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by

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# Microstructural and Chemical Constitution of the Oxide Scale formed on a Pesting-Resistant Mo-Si-Ti Alloy

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## Abstract

1 The oxidation behaviour of the pesting-resistant eutectic alloy Mo-20Si-52.8Ti was investigated by  
2 addressing the microstructural and chemical constitution by grazing incidence X-ray diffraction GIXRD  
3 and atom probe tomography APT of oxide scales formed at 800 and 1200 °C in order to understand their  
4 protective character. The duplex Si-Ti-oxide scale formed at 800 °C in air, i.e. within the so-called  
5 “*pestring regime*”, is considerably slow growing with a scale thickness of  $(11 \pm 3) \mu\text{m}$  after 1000 h of  
6 exposure. It is composed of a Ti(+IV)-oxide with the chemical composition of approximately  $\text{TiO}_{2.1}$   
7 confirmed by APT and  $\text{SiO}_2$  islands, which are most likely amorphous. The oxide scale formed at  
8 1200 °C, a potential application temperature, is characterised by a top single-phase scale and an  
9 underlying duplex scale with a considerably increased thickness of  $(68 \pm 11) \mu\text{m}$  in total. It consists of  
10 rutile  $\text{TiO}_2$  and some cristobalite  $\text{SiO}_2$  as determined by GIXRD. APT analysis of the top Ti-oxide scale  
11 confirms the stoichiometry  $\text{TiO}_{2.2}$ . The underlying duplex scale comprising Ti- and Si-oxide is  
12 characterised by strongly off-stoichiometric compounds, namely  $\text{TiO}_{1.4}$  and  $\text{SiO}_{1.6}$ . Initial linear oxide  
13 scale growth kinetics are found at 800 °C, which change to cubic kinetics for exposure times longer than  
14 100 h. At higher temperatures of 1100 and 1200 °C, diffusion-controlled, almost parabolic kinetics  
15 prevail.

## Keywords

16 refractory alloys; oxide scale; microstructure; chemical composition; crystal structure; oxidation  
17 kinetics

## 1. Introduction

18 The development of Mo-Si-based alloys for high-temperature applications as potential alternatives to  
19 state-of-the-art Ni-based superalloys is challenged by a judicious combination of sufficient creep  
20 resistance with adequate oxidation resistance. At elevated temperatures, this oxidation resistance can be  
21 achieved by: (i) Micro-alloying with B leads to a decrease in oxide scale viscosity [1] enabling quick  
22 coverage of the substrate surface by a borosilicate layer retarding further O ingress [2-4]. (ii)  $M_5Si_3$   
23 silicides with a higher Si content compared to  $M_3Si$  silicides (with M representing Mo or Ti,  
24 respectively) can be stabilised [5], which facilitate formation of a  $SiO_2$  oxide scale [6]. However at  
25 temperatures below 1000 °C, catastrophic oxidation is characteristic for all Mo-Si-based alloys since  
26 the kinetics of  $SiO_2$  formation is too slow in order to outbalance the formation of volatile  $MoO_3$  leading  
27 to rapid mass loss [7, 8], called “*pestring*”. Among multiple alloy design approaches, the ternary Mo-Si-  
28 Ti alloys were found to be the most promising regarding suppression of pestring [9]. A fully eutectic Mo-  
29 20Si-52.8Ti (at%) alloy possessing a two-phase, fine-scaled microstructure of Mo solid solution  $Mo_{SS}$   
30 and  $(Ti,Mo)_5Si_3$  was found *not* to undergo catastrophic oxidation at 800 °C [9]. An excellent oxidation  
31 resistance was observed with negligible specific mass changes in the order of 2 mg/cm<sup>2</sup> (isothermal)  
32 and 0.3 mg/cm<sup>2</sup> (cyclic) at 800 °C after 100 h [9]. This unexpected, outstanding oxidation behaviour has  
33 been attributed to the formation of a mixed  $SiO_2$ - $TiO_2$  layer with a scale thickness of less than 10 µm  
34 [9]. These observations were in striking contrast to the eutectoid Mo-Si-Ti alloy Mo-21Si-34Ti, being  
35 composed of  $Mo_{SS}$  and  $(Mo,Ti)_5Si_3$ , which suffered from severe pestring [9].

36 To summarise, our previous studies focused on the chemical and microstructural conditions for  
37 achieving pestring-resistance in eutectic-eutectoid Mo-Si-Ti alloys. It turned out that a threshold in  
38 nominal Ti content of minimum 43 at% is mandatory in order to obtain adequate oxidation resistance in  
39 the pestring regime [10, 11]. Moreover, it was found that the fine length scale of the eutectic  
40 microstructure is not required in order to achieve pestring-resistance since a considerably, artificially  
41 coarsened eutectic alloy exhibited a similarly good oxidation behaviour [11]. Thus, the chemical  
42 composition of the individual phases proved to be decisive whether pestring could be suppressed or not.  
43 While both  $M_5Si_3$  silicides (with “M” being either Ti or Mo or a combination of both), hexagonal  
44  $(Ti,Mo)_5Si_3$  and tetragonal  $(Mo,Ti)_5Si_3$ , exhibit an adequate oxidation resistance in the pestring regime  
45 [12, 13], it is the pestring-critical  $Mo_{SS}$  phase which is responsible for the dominance of  $MoO_3$   
46 evaporation [11]. Continuous pathways of the Ti-oxide are present in the duplex scale connecting the  
47 alloy substrate with the outer  $TiO_2$  oxide scale among all investigated Mo-Si-Ti alloys [10]. This is  
48 surprising with regard to the anticipated minor oxidation resistance of  $TiO_2$ , which is well known to  
49 exhibit scale cracking and spallation [14-17].

50 In conclusion, the reasons for the passivating character of the mixed Si-Ti-oxide scale formed on the  
51 eutectic alloy at 800 and 1200 °C, and especially the non-detrimental character of Ti-oxide still remain  
52 unclear. Therefore, this article addresses the crystallographic and chemical appearance of the oxide

53 scales and their growth characteristics. In particular, focus is placed on the solubility of the species Si,  
54 Ti and Mo in the oxide phases by means of atom probe tomography (APT), in order to analyse its impact  
55 on the peeling stability.

## 2. Experimental

56 The alloys were manufactured by repetitive arc-melting of the bulk high-purity elements Mo, Si and Ti  
57 with purities of 99.95, 99.99 and 99.8 %, respectively. Therefore, an AM/0,5 device provided by  
58 Edmund Bühler equipped with a button-shaped, water-cooled Cu crucible was used. Subsequent to  
59 multiple evacuating ( $< 2 \times 10^{-4}$  mbar) and Ar-flooding steps, a final Ar atmosphere of 600 mbar was  
60 established, which was further cleaned from O residuals by pre-melting a Zr lump. Repetitive melting  
61 (min. five times) ensured a homogenous element distribution. The resulting composition was confirmed  
62 to vary less than 0.5 wt% from the initial nominal composition by inductively coupled plasma optical  
63 emission spectroscopy.

64 Cyclic oxidation experiments were performed on samples with dimensions of  $(5 \times 5 \times 4)$  mm<sup>3</sup> and a  
65 surface finish of SiC grit P2500. Oxidation testing was conducted at laboratory air in muffle furnaces  
66 by Carbolite Gero and Nabertherm at 800 and 1200 °C for a test duration in total of 1000 and 100 h,  
67 respectively, with cycle durations varying between 1 to 10 h. The samples were cooled down to room  
68 temperature between each cycle and their mass change was recorded by means of a balance (Sartorius  
69 precision of  $\pm 1$  µg). The samples were maintained in Al<sub>2</sub>O<sub>3</sub> crucibles during testing, but turned around  
70 after each cycle to allow uniform oxidation of all surfaces.

71 The cross sections of the oxidation samples were analysed by scanning electron microscopy (SEM) after  
72 representative oxidation durations. Therefore, the oxidation samples were cold mounted and prepared  
73 by grinding steps down to SiC grit P2500 and subsequent polishing with 3 and 1 µm diamond suspension  
74 and finally with stabilised silica suspension provided by Struers. A LEO EVO 50 SEM by Zeiss was  
75 used at an acceleration voltage of 20 kV. Backscattered electron (BSE) imaging contrast, providing  
76 atomic number and thus material contrast, allowed the characterisation of the oxide scale morphology.  
77 The used SEM was equipped with an energy dispersive X-ray spectroscopy (EDX) system, which  
78 allowed for an estimation of the chemical composition of the phases within the substrate. Quantitative  
79 evaluation of the oxide scale thickness and the areal fractions of the respective oxides was performed  
80 by applying image processing techniques, based on thresholding greyscale values and pixel connectivity  
81 analysis using the software ImageJ and a self-written Matlab script.

82 In order to investigate the crystal structure of the formed oxide scales, grazing incidence X-ray  
83 diffraction (GIXRD) analyses were performed. Therefore, a Rigaku SmartLab diffractometer was used,  
84 equipped with a HyPix-3000 detector in 0D mode and a Cu K $\alpha$  radiation source. The sample was aligned  
85 by the usage of an Rx/Ry stage. The measurements were performed with a parallel beam and a 5° soller  
86 slit in the primary beam path at incident angles  $\omega$  varying between 1.2 and 2.5°.

87 Further analysis of the elemental distribution within the oxide scales was performed by means of 3D  
88 atom probe tomography (APT). The tips from the oxide layers were prepared in a Strata dual beam  
89 SEM/focused ion beam device by FEI. Firstly, the regions of interest were protected by a Pt layer to  
90 avoid damage caused by the Ga<sup>+</sup> ion beam. Parts of an originally (25 x 4 x 3) μm<sup>3</sup> sized rod were set to  
91 Si micro-posts provided by Cameca. Next, tips were shaped by annular milling at 30 kV with decreasing  
92 inner diameter down to 0.2 μm. Final milling with a closed circular pattern was performed at 5 kV  
93 acceleration voltage to minimize the Ga<sup>+</sup> affected layer at the surface.

94 Atom probe analyses were conducted in a LEAP 4000X HR by Cameca. The device was operated in  
95 laser mode (UV laser with λ = 355 nm) at a pulse energy of 50 or 100 pJ and a pulse repetition rate of  
96 100 or 125 kHz. The temperature was set to 50 K and the standing high voltage was controlled according  
97 to a detection rate of 0.3 to 0.5 %.

98 Atom probe data were reconstructed and analysed by the IVAS 3.6.14 software by Cameca. The  
99 chemical composition was determined using the peak deconvolution analysis to take the possible overlap  
100 of peaks into account, especially, the overlap of TiO<sup>2+</sup> and O<sub>2</sub><sup>+</sup> at 32 Da. Furthermore, APT analyses of  
101 oxides, as well as carbides and nitrides, have shown that the quantification of the chemical composition  
102 may depend on the experimental conditions [18-21]. An underestimation of the O content could be  
103 caused by preferential co-evaporation of O or O-containing ions during the same laser pulse leading to  
104 multiple signals on the detector, which cannot be separated [20]. Hence, a critical discussion of the  
105 obtained compositions is necessary. It can be assumed that a possible O underestimation is consistent  
106 for experimental conditions not varying substantially. These conditions are strongly influenced by the  
107 evaporation field which depends on, e.g. the pulse energy, tip radius and material. Varying evaporation  
108 fields can lead to significant changes in (i) the fraction of pulses leading to multiple signals and/or (ii)  
109 the ratio of detected ions of the same species with different charge. The tips discussed in this article  
110 exhibit about 80 % single signals and comparable ratios of ions at different charge states. Hence, similar  
111 experimental conditions can be assumed for the APT investigations. Additionally, it was guaranteed that  
112 no significant co-evaporation of O ions occurred during laser pulses. Therefore, a self-written software  
113 by Boll et al. [22] was used to create separate mass spectra containing ions from single signals or  
114 multiple signals, respectively. It was found that (i) the overall O content in the mass spectra derived  
115 from multiple signals was lower than that from single signals and (ii) no disproportionately high amount  
116 of O or O<sub>2</sub> ions occurred. Hence, it is unlikely that the APT analysis conditions cause a significant O  
117 underestimation in the APT results.

118 The coefficient of thermal expansion (CTE) was determined by an optical dilatometer heating  
119 microscope by LINSEIS. Here, the sample was compared to an Al<sub>2</sub>O<sub>3</sub> reference during measurement.  
120 The length difference was detected by a CCD camera. The CTE was analysed with a heating rate of  
121 10 °C/min over the temperature range from 300 to 1200 °C under Ar flow of 3 sccm/min.

### 3. Results and discussion

122 In the following paragraphs we present structural (Sect. 3.1) and chemical investigations (Sect. 3.2) of  
123 the oxide scales formed on the eutectic Mo-20Si-52.8Ti alloy (at%) at 800 and 1200 °C. Thereafter,  
124 oxide scale growth kinetics will be evaluated in order to assess the rate-controlling processes (Sect. 3.3).  
125 In contrast to our previous article [10], where the distribution of the solid and volatile oxide forming  
126 species Ti, Si and Mo within the (sub-)oxide scales was evaluated, the evolution of the oxide scale  
127 thickness with time at different temperatures is focused on. In the following, oxides, in which Ti cations  
128 represent the major cationic component, are referred to as Ti-oxide, whereas oxides possessing majority  
129 Si cations as metal ions will be designated as Si-oxide. These terms are only meant as general,  
130 qualitatively distinction and are not to be misinterpreted by oxidation levels, or stoichiometry relations.  
131 These will be named and discussed where they are of particular interest (Sect. 3.2).

#### 132 *3.1. Structural characterisation of the oxide scales formed at 800 and 1200 °C*

133 The general oxidation behaviour of the eutectic Mo-20Si-52.8Ti alloy has been studied in detail in Refs.  
134 [9, 11] for the as-cast and homogenised heat-treated condition with no significant differences in oxide  
135 scale formation and oxidation behaviour observed. Thus, we now focus on the detailed investigation and  
136 understanding of the formed oxide scales of the as-cast (ac) condition. The two-phase eutectic  
137 microstructure is differently fine-scaled and textured depending on the temperature profile during  
138 cooling after arc melting, and thus also partially degenerated (see Fig. 1: Mo<sub>5</sub>Si<sub>3</sub> white and (Ti,Mo)<sub>5</sub>Si<sub>3</sub>  
139 bright grey in BSE contrast). After being cyclically exposed to air at 800 °C for 100 h a thin duplex  
140 oxide scale of approximate  $(5 \pm 2)$  μm in thickness is formed (see Fig. 1b), which grows to a thickness  
141 of  $(11 \pm 3)$  μm after 1000 h of oxidation (see Fig. 1c). It consists of a Ti-oxide (grey in BSE contrast)  
142 with embedded islands of oxides rich in Si (dark-grey in BSE contrast) (see Fig. 1a to c). At 1200 °C  
143 after 100 h, a significantly thicker oxide scale (approximately 70 μm in total) is observed. Two distinct  
144 sub-scales are identified: (i) a single-phase, top Ti-oxide scale and (ii) a duplex scale comprising Ti- and  
145 Si-oxide underneath (see Fig. 1d and e). The duplex oxide scale was found to comprise a considerable  
146 fraction of Si-oxide of  $(52 \pm 6)$  vol% [10]. The top Ti-oxide scale reveals a rather low porosity of  $(1.3$   
147  $\pm 0.2)$  vol%.

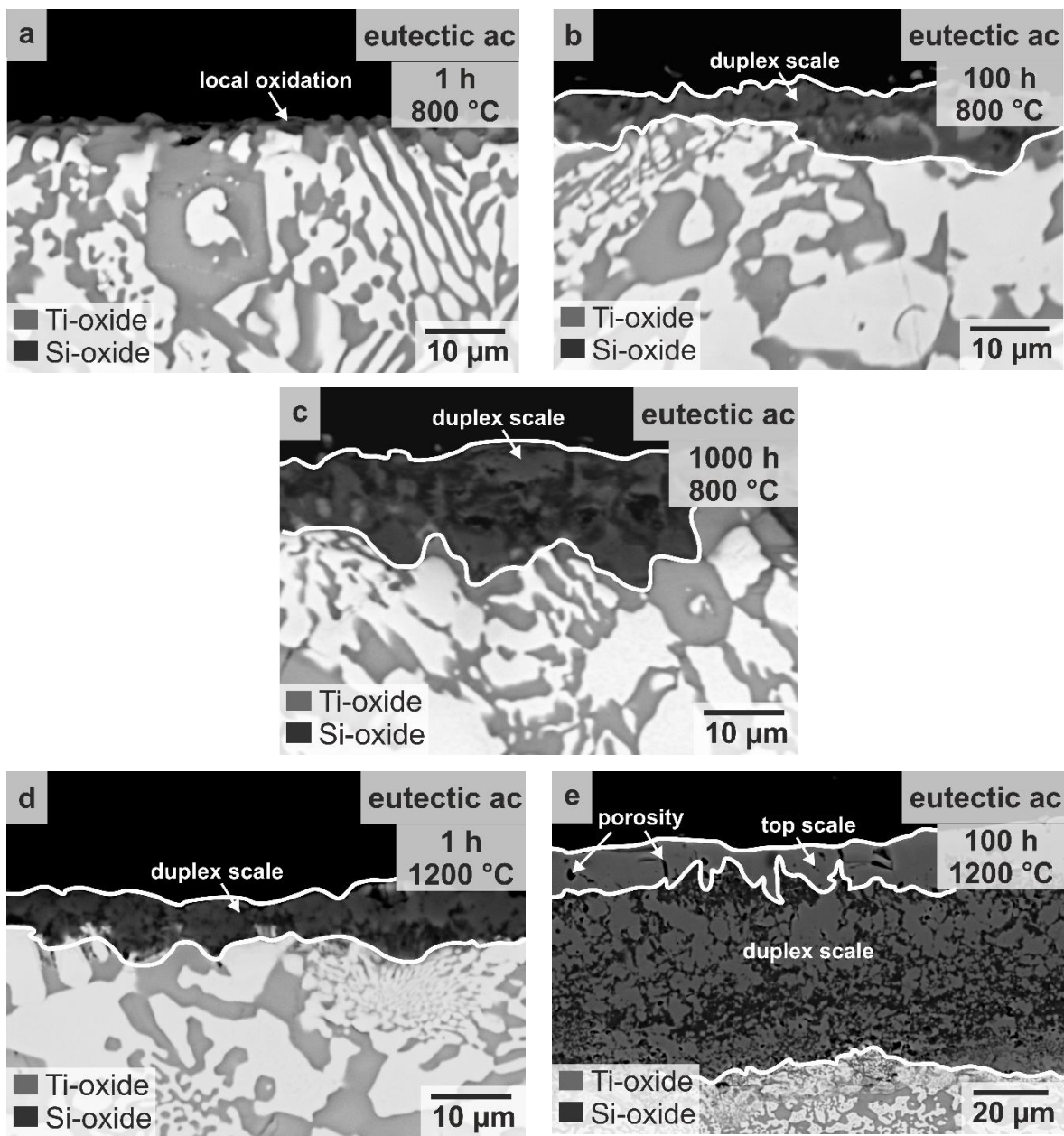


Fig. 1 BSE micrographs of the eutectic alloy Mo-20Si-52.8Ti after cyclic oxidation in laboratory air for 1, (a) 100 (b) and 1000 h (c) at 800 °C as well as 1 (d) and 100 h (e) at 1200 °C. Dark grey is the Si-oxide, while the Ti-oxide is light grey.

149 GIXRD measurements at an incident angle of  $\omega = 1.2^\circ$ , presented in Fig. 2, confirmed the oxide scales  
 150 formed at 800 and 1200 °C to be mainly composed of rutile  $\text{TiO}_2$ , Ti(+IV)-oxide (space group P  $4_2/m n$   
 151 m) and small amounts of cristobalite  $\text{SiO}_2$ , Si(+IV)-oxide (space group P  $4_1 2_1 1$ ). Thus, with respect to  
 152 the considerable volume fraction of the (dark-grey) Si-oxide within the Si-Ti-oxide duplex scale formed  
 153 at 1200 °C (see Fig. 1e), it is expected that  $\text{SiO}_2$  is mostly amorphous. This is in good agreement with  
 154 the results presented in Ref. [9] by electron back-scatter diffraction (EBSD). Besides, rutile  $\text{TiO}_2$ , some  
 155 peaks at  $2\theta = 26.78, 42.82, 63.04$  and  $65.57^\circ$  can be assigned to ordered TiO (space group C  $1 2/m 1$ ).  
 156 While the peaks at  $2\theta = 42.82, 63.04$  and  $65.57^\circ$  are either superimposed by  $(\text{Ti},\text{Mo})_5\text{Si}_3$  (in the case of

157 the 800 °C oxidation sample), or cristobalite SiO<sub>2</sub>, the peak at 2 $\Theta$  = 26.78° only matches the plane group  
 158 ( $\bar{1}11$ ) of ordered TiO. However, more characteristic peaks of ordered TiO, for instance at 2 $\Theta$  = 30.29,  
 159 or 46.74° of plane groups (111) and (021), respectively, would be expected, if a representative fraction  
 160 is prevalent in the oxide scale. Thus, the GIXRD results do not confirm the presence of TiO.  
 161 Additionally, some weak peaks at 2 $\Theta$  = 35.36, 39.85 and 69.90° are assigned to the plane groups (410),  
 162 (501) and (621) of MoO<sub>3</sub> (space group P b n m). Note that the peak at 2 $\Theta$  = 69.90° is superimposed  
 163 by a rutile peak at 69.09° at 1200 °C. The detection of MoO<sub>3</sub> is attributed to re-deposition of volatile  
 164 MoO<sub>3</sub> on the oxide surface and partial incorporation into the growing oxide scale. Additionally, the  
 165 800 °C oxidation sample exhibits numerous peaks that can be assigned to (Ti,Mo)<sub>5</sub>Si<sub>3</sub>. This is reasonable  
 166 as the oxide scale possesses a rather low thickness and sub-oxide regions of the substrate were likely  
 167 detected even by GIXRD. This is confirmed by additional measurements with increasing incident angles  
 168 and therefore increased information depth, as the respective peaks become more pronounced (see Supp.  
 169 1 for GIXRD results with an increased incident angle of  $\omega$  = 2.5°). Furthermore, peaks corresponding  
 170 to bcc Mo<sub>SS</sub> are not detected, which is in good agreement with the observations made by SEM analysis  
 171 (see Fig. 1a and b), showing that surface-near Mo<sub>SS</sub> regions suffer from oxidation while the (Ti,Mo)<sub>5</sub>Si<sub>3</sub>  
 172 regions remain almost unaffected. Moreover, there are two weak peaks at 2 $\Theta$  = 24.67 and 31.32° in the  
 173 GIXRD pattern of the 1200 °C oxidation sample, which cannot be assigned unambiguously. However,  
 174 these peaks neither correspond to the already discussed crystal structures, nor to further verified ones  
 175 (see Table 1).

Table 1 Examined crystal structures for evaluation of the GIXRD patterns (see Fig. 2).

type	crystal structure	space group	matching peaks with GIXRD patterns
Ti-oxides	rutile TiO <sub>2</sub>	P 4 <sub>2</sub> /m n m	yes
	ordered TiO	C 1 2/m 1	yes (superimposed by peaks of other crystal structures)
	NaCl-type TiO	F m $\bar{3}$ m	-
	monoclinic Ti <sub>3</sub> O <sub>5</sub>	C 1 2/m 1	-
	pseudobrookite Ti <sub>3</sub> O <sub>5</sub>	C m c m	-
	corundum Ti <sub>2</sub> O <sub>3</sub>	R $\bar{3}$ c	-
	anatase TiO <sub>2</sub>	I 4 <sub>1</sub> /a m d	-
brookite TiO <sub>2</sub>	P b c a	-	
Si-oxides	cristobalite SiO <sub>2</sub>	P 4 <sub>1</sub> 2 <sub>1</sub> 1	yes
	rutile SiO <sub>2</sub>	P 4 <sub>2</sub> /m n m	-
Mo-oxides	MoO <sub>3</sub>	P b n m	yes

	VO <sub>2</sub> -type MoO <sub>2</sub>	P 1 2 <sub>1</sub> /c 1	-
	rutile MoO <sub>2</sub>	P 4 <sub>2</sub> /m n m	-

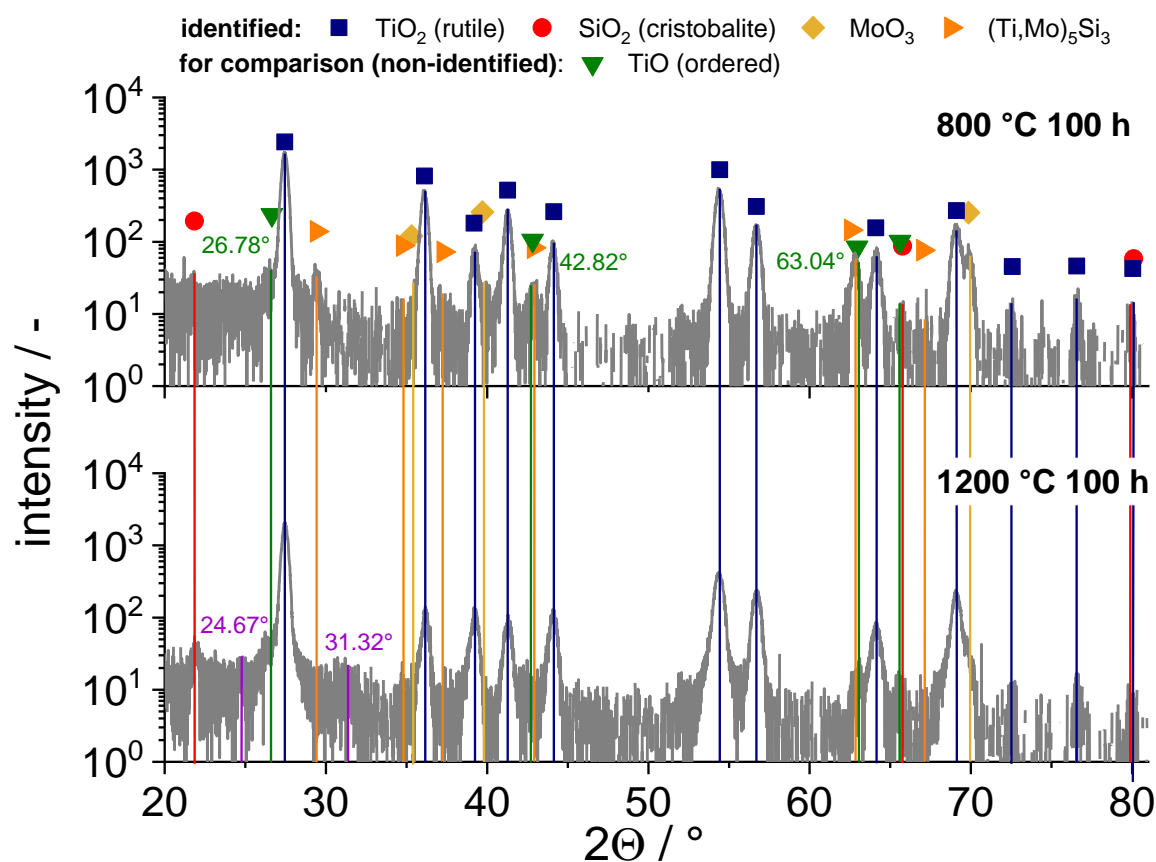


Fig. 2 GIXRD pattern of the surface of the oxidised sample at 800 (top) and 1200 °C (bottom) for 100 h. Note that the intensities are plotted in log scale. Diffraction angles that might correspond to ordered TiO (whose crystal structure cannot be identified unambiguously) are additionally labelled in green, whereas the non-assigned ones are labelled in violet colour.

### 3.2. Chemical analysis of the oxide scales formed at 800 and 1200 °C

176 The mass spectra of the investigated atom probe tips are displayed in Fig. 3, showing the characteristic  
 177 parts with the main peaks indicated. At 800 °C, the Si-oxide tip could not be evaluated due to instabilities  
 178 of tips manufactured from the oxide scale during APT analysis. Therefore, only the Ti-oxide tip was  
 179 analysed (see Fig. 3a). For the 1200 °C sample, three regions of interest were evaluated (compare to  
 180 BSE micrograph in Fig. 1e): (i) the top Ti-oxide scale (see Fig. 3b) and the underlying duplex scale of  
 181 both, (ii) the Ti- and (iii) the Si-oxide region (see Fig. 3c and d).

182 The mass spectrum of the Ti-oxide region formed at 800 °C (Fig. 3a) mainly exhibits TiO and TiO<sub>2</sub> as  
 183 well as O ion-related peaks. Additionally, the spectrum contains the main peak of Si<sup>+</sup> (28 Da) but no  
 184 side peaks or other O-containing Si peaks are identified. Furthermore, no peaks related to Mo are present,  
 185 which might have indicated the formation or incorporation of Mo-oxide. Thus, it can be concluded that  
 186 the peak at 32 Da predominantly results from TiO<sub>2</sub><sup>+</sup> ions. Nevertheless, the peak at 34 Da (a side peak  
 187 of O<sub>2</sub><sup>+</sup>) indicates a significant contribution of O<sub>2</sub><sup>+</sup> to the peak at 32 Da, which has to be taken into account

188 for the determination of the chemical composition. After peak deconvolution the chemical composition  
189 was found to be 34.4 at% Ti and 66.4 at% O (see Table 2), confirming the presence of TiO<sub>2</sub>, Ti(+IV)-  
190 oxide as already indicated by GIXRD analyses (see Fig. 2).

191 The mass spectrum of the top Ti-oxide region formed at 1200 °C (see Fig. 3b) exhibits similar peaks to  
192 the spectrum of the 800 °C sample, except the ones for Al<sup>+2+</sup> (27 and 13.5 Da) and AlO<sup>2+</sup> (21.5 Da).  
193 These peaks presumably result from a reaction with the alumina crucible during oxidation. The main  
194 peak of Si<sup>+</sup> (28 Da) is identified as well and no Mo-related peaks are detected. Peak deconvolution  
195 reveals the chemical composition to be 31.7 at% Ti and 68.3 at% O in the top Ti-oxide, 1200 °C sample  
196 (see Table 2). Assuming no experimentally caused underestimate of the O content, (see Sect. 2), the  
197 presence of TiO<sub>2</sub>, Ti(+IV)-oxide, is confirmed in the top layer by APT. This was also expected from the  
198 GIXRD analyses performed in this study (see Fig. 2) and from the EBSD results of the top Ti-oxide  
199 scale revealing rutile TiO<sub>2</sub>, see Ref. [9]. Although respective peaks are observed in the mass spectrum,  
200 the concentration of Si and Al is below 0.1 at%.

201 The mass spectra of the Ti-oxide of the underlying duplex scale (see Fig. 3c) exhibits the same peaks  
202 found in the mass spectra of the top layer tips, including a small Si<sup>+</sup> peak at 28 Da. Again, no Mo peaks  
203 are observed and the duplex layer shows no peaks related to Al. The latter suggests that no reaction with  
204 the alumina crucible has occurred during oxidation testing. This is reasonable as the duplex scale is  
205 assumed to grow inwards and is separated from the atmosphere by the top Ti-oxide scale. Thus, it is not  
206 in contact with the crucible. In comparison to the top Ti-oxide, 1200 °C sample, a lower O content of  
207 only 59.0 at% (equiv. to 41.0 at% Ti) is determined after peak deconvolution. As discussed, it can be  
208 assumed that the APT analysis conditions did not cause an underestimation of the O content. EBSD  
209 analyses by Schliephake et al. [9] unambiguously confirmed the top oxide scale to be rutile TiO<sub>2</sub>,  
210 Ti(+IV)-oxide. However, in the underlying duplex scale, besides some rutile-assigned portions, multiple  
211 un-indexed regions were assumed to be amorphous SiO<sub>2</sub>. These un-assigned regions might represent  
212 another Ti-oxide than rutile TiO<sub>2</sub>, Ti(+IV)-oxide.

213 The mass spectrum of the Si-oxide (see Fig. 3d) mainly exhibits peaks, which can be assigned to Si and  
214 O or combinations of both. Again, no Mo- or Al-related peaks are found. In contrast to all earlier  
215 discussed mass spectra, the peak at 32 Da results predominantly from O<sub>2</sub><sup>+</sup> ions. Small side peaks of  
216 TiO<sup>2+</sup> ions can be observed at 31, 31.5, 32.5 and 33 Da. Using peak deconvolution, a total Ti content of  
217 about 0.4 at% is obtained for the Si-oxide. The concentrations of Si (38.0 at%) and O (61.6 at%) are  
218 close to the stoichiometry of Si(+IV)-oxide SiO<sub>2</sub>, but this phase seems to be slightly depleted in O, too,  
219 like the Ti-oxide in the duplex layer.

220 The corresponding subsets of the Ti-oxide, as well as of the Si-oxide regions within the duplex oxide  
221 scale, which were taken to determine the chemical composition of the phases, are included in Fig. 3e.

222 The reconstructions of tip from the top Ti-oxide scales at 800 and 1200 °C are included in Supp. 2 for  
 223 the sake of completeness.

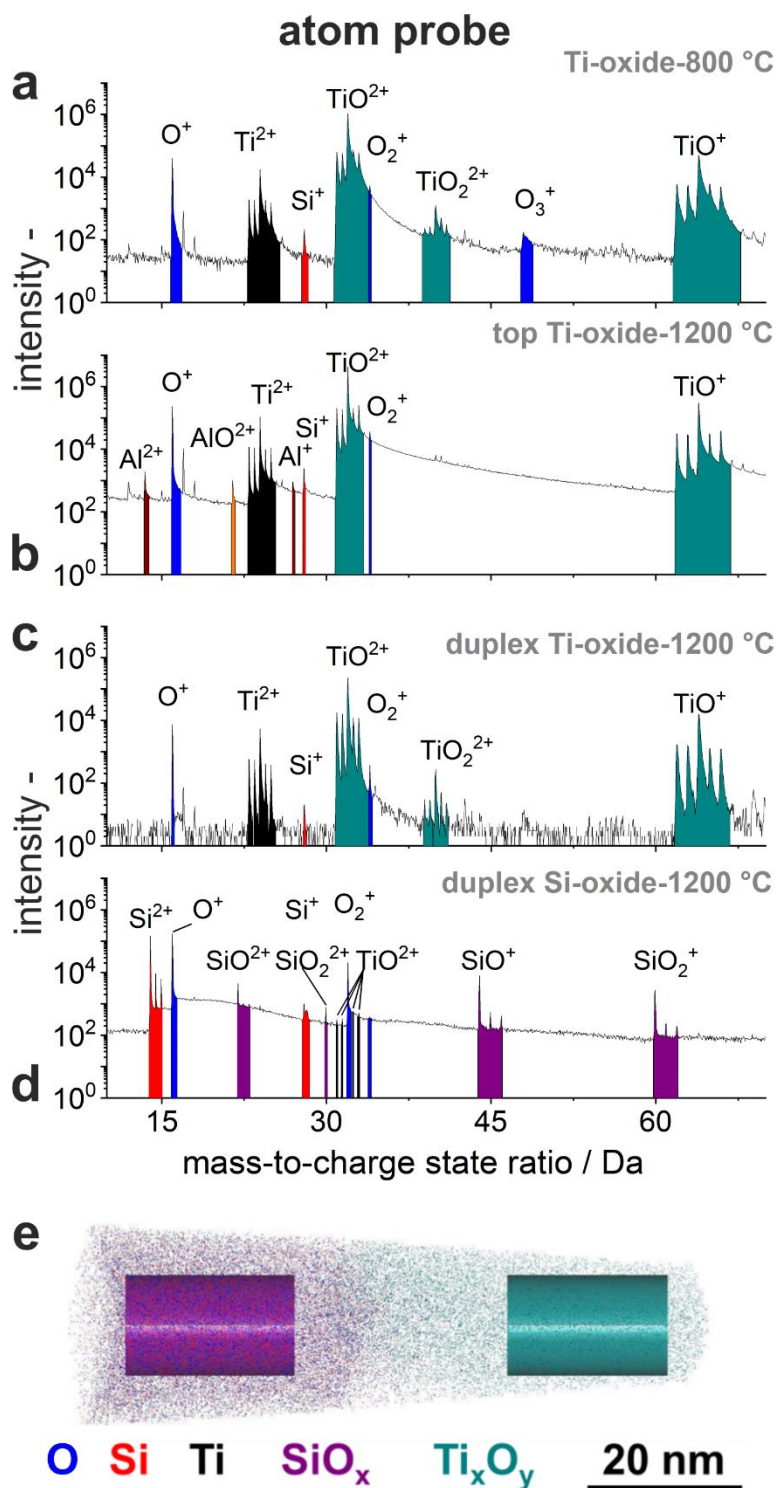


Fig. 3 Characteristic parts of the mass spectra of the top layer of the Ti-oxide-800 °C sample (a), the top Ti-oxide-1200 °C sample (b), as well as the duplex Si-oxide-1200 °C (c) and the duplex Ti-oxide-1200 °C (d) regions of the duplex layer formed at 1200 °C. Corresponding visualisation of the subsets for the analyses of the duplex oxide scale at 1200 °C (e), for reasons of clarity only 1 % of all identified ions is shown here.

Table 2 Chemical composition of the oxides in the investigated tips determined by APT after peak deconvolution (in at%) and comparison to the predominant oxide stoichiometry. \* In this case, several presumable oxide stoichiometries are compared based on the experimental results.

/ at%	Ti	Si	O	Al	predominant oxide	
Ti-oxide- 800 °C	32.4	< 0.1	67.6	-	TiO <sub>2.1</sub>	Ti(+IV)
top Ti-oxide-1200 °C	31.7	< 0.1	68.3	< 0.1	TiO <sub>2.2</sub>	Ti(+IV)
duplex Ti-oxide- 1200 °C*	41.0	< 0.1	59.0	-	TiO <sub>1.4</sub> Ti <sub>2</sub> O <sub>2.9</sub> Ti <sub>3</sub> O <sub>4.3</sub>	Ti(+II) or Ti(+III) Ti(+III) Ti(+IV/+III)
duplex Si-oxide-1200 °C	0.4	38.0	61.6	-	SiO <sub>1.6</sub>	Si(+IV)

224 The experimental results of the Ti- and Si-oxide regions of the duplex scale are corroborated by literature  
 225 data proving that SiO<sub>2</sub> (Si(+IV)-oxide) and TiO<sub>2</sub> (Ti(+IV)-oxide) are in equilibrium at ambient pressure  
 226 in air at 1100 [23] and 1200 °C [24], respectively. Moreover, there is only a solubility of 0.85 at% Si in  
 227 rutile TiO<sub>2</sub> reported at 1300 °C for pressures of 3 GPa and higher [25]. Assuming a linear dependence  
 228 of solved Si in TiO<sub>2</sub> with pressure, a solubility at ambient pressure of less than 0.57 at% can be  
 229 extrapolated [25].

230 However, the unexpected stoichiometry and crystal structure of the Ti-oxide in the duplex scale at  
 231 1200 °C remains unsolved. As it is not clear what kind of oxidation level is prevalent in this oxide (see  
 232 Table 2, third row), for instance Ti(+II), Ti(+III) or Ti(+IV), the oxide is designated as Ti<sub>x</sub>O<sub>y</sub> with the  
 233 general description of the oxidation level Ti(+2y/x). This off-stoichiometric Ti<sub>x</sub>O<sub>y</sub> is present as rutile  
 234 TiO<sub>2</sub> as confirmed by GIXRD in this work, because other crystal structure types cannot be assigned.  
 235 Additionally, the presence of rutile was confirmed by EBSD in Ref. [9], whereas sub-surface regions  
 236 are not indexed and might represent Ti-oxide other than rutile Ti(+IV)-oxide. However, the chemical  
 237 composition determined by APT is not in agreement with the stoichiometry range of stable rutile TiO<sub>2</sub>  
 238 reported in literature (TiO<sub>2-x</sub> with  $x = 0$  to 0.04 [26, 27]). From a thermodynamic point of view, besides  
 239 TiO<sub>2</sub>, the presence of Ti<sub>3</sub>O<sub>5</sub> would be expected (solubility range Ti<sub>3</sub>O<sub>5+x</sub> with  $x = 0$  to 0.1 [26, 28]) as  
 240 illustrated by the isothermal sections of the ternary Ti-Si-O (see Fig. 4a) and Mo-Si-O systems (see Fig.  
 241 4b) at the relevant temperatures of 1200 and 700 to 1000 °C, respectively. The possibly formed oxidation  
 242 products of the phases Mo<sub>5</sub>Si<sub>3</sub> and Ti<sub>5</sub>Si<sub>3</sub> (when neglecting the influence of dissolved Mo of (11 ± 3) at%  
 243 (determined by EDX) in (Ti,Mo)<sub>5</sub>Si<sub>3</sub>) can be seen when the O concentration (comparably to the oxygen  
 244 partial pressure) is increased (dotted line). A stability region of Ti<sub>5</sub>Si<sub>3</sub>, SiO<sub>2</sub> and Ti<sub>3</sub>O<sub>5</sub> (highlighted in  
 245 blue in Fig. 4a) can be reached when Ti<sub>5</sub>Si<sub>3</sub> is significantly enriched with O. With higher O concentration  
 246 or increased oxygen partial pressure, SiO<sub>2</sub> and TiO<sub>2</sub> are in equilibrium with O (highlighted in green in  
 247 Fig. 4a). Ti<sub>4</sub>O<sub>7</sub> is here excluded, as it is not in equilibrium with (Ti,Mo)<sub>5</sub>Si<sub>3</sub> and as the APT results do  
 248 not match the stoichiometry. During oxidation of Mo<sub>5</sub>Si<sub>3</sub> the formation of MoO<sub>2</sub>, SiO<sub>2</sub> and MoO<sub>3</sub> occurs  
 249 depending on the O concentration and oxygen partial pressure. Based on thermodynamics, it is likely

250 that at the substrate surface  $\text{SiO}_2$  (solid) +  $\text{Ti}_3\text{O}_5$  (solid) +  $\text{MoO}_3$  (volatile) are forming, while the  
 251 composition of the duplex oxide scale of  $\text{SiO}_2$  +  $\text{Ti}_3\text{O}_5$  +  $\text{MoO}_3$  (volatile) changes to  $\text{SiO}_2$  and  $\text{TiO}_2$  with  
 252 increasing thickness. The presence of the top  $\text{TiO}_2$  oxide scale seems to be determined by the kinetics  
 253 due to its observed fast-growing nature [13, 29] and the fast diffusion of Ti cations within  $\text{TiO}_2$  [30].

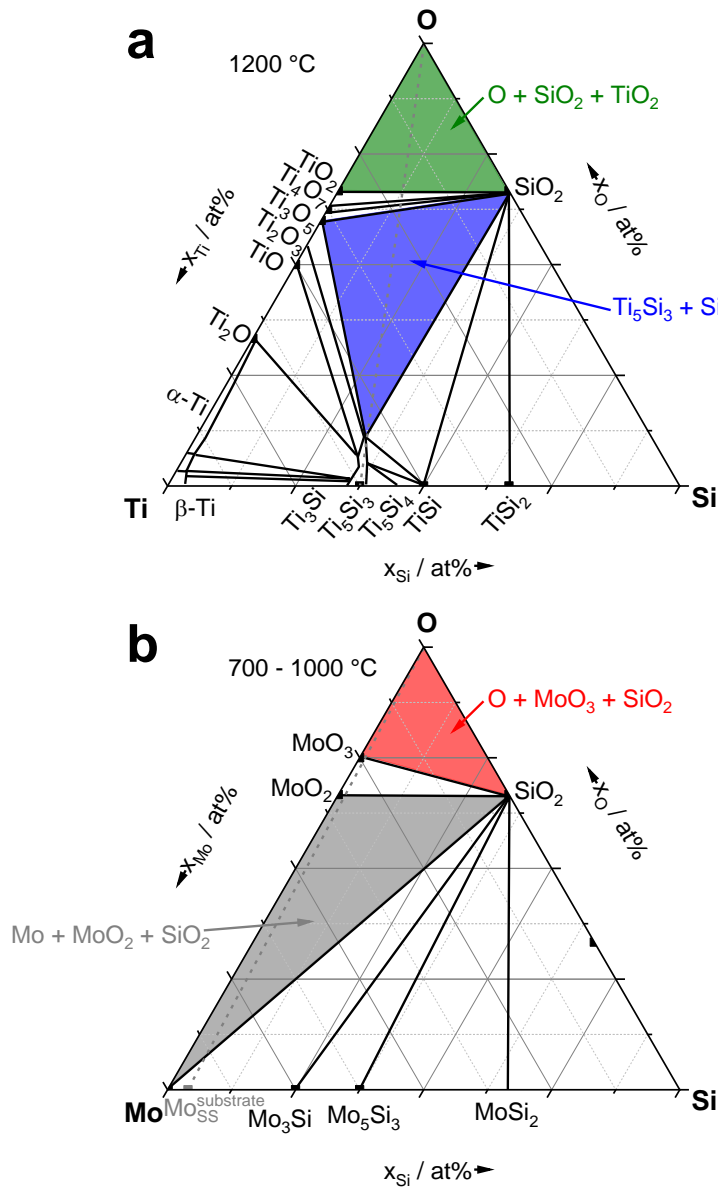


Fig. 4 Isothermal sections of the ternary Ti-Si-O (a) and Mo-Si-O (b) systems at 1200 and 700 to 1000 °C, respectively, including selected, highlighted phase equilibria along the stability line of  $\text{Ti}_5\text{Si}_3$  or  $\text{Mo}_5\text{Si}_3$  (dotted grey line) with enrichment of O [23, 31].

### 3.3. Analysis of the oxidation kinetics

254 In the following, the oxidation kinetics will be referred to as the kinetics of oxide scale growth, if not  
 255 otherwise stated. Literature data on weight change oxidation kinetics, which are considered for  
 256 comparison, are explicitly highlighted.

257 The evolution of the (sub-)oxide scale thickness  $d$  (internal oxidation  $d_{int}$ , duplex  $d_{duplex}$  and top scale  
 258  $d_{top}$ ) at 1200 °C is plotted in Fig. 5a as a function of time in double logarithmic manner (data at 100 h

259 taken from our previous article [10]). The following power fit function for the oxide scale thickness  $d$   
260 in dependence of the exposure time  $t$  with the oxidation rate constant  $k_n$  for a specific exponent  $n$  was  
261 applied:

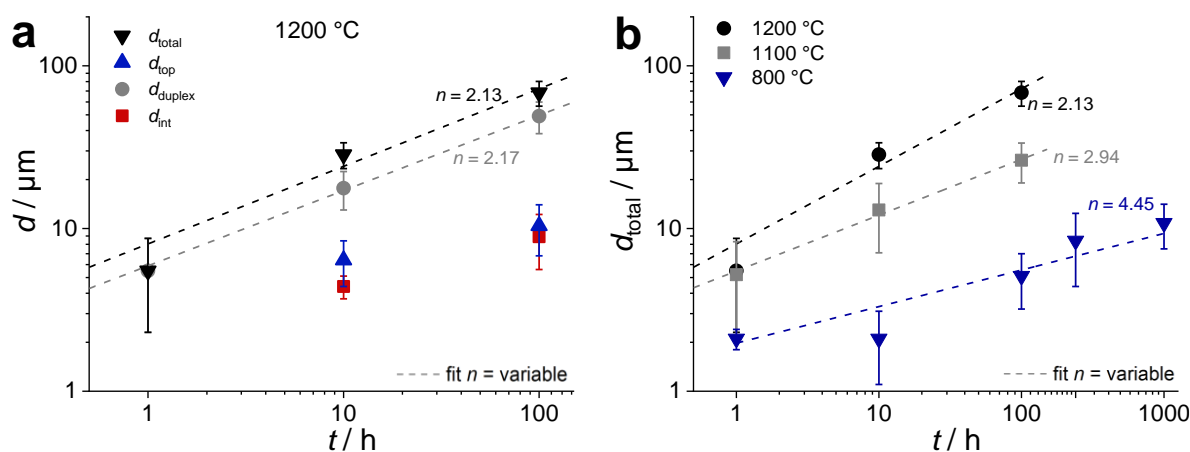
$$d^n = k_n \cdot t \quad \text{Eq. 1}$$

262 First, the fit was performed with the exponent  $n$  being fixed to 2, which is equal to a parabolic oxide  
263 scale growth law [32]. Additionally,  $n$  was adjusted individually in order to achieve optimum fit quality  
264 for comparison (dotted fit lines in Fig. 5a). It is revealed that: (i) The overall oxide scale growth at  
265 1200 °C is dominated by the growth of the duplex scale (green circles). (ii) Both, the evolution of the  
266 oxide scale in total  $d_{total}$  (violet triangles) and the duplex scale  $d_{duplex}$  (green circles) are parabolic  
267 with  $n$  values close to 2. (iii) Subtraction of the duplex scale data from the total oxide scale yields the  
268 change of the top single-phase oxide scale with time (blue triangles), which also seems to follow a  
269 parabolic rate law. However, a fit itself for the data points of the top single-phase was not possible since  
270 only two data points could be validly determined as for short oxidation times no separation of a top  
271 single-phase oxide scale was observed. In conclusion, the oxidation kinetics are determined to be  
272 parabolic and thus, the oxidation mechanism is regarded as bulk diffusion rate-controlled by either the  
273 oxidant (O anion) or the reactant (metal cation) through the (sub-)oxide scales.

274 In order to assess whether there is a change in oxidation mechanism with decreasing temperature and  
275 thus, less thermal activation for diffusion processes, the evolution of the total oxide scale thickness  
276  $d_{total}$  at 1200 °C is compared to the observations made at 800 and 1100 °C (see Fig. 5b). It is  
277 demonstrated that the oxide scales are considerably thicker at elevated temperatures, namely  $(26 \pm 7)$   
278 and  $(68 \pm 11)$   $\mu\text{m}$  at 1100 and 1200 °C, respectively, as compared to only  $(5 \pm 2)$   $\mu\text{m}$  at 800 °C after  
279 100 h of cyclic oxidation. Moreover, it is found that the oxide scale evolution might be associated with  
280 an almost cubic oxidation kinetics at 1100 °C as well, as revealed by an exponent of  $n = 2.94$  (see Table  
281 3). The cubic and parabolic growth observed at 1100 and 1200 °C, respectively, is attributed to diffusion  
282 processes, especially relevant at high temperatures. This is confirmed by the estimated diffusion distance  
283 of  $\text{Ti}^{4+}$  cations in  $\text{TiO}_2$ , Ti(+IV)-oxide at the respective temperatures, which is found to be 29 and 62  $\mu\text{m}$   
284 after 100 h at 1100 and 1200 °C, respectively, which is in excellent agreement to the experimental  
285 values. The impact of the temperature on the evolution of the oxide scale thickness is underlined by Fig.  
286 5c. The dependence of the total oxide scale thickness is highlighted as a function of temperature for  
287 specific exposure durations of 1, 10 and 100 h.

288 In contrast, the overall evaluation of the oxide scale growth at 800 °C does not yield parabolic kinetics,  
289 even after exposure times of 1000 h, as a considerably increased exponent of  $n = 4.45$  according to Eq.  
290 1 is noted. Such high exponents in power-law oxidation kinetics are neither widely reported, nor  
291 discussed in literature. Additionally, as only a moderate fit quality ( $R_{adj}^2 = 0.82$ ) is obtained, it is

292 suggested that there are different oxidation stages with changing oxidation kinetics. This suggestion is  
 293 supported by considering the initial oxidation stage up to 100 h and the ongoing stage from 100 to 1000 h  
 294 separately. During the initial oxidation stage, it is likely that the prevalent oxidation mechanism is  
 295 reaction rate-controlled, as a linear fit leads to an excellent fit quality with  $R_{adj}^2 = 0.97$  (see Table 3).  
 296 The obedience to linear oxidation kinetics is further corroborated by the discontinuous morphology of  
 297 the oxide scale for exposure times shorter than 100 h (see BSE micrographs in Fig. 1). It is shown that  
 298 the oxidation occurs locally, especially in the surface-near  $Mo_{SS}$  regions, although not providing full  
 299 coverage of the alloy substrate (see Fig. 1a and b). Therefore, the kinetics up to 100 h are most likely to  
 300 be rate-determined by surface reactions occurring either at the oxide scale/atmosphere interface or at the  
 301 oxide scale/substrate interface. Other oxidation mechanisms leading to linear oxidation kinetics, such as  
 302 direct O access to the substrate through porous oxide scales or cracks, are unlikely, since neither  
 303 significant porosity nor cracks are observed in the oxide scale by SEM analysis (see Fig. 1a and b). Note  
 304 that this initial linear oxidation kinetics does not lead to catastrophic oxidation behaviour, as the  
 305 oxidation rate constant of  $8.25 \times 10^{-12} \text{ ms}^{-1}$  is significantly low. For longer exposure times than 100 h, a  
 306 continuous mixed Si-Ti-oxide scale is formed (see Fig. 1c), which accounts for the change in oxidation  
 307 kinetics. Fitting the respective values according to Eq. 1 leads to an exponent of 3.18 with a good fit  
 308 quality of  $R_{adj}^2 = 0.94$ . This reveals that the oxidation kinetics change from linear to cubic. In literature,  
 309 cubic oxidation kinetics are assumed to be determined by diffusion processes along grain boundaries  
 310 [33-35]. Thus, it might be that O inward diffusion along grain boundaries and Ti-oxide/Si-oxide phase  
 311 boundaries determines the oxidation mechanism for exposure times longer than 100 h. However, no  
 312 profound evidence can be given here for this assumption.



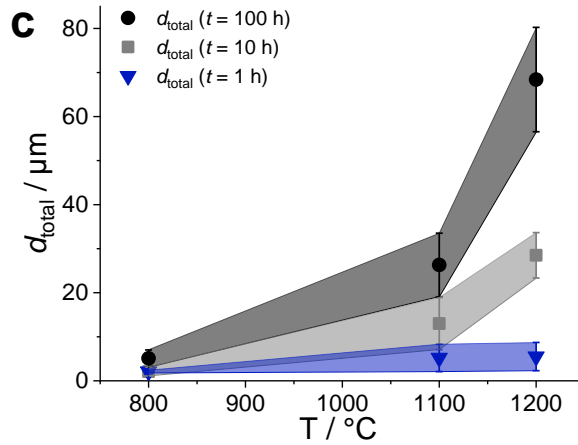


Fig. 5 Evolution of the oxide scale thickness in total  $d_{total}$  and of the respective sub-scales (top Ti-oxide  $d_{top}$ , duplex Si- and Ti-oxide scale  $d_{duplex}$  and internal oxidation zone  $d_{int}$ ) in dependence of the exposure time  $t$  at 1200 °C for the eutectic alloy (a). Fit functions according to Eq. 1 with  $n$  being adjusted variably (dotted lines) are included. In comparison  $d_{total}$  is displayed logarithmically at 800, 1100 and 1200 °C (b) and fitted accordingly as well (b). The total oxide scale thicknesses are compared for different times at 800, 1100 and 1200 °C (c).

Table 3 Determined oxidation rate constants  $k_n$  for 800, 1100 and 1200 °C. For 1100 and 1200 °C referring to Eq. 1. For 800 °C  $k^*$ , referring to a linear fitting method, is included.  $R_{adj}^2$  values are provided as well.

$T / ^\circ\text{C}$	fitting range of $t / \text{h}$	$n / -$	$k_n / \text{m}^n\text{s}^{-1}$	$k^* / \text{ms}^{-1}$	$R_{adj}^2 / -$
800	1 – 1000	4.45	$1.16 \times 10^{-29}$	-	0.82
	1 – 100	1 (linear)	-	$8.25 \times 10^{-12}$	0.97
	100 – 1000	3.18	$4.51 \times 10^{-23}$	-	0.94
	100 – 1000	2 (parabolic)	$4.41 \times 10^{-17}$	-	0.61
1100	1 – 100	2.94	$8.64 \times 10^{-20}$	-	0.99
		2 (parabolic)	$2.38 \times 10^{-15}$	-	0.86
1200	1 – 100	2.13	$3.56 \times 10^{-15}$	-	0.96
		2 (parabolic)	$1.51 \times 10^{-14}$	-	0.96

313 The high-temperature parabolic oxidation behaviour of the eutectic alloy Mo-20Si-52.8Ti is  
 314 characterised by the parabolic oxidation rate constant  $k_{n=2} = 2.38 \times 10^{-15}$  (1100 °C) to  $1.51 \times 10^{-14} \text{ m}^2\text{s}^{-1}$   
 315 (1200 °C), which are thermally activated with an activation energy of 310 kJ/mol. These findings also  
 316 apply to certain eutectic-eutectoid alloys from Ref. [11] (see App. 1 for their chemical compositions),  
 317 as well as to the eutectoid alloy from Ref. [9], as parabolic oxidation kinetics with similar oxidation rate  
 318 constants to the eutectic alloy were revealed with activation energies in the range of 200 to 410 kJ/mol.  
 319 Note that the determination of these activation energies is based on only two data points and thus, only  
 320 serves as estimates when interpreting the activation energies.

321 Moreover, no difference was found between the pesting-resistant and non-pesting-resistant Ti-rich and  
 322 Ti-lean (nominal Ti content < 43 at%) alloys, respectively, which could have been taken into

323 consideration for further understanding the root causes of pesting resistance. However, in order to  
 324 classify the oxidation behaviour of these Mo-Si-Ti alloys, their parabolic oxidation rate constants  $k_{n=2}$   
 325 are compared to the relevant diffusion coefficients of this systems. Since the oxidation rate constants  
 326 are known to be thermally activated [36], these can be visualised by an Arrhenius plot in Fig. 6. The  
 327 following correlation between the oxidation rate constant and the diffusion coefficient  $D$  allows a direct  
 328 comparison of the respective diagrams (see Eq. 2 [37]):

$$k_{n=2} = \frac{2 D C_0}{N} \quad \text{Eq. 2}$$

329 Here,  $D$  is the diffusion coefficient of a specific species diffusing in the oxide,  $C_0$  is the oxidant  
 330 concentration at the scale surface and  $N$  is the number of oxidant species incorporated in the newly  
 331 grown oxide of unit volume [37].

332 Generally, it is seen in Fig. 6 that Ti ion diffusion (solid blue line) is considerably faster than O ion  
 333 diffusion in  $\text{TiO}_2$  (dotted, dashed and solid red lines). This is in good agreement with the assumption  
 334 that the top Ti-rich oxide scale is growing outward by Ti-cation outward diffusion, which has also been  
 335 experimentally verified by marker experiments by Azim et al. in Ref. [29] on Mo-Si-B-Ti alloys. In  
 336 contrast, the diffusion coefficient for Si bulk diffusion in  $\text{SiO}_2$  is significantly lower compared to the  
 337 diffusion coefficients for O. This is in accordance with the assessment of Deal and Grove in Ref. [38]  
 338 who stated that  $\text{SiO}_2$  formation proceeds rather by the inward diffusion of O, than by the outward  
 339 diffusion of Si. Furthermore, the respective oxidation rate constants of the eutectic alloy ( $k_{n=2}^{\text{eutectic}}$ ), of  
 340 the intermediate eutectic-eutectoid alloys ( $k_{n=2}^{\text{eutectic-eutectoid}}$ ) and of the eutectoid alloy ( $k_{n=2}^{\text{eutectoid}}$ )  
 341 are found to be in the range of the diffusion coefficient of Ti in  $\text{TiO}_2$ . Hence, it can be concluded that  
 342 the oxidation rate of these eutectic-eutectoid Mo-Si-Ti alloys is determined by the Ti diffusion in  $\text{TiO}_2$ .

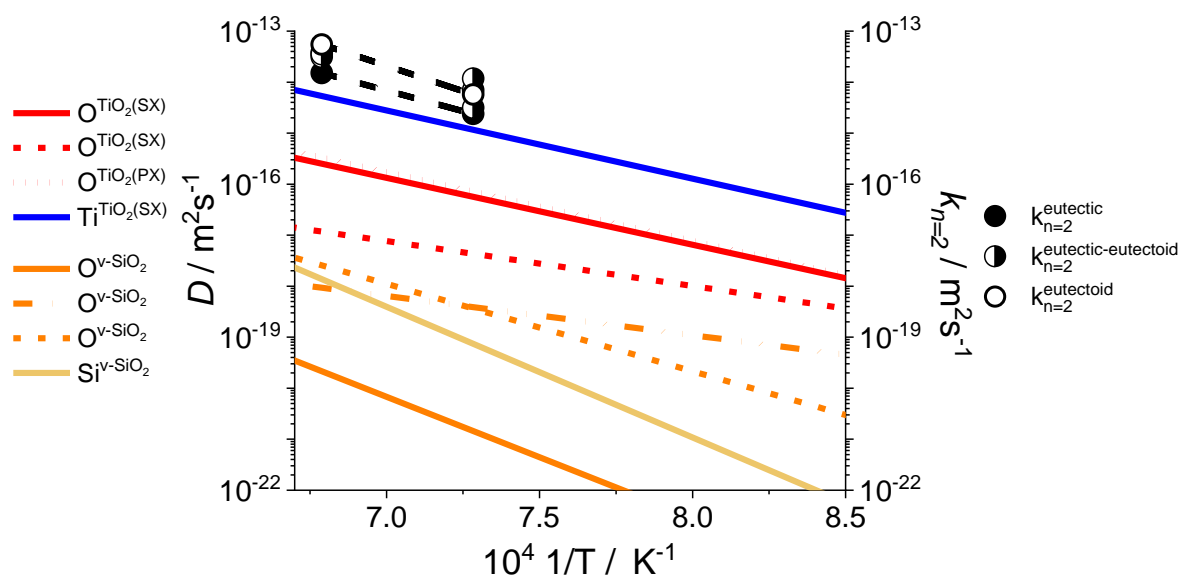


Fig. 6 Temperature-dependence of the diffusion coefficients  $D$  of Ti and O ions in single-crystalline (SX) and polycrystalline (PX)  $\text{TiO}_2$  (blue and red lines) and Si- and O ions in vitreous (v)  $\text{SiO}_2$  (yellow and orange lines), respectively. Data taken from [39-44]. For comparative reasons, the values of  $k_{n=2}$  for the eutectic (black solid circle), eutectic-eutectoid (half-opened circles) alloys and the eutectoid alloy (open black circle) are added.

343 In order to understand the observed oxidation kinetics in the Mo-Si-Ti system, the individual oxidation  
344 behaviour of the constitutional phases  $\text{Mo}_{\text{SS}}$  and  $(\text{Ti},\text{Mo})_5\text{Si}_3$  will be discussed in the following. Mo is  
345 known to undergo catastrophic oxidation due to volatilisation of  $\text{MoO}_3$  at temperatures above 500 °C  
346 [45-47]. The respective activation energy for temperatures beyond 800 °C was associated with a  
347 diffusion-controlled process through the gas phase [45, 47, 48] with 82 kJ/mol [45]. However, the  
348 tendency of forming volatile  $\text{MoO}_3$  can be counterbalanced by the formation of solid Ti-rich oxides,  
349 when alloyed with Ti [11]. Thus, the linear mass loss oxidation rate can be considerably decelerated at  
350 800 °C, namely from -33 to -14 mg/cm<sup>2</sup>h<sup>-1</sup>, when increasing the Ti content from 20 to 40 at% [11]. The  
351 here discussed eutectic alloy comprises a Ti-rich  $\text{Mo}_{\text{SS}}$  with an approximate Ti content of 45 at% [10].  
352 This supports the observed pesting-resistance in Ti-rich Mo-Si-Ti and Mo-Si-B-TiC alloys at 800 °C  
353 with considerable volume fractions of Ti-containing  $\text{Mo}_{\text{SS}}$  [10, 11, 49]. Therefore, the improvement in  
354 oxidation behaviour is attributed to the formation of a (relatively) dense  $\text{TiO}_2$  oxide scale [49].

355 In comparison, the silicide phase  $\text{Ti}_5\text{Si}_3$  reveals different weight change oxidation kinetics, which are  
356 dependent on the Si content and the oxidation duration [50]. The  $(\text{Ti},\text{Mo})_5\text{Si}_3$  phase present in the  
357 investigated eutectic alloy exhibits a constant Si ratio close to the ideal stoichiometry due to ingot  
358 metallurgical manufacturing. Furthermore, there is a considerable Mo concentration of  $(13 \pm 4)$  at%  
359 [11]. Therefore, the phase composition is regarded to be comparable to the studies made by Majumdar  
360 et al. in Ref. [12] on an Mo-30Si-40Ti alloy, which comprises a  $(\text{Ti},\text{Mo})_5\text{Si}_3$  matrix, but with an increased  
361 Mo content of 26 at%. The oxidation behaviour was reported to obey parabolic weight gain and oxide  
362 scale growth kinetics in the temperature range of 900 up to 1300 °C [12]. Thereby, the formation of an  
363 outer  $\text{TiO}_2$  scale and an underlying  $\text{SiO}_2$ - $\text{TiO}_2$  duplex scale was observed [12] like for the investigated  
364 Mo-Si-Ti alloys from the present study (the eutectic alloy Mo-20Si-52.8Ti, as well as the other  
365 derivatives from the Mo-Si-Ti system listed in App. 1). The authors concluded that the formation of  
366 volatile  $\text{MoO}_3$  is suppressed in  $(\text{Ti},\text{Mo})_5\text{Si}_3$  [12]. The parabolic oxidation rate constant was found to be  
367 about half an order of magnitude lower than in the eutectic alloy at 1200 °C in Ref. [12] (compare with  
368 Table 2). The corresponding activation energies were determined to be 72 and 325 kJ/mol in the  
369 temperature range between 900 to 1200 °C and 1200 to 1300 °C, respectively [12]. This first seems  
370 comparably low, but was interpreted by the authors on the basis of the activation energy for diffusion of  
371 oxygen in fused  $\text{SiO}_2$  which was regarded to be in the same order [12]. At higher temperatures instead,  
372 the activation energy is comparable to the activation energies found for the Mo-Si-Ti alloys in this study  
373 (see App. 1). The difference in activation energies was attributed to a change in microstructural set-up  
374 of the duplex oxide scale with an increased volume fraction of  $\text{TiO}_2$ , which might lead to accelerated O  
375 inward diffusion [12]. Conclusively,  $(\text{Ti},\text{Mo})_5\text{Si}_3$  exhibits a diffusion-controlled oxidation behaviour,  
376 which is mainly attributed to the inward diffusion of O through the  $\text{SiO}_2$ - $\text{TiO}_2$  duplex scale [12].

377 This comparative study reveals that the oxidation kinetics are combined kinetics of the constituting  
378 phases  $\text{Mo}_{\text{SS}}$  and  $(\text{Ti},\text{Mo})_5\text{Si}_3$ . At high temperatures the diffusion processes are fast enough to form

379 continuous, solid oxide scales, which can be accounted for the parabolic bulk diffusion-controlled  
380 oxidation, comparable to the oxidation kinetics of  $(\text{Ti},\text{Mo})_5\text{Si}_3$ . By contrast, the oxidation kinetics at  
381 800 °C are different to the ones observed for the constituting phases  $\text{Mo}_{\text{SS}}$  and  $(\text{Ti},\text{Mo})_5\text{Si}_3$ , as the  
382 eutectic alloy reveals linear oxidation kinetics at the beginning, turning into cubic kinetics for oxidation  
383 times longer than 100 h.

384 These fundamental differences might be rationalised as follows: Generally, the defect structure of the  
385 oxide determines the oxidation kinetics. In the case of rutile  $\text{TiO}_2$  the defect structure depends on  
386 temperature, oxygen partial pressure, the exact stoichiometry [51] and impurities [52]. At 1100 and  
387 1200 °C, the main defects are O vacancies and Ti cations of different valences ( $\text{Ti}^{3+}$ ,  $\text{Ti}^{4+}$ ) [53]. While  
388 the first primarily contribute to the non-stoichiometry [53, 54], the latter are the defects dominating scale  
389 formation.

#### 390 *3.4. The role of the Ti-oxide within the oxide scales formed on the eutectic alloy Mo-20Si-52.8Ti*

391 The good oxidation resistance of the Ti-oxide formed on the eutectic alloy Mo-20Si-52.8Ti (see Fig. 1)  
392 in comparison to pure Ti is unexpected [36, 55]. Therefore, possible explanations are discussed in the  
393 following: In essence, the oxidation resistance of Ti is improved by reducing its O solubility [55], e. g.  
394 by alloying with Al or Si [16, 56]. A reduction in oxidation rate is attained in Ti-xSi alloys with  $x = 0.4$   
395 to 1.7 or 12.7 at% Si at 500 to 700 and 850 °C, respectively [16, 56]. Moreover, a parabolic oxidation  
396 behaviour is observed for Ti-Si alloys in contrast to a linear one, which is present in pure Ti [56]. When  
397 3.3 at% Si or less are added, Si was found to be homogeneously distributed within the oxide scale, either  
398 solved as solid solution in rutile  $\text{TiO}_2$  or as embedded  $\text{SiO}_2$  islands with diameters of less than 1  $\mu\text{m}$  at  
399 850 °C [56]. In contrast, higher additions up to 13 at% Si were found to be inhomogeneous distributed  
400 within the oxide scale and even led to cracking at the substrate/oxide interface [16]. Hence, the Si  
401 concentration presumably accounts for a transition in oxide scale morphology preventing pore formation  
402 and spallation, which typically occurs in  $\text{TiO}_2$  formed on pure Ti [56]. There are several impacts of Si  
403 on the oxidation behaviour of Ti-Si alloys proposed: (i) Si might retard the inward diffusion of O and  
404 therefore lead to a reduction in penetration depth [56], as interstitially solved Si ions might reduce the  
405 amount of available O vacancy sites decelerating the diffusion rate of O in rutile  $\text{TiO}_2$  [56]. (ii) The  
406 presence of  $\text{SiO}_2$  facilitates the formation of a denser, less porous oxide scale and prevents  
407 recrystallisation and stratification of  $\text{TiO}_2$  due to the change in stress relaxation processes within the  
408 oxide scale [16, 56]. However, it is questionable whether the very low amount of Si/ $\text{SiO}_2$  in  $\text{TiO}_2$ /Ti-  
409 oxide below 0.1 at% formed on the eutectic alloy (see Table 2 and Fig. 2) can be taken into account for  
410 a reduction in O vacancies due to preoccupation by Si ions. For comparison, in Ti-Nb alloys, solution  
411 of  $\text{Nb}^{5+}$  ions was observed in rutile  $\text{TiO}_2$  leading to a significant deceleration of oxide scale growth at  
412 900 and 1000 °C in static air [57]. Thereby,  $\text{Nb}^{5+}$  ions were found to substitute  $\text{Ti}^{4+}$  ions with an  
413 estimated ratio of less than 0.14 % [57].

414 Although, TiO<sub>2</sub> formed on Ti or Ti-based alloys often suffers from cracking [16, 55, 58-60], the oxide  
 415 scales (especially the Ti-oxide) formed on the eutectic alloy are crack-free with very low porosity of  
 416 less than 1.5 vol% along the oxide scale substrate interface [11]. This indicates that a change in density  
 417 and adherence of the oxide scales allow for the high oxidation resistance. The crack formation is often  
 418 caused by the formation of sub-layers like TiN [16], but none were observed on the current eutectic  
 419 alloy Mo-20Si-52.8Ti. Moreover, the mismatch of the CTE needs to be considered with regard to the  
 420 oxide/substrate compatibility. For this purpose, CTE values are compared in Table 4. There is no  
 421 considerable difference in CTE, no matter whether TiO<sub>2</sub> is growing on Ti or on the eutectic alloy.  
 422 However, especially at longer exposure times and higher temperatures, the relationship between the top  
 423 TiO<sub>2</sub>, the duplex scale and the eutectic alloy substrate has to be taken into account. The CTE of thermally  
 424 grown SiO<sub>2</sub> is about one order of magnitude lower, so it is likely that the SiO<sub>2</sub> portions balance the  
 425 thermal expansion of TiO<sub>2</sub> within the (duplex) oxide scale and suppress crack formation during cyclic  
 426 oxidation testing.

427 *Table 4 Comparison of the coefficients of thermal expansions (CTE) of Ti, TiO<sub>2</sub>, SiO<sub>2</sub> and the eutectic alloy Mo-20Si-52.8Ti.*

	CTE / K <sup>-1</sup>	Refs.
Ti	10.5 x 10 <sup>-6</sup> (20 – 700 °C)	[61]
TiO <sub>2</sub>	<i>a</i> -axis: 8.1 x 10 <sup>-6</sup> (276 °C) <i>c</i> -axis: 10.6 x 10 <sup>-6</sup> (276 °C)	[62]
SiO <sub>2</sub>	5 x 10 <sup>-7</sup> (RT – 300 °C)	[63]
eutectic alloy	7.0 – 9.1 x 10 <sup>-6</sup> (300 – 1200 °C)	this study

428 In conclusion, the beneficial impact of the Ti-oxide on the oxidation behaviour is attributed to the  
 429 interaction with the Si-oxide, which might lead to a reduction in available vacancies for O inward  
 430 diffusion. Additionally, with regard to the diffusion of O, Si and Ti, the O concentration being available  
 431 for the formation of the duplex oxide scale at 1200 °C is determined by the O ion diffusion flux through  
 432 the top TiO<sub>2</sub> oxide scale. Once the duplex scale is formed, Ti ion diffusion (which might be faster along  
 433 the penetrating Ti-oxide regions through the oxide scale) to the top TiO<sub>2</sub> scale is necessary for further  
 434 growth of the top TiO<sub>2</sub> oxide scale. Therefore, it is concluded that the fast formation of the top TiO<sub>2</sub>  
 435 scale is triggered by kinetics and that its growth is slowed down with ongoing formation of the  
 436 underlying duplex scale.

#### 4. Summary and Conclusion

437 The analysis of the microstructural constitution of the oxide scales formed on the eutectic Mo-20Si-  
 438 52.8Ti alloy at 800 °C revealed a single-layered mixed oxide scale comprising Ti- and Si-oxide. At  
 439 1200 °C, a top Ti-oxide scale with an underlying mixed duplex Ti- and Si-oxide scale is observed.  
 440 Besides rutile TiO<sub>2</sub> and some cristobalite SiO<sub>2</sub>, GIXRD analyses indicate the presence of some MoO<sub>3</sub>  
 441 in the oxide scale formed at 1200 °C. However, the formation of MoO<sub>3</sub> is outbalanced and

442 overcompensated by solid oxide scale formation as documented by negligible mass changes even after  
443 test durations of 100 h. The assessment of the compositional constitution of the oxide scales by APT  
444 leads to the following conclusions: (i) The chemical composition of the (top) Ti-oxide scales formed at  
445 800 and 1200 °C is found to be comparable with a stoichiometry matching rutile-type TiO<sub>2</sub> Ti(+IV)-  
446 oxide. (ii) The duplex scale formed at 1200 °C is composed of an O-depleted Ti-oxide region off-  
447 stoichiometric to typical known Ti-oxide, among which Ti<sub>3</sub>O<sub>5</sub> is the most likely one to be present. (iii)  
448 The Si-oxide region within the duplex scale is depleted in O as well, with a stoichiometry of SiO<sub>1.6</sub>  
449 closest to SiO<sub>2</sub>. It is unlikely that this observed depletion in O is caused by an underestimation caused  
450 by the measurement conditions. (iv) Virtually no solubility of Mo is found in the Ti- and Si-oxide,  
451 respectively, for both oxide scales formed at 800 and 1200 °C. (v) There is a negligible amount of Si  
452 solved in the Ti-oxide formed at 800 and 1200 °C.

453 The study of the oxide growth kinetics revealed that the oxide scale growth obeys a linear rate law at  
454 800 °C up to 100 h pointing to a surface reaction-controlled oxidation. Longer exposure times facilitate  
455 the formation of a continuous mixed oxide scale, which results in cubic oxidation kinetics. In contrast,  
456 at 1100 and 1200 °C the thickness of the overall oxide scale and of the duplex scale grows with almost  
457 parabolic oxidation kinetics. This is also found for the eutectoid and eutectic-eutectoid Mo-Si-Ti alloys.  
458 The activation energies of the parabolic oxidation rate constants are in good agreement with published  
459 data on activation energies for self-diffusion of O, Ti and Si in the respective oxides [39-44, 64]  
460 confirming the oxidation rate to be diffusion-controlled. The observed change in oxidation mechanism  
461 between 800 and 1100 °C correlates with the oxidation kinetics of the microstructural constituents Mo<sub>SS</sub>  
462 and (Ti,Mo)<sub>5</sub>Si<sub>3</sub>. While Mo<sub>SS</sub> is known to undergo catastrophic oxidation with linear mass loss [45, 46],  
463 which is decelerated with increasing Ti content [11], above 600 °C, (Ti,Mo)<sub>5</sub>Si<sub>3</sub> was found to obey  
464 parabolic oxide growth kinetics in the temperature range of 900 to 1300 °C [12].

465

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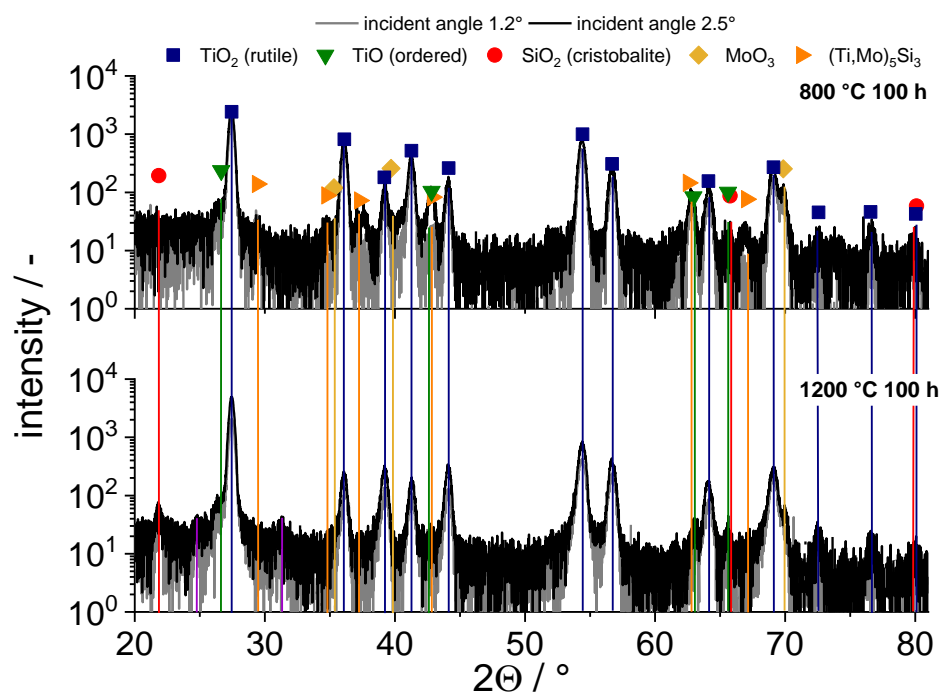
474

## Appendix

App. 1 Nominal chemical composition of eutectic-eutectoid Mo-Si-Ti alloys corresponding to Refs. [9, 11].

eutectic-eutectoid alloys	nominal composition / at%
alloy #1	Mo-21Si-47Ti
alloy #2	Mo-21Si-43.4Ti
alloy #3	Mo-21.5Si-41.5Ti
alloy #4	Mo-21Si34Ti

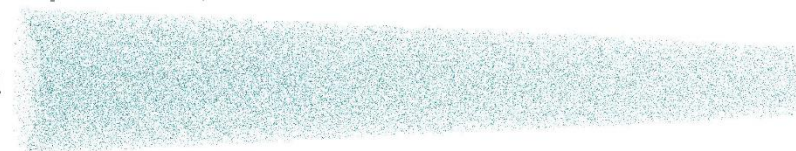
## Supplementary



Supp. 1 GIXRD diffraction patterns of the cyclically oxidised samples at 800 (top) and 1200 °C (bottom) for 100 h with incident angles of 1.2 (grey) and 2.5° (black). Note that the intensities are plotted with logarithmic scale.

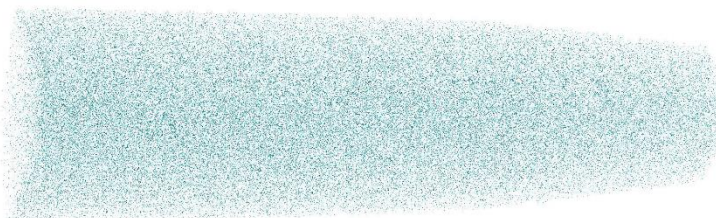
top Ti-oxide, 800 °C

a



top Ti-oxide, 1200 °C

b



O Si Ti  $Ti_xO_y$  50 nm

475 *Supp. 2 Visualisation of the subsets for the APT analyses of the top Ti-oxide scale at 800 (a) and 1200 °C (b). For reasons of*  
476 *clarity only 1 % of all identified ions is shown here. No  $SiO_x$  ions were identified.*

### Data availability statement

477 The raw and processed data required to reproduce these findings are available on request to  
478 alexander.kauffmann@kit.edu.

### References

- 479 1. M. F. Yan, J. B. MacChesney, S. R. Nagel, W. W. Rhodes, Sintering of optical wave-guide  
480 glasses. *Journal of Materials Science*, 1980. 15(6): p. 1371-1378. DOI: 10.1007/BF00752116.
- 481 2. M. Meyer, M. Kramer, M. Akinc, Boron-doped molybdenum silicides. *Advanced Materials*,  
482 1996. 8(1): p. 85-88. DOI: 10.1002/adma.19960080118.
- 483 3. M. K. Meyer, A. J. Thom, M. Akinc, Oxide scale formation and isothermal oxidation behavior  
484 of Mo–Si–B intermetallics at 600–1000°C. *Intermetallics*, 1999. 7(2): p. 153-162. DOI:  
485 10.1016/S0966-9795(98)00058-2.
- 486 4. K. Yoshimi, S. Nakatani, T. Suda, S. Hanada, H. Habazaki, Oxidation behavior of  $Mo_5SiB_2$ -  
487 based alloy at elevated temperatures. *Intermetallics*, 2002. 10(5): p. 407-414. DOI:  
488 10.1016/S0966-9795(02)00013-4.
- 489 5. Y. Yang, H. Bei, S. Chen, E. P. George, J. Tiley, Y. A. Chang, Effects of Ti, Zr, and Hf on the  
490 phase stability of  $Mo_{SS} + Mo_3Si + Mo_5SiB_2$  alloys at 1600°C. *Acta Materialia*, 2010. 58(2): p.  
491 541-548. DOI: 10.1016/j.actamat.2009.09.032.
- 492 6. A. Rahmel, P. J. Spencer, Thermodynamic Aspects of TiAl and  $TiSi_2$  Oxidation: The Al-Ti-O  
493 and Si-Ti-O Phase Diagrams. *Oxidation of Metals*, 1991. 35(1-2): p. 53-68. DOI:  
494 10.1007/BF00666500.
- 495 7. T. A. Parthasarathy, M. G. Mendiratta, D. M. Dimiduk, Oxidation mechanisms in Mo-  
496 reinforced  $Mo_5SiB_2$  (T2)– $Mo_3Si$  alloys. *Acta Materialia*, 2002. 50(7): p. 1857-1868. DOI:  
497 10.1016/S1359-6454(02)00039-3.
- 498 8. S. Paswan, R. Mitra, S. K. Roy, Oxidation behaviour of the Mo–Si–B and Mo–Si–B–Al alloys  
499 in the temperature range of 700–1300°C. *Intermetallics*, 2007. 15(9): p. 1217-1227. DOI:  
500 10.1016/j.intermet.2007.02.012.
- 501 9. D. Schliephake, A. Kauffmann, X. Cong, C. Gombola, M. A. Azim, B. Gorr, H.-J. Christ, M.  
502 Heilmaier, Constitution, oxidation and creep of eutectic and eutectoid Mo-Si-Ti alloys.  
503 *Intermetallics*, 2019. 104: p. 133-142. DOI: 10.1016/j.intermet.2018.10.028.
- 504 10. S. Obert, A. Kauffmann, M. Heilmaier, Characterisation of the oxidation and creep behaviour  
505 of novel Mo-Si-Ti alloys. *Acta Materialia*, 2020. 184: p. 132-142. DOI:  
506 10.1016/j.actamat.2019.11.045.

- 507 11. S. Obert, A. Kauffmann, S. Seils, S. Schellert, M. Weber, B. Gorr, H.-J. Christ, M. Heilmaier,  
508 On the chemical and microstructural requirements for the pesting-resistance of Mo-Si-Ti alloys.  
509 JMR&T, 2020. 9(4): p. 8556-8567. DOI: 10.1016/j.jmrt.2020.06.002.
- 510 12. S. Majumdar, P. K. Singh, A. K. Pandey, G. V. S. N. Rao, Kinetics of oxide scale growth on a  
511 (Ti,Mo)<sub>5</sub>Si<sub>3</sub> based oxidation resistant Mo-Ti-Si alloy at 900-1300°C. High Temperature  
512 Materials and Processes, 2019. 38(2019): p. 533-540. DOI: 10.1515/htmp-2019-0056.
- 513 13. M. A. Azim, B. Gorr, H.-J. Christ, O. Lenchuk, K. Albe, D. Schliephake, M. Heilmaier, Effect  
514 of Ti content and nitrogen on the high-temperature oxidation behavior of (Mo,Ti)<sub>5</sub>Si<sub>3</sub>.  
515 Intermetallics, 2017. 90: p. 103-112. DOI: 10.1016/j.intermet.2017.05.023.
- 516 14. J. Dai, J. Zhu, C. Chen, F. Weng, High temperature oxidation behavior and research status of  
517 modifications on improving high temperature oxidation resistance of titanium alloys and  
518 titanium aluminides: A review. Journal of Alloys and Compounds, 2016. 685: p. 784-798. DOI:  
519 10.1016/j.jallcom.2016.06.212.
- 520 15. J. Unnam, R. N. Shenoy, R. K. Clark, Oxidation of commercial purity titanium. Oxidation of  
521 Metals, 1986. 26(3-4): p. 231-252. DOI: 10.1007/BF00659186.
- 522 16. D. Vojtěch, B. Bártová, T. Kubátík, High temperature oxidation of titanium–silicon alloys.  
523 Materials Science and Engineering: A, 2003. 361(1-2): p. 50-57. DOI: 10.1016/S0921-  
524 5093(03)00564-1.
- 525 17. M. Yoshihara, Y.-W. Kim, Oxidation behavior of gamma alloys designed for high temperature  
526 applications. Intermetallics, 2005. 13(9): p. 952-958. DOI: 10.1016/j.intermet.2004.12.007.
- 527 18. J. Angseryd, F. Liu, H.-O. André, S. S. A. Gerstl, M. Thuvander, Quantitative APT analysis  
528 of Ti(C, N). Ultramicroscopy, 2011. 111(6): p. 609-614. DOI: 10.1016/j.ultramic.2011.01.031.
- 529 19. R. Kirchhofer, D. R. Diercks, B. P. Gorman, J. F. Ihlefeld, P. G. Kotula, C. T. Shelton, G. L.  
530 Brenneka, Quantifying Compositional Homogeneity in Pb(Zr, Ti)O<sub>3</sub> Using Atom Probe  
531 Tomography. Journal of the American Ceramic Society, 2014. 97(9): p. 2677-2697. DOI:  
532 10.1111/jace.13135.
- 533 20. F. Liu, K. Stiller, Atom probe tomography of thermally grown oxide scale on FeCrAl.  
534 Ultramicroscopy, 2013. 132: p. 279-284. DOI: 10.1016/j.ultramic.2013.02.004.
- 535 21. F. Tang, B. Gault, S. P. Ringer, J. M. Cairney, Optimization of pulsed laser atom probe (PLAP)  
536 for the analysis of nanocomposite Ti–Si–N films. Ultramicroscopy, 2010. 110(7): p. 836-843.  
537 DOI: 10.1016/j.ultramic.2010.03.003.
- 538 22. T. Boll, M. Thuvander, S. Koch, J. N. Wagner, N. Nedfors, U. Jansson, K. Stiller, An APT  
539 investigation of an amorphous Cr–B–C thin film. Ultramicroscopy, 2015. 159: p. 217-222. DOI:  
540 10.1016/j.ultramic.2015.01.001.
- 541 23. J. I. Goldstein, S. K. Choi, F. J. J. V. Loo, G. F. Bastin, R. Metselaar, Solid-state Reactions and  
542 Phase Relations in the Ti-Si-O System at 1373 K. Journal of the American Ceramic Society,  
543 1995. 78(2): p. 313-322. DOI: 10.1111/j.1151-2916.1995.tb08802.x.
- 544 24. A. Abba, A. Galerie, M. Caillet, High-temperature oxidation of titanium silicide coatings on  
545 titanium. Oxidation of Metals, 1982. 17(1-2): p. 43-54. DOI: 10.1007/BF00606192.
- 546 25. A. Escudero, F. Langenhorst, Incorporation of Si into TiO<sub>2</sub> phases at high pressure. American  
547 Mineralogist, 2012. 97(4): p. 524-531. DOI: 10.2138/am.2012.3941.
- 548 26. S. Andersson, B. Collén, U. Kuylenstierna, A. Magnéli, Phase analysis studies on the titanium-  
549 oxygen system. Acta Chemica Scandinavica, 1957. 11(10): p. 1641-1652.
- 550 27. P. G. Wahlbeck, P. W. Gilles, Reinvestigation of the Phase Diagram for the System Titanium–  
551 Oxygen. Journal of the American Ceramic Society, 1966. 49(4): p. 180-183. DOI:  
552 10.1111/j.1151-2916.1966.tb13229.x.
- 553 28. R. R. Merritt, B. G. Hyde, L. A. Bursill, D. K. Philp, The thermodynamics of the titanium +  
554 oxygen system: An isothermal gravimetric study of the composition range Ti<sub>3</sub>O<sub>5</sub> to TiO<sub>2</sub> at 1304  
555 K. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and  
556 Physical Sciences, 1973. 274(1245): p. 627-661. DOI: 10.1098/rsta.1973.0078.
- 557 29. M. A. Azim, S. Burk, B. Gorr, H.-J. Christ, D. Schliephake, M. Heilmaier, R. Bornemann, P.  
558 H. Bolívar, Effect of Ti (Macro-) Alloying on the High-Temperature Oxidation Behavior of  
559 Ternary Mo–Si–B Alloys at 820–1300°C. Oxidation of Metals, 2013. 80(3-4): p. 231-242. DOI:  
560 10.1007/s11085-013-9375-1.

- 561 30. D. A. Venkatu, L. E. Poteat, Diffusion of titanium of single crystal rutile. *Materials Science and*  
562 *Engineering*, 1970. 5(5): p. 258-262. DOI: 10.1016/0025-5416(70)90014-5.
- 563 31. R. Beyers, Thermodynamic considerations in refractory metal-silicon-oxygen systems. *Journal*  
564 *of Applied Physics*, 1984. 56(1): p. 147-152. DOI: 10.1063/1.333738.
- 565 32. G. B. Gibbs, Vacancy generation and the kinetics of oxidation. *Philosophical Magazine*, 1968.  
566 18(156): p. 1175-1180. DOI: 10.1080/14786436808227748
- 567 33. Z. Liu, W. Gao, Y. He, Modeling of oxidation kinetics of Y-doped Fe–Cr–Al alloys. *Oxidation*  
568 *of Metals*, 2000. 53(3-4): p. 341-350. DOI: 10.1023/A:1004545421739.
- 569 34. D. Naumenko, B. Gleeson, E. Wessel, L. Singheiser, W. J. Quadackers, Correlation between  
570 the microstructure, growth mechanism, and growth kinetics of alumina scales on a FeCrAlY  
571 alloy. *Metallurgical and Materials Transactions A*, 2007. 38(12): p. 2974-2983. DOI:  
572 10.1007/s11661-007-9342-z.
- 573 35. W. J. Quadackers, Growth mechanisms of oxide scales on ODS alloys in the temperature range  
574 1000–1100°C. *Materials and Corrosion*, 1990. 41(12): p. 659-668. DOI:  
575 10.1002/maco.19900411204.
- 576 36. P. Kofstad, Oxidation of Metals: Determination of Activation Energies. *Nature*, 1957.  
577 179(4574): p. 1362-1363. DOI: 10.1038/1791362a0.
- 578 37. C.-J. Han, C. R. Helms, Parallel oxidation mechanism for Si oxidation in dry O<sub>2</sub>. *Journal of The*  
579 *Electrochemical Society*, 1987. 134(5): p. 1297.
- 580 38. B. E. Deal, A. S. Grove, General Relationship for the Thermal Oxidation of Silicon. *Journal of*  
581 *Applied Physics*, 1965. 36(12): p. 3770-3778. DOI: 10.1063/1.1713945.
- 582 39. M. Dechamps, P. Lehr, Sur l'oxydation du titane  $\alpha$  en atmosphère d'oxygène: Rôle de la couche  
583 oxydée et mécanisme d'oxydation. *Journal of the Less Common Metals*, 1977. 56(2): p. 193-  
584 207. DOI: 10.1016/0022-5088(77)90041-8.
- 585 40. J. C. Mikkelsen, Self-diffusivity of network oxygen in vitreous SiO<sub>2</sub>. *Applied Physics Letters*,  
586 1984. 45(11): p. 1187-1189. DOI: 10.1063/1.95086.
- 587 41. D. K. Moore, D. J. Cherniak, E. B. Watson, Oxygen diffusion in rutile from 750 to 1000 degrees  
588 C and 0.1 to 1000 MPa. *American Mineralogist*, 1998. 83(7-8): p. 700-711. DOI: 10.2138/am-  
589 1998-7-803.
- 590 42. J. Rodríguez-Viejo, F. Sibieude, M. T. Clavaguera-Mora, C. Monty, <sup>18</sup>O diffusion through  
591 amorphous SiO<sub>2</sub> and cristobalite. *Applied Physics Letters*, 1993. 63(14): p. 1906-1908. DOI:  
592 10.1063/1.110644.
- 593 43. E. W. Suvov, Diffusion of Oxygen in Vitreous Silica. *Journal of the American Ceramic Society*,  
594 1963. 46(1): p. 14-20. DOI: 10.1111/j.1151-2916.1963.tb13763.x.
- 595 44. T. Takahashi, S. Fukatsu, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi,  
596 K. Shiraiishi, Self-diffusion of Si in thermally grown SiO<sub>2</sub> under equilibrium conditions. *Journal*  
597 *of Applied Physics*, 2003. 93(6): p. 3674-3676. DOI: 10.1063/1.1554487.
- 598 45. E. A. Gulbransen, K. F. Andrew, F. A. Brassart, Oxidation of Molybdenum 550° to 1700°C.  
599 *Journal of the Electrochemical Society*, 1963. 110(9): p. 952-959. DOI: 10.1149/1.2425918.
- 600 46. E. S. Jones, J. F. Mosher, R. Speiser, J. W. Spretnak, The Oxidation of Molybdenum. *Corrosion*,  
601 1958. 14(1): p. 20-26. DOI: 10.5006/0010-9312-14.1.20.
- 602 47. M. Simnad, A. Spilners, Kinetics and Mechanism of the Oxidation of Molybdenum. *JOM*, 1955.  
603 7(9): p. 1011-1016. DOI: 10.1007/BF03377603.
- 604 48. R. W. Bartlett, Molybdenum Oxidation Kinetics at High Temperatures. *Journal of The*  
605 *Electrochemical Society*, 1965. 112(7): p. 744-746.
- 606 49. T. Hatakeyama, S. Ida, N. Sekido, K. Yoshimi, Significant improvement of the oxidation  
607 resistance of MoSiBTiC-based multiphase alloys by Ti enrichment. *Corrosion Science*, 2020:  
608 p. 108937. DOI: 10.1016/j.corsci.2020.108937.
- 609 50. Z. Tang, J. J. Williams, A. J. Thom, M. Akinc, High temperature oxidation behavior of Ti<sub>5</sub>Si<sub>3</sub>-  
610 based intermetallics. *Intermetallics*, 2008. 16(9): p. 1118-1124. DOI:  
611 10.1016/j.intermet.2008.06.013.
- 612 51. J. He, R. K. Behera, M. W. Finnis, X. Li, E. C. Dickey, S. R. Phillpot, S. B. Sinnott, Prediction  
613 of high-temperature point defect formation in TiO<sub>2</sub> from combined ab initio and thermodynamic  
614 calculations. *Acta Materialia*, 2007. 55(13): p. 4325-4337. DOI:  
615 10.1016/j.actamat.2007.04.005.

- 616 52. P. Kofstad, Note on the defect structure of rutile (TiO<sub>2</sub>). *Journal of the Less Common Metals*,  
617 1967. 13(6): p. 635-638. DOI: 10.1016/0022-5088(67)90111-7.
- 618 53. P. Kofstad, Thermogravimetric studies of the defect structure of rutile (TiO<sub>2</sub>). *Journal of Physics*  
619 *and Chemistry of Solids*, 1962. 23(11): p. 1579-1586. DOI: 10.1016/0022-3697(62)90240-8.
- 620 54. F. Millot, C. Picard, Oxygen self-diffusion in non-stoichiometric rutile TiO<sub>2-x</sub> at high  
621 temperature. *Solid State Ionics*, 1988. 28: p. 1344-1348. DOI: 10.1016/0167-2738(88)90384-0.
- 622 55. P. Kofstad, P. B. Anderson, O. J. Krudtaa, Oxidation of titanium in the temperature range 800–  
623 1200°C. *Journal of the Less Common Metals*, 1961. 3(2): p. 89-97. DOI: 10.1016/0022-  
624 5088(61)90001-7.
- 625 56. A. M. Chaze, C. Coddet, Influence of silicon on the oxidation of titanium between 550 and  
626 700°C. *Oxidation of metals*, 1987. 27(1-2): p. 1-20. DOI: 10.1007/BF00656726.
- 627 57. M. Yoshihara, K. Miura, Effects of Nb addition on oxidation behavior of TiAl. *Intermetallics*,  
628 1995. 3(5): p. 357-363. DOI: 10.1016/0966-9795(95)94254-C.
- 629 58. Z. Alam, D. K. Das, Effect of cracking in diffusion aluminide coatings on their cyclic oxidation  
630 performance on Ti-based IMI-834 alloy. *Corrosion Science*, 2009. 51(6): p. 1405-1412. DOI:  
631 10.1016/j.corsci.2009.03.027.
- 632 59. A. Ashrafizadeh, F. Ashrafizadeh, Structural features and corrosion analysis of thermally  
633 oxidized titanium. *Journal of Alloys and Compounds*, 2009. 480(2): p. 849-852. DOI:  
634 10.1016/j.jallcom.2009.02.079.
- 635 60. J. Stringer, Some observations on the kinetics of oxidation of titanium at high temperatures.  
636 *Journal of the Less Common Metals*, 1964. 6(3): p. 207-213. DOI: 10.1016/0022-  
637 5088(64)90100-6.
- 638 61. P. Hidnert, Thermal expansion of titanium. *J. Res. Natl. Bur. Stand*, 1943. 30(1934): p. 101-  
639 105.
- 640 62. R. K. Kirby, Thermal expansion of rutile from 100 to 700 K. *Journal of Research of the National*  
641 *Bureau of Standards. Section A, Physics and Chemistry*, 1967. 71(5): p. 363-369. DOI:  
642 10.6028/jres.071A.041.
- 643 63. I. Blech, U. Cohen, Effects of humidity on stress in thin silicon dioxide films. *Journal of applied*  
644 *physics*, 1982. 53(6): p. 4202-4207. DOI: 10.1063/1.331244.
- 645 64. P. F. Dennis, R. Freer, Oxygen self-diffusion in rutile under hydrothermal conditions. *Journal*  
646 *of Materials Science*, 1993. 28(17): p. 4804-4810. DOI: 10.1007/BF00414275.
- 647