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Elemental Effects on the Oxidation of Refractory

Compositionally Complex Alloys

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Abstract

The oxidation of refractory compositionally complex alloys (RCCAs) is one of the most critical subjects for their high temperature applications. In this work, several RCCAs were systematically designed and isothermally oxidised at 1000 °C for up to 24 hours; the elemental effects of Al, Cr, Mo, Nb Ta, Ti, V, and Zr on the oxidation of the RCCAs were studied. It was found that Al, Cr, Ti could enhance the oxidation resistance of the RCCAs by promoting the formation of rutile-type AlTaO₄, CrTaO₄, and their related oxides, while Zr and V formed non-protective oxides such as Nb₂Zr₆O₁₇, Ta₂Zr₆O₁₇, ZrTiO₄, and VTa₉O₂₅, resulting in severe internal oxidation. Mo appeared to be effective in suppressing internal oxidation, but it could form non-protective MoTiTa₈O₂₅. Ta was slightly more beneficial than Nb for reducing the oxidation mass gain. This study provides insights on the elemental effects on the oxidation and guidelines for improving the oxidation resistance of RCCAs.

Keywords: Refractory alloys; Compositionally complex alloys; Oxidation.

37

38 **1. Introduction**

39 The development of materials for turbine engine is crucial for reducing fossil fuel
40 consumption and global warming, since the increase in operation temperature of
41 turbine engine can enhance its efficiency, potential materials with higher temperature
42 capability than that of superalloys are intensively studied. Nowadays, Ni-based
43 superalloys are widely used in the hottest sections of a gas turbine owing to their
44 outstanding mechanical properties and surface stability. However, the temperature
45 capability of the Ni-based superalloys has reached its limit due to the melting point of
46 the solvent element Ni, which is 1455 °C. Therefore, developing new alloys with even
47 higher melting points than Ni-based superalloys is important. Recently, RCCAs have
48 been proposed as potential candidates for advanced high temperature applications. By
49 combining multiple refractory elements, such as W, Ta, Mo, Nb, etc., in similar
50 atomic ratio, RCCAs can exhibit extraordinary strength at extremely high temperature
51 [1-7]. Although the high temperature strength of RCCAs is promising, they show poor
52 environmental resistance in general owing to the inability to form a protective oxide
53 scale at high temperature. While an advanced Ni-based superalloy containing Al
54 content as low as 8.7 at% could possess excellent surface stability by forming a
55 protective Al₂O₃ scale [8-12], RCCAs do not show such property even with 20 at% of
56 Al content [13-27]. One of the latest developments in enhancing the oxidation
57 resistance of RCCAs is attributed to the formation of CrTaO₄-based oxide scale,
58 which has been studied at the temperature range of 900 to 1500 °C and up to 200
59 hours [20, 21, 23, 24, 28]; the formation of continuous CrTaO₄-based oxide scale
60 could decrease oxidation mass gain [21, 23], but the substrate beneath it still shows
61 certain degree of internal oxidation, which is not observed in the Al₂O₃-forming
62 substrate [10, 11, 29-31]. Detailed examination on the internally oxidised region in the
63 CrTaO₄-based-oxide-forming substrate shows strong presence of nitrides in addition
64 to oxides [20, 21, 23, 24], indicating such oxide scale might not stop nitrogen intake
65 and thus the nitridation of the substrate, which usually leads to its embrittlement [32].
66 For an advanced Ni-based superalloy, the formation of a protective Al₂O₃ scale can be
67 achieved by means of alloying, such as adding Al, Cr, and Si [33-36]. While the
68 alloying strategy for tuning the surface stability of Ni-based superalloys have already
69 been well-established, the alloying effects on oxidation behaviour for RCCAs is still
70 scarce. In this study, the oxidation behaviours of several RCCAs have been designed
71 and analysed with respect to compositions and thermodynamic simulation. The aim of
72 this study is to provide an understanding on the compositional effects on the oxidation
73 of RCCAs and guidelines for designing oxidation-resistant RCCAs.

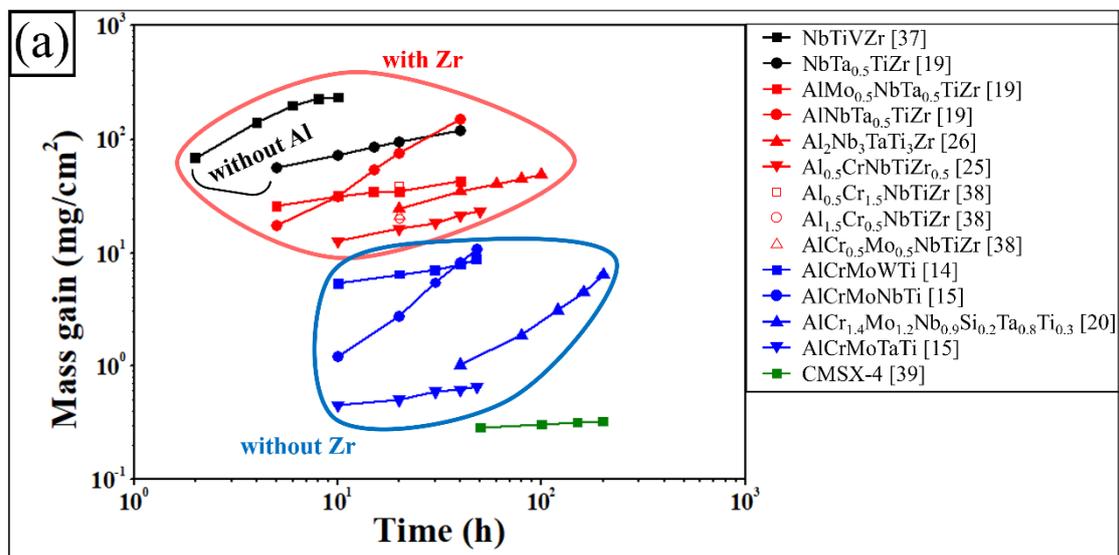
74

75 **2. Material and methods**

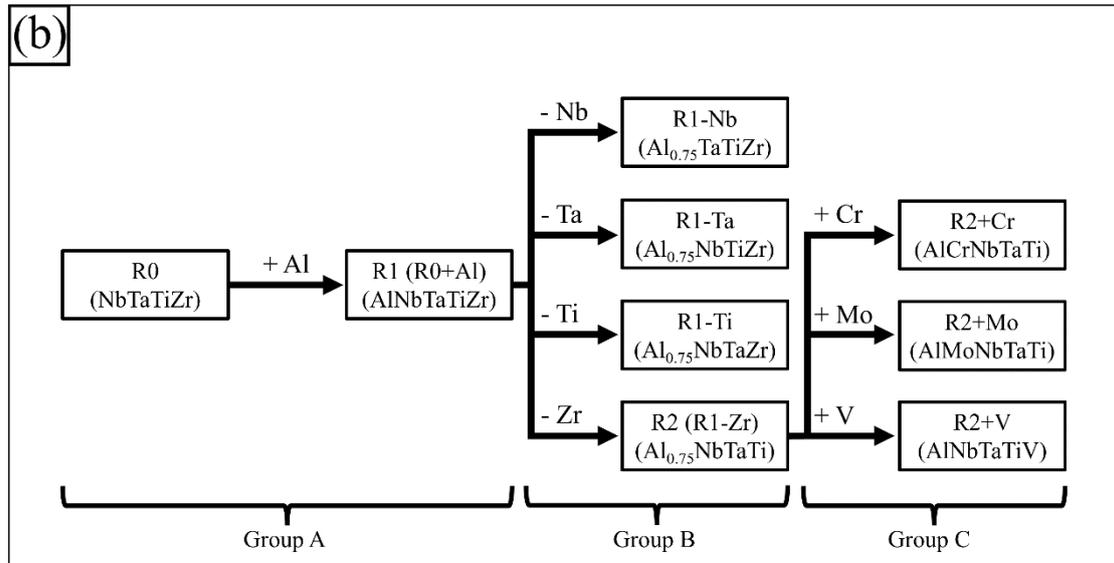
76 **2.1 Alloy design**

77 To have an overview of alloying strategy, the oxidation mass gain curves based
 78 on literature data of several representative RCCAs and a Ni-based superalloy
 79 CMSX-4 at 1000 °C were plotted and shown in Figure 1(a) [14, 16, 19, 20, 25, 26,
 80 37-39]. The oxidation mass gain curves of RCCAs with short testing duration [25, 38]
 81 or microalloying [18, 40] were not included. According to composition and mass gain,
 82 these RCCAs could be divided into 3 groups: RCCAs with only Zr and other
 83 non-protective-oxide-forming elements (black lines), RCCAs with both Al and Zr (red
 84 lines), and RCCAs with Al but no Zr (blue lines).

85 The general trends deduced from Figure 1(a) indicate that the Al-bearing RCCAs
 86 have reduced oxidation mass gain, while Zr-bearing RCCAs have increased oxidation
 87 mass gain. In order to further elucidate the compositional effects of individual
 88 elements on the oxidation behaviour of RCCAs, new compositions were designed
 89 based on quasi-binary technique in this work: Al content was fixed at 20 at%, while
 90 the rest of the components were selected refractory elements combined in equi-molar
 91 ratio. The Al content was specifically controlled since it was considered the reference
 92 element for the formation of Al₂O₃. The deduction of compositional effects for a
 93 specific element was done by adding or removing that element from a mother
 94 composition, then comparing the results of these two alloys. Figure 1(b) shows the
 95 compositions and designations of the new alloys. NbTaTiZr was the base alloy since
 96 this composition contains frequently used elements for RCCAs [7, 41-46].
 97 Additionally, Al, Cr, Mo, V were selected since these elements are commonly used for
 98 enhancing either the oxidation resistance [45-48] or mechanical properties [2, 4, 5, 41,
 99 43, 44, 48-50] of RCCAs. New compositions that were investigated in order to
 100 elucidate elemental effects could be categorized into Group A, Group B and Group C.



101



102

103 **Figure 1** (a) The oxidation mass gain curves or the terminal oxidation mass gain of
 104 the selected RCCAs reported in the literature and (b) the flow chart for the design of
 105 the studied RCCAs in this work.

106

107 *2.2 Experimental procedures*

108 The ingots of the alloys of interest shown in Figure 1(b) were prepared by
 109 arc-melting high purity elements (> 99.9 wt%) under Ti-gettered pure argon
 110 atmosphere on a water-cooled copper hearth according to their nominal compositions.
 111 The as-cast compositions of the ingots are listed in Table 1. Each button-shaped,
 112 20-gram ingot was flipped and re-melted 4 times to ensure the chemical homogeneity.
 113 The ingots had shiny surfaces and showed no sign of oxidation after the melting
 114 process. The ingots were subsequently electric-discharge-machined into $6 \times 5 \times 5$ mm
 115 blocks of specimens. The top surfaces of all specimens were ground with #1200 SiC
 116 abrasive paper prior to any subsequent tests. Isothermal oxidation was performed with
 117 a muffle furnace at 1000 °C for various duration. The specimens were spaced 10 mm
 118 apart from each other in an Al₂O₃ boat crucible and positioned into the furnace after
 119 the furnace interior was heated to 1000 °C and furnace-cooled to ambient temperature
 120 upon reaching the desired testing duration. At least 2 specimens were used per alloy
 121 for the isothermal oxidation test to ensure the repeatability of the testing results. Here,
 122 2-hour isothermal oxidation was mainly for observation on the cross-sectional
 123 microstructure, while 24-hour isothermal oxidation was mainly for X-ray diffraction
 124 (XRD) of the oxidised specimens, which was carried out with Bruker D2 Phaser
 125 equipped with Cu target. Goniometer scanning was performed between $2\theta = 20^\circ \sim$
 126 100° with a scanning rate of 5.7° per minute. The oxide scales of the specimens were
 127 either ground into fine powder (for specimens oxidised for 24 hours) or kept on the
 128 top surfaces of the specimens (for specimens oxidised for 2 hours) for XRD analysis.

129 Thermogravimetric analysis (TGA) was also carried out in flowing dry air at 1000 °C
 130 for up to 2 hours with SETARAM TAG 24- 18S simultaneous symmetrical
 131 thermoanalyser to investigate the oxidation kinetics of the studied RCCAs. Specimens
 132 for TGA had dimensions of $6 \times 3 \times 2 \text{ mm}^3$ with each surface ground with #1200 SiC
 133 abrasive paper. Each specimen was carefully placed in a micro Al_2O_3 cylindrical
 134 crucible to minimize its contact with the crucible, then the crucible with specimen was
 135 hung by a Pt wire vertically. The mass gain of the specimen was recorded
 136 automatically every 0.02 minute up to 2 hours with an accuracy of 0.023 μg . Each
 137 tested TGA specimen was compared with that of isothermal oxidation tests to ensure
 138 the consistency between the results. The mass of the tested TGA specimen itself and
 139 the total mass of the tested TGA specimen with the crucible were also measured to
 140 evaluate the spallation of the specimens. The specimens were polished with 0.02 μm
 141 colloidal silica prior to metallographic observation with a JEOL-JSM 7610F scanning
 142 electron microscope (SEM) equipped with back-scattered electron (BSE) and
 143 energy-dispersive X-ray spectroscopy (EDS) detectors. Image analysis for estimating
 144 the porosity of the external oxide scale was carried out with ImageJ software by
 145 averaging the area fraction of the porosity in 3 random regions which covered over
 146 $800 \mu\text{m}^2$ area each within the external oxide scale.

147

148 **Table 1**

149 Compositions (in at%) of the studied alloy samples determined by EDS.

Alloy	Al	Cr	Mo	Nb	Ta	Ti	V	Zr
R0	-	-	-	24.9±0.6	27.1±1.4	22.8±1.2	-	25.3±1.2
R1	18.0±1.1	-	-	21.0±0.0	20.1±2.1	19.3±0.2	-	22.1±1.5
R1-Nb	19.0±0.8	-	-	-	25.6±2.3	25.7±0.5	-	29.8±1.5
R1-Ta	18.1±0.4	-	-	27.2±0.4	-	26.4±0.5	-	28.3±0.3
R1-Ti	19.3±0.9	-	-	24.0±0.8	24.9±0.2	-	-	31.8±0.1
R2	21.4±1.6	-	-	26.4±0.4	27.9±0.7	24.4±0.5	-	-
R2+Cr	19.5±0.0	19.5±0.4	-	20.2±0.1	21.4±0.4	19.5±0.3	-	-
R2+Mo	20.1±2.9	-	20.4±1.1	19.9±0.7	20.7±0.7	19.0±0.5	-	-
R2+V	18.7±0.4	-	-	20.9±0.3	22.2±0.4	19.0±0.2	19.2±0.1	-

150

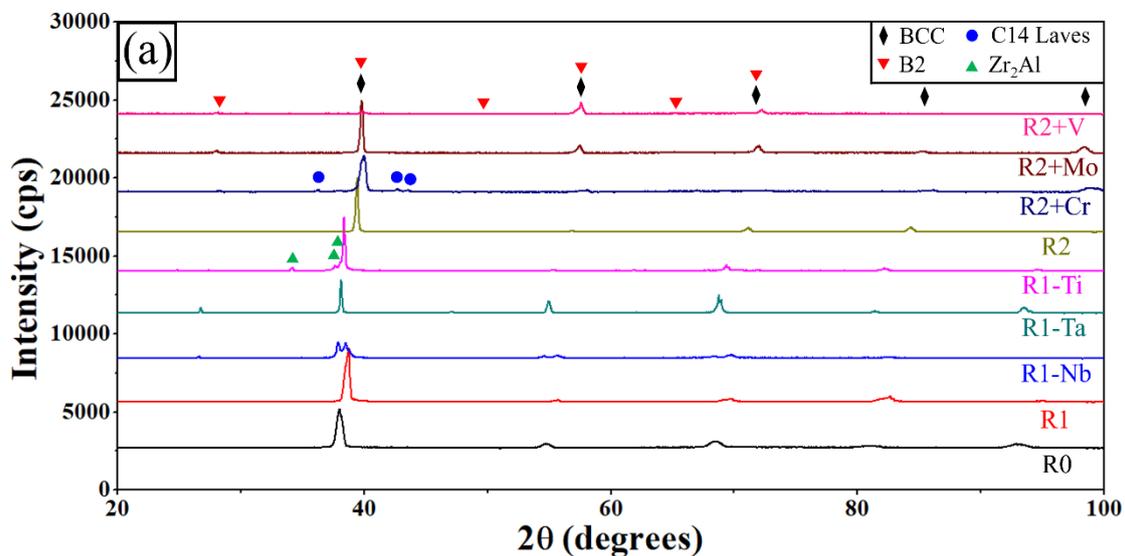
151 3. Results

152 3.1 Microstructures prior oxidation

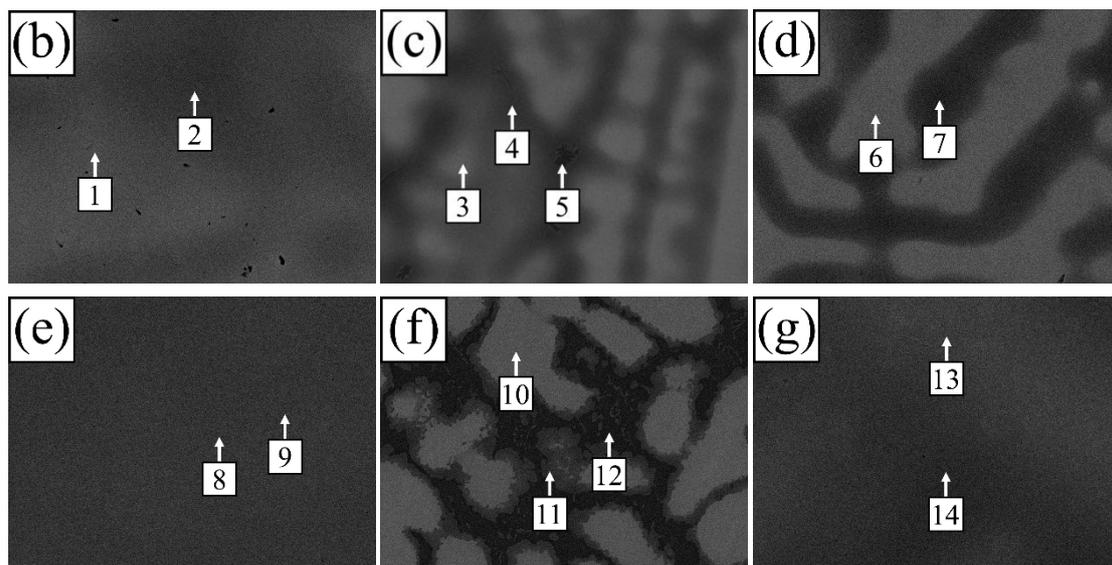
153 According to Figure 2(a), XRD analysis indicated that all alloys of interest in
 154 as-cast state have mainly body-centred-cubic (BCC) structure. Minor intermetallic
 155 phases, including C14 Laves and tetragonal Zr_2Al phases, are observed in R2+Cr and

156 R1-Ti, respectively. Additionally, diffraction peaks from B2 phase are detected in
 157 R1-Nb, R1-Ta, R2+Cr, R2+Mo, and R2+V, suggesting that chemical ordering may
 158 occur in these alloys.

159 SEM microstructures are shown in Figure 2(b)~(j) and EDS analysis are
 160 summarized in Table 2. It is evident that elements with high melting point, such as Ta,
 161 Mo, and Nb, tend to segregate toward dendrite arms (Region 1, 3, 6, 8, 10, 13, 15, 18,
 162 20), while those with relatively low melting points, such as Zr, Ti, and Al, prefer to
 163 segregate toward inter-dendritic regions (Region 2, 4, 7, 9, 12, 14, 17, 19, 21). Region
 164 11 in Table 2 shows an example of compositions in-between the dendrite arms and
 165 inter-dendritic regions of R1-Ti. Further examination showed that in addition to the
 166 tetragonal Zr_2Al (Region 12) and C14 Laves phase (Region 16) detected by XRD, (Zr,
 167 Al)-rich phase existed in the inter-dendritic regions of R1, Region 5. The low volume
 168 fraction of such phase is likely the reason why it was not detected by XRD.

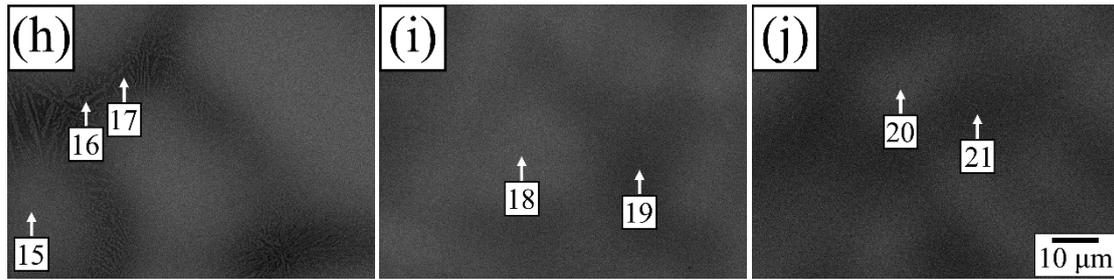


169



170

171



172

173 **Figure 2** (a) XRD patterns of all studied RCCAs and microstructural BSE images of
 174 the as-cast (b) R0 (c) R1 (d) R1-Nb (e) R1-Ta (f) R1-Ti (g) R2 (h) R2+Cr (i) R2+Mo
 175 (j) R2+V.

176

177 **Table 2**

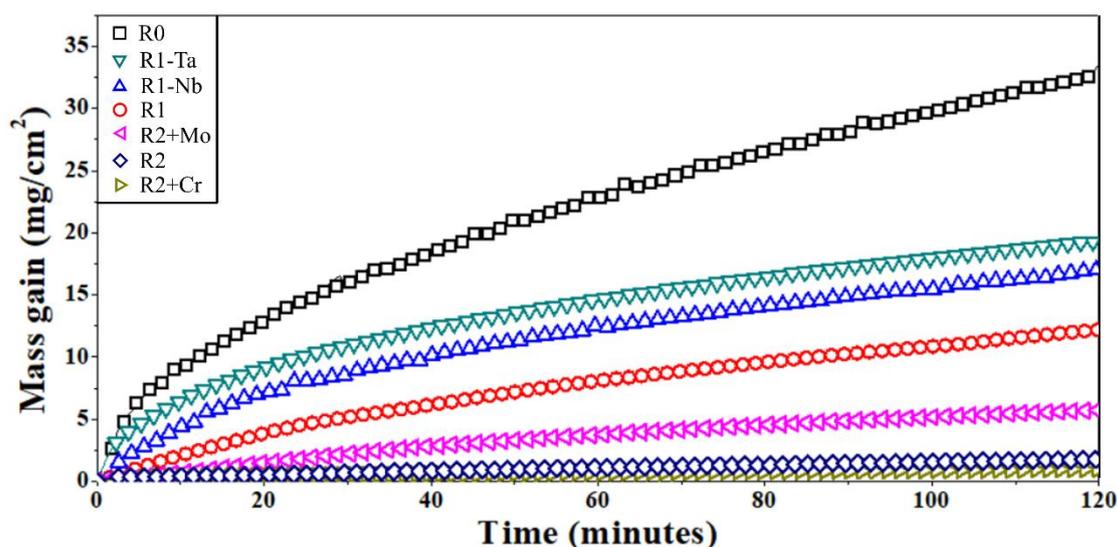
178 Chemical compositions (in at%) of the indicated regions in Figure 2(b)~(j).

Region	Al	Cr	Mo	Nb	Ta	Ti	V	Zr
1 (R0)	-	-	-	28.8±0.5	36.9±0.3	18.1±0.3	-	16.3±0.5
2 (R0)	-	-	-	24.0±1.3	20.6±2.6	23.4±1.0	-	32.1±3.0
3 (R1)	11.0±0.6	-	-	26.5±0.3	33.3±1.2	18.5±0.6	-	10.7±0.2
4 (R1)	26.4±0.2	-	-	12.0±1.9	6.0±2.2	19.4±1.0	-	36.3±3.8
5 (R1)	34.2±0.4	-	-	8.3±0.5	3.4±0.4	10.6±0.4	-	43.6±1.1
6 (R1-Nb)	12.2±0.6	-	-	-	44.5±0.1	26.7±0.3	-	16.7±0.2
7 (R1-Nb)	22.5±0.2	-	-	-	14.8±1.0	25.2±0.0	-	37.6±0.8
8 (R1-Ta)	16.9±0.9	-	-	30.1±0.9	-	27.0±0.8	-	26.0±0.7
9 (R1-Ta)	18.1±0.4	-	-	27.2±0.4	-	26.4±0.5	-	28.3±0.3
10 (R1-Ti)	8.1±0.3	-	-	35.3±0.3	46.4±0.3	-	-	10.3±0.5
11 (R1-Ti)	24.0±1.7	-	-	21.5±1.7	11.4±2.4	-	-	43.0±3.9
12 (R1-Ti)	35.3±0.4	-	-	13.0±0.5	5.7±0.0	-	-	46.0±0.5
13 (R2)	18.6±0.4	-	-	27.1±0.0	33.7±0.8	20.6±0.7	-	-
14 (R2)	21.7±1.1	-	-	26.4±0.3	26.6±2.1	25.5±1.1	-	-
15 (R2+Cr)	16.1±0.0	13.4±0.1	-	23.4±0.6	31.1±0.2	16.0±0.3	-	-
16 (R2+Cr)	19.4±0.3	33.8±2.1	-	15.4±0.6	15.3±0.9	16.3±1.7	-	-
17 (R2+Cr)	24.4±1.0	13.3±2.5	-	20.4±1.1	12.4±2.0	29.5±2.9	-	-
18 (R2+Mo)	11.5±1.9	-	24.8±1.0	20.6±0.2	28.8±2.1	14.3±1.2	-	-
19 (R2+Mo)	22.3±2.1	-	17.6±1.4	20.7±0.4	15.6±2.1	23.8±1.7	-	-
20 (R2+V)	17.8±0.2	-	-	21.0±0.2	25.5±0.7	17.4±0.5	18.4±0.3	-
21 (R2+V)	19.7±0.2	-	-	20.5±0.2	19.0±0.8	20.8±0.3	20.0±0.3	-

179

180 *3.2 Thermogravimetric analysis*

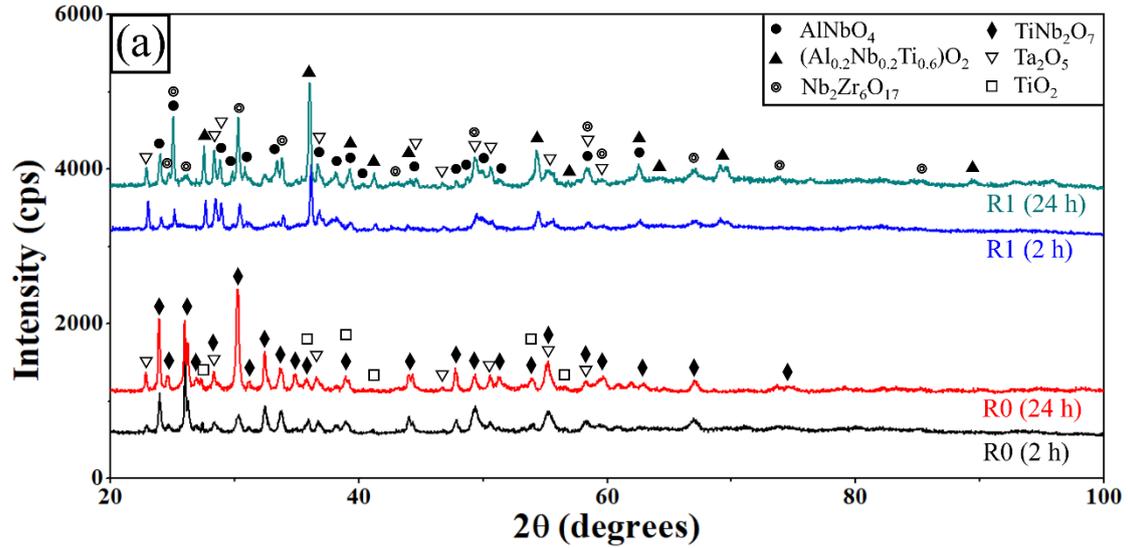
181 Figure 3 illustrates the oxidation kinetics of the studied RCCAs at 1000 °C for
 182 up to 2 hours. The TGA for R1-Ti and R2+V was waived owing to heavy oxidation or
 183 contamination of these alloys that could damage the instrument. The oxidation mass
 184 gain after 2 hours of isothermal oxidation at 1000 °C was 33.4, 19.3, 17.0, 12.2, 5.7,
 185 1.8, and 1.0 mg/cm² for R0, R1-Ta, R1-Nb, R1, R2, R2+Mo, and R2+Cr, respectively.
 186 All tested RCCAs showed no noticeable spallation, except R0 had spallation from the
 187 extruding oxide formed along the corners of the specimen. But since the
 188 metallographic observation was carried out at the flat surfaces of the specimen, such
 189 spallation is not expected to affect the observation and measurement in the following
 190 sections.



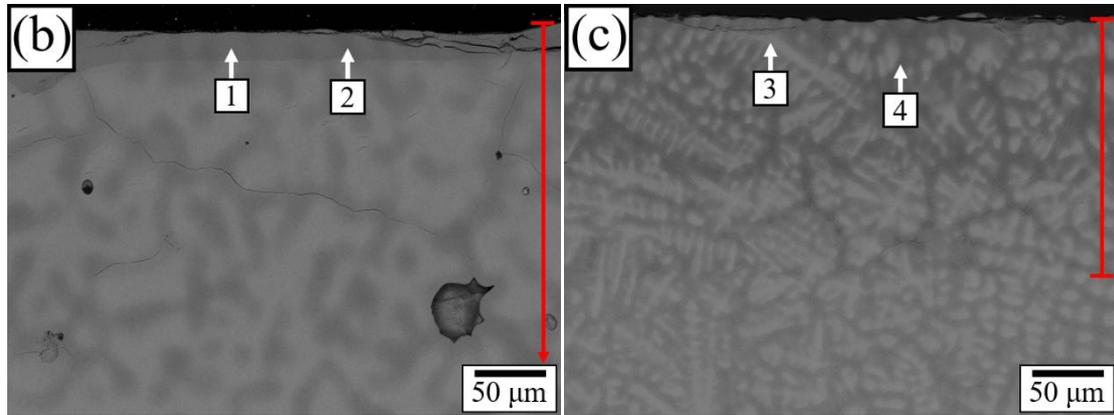
191
 192 **Figure 3** Oxidation mass gain curves of the studied RCCAs measured at 1000 °C for
 193 120 minutes.

194
 195 **3.3 Oxidation: R0 and R1 alloys (Group A)**

196 Comparing XRD results of both R0 and R1 after 2 and 24 hours of isothermal
 197 oxidation at 1000 °C, all conditions appeared to render the same oxide products,
 198 Figure 4(a). Based on the relative intensity of the diffraction peaks, the main oxide
 199 product for R0 was TiNb₂O₇, while that for R1 were (Al_{0.2}Nb_{0.2}Ti_{0.6})O₂ and Nb₂Zr₆O₁₇
 200 under both oxidation condition. Ta₂O₅ was also found in both alloys, while TiO₂ and
 201 AlNbO₄ were identified in R0 and R1, respectively. Figure 4(b)(c) and Table 3 show
 202 both alloys were oxidised prominently in the manner of internal oxidation since the
 203 morphology and chemical profile of the metallic substrate were preserved within the
 204 oxidised region, while no obvious external oxide scale was observed. Interestingly,
 205 the scales of the oxidised regions were significantly different between these alloys:
 206 The thickness of internal oxidation region (t_{IO}) was ~358 μm for R0, which was over
 207 twice as large as ~168 μm t_{IO} of R1, Figure 4(b)(c).



208



209

210 **Figure 4** (a) XRD patterns of R0 and R1 after 2 and 24 hours of isothermal oxidation
 211 and cross-sectional BSE images of (b) R0 and (c) R1 after 2 hours isothermal
 212 oxidation at 1000 °C. The red lines in (b)(c) represent t_{ox} .

213

214 **Table 3**

215 Chemical compositions (in at%) of the indicated regions in Figure 4(b)(c). Region 1,
 216 3 and 2, 4 are respectively the oxidised dendrite arms and inter-dendritic regions of
 217 Group A alloys.

Region	O	Al	Nb	Ta	Ti	Zr
1 (R0)	66.8±0.9	-	8.9±0.4	10.5±0.5	7.2±0.7	6.6±0.2
2 (R0)	69.1±0.5	-	7.7±0.6	6.6±0.6	7.0±0.8	9.6±0.8
3 (R1)	67.1±0.5	3.0±0.5	8.4±0.6	11.0±1.2	5.3±0.4	5.2±1.5
4 (R1)	61.8±1.5	8.4±0.8	6.0±0.7	4.7±1.0	7.5±1.0	11.6±1.5

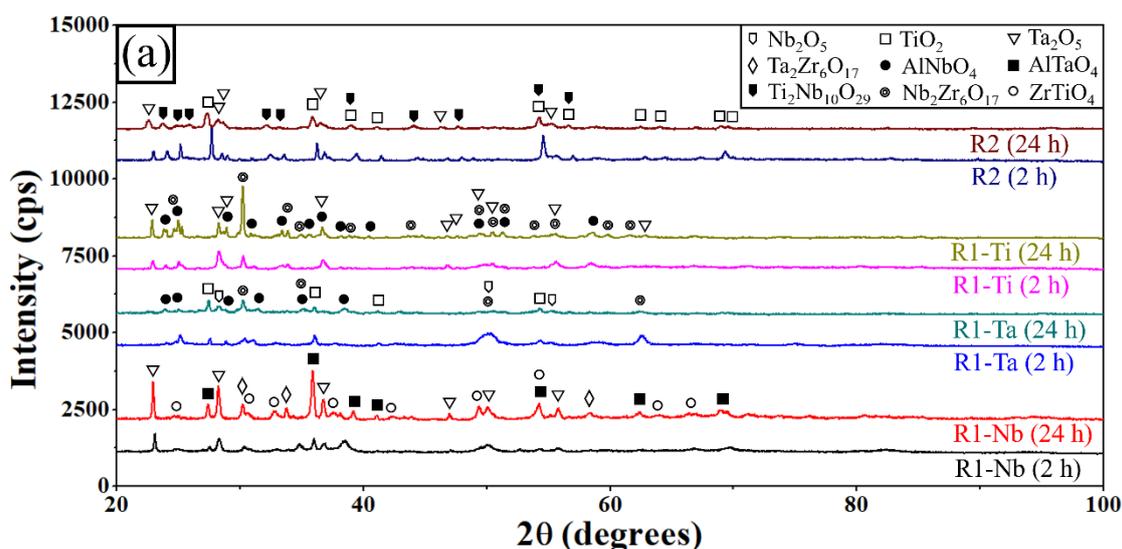
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219 **3.4 Oxidation: R1-Nb, R1-Ta, R1-Ti, and R2 alloys (Group B)**

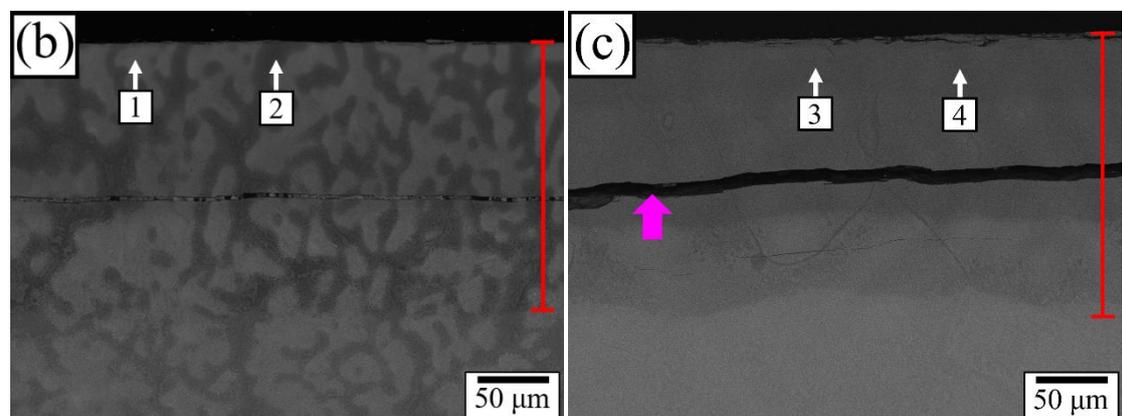
220 Similar to that of R0 and R1, XRD analysis suggested that oxide products
 221 appeared to be the same after 2 and 24 hours of isothermal oxidation at 1000 °C for

222 R1-Nb, R1-Ta, R1-Ti, and R2, Figure 5(a). It is noteworthy that rutile-type oxides,
 223 such as AlTaO₄, were absent in the oxide scale of R1-Ti, which was thoroughly
 224 oxidised without any metallic part left after 24 hours of isothermal oxidation at 1000
 225 °C. For R1-Nb, diffraction peaks of AlTaO₄ and Ta₂O₅ were prominent, while that of
 226 Ta₂Zr₆O₁₇ and ZrTiO₄ were also identified; for R1-Ta, TiO₂ and Nb₂Zr₆O₁₇ exhibited
 227 the highest diffraction peaks, while that of Nb₂O₅ and AlNbO₄ were also present. For
 228 R1-Ti, Nb₂Zr₆O₁₇ was the dominant oxide since its diffraction peaks were the highest
 229 among all other detected oxides. TiO₂ and Ta₂O₅ were found with high diffraction
 230 intensity for the oxide scale of R2, while Ti₂Nb₁₀O₂₉ was also observed.

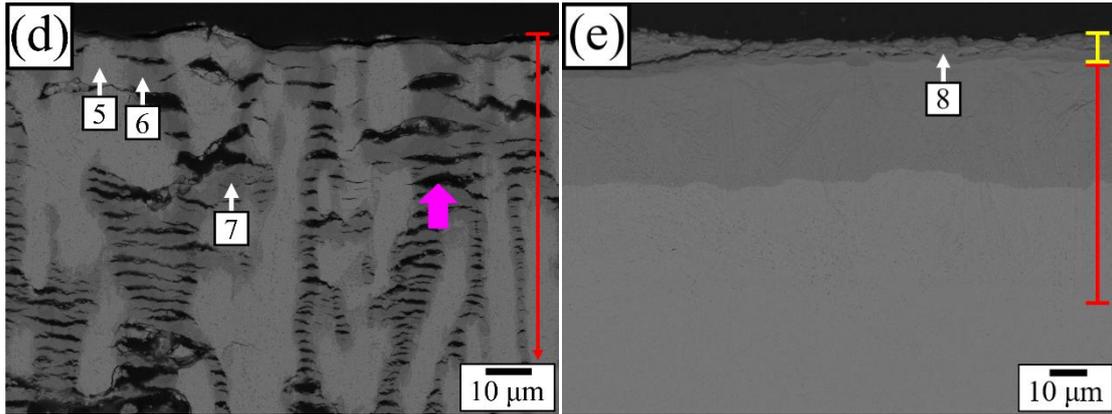
231 Cross-sectional SEM-EDS analysis revealed R2 was the least oxidized, while
 232 R1-Ti was the most affected by oxidation at 1000 °C, Figure 5(b)~(e) and Table 4.
 233 Furthermore, Zr-containing alloys, such as R1-Nb, R1-Ta, and R1-Ti, were mainly
 234 oxidised internally while R2 showed a visible external oxidation scale and greatly
 235 reduced internal oxidation region, Figure 5(b)~(e). This could be confirmed by the
 236 strong correlation of chemical profiles between the metallic substrates and oxidised
 237 regions for R1-Nb, R1-Ta, and R1-Ti, as well as the Ti-lean external oxide scale
 238 comparing to the composition of the metallic substrate for R2, Table 2 and 4.



239



240



241

242 **Figure 5** (a) XRD patterns of R1-Nb, R1-Ta, R1-Ti, and R2 after 2 and 24 hours of
 243 isothermal oxidation and cross-sectional BSE images of (b) R1-Nb (c) R1-Ta (d)
 244 R1-Ti (e) R2 after 2 hours of isothermal oxidation at 1000 °C. The yellow line in (e)
 245 marks the thickness of external oxide scale (t_{EO}) while red lines in (b)~(e) mark t_{10} .
 246 The width of the cracks (magenta arrowheads in (c)(d)) was excluded during the
 247 thickness measurement.

248

249 **Table 4**

250 Chemical compositions (in at%) of the indicated regions in Figure 5(b)~(e). Region 1,
 251 3, 5 and 2, 4, 7 are respectively the oxidised dendrite arms and inter-dendritic regions
 252 of R1-Nb, R1-Ta, and R1-Ti, while Region 6 and 8 are respectively the oxidised
 253 inter-diffusion zone of R1-Ti and the external oxide scale of R2.

Region	O	Al	Nb	Ta	Ti	Zr
1 (R1-Nb)	48.7±2.4	5.4±0.7	-	25.9±2.3	12.5±0.6	7.4±0.4
2 (R1-Nb)	61.2±1.6	9.2±0.9	-	5.9±1.6	9.2±1.4	14.4±0.9
3 (R1-Ta)	55.8±1.4	8.5±0.5	13.0±1.2	-	11.1±0.2	11.5±0.3
4 (R1-Ta)	57.5±2.2	8.7±0.4	9.9±2.0	-	9.2±1.6	14.8±1.7
5 (R1-Ti)	68.9±0.1	0.7±0.3	11.2±0.2	15.8±0.2	-	3.4±0.1
6 (R1-Ti)	65.0±0.4	8.5±0.5	7.0±0.3	4.5±0.4	-	15.0±0.5
7 (R1-Ti)	62.4±1.6	12.9±1.3	4.2±1.0	1.8±0.7	-	18.8±1.3
8 (R2)	68.5±0.7	6.9±1.1	9.1±0.8	10.2±0.9	5.3±0.5	-

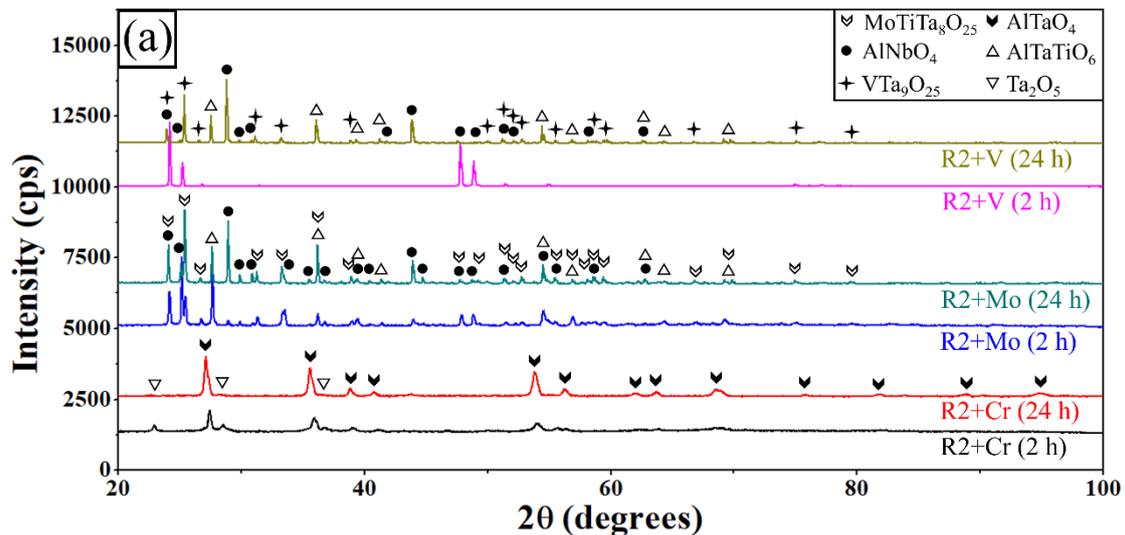
254

255 **3.5 Oxidation: R2+Cr, R2+Mo, and R2+V alloys (Group C)**

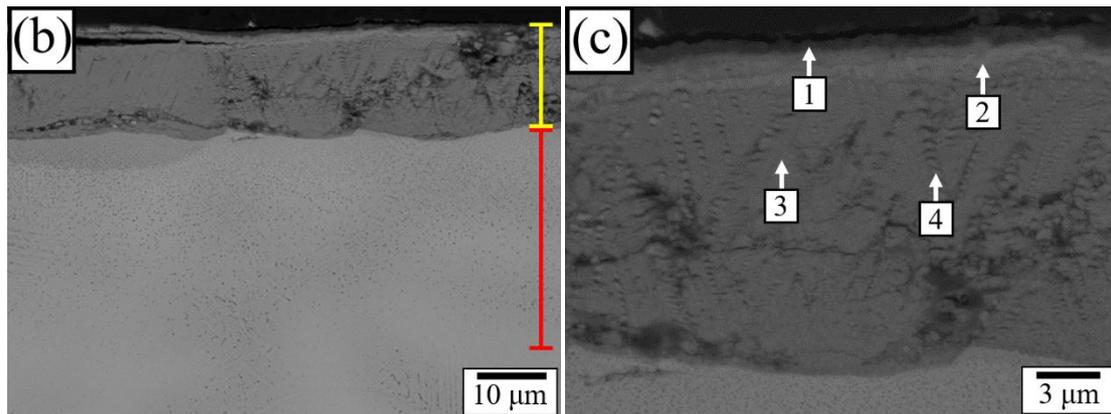
256 XRD analysis indicated that R2+Mo formed $MoTaTi_8O_{25}$, $AlTiTaO_6$, and
 257 $AlNbO_4$ after both 2 and 24 hours of isothermal oxidation, while the oxides observed
 258 in R2+Cr and R2+V were slightly different under these oxidation conditions, Figure
 259 6(a). For R2+Cr, diffraction peaks of $AlTaO_4$ were pronounced under both conditions,
 260 while that of Ta_2O_5 were only found after 2 hours of isothermal oxidation. In the case

261 of R2+V, only the diffraction peaks from AlNbO_4 were identified after 2 hours, while
 262 that of $\text{VTa}_9\text{O}_{25}$ and AlTaTiO_6 were detected after 24 hours of isothermal oxidation.

263 Cross-sectional SEM-EDS analysis showed all alloys in this group formed
 264 external oxide scale within 2 hours at 1000 °C, Figure 6(b)(d)(f) and Table 5. In
 265 addition to minor Al-rich oxide (Region 1) and Ta_2O_5 (Region 2), the external oxide
 266 scale of R2+Cr contained AlTaO_4 (Region 3) with CrTaO_4 dispersion (Region 4) and
 267 it was $\sim 14 \mu\text{m}$ in thickness, which was the thinnest t_{EO} in this group. The external
 268 oxide scale of R2+Mo was $\sim 48 \mu\text{m}$ thick and mainly composed of AlTiTaO_6 (Region
 269 5) and $\text{MoTiTa}_8\text{O}_{25}$ (Region 6), while that of R2+V was 267 μm thick and consisted
 270 of AlNbO_4 (Region 7), $\text{VTa}_9\text{O}_{25}$ (Region 8), and AlTiTaO_6 (Region 9), Figure
 271 6(c)(e)(g). In terms of internal oxidation, R2+Mo showed only $\sim 4 \mu\text{m}$ of t_{IO} , which
 272 was the thinnest t_{IO} in all studied alloys.

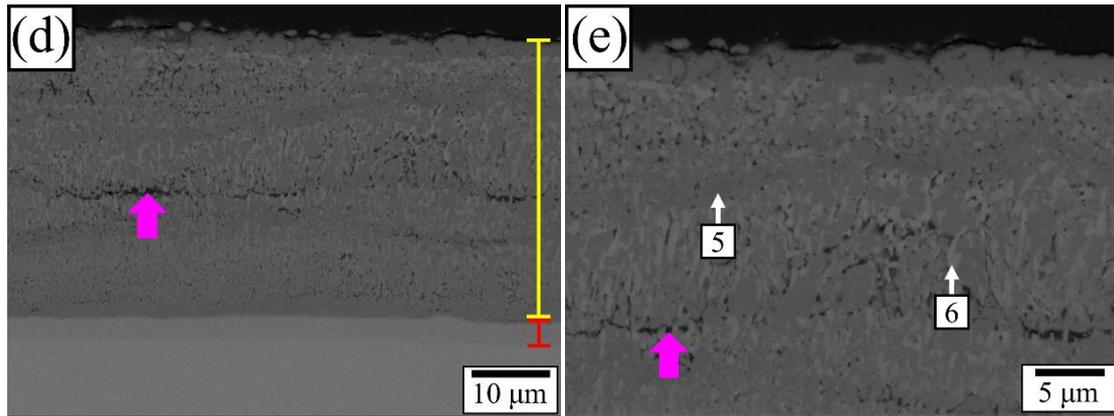


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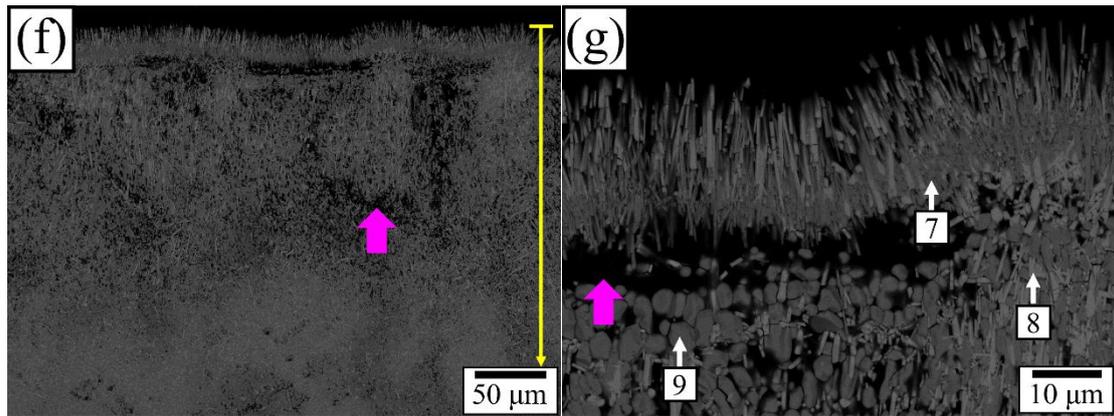


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275



276



277 **Figure 6** (a) XRD patterns of R2+Cr, R2+Mo, and R2+V after 2 and 24 hours of
 278 isothermal oxidation and cross-sectional BSE images of (b)(c) R2+Cr (d)(e) R2+Mo
 279 (f)(g) R2+V after 2 hours of isothermal oxidation at 1000 °C. The yellow and red lines
 280 in (b)(d)(f) respectively mark t_{EO} and t_{IO} , while the magenta arrowheads in (d)~(g)
 281 indicate the pores caused by evaporation of volatile oxides in the external oxide scale.

282

283 **Table 5**

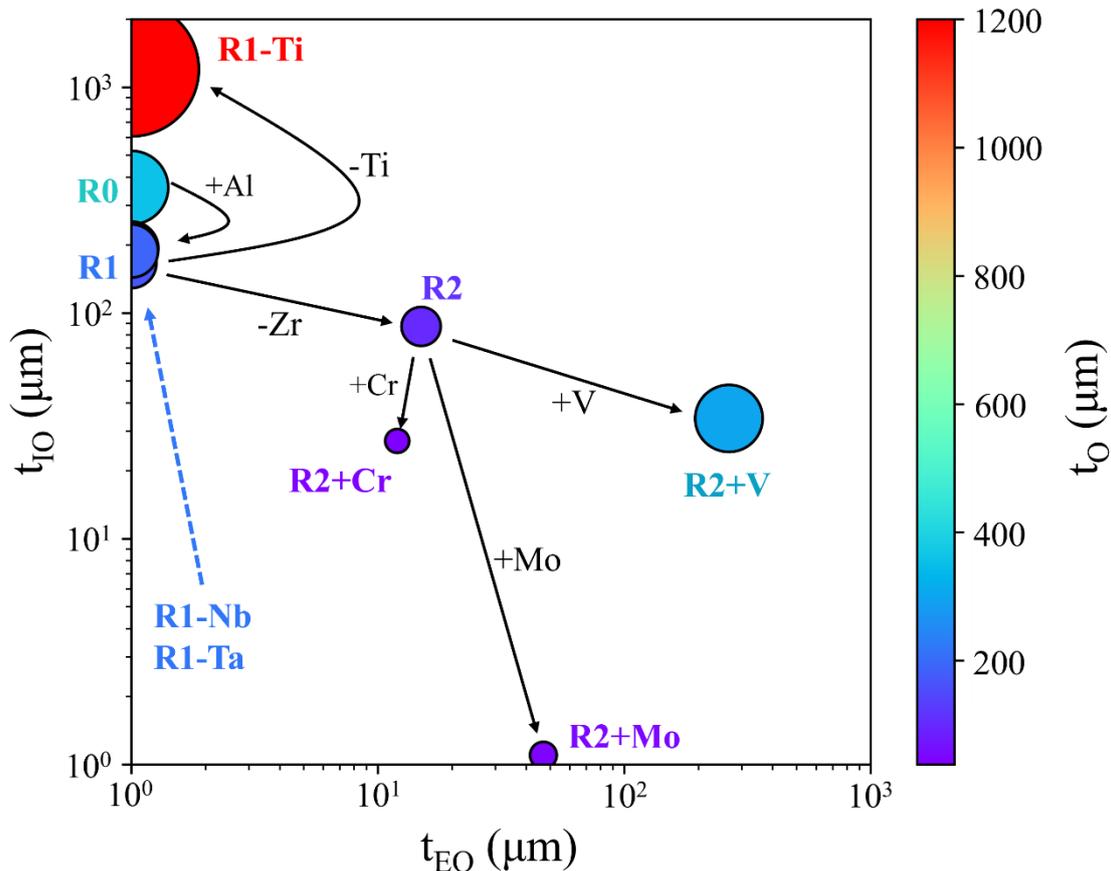
284 Chemical compositions (in at%) of the indicated regions in Figure 6(c)(e)(g).

Region	O	Al	Cr	Mo	Nb	Ta	Ti	V
1 (R2+Cr)	69.9±1.9	13.7±1.6	6.5±0.6	-	1.5±0.2	1.0±0.2	7.3±1.7	-
2 (R2+Cr)	69.4±0.3	5.4±0.5	1.3±0.0	-	8.8±0.2	9.3±0.3	5.8±0.5	-
3 (R2+Cr)	67.1±0.9	6.9±0.7	6.2±0.5	-	6.6±0.4	7.4±0.2	5.8±0.3	-
4 (R2+Cr)	66.1±1.1	7.0±0.3	8.7±0.8	-	6.1±0.4	7.9±0.6	4.3±0.6	-
5 (R2+Mo)	65.9±0.6	12.6±0.7	-	0.5±0.2	7.5±0.9	6.3±0.4	7.1±1.3	-
6 (R2+Mo)	69.0±0.8	3.9±1.0	-	2.8±0.5	10.6±0.8	9.7±0.6	4.0±0.7	-
7 (R2+V)	58.5±5.0	14.1±1.1	-	-	10.1±1.3	6.9±1.0	6.7±1.1	3.8±0.7
8 (R2+V)	66.7±2.4	0.4±0.3	-	-	15.0±1.7	12.0±0.7	1.9±0.2	4.0±0.5
9 (R2+V)	62.1±1.6	9.8±0.4	-	-	4.8±0.3	7.4±0.2	10.8±0.9	5.2±0.8

285

286 **4. Discussion**

287 Experimental results suggest that TGA and the total thickness of
 288 oxidation-affected region ($t_O = t_{EO} + t_{IO}$) measurement generally show good
 289 agreement with each other, Figure 3 and 7. The addition of Al decreases, while Zr
 290 addition could increase both oxidation mass gain and t_O in this work. For Group A, t_O
 291 of R1 was 53 % thinner and oxidation mass gain was 63 % lower than that of R0
 292 following Al addition; for Group B, t_O of R2 was 53 % thinner and oxidation mass
 293 gain was 53 % lower than that of the other Zr-bearing RCCAs following the removal
 294 of Zr. Furthermore, the results suggest that Ti might be crucial for the oxidation
 295 resistance of RCCAs since R1-Ti, which was the only Ti-free RCCA in this study,
 296 thoroughly oxidised with no metallic part left after 24 hours of isothermal oxidation at
 297 1000 °C. The results of R2+Mo and R2+V further reveal that Mo addition might
 298 suppress internal oxidation but form an external oxide scale with porosity, while V
 299 addition was clearly devastating for oxidation resistance. Cr addition appeared to
 300 greatly improve oxidation resistance since R2+Cr showed the lowest oxidation mass
 301 gain and t_O among all studied alloys. The oxides observed in the present study rarely
 302 possessed simple compositions, such as Al_2O_3 and Cr_2O_3 . Since current understanding
 303 on the properties of these complex oxides is still strictly limited, it is important to
 304 examine and deduce the characteristics of these oxides that could be important for
 305 future alloy design.



307 **Figure 7** t_{EO} , t_{IO} , and t_O of the studied RCCAs after 2 hours of isothermal oxidation at
308 1000 °C.

309

310 4.1 *The effects of Al, Cr, Nb, Ta, and Ti addition*

311 Traditionally, the surface stability of an alloy can be related to the formation of a
312 continuous and protective oxide scale [8, 33, 34], which can be achieved by alloying
313 with protective-oxide-forming elements or modified matrix properties, such as the
314 oxygen solubility [8, 33, 51]. For Al and Cr, both elements are frequently added to
315 enhance oxidation resistance, since Al_2O_3 and Cr_2O_3 scales have been proven to be
316 effective barriers [34]. However, in the present study, both protective oxide scales
317 were not observed. Instead, rutile-type Al- and Cr- bearing complex oxides, such as
318 $AlTaO_4$ and $CrTaO_4$ or their related oxides, were observed in most of the studied
319 alloys.

320 Despite the absence of Al_2O_3 and Cr_2O_3 , these complex oxides seem to provide
321 reasonable protection against oxidation, especially in the case of R2+Cr, since it
322 formed a continuous rutile-type complex oxide scale, Figure 6 and 7. The prominent
323 peak intensity of rutile-type $(Al_{0.2}Nb_{0.2}Ti_{0.6})O_2$ for R1 also corresponded with its
324 greatly reduced t_O and oxidation mass gain comparing to R0, Figure 4(a) and 7. This
325 observation agrees with that observed in previous literatures [20, 21, 23, 24], in which
326 the formation of rutile-type $CrTaO_4$ -based oxide could improve the oxidation
327 resistance of RCCAs. It is also proposed that while Cr addition could promote
328 formation of rutile-type oxides such as $CrNbO_4$ and $CrTaO_4$, the formation of $CrTaO_4$
329 would be more favourable than that of $CrNbO_4$ owing to its more negative formation
330 free energy [21]. But since other factors, such as the kinetics of oxide growth and
331 oxygen permeability of the oxide, are also essential for the formation of a protective
332 oxide layer, whether $CrTaO_4$ is preferable to $CrNbO_4$ as the protective oxide layer
333 requires further study to be clarified.

334 Interestingly, while the oxidation of R1-Nb and R1-Ta showed no noticeable
335 difference in terms of t_{EO} , t_{IO} , and t_O , the mass gain of R1-Nb was 2.3 mg/cm² lower
336 than that of R1-Ta after isothermally oxidised at 1000 °C for 2 hours, Figure 3 and 7.
337 It appears that the Ta-rich dendrite arms in R1-Nb had reduced oxygen intake, while
338 its interdendritic regions had similar oxygen intake comparing to that of the dendrite
339 arms and interdendritic regions of R1-Ta, Table 4. Given both RCCAs had similar t_O ,
340 R1-Nb would ingest less oxygen and thus have lower oxidation mass gain than R1-Ta.
341 While Ta and Nb are usually considered similar in terms of their chemical properties
342 owing to their adjacent locations in the Periodic Table, Ta was found to have more
343 pronounced effect on reducing the oxidation mass gain of TiAl-based intermetallics at
344 1000 °C comparing to Nb by decreasing the diffusion rate of oxygen [52]. These

345 observations suggest that the addition of Ta could be slightly superior to Nb in terms
346 of oxidation resistance.

347 Furthermore, it appears that the formation of rutile-type oxides, including TiO₂,
348 AlTaO₄, CrTaO₄ and their related oxides is generally beneficial for oxidation
349 resistance since R1-Ti did not form rutile-type oxide and was severely oxidised within
350 2 hours at 1000 °C. While the positive effects of rutile-type oxides have been reported
351 previously [20, 21, 23, 24, 53-56], the origin for the formation of the rutile-type
352 oxides remains an intriguing subject for further investigation. TiO₂ is one of the most
353 common oxides that possesses rutile-type crystal structure; when more than 2
354 refractory elements are co-oxidised, Ti can also be solutioned in rutile-type complex
355 oxides [20, 24]. While Al and Ta can form rutile-type AlTaO₄ when their oxides react
356 with each other [57], rutile-type oxide was not detected in the oxide scale of R1-Ti.
357 Therefore, the presence of Ti could benefit the oxidation resistance of RCCAs by
358 promoting the formation of rutile-type oxide.

359

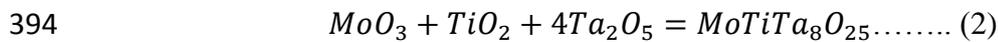
360 4.2 *The effects of Mo addition*

361 Since MoO₃ would sublime at 800 °C and above [58], the oxidation of Mo is
362 definitely not the reason behind the reduced t₀ of R2+Mo. Since R2+Mo showed the
363 thinnest t₁₀ among all tested RCCAs in the present study, it could be postulated that
364 the internal oxidation was suppressed due to the presence of Mo. Considering a binary
365 alloy system M-Al, in which M is an oxygen-soluble arbitrary metal nobler than Al
366 and Al is a dilute solute. Here, if Al₂O₃ is thermodynamically very stable and the
367 diffusivity of Al is significantly lower than that of oxygen, the time (t) dependency for
368 the depth of internal oxidation (ξ) of such alloy can be described as [8]:

369
$$\xi(t) \propto \sqrt{N_o^{(s)} t} \dots \dots \dots (1)$$

370 In which N_o^(s) is the oxygen solubility of the alloy substrate. Such relationship
371 indicates that reduced N_o^(s) would suppress internal oxidation. Generally, the internal
372 oxidation is not desirable for the oxidation resistance of an alloy since the protective
373 oxide scale is formed via external oxidation. Upon the formation of a continuous
374 external oxide scale, it could act as a barrier and retard the oxidation of the alloy.
375 Although the capabilities of such barrier depend on several factors, such as its
376 integrity, gas permeability, and gas diffusivity, the formation of an external oxide
377 scale and reduced internal oxidation are beneficial for the oxidation resistance of the
378 alloy. Previous study suggested Mo possesses extremely low oxygen and nitrogen
379 solubility as pure element [16] and it could improve the surface stability of
380 TiAl-based alloys by decreasing the solubility of oxygen and nitrogen in the alloy
381 substrate [59, 60]. Consequently, the reduced internal oxidation of R2+Mo might

382 result from the decreased $N_O^{(s)}$ caused by Mo addition. On the other hand, the
 383 external oxide scale of R2+Mo was relatively thick and full of rounded pores
 384 comparing to that of R2+Cr, indicating the former oxidised more severely than the
 385 later and might suffer from the formation and evaporation of volatile oxides, Figure 6.
 386 The area fraction of the rounded pores was estimated to be 2.4 % according to the
 387 image analysis. Since R2+Mo contains 20 at% of Mo, it is possible that volatile
 388 oxides, such as MoO_3 , would form during the isothermal oxidation at 1000 °C.
 389 Furthermore, the tetragonal $MoTiTa_8O_{25}$ was present in the oxide scale of R2+Mo
 390 alloy. Despite its presence was mentioned in the oxidation of $CrMo_{0.5}NbTa_{0.5}TiZr$ [47],
 391 no further description regarding to its properties was discussed. In this work, the
 392 formation of $MoTiTa_8O_{25}$ could result from a reaction among MoO_3 , TiO_2 , and Ta_2O_5
 393 in Ta_2O_5 -rich environment:



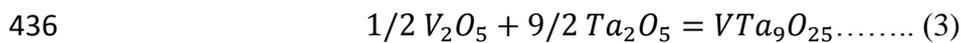
395 Since $MoTiTa_8O_{25}$ is largely preserved while MoO_3 is not found in the oxide
 396 scale of R2+Mo after the isothermal oxidation at 1000 °C, the thermal stability of
 397 $MoTiTa_8O_{25}$ should be superior to that of MoO_3 . It appears that $MoTiTa_8O_{25}$
 398 prevented heavy evaporation of MoO_3 by forming an external oxide scale since there
 399 was no obvious MoO_3 residue in the crucible after the oxidation test. Therefore, the
 400 oxidation mass loss caused by MoO_3 in the present study could be neglectable at least
 401 up to 2 hours of isothermal oxidation at 1000 °C. But considering the relatively thick
 402 oxide scale of R2+Mo comparing with that of R2+Cr, such oxide is not likely to be an
 403 efficient oxygen barrier. These could be the reasons why R2+Mo has thicker and more
 404 porous external oxide scale comparing to that of R2+Cr.

405

406 *4.3 The effects of Zr and V addition*

407 According to the oxidation behaviours of Zr- and V-bearing RCCAs, it appears
 408 that both alloying additions were detrimental since they are associated with large
 409 oxidation mass gain or t_O for RCCAs, Figure 1 and 7. While Zr is a common
 410 constituent in ductile RCCAs [41, 42, 44, 45, 61], ZrO_2 , which is a common form of
 411 Zr-related oxide, is known for its detrimental effects due to its polymorphism
 412 properties across a wide range of temperature [62, 63]. However, since ZrO_2 was not
 413 detected in this work, its role on oxidation might not be so direct. Alternatively, ZrO_2
 414 could react with other refractory oxides, such as TiO_2 and Nb_2O_5 , to form complex
 415 refractory oxides, such as $ZrTiO_4$ [63-66] and $Nb_2Zr_6O_{17}$ [37]. Interestingly, $Ta_2Zr_6O_{17}$
 416 was additionally found in the present study, presumably it was formed due to a
 417 reaction between ZrO_2 and Ta_2O_5 . Despite there has been no literature specifically
 418 describing the properties of these Zr-related complex refractory oxides, it is not likely
 419 that these oxides are protective against oxidation since these Zr-bearing alloys show

420 poor oxidation resistance [37, 63]. RCCAs containing Zr as main constituent could
421 suffer from heavy internal oxidation owing to the high affinity and solubility with
422 oxygen and nitrogen of Zr [67], which agrees with the observation in the present study,
423 Figure 3 and 7. On the other hand, although V has high solubility for oxygen [67, 68],
424 V_2O_5 could melt and become volatile at above 690 °C [69]. In this work, the Al_2O_3
425 crucible used as the container for R2+V was heavily contaminated after the 24 hours
426 of isothermal oxidation at 1000 °C. Along with large pores shown in Figure 6, which
427 were 8.2 % in area fraction within the oxide scale of R2+V, it is reasonable to assume
428 that the formation and melting of V_2O_5 occurred during the test. Another noticeable
429 V-related oxide found in R2+V was the tetragonal VTa_9O_{25} , which has not been
430 reported in the literature regarding to the oxidation of RCCAs. While its impact on the
431 surface stability of RCCAs is unknown, it has been suggested that VTa_9O_{25} is a stable
432 oxide at the Ta_2O_5 -rich end of V_2O_5 - Ta_2O_5 quasi-binary phase diagram and it could
433 melt at around 1800 °C [70]. Therefore, it is likely that some of the V_2O_5 reacted with
434 Ta_2O_5 and formed VTa_9O_{25} instead of melting away during the oxidation of R2+V at
435 1000 °C via the following reaction:



437 Since VTa_9O_{25} possesses much higher melting point than that of V_2O_5 , the
438 formation of VTa_9O_{25} might be less harmful to the surface stability of RCCAs than
439 that of V_2O_5 .

440

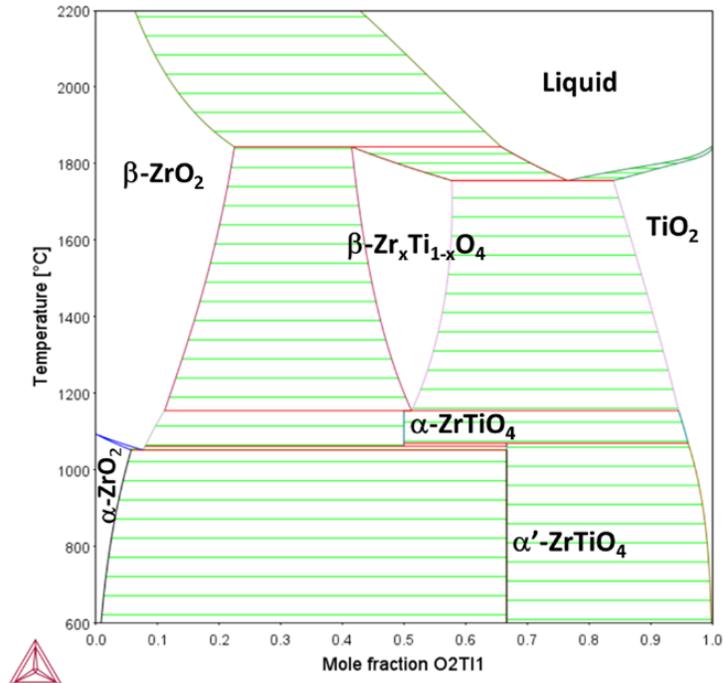
441 4.4 *The characteristics of complex oxides*

442 The other group of complex oxides identified in this work includes $AlNbO_4$,
443 $TiNb_2O_7$, and $Ti_2Nb_{10}O_{29}$. In previous studies, these oxides were found when Nb
444 content was high enough to reach its solubility limits in TiO_2 for TiAl-based alloys
445 [71, 72] or when Nb_2O_5 could react with Al_2O_3 in Nb-based alloys [56, 73].
446 Interestingly, the effects of these oxide on the surface stability of the reported alloys
447 can be either positive or negative. For TiAl-based alloys, the formation of $TiNb_2O_7$
448 could deteriorate oxidation resistance by interrupting the Nb-doped TiO_2 scale, which
449 could have assisted the formation of a continuous Al_2O_3 scale [71, 72]; on the other
450 hand, the formation of $AlNbO_4$ could enhance oxidation resistance of Nb-based alloys
451 by increasing the integrity of the oxide scale [56]. While the role of $Ti_2Nb_{10}O_{29}$ on the
452 surface stability has not been specifically described in the literature, it is frequently
453 found in the oxide scale of Ti-bearing and Nb-based alloys and could decompose into
454 $TiNb_2O_7$ [74, 75]. It is evident that these oxides would not be effective oxygen
455 barriers comparing to Al_2O_3 , Nb-doped TiO_2 , or rutile-type oxide like $CrNbO_4$ [71, 72,
456 76]. Therefore, the formation of these oxides should be avoided when designing
457 RCCAs that form protective oxide scale at high temperature, and this could be

458 achieved by limiting Nb content in RCCAs.

459 Multiple complex refractory oxides have been observed instead of simple
460 oxides, such as Al_2O_3 and ZrO_2 , in the present study. Here, the simple oxides might
461 react with each other and form complex oxides rather than existing independently, or
462 the complex oxides were directly formed as the stable oxides in the studied system. In
463 both cases, the formation free energy of the complex oxides could be more negative
464 than that of the simple oxides. However, such data cannot be retrieved from current
465 thermodynamic databases despite they do contain the constituents of the present
466 alloys. This is because these databases have been developed for a particular alloy
467 family, so each database can only accurately describe the corner region of the phase
468 diagram containing the main element. Although thermodynamic databases dedicated
469 to high entropy alloys has been intensively developed, they currently contain a very
470 limited number of assessed ternaries with oxygen. Still, the TCOX11 database for
471 Thermo-Calc Software dedicated to the thermodynamic simulation of oxides allows
472 the clarification to the formation of the intermediate oxide ZrTiO_4 in Ti-O-Zr bearing
473 alloys. As shown in Figure 8, three ternary oxides adjacent to both phase fields with
474 ZrO_2 and TiO_2 exist with different stability range. Above 1150 °C, the disordered
475 $\square\text{-Zr}_x\text{Ti}_{1-x}\text{O}_4$ crystallizes in an orthorhombic structure. At lower temperatures, it
476 undergoes two ordering transitions to $\alpha\text{-ZrTiO}_4$, and $\alpha'\text{-ZrTiO}_4$ below 1050 °C. This
477 could help explaining the presence of ZrTiO_4 in the oxide layer of some (Zr,
478 Ti)-bearing alloys [63, 65, 66], including R1-Nb in this study.

479 In summary, the content of Al, Cr, and Ti in RCCAs could benefit the oxidation
480 resistance by forming rutile-type complex oxides, while Zr and V contents could
481 deteriorate surface stability by forming non-protective oxides and enhancing internal
482 oxidation; Mo addition could greatly suppress internal oxidation of the substrate, but
483 the formation of non-protective $\text{MoTiTa}_8\text{O}_{25}$ might lead to reduced resistance against
484 oxidation; Ta addition could be slightly more beneficial than Nb addition in terms of
485 oxidation resistance owing to reduced oxygen intake of the alloy bulk. The properties
486 and the parent alloys of the observed oxides in the present study are summarized in
487 Table 6. The formation of oxides and their growth kinetics are heavily composition
488 dependent, thus changing the alloying amount of each element could lead to different
489 oxidation kinetics. These results and discussions present in this article could provide
490 guidelines for the design of RCCA with improved oxidation resistance in the future.



491

492 **Figure 8** ZrO₂-TiO₂ ternary phase diagram calculated with Thermo-Calc Software
 493 equipped with TCOX11 database.

494

495 **Table 6**

496 The constituents, crystal structures, and the parent alloys of the observed oxides in
 497 this work.

Element	Combination	Oxide	Crystal Structure	Alloy(s)
Al	Nb	AlNbO ₄	Monoclinic	R1 R1-Ta R1-Ti R2+Mo R2+V
	Ta	AlTaO ₄	Tetragonal (rutile)	R2+Cr
	Nb, Ti	(Al _{0.2} Nb _{0.2} Ti _{0.6})O ₂	Tetragonal (rutile)	R1
	Ta, Ti	AlTaTiO ₆	Tetragonal (rutile)	R1-Nb R2+Mo R2+V
Cr	Ta	CrTaO ₄	Tetragonal (rutile)	R2+Cr
Mo	Ta, Ti	MoTiTa ₈ O ₂₅	Tetragonal	R2+Mo
V	Ta	VTa ₉ O ₂₅	Tetragonal	R2+V
Zr	Nb	Nb ₂ Zr ₆ O ₁₇	Orthorhombic	R1 R1-Ta R1-Ti

	Ta	Ta ₂ Zr ₆ O ₁₇	Orthorhombic	R1-Nb
	Ti	ZrTiO ₄	Orthorhombic	R1-Nb
Nb	Ti	TiNb ₂ O ₇	Monoclinic	R0
		Ti ₂ Nb ₁₀ O ₂₉		R2
	-	Nb ₂ O ₅	Monoclinic	R1-Ta
Ta	-	Ta ₂ O ₅	Orthorhombic	R0 R1 R1-Nb R1-Ti R2 R2+Cr
Ti	-	TiO ₂	Tetragonal (rutile)	R0 R1-Ta R2

498

499 5. Conclusions

500 Several RCCAs have been designed by systematic change in composition with
501 respect to Al, Cr, Mo, Nb, Ta, Ti, V, Zr and subjected to isothermal oxidation for up to
502 24 hours at 1000 °C in order to examine the effects of the individual elements on
503 oxidation. It is found that the addition of Al, Cr, and Ti could benefit the oxidation
504 resistance by forming rutile-type complex oxides instead of their individual oxides,
505 while the addition of Zr and V degraded the oxidation resistance by forming
506 non-protective oxides or promoting internal oxidation. Mo addition appeared to
507 suppress the internal oxidation, yet the formation of non-protective MoTiTa₈O₂₅ might
508 undermine the surface stability. Ta addition showed slightly reduced oxidation mass
509 gain comparing with Nb addition owing to the reduced oxygen intake of the alloy
510 bulk in the present study. This work has presented the effects of multiple elements on
511 the oxidation of RCCAs and their associated oxides formation, and it may provide
512 guidelines to design future RCCAs with enhanced oxidation resistance.

513

514 Declaration of Competing Interest

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

517

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529

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