

1 **Microstructural and mechanical behavior of second-phase hardened porous refractory Ti-**
2 **Nb-Zr-Ta alloys**

3 C. González-Guillén^a, L. Romero-Resendiz^{b, c, d, *}, M. Naeem^d, A. L. Vidilli^e, L. B. Otani^f, E.
4 Klyatskina^a, G. Gonzalez^{g, *}, V. Amigó^{a, *}

5 ^a Instituto de Tecnología de Materiales, Universitat Politècnica de València, Camino de Vera s/n,
6 46022 Valencia, Spain

7 ^b Facultad de Química, Departamento de Ingeniería Metalúrgica, Universidad Nacional
8 Autónoma de México, Mexico City, 04510, Mexico

9 ^c Department of Design and Engineering, Faculty of Science and Technology, Bournemouth
10 University, Poole, Dorset, BH12 5BB, UK

11 ^d School of Metallurgy and Materials, University of Birmingham, Birmingham, B15 2TT, UK

12 ^e Graduate Program in Materials Science and Engineering, Federal University of São Carlos, Rod.
13 Washington Luiz, Km 235, São Carlos -SP, 13564-905, Brazil

14 ^f Department of Materials Engineering (DEMa), Federal University of São Carlos, Rod.
15 Washington Luis, km 235, São Carlos –SP, 13565-905, Brazil.

16 ^g Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
17 Circuito exterior S/N, Cd. Universitaria, A. P. 70-360, Coyoacán, C.P. 04510, Mexico

18 *Corresponding authors: liliana.rom7@comunidad.unam.mx (L. R.-R.); joseggr@unam.mx (G.
19 G.); vamigo@mcm.upv.es (V. A.)

20 **Abstract**

21 Second-phase hardening in refractory high-entropy alloys (RHEAs) has been recognized as one
22 of the main routes to significantly improve their mechanical properties. However, their cost-
23 benefit should not be compromised. Thus, we designed second-phase strengthened RHEAs by a
24 low-cost powder metallurgy method. We induced the formation of FCC (face-centered cubic) ZrC
25 second phase, which has not been reported in Ti-Nb-Zr-Ta alloys before and may be easily
26 confused with the FCC-Zr due to the complexity of identifying carbon by conventional methods.
27 We used neutron diffraction and electron backscatter diffraction for microstructural studies, as
28 well as hardness, ultrasonic and compression techniques for assessing mechanical properties. Our
29 investigation centered on equiatomic and equimassic Ti-Nb-Zr-Ta alloys, both displaying similar
30 grain morphology and porosity but differing in grain sizes and phases. The variation in grain size
31 was attributed to the influence of Ta as a grain growth pinning element. Our second-phase ZrC
32 hardened alloys revealed higher stiffness and hardness, surpassing those documented in the
33 existing literature.

34

35 **Keywords**

36 Refractory alloy; High-entropy alloy; Intermetallic; Microstructure; Mechanical properties

37 **1. Introduction**

38 Refractory high-entropy alloys (RHEAs) were reported in 2010 with the objective to overcome
39 the technological challenge of building high-temperature-resistant components for aerospace,
40 nuclear and chemical reactors [1]. RHEAs answer the immediate need for high mechanical
41 properties at elevated temperatures, due to their high melting points, surpassing the commonly
42 used nickel-based superalloys [2]. Microstructural control and the introduction of second-phase
43 hardening in RHEAs have been recognized as the main routes to improve their mechanical
44 properties [2]. Besides, increasing the multidisciplinary applications of RHEA is highly sought
45 after area. So far, the effect of B2 and Laves phases as second-phase hardening of RHEAs has
46 been broadly studied, but their formation requires thermo-mechanical processing that decreases
47 the cost–benefit of the alloy. Seeking feasible and low-cost materials may be the biggest challenge
48 for the technological application of materials science, including the second-phase hardened
49 RHEAs.

50 In this work, we seek to explore the formation of carbides as a second-phase hardening route
51 during the processing of the alloy, i.e., without further thermo-mechanical treatment. We selected
52 a powder metallurgy method for promoting carbide formation during sintering. Powder metallurgy
53 routes have been proven successful for obtaining carbide-reinforced RHEAs [3]. Besides, powder
54 metallurgy is well recognized due to the minimized cost of machining complex-shaped
55 components, as well as lower temperature and energetic requirement during processing compared
56 to casting [4]. However, no multidisciplinary RHEA has explored this option yet. The Ti-Nb-Zr-
57 Ta (TNZT) alloy was selected as the starting material because of its high oxidation and wear
58 resistance [2], as well as low cytotoxic effect [5] of the constituent elements. Besides, Zr has a

59 high affinity to form carbides. Thus, the TNZT alloy is a RHEA with adequate physical,
60 mechanical and biological properties for assessing the effect of second-phase hardening carbides.

61 Considering that carbon is difficult to characterize by conventional techniques, especially at
62 low fraction content, we used neutron diffraction to demonstrate its presence and quantification in
63 our alloys. The existence of an FCC Zr phase has been predicted from the elastic stability criteria
64 [6]. Later, some works have reported its formation in pure elements [7,8] and alloys [9,10].
65 However, its phase transformation from the room-temperature-stable HCP-phase [10,11] is still
66 not well understood. It has been usually linked to strain-induced or thermally-induced phase
67 transformation [7,9,10]. The challenge in identifying carbon through conventional methods,
68 coupled with ease with which carbon gets introduced from the environment during processing,
69 may have previously obscured its role and impact in phase transformations.

70 In this work, we developed two second-phase hardened porous RHEAs based on TNZT alloy
71 with the addition of a C-rich organic $C_{18}H_{36}O_2$ compound. Equiatomic and equimassic TNZT
72 matrix were selected because they are the most commonly reported TNZT stoichiometries.
73 Moreover, they offer broad literature to compare the new alloys produced in this work. We used
74 neutron diffraction characterization to demonstrate the formation of FCC-ZrC phase.

75

76 **2. Experimental methods**

77 Before processing of the alloys, the phases predictions were carried out by thermodynamic
78 calculations (CALPHAD method) using ThermoCalc[®] software and the TCHEA5 database. Once
79 the formation of desired carbides was successfully simulated, commercial powders (Atlantic
80 Equipment Engineers and Alfa Aesar) of Ti, Nb, ZrH₂, and Ta were used as raw materials for

81 producing the TNZT alloys (Table 1). The powders were weighed to obtain two second-phase
 82 hardened TNZT alloys as shown in Table 2.

83 **Table 1.** Raw powder characteristics.

Raw material	Purity / wt.%	Average particle size / μm	Crystal structure
Ti	99.9	44	HCP
Nb	99.8	1 - 5	BCC
ZrH ₂	99.9	4.5 - 6.5	FCC
Ta	99.9	1 - 5	BCC

84

85 **Table 2.** Elemental composition of studied alloys.

Element	Equimassic TNZT		Equiatomic TNZT	
	Wt. %	At. %	Wt. %	At. %
Ti	24.75	43.22	11.34	24.65
Nb	24.75	22.27	22.25	24.91
Zr	24.75	22.68	21.84	24.91
Ta	24.75	11.43	43.57	25.05
C ₁₈ H ₃₆ O ₂	1.00	0.39	1.00	0.49

86

87 Mechanical alloying (MA) was carried out in a planetary ball mill (Retsch model PM 400/2)
 88 at 350 rpm for 40 h. The milling was divided in work stages of 8 minutes on and 10 minutes off to
 89 improve the homogenization of alloys after press and sintering. Standard stainless-steel jars and
 90 chromium-steel balls with a ball-to-powder weight ratio of 10:1 were used for milling. 1 wt.% of

91 stearic acid ($C_{18}H_{36}O_2$) was used as a carbon source and debinding agent to avoid powder
92 agglomeration. The powders were then compacted using a hydraulic press (Metallkraft model
93 WPP 50 M) and a floating die of 1.8 cm^3 at 1,000 MPa for 10 seconds. The specimens were sintered
94 in a high-vacuum tubular furnace (Carbolite HVT 15/75/450) at a pressure between 0.01 to 0.1 Pa
95 in Ar atmosphere. Sintering was performed in three steps: 1) temperature increment at $5\text{ }^\circ\text{C min}^{-1}$
96 until 800°C and holding for one hour, 2) temperature increment up to 1400°C and holding for three
97 hours, and 3) furnace-cooling at $10\text{ }^\circ\text{C min}^{-1}$ to room temperature.

98 Phase identification and estimation were carried out by neutron diffraction measurements at the
99 TAKUMI beamline of the Materials and Life Science Experimental Facility (MLF) at the Japan
100 Proton Accelerator Research Complex (J-PARC) with a collimator of $5\text{ mm} \times 5\text{ mm}$. For
101 microstructural and mechanical properties characterisation, samples were prepared by
102 conventional metallography and polishing with a colloidal solution of $0.3\text{ }\mu\text{m}$ silica.
103 Morphological observations were done by electron backscatter diffraction (EBSD) in a Zeiss
104 Auriga model scanning electron microscope with an HKLNordlys EBSD detector (15 KV). Energy
105 dispersive X-ray spectroscopy (EDS) point and mapping analyses were performed in a scanning
106 electron microscope (SEM) Zeiss ULTRA 55. Phase discrimination was performed by EBSD
107 phase mappings through the “TruPhase” post-processing algorithm of Aztec software, which
108 matches regions with similar chemical composition based on referenced EDS spectra previously
109 obtained in the same sample. The content of C was inspected by a LECO ON836 Elemental
110 Oxygen and Nitrogen Detection Analyzer. Porosity was estimated by the Archimedes method
111 according to ASTM B962-17. At least five measurements were averaged for each sample.

112 The elastic modulus (E) was measured by ultrasonic non-destructive technique (Echograph
113 1090 from Karl Deutsch equipment) considering a Poisson’s ratio of 0.34. At least 3 elastic

114 modulus measurements were obtained for statistical purposes. A Shimadzu Vickers HMV-2
115 microhardness tester was used for microhardness measurements (HVN_{0.3}) by applying 3 N for 15
116 s. At least 5 measurements were obtained per sample. A Shimadzu Autograph AG-100 KN Xplus
117 universal testing machine was used for uniaxial compression testing at a strain rate of 0.5 mm min⁻¹.
118 The tests were stopped before the barreling generated due to friction between the discs and the
119 sample, which causes triaxial stress states and experimental errors in the stress-strain curves [12].
120 Yield strength was approximated by the 0.2% offset method. At least 3 compression tests were
121 performed for statistical purposes.

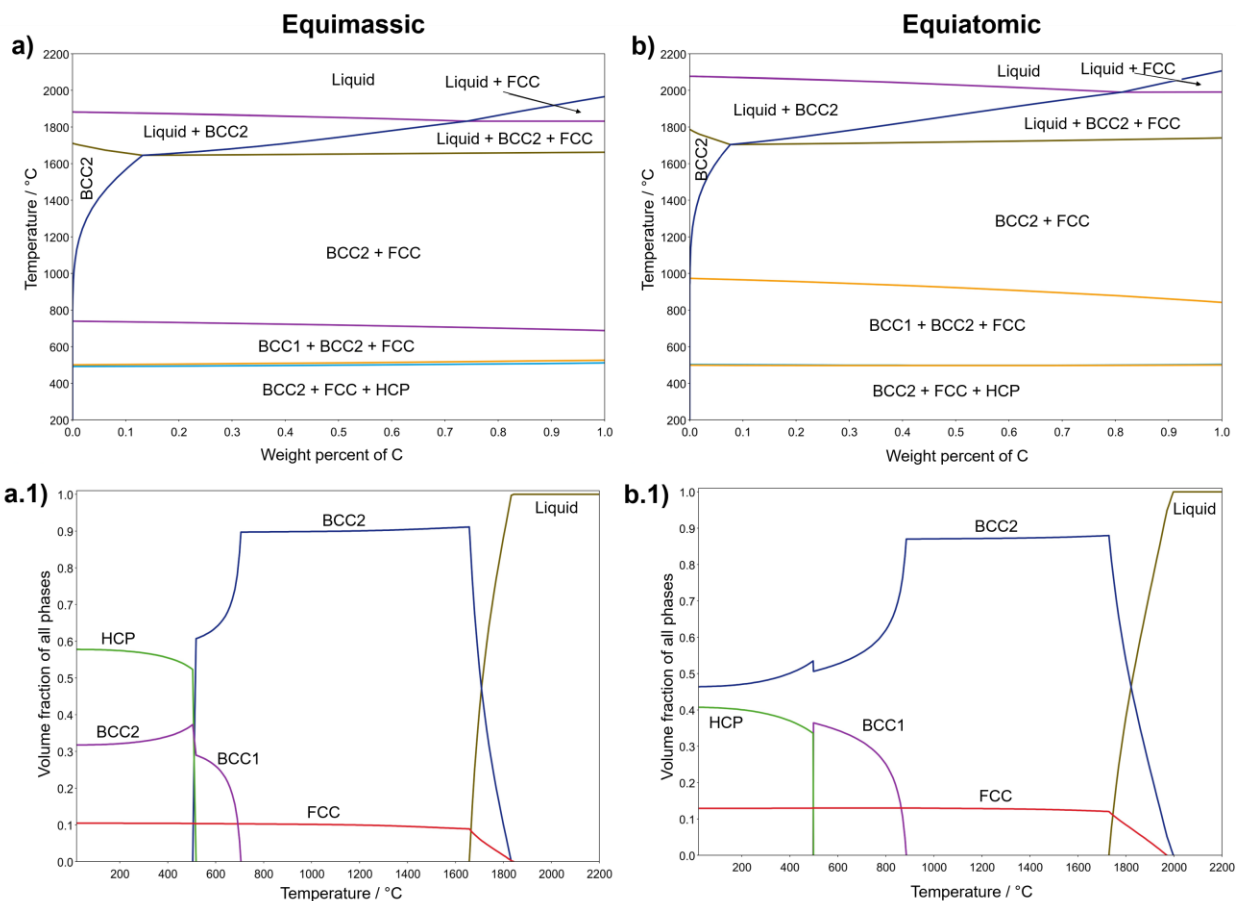
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123 3. Results and discussion

124 Based on the ThermoCalc® calculations presented in Fig. 1, it is anticipated that equimassic
125 and equiatomic alloys will exhibit three phases, including the desired FCC-ZrC. The initial
126 composition of 1.0 wt.% C₁₈H₃₆O₂ yields 0.76 wt.% of carbon. This specific carbon content was
127 taken into account for generating Fig. 1a.1 and Fig. 1b.1, as well as the phase compositions detailed
128 in Table 3. Both alloys are expected to form BCC2 and FCC in the region 1500 to 600 °C. BCC2
129 phase have nearly equiatomic Ti, Nb and Ta contents, and a lower Zr concentration. FCC phase is
130 enriched in C and Zr with depletion of Ti, Nb, and Ta. From 600 to 200 °C, BCC2, FCC, and
131 BCC1 phases are formed in both alloys. BCC2 phase is mainly enriched in Nb and Ta with
132 somewhat depletion of Ti and a low content of Zr between 3 to 4 at.%. The Nb, Ti, and Ta diffused
133 out of the FCC phase, leaving a ZrC with 60 at.% of Zr and 40 at.% of C. The BCC1 phase is rich
134 in Ti and Zr with lower contents of Nb and Ta. Below 200 °C, the FCC remains stable, while Zr
135 and Ti have diffused from the BCC2 phase to form a new HCP phase, which has 62 to 75 at.% of

136 Ti and 25 to 38 at.% of Zr. Both equiatomic and equimassic alloys showed similar phase formation
137 tendencies.

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140 **Fig. 1.** a,b) Phase diagram and a.1., b.1.) cooling path of the a, a.1) equimassic and b, b.1)
141 equiatomic TNZT alloys calculated by CALPHAD method.

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146 **Table 3.** Chemical composition at the isopleth of 0.76% C from the phase diagram of equiatomic
 147 and equimassic TNZT alloys.

Alloy	Temperature / °C	Phase	Composition	
Equimassic TNZT	1500	BCC2	$Ti_{46}Nb_{23}Zr_{18}Ta_{12}C_1$	
		FCC	$Ti_{10}Nb_4Zr_{44}Ta_3C_{39}$	
	1000	BCC2	$Ti_{47}Nb_{24}Zr_{17}Ta_{12}$	
		FCC	$Ti_1Nb_1Zr_{57}Ta_1C_{40}$	
	600	BCC1	$Ti_{57}Nb_{15}Zr_{21}Ta_7$	
		BCC2	$Ti_{23}Nb_{46}Zr_4Ta_{27}$	
		FCC	$Zr_{60}C_{40}$	
	200	HCP	$Ti_{75}Zr_{25}$	
		BCC2	$Ti_1Nb_{65}Ta_{34}$	
		FCC	$Zr_{60}C_{40}$	
	Equiatomic TNZT	1500	BCC2	$Ti_{27}Nb_{27}Zr_{18}Ta_{27}$
			FCC	$Ti_4Nb_3Zr_{50}Ta_4C_{39}$
1000		BCC2	$Ti_{28}Nb_{27}Zr_{17}Ta_{28}$	
		FCC	$Ti_1Nb_1Zr_{58}Ta_1C_{39}$	
600		BCC2	$Ti_{16}Nb_{39}Zr_3Ta_{42}$	
		BCC1	$Ti_{48}Nb_9Zr_{38}Ta_5$	
		FCC	$Zr_{60}C_{40}$	
200		BCC2	$Ti_2Nb_{49}Ta_{49}$	
		HCP	$Ti_{62}Zr_{38}$	
		FCC	$Zr_{60}C_{40}$	

148

149 From neutron diffraction results, shown in Fig. 2 and Table 4, the equimassic TNZT sample
150 (Fig. 2a) consisted of three phases, including two BCC ($\text{Im}\bar{3}\text{m}$) phases of lattice parameter 3.3060
151 Å (BCC1) and 3.3359 Å (BCC2), and one FCC ($\text{Fm}\bar{3}\text{m}$) phase with lattice parameter of 4.6016 Å.
152 The larger lattice parameter of BCC2 compared to BCC1 agrees with its higher Ta content (Table
153 3), which is the constituent element with the largest atomic size. The equiatomic TNZT sample
154 consisted of BCC1, FCC and HCP phases (Fig. 2b) with lattice parameters of 3.3148, 4.6092, and
155 $a=2.8960$ and $c=4.8999$ Å, respectively. Some peaks remained unidentified in both patterns due to
156 the probable oxidation during sintering and formation of complex oxides or carbides [13,14]. The
157 unidentified peaks are very low in intensity and due to the structural complexity of the potential
158 phases, they are expected in low amounts.

159 The predicted phases below 200 °C in Fig. 1 are different from the experimentally observed
160 phases in Fig. 2. The difference between predicted and experimentally observed phases may come
161 from the theoretical assumptions. The calculations in Fig. 1 did not consider that the starting
162 powders do not melt during the press and sintering method. Thus, the TNZT alloys processed here
163 by powder metallurgy route might have followed a different atomic diffusion path than the
164 theoretical calculations. The predictions made by the CALPHAD method only show the
165 thermodynamically stable phases and their quantities. The rate of solid-state diffusion (during
166 sintering) is lower than in liquid state (assumption during the calculations). Therefore, the limited
167 atomic diffusion could restrict the formation of the stable phases. The experimental results from
168 Fig. 2 showed that the limited solid-state diffusion generated an equivalent effect to extending the
169 BCC2 + BCC1 + FCC phase region to the room temperature in the equimassic TNZT alloy, and
170 limiting HCP (only 4%) formation in the equiatomic alloy.

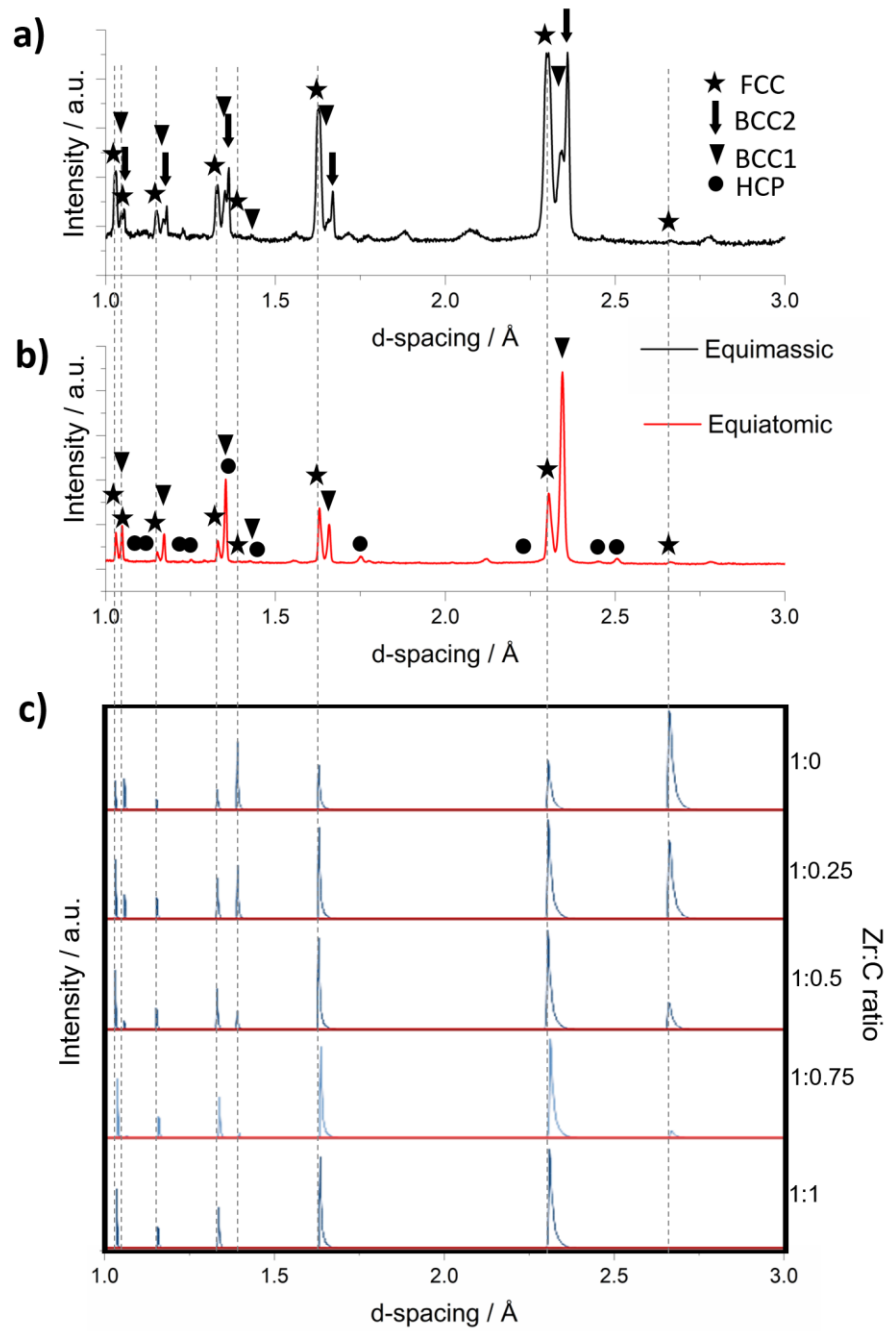
171 From the neutron diffraction data in Fig. 2, the FCC phase in the equimassic alloy (32.2%) is
172 higher compared to the equiatomic alloy (25.3%) (Table 4). From Fig. 1 and Fig. 2, the FCC-ZrC
173 phase is stable either at high-activated diffusion processes, like by assuming melting in the
174 CALPHAD calculations, or during lower atomic diffusion processes like sintering at 1400 °C.

175 Figure 2c shows the simulated neutron diffraction profiles for Zr and ZrC with different Zr:C
176 ratios. Increasing the carbon contents in the intermetallic ZrC causes the disappearance of three
177 peaks located at 1.06, 1.39, and 2.66 Å. Despite the peak located at 2.66 Å is the most intense in
178 the simulated patterns for 1:0.25 Zr:C ratio, neither the equimassic nor the equiatomic samples
179 showed the presence of any of those three peaks. This evidence suggests that the ZrC has a high C
180 percentage, while its similar lattice parameter in the equimassic (4.6016 Å) and equiatomic (4.6092
181 Å) alloys suggest a similar stoichiometry. Considering the significantly higher atomic mass of Zr
182 (91.2 amu) compared to that of C (12.0 amu), a higher number of C atoms is expected for
183 equivalent weights of Zr and C. Thus, a near-1:1 Zr:C atomic ratio may be possible for Zr-enriched
184 regions. This stoichiometry agrees well with the refined carbon occupancy ratio of 0.475Zr:0.525C
185 in the equiatomic alloy and 0.43Zr:0.57C in the equimassic alloy. Similar stoichiometry has been
186 reported for FCC-ZrC with C distributed among octahedral interstitial sites [15]. Evidence of local
187 Zr enrichments will allow observing the FCC-ZrC distribution and morphology.

188 Energy-dispersive X-ray spectroscopy (EDS) elemental mapping for equimassic and
189 equiatomic TNZT alloys are shown in Fig. 3. A part of Zr is distributed in the matrix forming solid
190 solution with Ti, Nb and Ta, i.e., forming the BCC phases. However, Zr-enriched zones were
191 evident by the higher Zr presence at Ti, Nb and Ta-depleted zones. Thus, Zr-enriched zones may
192 correspond to FCC-ZrC intermetallic and HCP-phase predicted by thermocalc simulations in Fig.
193 1 and confirmed by neutron diffraction in Fig. 2. Thus, the light regions in Fig. 3 correspond to

194 BCC phases while the dark regions correspond to FCC and HCP phases. The identification of these
195 regions agrees well with point EDS analyses shown in [Table 5](#) which showed Zr-enriched dark
196 regions, which correspond to the HCP and FCC compositions ([Table 3](#)). Besides, homogeneously
197 dispersed BCC1, BCC2, and FCC phases in the TNZT alloys were confirmed by EBSD shown in
198 [Fig. 4](#).

199 The presence of C was shown by an organic-elements analyzer, resulting in 0.814 and 0.851
200 wt.% for the equiatomic and equimassic TNZT alloys, respectively. These values are close to the
201 nominal content of C of 0.76 wt% according to the nominal stearic acid content of 1.0 wt.% in
202 each sample.



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Fig. 2. Neutron diffraction patterns of a) equimassic and b) equiatomic TNZT alloys and their comparison with c) simulated patterns of different Zr:C atomic ratios.

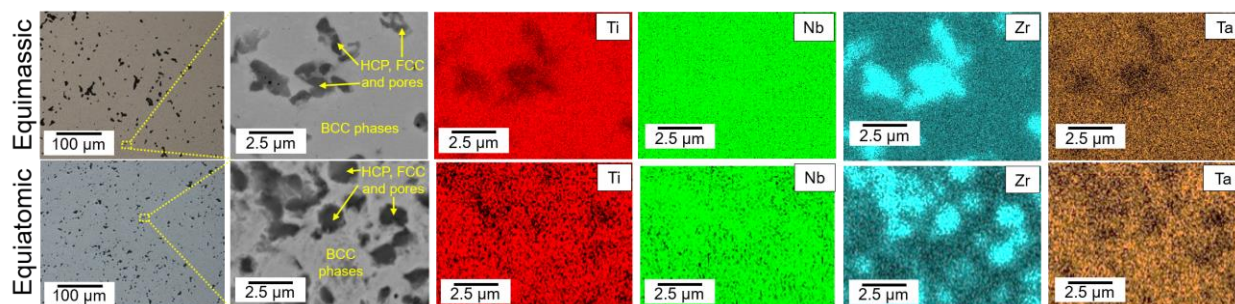
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207 **Table 4.** Experimental lattice parameter of equimassic and equiatomic TNZT alloys calculated
 208 from neutron diffraction measurements.

Phase	Equimassic TNZT		Equiatomic TNZT	
	Lattice parameter Å	Phase percentage vol. %	Lattice parameter Å	Phase percentage vol. %
BCC1	a = 3.3060	30.4	a = 3.3148	70.7
BCC2	a = 3.3359	37.4	-	-
HCP	-	-	a = 2.8960 c = 4.8999	4.0
FCC	a = 4.6016	32.2	a = 4.6092	25.3

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210

211 **Fig. 3.** EDS mapping of equimassic (upper panel) and equiatomic (lower panel) TNZT alloys.

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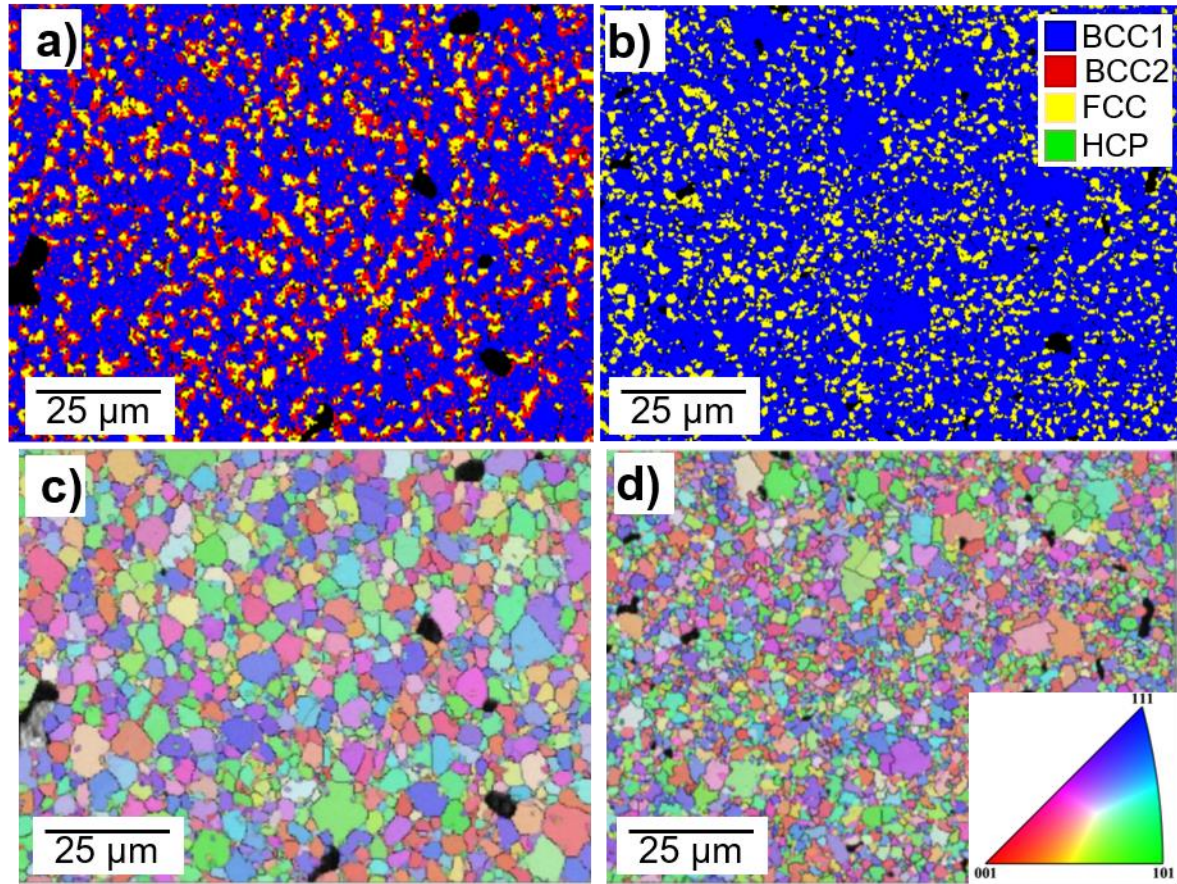
213 **Table 5.** EDS point analyses of equimassic and equiatomic TNZT samples.

Element	Dark zones		Light zones	
	Wt.%	At.%	Wt.%	At.%
Ti	7.0 ± 0.1	13.2 ± 0.3	12.7 ± 0.3	28.2 ± 0.6
Nb	5.7 ± 0.1	5.6 ± 0.1	24.8 ± 0.5	28.4 ± 0.6
Zr	76.4 ± 1.5	75.8 ± 1.5	11.3 ± 0.2	13.2 ± 0.3
Ta	10.9 ± 0.2	5.5 ± 0.1	51.2 ± 1.0	30.2 ± 0.6

214

215

216 From Fig. 4c,d, both alloys showed nearly equiaxed grain morphology. The grain size of the
217 equimassic is bigger than the equiatomic TNZT alloy. The quantitative differences in grain size
218 are shown in Table 6, where there are two types of averages, the standard and the area-weighted.
219 The first one represents the average when the maximum grain size is dominated by the diameter
220 of the grains that exist in higher number. On the other hand, in the second type the maximum grain
221 size is dominated by the diameter of the largest grains. The larger grain size of the equimassic
222 alloy agrees with the lower quantity of Ta compared to those in the equiatomic alloy (Table 2). As
223 the Ta atomic weight (180.9 amu) is the highest among the constituent elements (Ti = 47.8; Nb =
224 92.9; Zr = 91.2; C = 12.0 amu), a lower quantity of Ta atoms corresponds to the same weight
225 percent in the equimassic TNZT alloy. The lower Ta diffusion compared to the other constituent
226 elements in TNZT alloys has been reported [16]. Due to the large difference of Ta atomic weight,
227 many physical phenomena, including higher density and lower diffusion are expected. Low
228 element diffusion is commonly correlated with grain growth anchor due to pinning effect. This has
229 been observed in powder metallurgy processed $Ti_{25+x}Nb_{25}Zr_{25}Ta_{25-x}$ (X = 0, 5, and 10) alloys,
230 where the higher the Ta, the lower the grain size [16]. To evaluate the effect of the microstructural
231 features on the mechanical properties, hardness, compression and ultrasonic techniques were
232 applied.



233

234 **Fig. 4.** EBSD a,b) phase contrast mappings and c,d) inverse pole figure mapping of the a,c)

235 equimassic and b,d) equiatomic TNZT alloys.

236

237 **Table. 6.** Grain size of the equimassic and equiatomic TNZT alloys.

Alloy	Min / μm	Max / μm	Standard mean / μm	Area-weighted mean / μm	Standard deviation / μm
Equimassic	1.4	10.6	3.0	4.6	1.5
Equiatomic	1.1	7.9	1.9	3.0	0.9

238

239 [Table 7](#) shows the results of mechanical properties, where it can be observed that the equimassic

240 alloy has 6.9% higher hardness than the equiatomic alloy. Meanwhile, the stiffness indicated by

241 the elastic modulus is 16.4% higher for the equiatomic. A directly proportional trend between
 242 hardness and stiffness can be expected in dense materials. However, porous materials, such as the
 243 studied TNZT alloys, might follow a different trend as a function of the applied load during
 244 mechanical testing. In a similar way, porous zirconia toughened alumina has been reported with
 245 variable hardness values depending on the indentation load [17]. This phenomenon is related to
 246 densification and pore collapse during loading. As shown in Fig. 4, both equimassic and
 247 equiatomic alloys possess the typical porous microstructure by powder metallurgy processing
 248 route (Table 8). Thus, the different tendency between hardness and elastic modulus might be
 249 related to the applied load during hardness measurements, while the ultrasonic testing does not
 250 involve the application of mechanical loads. This hypothesis is also in agreement with the higher
 251 precision for determination of elastic properties reported by dynamic methods compared to
 252 mechanical tests [18]. It is noteworthy that the hardness values of the equiatomic and equiatomic
 253 alloys might overlap considering the measurement deviation indicated in Table 7. The comparable
 254 hardness of both alloys could be due to their similar total porosity (Table 8), equiaxed grain
 255 morphology (Fig. 4), and elemental distribution (Fig. 3).

256

257 **Table 7.** Mechanical properties of ZrC-containing TNZT alloys evaluated by microhardness,
 258 ultrasonic and compression testing.

TNZT alloy	HVN_{0.3}	E / GPa	Ultimate strength / MPa	Yield strength / MPa
Equimassic	489.1 ± 35.0	111.2 ± 0.0	1178.9 ± 149.7	865 ± 109.8
Equiatomic	455.2 ± 20.7	133.0 ± 0.0	1229.2 ± 158.2	1005 ± 129.3

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Table 8. Porosity of the studied TNZT alloys.

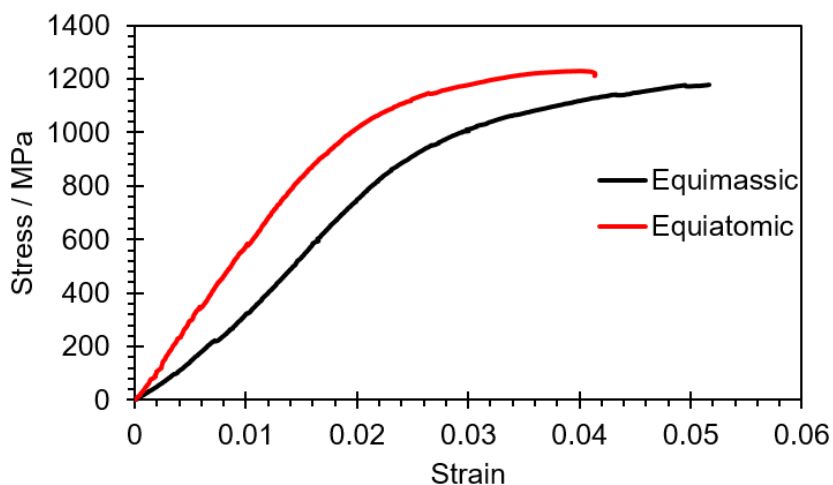
TNZT alloy	Open porosity / %	Closed porosity / %	Total porosity / %
Equimassic	2.71 ± 1.07	2.53 ± 0.39	5.86 ± 0.70
Equiatomic	0.95 ± 0.90	4.17 ± 0.11	5.12 ± 0.97

262

263 On the other hand, the strongest contribution to elastic modulus of metallic materials comes
 264 from the atomic bonding instead of from microstructural features, such as grain size [19]. Then,
 265 the higher elastic modulus (Table 7) in the equiatomic alloy may be related to local interatomic
 266 bonding disparities due to the presence of HCP phase in addition to the FCC phase that is present
 267 in both alloys (Table 4). As the BCC matrix contents of both alloys is similar (67.8 and 70.7% for
 268 equimassic and equiatomic alloys), its effect has been discussed with the reported TNZT alloys in
 269 literature. As shown in Fig. 6, reported TNZT alloys with at least 90% of BCC phase produced by
 270 melting or powder metallurgy have elastic moduli ranging from 73 to 91 GPa [16,20].
 271 Contrastingly, the TNZT alloys with 67.8 to 70.7% of BCC phase produced in this work, showed
 272 higher elastic moduli ranging from 11.2 to 133 GPa. Thus, the highest contribution to the elastic
 273 modulus of the TNZT alloys came from the phase contents, where the BCC phase seems to
 274 decrease the elastic modulus of TNZT alloys. Besides, phase contents, the TNZT alloys also
 275 showed different grain sizes. However, its effect can be considered negligible when the grain is
 276 larger than some dozens of nanometers [19,21]. To distinguish better the effect of the
 277 microstructural differences between both alloys, i.e., phase contents and grain size, compression
 278 testing was performed.

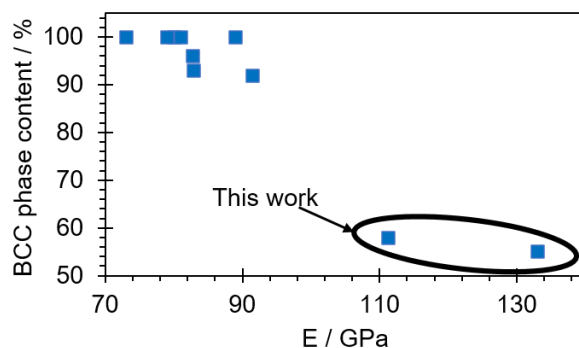
279 Figure 5 shows the stress vs. strain curves obtained from compression testing in the equimassic
 280 and equiatomic TNZT alloys. The mechanical properties obtained from compression testing are
 281 included in Table 7. The 4.1 and 13.9% higher ultimate and yield strength for the equiatomic alloy

282 compared to the equimassic one are within the experimental errors. Thus, as hardness, the ultimate
283 and yield strengths of both TNZT alloys are comparable. From hardness and compression testing,
284 which are techniques with a strong dependence on microstructural features, it is suggested that the
285 microstructural differences between both samples (given by grain size and phases contents) did
286 not have a significant contribution to cause a substantial change of mechanical properties.



287
288 **Fig. 5.** Stress vs strain curves obtained from compression testing in the equimassic and
289 equiatomic TNZT alloys.

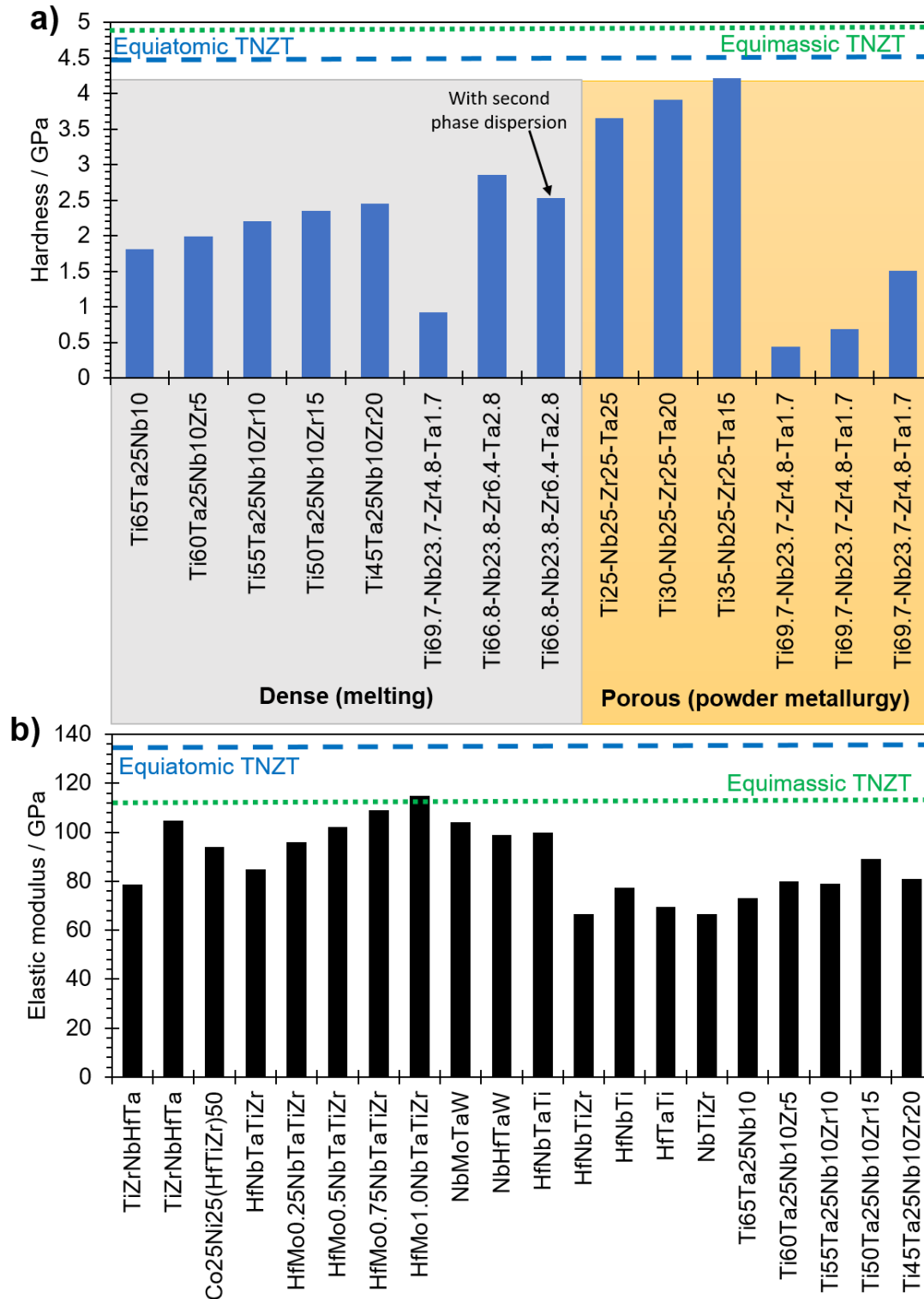
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291
292 **Fig. 6.** Elastic modulus as a function of the BCC phase contents on reported TNZT alloys
293 [16,20] and the ones produced in this work.

294

295 The strong effect of second-phase hardening particles can also be observed by comparing the
296 hardness and stiffness of reported RHEA with the equimassic and equiatomic second-phase
297 hardened TNZT alloys of this work (Fig. 7). Despite the alloys from the literature have similar
298 chemical composition to the second-phase hardened TNZT alloys in this work, they have shown
299 somewhat lower hardness and Young's modulus. Thus, the FCC-ZrC second-phase hardening was
300 proven as a successful strategy for improving mechanical properties of refractory TNZT alloys.
301 This hardening strategy in TNZT alloys was more efficient than the use of dispersed α -Ti particles
302 reported elsewhere (Fig. 7a) [22].



303

304 **Fig. 7.** Comparison of a) hardness [16,20,22–24] and b) elastic modulus [20,25–29] of the TNZT

305 alloys of this study (blue and green dashed lines) with other RHEAs from the literature.

306

307 **Conclusions**

308 Equimassic and equiatomic second-phase hardened TiZrNbTa alloys were produced by powder
309 metallurgy method. An organic C₁₈H₃₆O₂ compound was added before sintering for promoting the
310 formation of FCC-ZrC intermetallic in the BCC matrix. Both alloys showed similar grain
311 morphology and porosity but different grain size and phases. Equimassic alloy showed two BCC
312 and one FCC phase with mean grain size of 4.6 μm, while the equiatomic alloy showed BCC,
313 HCP, and FCC phases with mean grain size of 3.0 μm. The different grain size was related to the
314 effect of Ta as grain growth pinning element. The equimassic alloy showed a higher FCC-phase
315 content and larger area-weighted grain size (32.2 % and 4.6 μm) compared to the equiatomic alloy
316 (20.20 % and 3.0 μm). While the hardness and strength of both alloys can be considered
317 comparable considering porosity and statistical deviation effects, the stiffness slightly increased in
318 the equiatomic alloy (133.0 GPa) compared to the equimassic alloy (111.2 GPa). The higher
319 stiffness may be related to local interatomic bonding disparities promoted by the presence of HCP
320 phase in addition to the FCC phase which is present in both alloys.

321

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334

335 **Data Availability**

336 The raw data related to this manuscript would be made available on request.

337

338 **Conflict of interest**

339 The authors declare that there are no conflicts of interest.

340

341 **CRedit author statement**

342 **C. González-Guillén:** Conceptualization, Methodology, Investigation. **L. Romero-Resendiz:**
343 Supervision, Visualization, Writing-Original Draft. **M. Naeem:** Investigation (neutron
344 diffraction), Formal analysis, Writing - Review & Editing. **A. Vidilli:** Methodology (diagram
345 phase simulation), Writing - Review & Editing. **L. B. Otani:** Resources (Thermocalc), Writing -
346 Review & Editing. **E. Klyatskina:** Conceptualization, Writing - Review & Editing. **G. Gonzalez:**
347 Supervision, Visualization, Writing - Review & Editing. **V. Amigó:** Resources, Supervision,
348 Visualization, Funding acquisition, Writing - Review & Editing.

349 **References**

- 350 [1] O.N. Senkov, G.B. Wilks, D.B. Miracle, C.P. Chuang, P.K. Liaw, Refractory high-entropy
351 alloys, *Intermetallics*. 18 (2010) 1758–1765.
352 <https://doi.org/10.1016/j.intermet.2010.05.014>.
- 353 [2] W. Xiong, A.X.Y. Guo, S. Zhan, C.T. Liu, S.C. Cao, Refractory high-entropy alloys: A
354 focused review of preparation methods and properties, *J. Mater. Sci. Technol.* 142 (2023)
355 196–215. <https://doi.org/10.1016/j.jmst.2022.08.046>.
- 356 [3] S. Lv, Y. Zu, G. Chen, X. Fu, W. Zhou, An ultra-high strength CrMoNbWTi-C high
357 entropy alloy co-strengthened by dispersed refractory IM and UHTC phases, *J. Alloys*
358 *Compd.* 788 (2019) 1256–1264. <https://doi.org/10.1016/j.jallcom.2019.02.318>.
- 359 [4] W.B. James, *Powder Metallurgy Methods and Applications*, *Powder Metall.* 7 (2018) 9–
360 19. <https://doi.org/10.31399/asm.hb.v07.a0006022>.
- 361 [5] S.S. Sidhu, H. Singh, M.A.H. Gepreel, A review on alloy design, biological response, and
362 strengthening of β -titanium alloys as biomaterials, *Mater. Sci. Eng. C*. 121 (2021) 111661.
363 <https://doi.org/10.1016/j.msec.2020.111661>.
- 364 [6] A. Aguayo, G. Murrieta, R. de Coss, Elastic stability and electronic structure of fcc Ti, Zr,
365 and Hf: A first-principles study, *Phys. Rev. B - Condens. Matter Mater. Phys.* 65 (2002)
366 921061–921064. <https://doi.org/10.1103/PhysRevB.65.092106>.
- 367 [7] X. Hu, H. Zhao, S. Ni, M. Song, Grain refinement and phase transition of commercial
368 pure zirconium processed by cold rolling, *Mater. Charact.* 129 (2017) 149–155.
369 <https://doi.org/10.1016/j.matchar.2017.04.037>.
- 370 [8] W. Guo, F. Han, G. Li, Y. Zhang, M. Ali, J. Ren, Q. Wang, F. Yuan, Atomic scale
371 investigation of FCC \rightarrow HCP reverse phase transformation in face-centered cubic
372 zirconium, *J. Mater. Sci. Technol.* 137 (2022) 8–13.
373 <https://doi.org/10.1016/j.jmst.2022.07.032>.
- 374 [9] C. Liu, G. Li, H. Gu, F. Yuan, F. Han, M. Ali, Y. Zhang, W. Guo, Observation of FCC-Zr
375 phase in as-cast Zircaloy-4 alloy, *Mater. Lett.* 267 (2020) 127551.
376 <https://doi.org/10.1016/j.matlet.2020.127551>.
- 377 [10] B. Tao, R. Qiu, Y. Liu, X. Tan, Q. Liu, FCC phase transformation of Zr alloy during air
378 cooling and aging, *J. Nucl. Mater.* 551 (2021) 152989.
379 <https://doi.org/10.1016/j.jnucmat.2021.152989>.
- 380 [11] M.T. Pérez-Prado, A.A. Gimazov, O.A. Ruano, M.E. Kassner, A.P. Zhilyaev, Bulk
381 nanocrystalline ω -Zr by high-pressure torsion, *Scr. Mater.* 58 (2008) 219–222.
382 <https://doi.org/10.1016/j.scriptamat.2007.09.043>.
- 383 [12] X. Wang, H. Li, K. Chandrashekhara, S.A. Rummel, S. Lekakh, D.C. Van Aken, R.J.
384 O'Malley, Inverse finite element modeling of the barreling effect on experimental stress-
385 strain curve for high temperature steel compression test, *J. Mater. Process. Technol.* 243
386 (2017) 465–473. <https://doi.org/10.1016/j.jmatprotec.2017.01.012>.

- 387 [13] L.N. Miotto, L.M.G. Fais, A.L.R. Ribeiro, L.G. Vaz, Surface properties of Ti-35Nb-7Zr-
388 5Ta: Effects of long-term immersion in artificial saliva and fluoride solution, *J. Prosthet.*
389 *Dent.* 116 (2016) 102–111. <https://doi.org/10.1016/j.prosdent.2015.10.024>.
- 390 [14] S.J. Li, R. Yang, S. Li, Y.L. Hao, Y.Y. Cui, M. Niinomi, Z.X. Guo, Wear characteristics
391 of Ti-Nb-Ta-Zr and Ti-6Al-4V alloys for biomedical applications, *Wear.* 257 (2004) 869–
392 876. <https://doi.org/10.1016/j.wear.2004.04.001>.
- 393 [15] T. Davey, K. Suzuki, H. Miura, Y. Chen, Stability and structural properties of vacancy-
394 ordered and -disordered ZrCx, *RSC Adv.* 11 (2021) 32573–32589.
395 <https://doi.org/10.1039/d1ra06362f>.
- 396 [16] G. Al Hawajreh, G. Gonzalez, L. Romero-Resendiz, A. Vidilli, L.B. Otani, V. Amigó,
397 Effect of the Ti/Ta ratio on the feasibility of porous Ti_{25+x}-Nb₂₅-Zr₂₅-Ta_{25-x} (X= 0, 5,
398 and 10) alloys for biomedical applications, *J. Mater. Res. Technol.* (2023) 109181.
399 <https://doi.org/10.1016/j.jmrt.2023.04.070>.
- 400 [17] A. Nastic, A. Merati, M. Bielawski, M. Bolduc, O. Fakolujo, M. Nganbe, Instrumented
401 and Vickers Indentation for the Characterization of Stiffness, Hardness and Toughness of
402 Zirconia Toughened Al₂O₃ and SiC Armor, *J. Mater. Sci. Technol.* 31 (2015) 773–783.
403 <https://doi.org/10.1016/j.jmst.2015.06.005>.
- 404 [18] M. Radovic, E. Lara-Curzio, L. Riester, Comparison of different experimental techniques
405 for determination of elastic properties of solids, *Mater. Sci. Eng. A.* 368 (2004) 56–70.
406 <https://doi.org/10.1016/j.msea.2003.09.080>.
- 407 [19] H.S. Kim, M.B. Bush, Effects of grain size and porosity on the elastic modulus of
408 nanocrystalline materials, *Nanostructured Mater.* 11 (1999) 361–367.
409 [https://doi.org/10.1016/S0965-9773\(99\)00052-5](https://doi.org/10.1016/S0965-9773(99)00052-5).
- 410 [20] G. Ji, Z. Zhou, F. Meng, X. Yang, R. Sheng, J. Qiao, P.K. Liaw, M. Li, L. Jiang, S. Chen,
411 Y. Tong, Effect of Zr addition on the local structure and mechanical properties of Ti-Ta-
412 Nb-Zr refractory high-entropy alloys, *J. Mater. Res. Technol.* 19 (2022) 4428–4438.
413 <https://doi.org/10.1016/j.jmrt.2022.06.160>.
- 414 [21] P. Sharma, S. Ganti, On the grain-size-dependent elastic modulus of nanocrystalline
415 materials with and without grain-boundary sliding, *J. Mater. Res.* 18 (2003) 1823–1826.
416 <https://doi.org/10.1557/JMR.2003.0253>.
- 417 [22] S. Nag, R. Banerjee, H.L. Fraser, Microstructural evolution and strengthening
418 mechanisms in Ti-Nb-Zr-Ta, Ti-Mo-Zr-Fe and Ti-15Mo biocompatible alloys, *Mater. Sci.*
419 *Eng. C.* 25 (2005) 357–362. <https://doi.org/10.1016/j.msec.2004.12.013>.
- 420 [23] M.C. Rossi, B.N. Ventura, L. Milián, A.V. Escuder, V.A. Borrás, Study of
421 Electrochemical and Biological Characteristics of As-Cast Ti-Nb-Zr-Ta System Based on
422 Its Microstructure, *Metals (Basel)*. 12 (2022). <https://doi.org/10.3390/met12030476>.
- 423 [24] J. Rehtin, E. Torresani, E. Ivanov, E. Olevsky, Fabrication of Titanium-Niobium-
424 Zirconium-Tantalum Alloy (TNZT) bioimplant components with controllable porosity by
425 spark plasma sintering, *Materials (Basel)*. 11 (2018). <https://doi.org/10.3390/ma11020181>.
- 426 [25] M. Moschetti, A. Xu, B. Schuh, A. Hohenwarter, J.P. Couzinié, J.J. Kruzic, D.

- 427 Bhattacharyya, B. Gludovatz, On the Room-Temperature Mechanical Properties of an
428 Ion-Irradiated TiZrNbHfTa Refractory High Entropy Alloy, *Jom.* 72 (2020) 130–138.
429 <https://doi.org/10.1007/s11837-019-03861-6>.
- 430 [26] Q. He, S. Yoshida, N. Tsuji, Characteristic strengthening mechanisms in body-centered
431 cubic refractory high/medium entropy alloys, *Scr. Mater.* 231 (2023) 115442.
432 <https://doi.org/10.1016/j.scriptamat.2023.115442>.
- 433 [27] C.C. Juan, K.K. Tseng, W.L. Hsu, M.H. Tsai, C.W. Tsai, C.M. Lin, S.K. Chen, S.J. Lin,
434 J.W. Yeh, Solution strengthening of ductile refractory HfMoxNbTaTiZr high-entropy
435 alloys, *Mater. Lett.* 175 (2016) 284–287. <https://doi.org/10.1016/j.matlet.2016.03.133>.
- 436 [28] Q.F. He, J.G. Wang, H.A. Chen, Z.Y. Ding, Z.Q. Zhou, L.H. Xiong, J.H. Luan, J.M.
437 Pelletier, J.C. Qiao, Q. Wang, L.L. Fan, Y. Ren, Q.S. Zeng, C.T. Liu, C.W. Pao, D.J.
438 Srolovitz, Y. Yang, A highly distorted ultraelastic chemically complex Elinvar alloy,
439 *Nature.* 602 (2022) 251–257. <https://doi.org/10.1038/s41586-021-04309-1>.
- 440 [29] J. Mo, Y. Wan, Z. Zhang, B. Shen, X.B. Liang, The structure and mechanical properties of
441 NbHfTaW refractory high-entropy alloy: A combined theoretical and experimental study,
442 *Int. J. Refract. Met. Hard Mater.* 111 (2023) 106067.
443 <https://doi.org/10.1016/j.ijrmhm.2022.106067>.
- 444