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Probing grain size effect in the superelastic Ti-20Zr-3Mo-3Sn alloy using spherical nanoindentation

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1 **Abstract**

2 Grain size effect on superelasticity was investigated in Ti-20Zr-3Mo-3Sn alloys for the same
3 crystallographic texture and for a broad grain size range from 7 μm to 180 μm . The
4 dependence of superelasticity on grain size was studied by spherical nanoindentation.
5 Results displayed the same tendency as that observed during tensile tests. The small-sized β
6 grains favored the martensitic transformation, and exhibited the greater superelasticity. It is
7 confirmed that spherical nanoindentation is capable of characterizing superelasticity and is
8 sensitive enough to probe grain size effect in superelastic alloys. It is also shown that β grain
9 size evidently affects indentation hardness and modulus.

10

11 **Keywords:** Titanium alloys; Nanoindentation; Grain size; Superelasticity; Stress-induced
12 martensitic transformation.

13

14 **1. Introduction**

15 Metastable β -Ti alloys are well-known to display superelastic behavior which arises
16 from a reversible stress-induced martensitic (SIM) transformation between the
17 body-centered cubic (bcc) β phase and the orthorhombic α'' phase when they are deformed
18 cyclically upon loading and unloading within the first yielding region of their macroscopic
19 engineering tensile stress-strain curves [1, 2].

20 The occurrence of SIM transformation in superelastic metastable β -Ti alloys depends
21 on: (i) the metastability of β phase determined by the concentration of alloying elements; (ii)
22 the difference between test temperature and martensite start (M_s) temperature which
23 determines the required driving force for the transformation; (iii) the microstructure
24 characteristics of β phase such as crystallographic texture and grain size. The above variables
25 are influenced mutually and reciprocally, and can be tailored by the nature and concentration
26 of alloying elements and by the thermo-mechanical treatment conditions. For instance,
27 addition of alloying elements strongly affects the M_s temperature and the transformation
28 strain which arises from the lattice distortion between the parent β phase and the
29 stress-induced α'' phase, and subsequently affects the superelastic response. It was reported
30 that alloying with Zr and Mo elements is effective to increase the superelastic recovery strain
31 [3, 4]. The texture control is another efficient way to improve the superelasticity since the
32 martensitic transformation strain is strongly anisotropic and addition of a small amount of Sn,
33 as low as 1 to 4 at. %, in metastable β -Ti alloys is favorable for developing $\langle 110 \rangle_\beta$

34 recrystallization texture which is desirable for large transformation strain and subsequently
35 for large superelastic recovery strain [5]. Addition of Sn is also very effective at suppressing
36 the formation of athermal ω precipitates which adversely affect the superelasticity [6].
37 Ti-20Zr-3Mo-3Sn (at. %, Ti2033 for short) alloy has been proposed to show excellent
38 superelasticity, and occurrence of the reversible SIM transformation has been evidenced in
39 this alloy system by synchrotron X-ray diffraction [7, 8].

40 The superelastic performances of metastable β -Ti alloys are also largely dependent on
41 the grain size [11-13]. In the last twenty years, research topics on grain refinement in
42 superelastic alloys have attracted much attention since combinational properties such as
43 good superelasticity, small hysteresis (low dissipation energy), high cyclic stability and high
44 fatigue resistance can be expected to achieve so that new potential applications can be
45 explored [14]. An earlier study conducted by Grosdidier et al. [15] showed that reduced
46 grain size of the parent β phase lowers the M_s temperature, and thus increases the critical
47 stress for triggering the SIM transformation. The free energy change during such
48 transformation is responsible for the dependence of the triggering stress on grain size [16].
49 Bian et al. [17] proposed that smaller grain size causes higher grain boundary constraint
50 which restrains the shear deformation within grain interiors, and thus enhances the plasticity
51 resistance. It has also been reported that the reduced grain size could lower the martensitic
52 transformation strain, change the phase transformation path and improve the mechanical
53 properties of superelastic alloys [11, 18].

54 Bulk mechanical properties of materials are commonly measured under uniaxial
55 loading conditions such as uniaxial tension or compression. Recently, nanoindentation is
56 considered as a suitable and powerful technique for the characterization of local mechanical
57 properties and nanoscale deformation behavior owing to its capability of sensitively probing
58 indentation responses from small volumes of materials. By coupling with electron
59 backscattered diffraction (EBSD) analysis, nanoindentation also can be used to evaluate the
60 superelasticity of targeted individual grains with orientation indexed by EBSD [19]. It offers
61 an opportunity to independently investigate the influence of grain size on the superelasticity
62 by dissociating the texture factor.

63 The present study establishes a correlation concerning the capability of characterizing
64 the superelasticity between tensile testing and nanoindentation measurement, and elucidate
65 the influence of grain size on the superelasticity, indentation hardness and modulus at local
66 scale in the metastable β Ti2033 alloy. It would be valuable to use the coherency of
67 superelastic characteristics measured by macroscopic tensile testing and nanoindentation
68 technique to facilitate the evaluation of superelasticity on small-sized materials in the

69 absence of the ability to perform macroscopic tensile, compression or bending tests.

70 **2. Materials and methods**

71 The Ti2033 alloy ingots were elaborated by cold crucible levitation melting (CCLM)
72 technique from pure metals, homogenized at 1223 K for 20 h followed by water quenching,
73 cold-rolled into 0.5 mm thickness sheet with a thickness reduction rate of 95%, and then
74 machined into flat tensile specimens in dog-bone shape with 3 mm × 15 mm × 0.5 mm
75 gauge dimensions. These specimens were recrystallized at 973 K, 1073 K and 1173 K for 0.5
76 h, respectively, followed by water quenching to retain the metastable β phase. The specimens
77 were denoted as Ti2033-973K, Ti2033-1073K and Ti2033-1173K. It is worth to mention that
78 the β transus temperature of Ti2033 alloy has been detected by resistivity measurements to
79 be 963 K [7]. After thermal treatments, the specimens were treated in an HF/ HNO₃ solution
80 (1/1 ratio) to remove the surface oxide layer.

81 Macroscale mechanical properties of Ti2033 specimens were evaluated by tensile
82 testing on an INSTRON 3369 tensile machine in a strain control mode at a rate of 10^{-4} s⁻¹.
83 Cyclic tensile tests were conducted at room temperature with a strain increment of 0.5% by
84 steps until an elongation of 5.0% and each step was followed by a complete stress release.
85 The tensile direction was chosen parallel to the cold rolling direction. The grain size and
86 crystallographic orientations of individual grains were identified by EBSD on a scanning
87 electron microscope (SEM, JEOL JSM 7100F) equipped with an Oxford HKL EBSD system
88 and were analyzed by the HKL Channel 5 package. The surface of the specimens was
89 prepared by electrochemical polishing in an electrolyte composed of perchloric acid (6
90 vol. %) and methanol (94 vol. %) at -15 °C and 0.2 A current for 45 s. Superelastic response
91 of the Ti2033 alloy in all heat-treated states was investigated by nanoindentation using the
92 instrumented NHT Anton Paar nanoindentation test system. Nanoindentation measurements
93 were performed on selected grains along the surface normal direction at different penetration
94 depths. Spherical indenter with nominal tip radius of 50 μ m was used and calibrated on fused
95 silica sample to take into account the real shape of the tip. Individual grains with targeted
96 orientations were located by an optical microscope attached in the instrumented
97 nanoindentation test system, with the aid of EBSD orientation maps.

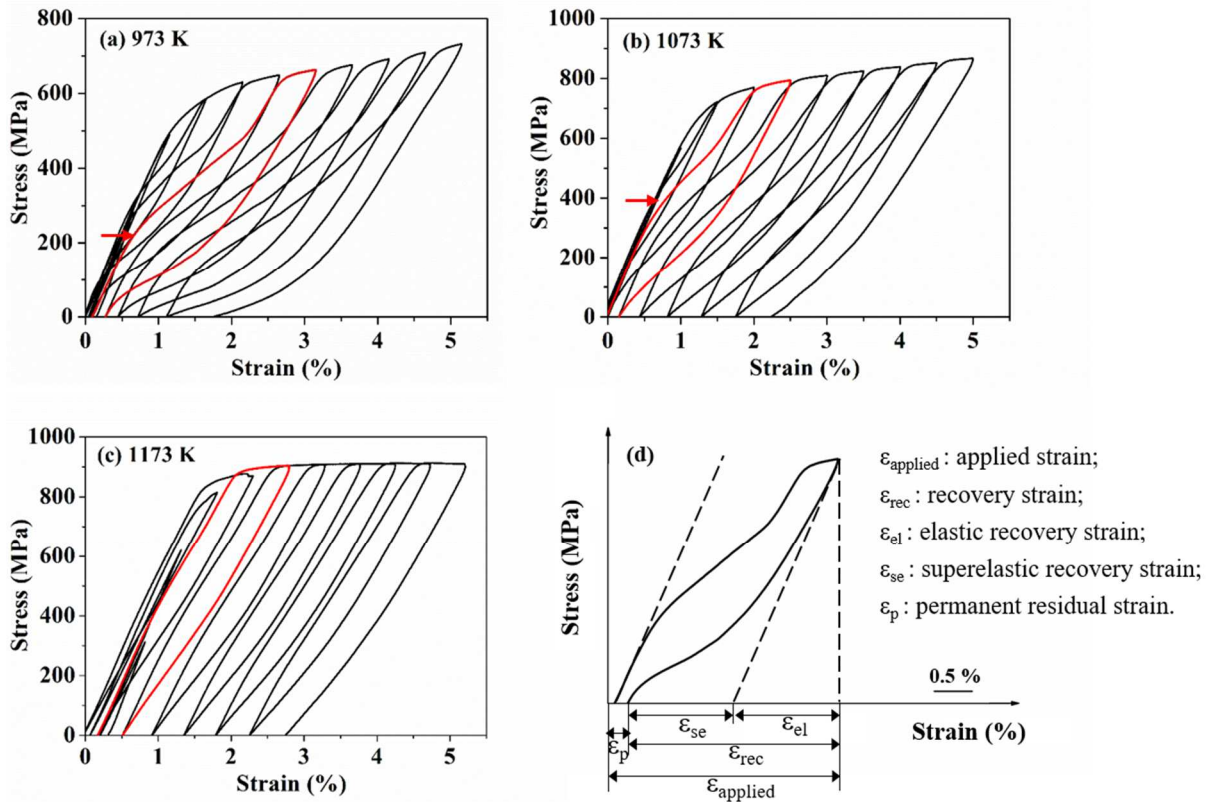
98 **3. Results and discussion**

99 **3.1 Grain size effect on superelasticity by tensile testing**

100 The tensile cyclic stress-strain curves of Ti2033 specimens recrystallized at 973 K,

101 1073 K and 1173 K for 0.5 h, respectively, are shown in Fig. 1. The stress-strain curves
 102 exhibit deformation characteristics of the double yielding and the stress hysteresis
 103 phenomenon associated with the occurrence of reversible SIM transformation between β and
 104 α'' phases [20, 21], demonstrating the superelasticity in Ti2033 alloy. The stress
 105 corresponding to the first yielding denotes the critical stress for SIM transformation, σ_{SIM} , as
 106 indicated by the arrow on the cycles highlighted in red. It is noticed that the σ_{SIM} increases
 107 with increasing heat treatment temperature. The yielding for SIM transformation becomes
 108 less distinct and the σ_{SIM} cannot be well defined for Ti2033-1173K specimen. The occurrence
 109 of SIM transformation can be understood regarding the competition among different possible
 110 accommodating deformation mechanisms in metastable β phase, such as slip, twinning and
 111 SIM transformation. Thus, SIM transformation is the earlier and dominant mechanism at
 112 lower grain sizes, and at higher grain sizes the σ_{SIM} tends towards the critical stress for
 113 dislocation slips σ_{CSS} , masking the SIM transformation altogether.

114 As indicated in Fig. 1d, for each individual loading-unloading cycle, the maximum
 115 applied strain ($\epsilon_{applied}$), and other four types of strain, elastic recovery strain (ϵ_{el}), superelastic
 116 strain (ϵ_{se}), total recovery strain (ϵ_{rec}) which is the summation of ϵ_{el} and ϵ_{se} , and permanent
 117 residual strain (ϵ_p) after complete unloading were evaluated from the stress-strain curves to
 118 characterize superelastic properties [5, 9].



119

120 Fig. 1 Tensile cyclic stress-strain curves of Ti2033 specimens recrystallized at (a) 973 K, (b) 1073 K and
 121 (c) 1173 K for 0.5 h, respectively. The curves were reorganized from [7]. (d) measurement scheme of the

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different strains from the red cycle presented in (a).

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The magnitudes of total recovery strain ε_{rec} and superelastic recovery strain ε_{se} extracted from the cyclic stress-strain curves for the three specimens were plotted as a function of applied strain $\varepsilon_{applied}$ of each cycle (Fig. 2a). The diagonal line in Fig. 2a represents the 100% full recovery. Almost perfect recovery is exhibited up to 2.5% for the Ti2033-973K alloy. At high $\varepsilon_{applied}$, the deviation of ε_{rec} from the diagonal line indicates the permanently residual strain ε_p , due to the occurrence of irreversible martensitic transformation and plastic deformation. For the Ti2033-973K alloy, the total recovery strain ε_{rec} firstly increases with increasing $\varepsilon_{applied}$ until reaches the maximum ε_{rec} of 3.5% and also obtains the maximum superelastic recovery strain ε_{se} of 2.3%. ε_{rec} and ε_{se} are clearly higher than those measured for Ti2033-1073K and Ti2033-1173K alloys. The strain recovery ratios were calculated as the ratio of strain recovery to the applied strain on each cycle:

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$$\eta_{\varepsilon_{rec}} = 100 * \frac{\varepsilon_{rec}}{\varepsilon_{applied}} \quad (1)$$

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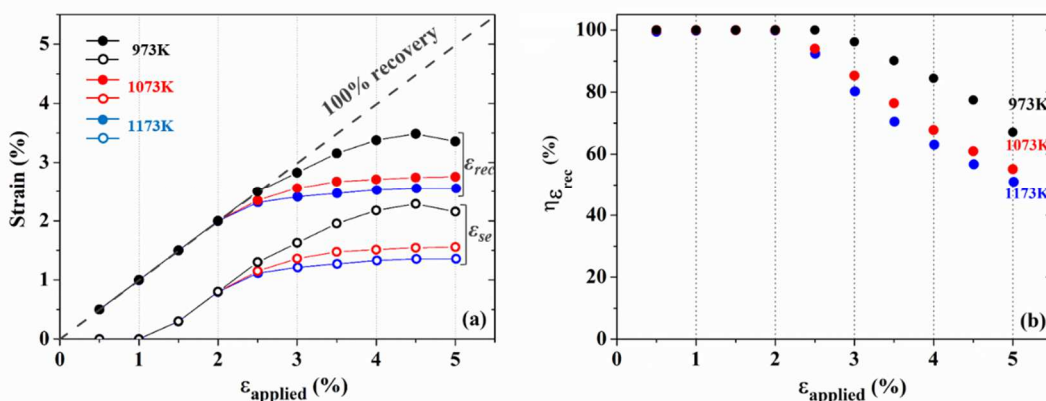
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The variation of strain recovery ratio $\eta_{\varepsilon_{rec}}$ with respect to the applied stress $\varepsilon_{applied}$ at each cycle is presented in Fig. 2b. It shows that the three alloys follow the same tendency: the magnitudes of $\eta_{\varepsilon_{rec}}$ remain at 100% to a certain strain level and then decrease with the increasing $\varepsilon_{applied}$. It also shows that the strain recoverability is dependent on the thermal treatments. It can be concluded that by tensile testing, the recovery performances of the studied specimens behave as the following sequence: Ti2033-973K > Ti2033-1073K > Ti2033-1173K.



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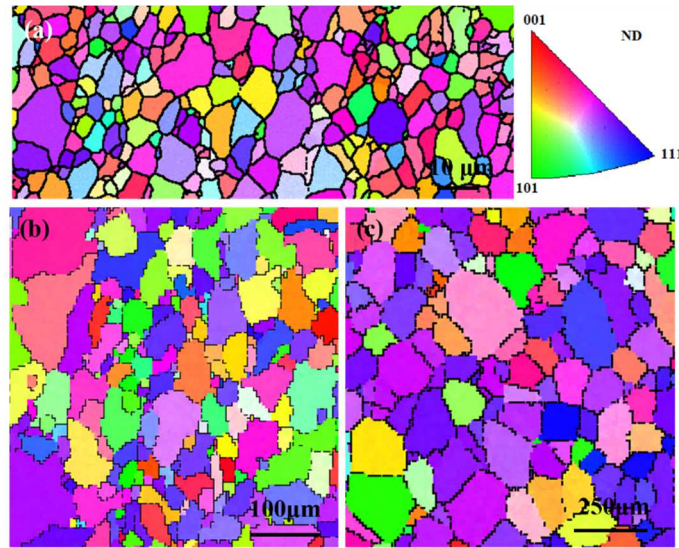
Fig. 2 (a) Total recovery strain ε_{rec} , superelastic strain ε_{se} , and (b) recovery strain ratios $\eta_{\varepsilon_{rec}}$ extracted from cyclic loading-unloading tensile curves as shown in Fig.1, and plotted as a function of the applied strain $\varepsilon_{applied}$ of each cycle.

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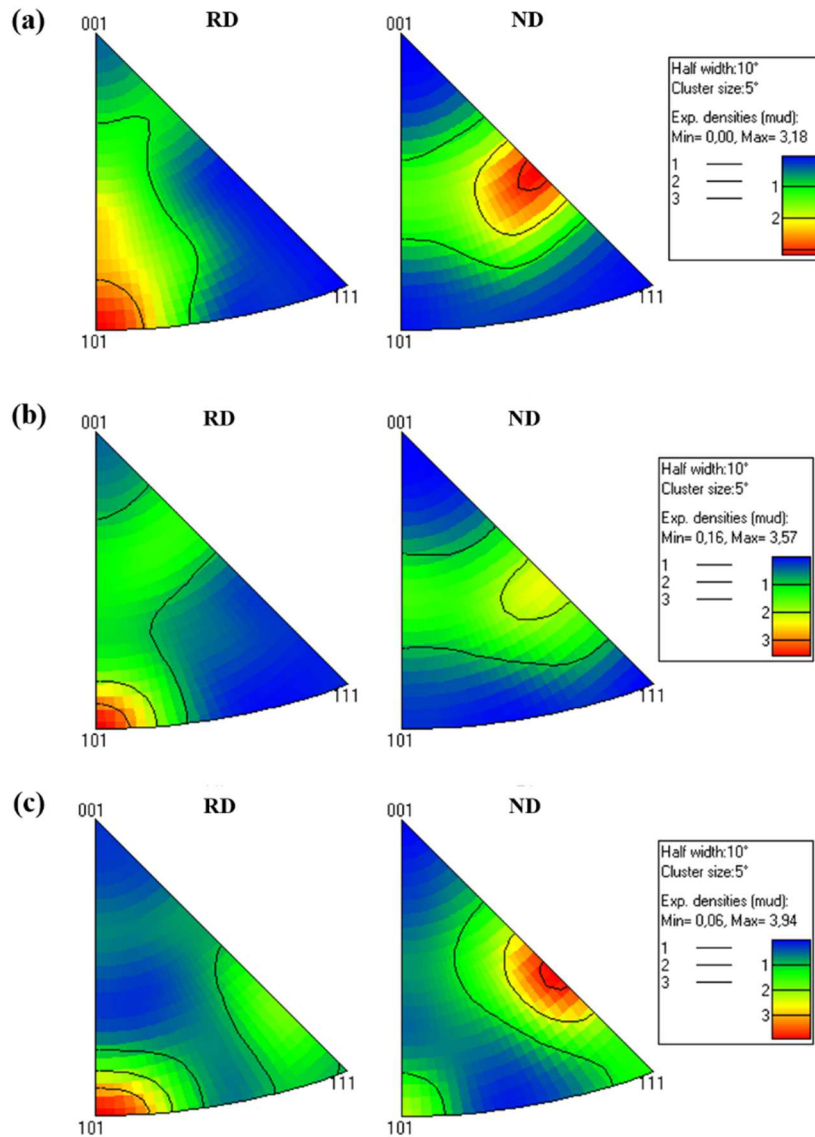
The different levels of recoverability in superelastic alloys can be attributed as many influencing factors, such as texture [5, 7, 8, 22, 23], phase composition [5, 24],

148 transformation strain [23, 25], competition between the critical stresses for SIM
149 transformation σ_{SIM} and for dislocation slip σ_{css} [13, 24, 26], and grain size [12, 13]. It is
150 likely that the observed differences in the strain recoverability of Ti2033 alloys arise from
151 the different heat treatments causing the difference in grain sizes. Thus, it is of great interest
152 to elucidate the influence of heat treatment temperature on the microstructure and
153 superelasticity of Ti2033 alloys. Fig. 3 presents the EBSD orientation maps along the normal
154 direction (ND) for Ti2033 alloys recrystallized at 973K, 1073K, and 1173K. All specimens
155 display typical equiaxed β -grain microstructures. The average grain size determined from the
156 EBSD maps was calculated to be 7 μm , 70 μm and 180 μm , for the Ti2033-973K,
157 Ti2033-1073K, and Ti2033-1173K, respectively, with standard deviation of 2 μm , 16 μm and
158 41 μm , respectively. That is, grain size decreases with decreasing heat treatment temperature.



159
160 Fig. 3 EBSD orientation maps along the normal direction (ND) for recrystallized Ti2033 alloys at: (a) 973
161 K; (b) 1073 K; (c) 1173 K.

162 To furthermore compare the crystallographic orientation of the three specimens, the
163 corresponding inverse pole figures (IPF) are shown in the rolling direction (RD) and ND for
164 each specimen in Fig. 4. It can be seen that although the specimens were subjected to
165 different heat treatments, all displayed the same $\{113\}_\beta \langle 110 \rangle_\beta$ strong recrystallization
166 texture. It offers an opportunity to independently investigate the influence of grain size on
167 the superelasticity by dissociating the texture factor. Therefore, it is reasonable to accept that
168 during tensile test the increased superelasticity observed in the Ti2033 alloy recrystallized at
169 lower temperature is predominantly attributed to the reduced grain size. It might be very
170 interesting to investigate the grain size effect on superelastic behaviors of Ti2033 alloys
171 under compression at the local scale using nanoindentation.



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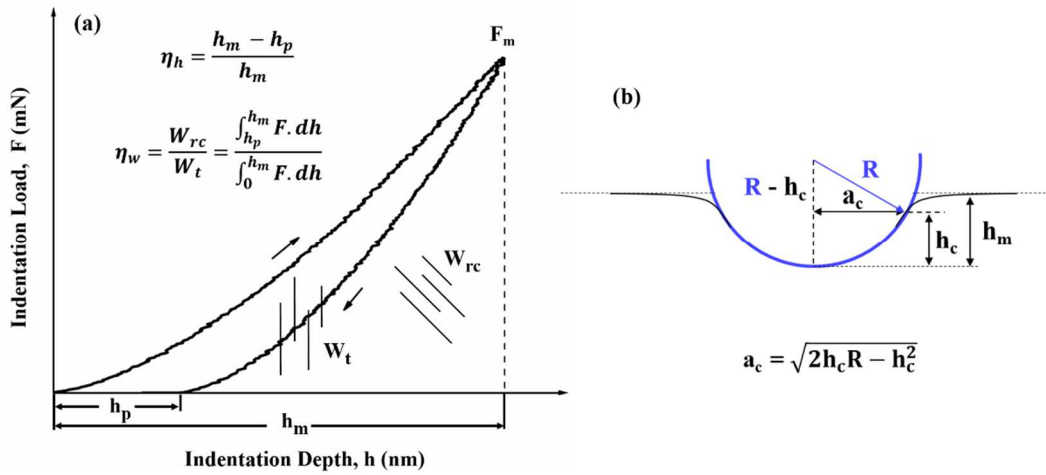
Fig. 4 EBSD inverse pole figures for recrystallized Ti2033 alloys at: (a) 973 K; (b) 1073 K; (c) 1173 K.

174 3.2 Grain size effect on superelasticity by nanoindentation

175 Combining EBSD orientation maps and nanoindentation tests, it is practically feasible
176 to probe the superelasticity at the grain scale in localized region. The differently orientated
177 grains show traceable grain boundaries under the microscope attached in nanoindentation
178 platform, which facilitates the localization of the target grains with specific orientation
179 identified from EBSD maps. Among the three specimens with different grain sizes, the areas
180 with grains oriented or closely oriented in $\langle 113 \rangle_{\beta}$ direction were selected and
181 nanoindentation measurements were performed on those selected grains, so as to investigate
182 the grain size effect on the superelastic behavior at grain scale.

183 To characterize the superelasticity of materials by nanoindentation, the depth recovery
184 ratio η_h and the work recovery ratio η_w can be extracted from nanoindentation load-depth

185 ($F-h$) curve [27], as highlighted in the schematic in Fig. 5a. Here, h_m denotes the maximum
 186 indentation depth, h_p denotes the permanently residual depth. The total energy W_t and the
 187 recoverable work W_{rc} are the integration area performed along the loading curve and the
 188 unloading curve, respectively. The magnitude of W_{rc} indicates the capability of a superelastic
 189 material to accommodate the deformation energy during indentation causing no damage
 190 [28].



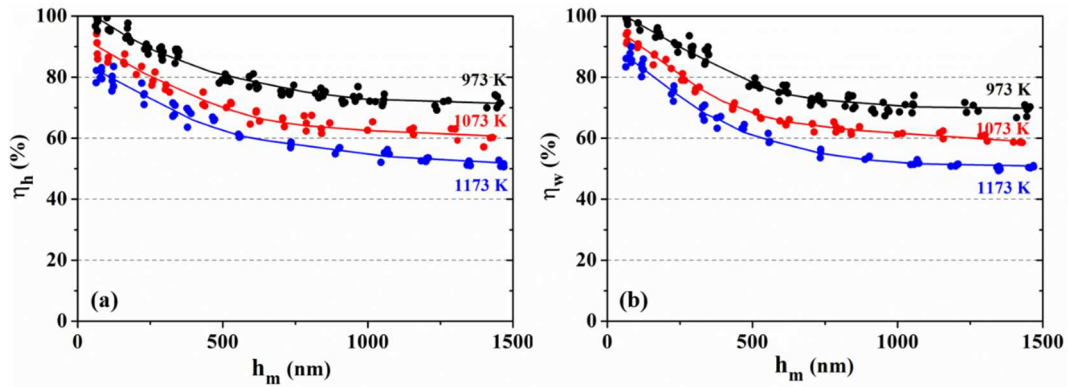
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192 Fig. 5 (a) Schematic nanoindentation $F-h$ curve and (b) schematic illustration of indentation upon loading
 193 showing the parameters used for the analysis.

194 Nanoindentation matrices were performed with maximum indentation depth h_m varying
 195 in the range of 50 - 1500 nm. The contact radius between the indenter and the specimen,
 196 $a_c = \sqrt{2h_c R - h_c^2}$, has been correspondingly calculated to be in range of 1.6 - 9.2 μm . Here, h_c
 197 is the contact depth and R is the tip radius, as shown in Fig. 5b. Therefore, it is worth noting
 198 that the real contact is mainly limited to the core of individual grains.

199 The η_h and η_w measurements were plotted as a function of h_m for the three Ti2033
 200 specimens in Fig. 6. Each point represents the average value of at least 5 measurements.
 201 Magnitudes of η_h and η_w deviate initially from the 100% line at very shallow depths, instead
 202 of remaining at 100% value like the case of $\eta_{\epsilon_{rec}}$ in Fig. 2b. It is probably due to the different
 203 loading conditions applied during tensile testing and during nanoindentation. The tensile
 204 testing corresponds to uniaxial stress condition while the nanoindentation produces rather
 205 complex loading conditions with triaxial stress state and constant change of the deformed
 206 volume. The stress of uniaxial tension testing is applied homogeneously in bulk and
 207 increases gradually with applied strain $\epsilon_{applied}$, whereas during nanoindentation the spatial
 208 stress field under indenter tip is distributed radially, decreasing along the radial direction.
 209 Various studies [27, 29-31] modeled the deformation process underneath the indenter tip
 210 using four concentric shells: a fully transformed and plastically deformed martensite region

211 right beneath the tip, surrounded by a fully transformed and reversible martensite region, a
 212 partially transformed region and an untransformed parent β phase region. Therefore, once the
 213 stress state beneath the indenter tip is beyond the critical stress for dislocation slips σ_{CSS} ,
 214 plastic deformation occurs and, therefore, the recoverability decreases, even at very shallow
 215 h_m .



216

217 Fig. 6 Variations of depth recovery ratio η_h (a) and work recovery ratio η_w (b) versus maximum
 218 indentation depth h_m for Ti2033 specimens recrystallized at 973 K, 1073 K and 1173 K, respectively.

219 Besides, it is also shown that the recovery ratios, η_h and η_w , for the three Ti2033 alloys
 220 behave in the same way: decrease dramatically at low depths and saturate gradually at high
 221 depths. The values of η_h and η_w vary from 100% to 70% for the Ti2033-973K alloy, from 95%
 222 to 60% for the Ti2033-1073K alloy, and from 82% to 50% for the Ti2033-1173K alloy,
 223 respectively. By comparison, the Ti2033 alloy subjected to different heat treatments
 224 demonstrates the superelasticity characterized by nanoindentation in the following sequence:
 225 Ti2033-973K > Ti2033-1073K > Ti2033-1173K, which is in agreement with the macroscale
 226 recovery responses evaluated by tensile tests.

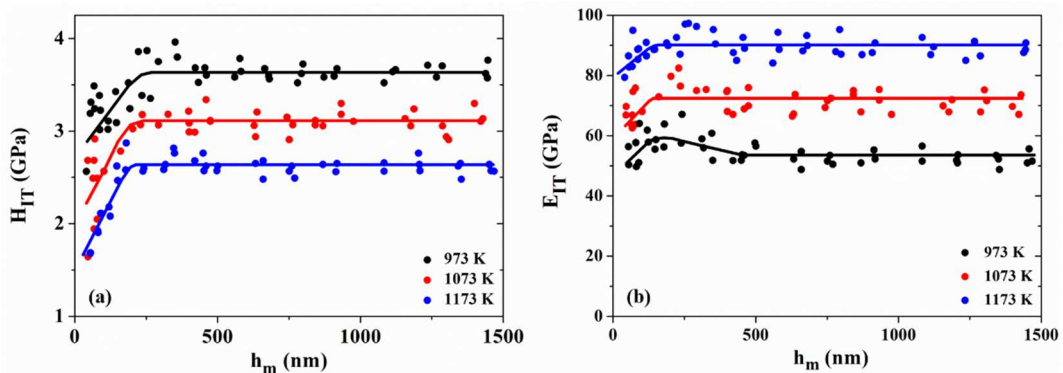
227 Nanoindentation is sensitive enough to probe the influence of grain size on the
 228 recoverability. The grain size indeed affects the superelasticity in Ti2033 alloys. The
 229 Ti2033-973K alloy with the smallest grain size exhibits the highest values of η_h and η_w ,
 230 showing the highest superelasticity. Similar observation has been reported in β
 231 Ti-20Zr-12Nb-2Sn alloy [12]. It is due to that the critical stress for SIM transformation σ_{SIM}
 232 for the Ti2033-973K alloy has the lowest value and it increases with the increasing grain size
 233 tailored by heat treatments, as discussed above. It has been sufficiently evidenced that the
 234 σ_{SIM} depends on various factors, such as alloying elements [32], test temperature [20],
 235 presence of second phase [26, 33, 34], the strain rate [35], and grain size of β phase [16,
 236 36-38]. In the present study, the focus is mainly on the analysis of the grain size effect on the
 237 σ_{SIM} . Several studies have made the supportive reports in agreement with our observations.
 238 Bhattacharjee et al. [16] pointed out that the σ_{SIM} increases with increasing β grain size up to

239 300 μm in Ti-10V-2Fe-3Al alloy. The dependence of σ_{SIM} on β grain size is related to the
 240 free energy changes for the SIM transformation. Similarly, Gil et al. [37] observed a linear
 241 increase in σ_{SIM} with increasing grain size. The elastic energy stored in grain boundary favors
 242 SIM transformation. The transformed martensite interacts with grain boundaries, increases
 243 the local elastic energy, and promotes the nucleation of new martensite. Wayman et al. [39]
 244 also stated that grain boundaries could act as one of the most preferential nucleation sites in
 245 martensitic transformation. Thus, grain refinement with higher density of grain boundaries
 246 facilitates the SIM transformation.

247 In addition, the grain size influences the relative mobility of dislocations in the parent
 248 and martensitic phases since the grain boundaries act as barriers for the dislocation
 249 movements. Grain refinement increases the critical stress for dislocation slips σ_{CSS} , and thus
 250 enhances the resistance to permanent plasticity deformation. Larger difference between the
 251 critical stresses for plasticity deformation and for SIM transformation results in a larger
 252 recovery strain in superelastic Ti-Nb-Ta alloy [40].

253 Therefore, it can be concluded that the higher critical stress for dislocation slips σ_{CSS} and
 254 the lower critical stress for SIM transformation σ_{SIM} contribute to the excellent
 255 superelasticity with a larger recovery strain in Ti2033-973K alloy with the smaller grain size.

256 The indentation hardness H_{IT} and modulus E_{IT} as a function of h_m have been extracted
 257 according to Oliver-Pharr method [41], and plotted for the three Ti2033 alloys in different
 258 grain sizes in Fig. 7. The smaller the grain size, the more grain boundaries underneath the
 259 indenter tip. For instance, in the case of Ti2033-973K, the highest density of grain
 260 boundaries will be involved during the indentation process. It is shown that Ti2033-973 K
 261 with smallest grain size exhibits the highest H_{IT} and the lowest E_{IT} .



262
 263 |Fig. 7 Indentation hardness H_{IT} (a) and modulus E_{IT} (b) versus maximum indentation depth h_m for Ti2033
 264 specimens recrystallized at 973 K, 1073 K and 1173 K, respectively.

265 The variation of indentation hardness versus grain size is in agreement with Hall-Petch
 266 relationship, which is also called grain refinement strengthening effect. This strengthening is
 267 attributed to the blockage of dislocation motions by the high density of grain boundaries. For

268 superelastic materials involving the SIM transformation, indentation hardness reflects not
269 only the resistance for the plastic deformation, but also the resistance for the phase
270 transformation, and indentation modulus is the apparent modulus associated with the
271 transformed volume fractions of β and α'' phases. The Ti2033-973 K alloy shows lowest E_{IT} ,
272 probably due to its more prominent superelastic recovery accompanied by reversible SIM
273 transformation that makes the material soft from the pseudo-elastic view.

274 **4 Conclusion**

275 In the present study, the superelastic Ti-20Zr-3Mo-3Sn (at. %) alloy was elaborated and
276 subjected to different heat-treatments, and their microstructure presented the same strong
277 $\{113\}_{\beta}<110>_{\beta}$ recrystallization texture but different average grain sizes were evidenced by
278 EBSD. Investigation was performed to shed lights on the β grain size effect on the
279 superelastic and mechanical properties. The main conclusions were made as follows:

280 (1) The evolution in the magnitude of the superelastic response probed by
281 nanoindentation is in agreement with that measured by tensile tests. It confirms that
282 nanoindentation can be used as an efficient tool to characterize the superelasticity and is
283 sensitive enough to probe the grain size effect on the superelasticity.

284 (2) The superelastic behavior based on the reversible stress-induced martensitic
285 transformation can be influenced by the grain size. The small-sized grains favor the
286 martensitic transformation, resulting in high superelasticity.

287 (3) The alloy with smallest grain size exhibits the highest H_{IT} and the lowest E_{IT} .

288

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