Research Article

Victor Grishkov, Vladimir Kopylov, Alexander Lotkov*, Svetlana Latushkina, Anatoly Baturin, Natalia Girsova, Victor Timkin, and Dorzhima Zhapova

Effect of warm equal channel angular pressing on the structure and mechanical properties of Ti_{0.16}Pd_{0.14}Fe (wt%) alloy

<https://doi.org/10.1515/rams-2019-0005>

Received Aug 28, 2018; accepted Oct 4, 2018

Abstract: Here we analyze the microstructure and phase composition of a Ti alloy with 0.16Pd and 0.14Fe (wt%) alloy exposed to warm equal channel angular pressing (ECAP) at 648 K. The analysis shows that after four ECAP passes, the material assumes a submicrocrystalline structure with an average grain size of 0.28 μm , as against its initial value 10 μm , and that the α phase dominates in the alloy both before and after ECAP. The initial alloy reveals a high content of Fe and Pd atoms near grain boundaries compared to central grain regions. Such near-boundary zones contain orthorhombic α'' martensite in addition to the α phase, and β or $\alpha + \beta$ particles are found directly at the grain boundaries. These features of the phase composition are inherited after ECAP. The yield strength of the ECAP treated alloy is 500 MPa, being greater than the initial strength 350 MPa, and its margin of plasticity is rather high. The torsional strain up to fracture in the initial and in the ECAP treated alloy is 70% and 50%, respectively.

1 Introduction

Titanium and its alloys hold the lead in medicine over other metal materials [1–3] due to their high strength, high corrosion resistance, and biocompatibility. The best corrosion resistance in saline solutions and other corrosive media is displayed by Ti alloys of grade 7 containing 0.14–

0.20Pd (wt%) [4, 5]. Research data show that Ti alloys with a small Pd content are highly resistant to corrosion even in saline solutions with fluorine compounds, which greatly speed up the corrosion of other Ti alloys used in medicine [6]. Such Ti–Pd alloys are produced in different countries of the world (USA, Great Britain, Russia, Japan, China, etc.) as they serve to produce devices and constructions for operation with chemically active media [4, 7], and their use is expected in shipbuilding [8] and in manufacturing storage containers for high-level nuclear waste [9]. However, Ti–Pd alloys have low mechanical properties (yield strength ~ 400 MPa), being a barrier on the way to their wider application, including medical. By now, technologies of severe plastic deformation are available allowing the formation of a submicro- or a nanocrystalline structure in metals and alloys as well as improvement of their mechanical properties [10–12]. Among these technologies is the equal channel angular pressing (ECAP). Unfortunately, we are aware of only one paper [13] which reports on the structure and properties of an ECAP treated alloy of grade 7 (Ti–0.14Pd–0.03Fe, wt%), showing that two ECAP passes with a channel angle of 105° at 673 K provide a microcrystalline structure with a grain size of ~ 3.8 μm in the material and improve its corrosion resistance compared to the initial coarse-grained state.

Here we present research data on the structure, phase state, and mechanical properties of a Ti alloy containing 0.16Pd and 0.14Fe wt% after equal channel angular pressing with a channel angle of 90° at 648 K.

2 Experimental procedure

The test alloy contained 0.16Pd, 0.14Fe, 0.02C, 0.01N, 0.001H, 0.12O₂, and balance Ti (wt%). The alloy was produced in China; its analogues are alloy 4200 and alloy of grade 7. The alloy was shaped into specimens of cross-section 14×14 mm² and length 160 mm from bars of diameter 20 mm and were exposed to ECAP in dies with a

***Corresponding Author: Alexander Lotkov:** Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademicheskoy Ave., Tomsk, 634055, Russia; Email: lotkov@ispms.tsc.ru

Victor Grishkov, Anatoly Baturin, Natalia Girsova, Victor Timkin, Dorzhima Zhapova: Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademicheskoy Ave., Tomsk, 634055, Russia

Vladimir Kopylov, Svetlana Latushkina: Physical Technical Institute NASB, 10 Kuprevich St., Minsk, 220141, Belarus

channel angle of 90° at a temperature of 648 K. The strain rate was 1 s^{-1} , and the true (logarithmic) strain was 0.7 per pass. The specimens were examined after one pass, two passes by route A, and three and four passes by route B. The grain structure of the initial material was examined by optical metallography (AXIOVERT-200MAT) and scanning electron microscopy (LEO EVO 50). The phase state of the initial and treated materials was examined on their lateral and longitudinal sections by X-ray diffraction analysis (DRON-7) and TEM – transmission electron microscopy (JEM-2100 with energy-dispersive X-ray spectroscopy). The foils for transmission microscopy were cut from longitudinal and lateral sections of the initial and treated materials, were mechanically thinned to 0.2 mm, and were polished in an electrolytic solution containing H_2SO_4 , HF, and HNO_3 with a volume percentage of 30, 64, and 6, respectively. The mechanical properties of the material after ECAP were investigated on specimens of cross-section $1 \times 1 \text{ mm}^2$ with a gage length of 9 mm. Preliminarily, the specimens were exposed to mechanical grinding and electrolytic polishing.

3 Research results

Our research suggests that the initial alloy has a microcrystalline structure. The maximum grain sizes in its longitudinal and lateral sections are close, measuring 24 and $19 \mu\text{m}$, respectively. The grains are near-equiaxed, and their maximum to minimum size ratio is 1.4 and 1.2 length- and cross-wise, respectively. The average grain size in the direction of maximum elongation in both sections are also close: $10 \mu\text{m}$ for longitudinal and $8 \mu\text{m}$ for lateral. According to X-ray diffractometry, the main phase in the alloy is α , and its lattice parameters ($a = 2.951 \text{ \AA}$, $c = 4.686 \text{ \AA}$) correspond to those in $\alpha\text{-Ti}$ ($a = 2.945\text{--}2.953 \text{ \AA}$, $c = 4.679\text{--}4.730 \text{ \AA}$ [2]). Any other reflection distinct from the α phase, except for TiC, is not found.

The X-ray diffraction data agree with transmission electron microscopy data. In the volume of most grains, the main phase is α whose typical microdiffraction patterns are shown in Figure 1a. At the same time, as can be seen from Figure 1, an intragranular structure composed of submicro- and nanosized crystallites is found inside the grains, suggesting the presence of not only the α phase but also α' arising in Ti alloys due to $\beta \rightarrow \alpha'$ martensite transformation [4, 14]. The α' phase has the same hcp (hexagonal close packet) structure as the α phase, and the parameters of both structures differ slightly. In our study, any difference in their lattice parameters escaped detection,

and we will further refer to the α phase as the main hcp phase of Ti0.16Pd0.14Fe (wt%). Our TEM analysis reveals specific features in the phase state of the alloy near and at the boundaries of grains which are not detected by X-ray diffractometry. In particular, the microdiffraction pattern of a microvolume near a grain junction (Figure 1b, upper arrow) points to the presence of orthorhombic α'' martensite in addition to the α phase. Similar microvolumes with a two-phase $\alpha + \alpha''$ structure are observed directly near the grain boundaries (zone $\pm 1 \mu\text{m}$) and at a distance of 2–3 μm from them. Moreover, part of the grain boundaries and grain junctions contains particles with a structure distinct from α and α' (Figure 2). The fraction of such grain boundaries is small, and its quantitative estimation fails. Such precipitates at grain junctions are most often shaped as a truncated ellipsoid, and their size ranges from 50 nm to $\sim 1 \mu\text{m}$. Along the grain boundaries, either single spheroidal or ellipsoidal particles and more rarely the chains of similar particles are observed. In some cases, coarser plate-like particles with a lateral size of up to $0.5 \mu\text{m}$ and length of up to $\sim 3 \mu\text{m}$ occur at the grain boundaries.

Figure 1: Bright field TEM initial microstructure of Ti0.16Pd0.14Fe (wt%) alloy and diffraction patterns from central grain regions in α state (a) and near-junction regions in $\alpha + \alpha''$ state (b).

According to microdiffraction patterns, the particles differ in phase state. The structure of spherical particles with a size of $1 \mu\text{m}$ and less corresponds to the monophase bcc structure of $\beta\text{-Ti}$ with a lattice parameter of $3.25\text{--}3.28 \text{ \AA}$; according to available data [2], the lattice parameter of

Figure 2: Bright field TEM grain boundary particle with $\alpha + \alpha''$ phase structure (a) and diffraction pattern from its center (inset); dark field image in coincident (011) and (002) reflections of β and α'' phases, respectively (b)

β -Ti at 300 K is 3.269–3.271 Å. Coarser particles can have both a β structure and a two-phase $\beta + \alpha''$ structure, like the particle in Figure 2. By estimates, the lattice parameters of α'' martensite in near-boundary zones and in $\beta + \alpha''$ precipitates are $a = 2.94$ – 3.02 Å, $b = 4.96$ – 5.17 Å, and $c = 4.58$ – 4.68 Å. In general, these values are close to the lattice parameters of α'' martensite in Ti alloys [13, 14]. The presence of $\alpha + \alpha''$ or α'' microvolumes in near-boundary regions and in grain boundary particles evidences that these microvolumes differ in elemental composition from both central grain regions and nominal state of the alloy.

Our energy dispersive X-ray analysis of the elemental composition of alloy microvolumes in central grain regions, in near-boundary regions, including those with β precipitates, and in particles at grain boundaries and junctions suggests the following. In central grain regions, the content of Fe and Pd is either coincident with or markedly lower than their nominal content in the alloy: 0.05–0.09 at% for Pd and 0.08–0.12 at% for Fe. In near-boundary $\alpha + \alpha''$ and α'' regions similar to those in Figure 2, the content of Fe and Pd is 1.5–3 times higher than their nominal content in the alloy. In particular, the Fe content reaches 0.17–0.43 at% in these regions, and the Pd content measures 0.04–0.24 at%. The highest Fe and Pd content falls on grain boundary particles. In the microvolumes of these precipitates, the Fe content is 5–11.8 at%, and the Pd content is 0.4–0.9 at%. By and large, the elemental composition of the particles at the boundaries corresponds to a

ternary $\text{Ti}_{1-x-y}\text{Fe}_x\text{Pd}_y$ alloy, where $x \approx 6$ –14 wt% (5–12 at%) and $y \approx 0.09$ –1.9 wt% (0.4–0.9 at%).

Thus, the initial Ti0.16Pd0.14Fe (wt%) alloy has a microcrystalline structure with an average grain size of ~ 10 μm , and its main phase is α . Compared to the nominal composition of the alloy, the Fe and Pd content in its central α -structured grain regions is lower, and in near-boundary regions, it is higher, which is responsible for their two-phase $\alpha + \alpha'$ or single-phase α'' states. The most intense segregation of Fe and Pd atoms falls on grain boundaries and junctions such that these microvolumes can contain β -Ti(Pd, Fe) precipitates with a size of 0.6–3.5 μm in which the Fe and Pd content is 6–14 wt% (5–12 at%) and 0.9–1.9 wt% (0.4–0.9 at%), respectively.

According to X-ray diffraction data, the phase state of the alloy after ECAP at 648 K remains the same. The diffraction patterns of all specimens, irrespective of the number of passes, are qualitatively similar to those of the initial alloy, showing only reflections of the hexagonal α phase. However, the peak intensities and their ratio change, as the pressing changes the texture of the alloy, and the peak half-width increases compared to the initial state, which is typical for deformed materials.

Our TEM analysis shows that the ECAP treated alloy inherits the features of the initial phase state such as β or $\beta + \alpha''$ particles of size ~ 1 μm (Figures 3, 4). The precipitates hold their size and spheroidal or ellipsoidal shape at any number of passes. After one ECAP pass, the boundaries of

Figure 3: Bright field TEM of β particles in Ti0.16Pd0.14Fe (wt%) alloy after one (a), two (b), three (c), and four (d) ECAP passes

adjacent grains still reveal their traces, and as the number of passes is increased, the size of fragments (grains and subgrains) in the volume surrounding the particles decreases and the microstructure becomes more and more homogeneous. After three and four ECAP passes, the material assumes a homogeneous submicrocrystalline structure free of signs of the initial grain boundaries. However, the treated alloy reveals α'' and $\alpha + \alpha''$ microvolumes near the particles, as is the case in the initial state (Figure 4). The particles are enriched in Fe up to 10–11 at% and in

Pd up to 1–1.3 at%, like similar precipitates in the initial alloy. In a near-precipitate region 0.5–1 μm thick, the Fe and Pd content is also higher than the nominal content of these elements in the alloy, measuring from 0.12 to 0.4–0.6 at%. The immediate surroundings of β particles reveal microvolumes with a three-phase structure: α , α'' , and β . The β phase is represented by nanosized (20–40 nm) fragments whose presence in the zones with a high initial content of Fe and Pd is likely due to local nanosized segregation which occurs under severe plastic deformation at 648

Figure 4: Bright field TEM image of β particle (a, region 1) and its diffraction pattern (inset); diffractions patterns from local regions 2 and 3 (b, c, respectively), and dark field image in (021) reflection of α'' phase (d). Two ECAP passes, route A

K and in which the content of these elements is even higher than the initial one.

Figure 5 and 6 show typical microstructures without coarse β or $\alpha'' + \beta$ particles in the alloy after ECAP at 648 K. It should be noted that after one ECAP pass, the initial microcrystalline structure transforms to a fragmented structure with a maximum fragment size of $2\text{ }\mu\text{m}$. However, after two passes, the material assumes a more homogeneous

microband structure with mostly submicrocrystalline non-equiaxed fragments (Figure 5). Any clearly defined traces of the initial grain boundaries are not found. After two passes, both α and $\alpha + \alpha''$ fragments are detected on microdiffraction patterns (Figure 5a, inset). As it follows from dark field images in coincident reflections of α and α'' , the two-phase regions appear as bands of width $\sim 1\text{ }\mu\text{m}$ (Figure 5b). Increasing the number of passes to 3 and 4 (route B) in-

Figure 5: Bright field TEM microstructure of Ti0.16Pd0.14Fe (wt%) alloy after two ECAP passes by route A at 648 K (a) and diffraction pattern of its local central region (inset); dark field image in coincident (112) and (012) reflections of α'' and α phases, respectively (b)

creases the grain-subgrain structure homogeneity, and the fragment shape tends to equiaxial (Figure 6). At the same time, the structure likely retains the high content of Fe and Pd in wide (up to 1.5 μm) near-boundary grain regions after ECAP, which determines their phase state. Evidence of this can be found from changes in the phase state of structural fragments after three and four ECAP passes. In particular, after three passes, the region of width $\pm 1 \mu\text{m}$ each way from a bright line in Fig. 6a reveals frequent local ($\sim 200 \text{ nm}$) zones of either α'' fragments (e.g., symbols “x” in Figure 6a, diffraction pattern in Figure 6b) or $\alpha + \alpha''$ fragments. The amount of α fragments in this region is small (Figure 6c, d). Directly on the bright line, a β fragment of size $\sim 0.5 \mu\text{m}$ (fragment 1) similar to grain boundary particles in the initial material is found. The microdiffraction patterns of microvolumes more distant from the bright line in Figure 6a (e.g., symbols “+”) are characteristic of the α phase.

Figures 7, 8 present diagrams plotted from bright and dark field TEM images to illustrate the effect of warm ECAP on the size of structural fragments (grains and subgrains) in Ti-0.16Pd wt%. It is seen from Figure 7 that after the first pass, the largest fragment sizes in the direction of maximum elongation and perpendicular to it are more than 10 times smaller than the average grain size in the initial alloy. As the number of passes is increased from 1 to 4, the decrease in the size of fragments is less steep, and their shape tends to equiaxial. Figure 8 shows the average fragment sizes $\langle d \rangle$ calculated from fragment size distributions versus

the number of passes. It is seen from the figure that the first two passes provide an efficient decrease in $\langle d \rangle$, and after three and four passes, $\langle d \rangle$ is almost the same. Thus, warm (648 K) equal channel angular pressing provides a sub-microcrystalline structure with an average grain/subgrain size of 0.28 μm in which the main phase is α -Ti. The deformed material inherits the features of the initial phase state due to the segregation of Fe and Pd atoms at the initial grain boundaries. In particular, its structure contains α'' fragments, $\alpha + \alpha''$ fragments, and β -Ti(Fe, Pd) precipitates (at least partly) in which the Fe and Pd content can reach respectively 10–11 at% and 1–1.3 at% at a maximum particle size of 1.5 μm .

Figure 9 shows stress–strain curves (τ – γ) under torsion for Ti0.16Pd0.14Fe (wt%) before and after ECAP. The dependences have a near-parabolic form typical of materials which pass from the elastic to the plastic range and experience an almost linear increase in severe plastic strains with applied stress up to fracture. It is seen from Figure 9 that the material after ECAP becomes hardened and requires a higher applied stress to be deformed to the same level as the initial material. The data of Figures 9 and 10 suggest that compared to route B, route A provides more efficient hardening of Ti0.16Pd0.14Fe (wt%). After the second pass by route A, the τ – γ curve lies in the higher stress range than that after three passes by route B, approximating the curve for this route after four passes (Figure 9). This finds evidence in Figure 10 from which it follows that the

Figure 6: Bright field TEM microstructure of Ti0.16Pd0.14Fe (wt%) alloy after three ECAP passes (a), typical diffraction pattern of α'' fragments marked as “x” (b), diffractions from α fragment 2 (c), and dark field image in $(01\bar{2})$ reflection of α phase (d). Other notation in (a): β particle (1) and α fragments (+)

failure stress τ_f is maximal after the second pass by route A (~ 900 MPa), whereas the increment in τ_f after four passes by route B is lower (~ 30 MPa). For the alloy in the initial state and after the first pass and the second pass by route A, the failure strain γ_f (margin of plasticity or elongation δ at the point of tensile fracture) is almost the same and high, measuring $\gamma_f \sim 70\%$. After three and four passes by route B, γ_f decreases almost linearly from $\sim 70\%$ to $\sim 50\%$ (Figure 10), *i.e.*, its decrease with respect to γ_f in the initial

alloy is 29%. An important characteristic of materials is the yield strength ($\tau_{0.3}$ under torsion and $\sigma_{0.2}$ under tension) whose increase greatly extends the range of their possible practical applications. How the yield strength $\tau_{0.3}$ changes in Ti0.16Pd0.14Fe (wt%) upon its transition from micro- to submicrocrystalline structure during ECAP at 648 K can be judged from Figure 10. It is seen that the dependence of $\tau_{0.3}$ on the number of ECAP passes is generally close to linear. The yield strength $\tau_{0.3}$ increases from 370 MPa in the

Figure 7: Maximum sizes of coarse fragments vs number of ECAP passes (TEM data): longitudinal (1) and transverse (2) directions

Figure 8: Average grain/subgrain size vs number of ECAP passes at 648 K

initial alloy to 500 MPa after four passes by route B. Thus, the increase in $\tau_{0.3}$ after ECAP at 648 K is 46% while γ_f decreases by ~29%.

Figure 9: Stress–strain (τ – γ) curves of Ti0.16Pd0.14Fe (wt%) alloy under torsion in its initial state (1) and after one (2), two (3), three (4), and four (5) ECAP passes

Figure 10: Failure stress τ_f , failure strain γ_f , and yield strength $\tau_{0.3}$ of Ti0.16Pd0.14Fe (wt%) alloy under torsion vs number of ECAP passes

4 Discussion

Our research data on the structure and phase state of Ti0.16Pd0.14Fe (wt%) correlate with those obtained for Ti alloys of grades 2 and 4 with no Pd [15–17], for alloys of grade 7 with a Pd content of 0.15–0.20 wt% [15, 16, 18], and similar powder metallurgy alloys both with no Pd [16, 19] and with Pd in amount of 0.15 wt% [16]. The presence of β precipitates with a Fe content of 5.7 to 10–12 at% is detected in grade 2 alloy containing 0.127 wt% Fe [16] and grade 4 alloy containing 0.5 wt% Fe [15], in alloys with 0.088 and 0.285 wt% Fe (Egypt) [16, 19], being analogues of grade 1 and grade 2 alloys, respectively, and in Ti alloys with 0.04–0.128 wt% Fe [16, 19]. The presence of bcc β particles with

5–12 at% Fe and 0.4–4 at% Pd is found at grain boundaries in grade 7 alloys containing 0.07–0.3 at% Fe and 0.4–4 at% Pd [15, 16].

The increase in the fraction of β -Ti particles at grain boundaries of Ti alloys, no matter whether Pd is present, is associated with an increase in Fe content [2, 17, 19]. In alloys sintered from high-purity Ti powders with 0.004 wt% Fe, no such particles are detected at grain boundaries [16]. They are also not detected in grade 1 alloy with 0.2 wt% Fe [15]. In grade 7 alloy (0.05 wt% Fe, 0.18 wt% Pd), which is dominated by the α phase after quenching from 1173 K, grain boundary β precipitates are also absent. However, at the grain boundaries of the α phase, zones of width $\sim 25\ \mu\text{m}$ are found in which the Pd content increases from 0.1 to 1.2 wt% [18]. These zones have the structure of α' martensite with needle-like crystallites. Such a phase in Ti0.16Pd0.14Fe (wt%), which is also dominated by the α phase, is identified neither in its initial state nor after ECAP at 648 K. However, the initial alloy reveals β -Ti and $\beta + \alpha''$ particles at its grain boundaries and α'' and $\alpha + \alpha''$ microvolumes in its near-boundary regions. The presence of the β and α'' phases owes to the higher Fe content in Ti0.16Pd0.14Fe (wt%) as a whole (0.14 wt% Fe and 0.05 wt% Fe [18]), in its near-boundary regions (up to 0.43 at% Fe, 0.24 at% Pd), and in particles (up to 12 at% Fe, 0.9 at% Pd). These features of the initial phase composition, which are associated with specific distributions of Fe and Pd atoms, are inherited after warm ECAP. Undeniably, further research is required to identify the factors responsible for the enrichment of grain boundaries with Fe and Pd atoms and the temperature intervals of such segregation in Ti alloys. At the same time, our analysis of Fe- and Pd-rich zones and particles inherited by Ti0.16Pd0.14Fe (wt%) after warm ECAP suggests that they are formed at temperatures higher than the ECAP temperature 748 K. This conclusion correlates with phase transformation diagrams for Ti(Fe) and Ti(Pd) solid solutions [4, 20, 21]. The least soluble element in α -Ti is iron (0.05 and 0.01 at% at 973 and 773 K, respectively [20]) which is simultaneously the most efficient β phase stabilizer: increasing the Fe content to 3.5–4 wt% (3.0–3.6 at%) steeply decreases the $\beta \rightarrow \alpha$ transition temperature from 1155 to $\sim 423\ \text{K}$ [4]. The influence of palladium on the $\beta \rightarrow \alpha$ temperature is much weaker. At a Pd content of 0.2 wt%, this temperature is almost the same as that in pure Ti (1155 K) [18]. Increasing the Pd content to $\sim 2\ \text{at\%}$ (4.3 wt%) decreases the $\beta \rightarrow \alpha$ temperature by $\sim 20^\circ$, and with a Pd content of 10 at% (19.9 wt%), the α phase appears at 868 K [21]. Most likely, when heated to 648 K and pressed, the central regions of the initial grains preserve their α structure because the Fe and Pd concentration there is low (equal to or even less than the total

content of Fe and Pd in the alloy) and because the $\alpha \rightarrow \beta$ temperature is higher. In near-boundary regions and in particles with the initial $\beta + \alpha''$ structure, the situation is not so unambiguous. On heating to 648 K, they can experience $\alpha'' \rightarrow \beta$ transformations, but high plastic strains in pressing can stimulate their reverse $\beta \rightarrow \alpha''$ martensite transformation. Such a reverse transition under external stress is observed in metastable β -Ti alloys, including Ti-V [22], Ti-Nb [23], Ti-Mo [24], and in other alloys with a more complex elemental composition [25, 26]. The data agree with experimental results demonstrating the absence of any substantial changes in the phase composition of Ti0.16Pd0.14Fe (wt%) after ECAP at 648 K. However, by and large, ECAP at 648 K provides the transformation of a microcrystalline structure with an average grain size of $\sim 10\ \mu\text{m}$ to a homogeneous submicrocrystalline structure with an average grain size of $0.28\ \mu\text{m}$, increases the yield strength, and retains the margin of plasticity at a rather high level. In general, the research results agree with data concerning the effect of warm ECAP (673–723 K) on the mechanical properties of Ti alloys [12, 27–29]. In Ti alloys, like in Ti0.16Pd0.14Fe (wt%), such pressing forms a submicrocrystalline structure with an average grain size of $0.35\text{--}0.26\ \mu\text{m}$ and provides an increment in $\sigma_{0.2}$ by 48–68% under tension and a decrease in their elongation δ by 25–50% at the instant of fracture. In particular, in VT1-0 Ti alloy, $\sigma_{0.2}$ increases from 360 to 654 MPa, and δ decreases from 24.8 to 18.9% [29].

5 Conclusion

Thus, our study shows that warm equal-channel angular pressing at 648 K (channel angle 90° , route B, four passes) allows one to transform the microcrystalline structure of Ti–0.16Pd–0.14Fe (wt%) with an average grain size of $10\ \mu\text{m}$ to a submicrocrystalline structure with an average grain size of $0.28\ \mu\text{m}$. The main phase of the alloy both in the initial state and after equal-channel angular pressing (ECAP) is α with its hexagonal close-packed structure. In the initial alloy, zones of width up to $1\ \mu\text{m}$ from grain boundaries and grain junctions are oversaturated with Fe up to 0.43 at% and with Pd up to 0.24 at% compared to central grain regions in which the content of Fe and Pd is either close to or lower than their nominal content in the alloy ($\sim 0.1\ \text{at\% Fe}$, $0.05\text{--}0.1\ \text{at\% Pd}$). Part of these grain boundaries in the initial alloy contains either β particles or $\beta + \alpha''$ particles (orthorhombic martensite). After ECAP at 648 K, the initial boundaries are not detected but chemical and phase inhomogeneities near them are inherited as

extended bands of width up to 2 μm with homogeneous submicrocrystalline fragments with either α , α'' , or $\alpha + \alpha''$ structures. Such bands also contain inherited β particles or $\beta + \alpha''$ particles. The elemental composition of particles both in the initial alloy and after ECAP corresponds to Ti(Pd,Fe) with a Pd content of 0.4–1.3 at% and Fe content of 5–12 at%. In general, any substantial changes in the phase composition of Ti0.16Pd0.14Fe (wt%) after warm ECAP at 648 K are not found.

Warm ECAP at 648 K provides hardening of Ti0.16Pd0.14Fe (wt%). After four passes, the torsional yield strength of the alloy $\tau_{0.3}$ increases from 370 to 500 MPa (by 46%), and the margin of its plasticity γ_p (failure strain) decreases from 70 to 50% (by 29%). The results agree with data on other submicrocrystalline Ti alloys with $\langle d \rangle = 0.35\text{--}0.26\ \mu\text{m}$ after warm ECAP at 673–723 K, showing that their tensile yield strength $\sigma_{0.2}$ increases by 46–68% and the elongation decreases by 25–50% compared to the initial coarse-grained state.

Acknowledgement: The work was supported by Fundamental Research Program of the State Academies of Sciences for 2013–2020 (priority direction III.23) and Russian Foundation for Basic Research (grant No. 18-58-00036).

References

- [1] H.J. Rack and J.I. Qazi, *Mater. Sci. Eng. C.*, **26** (2006) 1269-1277.
- [2] C.N. Elias, M.A. Meyers, R.Z. Valiev, and S.N. Monteiro, *J. Mater. Res. Technol.*, **2** (2013) 340-350.
- [3] S. Shrestha and S. Joshi, *Sci. Res.*, **2** (2014) 7-12.
- [4] U. Zwicker, *Titan und Titanlegierungen*, Springer – Verlag, Berlin – Heidelberg, (1974).
- [5] N.D. Tomashov, *Titanium and its Corrosion-Resistant Alloys*, Metallurgia, Moscow, (1985).
- [6] M. Nakagawa, S. Matsuya, and K. Udoh, *Dental Mater. J.*, **20** (2001) 305-314.
- [7] M.N. Fokin, Yu.S. Rusko, and A.V. Mosolov, *Titanium and its Alloys in Chemical Industry*, Khimia, Leningrad, (1978).
- [8] D.K. Peacock, *Underwater Technol.*, **21** (1996) 23-30.
- [9] A. Michaelis, S. Kudelka, and J.W. Schultze, *Corrosion Rev.*, **18** (2000) 395-423.
- [10] Y.J. Chen, Y.J. Li, J.C. Walmsley, S. Dumoulin, P.S. Skaret, and H.J. Roven, *Mater. Sci. Eng. A.*, **527** (2010) 789-796.
- [11] Y.T. Zhu, T.G. Langdon, Z. Horita, M.J. Zehetbauer, S.L. Semiatin, and T.C. Lowe, editors, *Ultrafine Grained Materials IV*, The Minerals, Metals and Materials Society, Warrendale (PA), (2006).
- [12] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M.J. Zehetbauer, and Y.T. Zhu, *Mater. Res. Lett.*, **4** (2016) 1-21.
- [13] Liu Bing, Zhou Qing, Qu Rui-Feng, and Chang Wang-Tao, *Chin. J. Nonferrous Metals*, **25** (2015) 959-966.
- [14] K. Mukherjee and M. Kato, *J. de Physique Colloques*, **43** C4 (1982) C4-297-C4-302.
- [15] M. Yan, M. Qian, T.T. Song, M. Yan, M.S. Dargusch, and X.S. Wei, *MRS Commun.*, **4** (2014) 183-188.
- [16] M.A. Ashworth, A.J. Davenport, R.M. Ward, and H.G.C. Hamilton, *Corrosion Sci.*, **52** (2010) 2413-2421.
- [17] M. Mhaede, L. Wagner, and K. Ibrahim, *Int. J. Mater. Res.*, **104** (2013) 713-720.
- [18] F.J. Gill, J.A. Picas, M.J. Manero, A. Forn, and J.A. Planell, *J. Alloys Comp.*, **260** (1997) 147-152.
- [19] M. Yan, S.D. Luo, G.B. Schaffer, and M. Qian, *Metall. Mater. Trans. A*, **44** (2013) 3961-3969.
- [20] E. Raub, Ch.J. Raub, E. Roschel, U.B. Compton, T.H. Geballe, and B.T. Matthias, *J. Less Common Met.*, **12** (1967) 36-40.
- [21] H. Okamoto, *J. Phase Equilibria*, **14** (1993) 128-129.
- [22] E.S.K. Menon, J.K. Chakravarty, S.L. Wadkar, and S. Banerjee, *J. de Physique, Coll. C4 43* (1982) 321.
- [23] P. Hoshtukl and B. Obst // *J. de Physique, Coll. C4 43* (1982) 133
- [24] A. Zafari, X.S. Wei, W. Xu, and K. Xia // *Acta Mater.* **97** (2015) 146.
- [25] A.I.P. Nwobu, H.M. Flower, and D.R.F. West // *J. de Physique Colloques*, **43** C4 (1982) C4-315-C4-320.
- [26] V. Braibowski, S. Prokoshkin, K. Inaekyan et al. // *Mater. Sci. Found.*, **81-82** (2015) 342-405.
- [27] R.Z. Valiev and I.V. Alexandrov, *Bulk Nanostructured Metallic Materials: Processing, Structure and Properties*, Akademkniga, Moscow (2007).
- [28] Yu.R. Kolobov, R.Z. Valiev, G.P. Grabovetskaya et al., *Grain Boundary Diffusion and Properties of Nanostructured Materials*, Nauka, Novosibirsk (2001).
- [29] Yu.R. Kolobov, O.A. Kashin, E.E. Sagymbaev, E.F. Dudarev et al., *Russ. Phys. J.*, **43** (2000) 71-78.