

# 1 On the oxidation mechanism of refractory high entropy alloys

## 2 Authors

3 Franz Müller<sup>a</sup>, Bronislava Gorr<sup>a</sup>, Hans-Jürgen Christ<sup>a</sup>, Julian Müller<sup>a</sup>, Benjamin Butz<sup>a</sup>, Hans Chen<sup>b</sup>,  
4 Alexander Kauffmann<sup>b</sup> and Martin Heilmaier<sup>b</sup>

## 5 Affiliation

6 <sup>a</sup>Institut für Werkstofftechnik, Universität Siegen, Siegen, Germany; <sup>b</sup>Institut für Angewandte  
7 Materialien, Karlsruher Institut für Technologie (KIT), Karlsruhe, Germany; <sup>c</sup>

## 8 Abstract

9 The high-temperature oxidation mechanism of a series of refractory high entropy alloys: TaMoCrTiAl,  
10 NbMoCrTiAl, NbMoCrAl and TaMoCrAl at 1000°C in air was studied. A complex protective oxide  
11 layer consisting of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and CrTaO<sub>4</sub> oxides was observed for the quinary Ta-containing alloy.  
12 The formation of CrTaO<sub>4</sub> in this alloy after a short incubation period decreased the oxidation kinetics  
13 from a parabolic to a quartic rate law. Ti was found to support the formation of CrTaO<sub>4</sub>. In the Nb-  
14 containing alloys, the formation of different Nb<sub>2</sub>O<sub>5</sub> polytypes near the metal/oxide interface caused a  
15 highly porous oxide scale and severe oxide spallation.

16 **Keywords:** Refractory high entropy alloy, High temperature corrosion, Compositionally complex alloy,  
17 Quartic rate law, CrTaO<sub>4</sub> formation

## 18 1. Introduction

19 The development of new high temperature structural materials is confronted with the common problem  
20 to realize a favourable combination of elevated temperature (creep and fatigue) strength, room  
21 temperature ductility and high temperature oxidation resistance in a single alloy. Recently, the discovery  
22 of novel multicomponent alloys, so-called High Entropy Alloys (HEAs) or Compositionally Complex  
23 Alloys (CCAs) has led to the development of a large number of new alloy systems with unique and,  
24 thus, attractive property combinations [1]. In contrast to the classical alloy design approach, HEAs do  
25 not have a certain base element but consist of five or more elements in nearly equimolar ratios. As a  
26 result, from a thermodynamic point of view, HEAs exhibit a higher mixing entropy compared to that of  
27 classical alloys which may suppress the formation of ordered intermetallic compounds and favour the  
28 formation of a single-phase with simple crystal structure instead. However, it was demonstrated recently,  
29 that this approach is by far too simple to predict single-phase HEAs and further physical and chemical  
30 effects have to be considered [2]. Rather, proper element selection is more important than the increase  
31 of the number of participating elements only [3, 4].

32 Recently, HEAs with high concentrations of refractory metals, typically greater than 50 at.%, have been  
33 suggested to possibly fulfill the initially mentioned property portfolio for high-temperature structural  
34 materials, mainly because of their high melting points, strength retention at elevated temperatures and  
35 reasonable room temperature ductility and toughness [5-7]. While microstructure and mechanical  
36 properties of refractory HEAs merit great attention among material scientists, studies on the oxidation  
37 behavior of these materials are still scarce [8]. Moreover, these studies often represent merely a cursory  
38 scan of alloy oxidation properties, in other words, the oxidation mechanisms are not thoroughly  
39 elucidated [9-11].

40 In classical metallurgical approaches, the oxidation resistance of high-temperature alloys relies on  
41 additions of Cr, Al and Si enabling the formation of protective Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> scales. In

42 commercially available Ni-base and Fe-base high-temperature alloys, the concentrations of Cr, Al and  
43 Si usually do not exceed 25 at.% (e.g. the NiCrofer 3228 alloy), 11 at.% (B1914 alloy), 3.3 at.%  
44 (GX40CrSi29 alloy), respectively [12,13]. These (maximum) concentrations, on the one hand, ensure  
45 the formation of protective oxide layers and, on the other hand, guarantee that undesirable intermetallic  
46 phases such as Laves and Sigma phases as well as aluminides and silicides do not form. If such an alloy  
47 contains both, Cr and Al, the concentrations of these elements can be reduced as Cr and Al act  
48 synergistically and alloy passivation usually occurs very fast [14]. In many cases, small amounts of Si  
49 (max. 3 at.%) are added to further alleviate the formation of a protective chromia scale. In Nb- and Mo-  
50 based alloys, however, higher nominal concentrations of Si in conjunction with the formation of silicides  
51 as Si reservoirs are mandatory to form silica as a protective scale [15-17].

52 Obviously, decent oxidation resistance requires the addition of significant amounts of Al, Cr and  
53 possibly Si to HEAs. So far this has been scarcely done in literature [9-11, 18-22]. Our own exploratory  
54 work indicates the positive effects of Ta-substitution for Nb within the alloy system NbMoCrTiAl. In  
55 these preliminary studies, however, the mechanisms of oxidation behaviour were not fully rationalized  
56 [9, 11].

57 Based on these promising, albeit tentative results, we aim to elucidate the key role of the elements Ti,  
58 Nb and Ta on oxidation resistance by studying a systematic series of quaternary and quinary alloys. As  
59 a consequence, two equiatomic 5-component alloys (NbMoCrTiAl, TaMoCrTiAl) as well as two  
60 equiatomic quaternary alloys (NbMoCrAl, TaMoCrAl, i.e. without Ti), were studied. As a long-term  
61 objective, a more comprehensive understanding of the complex oxidation mechanisms may foster  
62 accelerated alloying strategies for oxidation resistant high strength refractory high entropy alloys.

## 63 **2. Experimental Procedures**

64 All alloys were cast from elemental bulk material by arc-melting (arc-melter AM 0.5 by Edmund Bühler  
65 GmbH) in ~0.6 atm. of Ar. The purities of the used elemental bulk materials Ta, Nb, Mo and Al were  
66 99.9%, while Cr and Ti had purities of 99 % and 99.8%, respectively. The prepared buttons were flipped  
67 over and remelted at least five times in a water-chilled copper mold to facilitate alloy homogenization.  
68 All alloys were subsequently heat-treated at 1300-1400°C depending on alloy composition (see Tab.1)  
69 for 20 h in Ar atmosphere to dissolve the dendritic microstructure and achieve near-equilibrium  
70 microstructures at operating conditions. The alloys were cooled in the furnace after the heat treatment  
71 in (streaming) Ar atmosphere with a cooling rate of 4.2 K/min. The ingots were then cut by electrical  
72 discharge machining (EDM) to dimensions of 5 mm x 5 mm x 2 mm, polished up to grit P1200 and  
73 ultrasonically cleaned in ethanol directly before high-temperature exposure. Oxidation tests were carried  
74 out in a Rubotherm thermogravimetric system under isothermal conditions at 1000°C for 24 – 100 hours  
75 in laboratory air. To analyse the oxide morphology, a Focused Ion Beam - Scanning Electron  
76 Microscope (FIB-SEM) DualBeam system of type FEI Helios Nanolab 600 was used. It is equipped  
77 with techniques such as backscatter electron (BSE) imaging, energy-dispersive X-ray spectroscopy  
78 (EDX) as well as electron backscatter diffraction (EBSD). The mean oxide scale thickness and the mean  
79 depth of the internal corrosion zone of the investigated alloys after various exposure times were  
80 determined using three BSE cross-section images in each of which 20 individual measurements were  
81 carried out using the software ImageJ. The preparation of the pre-cut samples for transmission electron  
82 microscopy (TEM) was done by ion milling with Ga<sup>+</sup>-ions at 5-30kV depending on the lamella thickness  
83 using the FEI Helios Nanolab 600. Subsequent TEM investigations were conducted using a TEM FEI  
84 Talos F200X with 200kV acceleration voltage. The crystal structures of the formed oxides in the surface  
85 scales were analysed by X-ray diffraction (XRD). These XRD measurements were carried out using an  
86 X'Pert Pro MPD diffractometer operating in Bragg-Brentano geometry with Cu-K $\alpha$  radiation as  
87 described in Ref. [11]. Oxide scales formed on the alloys were removed mechanically from the oxidized

88 samples using a scalpel and pestled into powders with particle sizes smaller than 40  $\mu\text{m}$  before XRD  
89 investigations.

90

### 91 **3. Results**

#### 92 **3.1 Microstructure**

93 Figure 1 exemplifies the microstructure of the four investigated alloys after suitable annealing as given  
94 in Table 1. None of the alloys is entirely single-phase after annealing. Specifically, the alloys NbMoCrAl  
95 and TaMoCrAl exhibit a noticeable amount of secondary, intermetallic phases which were subsequently  
96 characterized by combined EDX and EBSD (Figs. 2 a.,b.) as well as XRD analysis (see supplementary  
97 materials Figs. S1 a, b). The powder XRD measurements of both alloy NbMoCrAl and TaMoCrAl  
98 revealed a C14-type Laves phase ( $\text{Cr}_2\text{Ta}/\text{Cr}_2\text{Nb}$ ) and an A15 phase ( $\text{AlMo}_3/\text{Al}(\text{Mo}, \text{Nb})_3$ ) (Figs. S1 a,  
99 b). Further, ordering of the bcc solid solution (A2) towards a B2-type crystal structure of is assumed;  
100 this is indicated by the exclusive B2 superlattice peaks (open diamonds) in the supplementary materials  
101 Figs. S1. In agreement with the XRD measurements, the EDX and EBSD results (Fig. 2) confirm the  
102 presence of C14-type Laves phase in both alloys, however reliable identification between the cubic A15,  
103 A2 and B2 phases seems difficult during automated acquisition and indexing of EBSD patterns.

104 The microstructure investigations of both quinary alloys NbMoCrTiAl and TaMoCrTiAl were already  
105 published in our latest works [11, 23] and are, thus, only summarized shortly. In contrast to the  
106 quaternary alloys, only minor amounts of both i.e. A15 and C14 secondary phases were observed for  
107 NbMoCrTiAl, appearing as a fringe of tiny dimensions in the vicinity of some grain boundaries (see  
108 Fig. 1). Large grains with an ordered B2-type crystal structure were observed by TEM measurements as  
109 presented in our other work [23]. The alloy TaMoCrTiAl, however, showed after annealing at 1400°C  
110 for 20h merely  $\text{Cr}_2\text{Ta}$  Laves phase (20% area fraction) of C14-type (Tab. 1), predominantly located at  
111 grain boundaries, but no evidence of the A15 phase [11]. Volume fractions of the studied alloys were  
112 assessed by BSE-contrast or EBSD measurements if possible and are listed in Tab. 1.

113

#### 114 **3.2 Oxidation kinetics**

115 In Figs. 3 a-b, the mass change versus time curves of the alloys NbMoCrAl, NbMoCrTiAl, TaMoCrAl,  
116 TaMoCrTiAl during isothermal exposure in air at 900-1100°C are displayed. The mass change during  
117 isothermal exposure can be rationalized through:

$$118 \quad (\Delta W/A)^n = k \cdot t \quad (1)$$

119 where  $\Delta W/A$  is the mass change per unit area,  $t$  the exposure time,  $n$  the oxidation rate exponent and  $k$   
120 the oxidation constant. A linear plot of  $(\Delta W/A)^n$  vs.  $t$  yields the oxidation constant  $k$  as the slope of the  
121 straight. From a logarithmic representation of this relation the rate exponent ( $n$ ) can be derived according  
122 to

$$123 \quad \ln \Delta W/A = \frac{1}{n} \ln k + \frac{1}{n} \ln t \quad (2)$$

124 as the slope of a double logarithmic plot of mass change versus time. This is depicted for the investigated  
125 alloys at 1000°C in air in Figs. 4a and b and the corresponding  $n$  and  $k$  values are listed in Tab. 2. Both  
126 Ta-containing alloys, Fig. 3a, exhibited the lowest mass gain during oxidation at 1000°C. In the early  
127 oxidation stage ( $t=0.5-4.5\text{h}$ ), TaMoCrTiAl showed mass gain with a parabolic rate ( $n=1.82$ ) which later

128 on decreased to a quartic oxidation rate ( $t=4.5\text{h}-100\text{h}$ ,  $n=4.55$ ) yielding a very low mass gain up to 300h  
129 (see Fig. 3a). Interestingly, the Ti-free alloy TaMoCrAl behaved differently with oxidation kinetics  
130 obeying a quartic rate law at the very beginning ( $t=0.14\text{h}-3\text{h}$ ,  $n=4.35$ ), subsequently increasing towards  
131 a parabolic oxidation rate ( $t=3\text{h}-48\text{h}$ ,  $n=2.08$ ). After 48h of exposure, the TaMoCrAl alloy showed an  
132 abrupt increase in oxidation rate, similar to break-away behavior which resulted in complete oxidation  
133 of the sample after 100h oxidation (see Fig. 3a).

134 Both Nb-containing alloys (Fig. 3b) generally exhibited substantially higher mass changes and different  
135 oxidation kinetics compared to those of the Ta-containing alloys. The oxidation kinetics of NbMoCrTiAl  
136 increased from near-parabolic kinetics ( $t=0.17\text{h}-8.17\text{h}$ ,  $n=1.49$ ) to linear one ( $n=0.82$ ) during exposure  
137 in air at 1000°C (see Tab. 2). For the Ti-free NbMoCrAl, the decrease of oxidation rate exponent was  
138 even more pronounced from  $n=2.08$  to  $n=0.30$  after 7h of exposure to air at 1000°C. Further, after 24h  
139 of oxidation, the mass gain suddenly stopped and subsequent mass loss was observed. After 48h of  
140 exposure to air at 1000°C, the complete sample of NbMoCrAl was oxidized and no residual metal  
141 substrate could be found.

142 In agreement with the thermogravimetric analyses, inspection of the formed oxide layers of both Ta-  
143 containing alloys yielded these to be substantially thinner compared to those on the Nb-containing  
144 variants (see Fig.5a). In addition, the internal corrosion process for both Ta-containing alloys proceeded  
145 distinctly slower during the first 24h compared to NbMoCrTiAl and NbMoCrAl (Fig. 5b). As described  
146 further below, the internal corrosion zone was defined as the area below the oxide scale where corrosion  
147 products, mainly  $\text{Al}_2\text{O}_3$ , CrN and TiN were detected. For the NbMoCrAl and NbMoCrTiAl alloys, the  
148 internal corrosion zone thickness is interestingly reduced or even disappeared after more than 3h (see  
149 Fig. 5b.); this zone was rarely detected in the cross-sectional images.

150 According to Fig. 4 and Table 2, oxidation rates of the two Nb-containing alloys are low at the beginning  
151 of the oxidation process indicating the formation of relatively protective scales. In turn, the precipitation  
152 of corrosion products in the metallic substrate which were predominately  $\text{Al}_2\text{O}_3$  or TiN is facilitated (as  
153 shown in Figs. 6 and 7). When the oxide scales become non-protective and the oxygen partial pressure  
154 below the oxide scale increases, residual metal and nitrides in the internal corrosion zone were oxidized.  
155 Obviously, the oxidation process became dominant compared to the internal corrosion, i.e. nitridation,  
156 after prolonged oxidation.

### 157 **3.3 Microstructural analysis of oxide scales**

#### 158 **3.3.1. NbMoCrTiAl and NbMoCrAl**

159 As a follow up of our preliminary results [9], we will focus here on elucidating the high-temperature  
160 oxidation mechanism of the Nb-containing HEAs during short term and long term exposure in air up to  
161 100h at 1000°C. Three oxides were identified after 48h oxidation at 1000°C by powder XRD  
162 measurements: Rutile, corundum and  $\text{Nb}_2\text{O}_5$  (see supplementary materials Fig. S2). According to our  
163 Rietveld analyses [9], rutile was the dominant oxide phase which formed during high-temperature  
164 oxidation at 1000°C and the volume fractions of the other oxides were much lower (being around 15  
165 Vol.% after 48h) [9]. In Figs. 6a-c, the BSE cross-section images of NbMoCrTiAl present the course of  
166 the complex oxide layer formation after exposure to air for 3h, 48h and 100h, respectively, at 1000°C.  
167 Figure 6d exemplifies the EDX analysis of this alloy after oxidation for 48h. Already after 3h (Fig. 6a)  
168 both, a sequence of thick and thin oxide layers was observed. The thick sublayers are enriched in Nb  
169 and contain pores and cracks. The thin parts exhibit a dense multi-layer structure with Ti-, Al- and Cr-  
170 rich oxides. After 48h of oxidation, similar results were observed [9]. Concerning the thin oxide layers  
171 (see the outermost part of the scale in Fig. 6b) pure rutile  $\text{TiO}_2$  was identified by XRD and EDX (see  
172 also supplementary material Fig. S2.). Underneath, in the order from outside to inside, a multi-layer

173 consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{CrNbO}_4$  oxides was identified (Figs. 6). Below the oxide scale,  
174 internal corrosion products like fine  $\text{Al}_2\text{O}_3$  particles and predominately coarse, spherical TiN particles  
175 are found (Fig. 6 b.), of which the phases were confirmed by previous XRD measurements [9]. After  
176 100h of oxidation (Fig. 6c), thick and porous multiphase oxide scales of mostly rutile-type oxide layers  
177 are present, whereas the internal corrosion zone appears much thinner (compared to Fig. 5b) and only  
178 fine TiN and  $\text{Al}_2\text{O}_3$  particles were observed (not presented here).

179 To study the importance of Ti for oxidation resistance in this alloy system, samples of Ti-free equimolar  
180 alloy NbMoCrAl were oxidized under similar conditions at  $1000^\circ\text{C}$  in air. Different to NbMoCrTiAl, a  
181 substantial amount of the intermetallic phases A15 and Laves phases (see. Tab. 1) was found after heat-  
182 treatment in NbMoCrAl which may impact scale formation.

183 XRD-analysis after 3h of exposure (not shown here) reveals the formation of the following oxides:  
184 corundum-type chromia and alumina, rutile-type solid solutions of  $\text{MO}_2$  with major solvents of  $\text{M}=\text{Cr}$ ,  
185 Mo, Nb but also pure  $\text{Nb}_2\text{O}_5$  oxides. No further oxides are found after prolonged oxidation times,  
186 however, the intensity of the rutile-type oxide increased compared to corundum-type oxide.

187 Fig. 7 exemplifies BSE-images of NbMoCrAl after 3h and 24h of exposure to air at  $1000^\circ\text{C}$ . After 3h  
188 of exposure, the  $4.6 \pm 0.5\mu\text{m}$  thick scale essentially contains oxides of  $\text{MO}_2$  rutile-type solid solutions  
189 and to a lesser extent of  $\text{Nb}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  (Fig. 7a). Further precipitates of alumina forming a sparse  
190 scale within the rutile-type layer were identified. Below the oxide scale, the EDX and XRD  
191 investigations reveal the formation of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{N}$ , generally located at the phase boundaries and  
192 within the grains of the  $\text{Cr}_2\text{Nb}$  Laves phase (Fig. 7a).

193 After 24h, the structure of consecutive layers within the scale is clearly seen (see Fig. 7b). Between the  
194 layers, significant porosity is observed that apparently led to delamination of layers. The layers consist  
195 of alternating rutile,  $\text{Nb}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$  as well as semi-continuous layers with  $\text{Al}_2\text{O}_3$ . Severe crack  
196 formation and spallation occurred in the  $\text{Nb}_2\text{O}_5$ -rich layers and at the metal/oxide interface (see the lower  
197 area in Fig. 7b). Interestingly, the amount of internal nitridation was clearly reduced after prolonged  
198 oxidation time and no corrosion products were found below the oxide scale (see Fig. 7c).

### 199 3.3.2 TaMoCrTiAl and TaMoCrAl

200 The XRD-measurements of TaMoCrTiAl after 3h and 300h of oxidation at  $1000^\circ\text{C}$  in air (Fig. 8) both  
201 yield the formation of titania, alumina, chromia and  $\text{CrTaO}_4$ . In order to investigate the corrosion  
202 products in detail, TEM analyses were performed on a sample oxidized for 3h at  $1000^\circ\text{C}$  (see  
203 supplementary materials Fig. S3). A multi-layered oxide scale consisting of outer  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$   
204 and inner  $\text{CrTaO}_4$  could be confirmed. Several round-shaped  $\text{Al}_2\text{O}_3$  precipitates below the oxide scale  
205 and within the Laves phase were identified by EDX measurements and TEM diffraction patterns  
206 (displayed in supplementary materials Fig. S3 b-d).

207 Figure 9 displays the cross-section BSE images after 48h (a), 100h (b) and 300h (c) of oxidation at  
208  $1000^\circ\text{C}$  in air and an enlarged EDX-mapping (d) of the zone framed in dashed lines in (a). By  
209 combination of the EDX and XRD investigations (also see Fig. 8), it was found that the oxide scale  
210 composition during 3h till 300h of exposure to air was comparable. As demonstrated in the EDX  
211 mapping in Figure 9d, titania was formed as the top layer, alumina and chromia were identified  
212 underneath. The inner layer consisted of  $\text{CrTaO}_4$  which became clearly thicker (approx.  $8\mu\text{m}$ ) with  
213 oxidation time, whereas the other layers remained unchanged (compare Fig. 9a-c).

214 Since several oxide layers formed during oxidation, it is mandatory to explore which of these oxides  
215 may finally be responsible for the high oxidation resistance of the alloy TaMoCrTiAl. While  $\text{Al}_2\text{O}_3$  and

216 Cr<sub>2</sub>O<sub>3</sub> are generally considered as protective oxides in literature, little is known about the protectiveness  
217 of CrTaO<sub>4</sub>. Hence, to study this, the alloy TaMoCrTiAl was oxidized in a separate discontinuous  
218 experiment for 6h at 1000°C. Subsequently, the upper oxide scale consisting of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>  
219 was removed by mechanical grinding leaving a thin CrTaO<sub>4</sub> layer on the surface (see Fig. 10a). Then,  
220 the oxidation of the sample continued in air at 1000°C for 24h (see Fig. 10b). The BSE cross-section  
221 images reveal that no additional oxides were observed on top of the (now “outermost”) CrTaO<sub>4</sub> layer  
222 (see Fig. 10b). Only the thickness of the CrTaO<sub>4</sub> layer and of the internal corrosion zone, containing  
223 mostly Ti-nitrides and alumina, increased by 4 μm and 14 μm, respectively. This suggests that the  
224 outward diffusion of cations through the CrTaO<sub>4</sub> layer was clearly inhibited, while the inward diffusion  
225 of oxygen and nitrogen was not suppressed. It can, therefore, be assumed that the metallic substrate is  
226 effectively protected by the slow growth of CrTaO<sub>4</sub> which explains the lower oxidation rates of both Ta-  
227 alloys compared to the Nb-alloys (see Tab. 2).

228 To evaluate the importance of Ti on the high temperature oxidation resistance on TaMoCrTiAl, we  
229 comparatively investigated the quaternary Ti-free TaMoCrAl alloy being exposed to air at 1000°C for  
230 up to 100h. The XRD measurements after 3h of oxidation (see supplementary materials Fig. S4)  
231 identified various oxides: Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CrTaO<sub>4</sub>. After 48h of oxidation, also Ta<sub>2</sub>O<sub>5</sub> was found in  
232 XRD investigations (not shown here).

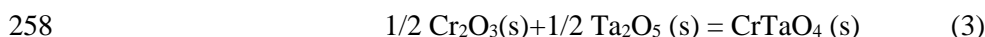
233 In Figures 11a-b, the BSE cross-section images of TaMoCrAl after 3h and 48h exposure to air at 1000°C  
234 are displayed. The average oxide layer thickness after 3h oxidation was only 2.1 μm and the layers  
235 appeared adherent with no or minor visible pores or cracks. EDX investigations (not presented here) and  
236 XRD measurements (see supplementary materials Fig. S3) revealed the formation of an upper layer  
237 consisting of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, as well as a thicker inner scale of CrTaO<sub>4</sub> (Fig. 11a).

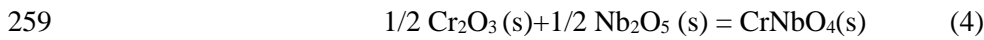
238 In contrast, after 48h of exposure, a much thicker (28.5μm in average) and porous oxide scale was  
239 observed (Fig. 11b). The outermost layer with a darker contrast in the BSE image is comprised of thin  
240 Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> oxides; see Fig. 11b. The inner layer, though, shows a multi-phase structure consisting  
241 essentially of CrTaO<sub>4</sub> and Ta<sub>2</sub>O<sub>5</sub> with semi-continuous scales of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> which appear in a  
242 darker contrast in the BSE cross-section image (as shown in Fig. 11b). Below the thick oxide scale,  
243 pronounced internal oxidation was additionally observed, especially at the phase boundaries which were  
244 decorated with alumina and Cr<sub>2</sub>N particles (Fig. 11b).

#### 245 4. Discussion

246 The results presented above clearly reveal a higher oxidation resistance for both Ta-containing alloys  
247 and inferior oxidation behavior for both Nb-containing alloys during exposure to air at 1000°C. Ta, Nb  
248 and Ti, which are present in relatively high concentrations (20 at.% in quinary and 25 at.% in quaternary  
249 alloys, respectively) in the studied alloys, obviously have a pronounced effect on the elevated  
250 temperature oxidation resistance.

251 The formation of the multi-layered oxide scales as observed in our experiments can be rationalized  
252 taking into account both, thermodynamic and kinetic aspects. In doing so, standard free energies of  
253 formation of the observed oxides at 1000°C were calculated using the commercial software FactSage.  
254 The formation of CrTaO<sub>4</sub> and CrNbO<sub>4</sub> oxides below the chromia and alumina layers was observed for  
255 the Ta- and Nb-containing alloys, respectively. Assuming the chemical reactions (3) and (4) according  
256 to [24], the standard free energies of formation of CrTaO<sub>4</sub> and CrNbO<sub>4</sub> were calculated as described in  
257 eqs. (5) and (6). The calculated ΔG<sup>0</sup> values are summarized in Tab.3.





260  $\Delta G^0_{\text{CrTaO}_4} = 1/2 (\Delta G^0_{\text{Cr}_2\text{O}_3} + \Delta G^0_{\text{Ta}_2\text{O}_5})$  (5)

261  $\Delta G^0_{\text{CrNbO}_4} = 1/2 (\Delta G^0_{\text{Cr}_2\text{O}_3} + \Delta G^0_{\text{Nb}_2\text{O}_5})$  (6)

262

263 According to Tab.3, the thermodynamic driving forces are highest for  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  amongst all  
 264 considered oxide species, which result in the formation of an initially multi-layered oxide scale,  
 265 consisting of the outer  $\text{TiO}_2$  and the inner  $\text{Al}_2\text{O}_3$ . According to Fig. 10, though, these oxides seem to be  
 266 a product of the transient oxidation only, and do not significantly influence the further oxidation process.

267 Generally, the impact of Ti on the oxidation resistance seems to be positive. Although the experiments  
 268 with the Ti-free alloys NbMoCrAl and TaMoCrAl first indicate superior, i.e. slower, oxidation kinetics  
 269 during initial oxidation as compared to their Ti-containing counterparts (see Fig. 3), after longer  
 270 oxidation times the oxide scales of both Ti-free alloys were thicker and less adherent (Fig. 5). This is  
 271 believed to be the effect of higher Mo-concentrations in the Ti-free alloys and, consequently, the higher  
 272 volume fraction of the Mo-rich A15 phase (see Fig. 1) which is known to be intrinsically not oxidation  
 273 resistant [25, 26]. The oxidation of the A15 phase causes the formation of volatile Mo-oxides, which  
 274 have a destructive effect on the macroscopic integrity of the initially protective oxide scale. As a further  
 275 consequence, the oxide scales which formed at prior A15 phase grains eventually became porous  
 276 evoking even severe evaporation of Mo-oxides (Fig. 2).

277 Though the elements Nb and Ta are known to have a similar chemical nature, their effect on the  
 278 oxidation behavior of the studied alloys is seemingly different. As the thermodynamic stability of  
 279  $\text{CrNbO}_4$  is almost the same as those of  $\text{Cr}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  (Tab. 3), this may apparently lead to a  
 280 competition in the formation between these oxides that can explain an only partial formation of  $\text{CrNbO}_4$ .  
 281 In contrast, the thermodynamic stability of  $\text{CrTaO}_4$  is clearly higher as of  $\text{Cr}_2\text{O}_3$ , thus the formation of  
 282 distinct and protective  $\text{CrTaO}_4$  layers below  $\text{Cr}_2\text{O}_3$  is facilitated.  $\text{CrNbO}_4$  oxides, however, have been  
 283 found to improve the oxidation resistance of various other alloys, e.g. Nb-Si-based alloys [27, 28.]. Chan  
 284 et al. reported enhanced thermal cycling oxidation resistance of Nb-Cr-Si-based alloy due to the  
 285 formation of adherent  $\text{CrNbO}_4$  layers instead of  $\text{Nb}_2\text{O}_5$  [29]. Qu et al. reported on enhanced adherence  
 286 between oxide scale and substrate of Nb-Si based alloys due to  $\text{CrNbO}_4$  formation at the metal/oxide  
 287 interface [30]. One can, therefore, expect a relatively high oxidation resistance of an alloy forming  
 288  $\text{CrNbO}_4$ .

289 In our study, both Nb-containing alloys first showed almost parabolic oxidation kinetics with rate  
 290 exponents of  $n=1.49-2.0$  suggesting the initial formation of protective oxide layers such as  $\text{CrNbO}_4$ ,  
 291  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . However, a severe increase of oxidation rates and high mass gain after prolonged  
 292 oxidation time indicate porous, fast-growing non-protective oxide scales (Tab 2). As illustrated  
 293 schematically in Fig. 12, the increase of the oxidation rates observed for both Nb-containing alloys can  
 294 be attributed to the formation of various polymorphic forms of  $\text{Nb}_2\text{O}_5$  which have been identified by  
 295 XRD (supplementary materials Fig. S2) and EBSD (not presented here).

296 Especially at temperatures below  $1100^\circ\text{C}$ , various monoclinic and orthorhombic polymorphs have been  
 297 observed which transform rapidly at temperatures above  $1100^\circ\text{C}$  to monoclinic H- $\text{Nb}_2\text{O}_5$ , the stable  
 298 high-temperature form [31, 32]. In the intermediate temperature range between  $1000-1100^\circ\text{C}$ , the  
 299 formation of different  $\text{Nb}_2\text{O}_5$  polymorphs will lead to severe anisotropic volume expansion and, thus, to  
 300 crack formation. In our findings, at least two polymorphic forms of  $\text{Nb}_2\text{O}_5$  have been identified by EBSD  
 301 and XRD, namely h- $\text{Nb}_2\text{O}_5$  and  $\beta$ - $\text{Nb}_2\text{O}_5$  (supplementary materials Fig. S2). Among all these,  $\beta$ - $\text{Nb}_2\text{O}_5$

302 is known to be the most expanding Nb<sub>2</sub>O<sub>5</sub> [27, 28, 33-35]. It is thus, by no means surprising that crack  
303 formation occurs at the interphase substrate/oxide (Fig. 12), hence leading to rapid oxygen ingress and  
304 explains the observed massive increase of mass gain (see Fig. 3), oxidation rates (see Tab. 2) and oxide  
305 scale growth (see Fig. 5) of both Nb-containing alloys. Consequently, the alloy with the highest Nb  
306 content (NbMoCrAl) exhibited the worst oxidation resistance and formed the thickest Nb-rich oxide  
307 scales (see Fig. 5). The effect of the Cr<sub>2</sub>Nb Laves phase on the oxide layer formation is rather small: the  
308 oxide layer formed on top of the Laves phase grains had a similar thickness as that one formed on top  
309 of the other phases. However, the effect of the Laves phase on internal corrosion is significant. First,  
310 Al<sub>2</sub>O<sub>3</sub> precipitates seem to form primarily in the Laves phase rather than in the matrix. A similar  
311 experimental finding was observed in the alloy TaMoCrTiAl (see supplementary material Fig. S3).  
312 Second, internal corrosion starts at the phase boundaries as TiN and CrN precipitations were abundantly  
313 found between the Laves phase and the matrix (Figs. 6a and 7a).

314 The CrTaO<sub>4</sub> oxide, identified during oxidation experiments of Ta-containing alloys, is supposed to form  
315 by the reaction, eq. 3, and, thus, first requires an incubation period for the formation of Cr<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub>.  
316 It should be noted, however, that no pure Ta<sub>2</sub>O<sub>5</sub> was observed for TaMoCrTiAl by XRD-analysis  
317 possibly due to the very fast reaction to CrTaO<sub>4</sub>. Ta<sub>2</sub>O<sub>5</sub>, though forming rapidly growing scales with  
318 PBR values of 2.5 [36], is stable only as monoclinic α-Ta<sub>2</sub>O<sub>5</sub> up to 1350°C in contrast to Nb<sub>2</sub>O<sub>5</sub> that  
319 yields numerous polymorphic modifications. Therefore, the oxide scales formed on Ta-containing alloys  
320 (see Fig. 10) generally show a better adherence compared to Nb<sub>2</sub>O<sub>5</sub>-forming alloys. After forming Ta-  
321 rich oxide scales it is rather unexpected that the alloy TaMoCrAl finally exhibits break-away oxidation  
322 after prolonged oxidation (see Fig. 11). We attribute this to the above-described formation of the Mo-  
323 rich A15 phase in the alloy TaMoCrAl (see Fig. 2) which led to enhanced formation of volatile Mo-  
324 oxides resulting in damaging the initially protective oxide scales (see Fig. 3). The influence of the Cr<sub>2</sub>Ta  
325 Laves phase on the oxidation resistance on both, microscopic and macroscopic level, is similar to that  
326 discussed for the alloy NbMoCrTiAl

327 Besides the positive effect of the Ti-addition on suppressing the formation of the A15 phase, Ti  
328 obviously plays a beneficial role by decreasing the amount of less favourable Ta<sub>2</sub>O<sub>5</sub> (or Nb<sub>2</sub>O<sub>5</sub>) and  
329 increasing the fraction of more favourable Ti-rich rutile-type solid solutions. Interestingly, various Ti-,  
330 Cr-, Ta- and Nb- oxides are known to form highly stable rutile phases and mixed solid solutions like  
331 TiO<sub>2</sub> (ICSD: 9161), TaO<sub>2</sub> (ICSD: 7624), CrTaO<sub>4</sub> (ICSD: 72276), TaTiO<sub>4</sub> (ICSD: 72278), CrNbO<sub>4</sub>  
332 (ICSD: 72275) and (Cr,Ti,Ta)O<sub>6</sub> (ICSD: 160795) to mention few of them. The PBR value of rutile-type  
333 TiO<sub>2</sub> generally is more favorable (1.7) [36], therefore the Ti-rich rutile-type oxides show improved  
334 adherence compared to Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub> based oxide scales.

335 The high-temperature oxidation kinetics for the formation of protective alumina or chromia layers is  
336 known to obey parabolic oxidation kinetics [12, 37]. The observed oxidation kinetics and oxide scale  
337 growth for the Ta-containing alloys, however, suggests the formation of a similarly highly protective  
338 oxide scale. After an incubation period that corresponds to the observed first 4.5h for TaMoCrTiAl, very  
339 low oxidation rates according to a quartic rate law were observed (see Tab. 2). The experiments further  
340 present that oxygen inward diffusion through the CrTaO<sub>4</sub> scale is rate-determining (see Fig. 9). The  
341 above-mentioned conclusions on the oxidation behavior of TaMoCrTiAl and TaMoCrAl are illustrated  
342 schematically in Fig. 13.

343 Recently Ren et al. reported on the enhanced oxidation resistance of Ni-based superalloys between 850  
344 and 900°C in air due to the formation of CrTaO<sub>4</sub> oxides that form below Cr<sub>2</sub>O<sub>3</sub> oxides after a short  
345 incubation time. The oxidation rate constants published by Ren et al. can be compared with the ones of  
346 our TaMoCrTiAl alloy in the temperature range 900-1100°C (see Tab. 2) [11]. Comparing the logarithm  
347 of oxidation rate constants of rutile-type CrTaO<sub>4</sub> comparable activation energies for the oxidation



348 process of  $Q=350$  kJ/mol for TaMoCrTiAl and  $Q=375$  kJ/mol for Ni-based alloy [38] can be  
349 accessed(see Fig. 14). Considering the activation energies for chromia (250 kJ/mol) [39] and alumina  
350 forming Ni-based superalloys (400 kJ/mol) [40], it can be stated that the activation energy for oxygen  
351 diffusion through CrTaO<sub>4</sub> and oxidation rate constant obviously lie in between, but advantageously  
352 closer to that of alumina.

## 353 **5. Conclusions**

354 Systematic comparative investigations of the oxidation behaviour of four refractory HEAs within the  
355 system Ta-Nb-Mo-Cr-Ti-Al in a temperature range between 900 and 1100°C lead to the following  
356 conclusions:

357 (i) The superior oxidation resistance of TaMoCrTiAl at 1000°C in air is the result of the formation of  
358 protective Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and CrTaO<sub>4</sub> oxide layers. The slow oxygen diffusion through CrTaO<sub>4</sub> seems to  
359 be rate determining which may pave the way for further development of oxidation-resistant refractory  
360 HEAs.

361 (ii) Although the initial formation of similar protective oxide layers consisting of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and  
362 CrNbO<sub>4</sub> were observed for NbMoCrTiAl and NbMoCrAl, the highly and anisotropic thermal expansion  
363 of the Nb<sub>2</sub>O<sub>5</sub> polymorphs leads to pore formation and scale spallation.

364 (iii) Ti-addition plays a crucial role in forming protective rutile type oxides (like CrTaO<sub>4</sub>),  
365 simultaneously decreasing the amount of less favorable oxides (Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>). Further, the volume  
366 fraction of the A15 phase can be reduced or even completely suppressed by the Ti-addition.

367 In our future works, the effect of Y additions aiming at the enhancement of oxidation resistance of  
368 NbMoCrTiAl alloy will be investigated. The oxidation behavior of both Ta-containing alloys is very  
369 promising, however, concerning the mechanical properties, the amount of brittle intermetallic  
370 compounds such as Laves Phases should be reduced. Therefore, the reduction of Cr- and Ta-  
371 concentrations in the TaMoCrTiAl system will be undertaken. The alloys with reduced Cr- and Ta-  
372 concentrations will be studied in terms of their microstructure and high-temperature corrosion behavior.

## 373 **Data availability**

374 The data that support the finding of this study are available as supplementary materials or from the  
375 corresponding author upon reasonable request.

## 376 **Acknowledgment**

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378 2283/4-1, is gratefully acknowledged. Part of this work was performed at the Micro- and Nanoanalytics  
379 Facility (MnaF) of the University of Siegen.

## 380 **Appendix A. Supplementary material**

381 Supplementary material related to this article can be found in the attachment.

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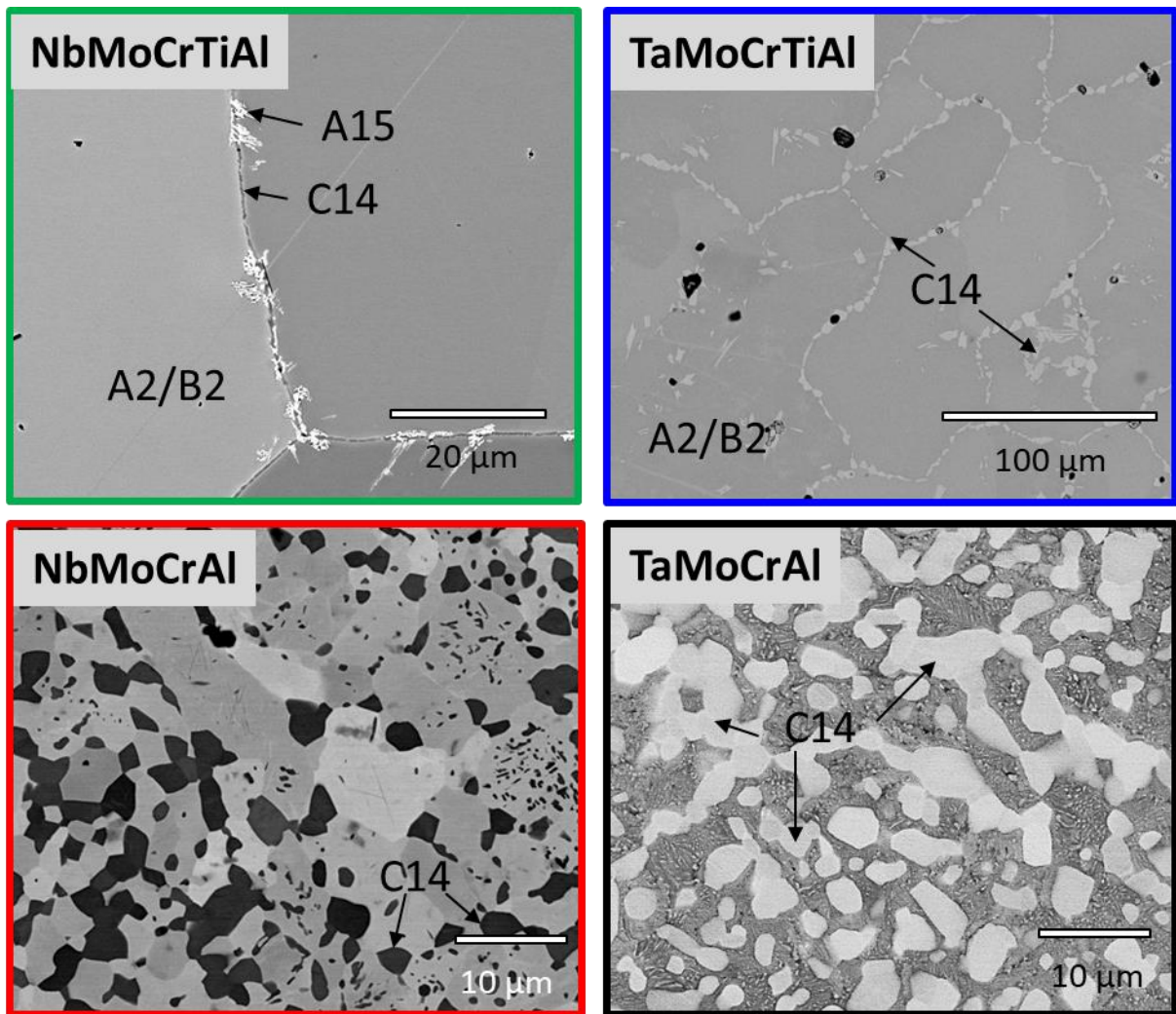
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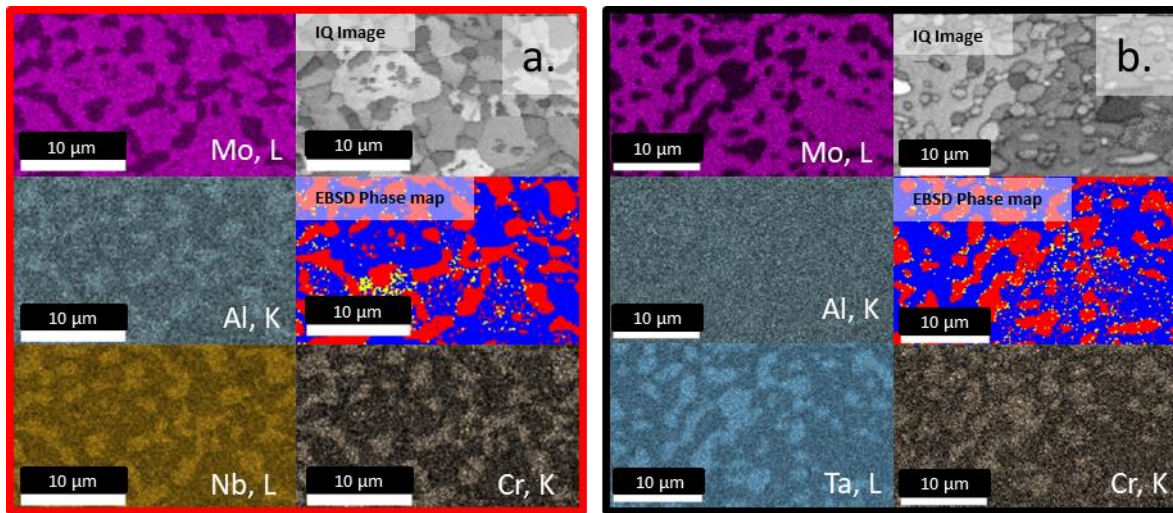
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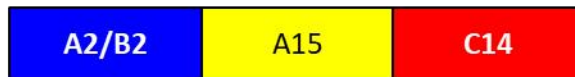


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487 Fig. 1: BSE images of the investigated alloys TaMoCrTiAl, NbMoCrTiAl, NbMoCrAl and TaMoCrAl  
488 after annealing conditions (see Tab. 1).

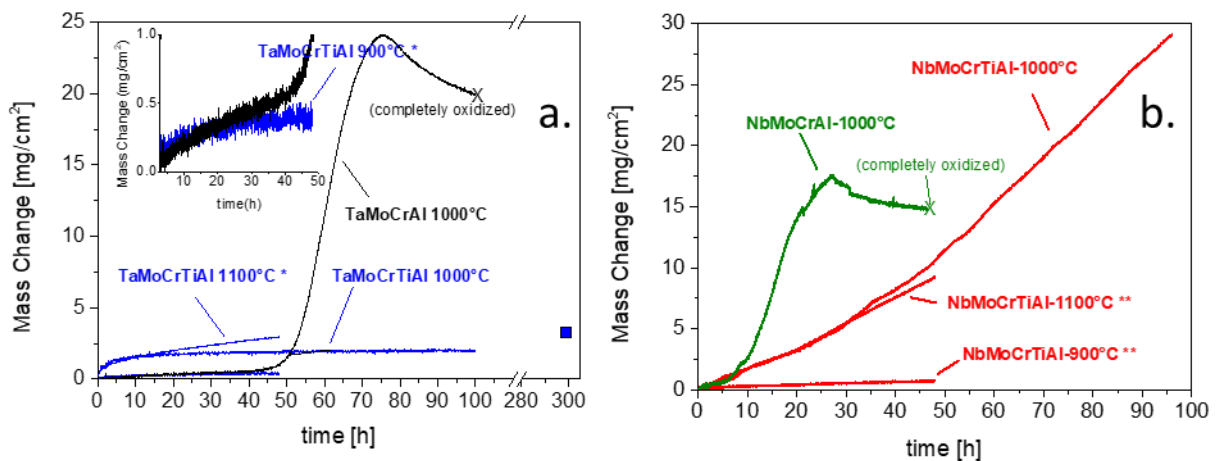


EBSD Phase map color code:



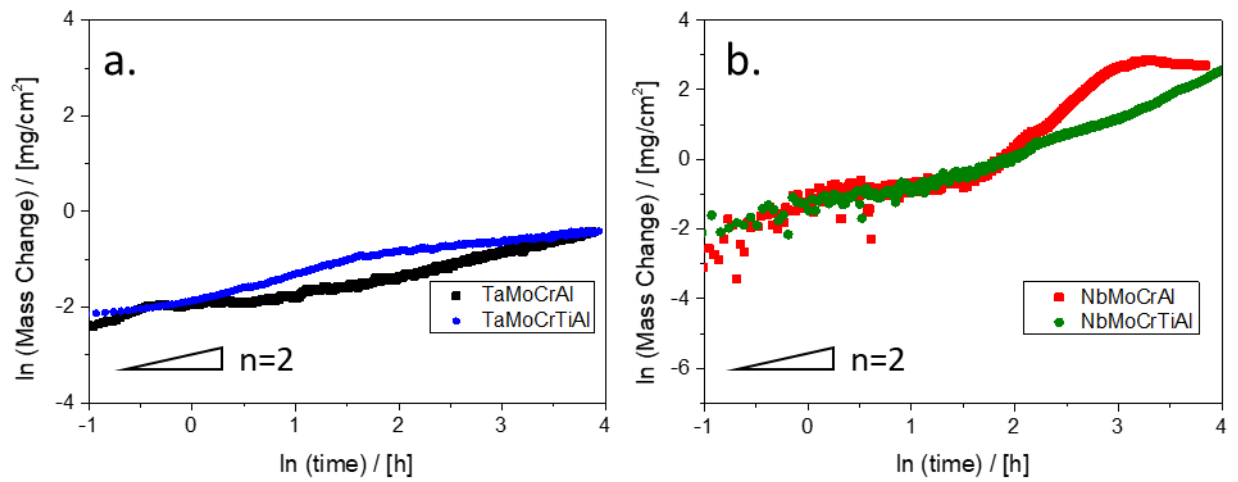
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490 Fig. 2: Characterization of NbMoCrAl (a.) and TaMoCrAl (b.) by combined EDX and EBSD analysis



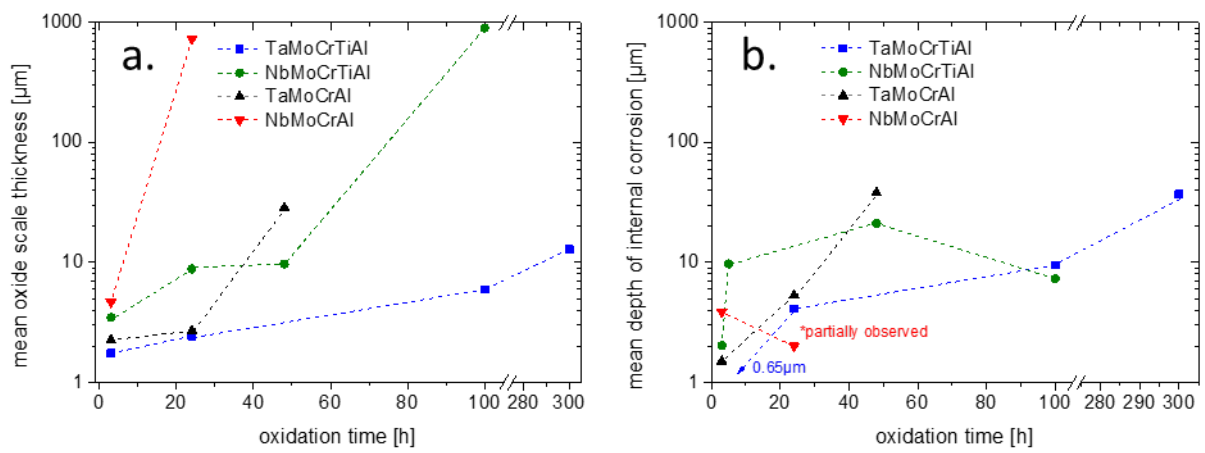
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492 Fig. 3: Specific mass change as a function of time for TaMoCrTiAl and TaMoCrAl (a.) and  
 493 NbMoCrTiAl and NbMoCrAl (b.) during isothermal exposure to air at 900 - 1100°C. Measurements  
 494 denoted with \* are taken from [11] and those with \*\* from [9].



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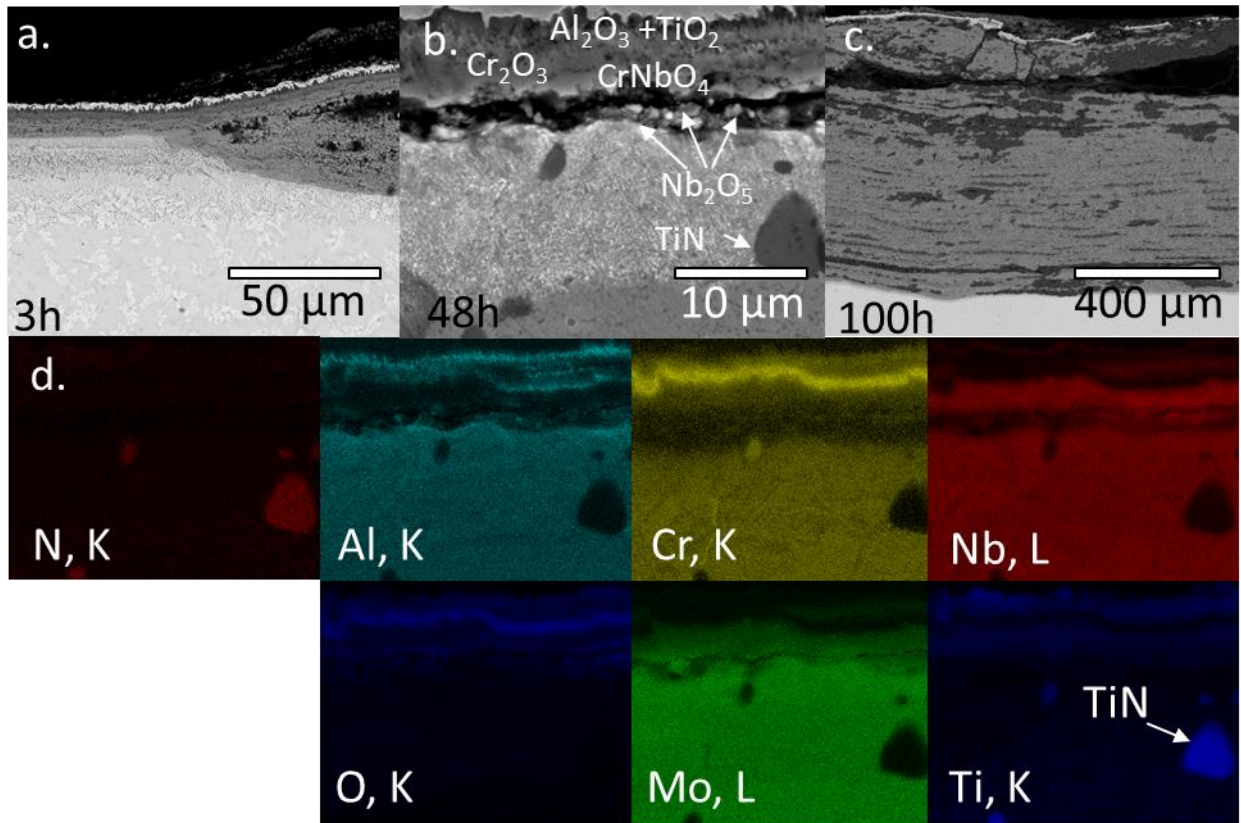
496 Fig. 4: Double logarithmic plots of mass change against time for TaMoCrTiAl, TaMoCrAl (a.) and for  
 497 NbMoCrTiAl and NbMoCrAl (b.) during isothermal oxidation at 1000°C in air up to 48h.



498

499 Fig. 5: Mean oxide scale thickness (a.) and mean depth of internal corrosion (b.) for TaMoCrTiAl,  
 500 NbMoCrTiAl, TaMoCrAl, and NbMoCrAl during isothermal exposure to air at 1000°C.

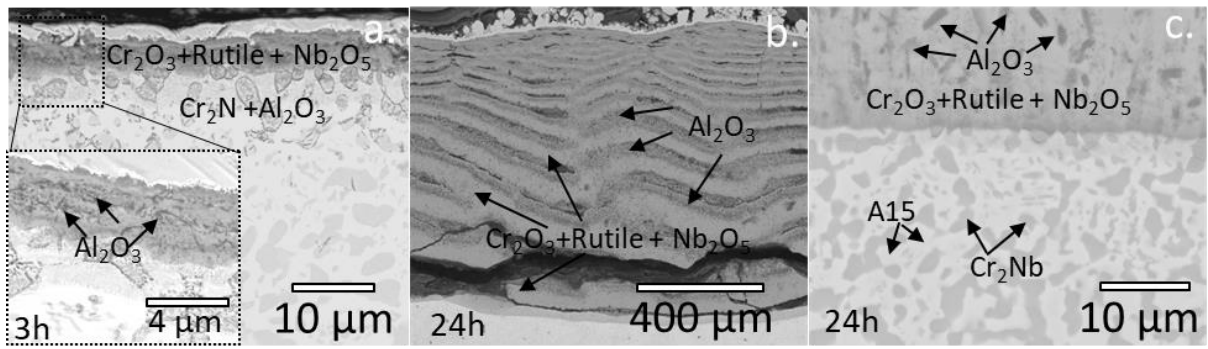




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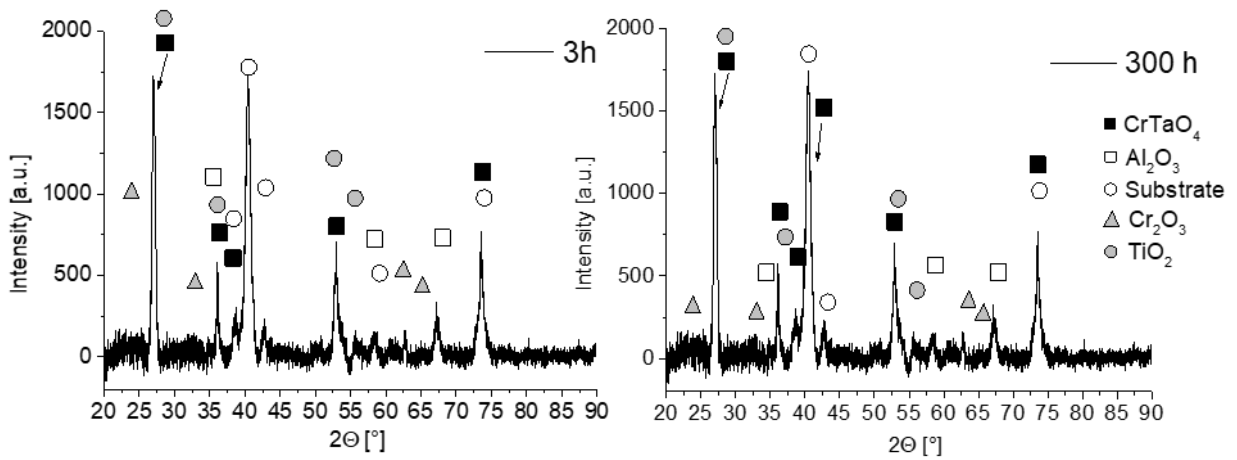
502 Fig. 6: BSE images of NbMoCrTiAl after 3h (a.), 48h (b.) and 100h (c.) of exposure to air at 1000°C  
 503 and (d.) the corresponding EDX-mappings of (b.).





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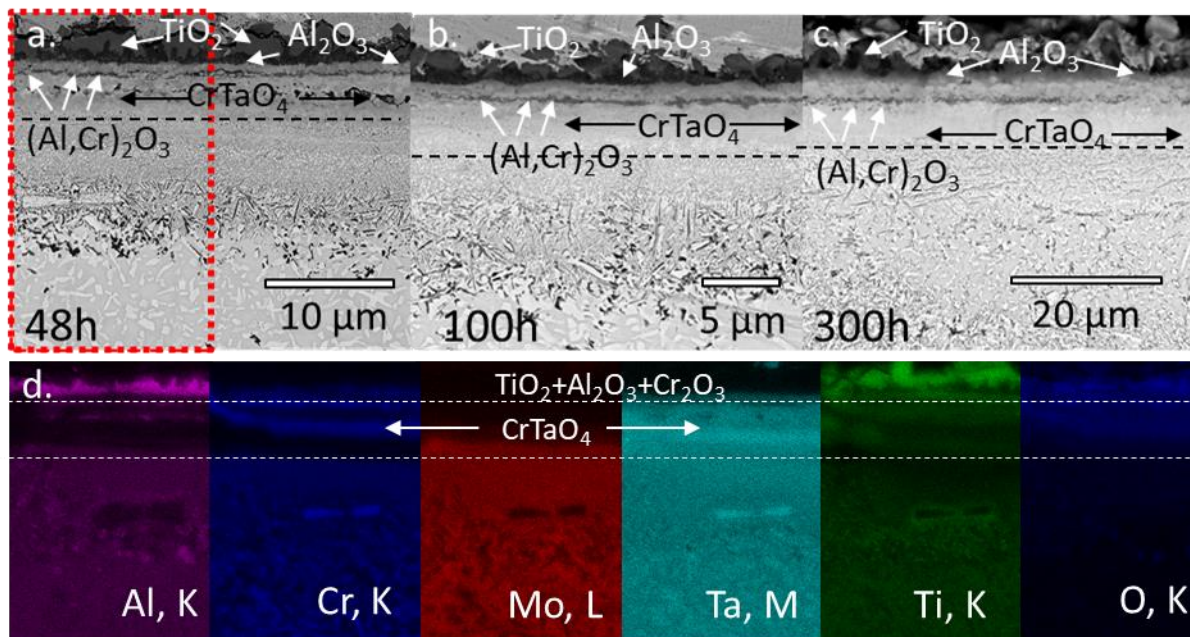
505 Fig. 7: BSE images of NbMoCrAl after 3h (a.) and 24h (b.) of exposure to air at 1000°C. A higher  
 506 magnification BSE image of the metal/oxide interface of (b.) is displayed in (c.).



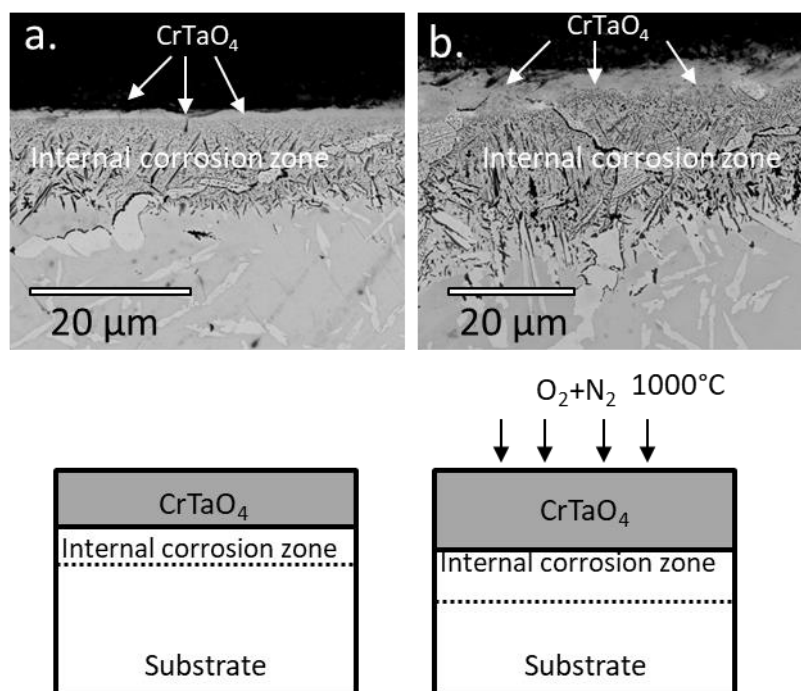
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508 Fig. 8: XRD plots of TaMoCrTiAl after 3h and 300h oxidation at 1000°C in air.

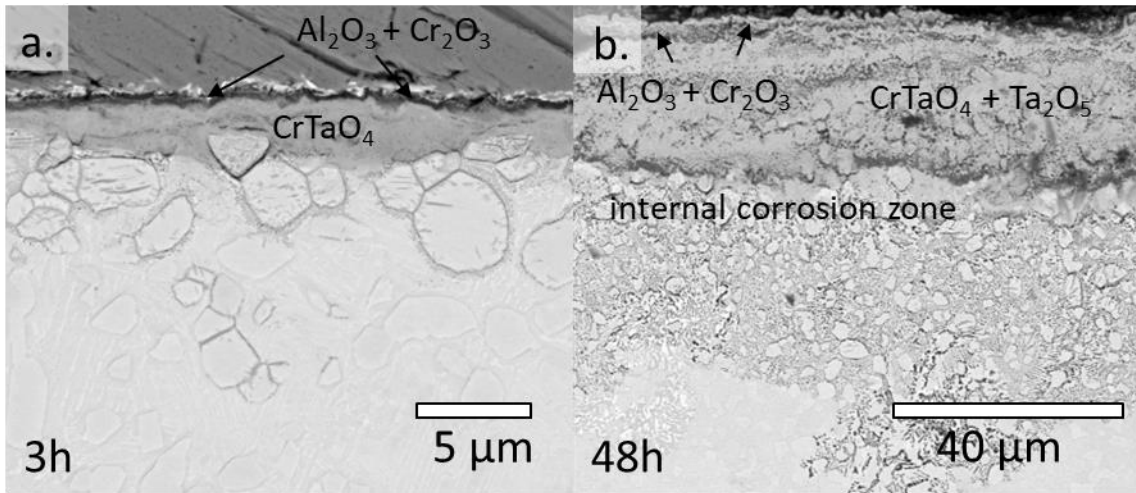
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510  
 511 Fig. 9: BSE images of TaMoCrTiAl after 48h (a.), 100h (b.), 300h (c.) exposure to air at 1000°C and  
 512 EDX mapping (d.) of cross-section marked in (a.). The horizontal lines indicate the interface between  
 513 the oxide layer and the internal corrosion zone.

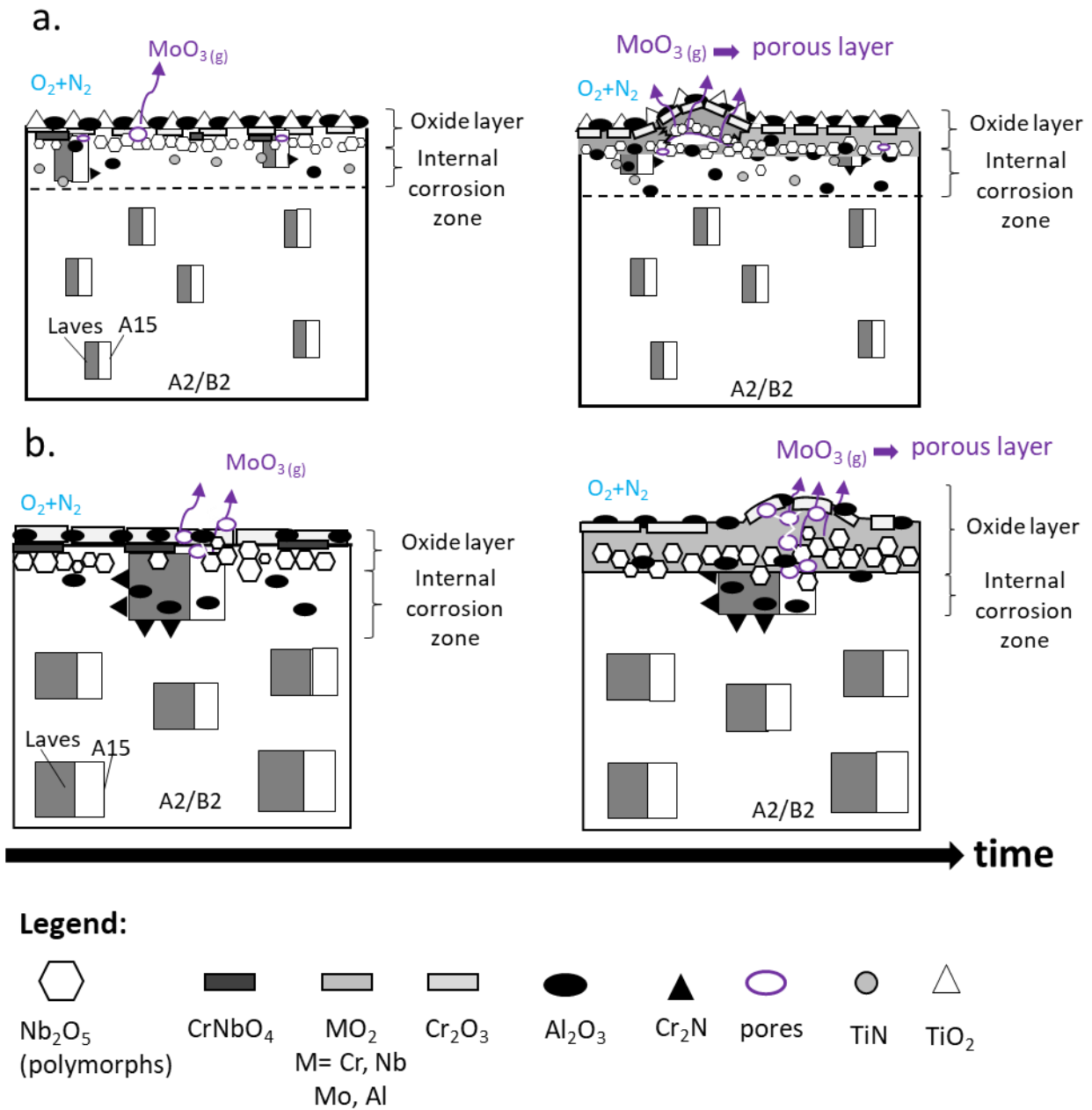


514  
 515 Fig. 10: Investigation of the protectiveness of the inner CrTaO<sub>4</sub> oxide layer during exposure to air at  
 516 1000°C. The darker upper oxide layer consisting of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> was removed, i.e. the CrTaO<sub>4</sub>  
 517 is the outer oxide layer here (a.), after subsequent 24h oxidation at 1000°C in air no additional oxides  
 518 visible on top of CrTaO<sub>4</sub> (b.)



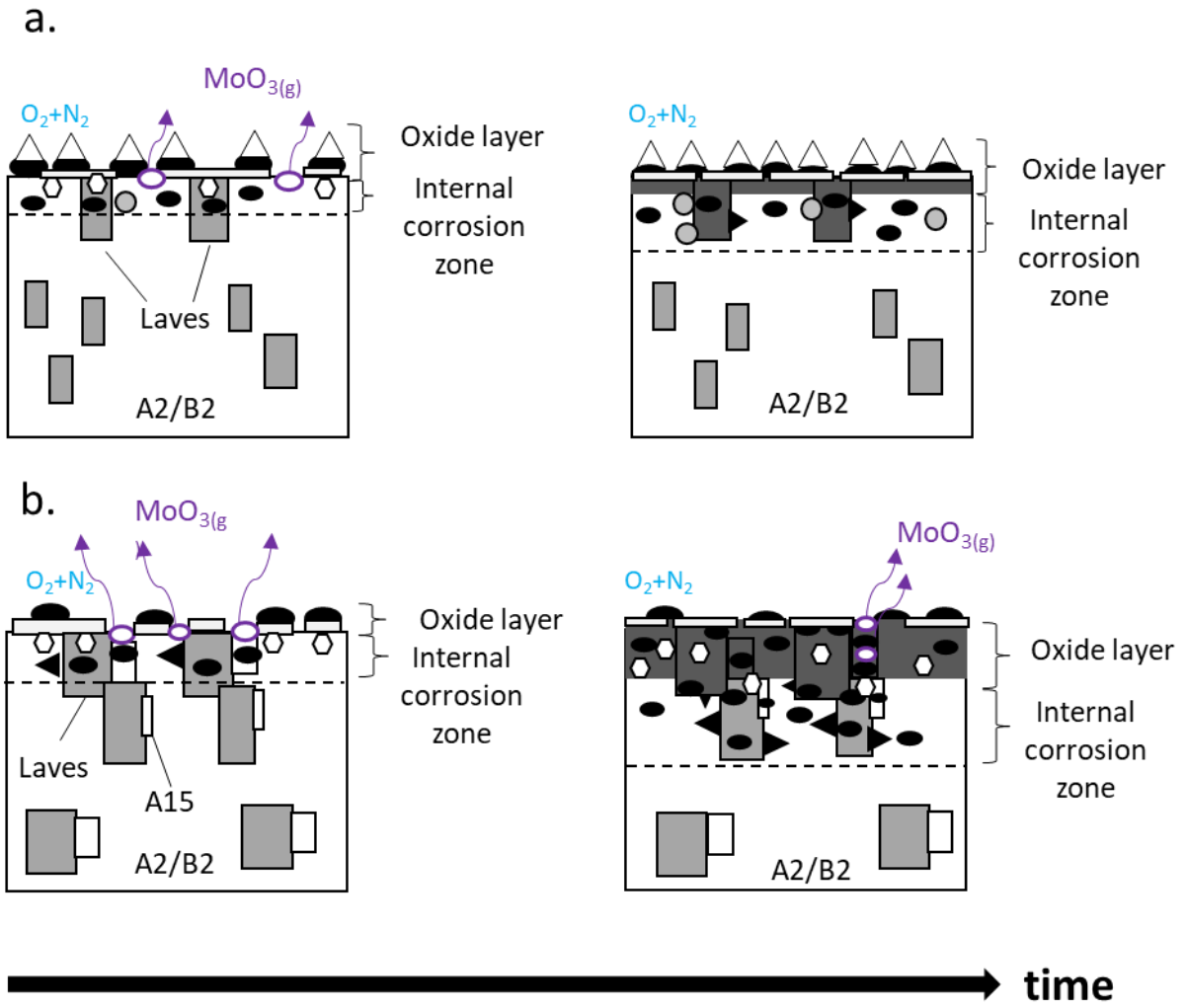
519

520 Fig. 11: BSE images of TaMoCrAl after 3h (a.) and 48h (b.) of exposure to air at 1000°C in air.

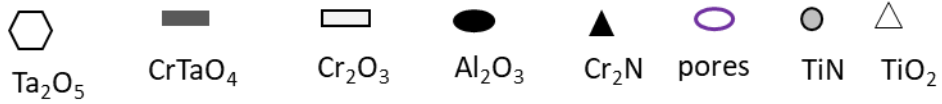


521

522 Fig. 12: Oxidation behavior of NbMoCrTiAl (a.) and NbMoCrAl (b.) during exposure at 1000°C in air

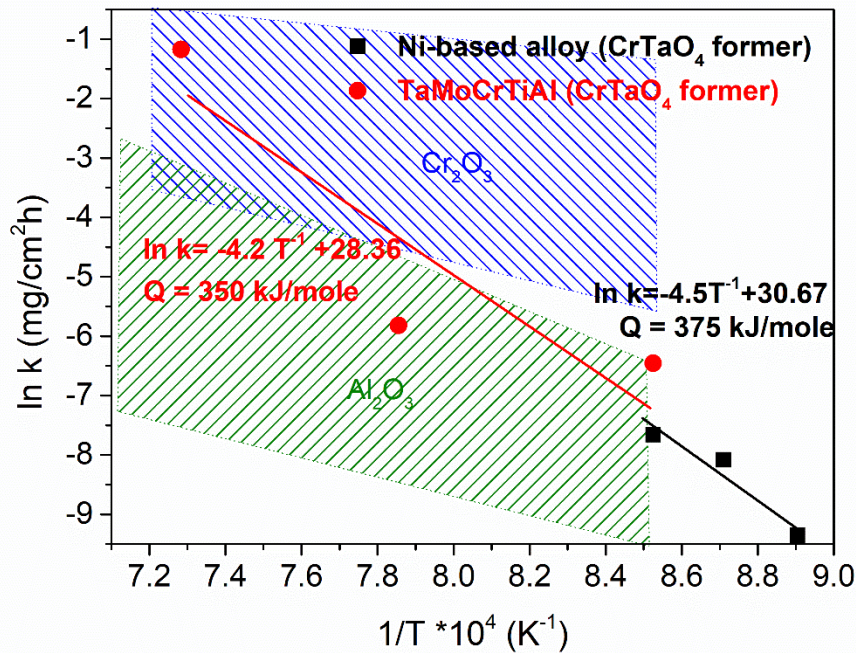


**Legend:**



523

524 Fig. 13: Oxidation behavior of TaMoCrTiAl (a.) and TaMoCrAl (b.) during exposure at 1000°C in air



525

526 Fig. 14: Logarithm of the oxidation rate over reciprocal temperature during steady-state oxidation (after  
 527 CrTaO<sub>4</sub> formation) of TaMoCrTiAl and CrTaO<sub>4</sub>-forming Ni-based superalloy [39]. Scatter regions of  
 528 oxidation rate for Al<sub>2</sub>O<sub>3</sub> (olive shaded area) and Cr<sub>2</sub>O<sub>3</sub> (blue shaded area) forming alloys after [41]

529 **Table captions**

530 Tab.1 Annealing conditions and identified phases of the investigated alloys. Volume fractions were  
 531 accessed by means of BSE-contrast (denoted with \*) or EBSD measurements (marked as †). The A2/B2  
 532 and A15 phases cannot be distinguished by means of BSE contrast or EBSD.

alloy	annealing conditions	identified phases	area fractions /method
NbMoCrTiAl	1300°C, 20 h	A2/B2 Al(Mo,Nb) <sub>3</sub> (A15) Laves phase, Cr <sub>2</sub> Nb (C14)	99% * 0.5% * 0.5% *
NbMoCrAl	1300°C, 20 h	A2/B2+Al(Mo,Nb) <sub>3</sub> (A15) Laves phases, Cr <sub>2</sub> Nb (C14)9	60% † 40% †
TaMoCrTiAl	1400°C, 20 h	A2/B2 Laves phases, Cr <sub>2</sub> Nb (C14)	80% * 20% *
TaMoCrAl	1400°C, 20 h	A2/B2+AlMo <sub>3</sub> (A15) Laves phases, Cr <sub>2</sub> Nb, (C14))	65% † 35% †

533

534

535 Tab. 2 Oxidation rate exponents (n) with regression coefficient (R<sup>2</sup>) and oxidation constants (k)  
 536 calculated from the curves shown in Fig. 3

Alloy	t <sub>1</sub> [h]	t <sub>2</sub> [h]	n	R <sup>2</sup>	oxidation rate constant k
<b>TaMoCrTiAl</b>	0.4	4.5	1.82	0.99	$k_p=3.34 \cdot 10^{-2}$ [mg <sup>2</sup> /cm <sup>4</sup> h <sup>2</sup> ]
	4.5	100.0	4.55	0.96	$k_q=2.97 \cdot 10^{-3}$ [mg <sup>4</sup> /cm <sup>8</sup> h <sup>4</sup> ]
<b>TaMoCrAl</b>	0.4	3.0	4.35	0.96	$k_q=1.91 \cdot 10^{-4}$ [mg <sup>4</sup> /cm <sup>8</sup> h <sup>4</sup> ]
	3.0	48.0	2.08	0.99	$k_p=7.96 \cdot 10^{-3}$ [mg <sup>2</sup> /cm <sup>4</sup> h <sup>2</sup> ]
<b>NbMoCrTiAl</b>	0.4	8.2	1.49	0.97	$k_l=1.24 \cdot 10^{-1}$ [mg/cm <sup>2</sup> h]
	8.2	100.0	0.82	0.99	$k_l=3.45 \cdot 10^{-1}$ [mg/cm <sup>2</sup> h]
<b>NbMoCrAl</b>	0.4	7.6	2.08	0.95	$k_p=6.95 \cdot 10^{-2}$ [mg <sup>2</sup> /cm <sup>4</sup> h <sup>2</sup> ]
	7.6	24.00	0.30	0.99	$k_l=1.12 \cdot 10^{-1}$ [mg/cm h]

537

538 Tab. 3 standard free energy of formation of relevant oxides at 1000°C

Oxide	Cr <sub>2</sub> O <sub>3</sub>	Ta <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub> (rutile)	Al <sub>2</sub> O <sub>3</sub>	MoO <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	CrTaO <sub>4</sub>	CrNbO <sub>4</sub>
ΔG <sup>0</sup> [kJ/mole O <sub>2</sub> ]	-538	-598	-713	-853	-293	-540	-568	-539

539

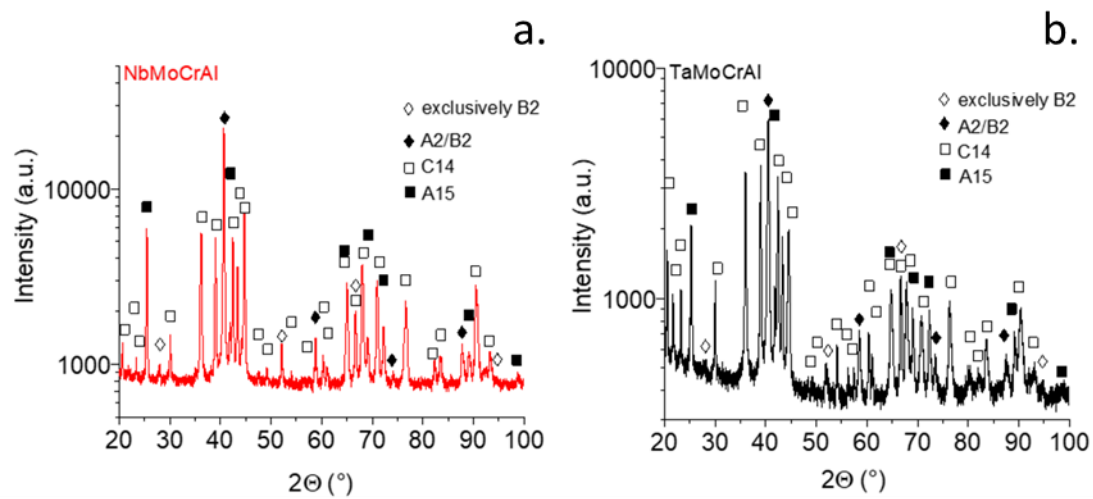
540



541 **Supplementary Material**

542

543

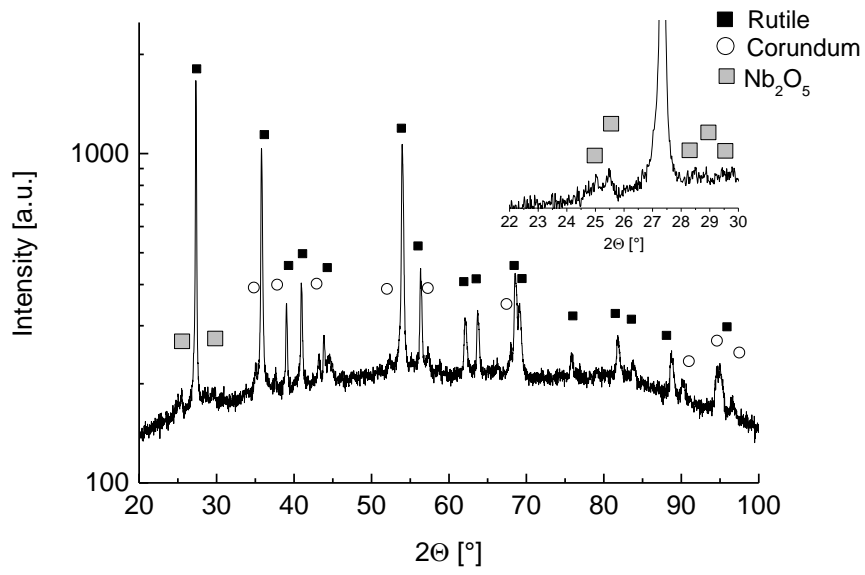


544

545 Fig. S1: Powder XRD patterns of NbMoCrAl (a.) and TaMoCrAl (b.). For better visibility of low-  
546 intensity peaks in the XRD, the intensity is plotted on a logarithmic scale.

547

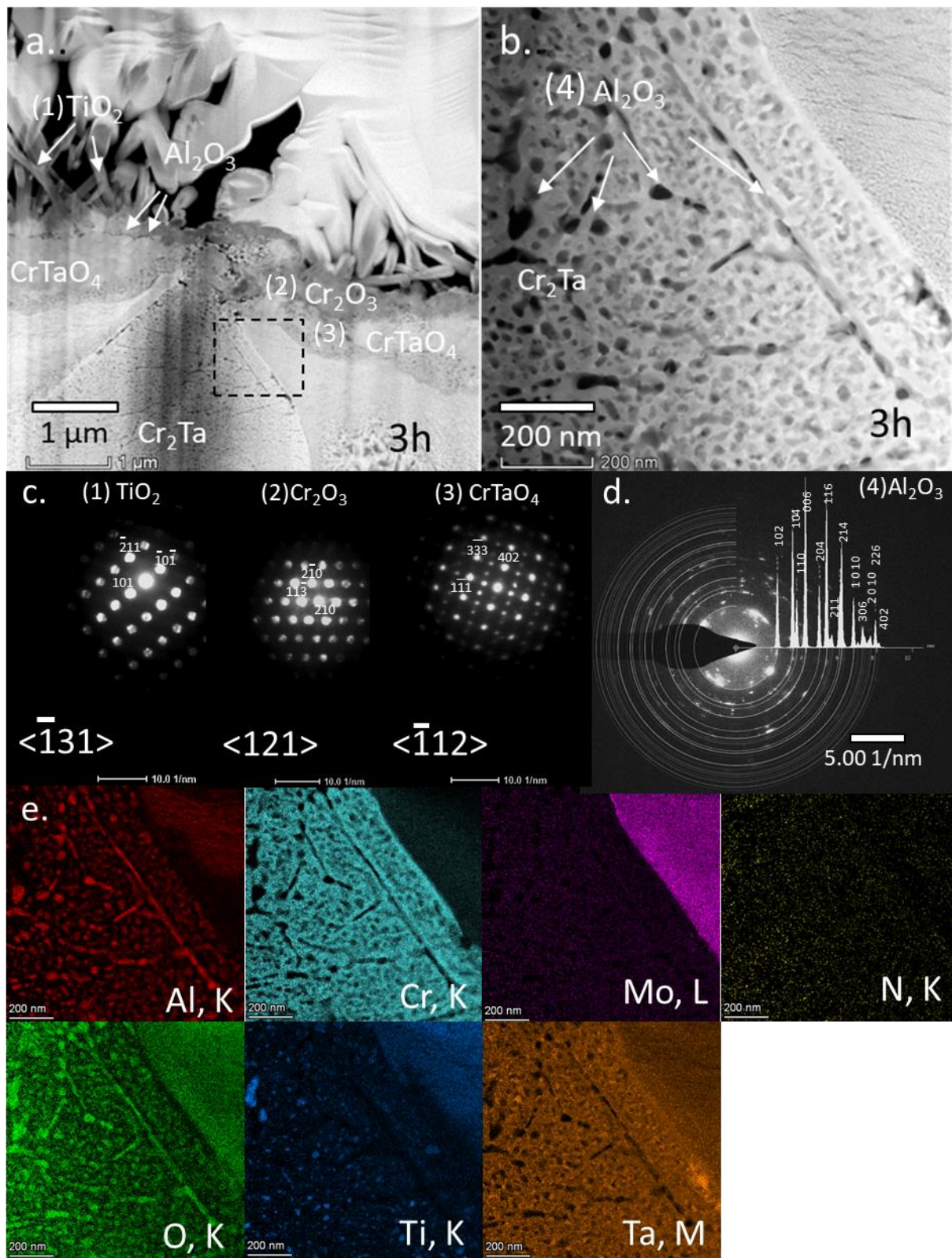




548

549 Fig. S2: Powder XRD analysis of the formed oxide scale of NbMoCrTiAl after 48h of exposure to air  
550 at 1000°C [9]. For better visibility of low-intensity peaks in the XRD, the intensity is plotted on a  
551 logarithmic scale.

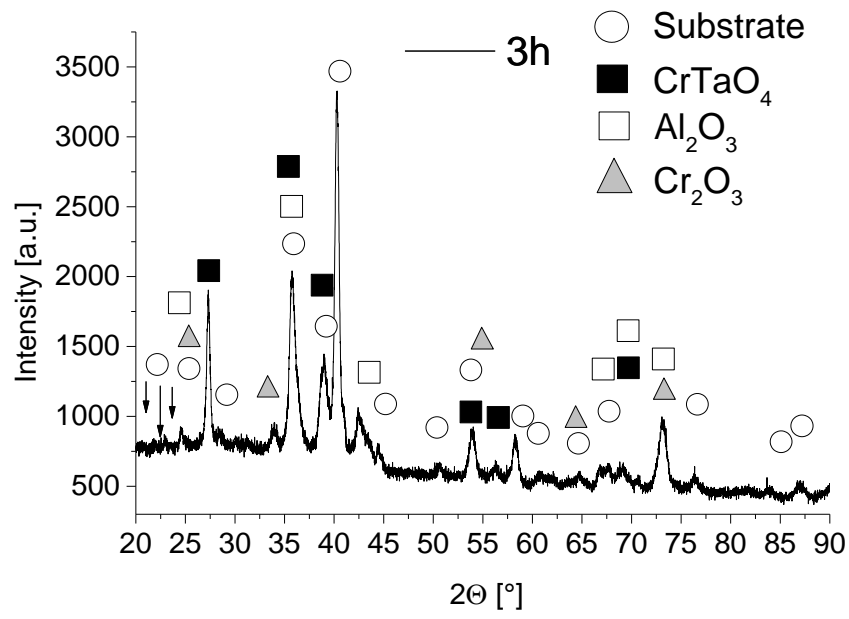
552



553

554 Fig. S3: STEM image (HAADF contrast) of TaMoCrTiAl after 3h exposure at 1000°C in air (a) as well  
 555 as a magnification of the oxidized Laves phase (Cr<sub>2</sub>Ta) in (b.). TEM diffraction pattern of the marked  
 556 oxides in (a.). TEM ring diffraction pattern of Al<sub>2</sub>O<sub>3</sub> (d.). EDX mapping of Fig. (b.) (e.).

557



558

559 Fig. S4: XRD measurement of TaMoCrAl after 3h exposure to air at 1000°C

560

561