

Application of Accelerators in High Temperature Materials Research

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Abstract: Components in high temperature technology have to withstand extreme service conditions with temperatures above 800°C. Two classes of materials are considered: TiAl-alloys and Ni-based superalloys. The fluorine effect offers an innovative way for oxidation protection. The increasing interest in Gamma-TiAl based alloys is motivated by their excellent specific strength at high temperatures which offers a high application potential in aerospace and automotive industries. To improve the insufficient oxidation resistance at temperatures above 750°C the fluorine effect is applied to stimulate the formation of a dense protective alumina scale. The parameters for the long time stability are determined and the conditions for the long time oxidation protection are formulated by using ion implantation and ion beam analysis (PIGE). The widely used Ni-base alloys form only a discontinuous non-protective alumina scale due to their low Al-content. By using the halogen effect a dense protective alumina scale can be established. Based on thermodynamical calculations the optimal parameters are determined by using ion implantation and non-destructive PIGE-analysis.

1. Introduction

Due to their high specific strength at high temperatures the γ -TiAl (46-50 at.-% Al) based alloys are believed to have a high application potential in high temperature technologies, especially in aerospace and automotive industries. In contrast to the presently used Ni-based superalloys their specific weight is reduced by about 50% leading to a lower moment of inertia for rotating parts like turbocharger rotors, exhaust valves or turbine blades. Thus lower mechanical stresses and a reduced fuel consumption can be expected. However the oxidation resistance of γ -TiAl inhibits an industrial use at temperatures above 750°C [1]. To reach higher service temperatures the surface modification is expected to avoid any detrimental influence to the excellent mechanical properties of the material. The oxidation resistance can be improved by using the so-called "halogen-effect". In [2-7] a dense alumina scale protecting the material against corrosion was formed on the surface after the application of small amounts of chlorine. However the alumina scale fails during thermocyclic loading. After fluorine ion implantation [8] or liquid phase treatment with diluted HF [9] in combination with oxidation at 900°C/air a dense alumina scale was achieved showing pronounced adherence even during cyclic oxidation. The halogen effect can be explained by a thermodynamic model assuming the preferred formation and transport of volatile Al-halides through pores and microcracks within the metal/oxide interface and their conversion into alumina forming a protective oxide scale on the surface [4]. This model was proofed by the F-depth profiles obtained by PIGE (Proton Induced Gamma-ray Emission) [8,9] showing a distinct maximum located at the metal/oxide interface [8-11]. In contrast to the initial F-concentration a pronounced fluorine decrease was found within the first hours of oxidation at 900°C. In [10,11] it was shown that dominant fluorine loss occurs during sample heating. The remaining fluorine content of less than 5 at.-% is essential for a stable fluorine effect. However technical use is only possible if the fluorine effect can be stabilized for a time of at least 1000 hours. This work is dedicated to the role of fundamental material parameters related to the stability of the fluorine effect.

At service temperatures above 900°C Ni-base superalloys with Al-contents of significantly less than 10 wt.-% Al are widely used in high temperature technology showing excellent mechanical properties. However instead of forming a dense protective alumina scale the metal is covered with a fast growing complex oxide scale [12-16] This complex mixed oxide

scale is characterized by an inward growing discontinuous alumina scale together with oxide and spinel phases which does not prevent the inward diffusion of oxygen and nitrogen. One way of oxidation protection is the use of Al-rich coatings to form a dense protective alumina scale [17-19]. Recently this method has become state of the art in industrial use for the manufacturing of turbine blades. In the second part of this paper a new method is presented which stimulates the formation of a dense protective alumina scale without increasing the Al content of the Ni base alloy. This method is based on the halogen effect which was successfully applied to TiAl-alloys.

2. Experimental

Cast γ -TiAl (Ti-50 at.-% Al) and the technical γ -Met (46.6 at.-% Al) manufactured by powder metallurgy were prepared as coupons of size $8*8*1 \text{ mm}^3$ and polished with SiC paper down to 4000 and 1200 grit resp. Microstructural investigations showed minor amounts of the α_2 -Ti₃Al phase (lamellar structure) within the γ -TiAl phase. For standard implantation a fluence of $2 \times 10^{17} \text{ F cm}^{-2}$ at 20 keV was used [8]. The mean projected range of the F-ions is about 34 nm [20]. All beam line implantations were carried out at the 60 kV implanter of the Institute of Nuclear Physics (IKF) of the Johann Wolfgang Goethe - University in Frankfurt/Main using CF₄ in the gas source. The samples were oxidized isothermally and thermocyclicly (cycles of 1h) in a furnace at 900°C and 1000°C in lab air. The fluorine concentration depth profiles were determined by using the non-destructive PIGE-technique [21]. The PIGE measurements were performed at the 2.5 MV Van de Graaff accelerator of the IKF using the nuclear reaction $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ at a resonance energy of proton energies $E_p=340 \text{ keV}$ and 484 keV resp., and detecting the high energetic γ -rays (5-6 MeV) with a 10 inch NaI-detector. The information depth of the PIGE depth profiling is within $1.4 - 1.5 \text{ }\mu\text{m}$, whereas the depth resolution near the surface is about 25 nm. Finally all samples were inspected by metallographic methods and SEM. The cast Ni-base superalloy IN738 (composition see tab. 1).was cut into coupons of $10*10*1 \text{ mm}^3$. The same polishing as for the TiAl-samples was chosen. The beamline implantation was performed by using F-ions of 38 keV energy corresponding to a mean projected range of 34 nm. The isothermal oxidation treatment at 1050°C/lab air and the post oxidation investigations were done with the furnaces and methods described above.

Element	Ni	Co	Cr	Al	W	Mo	C	Ti	Ta	Others
IN 738	61,13	9,0	16,00	3,3	1,70	2,60	0,17	3,50	1,70	0,90 Nb

Table 1: Composition of the Ni-base alloy IN 738 (in wt.-%).

3. Stability of the F-effect during oxidation of TiAl-alloys

The F-depth profiles performed by beam line implantation in TiAl can be calculated by using the Monte Carlo simulation software T-DYN [22]. The F-depth profiles were measured before and after oxidation by using PIGE. In fig. 1 implantation profiles of $1.23 \times 10^{17} \text{ F cm}^{-2}$ and $2 \times 10^{17} \text{ F cm}^{-2}$ at 20 keV are presented showing relatively high F concentrations within the near surface region. For the fluence of $2 \times 10^{17} \text{ F cm}^{-2}/20 \text{ keV}$ the F maximum of nearly 50 at.-% is located in a depth of about 35 – 40 nm. In contrast to this the F-profiles show a significantly different behaviour already after 1 hour of oxidation. The F content is reduced mostly by evaporation of TiF₄ during the heating process as reported in [10,11]. The F-profile can be divided into 3 different regions as illustrated in fig. 2. A negligible F content occurs within the formed initial alumina scale of about 200 nm thickness. This alumina scale – once formed – acts as a diffusion barrier and prevents further F loss from the surface. The F

maximum of about 3 at.-% is located at the metal/oxide interface, followed by a region which is characterized by a slight diffusion of F into the metal.

For longer oxidation times the F maximum drops to 1-2 at.-% after 500 h/900°C. (see fig. 1). These results suggest that the F-concentration at the metal/oxide interface is an important parameter for the stability of the fluorine effect. We define these parameter as c_F^{\max} (fig. 2). One focus of this work is on the time behaviour of c_F^{\max} . In the case of isothermal oxidation at 900°C first results have been reported in [23] encouraging to investigate the long time stability in more detail. In the present work the time for isothermal oxidation has been extended to 4000 h showing a nearly constant time behaviour of c_F^{\max} as depicted in fig. 3. The SEM inspection showed a dense alumina scale on the sample surface revealing that the F-effect is still working. The time dependence of c_F^{\max} after passing the heating phase can be expressed by an exponential decay function starting at $t=1$ hour of the following type (1):

$$c_F^{\max}(t) = c_0 + A \exp\left(-\frac{t}{t_1}\right) \quad (1)$$

The equation 1 suggests that after formation of a dense alumina scale c_F^{\max} decreases only slightly approaching a constant value of c_0 . The fit parameters summarized in fig. 3-4 allow the description of the F reservoir essential for the oxidation protection reaching a constant value of about 1 at.-%. By increasing the oxidation temperature to 1000°C the kinetics of c_F^{\max} corresponds also to eq. 1 as illustrated in fig. 4. The time behaviour indicates that a F content of about 0.3 at.-% stabilizes the F effect even at 1000°C at least within 1000 h. However components in aerospace and automotive environments undergo service conditions which are characterized by thermocyclic loading between 900°C and ambient temperature. Therefore cyclic oxidation tests (1 h-cycles/900°C/air) were performed to study the fluorine content up to an oxidation time of 2592 h. Before starting the cyclic process a preoxidation was done to establish a dense alumina scale on the surface. The oxide structure depicted in fig. 5 reveals the existence of a thin protective alumina scale of 1-2 μm thickness even after cyclic oxidation. The time behaviour of the F maximum illustrated in fig. 6 is also fitted by eq. 1, whereas the parameter c_0 reveals the presence of about 1 at.-% fluorine in the metal/oxide interface. The results for the cyclic loading at 1000 h/1000°C (fig. 7) indicate the stability of the F-content also at these extreme conditions. The F-maximum reaches values of about 0.7 at.-%. In agreement with the metallographic inspections it was demonstrated that an excellent oxidation resistance can be obtained already after a single F implantation. A detailed study for the case of fluorine double implantation leads to an increasing F-content c_0 for the oxidation parameters discussed above [24].

4. Diffusion coefficient of fluorine in TiAl and the stability of the fluorine effect

After the formation of an alumina scale the stability of c_F^{\max} depends on the inward diffusion of F into the metal. In [23] the F diffusion coefficient D in TiAl at 900°C was determined. By using the mean value of $1.56 \times 10^{-15} \text{ cm}^2/\text{s}$ a theoretical modelling of the dependence of c_F^{\max} from the oxidation time at 900°C was performed. c_F^{\max} was described by the solution of the diffusion equation

$$c(x,t) = \frac{Q}{2\sqrt{Dt\pi}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (2)$$

where Q denotes the number of fluorine atoms in at./cm^2 deposited at the metal/oxide interface and x the distance from the metal/oxide interface. The result in fig. 8 confirms the experimental behaviour suggesting long time stability of the fluorine maximum and the fluorine effect in TiAl.

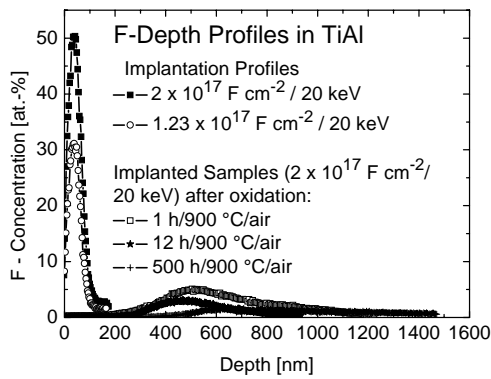


Fig. 1: The time behaviour of the F-depth profiles after implantation and after isothermal oxidation (900°C/air).

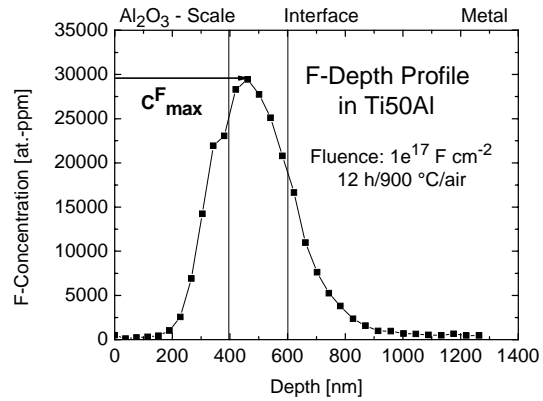


Fig. 2: F-depth profile of an implanted ($1 \times 10^{17} \text{ F cm}^{-2} / 20 \text{ keV}$) TiAl-sample after oxidation (12 h/900°C/air).

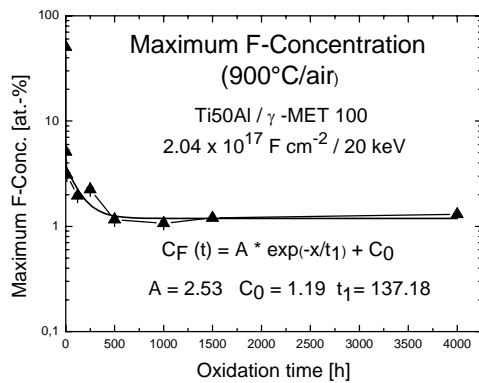


Fig. 3: The dependence of the F-maximum ($2.04 \times 10^{17} \text{ F cm}^{-2} / 20 \text{ keV}$) during isothermal oxidation (4000 h/900°C) is fitted by a decay function with a constant term.

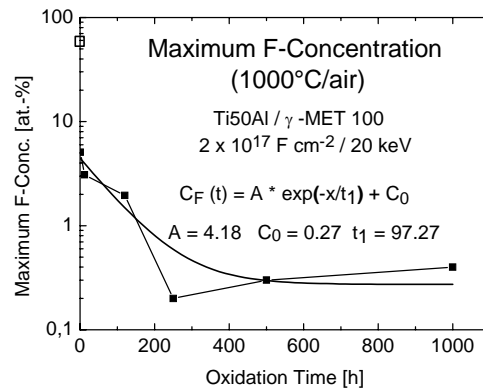


Fig. 4: An exponential decay function with a constant term describes the time behaviour of $c_{\text{max}}^{\text{F}}$ ($2 \times 10^{17} \text{ F cm}^{-2} / 20 \text{ keV}$) during isothermal oxidation (1000 h/1000°C/air).

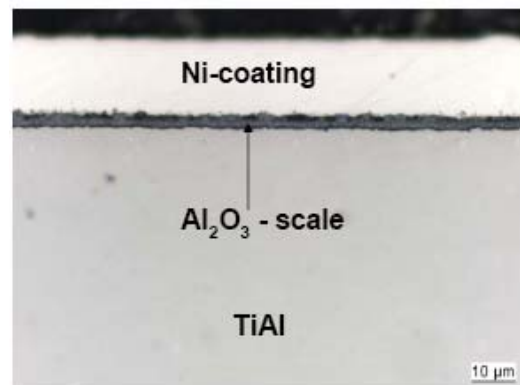
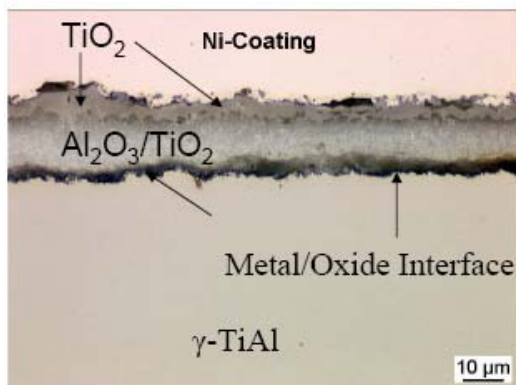


Fig. 5: Left micrograph: Fast growing mixed oxide scale on untreated TiAl after oxidation of 12 h/900°C. Right micrograph: Alumina scale on the surface of a γ -Met sample ($2 \times 10^{17} \text{ F cm}^{-2} / 20 \text{ keV}$) after cyclic oxidation (1h-cycle) of 2592 h/900°C/air.

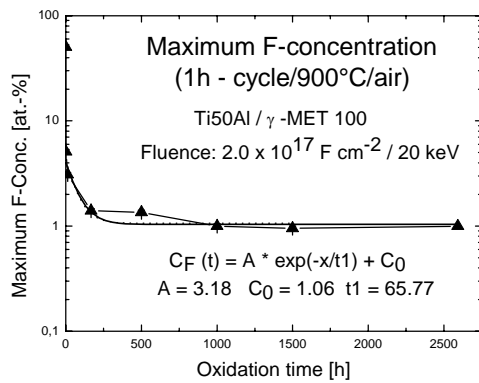


Fig. 6: An exponential decay function with a constant term describes the time behaviour of c_{\max}^F (2×10^{17} F cm⁻² / 20 keV) during cyclic oxidation (1-h-cycle) for 2592 h/ 900°C/air.

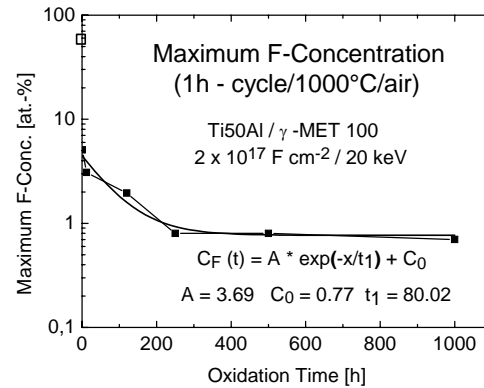


Fig. 7: An exponential decay function describes the time behaviour of c_{\max}^F (2×10^{17} F cm⁻² / 20 keV) during cyclic oxidation (1-h-cycle) for 1000 h/1000°C.

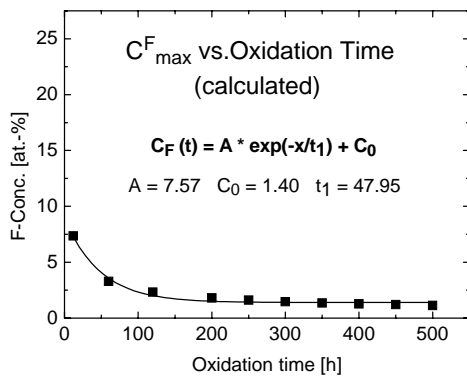


Fig. 8: Modelling of the F-maximum c_{\max}^F at the metal/oxide – interface during oxidation (900°C/air).

5. The Fluorine effect for Ni-base superalloys

The low Al-content of < 10 wt.-% (about 7 at.-% for IN738) hinders the formation of a dense protective alumina scale. Following Wagner's oxidation theory [25] a protective alumina scale can be formed if the Al activity is sufficiently high. The halogen effect allows an "artificial" increase of the Al content near the metal surface. Because of the good results for TiAl also fluorine was chosen. The condition for the fluorine effect is the selective formation of gaseous Al-fluorides at high temperatures in pores and microcracks near the surface of the alloy [4]. Therefore mainly Al-fluorides migrate to the surface. Due to the increasing oxygen partial pressure the Al-fluorides decay and Al₂O₃ is formed. The free fluorine gas returns into the metal and reacts to form Al-fluorides again. Once this cycle process is established a dense and pure protective alumina scale can be achieved. In contrast to this the other alloying elements, especially Ni, remain in the metal because of the relatively low partial pressure of the corresponding metal fluorides. To find a region of selective formation of Al-fluorides, thermodynamic calculations were performed [26] by using the software FactSage [27]. An interval of F-partial pressures was found showing the dominant formation of gaseous AlF within the temperature range of 900-1200°C. However for practical use the corresponding F-

concentrations within the near surface region have to be known. By using ion implantation with fluences from 10^{16} up to 4×10^{17} F cm⁻² a screening was performed to find the corresponding F- concentrations for the F-effect at Ni-base alloys. The F implantation profiles were calculated by using T-DYN [22], whereas the PIGE was used to validate the implantation. The results show the formation of a dense protective alumina scale on the metal surface (fig. 9). The lack of nitrides reveals that the inward diffusion of nitrogen is suppressed. As suitable parameters the range between 5×10^{16} and 2×10^{17} F cm⁻² was identified. The results show the potential of the fluorine effect for oxidation protection of Ni-base superalloys by using the halogen effect.

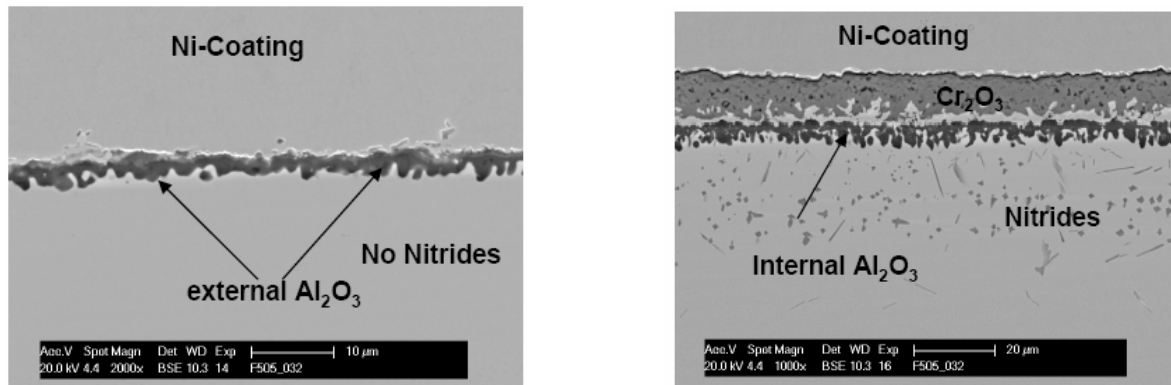


Fig. 9: Oxide scale of the Ni-base alloy IN 738 after oxidation (60 h/1050°C/air). Left: Implanted sample (2×10^{17} F cm⁻² / 38 keV). The Ni-coating is part of the metallographic preparation. Right: Non implanted side of the sample.

6. Conclusions

The F concentration at the metal/oxide interface c_F^{\max} was identified to be a fundamental material parameter for the stability of the fluorine effect for TiAl. Isothermal and thermocyclic loading were considered at 900°C and 1000°C. After single F implantation and F loss during heating the time behaviour of c_F^{\max} corresponds to an exponential decay function with a constant term reaching values between 0.3 and 1.1 at.-%. From the results a stable F amount at the metal/oxide interface can be concluded already after a single fluorine implantation leading to a stable oxidation resistance at temperatures of 900°-1000°C. The diffusion coefficient of F into TiAl at high temperatures was identified to be a second fundamental material parameter to establish a stable F effect. From the results the industrial use of the fluorine effect is in progress by using fluorine treatment via gas phase, liquid phase and plasma implantation.

Based on the thermodynamical calculations the conditions for the fluorine effect were investigated also for Ni-based superalloys. A screening by using fluorine ion implantation shows the optimal F concentrations. After oxidation at 1050°C a dense protective alumina scale was found on the surface. The results reveal the potential of the halogen effect also for Ni-base superalloys.

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References

- [1] A. Rahmel, et al., "Fundamentals of TiAl oxidation – A critical review ", *Materials and Corrosion*, 46 (1995) 271-285.
- [2] M. Kumagai, et al., "Influence of chlorine on the oxidation behavior of TiAl-Mn intermetallic compound", *Intermetallics*, 4 (1996) 557-566.
- [3] M. Schütze, et al., "Improvement of the oxidation resistance of TiAl alloys by using the chlorine effect", *Mat. Sci. Eng.*, A239-240 (1997) 847-858.
- [4] A. Donchev, et. al., "Thermodynamic considerations of the beneficial effect of halogens in the oxidation resistance of TiAl-based alloys", *Intermetallics* 11, (2003) 387-398.
- [5] G. Schumacher, et al., "Microalloying effects in the oxidation of TiAl materials", *Intermetallics*, 7 (1999) 1113-1120.
- [6] G. Schumacher, et al., "Improvement of the oxidation resistance of gamma titanium aluminides by microalloying with chlorine using ion implantation", *Materials and Corrosion*, 50 (1999) 162-165.
- [7] U. Hornauer, et al., "Improvement of the high temperature oxidation resistance of Ti50Al via ion-implantation ", *Nucl. Instr. & Meth. in Phys. Res.*, B 148 (1999) 858-862.
- [8] H.-E. Zschau, et al., "Investigation of the Fluorine Microalloying Effect in the Oxidation of TiAl at 900°C in Air", *Proc. International Symposium Turbomat*, June 17-19, 2002, Bonn, 210-214.
- [9] H.-E. Zschau, et al., "Investigation of the Fluorine Microalloying Effect in the Oxidation of TiAl at 900°C in Air", *Oxidation of Metals*, 59 (2003) 183-200.
- [10] H.-E. Zschau, et al., "Application of ion beam analysis for the control of the improvement of the oxidation resistance of TiAl at 900°C in air by fluorine ion implantation and HF-treatment", *Nucl. Instr. & Meth. in Phys. Res.*, B 240 (2005) 137-141.
- [11] H.-E. Zschau, et al., "The Quantitative Role of Surface Doped Fluorine for the Improvement of Oxidation Resistance of TiAl in Air", *Materials Science Forum* 461-464 (2004) 505-512.
- [12] D. Clemens, et al., "Effect of Si and Ti Additions on Alumina Scale Formation on NiCrAlY-Alloys" in *Electrochemical Society Meeting*, San Diego, California, May 3-8, 1998, Proc., P. Y. Hou, M. J. McNallan, R. Oltra, E. J. Opila and D. A. Shores (Eds.), *High Temperature Corrosion and Materials Chemistry*, Electrochem. Soc. Proc. Volume 98-9, 134-145.
- [13] L. Singheiser, et al., *Thermal Barrier Coatings for Gas Turbine Applications- Failure Mechanisms and Life Prediction*. in: 6th Liege Conference On Mat. For Adv. Power Engng., 5-7 Oct.1998, Liege, B, Proc. Europ. Comm., Edt. J. Lecomte-Beckers, F. Schubert, P.J. Ennis, vol. II, 977 – 996.
- [14] H. Nickel, et al., *Development of NiCrAlY Alloys for Corrosion-Resistant Coatings and Thermal Barrier Coatings of Gas Turbine Components* , *Journal of Pressure Vessel echnology*, 121 (1999) 384-387.
- [15] R. Munoz-Arroyo, et al., "Influence of Composition and Phase Distribution on the Oxidation Behaviour of NiCoCrAlY Alloys", *Materials Science forum*, Vols. 369-372 (2001) 165 – 172.
- [16] H. Li, et al., *Oxidation Behavior of a Single-Crystal Ni-Base Superalloy in Air. I: At 800 and 900°C* , *Oxidation of Metals* 59 (2003) no. 5/6 591-605.

- [17] C. Leyens, et al., Oxidation and lifetime of PYSZ and CeSZ coated Ni-base substrates with MCrAlY bond layers, Proc. MICROSCOPY OF OXIDATION (2003) p. 229-234 .
- [18] D. Strauss, et al., "Oxide Scale Growth on MCrAlY bond Coatings after Pulsed Electron Beam Treatment and Deposition of EBPVD-TBC", Surface and Coatings Technology, 135 (2001) 196 – 201.
- [19] Quadakkers, W.J. , et al., "Oxidation Characteristics of a Platinized MCrAlY Bond Coat for TBC Systems during Cyclic Oxidation at 1000°C ", Surface & Coatings Technology 1 (2005) 77-82.
- [20] J. Ziegler, et al., The stopping and range of ions in solids, Version 95, 1995, Pergamon Press, New York.
- [21] J. R. Tesmer, M. Nastasi (Eds.), Handbook of Modern Ion Beam Materials Analysis, Materials Research Society, Pittsburgh 1995, PA, USA.
- [22] J. Biersack, „TRIM-DYNAMIC applied to marker broadening and SIMS depth profiling”, Nucl. Instr. & Meth. in Phys. Res. B 153 (1999) 398-409.
- [23] H.-E. Zschau, et al., „Surface modification of titanium aluminides with fluorine to improve their application for high temperature service conditions“, Nucl. Instr. & Meth. in Phys. Res., B 257 (2007) 383-387.
- [24] H.-E. Zschau, et al., „Characterization of the long time oxidation protection of fluorine implanted technical TiAl-alloys using ion beams“, Nucl. Instr. & Meth. in Phys. Res., B 266 (2008) 2441-2445.
- [25] P. Kofstad: High Temperature Oxidation of Metals, Elsevier, New York, 1988
- [26] H.-E. Zschau, P.J. Masset, D. Renusch, M. Schütze, „Thermodynamical Considerations for applying the halogen effect to Ni-base superalloys“, Proc. TMS Annual Meeting, San Francisco, 15.-19.2.2009, 149-156.
- [27] Program system FactSage Version 4.5.1 Fa. GTT, Herzogenrath.