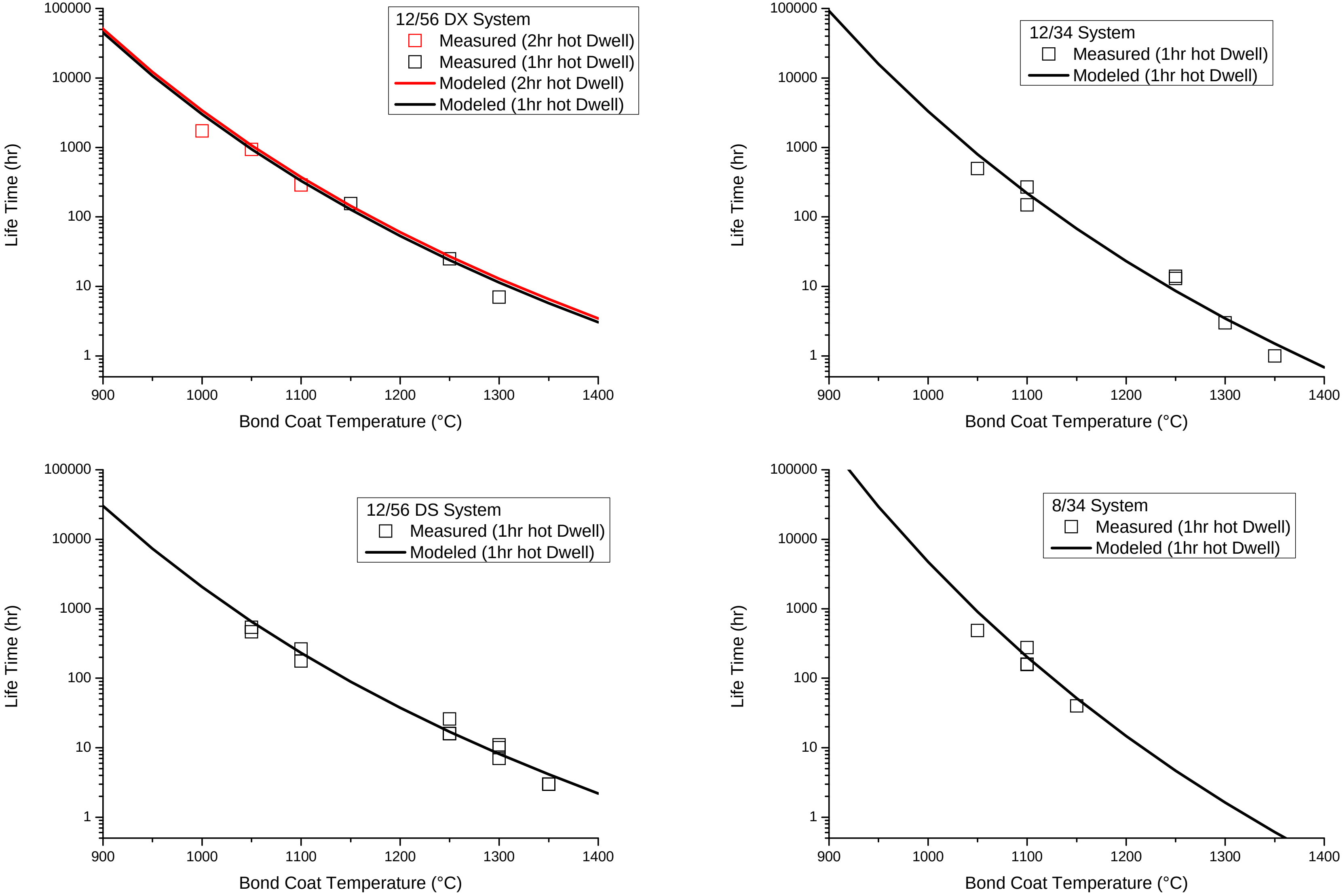


Figure 21: Measured and Modeled Spallation Life Times. The calculations were made by the "Thermal Barrier Coating Lifetime Analysis 1.0" software.

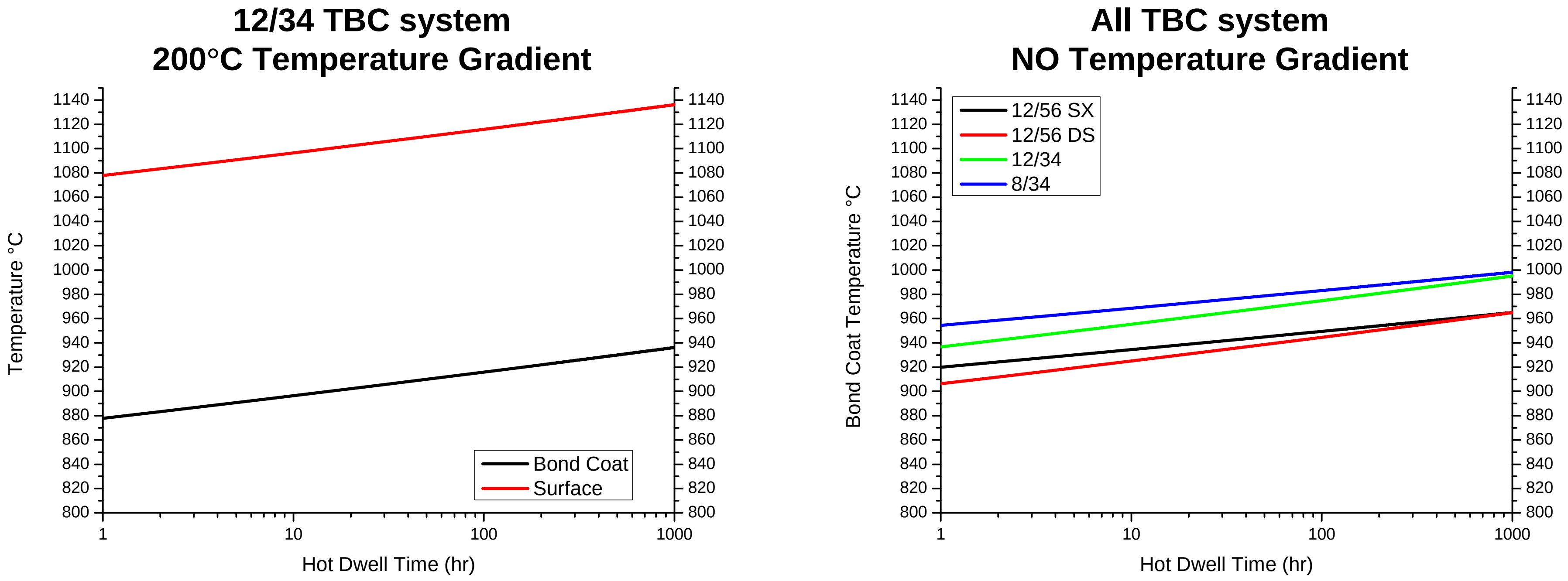
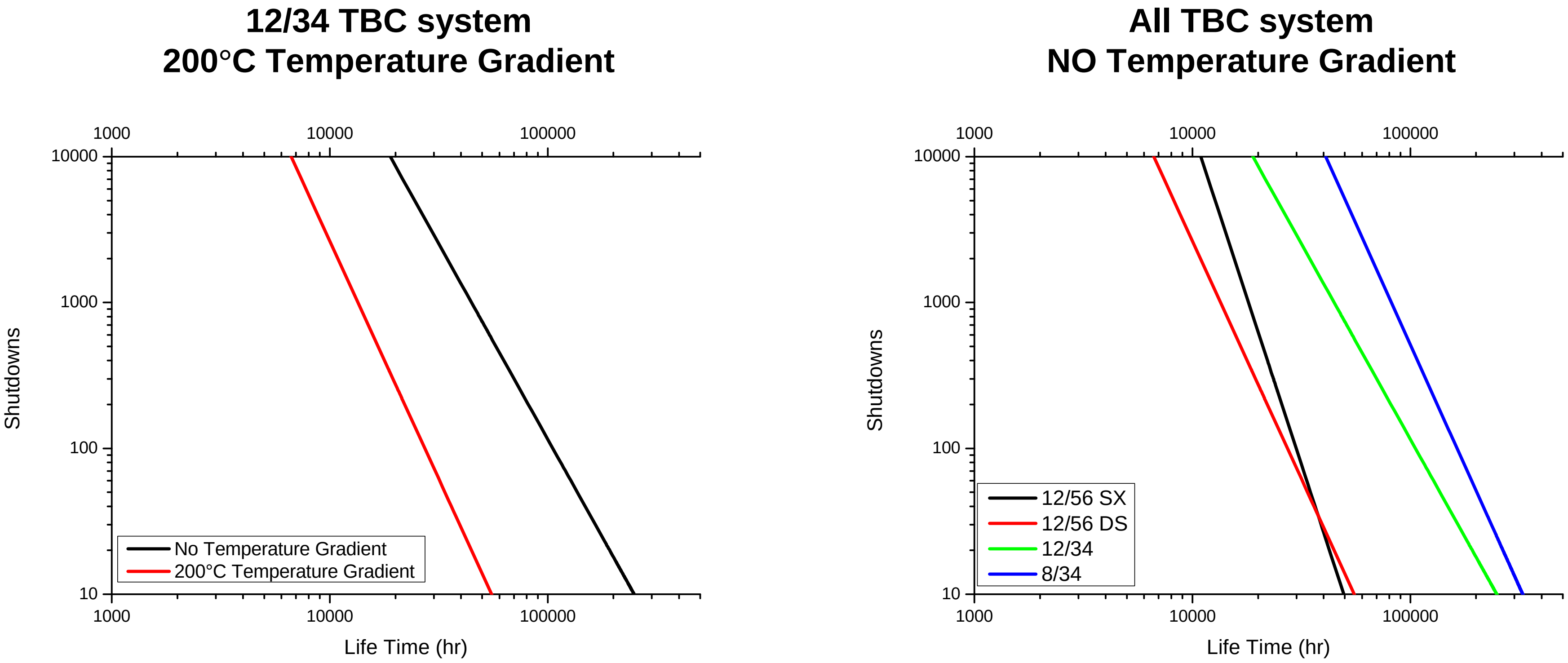


Figure 22: Calculated temperature limits for 25000h life time. Calculated by the “Thermal Barrier Coating Lifetime Analysis 1.0” software.



12/34 TBC system
200°C Temperature Gradient

All TBC system
NO Temperature Gradient

Figure 23: Number of Turbine Shutdowns vs. Spallation Life Time for operations at bond coat temperatures of 950°C. Calculated by the “Thermal Barrier Coating Lifetime Analysis 1.0” software.