

Microstructure and mechanical properties at elevated temperatures of a new Al-containing refractory high-entropy alloy Nb-Mo-Cr-Ti-Al

H. Chen^{a*}, A. Kauffmann^a, B. Gorr^b, D. Schliephake^a, C. Seemüller^a, J. N. Wagner^a, H.-J. Christ^b, and M. Heilmaier^a

^a Institute for Applied Materials (IAM-WK), Karlsruhe Institute of Technology (KIT), Engelbert-Arnold-Str. 4, D-76131 Karlsruhe, Germany

^b Institut für Werkstofftechnik, Universität Siegen, Paul-Bonatz-Str. 9-11, D-57068 Siegen, Germany

* corresponding author

mail: hans.chen@kit.edu, phone: +4972160846462

Keywords: high-entropy alloys, refractory metals, homogenization, deformation, secondary phases

1 Abstract

2 In the present investigation, we provide results on the casting, homogenization, and
3 deformation behavior of a new Al-containing refractory high-entropy alloy, namely the
4 equiatomic Nb-Mo-Cr-Ti-Al. The alloy shows a dendritic microstructure after arc melting.
5 The dendrites completely dissolve due to a heat treatment at 1300 °C for 20 h. Besides a
6 major phase in the form of a solid solution of W prototype structure, identified by X-ray
7 diffraction (XRD) measurements as well as electron backscatter diffraction (EBSD),
8 additional phases of small volume fraction within the grains and at the grain boundaries were
9 observed. Quasistatic compression tests, performed between room temperature and 1200 °C,
10 reveal sustaining and high yield strength up to 800 °C and an increasing ductility with
11 increasing test temperature. The dominant deformation mechanism for quasistatic
12 compression loading between 800 °C and 1200 °C is the $\langle 111 \rangle$ pencil glide of dislocations
13 within the solid solution which was proven by the according fiber texture components,
14 evolving during deformation.

15 1. Introduction

16 Materials, combining excellent mechanical strength at ambient as well as elevated
17 temperature with a suitable ductility and toughness, always are a reasonable optimization goal
18 of modern materials science in order to facilitate new applications in mechanical engineering.
19 In this respect, the recently proposed concept of suppression of intermetallic phases and
20 stabilization of a solid solution of simple crystal structure by minimizing the configurational

21 entropy term $-T \cdot \Delta S_{\text{config}}$ in the Gibb's free energy [1-5] seems to provide an approach. For this
22 purpose, equiatomic concentrations of mainly at least five alloying elements should be
23 established in the solid solution in order to fulfill this concept. Due to the suppression of
24 brittle intermetallic phases, ductility can in principle be improved. This is, of course, a rough
25 assumption when the typical embrittlement of body-centered cubic (bcc) solid solutions with
26 respect to the ductility and toughness of the base elements (for example Mo-Si or Mo-Re [6-
27 8]) is taken into account. Nevertheless, Senkov & Semiatin [9] recently presented a bcc high
28 entropy alloy which could be rolled up to a remarkable true strain of about 2.3 at room
29 temperature indicating that a simple extrapolation from binary or ternary solid solutions to
30 concentrated multicomponent systems with respect to ductility and toughness can be
31 misleading. In addition to the suppression of intermetallic phases, choosing base elements
32 with high melting points can lead to an enhanced melting point of the high-entropy alloy in
33 comparison to currently used high temperature materials. Thus, operation at higher
34 temperature is in principle possible. Moreover, adding alloying elements for improving
35 properties other than pure mechanical ones is possible, too – for example, by utilizing
36 elements facilitating the formation of a stable oxide scale for enhancing high temperature
37 corrosion resistance.

38 Before adding Al, the focus has mainly been on the microstructure, mechanical properties and
39 oxidation behavior of high-entropy alloys, solely based on elements with high melting points
40 from group 4 to 6 (frequently named refractory metals) of the periodic table of elements [10-
41 12]. Due to the high density of these alloys ranging up to 13.75 g/cm^3 for equiatomic W-Nb-
42 Mo-Ta, heavy elements were replaced by lighter ones such as Hf, Zr, Cr and Ti [6,13-20]. The
43 addition of Al to a high-entropy alloy changes its properties in different ways. With increasing
44 Al content, the density of the alloy decreases. Comparing the alloys Ta-Nb-Hf-Zr-Ti and
45 $\text{Al}_{0.4}\text{-Hf}_{0.6}\text{-Nb-Ta-Ti-Zr}$ which were introduced by Senkov et al. [20,21], the density drops
46 from about 9.9 g/cm^3 to 9.0 g/cm^3 . The mechanical properties, such as the yield strength and
47 the ductility, depend on the amount of Al in the HEA, investigated on Nb-Ti-V-Ta- Al_x [22]
48 and $\text{Al}_x\text{-Hf-Nb-Ta-Ti-Zr}$ [23]. Regarding high temperature oxidation, Al may form a stable
49 and dense Al_2O_3 oxide scale. Oxidation tests of the high-entropy alloy W-Mo-Al-Cr-Ti reveal
50 a scale growth following the parabolic growth law [24]. Having a similar atomic radius as
51 refractory metals, it can be expected that Al-addition allows the formation of a solid solution
52 in such an alloy, thus preventing the formation of intermetallic phases [21]. Nevertheless, it
53 has to be pointed out that several investigations already revealed various parameters other
54 than the configurational entropy or atomic size difference to be more or less decisive, such as
55 the mixing enthalpy ΔH_{mix} , the mixing entropy ΔS_{mix} [25], the parameter Ω which describes
56 the correlation between ΔH_{mix} and ΔS_{mix} [26], and the valence electron concentration VEC
57 [27]. Hence, the stability of a solid solution with simple crystals structure has to be verified
58 for each case.

59 In the present work, Nb-Mo-Cr-Ti-Al is investigated with respect to microstructural evolution
60 during annealing as well as mechanical properties at various temperatures. For that, Nb, Mo
61 and Ti are refractory metals for providing a suitable melting point for high temperature

62 application. Ti, again, and Al are chosen in order to achieve low density, as shown by Senkov
63 et al. [13,21], while Al and Cr are considered due to their ability to form stable oxide scales
64 for good oxidation resistance. Nb-Mo-Cr-Ti-Al is expected to have similar properties as the
65 W-containing counterpart, introduced above. CALPHAD calculations suggest that Nb-Mo-
66 Cr-Ti-Al (“PanNb with V” database using Pandat; single phase, solid solution at 788–
67 1712 °C) exhibits a similar melting temperature as W-Mo-Cr-Ti-Al (FactSage calculation;
68 single phase, solid solution at 1077–1700 °C [24]). Considering the lower atomic mass of Nb,
69 a lower density is to be expected when comparing Nb-Mo-Cr-Ti-Al with W-Mo-Cr-Ti-Al.

70 Generally, the investigated alloys show dendritic structure in the as-cast condition with
71 significant differences in atomic concentration between dendritic and interdendritic
72 regions [24,28]. An annealing step is typically performed after casting in order to homogenize
73 the microstructure as well as to establish a single phase solid solution with simple crystal
74 structure [13,14]. Despite the theory of stabilization of solid solutions by increasing the
75 configurational entropy, a macro- and mesoscopically homogeneous microstructure cannot be
76 reached in all cases of postulated high-entropy alloys. This is even more evident when
77 investigations down to atomic scale are performed [29]. In addition to these local
78 investigations, secondary phases are frequently found. XRD patterns of Ta-Nb-Hf-Zr-Ti show
79 a presumably hexagonal second phase besides the main body-centered cubic structure (bcc)
80 whereas Cr-Nb-Ti-(V-)Zr exhibits a Cr-rich face-centered cubic Laves phase [13,15].

81 In this publication, a detailed characterization of the alloy Nb-Mo-Cr-Ti-Al is presented,
82 especially regarding microstructure, its evolution after heat treatment, and deformation at
83 ambient and elevated temperature. Furthermore, the deformation mechanism by dislocation
84 slip during compression loading at elevated temperatures is explicitly examined and identified
85 by EBSD analysis.

86 **2. Experimental**

87 Nb-Mo-Cr-Ti-Al was melted from elemental bulk materials, mixed in equiatomic
88 concentration, using an arc-melter AM/0.5, provided by Edmund Bühler GmbH. The purities
89 of the starting materials Nb, Mo, Al, Cr and Ti were 99.9 %, 99.96 %, 99.9 %, 99 %, and
90 99.8 %, respectively. The Ar base pressure for arc-melting was 0.6 bar following several
91 alternating iterations of pumping and Ar flooding. A Zr lump in the vacuum chamber was
92 used in order to reduce residual oxygen by liquefying prior to every melting step. The
93 prepared buttons were flipped and remelted for at least five times for homogenization. After
94 the final melting step, the alloy was cast into a rod-shaped Cu mold. The diameter and the
95 length of the cast rod were 12 mm and 60 mm, respectively. The chemical alloy composition
96 was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) for
97 the elements Nb, Mo, Cr, Ti and Al. O and N content were determined by means of carrier
98 gas hot extraction analysis, using a TC500 by Leco. Heat treatments were performed using a
99 Gero HTRH 70-600/18 resistance heating tube furnace under Ar flow at 1100, 1200, and

100 1300 °C for 20 h. The heating and cooling rate were 4.2 K/min. The platelet shaped samples
101 with 12 mm in diameter were extracted from one and the same cast sample.

102 The cast as well as the heat-treated alloy conditions were investigated by means of SEM
103 utilizing backscatter electron (BSE) imaging and energy dispersive X-ray spectroscopy
104 (EDX) as well as EBSD for analytical purposes. All samples were prepared by a standard
105 metallographic procedure finalized by a vibratory polishing step, using a non-crystallizing
106 oxide polishing suspension with pH = 9.8, provided by Struers. Thereby, a combination of
107 mechanical and chemical preparation was achieved. SEM investigations were performed on a
108 Zeiss Auriga dual beam scanning electron and focused ion beam microscope equipped with an
109 EDAX DigiView EBSD system and EDAX Octane silicon drift detector EDX system as well
110 as a Zeiss EVO50 system equipped with a Thermo Scientific EDX system. X-ray diffraction
111 analyses were carried out on a D2 Phaser system by Bruker equipped with a Lynxeye line
112 detector. The Cu tube was operated at 30 kV and 10 mA. Quasistatic compression tests were
113 performed utilizing a Zwick Z100 electro-mechanical universal testing machine equipped
114 with a vacuum furnace by Maytec. After heating at a rate of 20 K/min, the test temperature
115 was stabilized for 30 min before testing. The heat-treated samples (1300 °C / 20 h) of $(3 \times 3 \times$
116 $4.5) \text{ mm}^3$ were tested under vacuum with an initial engineering strain rate of 10^{-3} s^{-1} . Strain
117 was determined using strain gauges attached to the samples. The punches were made of SiC
118 and hexagonal BN was used for lubrication. The specimens for compression tests shown in
119 this article were extracted from the same cast sample as the specimens for heat-treatment
120 experiments. For the reproduction of the deformation experiments, a second batch of material
121 was produced and treated in the same way as described before.

122 **3. Results and discussion**

123 **3.1 Casting and homogenization**

124 Tab. 1 summarizes the chemical composition of the different materials conditions investigated
125 in this article. For the as-cast state, wet chemical analysis by ICP-OES and EDX are in good
126 agreement and the deviation from the equimolar composition does not exceed 0.75 at% for all
127 elements. Hence, there is little evaporation during arc melting operations despite large
128 differences in melting and boiling point of the alloying elements. The microstructure of the
129 as-cast state, as it is shown in Fig. 1a, consists of dendritic and interdendritic regions within a
130 polycrystalline matrix. Even at high resolution, no evidence for secondary phases was found.
131 Previous investigations revealed that elements with high melting points tend to crystallize in
132 the early stages of solidification [19,28]. In accordance to that, EDX of the dendrites reveals
133 enrichment in Mo and Nb during primary solidification (Tab. 1). In contrast, the interdendritic
134 regions are enriched in Cr, Ti and Al. By analyzing the compositions of the dendritic and
135 inter-dendritic regions in comparison to the total composition, fractions of 46 at% dendritic as
136 well as 54 at% inter-dendritic region can be calculated, respectively. The XRD analysis of the

137 as-cast state is shown in Fig. 2. The major Bragg positions can be assigned to a bcc crystal
138 structure of the W prototype with a broad variation of possible lattice constants ranging from
139 about 0.312 nm up to 0.318 nm. The variation is most probably attributed to the
140 inhomogeneous element distribution within the solid solution as it was assumed in previous
141 investigations [24], too. This can be well described by assuming several bcc phases with
142 different lattice parameters. The obtained values are slightly higher than those of the
143 comparable W-Mo-Al-Cr-Ti alloy, which are between about 0.309 nm and 0.312 nm (for the
144 as-cast as well as heat-treated condition) [24]. Considering the larger atomic radius of Nb
145 (145 pm) compared to W (135 pm), an increase of the lattice parameter in Nb-Mo-Cr-Ti-Al is
146 conceivable [30]. Local analysis of the crystal structure of dendritic and interdendritic regions
147 within a single grain of the as-cast state (patterns are included in the online supplementary,
148 similar pattern to that in Fig. 3d), respectively, support the global XRD analysis by patterns of
149 bcc crystals with minor changes of the lattice constant (the determined variation of 0.312–
150 0.318 nm is below the resolution of the EBSD camera system in use).

151 In order to homogenize the material as well as to establish a single phase solid solution, heat
152 treatments of 20 h under Ar atmosphere were performed. The microstructure following an
153 annealing at 1100 °C does not exhibit a significant homogenization effect which can be seen
154 from microstructural imaging in Fig. 1b as well as global XRD analysis in Fig. 2. In Fig. 1b, a
155 combination of composition and orientation contrast is visible. The local analysis of crystal
156 structure reveals at least three different phases that can be identified as bcc (W prototype,
157 Strukturbericht designation A2, pattern is included in the online supplementary, similar to the
158 pattern in Fig. 3d), the hexagonal modification of the Cr₂Nb Laves phase (MgZn₂ prototype,
159 Strukturbericht designation C14, Fig. 3a) and an unknown phase (Fig. 3b). Due to the small
160 length scale of the obtained microstructure, a detailed investigation of the local chemistry of
161 the phases by SEM-EDX is not suitable, here. This is done for higher annealing temperatures
162 in the following.

163 Subsequent to a heat treatment at 1200 °C, the volume fraction of dendritic microstructure
164 was significantly reduced as visualized in Fig. 1c. Also, the number and intensity of Bragg
165 positions, not correlating with those of the bcc crystal structure, are significantly reduced, as
166 seen in the XRD pattern in Fig. 2a. The secondary phases are mainly located at the grain
167 boundaries. The Laves phase, which was identified by electron diffraction (pattern is included
168 in the online supplementary, similar to the pattern in Fig. 3a), appears dark-gray and an
169 unknown phase (Fig. 3c) appears bright in the inset of Fig. 1c. The diffraction pattern of the
170 unknown phase in Fig. 3c exhibits remarkable similarities to the pattern for the unknown
171 phase (Fig. 3b, indicated by arrows connecting similar zone axis) obtained following the
172 1100 °C annealing step. Thus, the unknown phase obtained subsequent to annealing at
173 1100 °C and 1200 °C seem to be the same. The grain size of the solid solution (W prototype,
174 see pattern in Fig. 3d) has grown to 50-100 μm as it can be seen from the SEM image in
175 Fig. 1d. According to Tab. 1, the solid solution approximately exhibits the equimolar
176 composition with deviations less than 0.6 at%. By analyzing the compositions of the obtained
177 phases in comparison to the total composition, the fraction of the solid solution can be

178 calculated to about 87 at%, which is in good agreement with the SEM image in Fig. 1c. The
179 hexagonal Laves phase is enriched in Cr. The presence of a Cr-rich Laves phase was already
180 observed in the alloys Cr-Nb-Ta-Ti-Zr and Cr-Nb-Ti-V-Zr [13,19]. However, the reported
181 Laves phases were identified as the face-centered cubic modification of Cr₂Nb (MgCu₂
182 prototype, Strukturbericht designation C15). A possible substitution of lattice sites can be
183 described by means of (Cr,Al,Mo)₂(Nb,Ti) according to the overall composition of the phase:
184 (i) ideal stoichiometry Cr:Nb = 66.6:33.3 and (ii) present sample (Cr,Al,Mo):(Nb,Ti) =
185 65.3:34.7 (see Tab. 1). Since the composition as well as crystallographic data suggest a
186 derivation of the present Laves phase from the binary Cr₂Nb, the following discussion is
187 based on the relation of these two elements to the others present in the HEA. Cr-Nb as well as
188 Cr-Ti form Laves phases. Nb-Ti as well as Cr-Mo exhibit complete solubility (Cr-Mo with
189 miscibility gap at low temperature). Al-Cr forms a Cr₂Al compound but the prototype system
190 is not related to a Laves phase (MoSi₂ prototype). It has to be emphasized, that Mo-Nb exhibit
191 complete solubility in contrast to the proposed substitution. Thus, a certain amount of Mo on
192 the Nb lattice site is to be expected, too. The XRD pattern shows a Bragg position at 25.22°,
193 which can perhaps be assigned to the unknown phases (Fig. 3b and c). The EDX analysis does
194 not provide indications for a suitable stoichiometric prototype structure since it exhibits a
195 similar composition as the solid solution.

196 A further increase of homogenization temperature up to 1300 °C, as shown in Fig. 1d, results
197 in a further reduction of secondary phases within the grains of the solid solution. The contrast
198 of Fig. 1d is mainly attributed to different orientations of the chemically homogeneous grains.
199 The chemical composition of the bcc solid solution (diffraction pattern in Fig. 3d) is shown in
200 Tab. 1. The deviation from the equimolar composition is less than 0.5 at%. Residual
201 intermetallic phases are found in the vicinity of the grain boundaries similar to observations
202 on comparable Al-containing refractory high-entropy alloys in Ref. [21]. Hence, Bragg
203 positions, not assignable to the bcc crystal structure, are still present as they are visualized in
204 the logarithmic intensity plot in Fig. 2b. Evidence for the local appearance of any
205 modification of the Laves phases was not found. The grain boundaries seem to be decorated
206 by the unknown phase, exclusively. The pattern of the unknown phase in Fig. 3e differs from
207 those observed for annealing at 1100 and 1200 °C (Fig. 3b and c). Based on image analysis
208 the fraction of secondary phase at the grain boundary could be determined to be well below
209 0.5 vol% while the spread of the acicular morphology into the matrix grains is always below
210 10 μm (inset of Fig. 1d). The grain size of the bcc solid solution increased to about 250 μm.
211 Abnormal grain growth has already started. A further increase of homogenization temperature
212 to maximum 1400 °C does not lead to a full suppression of secondary phases but further rapid
213 grain growth is observed (not shown here). In order to provide a reasonable orientation
214 distribution during the following analysis of the microstructure subsequent to quasistatic
215 compression tests, the following results were obtained on samples, homogenized at 1300 °C
216 for 20 h.

217 **3.2 Deformation at ambient and elevated temperature**

218 In order to evaluate the potential of the present Nb-Mo-Cr-Ti-Al alloy regarding high
219 temperature application, compression tests were performed at room temperature, 400 °C,
220 600 °C, 800 °C, 1000 °C and 1200 °C with a strain rate of 10^{-3} s^{-1} . Fig. 4 shows the according
221 stress-strain dependence and Tab. 2 summarizes the mechanical properties determined by
222 these tests.

223 At room temperature, there was no indication of plastic deformation. At elevated
224 temperatures, plastic deformation was observed. A minimum fracture strain of 0.02 was
225 reached at 400 °C. While strength remains stable, plastic deformability before failure rises up
226 to 0.135 by increasing the temperature to 800 °C. Beside a significant drop of stress by 40 %
227 at 1000 °C, stress-strain dependence shows a characteristic curve shape with an inflection
228 point after reaching maximum stress. At 1200 °C, a plastic strain of over 0.24 without
229 indication of internal cracks was obtained.

230 Regarding room temperature compression test, onset of plasticity could not be determined
231 unlike to comparable Al-containing high-entropy alloys, such as Al-Nb_{1.5}-Ta_{0.5}-Ti_{1.5}-Zr_{0.5}
232 which revealed a plastic strain of at least 0.035 at room temperature [21]. The maximum
233 stresses during compression tests up to 800 °C are most probably determined by defects of the
234 cast material as it can be exemplarily seen in the SEM micrographs in Fig. 1d. Thus, a large
235 standard deviation of the characteristic stresses is observed at a test temperature of 800 °C
236 (Tab. 2). As regularly seen in literature [14,16,21], temperature increase leads to higher
237 plasticity. At 1000 °C, the investigated alloy shows a similar curve shape as high-entropy
238 alloys by Senkov et al. [21], tested in the same temperature range. Dynamic recrystallization
239 as a possible reason for the softening behavior [31] can be excluded since no evidence for
240 microstructure restoration by nucleation at the grain boundary forming typical necklace
241 structures or particle stimulated nucleation was found (Fig. 5d).

242 After performing the quasistatic compression tests, microstructure of the deformed samples
243 was analyzed by means of EBSD. Therefore, orientation maps are shown in Fig. 5 as color-
244 coded images according to the inverse pole figure (inset in Fig. 5b) of the compression
245 direction (CD). Abnormal grain growth induced during the homogenization process is clearly
246 indicated by grains with diameter of more than 500 μm in the as-homogenized state.
247 Subsequent to deformation at 400 °C, cracks are observed with an orientation of about 45°
248 with respect to the compression direction. Discontinuous stress-strain dependence during
249 loading at 400 °C as well as 600 °C is caused by crack initiation within the material, which is
250 exemplarily seen in Fig. 5b. In the vicinity of the crack, increased local misorientation is
251 observed, revealing localized plastic deformation. In contrast, short cracks are oriented
252 parallel to the compression direction and local misorientation is homogeneously distributed at
253 800 °C. In all cases, 400 °C, 600 °C and 800 °C, occurring cracks are transgranular, implying
254 stable grain boundaries within the material. At 1000 °C as well as 1200 °C, cracks are absent,
255 plastic deformation occurs uniformly, and grains become flattened as it is expected for ductile
256 behavior during compression tests. In this temperature range, significant changes of the

257 microstructure were observed during the solution annealing experiments. Thus, further
258 analysis of changing microstructure and phases were performed after thermomechanical
259 loading. In contrast to deformation tests at 800 °C and below, the phases at the grain
260 boundaries of the as-homogenized microstructure tend to coarsen as can be seen by a
261 comparison of Fig. 6a with Figs. 6b and 6c. Moreover, additional phase formation within the
262 grains is observed at 1200 °C (Fig. 6c) within the deformed matrix (indicated by changes of
263 orientation contrast by localized deformation). The hexagonal Laves phase (patterns are
264 similar to that in Fig. 3a and are included in the online supplementary) and an unknown phase
265 (electron patterns in Fig. 7) could be identified as the secondary phases developing and
266 coarsening during deformation at 1000 °C as well as 1200 °C. The patterns of the unknown
267 phase exhibit similar zone axes (indicated by arrows) to those of the unknown phase observed
268 in the same temperature range during the solution annealing experiments. Nevertheless, the
269 zone axis distances in the case of Fig. 7b are slightly higher indicating changing lattice
270 parameter ratios or lattice angles. This might be attributed to the different time scales for the
271 compression tests at high temperature and for the solution annealing experiments. In
272 accordance to the evaluation of the homogenized material, the Laves phase is enriched in Cr
273 while the unknown phase exhibits a solute content similar to the solid solution. The local
274 chemical analysis is included in Tab. 1.

275 Despite a comparatively low number of investigated grains, the orientation distribution
276 plotted as contours in the inverse pole figure in Fig. 8 reveals an increase of orientation
277 density between $\langle 001 \rangle$ and $\langle 111 \rangle$ crystallographic axes parallel to the compression direction as
278 deformation temperature and, thus, plastic strain is increased. This can be explained by pencil
279 glide being the predominant deformation mechanism. The $\langle 111 \rangle$ crystallographic axes seem to
280 be the common slip directions. For the commonly observed slip systems of bcc metals,
281 namely with a $\langle 1\bar{1}1 \rangle$ slip direction and slip planes of type $\{110\}$, $\{121\}$, or $\{132\}$, a rotation
282 of the compression direction under single slip from an arbitrary orientation within the
283 standard triangle towards the trace between $\langle 001 \rangle$ and $\langle 111 \rangle$ is expected. The corresponding
284 orientation changes are illustrated in Fig. 9.

285 4. Conclusions

286 This study provides the following main results regarding microstructure and deformation at
287 elevated temperature of an equiatomic Nb-Mo-Cr-Ti-Al high-entropy alloy:

- 288 • The analysis of the microstructure of arc-melted Nb-Mo-Cr-Ti-Al subsequent to
289 homogenization treatments reveals that the dendritic-like as-cast microstructure can be
290 transformed into an equiaxed microstructure with minor secondary phases by
291 annealing at 1300 °C under Ar atmosphere for 20 h. The formation of the hexagonal
292 modification of the Cr₂Nb Laves phase can be suppressed by a homogenization
293 temperature of 1300 °C and above.

- 294 • Compression tests reveal a maximum strength of ≈ 1 GPa and increasing ductility up
295 to a plastic strain of 24 % with increasing test temperature up to 1200 °C. During
296 compression testing at 1000 °C as well as 1200 °C, secondary phases are formed and
297 coarsen, respectively.
- 298 • The analysis of fiber texture components subsequent to uniaxial compression testing at
299 elevated temperatures suggests that Nb-Mo-Cr-Ti-Al deforms by dislocation slip,
300 forming the common combined $\langle 001 \rangle$ and $\langle 111 \rangle$ fiber texture components along the
301 compression direction. These can be explained in terms of the orientation change
302 during slip deformation on slip systems with common $\langle 111 \rangle$ slip direction.

303 **Acknowledgements**

304 The authors gratefully acknowledge the financial support by the
305 Deutsche Forschungsgemeinschaft (DFG), grant no. HE 1872/31-1. AK thanks the Carl Zeiss
306 Foundation for financial support by a postdoc grant. This work was partly carried out with the
307 support of the Karlsruhe Nano Micro Facility (KNMF, www.knmf.kit.edu), a Helmholtz
308 Research Infrastructure at Karlsruhe Institute of Technology (KIT, www.kit.edu). The authors
309 acknowledge the chemical analysis by ICP-OES at the Institute for Applied Materials (IAM-
310 AWP), Karlsruhe Institute of Technology (KIT). Furthermore, we would like to express our
311 gratitude to S. Seils for experimental support.

312 **References**

- 313 [1] Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H. &
314 Chang, S.-Y.: "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel
315 Alloy Design Concepts and Outcomes" in *Advanced Engineering Materials* 6 (2004) 299-303
- 316 [2] Yeh, J.-W.; Chen, Y.-L.; Lin, S.-J. & Chen, S.-K.: "High-Entropy Alloys - A New Era of
317 Exploitation" in *Materials Science Forum* 560 (2007) 1-9
- 318 [3] Tsai, M.-H.: "Physical Properties of High Entropy Alloys" in *Entropy* 15 (2013) 5338-
319 5345
- 320 [4] Tsai, M.-H. & Yeh, J.-W.: "High-Entropy Alloys: A Critical Review" in *Materials*
321 *Research Letters* 2 (2014) 107-123
- 322 [5] Zhang, Y.; Zuo, T. T.; Tang, Z.; Gao, M. C.; Dahmen, K. A.; Liaw, P. K. & Lu, Z. P.:
323 "Microstructures and properties of high-entropy alloys" in *Progress in Materials Science* 61
324 (2014) 1-93
- 325 [6] Northcott, L.: "Molybdenum" (1956), Butterworths Scientific Publications, London

- 326 [7] Yu, X. J. Yu & Kumar, K. S.: "The tensile response of Mo, Mo–Re and Mo–Si solid
327 solutions" in *Int. Journal of Refractory Metals and Hard Materials* 41 (2013) 329-338
- 328 [8] Sturm, D.; Heilmaier, M.; Schneibel, J. H.; Jéhanno, P.; Skrotzki, B. & Saage, H.: "The
329 influence of silicon on the strength and fracture toughness of molybdenum" in *Materials*
330 *Science and Engineering A* 463 (2007) 107-114
- 331 [9] Senkov, O. N. & Semiatin, S. L.: "Microstructure and properties of a refractory high-
332 entropy alloy after cold working" in *Journal of Alloys and Compounds* 649 (2015) 1110-1123
- 333 [10] Senkov, O.; Wilks, G.; Miracle, D.; Chuang, C. & Liaw, P.: "Refractory high-entropy
334 alloys" in *Intermetallics* 18 (2010) 1758-1765
- 335 [11] Senkov, O.; Wilks, G.; Scott, J. & Miracle, D.: "Mechanical properties of
336 Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys" in
337 *Intermetallics* 19 (2011) 698-706
- 338 [12] Zhang, B.; Gao, M. C.; Zhang, Y.; Yang, S.; Guo, S. M.: „Senary refractory high entropy
339 alloy MoNbTaTiVW“
- 340 [13] Senkov, O.; Senkova, S.; Woodward, C. & Miracle, D. B.: "Low-density, refractory
341 multi-principal element alloys of the Cr–Nb–Ti–V–Zr system: Microstructure and phase
342 analysis" in *Acta Materialia* 61 (2013) 1545-1557
- 343 [14] Senkov, O.; Senkova, S.; Miracle, D. & Woodward, C.: "Mechanical properties of low-
344 density, refractory multi-principal element alloys of the Cr-Nb-Ti-V-Zr system" in *Materials*
345 *Science and Engineering A* 565 (2013) 51-62
- 346 [15] Senkov, O.; Scott, J.; Senkova, S.; Miracle, D. & Woodward, C.: "Microstructure and
347 room temperature properties of a high-entropy TaNbHfZrTi alloy" in *Journal of Alloys and*
348 *Compounds* 509 (2011) 6043-6048
- 349 [16] Senkov, O.; Scott, J.; Senkova, S.; Meisenkothen, F.; Miracle, D. & Woodward, C.:
350 "Microstructure and elevated temperature properties of a refractory TaNbHfZrTi alloy" in
351 *Journal of Materials Science* 47 (2012) 4062-4074
- 352 [17] Senkov, O. & Woodward, C.: "Microstructure and properties of a refractory
353 NbCrMo_{0.5}Ta_{0.5}TiZr alloy" in *Materials Science and Engineering A* 529 (2011) 311-320
- 354 [18] Senkov, O. N.; Zhang, F. & Miller, J. D.: "Phase Composition of a
355 CrMo_{0.5}NbTa_{0.5}TiZr High Entropy Alloy: Comparison of Experimental and Simulated
356 Data" in *Entropy* 15 (2013) 3796-3809
- 357 [19] Poletti, M. G.; Fiore, G.; Szost, B. A. & Battezzati, L.: "Search for high entropy alloys in
358 the X-NbTaTiZr systems (X= Al, Cr, V, Sn)" in *Journal of Alloys and Compounds* 620
359 (2015) 283-288

- 360 [20] Couzinié, J.; Dirras, G.; Perrière, L.; Chauveau, T.; Leroy, E.; Champion, Y. & Guillot,
 361 I.: "Microstructure of a near-equimolar refractory high-entropy alloy" in *Materials Letters* 126
 362 (2014) 285-287
- 363 [21] Senkov, O.; Woodward, C. & Miracle, D.: "Microstructure and Properties of Aluminum-
 364 Containing Refractory High-Entropy Alloys" in *JOM* 66 (2014) 2030-2042
- 365 [22] Yang, X.; Zhang, Y.; Liaw, P. K.: „Microstructure and Compressive Properties of
 366 NbTiVTaAl_x High Entropy Alloys” in *Procedia Engineering* 36 (2012) 292-298
- 367 [23] Lin, C. M.; Juan, C. C.; Chang, C. H.; Tsai, C. W.; Yeh, J. W.: “Effect of Al addition on
 368 mechanical properties and microstructure of refractory Al_xHfNbTaTiZr alloys” in *Journal of*
 369 *Alloys and Compounds* (2015) 100-107
- 370 [24] Gorr, B.; Azim, M.; Christ, H.-J.; Mueller, T.; Schliephake, D. & Heilmaier, M.: "Phase
 371 equilibria, microstructure, and high temperature oxidation resistance of novel refractory high-
 372 entropy alloys" in *Journal of Alloys and Compounds* 624 (2014) 270-278
- 373 [25] Zhang, Y.; Zhou, Y. J.; Lin, J. P.; Chen, G. L.; Liaw, P. K.: „Solid-Solution Phase
 374 Transformation Rules for Multi-component Alloys” in *Advanced Engineering Materials* 10
 375 (2008) 534-538
- 376 [26] Zhang, Y.; Yang, X.; Liaw, P. K.: „Alloy Design and Properties Optimization of High-
 377 Entropy Alloys“ in *JOM* 64 (2012) 830-838
- 378 [27] Guo, S.; Ng, C.; Lu, J.; Liu, C. T.: „Effect of valence electron concentration on stability
 379 of fcc or bcc phase in high entropy alloys” in *Journal of Applied Physics* 109 (2011) 103505
- 380 [28] Gorr, B.; Azim, M.; Christ, H.-J.; Chen, H.; Szabo, D. V. & Heilmaier, M.:
 381 "Microstructure evolution in a new refractory high-entropy alloy Mo-W-Al-Cr-Ti" in
 382 *Metallurgical and Materials Transactions A* (2015) submitted
- 383 [29] Laurent-Brocq, M.; Akhatova, A.; Perrière, L.; Chebini, S.; Sauvage, X.; Leroy, E. &
 384 Champion, Y.: "Insights into the phase diagram of the CrMnFeCoNi high entropy alloy" in
 385 *Acta Materialia* 88 (2015) 355-365
- 386 [30] Slater, J. C.: “Atomic radii in crystals” in *The Journal of Chemical Physics* 41 (1964)
 387 3199-3204
- 388 [31] Humphreys, F. J. & Hatherly, M.: "Recrystallization and Related Annealing
 389 Phenomena", Elsevier, Oxford (2004)

390 **Captions**

391 Tab. 1: Composition of the investigated alloy in different conditions determined by EDX.
 392 † Composition determined by ICP-OES (unbalanced) for comparison. Dendritic and

393 interdendritic regions are shown in the inset of Fig. 2a in detail. O content was determined to
394 be 92 ppm in the as-cast state. N content was below the detection limit. * Phase located at the
395 grain boundaries (see insets in Fig. 2c and d) and ** located within the grains (see Fig. 2c).

396 Fig. 1: SEM micrographs (BSE, orientation and composition contrast) of the microstructure of
397 Nb-Mo-Cr-Ti-Al in the: a) as-cast and annealed conditions after heat treatment at b) 1100 °C,
398 c) 1200 °C and d) 1300 °C for 20 h, respectively. All major micrographs are taken at the same
399 magnification. Inset magnification is specified, respectively. The inset in (b) highlights the
400 morphology of the at least three different phases at higher magnification. The insets in (c) and
401 (d) show secondary phases with continuous as well as acicular morphology at the grain
402 boundaries. The dark grain boundary phase in (c) is assigned to the EBSD pattern in Fig. 5g.

403 Fig. 2: Background subtracted XRD patterns of cross sections of Nb-Mo-Cr-Ti-Al in different
404 conditions: a) full pattern and b) section of the pattern with logarithmic intensity scale. Bragg
405 positions of bcc structures with varying lattice parameters (provided in nm) are indicated by
406 dashed lines in (a). Bragg positions of the hexagonal Laves phase are highlighted according to
407 the labels in (b) – positions with little intensity were excluded. Intensities may be influenced
408 by limited number of grain orientations within the samples. The lines, indicating the lattice
409 constant variation, are extended to the diffraction patterns of the annealed state in order to
410 ease comparison.

411 Fig. 3: EBSD patterns with corresponding zone axes of Nb-Mo-Cr-Ti-Al taken at 20 kV on
412 samples in different conditions (a complete set of patterns for all phases is included in the
413 online supplementary). The Laves phase is the hexagonal modification of Cr₂Nb (MgZn₂
414 prototype, Strukturbericht designation C14).

415 Fig. 4: Stress-strain dependence of quasistatic compression tests at: a) room temperature,
416 400 °C and 600 °C as well as b) 800 °C, 1000 °C and 1200 °C. Fracture is highlighted by X.
417 Arrows indicate tests deliberately stopped.

418 Fig. 5: Orientation imaging microscopy on longitudinal sections of Nb-Mo-Cr-Ti-Al
419 quasistatically deformed in compression: a) initial condition and deformed at b) 400 °C, c)
420 800 °C, d) 1000 °C and e) 1200 °C. Compression direction is vertical and the color code
421 corresponds to the inverse pole figure of the compression direction (inset in (b)). The maps
422 are of the same size and observed using a step size of 5 μm.

423 Fig. 6: Detailed SEM micrographs (BSE, orientation and composition contrast) of Nb-Mo-Cr-
424 Ti-Al subsequent to deformation at: a) 800 °C, b) 1000 °C, and 1200 °C. All SEM
425 micrographs are taken at the same magnification.

426 Fig. 7: EBSD patterns with corresponding zone axes of Nb-Mo-Cr-Ti-Al taken at 20 kV. A
427 complete set of patterns for all phases is included in the online supplementary.

428 Fig. 8: Orientation distribution as contours in the inverse pole figures of the compression
429 direction of Nb-Mo-Cr-Ti-Al quasistatically deformed in compression: a) initial condition,

430 deformed at b) 400 °C, c) 800 °C, d) 1000 °C, and e) 1200 °C. Scale in multiples of the
431 random distribution (inset in (a)) is kept constant.

432 Fig. 9: a) Maximum Schmid factors (active slip system under single slip) of the pencil slip
433 systems with common $\langle 1\bar{1}1 \rangle$ slip direction and $\{110\}$, $\{121\}$, and $\{132\}$ slip planes presented
434 in the inverse pole figure of the compression direction. b) Rotation of the compression
435 direction, indicated by arrows, in dependence of the initial orientation of a single crystal.
436 Under compression load, the compression direction tends to rotate towards to slip plane
437 normal. Dashed lines indicate the connection of slip plane normals when multiple slip is
438 preferred.

439 Tab. 2: Yield stress $\sigma_{0.2}$, maximum strength σ_{\max} and obtained plastic strain before fracture ε_p
440 as a function of temperature during compression tests; (X) marks those compression tests
441 which ended due to fracture of the respective sample