

PHASE EVOLUTION IN AND CREEP PROPERTIES OF NB-RICH NB-SI-CR EUTECTICS

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Abstract

In this work, the Nb-rich ternary eutectic in the Nb-Si-Cr system has been experimentally determined to be Nb-10.9Si-28.4Cr (in at.%). The eutectic is composed of three main phases, Nb solid solution (Nb_{ss}), β -Cr₂Nb and Nb₉(Si,Cr)₅. The ternary eutectic microstructure remains stable for several hundred hours at a temperature up to 1200 °C. At 1300 °C and above, the silicide phase Nb₉(Si,Cr)₅ decomposes into α -Nb₅Si₃, Nb_{ss} and β -Cr₂Nb. Under creep conditions at 1200 °C, the alloy deforms by dislocation creep while the major creep resistance is provided by the silicide matrix. If the silicide phase is fragmented and, thus, its matrix character is destroyed by prior heat treatment (e.g. at 1500 °C for 100 h), creep is mainly controlled by the Laves phase β -Cr₂Nb, resulting in increased minimum strain rates. Compared to state of the art Ni-based superalloys, the creep resistance of this three phase eutectic alloy is significantly higher.

Keywords: eutectic alloys, niobium silicides, intermetallics, refractory based alloys, creep

I. Introduction

Due to their high melting point and relatively low density, Nb-Si based alloys are promising novel materials for high temperature structural applications [1, 2]. Unfortunately, good mechanical strength and oxidation resistance at elevated temperatures, as well as sufficient fracture toughness at ambient temperature, are difficult to achieve simultaneously in a satisfactory manner, as the improvement of one property usually comes along at the expense of the other. This challenge may be met by e.g. combining different phases with complementary properties in a fine eutectic microstructure. For example, in the Nb-Si binary system, the binary eutectic Nb-18Si (in at.%) showed a combination of high creep strength subsequent to directional solidification [3] with reasonable fracture toughness [4] due to the presence of the silicide and Nb solid solution (Nb_{ss}), respectively. However, this alloying system did not provide acceptable oxidation resistance, as the bulky, porous and non-adherent oxide Nb_2O_5 is formed. Hence, further alloying additions are necessary to suppress the formation of Nb_2O_5 . For example, Ti, Al, Sn and Cr are known to increase the oxidation resistance [5–8]. However, only the system Nb-Si-Cr features a Nb-rich ternary eutectic as a prerequisite for later directional solidification.

For this reason, the model system Nb-Si-Cr was selected, where Cr is added to mainly improve the oxidation resistance, by replacing the fast forming, bulky, non-adherent oxide Nb_2O_5 by dense, adherent $CrNbO_4$ scales [9]. Si is known to improve the creep properties by formation of silicide phases while Nb solid solution (Nb_{ss}) provides suitable fracture toughness. However, a literature survey reveals contradictory information on the exact composition of the ternary eutectic in this system. In 2005, Shao calculated the ternary eutectic composition to be Nb-12Si-25Cr [10] (in at.%) using CALPHAD. In contrast, Bewlay et al. experimentally assessed the Nb-Si-Cr system in 2009 to determine the ternary eutectic composition to be close to Nb-8.7Si-33.1Cr [11]. Therefore, the exact location of the ternary eutectic is critically reviewed in this study with samples of different appropriate alloy compositions produced by arc melting. The identified composition of the ternary eutectic is thoroughly assessed in terms of phase evolution, as well as microstructure and phase stability. Moreover, the creep behavior at the potential operating temperature of 1200 °C is assessed.

II. Experimental

To determine the ternary eutectic composition, different alloys were synthesized from elemental granules (Cr, purity 99,0 wt.%; Si purity 99,9999 wt.%) and slug (Nb, purity 99,8 wt.%) using an arc melter AM/0.5 (Edmund Buehler GmbH, Hechingen, Germany) with tungsten electrode. Chemical analysis of cast ingots (mass 30 g) was carried out by means of inductively coupled plasma optical emission spectrometry (ICP-OES). For heat treatments and microstructure examinations, the ingots were cut into smaller pieces using electro discharge machining. Heat treatments were performed in a high temperature furnace Gero HTRH 70-600/18 (Carbolite Gero GmbH, Neuhausen, Germany) under Ar atmosphere. Metallographic samples were hot-mounted in “Duroplast” resin (ATM GmbH, Mammelzen, Germany) using a Simplimet 1000 (Buehler, Lake Bluff, IL, USA), prior to grinding using SiC paper with successively decreasing particle size and finally polished with a diamond suspension. To prepare samples for electron backscatter diffraction (EBSD), two additional semiautomatic polishing steps with both non-crystallizing, pH-neutral OPS (10 minutes) and alkaline stabilized OPS (1 minute) were performed to remove remaining surface-near plastic deformation by the prior polishing steps.

The microstructure was examined using an SEM EVO 50 (Carl Zeiss AG, Oberkochen, Germany) in backscattered-electron mode (BSE) to reveal the different phases. Phase fractions (vol.%, as material is expected to be isotropic) were determined on at least five SEM-BSE images each using the software ImageJ for quantitative image analysis by threshold segmentation. Local phase compositions were determined applying electron probe micro analysis (EPMA). Either the aforementioned SEM was used for standardless energy-dispersive spectroscopy (EDS) measurements or a SEM JEOL JXA-8100 (JEOL GmbH, Freising, Germany) was employed for wavelength-dispersive spectroscopy (WDS) measurements using the standards J13_Cr, J13_Si, J13_ZrO₂ and 9033Nb. EBSD was performed using an EDAX DigiView camera on a Zeiss Auriga 60 SEM (Carl Zeiss AG, Oberkochen, Germany). For analysis of the determined EBSD patterns, a commercial software provided by EDAX was used. Creep tests on cuboidal samples (size 3 mm x 3 mm x 5 mm) were performed in compression in an electro-mechanical universal testing machine Zwick Z100 (Zwick GmbH, Ulm, Germany) with attached vacuum furnace (Maytec GmbH, Singen, Germany) at constant true stress at 1200 °C in vacuum. All creep experiments were terminated before failure of the samples.

III. Results and Discussion

Determination of the ternary eutectic

Figure 1 compares the microstructures of the two different ternary eutectic compositions suggested in the literature [10,11]. It becomes obvious that Nb-12Si-25Cr (Figure 1a) is not a ternary eutectic, as a significant amount of primary solidifying Nb_{ss} (light-grey phase, phase fraction (25.1 ± 3.2) vol.%) is located between a subsequently solidified two-phase eutectic microstructure. According to EDS measurements, this eutectic consists of Nb_{ss} and a ternary silicide phase in the compositional range of Nb₉(Si,Cr)₅ (grey phase). However, at equilibrium, α-Nb₅Si₃ silicide is expected according to calculations by Shao [10]. The determined Nb₉(Si,Cr)₅ silicide composition matches quite well with the one reported by Bewlay et al. for the phase present in the vicinity of the ternary eutectic [11]. This mismatch between calculation and experiment might be due to an incomplete Calphad database, in which the ternary silicide has not been implemented. Despite of some Cr-rich segregations (dark grey phase), no other phases are detectable in Figure 1a.

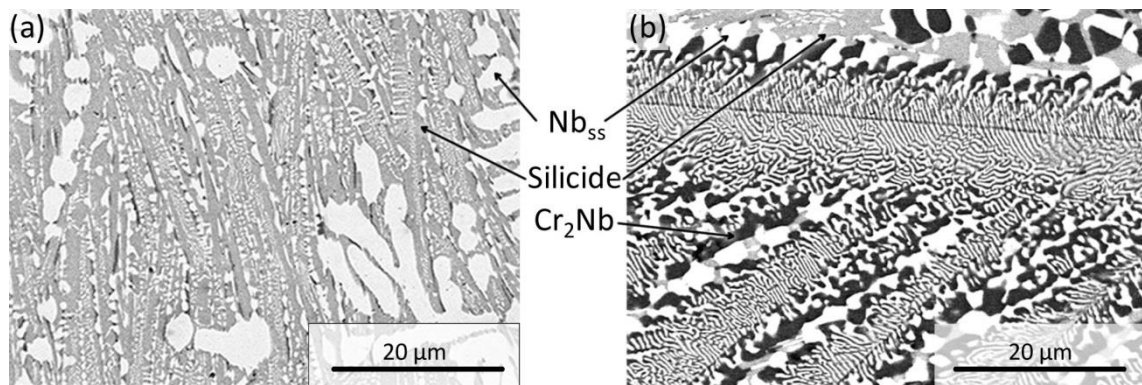


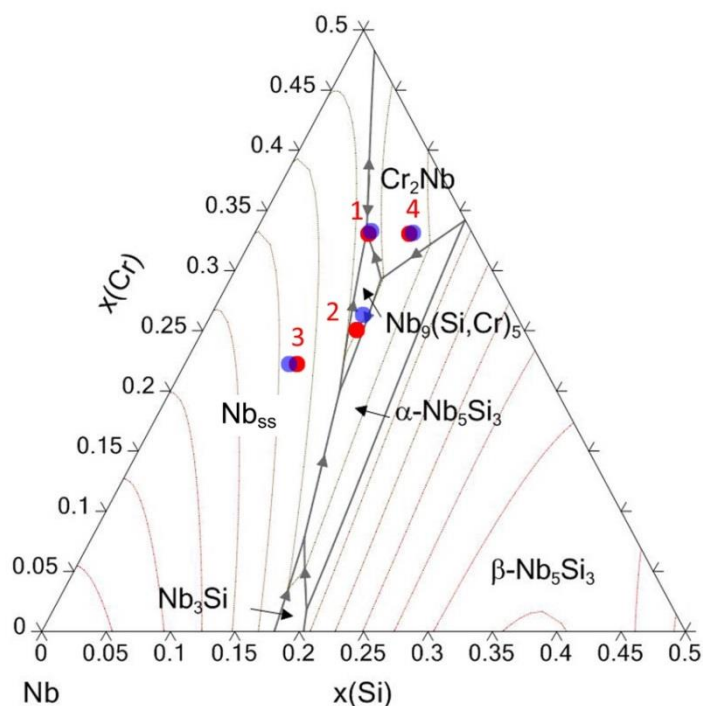
Figure 1: SEM-BSE micrographs of the alloys (a) Nb-12Si-25Cr and (b) Nb-8.7Si-33.1Cr, both in as cast condition

In contrast, the second proposed composition Nb-8.7Si-33.1Cr, shown in Figure 1b, does not exhibit primary solidification of a single phase, indicating close proximity to the ternary eutectic composition. The microstructure is characterized by two distinct features:

- (i) very fine two-phase lamellar eutectic cells, in which a coupled growth of Nb_{ss} (white phase) and Cr₂Nb (dark-grey phase) occurs;
- (ii) in between, coarse regions consisting of three different phases, i.e. Nb_{ss} (white phase), Cr₂Nb (black phase) and a third undetermined silicide phase (light-grey).

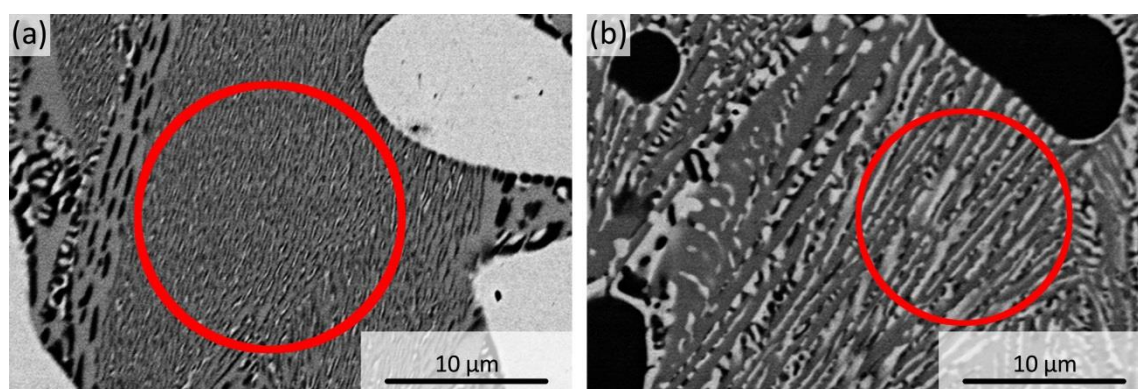
This ternary phase does not correlate with the compositional range of Nb₉(Si,Cr)₅, as its chemical composition was determined to be (50.2 ± 0.5) at.% Nb, (15.2 ± 0.2) at.% Si and (34.6 ± 0.3) at.% Cr, which does not match with any known phase in the Nb-Si-Cr system. However, the identification and the study of this unknown phase are beyond the scope of the present study and will not be addressed hereafter. Therefore, Nb-8.7Si-33.1Cr is also not the exact ternary eutectic composition.

To reduce the gap between literature results and experiments regarding the ternary eutectic composition, a triangulation scheme was carried out by examining compositions in the vicinity of Nb-8.7Si-33.1Cr. Starting from this composition, either the Si or Cr content was varied to achieve primary solidification of either Nb_{ss} or Cr₂Nb. The examined compositions are given in Table 1 and are additionally plotted in the partial liquidus projection in Figure 2. Comparison between nominal composition and actual composition reveals no deviation within the range of the measurement uncertainty (standard deviation SD ≤ 0.4 at.% for Si, and SD ≤ 0.45 at.% for Cr). For this reason, only nominal compositions will be used in the following.



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Figure 2: Partial liquidus projection of the Nb-Si-Cr system, including isothermal lines (calculated with PANDAT employing the PanNb database). Compositions according to the numbers are listed in Table 1. The red dots symbolize the nominal composition; blue ones represent the actual composition.

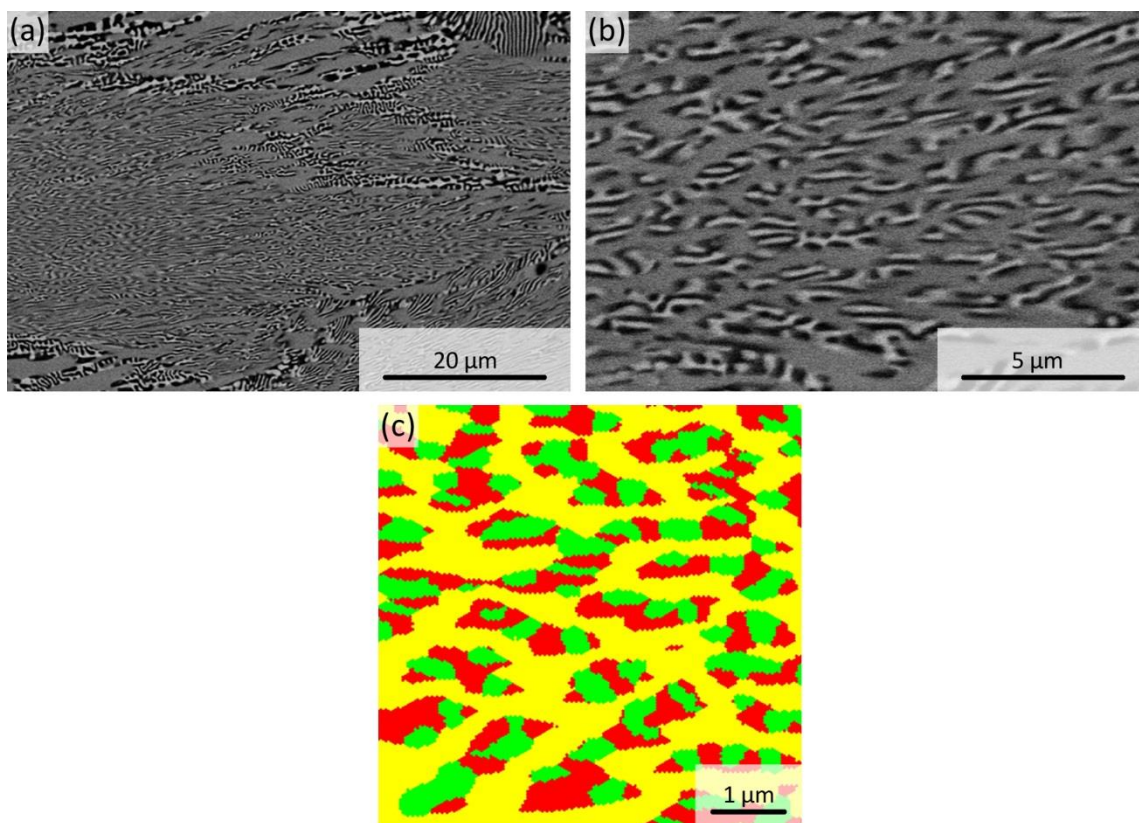
140 The microstructures of Alloys 1 (Nb-8.7Si-33.1Cr) and 2 (Nb-12Si-25Cr) have already been discussed.
141 For Alloy 3 (Nb-8.7-22Cr), Nb_{SS} primary solidification is expected. Indeed, growth of Nb_{SS} primary
142 dendrites (white phase) is visible in Figure 3a with a phase fraction of (36.6 ± 2.2) vol.%. Moreover,
143 ternary eutectic is present, comprising Nb_{SS}, Cr₂Nb and Nb₉(Si,Cr)₅. The expected binary eutectic,
144 which according to Figure 2 should consist of Nb_{SS} and Nb₉(Si,Cr)₅, cannot clearly be separated from
145 the ternary eutectic. Occasionally, binary eutectic structures of Nb_{SS} + Cr₂Nb and Cr₂Nb + Nb₉(Si,Cr)₅
146 can be observed, which are not likely to form along the expected solidification path in equilibrium and
147 may be attributed to segregation effects during solidification.
148 Conversely, Alloy 4 (Nb-12Si-33.1Cr), is expected to solidify from the Cr₂Nb phase region. This
149 feature is confirmed in Figure 3b, where Cr₂Nb dendrites (black phase) are identified, having a phase
150 fraction of (23.6 ± 0.6) vol.%. Adjacent to primary dendrites, the binary eutectic Nb_{SS} + Cr₂Nb is
151 formed. Subsequently, the remaining melt solidifies by formation of ternary eutectic cells.
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Figure 3: SEM-BSE micrographs of the alloys (a) Nb-8.7Si-22Cr and (b) Nb-12Si-33.1Cr. In both alloys ternary eutectic structures can be observed (marked with a red circle).

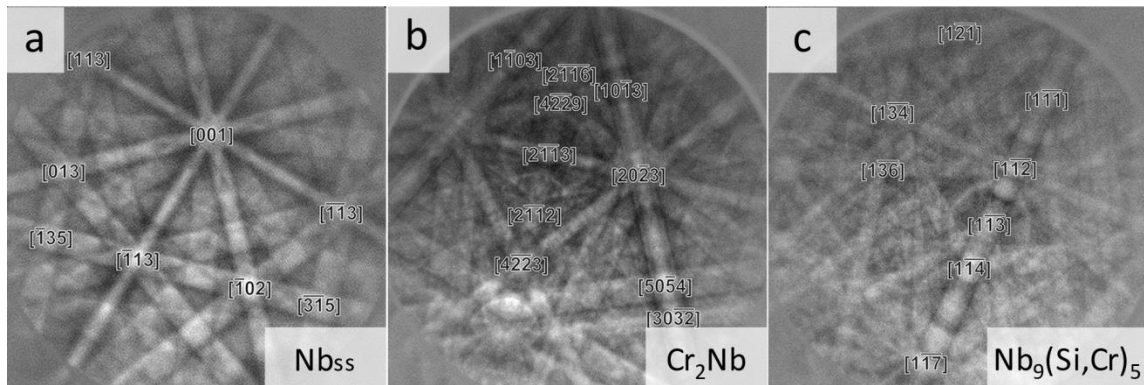
156 To determine the chemical composition of the ternary eutectic, EDS area scans of eutectic cells have
157 been performed on Alloys 3 and 4. Exemplarily analyzed regions are marked by red circles in Figure 3.
158 Quantitative results for these scans are given in Table 2. The compositions for eutectic cells in both
159 alloys are very similar. Accordingly, the “true” ternary eutectic composition has been approximated as
160 Nb-10.9Si-28.4Cr. This seems to be confirmed by the micrographs in Figure 4, where the
161 microstructure of an alloy with actual composition of Nb-10.8Si-28.8Cr consists almost entirely of

162 ternary eutectic cells. Within these cells, the silicide phase $\text{Nb}_9(\text{Si,Cr})_5$ forms a discontinuous matrix
163 (phase fraction (67.7 ± 4.2) vol.%), which is clearly underlined by Figure 4c and orientation analysis
164 that reveal uniform orientation of $\text{Nb}_9(\text{Si,Cr})_5$ within the colonies. Between this silicide matrix, Nb_{ss} and
165 Cr_2Nb grow in a coupled manner with phase fractions of (14.6 ± 4.7) vol.% and (17.7 ± 4.9) vol.%,
166 respectively. Distributed along the cell boundaries, coarse regions of $\text{Nb}_9(\text{Si,Cr})_5$ and the binary
167 eutectic $\text{Nb}_{\text{ss}} + \text{Cr}_2\text{Nb}$ are present, which must have solidified before the ternary eutectic. As this
168 slightly off-eutectic solidification occurs along the cell boundaries, the ternary eutectic composition was
169 double-checked within the cells and the composition Nb-10.9Si-28.4Cr was confirmed. Chemical
170 compositions of each individual phase were measured using WDS on the coarse regions. The results
171 are given in Table 3. The actual chemical composition of Nb_{ss} is in good agreement with previously
172 published solubility limits of Si (2.4 at.%) and Cr (16.0 at.%) in an isothermal section at 1500 °C of the
173 Nb-Si-Cr system [12]. For $\text{Nb}_9(\text{Si,Cr})_5$, the measured composition is close to the stoichiometry of the
174 phase.
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177 **Figure 4: Micrographs of the ternary eutectic alloy Nb-10.9Si-28.4Cr: (a-b) SEM-BSE mode and (c) EBSD, false-color image**
178 **of the phases $\text{Nb}_9(\text{Si,Cr})_5$ (yellow), Nb_{ss} (green) and Cr_2Nb (red).**

179 In Cr_2Nb , Si is significantly substituting for Cr. According to Ref. [13], up to 26 at.% of Si can substitute
180 Cr, stabilizing the hexagonal high temperature modification $\beta\text{-Cr}_2\text{Nb}$ (C14, hP12, $P6_3/mmc$) down to
181 ambient temperature. In contrast, the hexagonal, binary $\beta\text{-Cr}_2\text{Nb}$ phase would transform into its cubic
182 low temperature modification $\alpha\text{-Cr}_2\text{Nb}$ (C15, cF24, $Fd3m$) below 1600 °C for the binary Nb-Cr system
183 [14]. The presence of $\beta\text{-Cr}_2\text{Nb}$ in Nb-10.9Si-28.4Cr was additionally confirmed using EBSD; indexed
184 diffraction patterns for all phases present in Nb-10.9Si-28.4Cr are shown in Figure 5. For the sake of
185 simplicity, Cr_2Nb will refer to the $\beta\text{-Cr}_2\text{Nb}$ phase in the following.

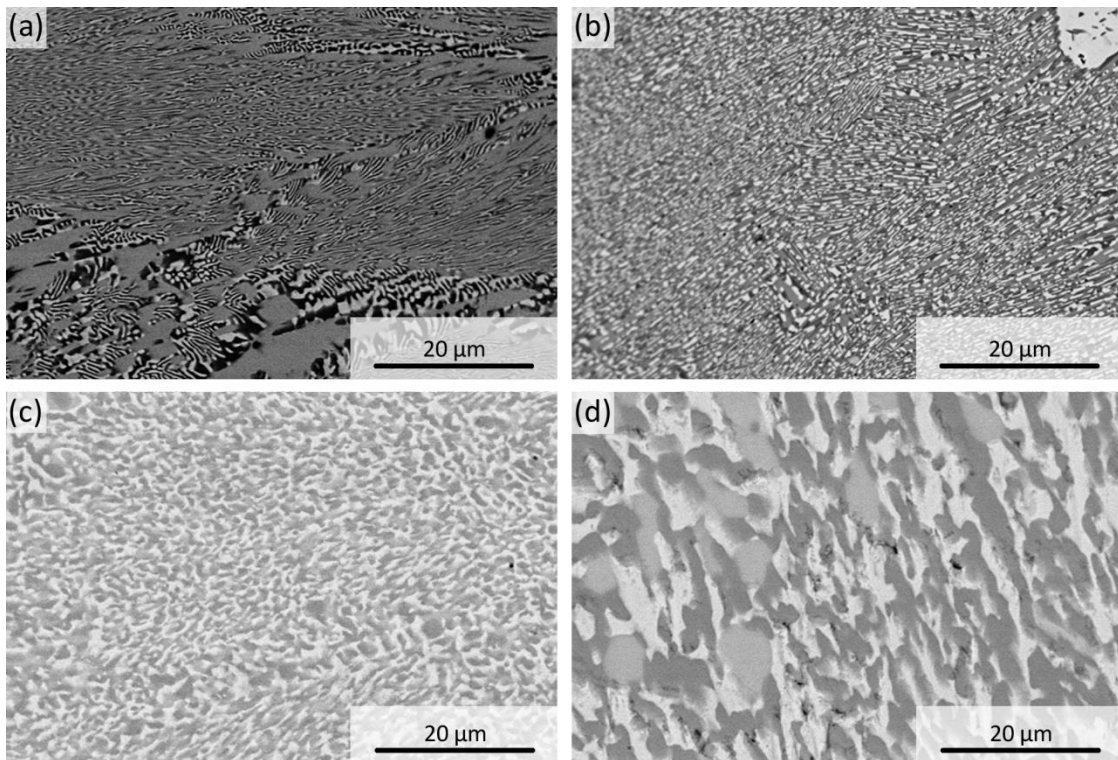


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Figure 5: Indexed EBSD patterns of the phases present in Nb-10.9Si-28.4Cr: (a) Nb_{ss}, (b) Cr₂Nb and (c) Nb₉(Si,Cr)₅.

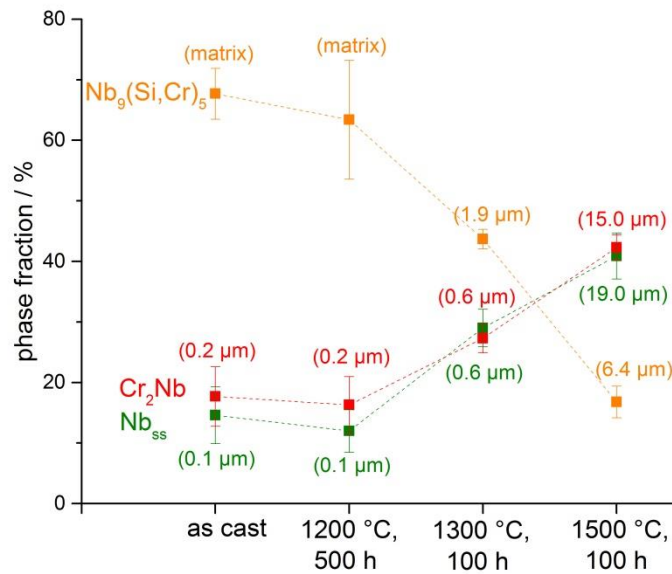
188 Phase stability

189 For high temperature applications, microstructural as well as phase stability at and above service
 190 temperature is a crucial requirement. Therefore, the evolution of microstructural parameters such as
 191 phase fraction and size was examined after exposure to high temperatures. Besides long term stability
 192 (500 h) at 1200 °C which may be a potential operation temperature for turbine applications higher
 193 temperatures (1300 °C and 1500 °C) were also considered for shorter periods of time (100 h). Figure
 194 6 shows the microstructure of Nb-10.9Si-28.4Cr in the as cast state as well as after such heat
 195 treatments. It is complemented by Figure 7 which illustrates the corresponding phase fractions and
 196 sizes.
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Figure 6: Phase evolution and stability in the alloy Nb-10.9Si-28.4Cr, starting from as cast state in (a) for different heat treatment conditions: (b) 1200 °C, 500 h; (c) 1300 °C, 100 h and (d) 1500 °C, 100 h.



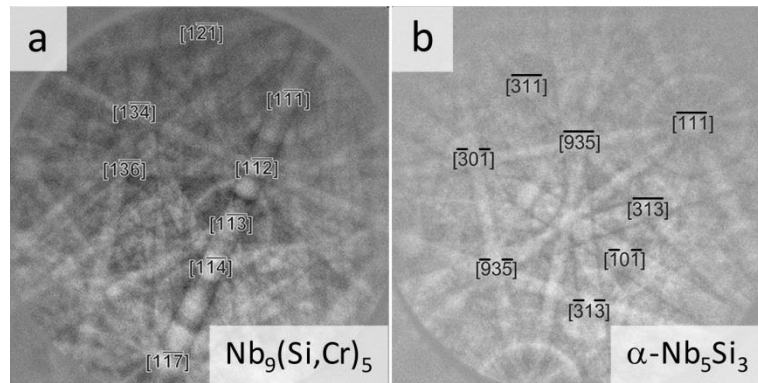
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202 **Figure 7: Evolution of phase fraction and -size in Nb-10.9Si-28.4Cr for different heat treatment conditions. Average phase**
 203 **size determined by segmentation of BSE images is provided in brackets. Connecting lines are to guide the eyes.**

204 Compared to the as cast state, homogenization of the microstructure occurs for all heat treatment
 205 conditions. The inhomogeneous boundaries of the eutectic cells disappear. Apart from
 206 homogenization, the microstructure remains stable for up to 500 h at 1200 °C. At 1300 °C, slight
 207 coarsening of the phases is observed. The phase fraction of $Nb_9(Si,Cr)_5$ decreases significantly, while
 208 the amounts of Nb_{ss} and Cr_2Nb increase simultaneously and uniformly. Moreover, the silicide phase
 209 loses its matrix character. These effects are even more pronounced at 1500 °C. Hence, the examined
 210 alloy undergoes profound morphological changes during heat treatments. Especially the pronounced
 211 decrease of the silicide phase fraction and the simultaneous increase of Nb_{ss} and Cr_2Nb fractions are
 212 worth mentioning. As this effect might result from possible phase transformations, the local chemical
 213 composition was checked again after heat treatments. Results subsequent to annealing at 1500 °C for
 214 100 h are shown exemplarily in Table 4. Even though slight compositional variations have occurred in
 215 Nb_{ss} and Cr_2Nb , these two phases are still present after heat treatment. In contrast, the silicide phase
 216 shows a significant change in terms of chemical composition. The Si content is increased to about
 217 38 at.% (as compared to roughly 16 at.% in the as cast state). However, the Cr content has been
 218 reduced dramatically (1.5 at.% as compared to 21 at.%). Thus, the stoichiometry of the silicide phase
 219 hints for the presence of Nb_5Si_3 instead of $Nb_9(Si,Cr)_5$ after heat treatment. EBSD diffraction patterns
 220 presented in Figure 8 reveal that the silicide phase identified is the tetragonal $\alpha-Nb_5Si_3$ (tI32, I4/mcm
 221 [15]). Figure 8b demonstrates that this evolution into $\alpha-Nb_5Si_3$ is already active at temperatures as low
 222 as 1300 °C.

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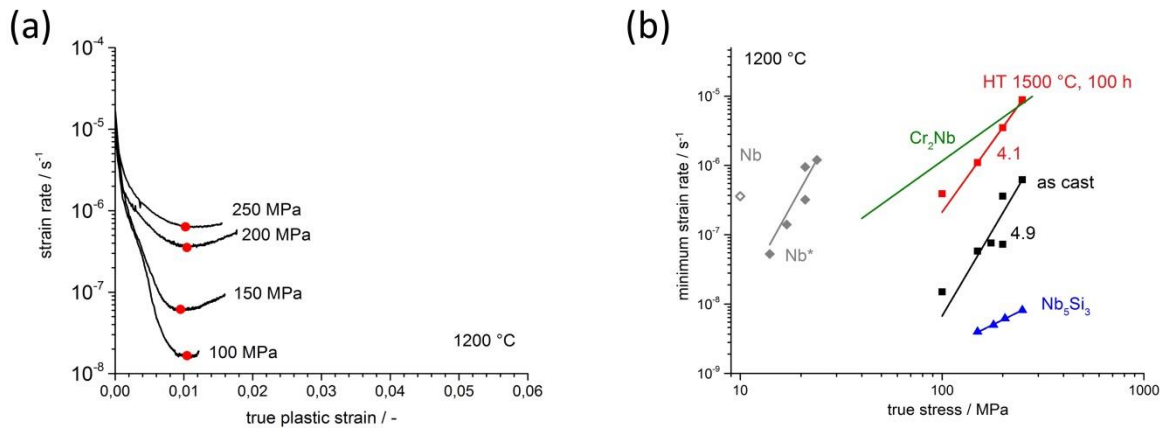
226 **Figure 8: indexed EBSD diffraction patterns showing the silicide phase evolution in Nb-10.9Si-28.4Cr for different heat**
 227 **treatment conditions: (a) $Nb_9(Si,Cr)_5$ in as cast state and (b) $\alpha-Nb_5Si_3$ after 1300 °C, 100 h**

228 Attempts to address this solid-state reaction, e.g. by DSC measurements, were not successful so far.
 229 Nevertheless, as the transformation from $Nb_9(Si,Cr)_5$ to $\alpha-Nb_5Si_3$ coincides with increasing phase
 230 fractions of Nb_{ss} and Cr_2Nb , a eutectoid-like decomposition is conceivable. A eutectoid decomposition
 231 is already known from the Nb-Si binary system, where Nb_3Si decomposes into Nb_{ss} and $\alpha-Nb_5Si_3$ at
 232 1763 °C [16]. However, this solid-state reaction follows very slow kinetics [17], where a full eutectoid
 233 decomposition of Nb_3Si cannot be achieved even after 1500 °C for 500 h [18]. Hence, the absence of
 234 distinct reaction peaks during DSC measurements (not shown here) is not uncommon.

235 Creep properties

236 For high temperature applications, considerable slow creep deformation under constant load at
 237 homologous temperature $T/T_m > 0.4$, where T_m is the melting temperature, is one of the major design
 238 criteria for structural applications.

239 From previous results, the microstructure of the ternary eutectic appears to be stable in terms of phase
 240 fraction and size for temperatures up to 1200 °C, which might be a potential service temperature.
 241 Therefore, compressive creep tests were performed at this temperature on as cast material. The
 242 evolution of strain rate in dependence of true plastic strain is shown in Figure 9a. As soon as constant
 243 true stress was applied, a decrease in strain rate indicates initial strain hardening. This effect is more
 244 pronounced with decreasing true stress. The strain rates decrease until a minimum strain rate is
 245 reached at about 1 % true plastic strain, which is similar for all true stresses tested. Immediately
 246 following the minimum, the strain rate slowly but continuously increases. Therefore, a stationary or so
 247 called “steady state” creep region where a dynamic equilibrium between strain hardening and recovery
 248 is established cannot be determined. Instead, a minimum creep rate has been defined at 1% plastic
 249 strain and is marked with red dots in Figure 9a. As true stress is applied in compression throughout
 250 the experiments and no significant microstructural changes were observed during creep (not shown
 251 here since similar to load-free heat treatment), only internal damage, e.g. cracking within the silicide or
 252 along the phase boundaries can cause the observed absence of stationary creep. This has already
 253 been reported by Bewlay et al. [19] and Seemueller et al. [20]. Even though cracking of the silicide,
 254 being still brittle at the temperature tested, is the most likely explanation for the observed effect, no
 255 significant damage could be observed, as the total strain achieved was < 2 % and therefore very
 256 small.



257

258 **Figure 9: Stress dependence of the strain response for Nb-10.9Si-28.4Cr, shown as (a) strain rate vs. true plastic strain**
 259 **(deliberately stopped subsequent to minimum) and (b) minimum strain rate vs. true stress (Norton plot). Data marked**
 260 **with "*" were determined at 1000 °C.**

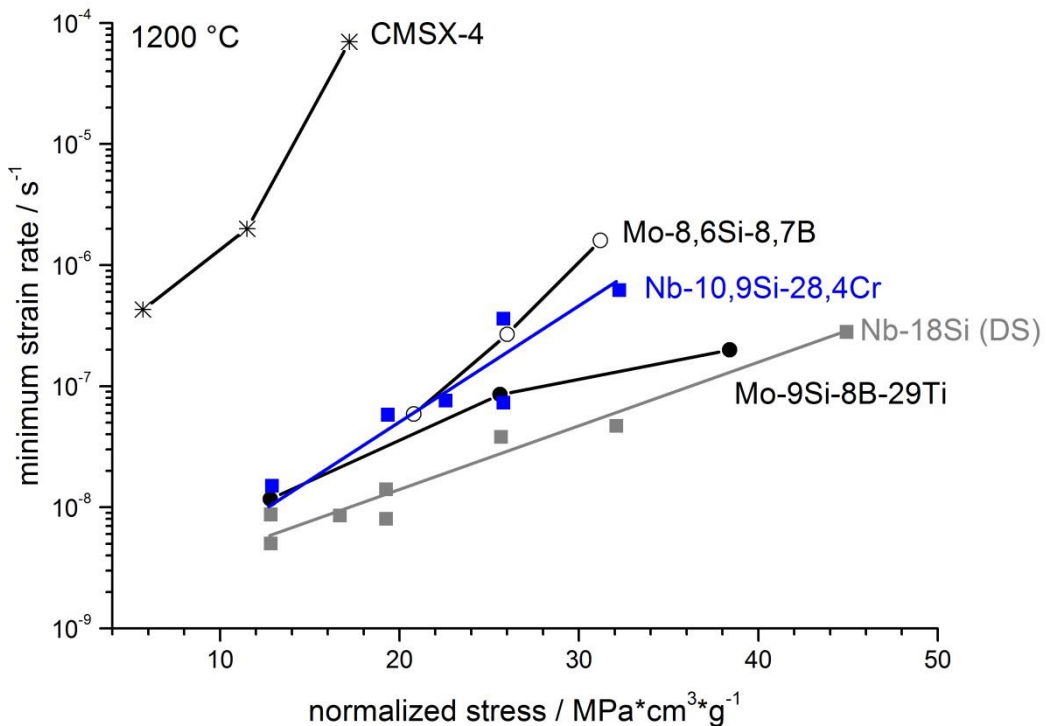
261 The Norton plot in Figure 9b depicts the minimum strain rate with respect to the applied true stress.
 262 For comparison, literature values of compressive creep data for monolithic Nb₅Si₃ [21] (as no literature
 263 data for Nb₉(Si,Cr)₅ is available), Cr₂Nb [19] and pure Nb [22] were added. Data for Nb-10.9Si-28.4Cr,
 264 heat treated at 1500 °C for 100 h are included as well since this microstructure should be stable at the
 265 testing temperature of 1200 °C.

266 Surprisingly, the as cast condition, which according to Figure 7 has a substantially lower phase size
 267 than the heat treated condition, exhibits the lowest creep rates. An explanation for this effect can be
 268 found in the matrix character of the silicide phase Nb₉(Si,Cr)₅ after casting (phase fraction of ≈ 68 %).
 269 This phase carries the load, supports the substantially less creep resistant phases Cr₂Nb and Nb_{ss} and
 270 thus controls the creep resistance in the former case. The mitigation of Nb₅Si₃ creep properties by
 271 Nb_{ss} using a rule of mixture approach could explain the intermediate position obtained for Nb-10.9Si-
 272 28.4Cr. Simulation based on such approach in binary Nb-Si alloys, consisting of Nb_{ss} and Nb₅Si₃,
 273 showing similar results, were already published [23, 24]. On the other hand, a difference in
 274 Nb₉(Si,Cr)₅ creep strength in the present alloy compared to monolithic Nb₅Si₃ may also explain strain
 275 rate variations.

276 Increased strain rates obtained for heat treated conditions could be attributed to the decreasing
 277 fraction of the silicide phase and the loss of its matrix character. This influence of the silicide phase
 278 fraction on the creep behavior has already been published in the literature for quaternary Nb-Si-Ti-Hf
 279 alloys [19]. The minimum strain rates shown in Figure 9b approach the values of the other phases
 280 involved in the microstructure, mainly the ones for Cr₂Nb. Due to the interpenetrating eutectic
 281 character of the microstructure, and since Nb_{ss} has no significant creep resistance at the present
 282 stress levels and temperature, the Laves phase Cr₂Nb carries the major part of load during creep and
 283 therefore determines the overall creep resistance of the alloy.

284 Stress exponents for both material conditions are in the order of magnitude expected for dislocation
 285 creep (n = 3 - 8). Supporting this finding, dislocation climb controlled creep has not only been reported
 286 in Nb and Cr₂Nb at temperatures above 1200 °C [25], but also for Nb₃Si [26]. Hence, the assumption
 287 of dislocation creep in the present silicide phase Nb₉(Si,Cr)₅ seems legitimate, even though no data for
 288 this monolithic phase are available.

289 Finally, the data obtained for Nb-10.9Si-28.4Cr are compared to compressive creep data for other
 290 refractory based silicides, as well as a state of the art Ni-based superalloy tested in tension, from the
 291 literature, in a density-normalized Norton plot in Figure 10, in order to critically assess the potential of
 292 the ternary eutectic alloy.



293
 294 **Figure 10: Density-normalized Norton plot, showing the potential of Nb-10.9Si-28.4Cr when compared to other refractory**
 295 **metals based alloys as well as Ni-based superalloys.**

296 The minimum strain rates for Nb-10.9Si-28.4Cr are comparable with molybdenum silicides Mo-8.6Si-
 297 8.7B [27] and Mo-9Si-8B-29Ti [28] in the measurement uncertainty range. When compared to
 298 directionally solidified Nb-18Si [3], the fraction of load-bearing silicide phases is similar ($\approx 66\%$ for Nb-
 299 18Si versus $\approx 68\%$ for Nb-10.9Si-28.4Cr). Hence the strain rate difference of one order of magnitude
 300 can be attributed to the phase alignment along the loading direction. Compared to the single-crystal
 301 Ni-based superalloy CMSX-4 [29], all refractory based alloys have up to two orders of magnitude lower
 302 strain rates. This is not surprising, as the testing temperature of 1200 °C is in the temperature range of
 303 γ' solvus in Ni-based superalloys, which leads to a significant loss of particle strengthening in these
 304 alloys.

305
 306 **IV. Conclusions**
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308 The chemical composition of the Nb-rich ternary eutectic in the system Nb-Si-Cr was
 309 experimentally determined to be Nb-10.9Si-28.4Cr. The phases present in the as cast state are Nb_{ss},
 310 β -Cr₂Nb and Nb₉(Si,Cr)₅, the later forming an interpenetrating matrix. Microstructure and phase
 311 stability could be confirmed up to 1200 °C for several hundred hours. At this temperature, creep
 312 properties are comparable to other refractory based silicide alloys, dislocation controlled creep being
 313 the predominant mechanism. As compared to CMSX-4, significantly improved creep strength could be
 314 observed. However, above 1200 °C, the Nb₉(Si,Cr)₅ undergoes a presumably eutectoid-like
 315 decomposition into Nb_{ss}, β -Cr₂Nb and α -Nb₅Si₃. Because of this decomposition, Nb-10.9Si-28.4Cr
 316 loses its load-bearing Nb₉(Si,Cr)₅ matrix, which results in a significant loss of creep strength.
 317 Therefore the temperature limit for structural applications is currently set below 1300 °C. To overcome
 318 this limitation, more profound knowledge of the decomposition process is necessary. So far, employing
 319 available analyzing methods (e.g. DSC) could not yield information on both the exact transformation
 320 path and the reversibility of the process. Moreover, it has to be clarified, whether Nb₉(Si,Cr)₅ may

321 possibly be a metastable high temperature phase. Finding answers to these questions is part of
322 ongoing research. Eventually, ways can be found to suppress either its formation or decomposition. As
323 stated previously, this ternary alloy in theory should exhibit well-balanced creep, oxidation and fracture
324 toughness properties. However, the two later properties have not been addressed so far and should
325 be thoroughly assessed in future work, to explore the capability and applicability of a ternary eutectic
326 Nb-Si-Cr alloys.

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330

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342 VI. References

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Tables

Table 1: Nominal and actual composition of the alloys used for triangulation. The numbers shown in Figure 2 are matched to the compositions accordingly.

alloy no.	nominal	actual (ICP-OES)
1	Nb-8.7Si-33.1Cr	Nb-9.0Si-33.3Cr
2	Nb-12Si-25Cr	Nb-12.5Si-26Cr
3	Nb-8.7 Si-22Cr	Nb-7.8Si-21.9Cr
4	Nb-12Si-33.1Cr	Nb-12.4Si-33.2Cr

404

Table 2: Quantitative EDS results for the ternary eutectic structures

alloy no.	alloy composition	Nb / at.%	Si / at.%	Cr / at.%
3	Nb-8.7Si-22Cr	60.7 ± 0.1	11.0 ± 0.5	28.3 ± 0.5
4	Nb-12Si-33.1Cr	60.7 ± 0.1	10.8 ± 0.6	28.5 ± 0.4

406

Table 3: Chemical composition of the phases in Nb-10.9Si-28.4Cr in the as cast state.

phase	Nb / at.%	Si / at.%	Cr / at.%
Nb _{ss}	84.6 ± 2.5	2.4 ± 0.8	13.0 ± 2.0
Cr ₂ Nb	39.9 ± 2.3	12.6 ± 0.9	47.5 ± 1.6
Nb ₉ (Si,Cr) ₅	62.8 ± 1.3	16.2 ± 0.4	21.0 ± 1.6

408

Table 4: Chemical composition of the phases present in Nb-10.9Si-28.4Cr after heat treatment at 1500 °C for 100 h.

phase	Nb / at.%	Si / at.%	Cr / at.%
Nb _{ss}	89.9 ± 0.2	0.4 ± 0.1	9.7 ± 0.2
Cr ₂ Nb	33.8 ± 0.2	12.4 ± 0.3	53.7 ± 0.4
Silicide	60.5 ± 0.1	38.0 ± 0.2	1.5 ± 0.1

410

411 Figures

412

413 Figure 1: SEM-BSE micrographs of the alloys (a) Nb-12Si-25Cr and (b) Nb-8.7Si-33.1Cr, both in as
414 cast condition

415

416 Figure 2: Partial liquidus projection of the Nb-Si-Cr system, including isothermal lines (calculated with
417 PANDAT employing the PanNb database). Compositions according to the numbers are listed in Table
418 1. The red dots symbolize the nominal composition; blue ones represent the actual composition.

419

420 Figure 3: SEM-BSE micrographs of the alloys (a) Nb-8.7Si-22Cr and (b) Nb-12Si-33.1Cr. In both
421 alloys ternary eutectic structures can be observed (marked with a red circle).

422

423 Figure 4: Micrographs of the ternary eutectic alloy Nb-10.9Si-28.4Cr: (a-b) SEM-BSE mode and (c)
424 EBSD, false-color image of the phases Nb₉(Si,Cr)₅ (yellow), Nbss (green) and Cr₂Nb (red).

425

426 Figure 5: Indexed EBSD patterns of the phases present in Nb-10.9Si-28.4Cr: (a) Nbss, (b) Cr₂Nb and
427 (c) Nb₉(Si,Cr)₅.

428 Figure 6: Phase evolution and stability in the alloy Nb-10.9Si-28.4Cr, starting from as cast state in (a)
429 for different heat treatment conditions: (b) 1200 °C, 500 h; (c) 1300 °C, 100 h and (d) 1500 °C, 100 h.

430

431 Figure 7: Evolution of phase fraction and -size in Nb-10.9Si-28.4Cr for different heat treatment
432 conditions. Average phase size determined by segmentation of BSE images is provided in brackets.
433 Connecting lines are to guide the eyes.

434

435 Figure 8: indexed EBSD diffraction patterns showing the silicide phase evolution in Nb-10.9Si-28.4Cr
436 for different heat treatment conditions: (a) Nb₉(Si,Cr)₅ in as cast state and (b) α-Nb₅Si₃ after 1300 °C,
437 100 h

438

439 Figure 9: Stress dependence of the strain response for Nb-10.9Si-28.4Cr, shown as (a) strain rate vs.
440 true plastic strain (deliberately stopped subsequent to minimum) and (b) minimum strain rate vs. true
441 stress (Norton plot). Data marked with "*" were determined at 1000 °C.

442

443 Figure 10: Density-normalized Norton plot, showing the potential of Nb-10.9Si-28.4Cr when compared
444 to other refractory metals based alloys as well as Ni-based superalloys.