Ultra fine grained Ti prepared by severe plastic deformation

F Lukáč¹, J Čížek¹, J Knapp¹, I Procházka¹, P Zháňal¹, R K Islamgaliev²
¹Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 18000 Praha 8, Czech Republic
²Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 K. Marx Street, 450000 Ufa, Russian Federation
E-mail: frantisek.lukac@mff.cuni.cz

Abstract. The positron annihilation spectroscopy was employed for characterisation of defects in pure Ti with ultra fine grained (UFG) structure. UFG Ti samples were prepared by two techniques based on severe plastic deformation (SPD): (i) high pressure torsion (HPT) and (ii) equal channel angular pressing (ECAP). Although HPT is the most efficient technique for grain refinement, the size of HPT-deformed specimens is limited. On the other hand, ECAP is less efficient in grain refinement but enables to produce larger samples more suitable for industrial applications. Characterisation of defects by positron annihilation spectroscopy was accompanied by hardness testing in order to monitor the development of mechanical properties of UFG Ti.

1. Introduction

Broad industrial applicability of titanium originates in its high strength, relatively low weight and high temperature stability. Moreover, by alloying titanium with other elements one can produce alloys with excellent mechanical properties, which are frequently used in biomedical applications. Since some alloying elements lack biocompatibility, there is a strong request for improved mechanical properties in pure titanium. Therefore, the ultra fine grained (UFG) metals attract interest of many researchers due to their superior mechanical properties consisting in a favourable combination of high strength and sufficient ductility [1, 2]. High pressure torsion (HPT) [1] is the most efficient technique for grain refinement by severe plastic deformation (SPD) methods and enables to achieve UFG structure with grain size around ~100 nm. However, size of HPT-deformed samples is limited to disk shape specimens with thickness up to ~1 mm and diameter up to ~20 mm. Moreover, strain distribution is not uniform across the HPT-deformed samples but increases from the centre of the sample towards the periphery [1, 2]. The Equal channel angular pressing (ECAP) [1] provide more massive samples in the form of rods which are more suitable for industrial applications. However, grain refinement by ECAP is lower compared to the HPT technique as a rule. SPD introduces a high density of defects, namely dislocations generated by plastic deformation and vacancies created by crossing dislocations. These deformation-induced defects play the key role in properties of UFG materials [3,4]. Hence, characterisation of defects in UFG samples prepared by SPD represents a very important task. Positron annihilation spectroscopy (PAS) has been frequently employed for defect studies of UFG metals but these studies covered mainly metals with cubic structure, see e.g. Refs. [3,4]. In particular there is a lack of PAS studies of UFG pure Ti despite that fact that Ti represents an important structural material. In the present work the positron lifetime (LT) spectroscopy was employed for characterisation of defects and their spatial distribution in UFG Ti samples prepared by HPT and ECAP.
2. Experimental details

A pre-rolled bar of titanium of commercial purity Grade IV (99.0% Ti) was deformed by ECAP method. No annealing of the Ti bar was performed prior to ECAP processing. The Ti bar was pressed through channels with an intersection angle of 105°. ECAP deformation was performed at temperature of 300°C following the route B_C, which was found to be the most effective in grain refinement [5]. The samples prepared by ECAP were rods having circle cross-section with the diameter of 12.5 mm.

High purity titanium (99.7%) was used for high pressure torsion (HPT) method. Similarly to the previous case, no annealing of Ti samples was performed prior to HPT processing. Two rotating anvils were pressed against each other by a pressure of 6 GPa. One of the anvils was slowly rotating and 5 revolutions were made at room temperature. The HPT-deformed sample is disc shaped with the diameter of 7 mm and the thickness of 0.5 mm. HPT samples were cleaned thoroughly before measurements.

The Vickers microhardness (HV) was measured by STRUERS DuraScan 50 Hardness Tester with automated indentation. The load of 100 g was applied for 10 seconds.

A digital LT spectrometer [6] with an excellent time resolution of 145 ps (FWHM 22Na) was employed for the LT investigations. A 22Na:CO3 positron source with the diameter less than 1 mm and with the activity of 1.5 MBq was deposited on a 2 mm thick Mylar foil. At least 10^7 positron annihilation events were accumulated in the LT spectra which were decomposed using a maximum likelihood based procedure [7]. The source contribution consisted of two weak components which come from positrons annihilated in the source spot and the covering Mylar foil and exhibit lifetimes of ~368 ps and ~1.5 ns and corresponding intensities of ~6 % and ~1 %, respectively.

3. Results and discussion

The homogeneity of commercially pure titanium prepared by ECAP method was checked in a transversal cut (i.e. in the cross-section of the sample perpendicular to the pressing direction) after one and ten ECAP passes. Figure 1a shows a colour coded HV map after one ECAP pass. Hardness is not uniform across the sample cross-section. Enhanced HV values observed at the periphery (outer radius) are most probably due to friction between the inner channel surface and the surface of the pressed sample. This makes deformation at the periphery higher than in the inner region of the sample. Fig. 1b shows a HV map of the sample deformed by 10 ECAP passes. One can see in the figure that the hardness of the sample substantially increased and moreover the homogeneity of hardness across the sample was remarkably improved.

Two reference samples were measured by LT spectroscopy: (i) high purity titanium annealed at 1000°C for 2 hour and slowly cooled and (ii) the same sample conventionally cold rolled at room temperature. The annealed sample exhibits a single component spectrum with positron lifetime of 144.6±0.6 ps. This value is in a good agreement with the Ti bulk lifetime of 147 ps obtained from theoretical calculations [8]. The cold rolled sample exhibits defect component with lifetime of 172±1 ps, which can be attributed to the lifetime of a positron trapped at a dislocation in titanium.

Figure 2 shows the development of positron lifetimes and relative intensities of the components resolved in the LT spectra of Ti samples subjected to various numbers of ECAP passes. The LT spectra of Ti deformed by one and two ECAP passes are three component consisting of: (i) a short-lived component with the lifetime τ1 significantly lower than the bulk Ti lifetime; (ii) a longer component with the lifetime τ2~170 ps; and (iii) a long-lived component with the lifetime τ3~255 ps. The short-lived component with the lifetime τ1 obviously comes from free positrons while the components with the lifetimes τ2 and τ3 represent contributions of positrons trapped at defects. ECAP deformation by four and more passes led to disappearance of the free positron component and virtually all positrons are trapped at defects. The lifetime τ2 = 170 ps corresponds well to the dislocation lifetime measured in the cold rolled reference sample and the component with lifetime τ2 can be therefore attributed to positrons trapped at dislocations introduced by SPD. The lifetime τ3 = 255 ps is higher than the lifetime of positrons trapped at monovacancies in Ti [8]. Hence, the appearance of the component with the lifetime τ3 suggests that larger open volume defects, namely vacancy clusters,
were created by ECAP deformation. The ab initio calculations of positron lifetimes for vacancy clusters of various sizes in titanium were performed in Ref. [8]. By comparison of the lifetime $\tau_3$ with the theoretical calculations in Ref. [8] one can conclude that vacancy clusters in ECAP-deformed titanium consist on the average of two vacancies.

Figure 1. Colour coded maps of microhardness in the plane perpendicular to the direction of the ECAP pressing in commercially pure titanium (a) after one pass (b) after 10 passes. HV mapping was performed on a half of the sample cross-section.

Figure 2. (a) The evolution of positron lifetime components distinguished in the spectra with respect to the number of ECAP presses. (b) The intensities of the positron lifetime components with respect to the number of ECAP presses.
The homogeneity of high purity titanium prepared by HPT was examined by HV mapping and a colour coded HV map of the HPT-deformed sample is shown in Figure 3a. The dependence of HV values (averaged over the whole angular range) on the radial distance \( r \) from the centre of the specimen is plotted in Fig. 3b. HV increases from the centre of the sample towards the periphery. This is caused by non-uniform strain imposed by HPT deformation which linearly increases from the centre of the sample towards the periphery [1, 2].

**Figure 3.** (a) A colour coded HV map of HPT-deformed titanium. Note that HV mapping was performed on a quarter of the sample disk. (b) The radial dependence of HV averaged over the whole angular range.

LT spectroscopy was employed to examine the spatial distribution of defects across the HPT-deformed sample. The HPT-deformed titanium sample exhibits a two-component LT spectrum. The first component with lifetime \( \tau_1 \approx 170 \) ps comes from positrons trapped at dislocations while the second component with lifetime \( \tau_2 \approx 280 \) ps represents a contribution of positrons trapped at vacancy clusters. From comparison of the lifetime \( \tau_2 \) with theoretical calculations in Ref. [8] one can deduce that vacancy clusters in HPT-deformed titanium consist on the average of three vacancies. Saturated positron trapping at dislocations and in vacancy clusters was observed in all points measured across the HPT-deformed sample. Fig. 4a shows the development of positron lifetimes \( \tau_1, \tau_2 \) with increasing...
radial distance from the centre of sample while the development of the relative intensity $I_2$ of positrons trapped at vacancy clusters is displayed in Fig. 4b. The intensity of the vacancy cluster component exhibits monotonic increase with the radial distance from the centre. It confirms that the concentration of vacancy clusters increases with $r$ due to increasing strain. One can see in Fig. 4a that the lifetime $\tau_2$ exhibits also a moderate increase with $r$. Hence, the average size of vacancy clusters slightly increases from the centre of the sample towards the periphery.

The lifetime of positrons trapped at vacancy clusters in HPT-deformed sample (~280 ps) is higher than the lifetime for vacancy clusters in the ECAP-deformed sample (~255 ps) indicating that open volume of vacancy clusters in the ECAP-deformed sample is lower. This is most probably caused by lower purity of the Ti sample deformed by ECAP. The commercial purity grade IV Ti used for ECAP deformation exhibits significantly higher concentration of interstitial oxygen compared to the high purity Ti used for HPT processing. The vacancy clusters introduced by ECAP processing are therefore likely coupled with interstitial oxygen atoms which reduce their open volume. The interaction of deformation-induced vacancies with interstitial oxygen is facilitated by the elevated temperature of ECAP processing (300 °C) which leads to a higher mobility of vacancies.

Comparing Figs. 2b and 4b one can notice that the intensity of positrons trapped at vacancy clusters is higher in the HPT-deformed sample than in the sample deformed by ECAP. It indicates that the HPT-deformed sample contains higher concentration of vacancy clusters than the sample deformed by ECAP. This is caused by the fact that that HPT imposes higher strain than ECAP processing. Note that no vacancy clusters could be detected in the Ti sample deformed by conventional cold rolling since the imposed strain was substantially lower than in case of SPD techniques and the concentration of deformation-induced vacancies is therefore too low.

4. Conclusions

UFG titanium samples produced by two different SPD methods (ECAP and HPT) were characterised by positron lifetime spectroscopy combined with microhardness mapping. Positron lifetime spectroscopy revealed that a high concentrations of dislocations are produced in ECAP and HPT-deformed samples of titanium. Moreover, vacancies produced during ECAP and HPT processing by crossing dislocations agglomerate into small vacancy clusters with different sizes. While the low temperature HPT processing produces vacancy clusters consisting on the average of three vacancies, the ECAP processing performed at elevated temperature induced vacancy clusters with smaller open volume most probably containing oxygen impurities. While the structure of ECAP-deformed sample becomes approximately uniform after sufficient number of passes, the HPT-deformed sample exhibits non-uniform structure due to non-uniform strain which increases from the centre towards the periphery. It is reflected by hardness increasing from the centre of the sample towards the periphery and the concentration and size of vacancy clusters which also increase with the radial distance from the centre.

5. Conclusions

This work was supported by the Czech Science Foundation (project P108/12/G043) and the Grant Agency of Charles University (Project No. 2002214).

References

[1] Zhilyaev A P and Langdon T G 2008 Prog. Mater. Sci. 53 893
[2] Valiev R, Islamgaliev R and Alexandrov I 2000 Progress in Materials Science 45 103
[3] Čížek J, Janeček M, Srba O, Kužel R, Barnovská Z, Procházka I and Dobatkin S 2011 Acta Mater. 59 2322
[4] Su L, Lu C, He L, Zhang L, Guagliardo P, Tieu A, Samarin S, Williams J and Li H 2012 Acta Mater. 60 4218
[5] Langdon T, Furukawa M, Nemoto M and Horita Z 2000 J. Organomet. Chem. 52 30
[6] Bečvář F, Čížek J, Procházka I and Janotová J 2005 Nucl. Instr. Meth. Phys. Res. A 539 372
[7] Procházka I, Novotný I and Beťavá F 1997 Mater. Sci. Forum 255-257 772
[8] Čížek J, Melikhova O, Barnovská Z, Procházka I and Islamgaliev R K 2013 J. Phys.: Conf. Ser. 443 012008