Defects in High Entropy HfNbTaTiZr Alloys Studied with Positrons

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High entropy alloys (HEAs) – called sometimes "materials cocktails" – are a class of new materials based on many (at least four or five) constituting metals mixed in equimolar concentrations. Important characteristics of these alloys are their large configurational entropy and a single, simple phase they exhibit. HEAs are nowadays frequently studied because of their interesting properties. HfNbTaTiZr alloys were introduced recently [1] as a candidate to replace current materials in high temperature applications (all involved metals are refractories), and biocompatible applications are also envisaged. Since the defects' structure, behavior and influence on HfNbTaTiZr alloys' properties are largely unknown, we bring here first information. At the beginning, we investigate theoretically the alloy structure stability, short range order and behavior of vacancies. In particular, we address the question of existence of structural vacancies. Theoretical considerations presented in [2] suggest that structural vacancies do not exist in HEAs, but our *ab initio* calculations give some indications that such vacancies could be found.

On the experimental side, the HfNbTaTiZr alloy studied was prepared by vacuum arc melting of corresponding pure metals (purity 99.9 %) in a water cooled copper crucible. Each element was added to the melt in equimolar proportion. The casting was performed six times and flipped for each melt to mix the elements thoroughly and suppress chemical heterogeneity. The X-ray diffraction phase analysis revealed that the cast sample is a single phase with the bcc structure and lattice parameter a = 3.4089(1) Å. Positron annihilation studies were performed using a digital positron lifetime (LT) spectrometer with the time resolution 144 ps and a digital coincidence Doppler spectrometer equipped with two HPGe detectors. The as-cast sample exhibits a two component LT spectrum. The shorter LT component comes from free positrons whereas the longer one with a lifetime of 165(1) ps represents a contribution from positrons trapped at defects. The defect component with an intensity of 94 % is dominating in the LT spectra of the as-cast sample. Annealing at 1000 ^{o}C for 1h caused a decrease in the intensity of the defect component indicating a partial recovery of defects. The theoretical bulk lifetime of HfNbTaTiZr alloys was estimated to be 142 ps from several fully relaxed model supercells using a parameter-free gradient-correction approach to electron-positron correlations [3]. Further calculations for various vacancy configurations are in progress, and their corresponding positron lifetimes will be compared to experimentally found LT components.

[1] O.N. Senkov et al., J. Alloys Comp. **509**, 6043 (2011).
[2] *High-Entropy Alloys: Fundamentals and Applications*, edited by M.C. Gao, J.-W. Yeh, P.K. Liaw and Y. Zhang, Springer (2016).
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Defects in high entropy alloy HfNbTaTiZr prepared by spark plasma sintering

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High entropy alloys exhibit various combinations of interesting physical properties due to the formation of solid solution stabilized by high configurational entropy. High entropy alloy HfNbTaTiZr exhibits single phase solid solution with BCC structure when prepared by arc melting [1]. Grain refinement achieved in cold rolled samples after recrystallization remarkably enhanced ductility of this alloy [2]. Mechanical alloying by milling and subsequent sintering is a frequent production way of preparing fine grained alloys from chemical elements with high melting temperature. In addition, spark plasma sintering (SPS) method with applied pressure serves as a unique tool of powder metallurgy thanks to fast heating rates and low time of exposition to elevated temperatures. Therefore, the deformation energy introduced during mechanical alloying may be effectively consumed during short sintering process and presents the additional parameter for grain refinement. The present work presents characterization of HfNbTaTiZr alloy prepared by SPS.

Microstructure of samples prepared by SPS was compared with as cast ingots. The samples were characterized by X-ray diffraction and scanning electron microscopy. Positron annihilation spectroscopy was employed for characterization of defects introduced by SPS and their thermal stability.

[1] O.N. Senkov, J.M. Scott, S.V. Senkova. D.B. Miracle, C.F. Woodward: Journal of Alloys and Compounds **509**, 6043-6048 (2011).
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Hydrogen-induced defects in Ti and their thermal stability

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Titanium readily absorbs hydrogen and undergoes phase transition into the hydride phase (TiH_2). In the hydride phase Ti is able to absorb the hydrogen concentration as high as 1.4 wt.%. These properties make Ti and Ti-based alloys attractive for hydrogen storage applications. Hydrogen absorption in titanium matrix may introduce open volume defects since the volume of TiH_2 phase exceeds that of titanium matrix. Absorbed hydrogen may segregate at these defects forming defect-hydrogen complexes.

In the present work positron annihilation spectroscopy was employed for characterization of hydrogen-induced defects in titanium. Defects created by hydrogen loading from the gas phase were compared with those introduced by electrochemical hydrogen charging. In general hydrogen loading introduces a high density of dislocations and vacancy clusters created by agglomeration of hydrogen-induced vacancies. The mean size of vacancy clusters depends on the hydrogen absorption temperature.

Thermal stability of hydrogen absorbed in titanium and recovery of hydrogen-induced defects were studied by positron lifetime spectroscopy combined with *in-situ* X-ray diffraction and thermal desorption spectroscopy. Fig. 1 shows the temperature dependence of positron lifetimes and relative intensities of individual components for hydrogen gas loaded titanium. The decomposition of TiH_2 phase is accompanied with introduction of additional vacancies agglomerating into vacancy clusters. Further annealing of the sample above 500 °C leads to recovery of dislocations.

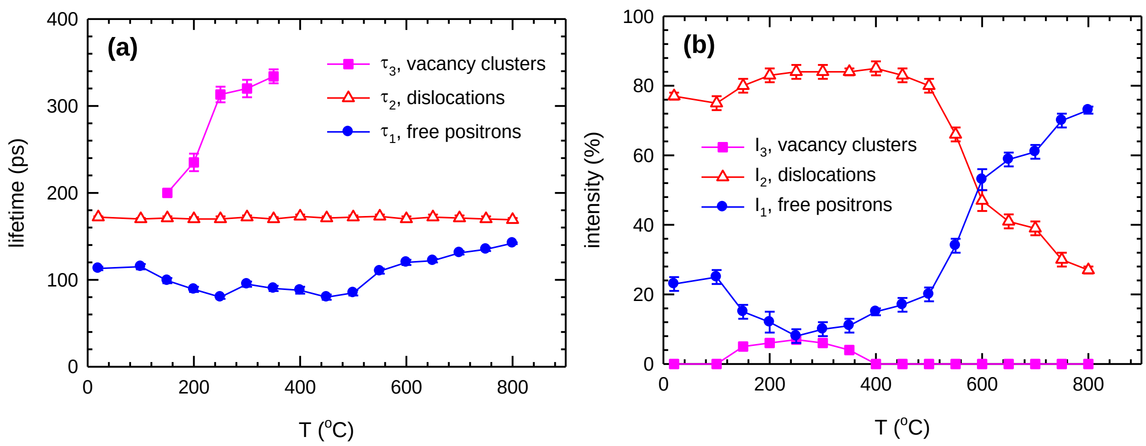

Fig. 1: Results of positron lifetime investigations of hydrogen loaded Ti (H_2 gas pressure 1 bar, temperature 400 °C): the development of (a) positron lifetimes and (b) corresponding relative intensities on the annealing temperature.

Doppler Broadening analysis of defect evolution in Eurofer97 and ODS Eurofer97 after He-implantation and annealing treatments

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The addition of nanosized Y_2O_3 particles in steels for nuclear fusion reactors is a new approach to improve performance at high temperatures (650-700 °C) and also to increase radiation damage resistance; however, the role of oxide nanoparticles is still not fully understood. In the present work, the formation and evolution of defects in Eurofer97 and Oxide Dispersion Strengthened (ODS) Eurofer97 alloys, after He implantation and at different working temperatures, is investigated. Samples of the two steels were He-implanted at room temperature, with 350 keV He ions and a dose of 10^{16} He ions.cm^{-2}. Then, the formation of defects in both steels was studied by Positron Annihilation Spectroscopy Doppler Broadening (PASDB), first at ambient temperature (23 °C) and then *in situ*, during annealing at temperatures up to 1200 °C (Eurofer97) and 1300 °C (ODS Eurofer97). The annealing treatments were made under a pressure of 10^{-7} mbar; the samples were heated gradually, with steps of 100 °C and duration of 5 min. At the end of each heating step and after cooling inside the furnace, the defect evolution was measured with PASDB.

The influence of the Y_2O_3 nanoparticles can primarily be observed by an increase in stability of voids in the ODS Eurofer97 steel. At critical temperatures – at which abrupt changes of state in defects take place – these more stable voids minimize undesired effects, such as volumetric expansion or embrittlement. These critical temperatures are 200 °C and 800 °C, which is in accordance with previous studies conducted on the same materials. The effect of He implantation doses, in comparison to previous studies with different doses, is highly influential on complex cluster formation and on triggering helium release mechanisms. An implantation dose of 10^{15} He ions.cm^{-2} is required to observe the significance of He bubbles in high He concentration regions in Eurofer97, while from implantation doses of 10^{16} He ions.cm^{-2} onwards, also low He concentration regions will undergo complex cluster formation.

A two-particle model for Positronium confined in sub-nanometric cavities

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In the last years, the electron-positron bound state, namely the positronium atom (Ps), has been widely used as a probe to test structural properties of porous materials. This is possible thanks to the strong connection between Ps annihilation rate and the electronic structure of the confining medium.

Accessible experimental measurements concern annihilation rates by pickoff processes and contact densities (the electron density at the positron position).

While the pickoff process is well understood, existing models describing Ps properties in nanometric or sub-nanometric cavities fail to justify the lowering of the contact density with respect to that of Ps in vacuum, as found in most materials.

For this reason we formulated a new two-particle model in which only the electron is confined in the cavity [1], while the positron is moving freely and feels the medium via a positive work function. We show that this model explains experimental data for a large class of materials and suggests a way to gain information on pore sizes and positron work functions.

[1] G. Marlotti Tanzi, F. Castelli, and G. Consolati, *Phys. Rev. Lett.* **116**, 033401 (2016)

P-6 **Mon/Tue, Sep-04/05, 15:00 - 15:30**

Identification of defects in high-entropy alloys by positron annihilation spectroscopy

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To be submitted …

Improvements in the Production of 22Na Positron Sources at iThemba LABS

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The poster shows the production of 22-Na at the iThemba Labs in Faure (near Cape Town) and the improvements recently obtained.

iThemba LABS has been producing ultra-high vacuum (UHV) 22-Na positron sources since the mid 1990's. Today, iThemba LABS is the only producer of these UHV 22-Na positron sources worldwide. These sources are produced by using the in-house produced high purity 22-Na radionuclide with a specification of >800 Ci 22-Na per gram of sodium together with the empty source capsules produced by Rehberg Electronics (Prof. Dr. Reinhard Krause- Rehberg) in Halle, Germany.

In the last quarter of 2014, we encountered a few problems from clients complaining about the low beta efficiency of the 22-Na positron sources. This paper will present the improvements made by Rehberg Electronics on the empty source capsule together with the improvements made by iThemba LABS on the dispensing of the 22-Na radionuclide during the manufacture of the 22-Na source capsule. Since the implementation of these improvements, the quality of the 22-Na positron sources has improved drastically and we have only received positive feedback from clients in this regard. In addition, upgrades of the current 22-Na production facility, the availability of the 22-Na stock levels together with the future vision of iThemba LABS will also be presented.

Positron Spectroscopy of Intermetallic Hydrogen Storage Alloys Synthesis Based on Ti-Cr with C14 and C36 Laves Phases

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The possibility of obtaining hydrogen storage materials based on $TiCr_2$ intermetallic compounds by melting in glow discharge plasma and electron beam melting is shown. Applying the glow discharge plasma method leads to the formation of the Laves phase with a C36 structural type, while electron beam melting allow to obtain the Laves phase with C14 type It has been established that the formation of Laves phases with different structural types is associated with different cooling rates, which is related to the synthesis methods peculiarities of intermetallic compounds.

Positron spectroscopy carries out by means of positron lifetime spectroscopy (PLS) and Coincidence Doppler broadening spectroscopy (DBS). To clarify the positrons lifetime for the C36 and C14 phases, theoretical calculations were performed in the framework of the density functional theory in the software package Abinit.

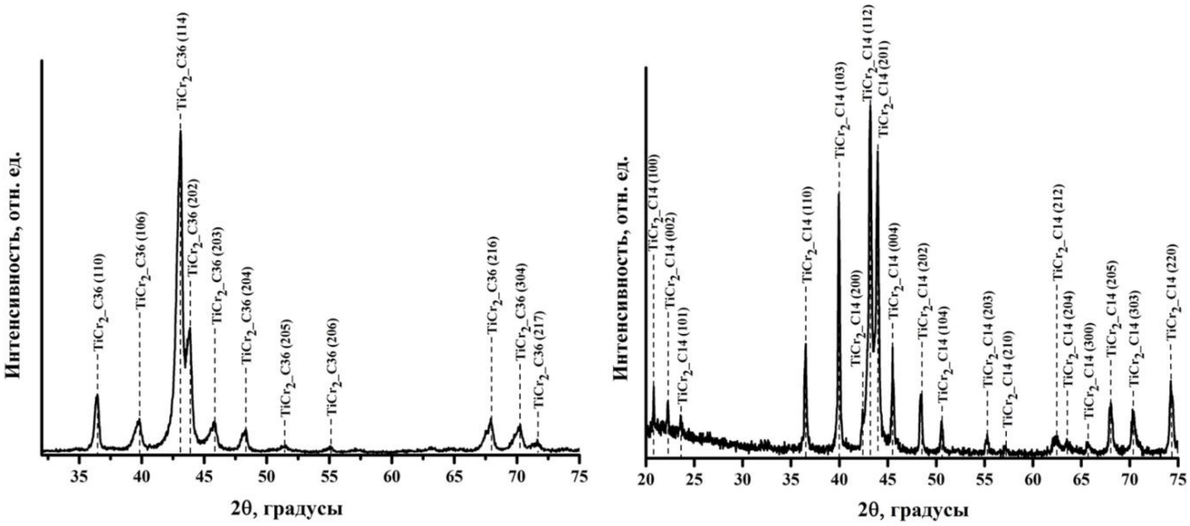

Fig1. Diffractograms of TiCr2 alloys obtained in an anomalous glow discharge plasma (a) and electron-beam melting (b)

The research is carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.

Positron Spectroscopy of Defect Structure Additively Manufactured Titanium Ti-6Al-4V

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Nowadays additive manufacturing (AM) is being actively implemented in many industries. Among the advantages of AM in metals are the possibility of creating unique product shapes, providing solid and lightweight (e.g. lattice) structures in a single manufacturing process and high quality of resulting materials. Additionally, electron beam manufacturing (EBM) technology today provides high rates of production and layer-to-layer component quality control. . The use of additive manufacturing also allows creating a new generation of materials with unique set of properties. The same time few issues related to the EBM process in already well established AM materials like Ti and Ti-6Al-4V remain not clear. Present paper reports results of the first studies into the hydrogen interaction with titanium Ti-6Al-4V parts produced by EBM.

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Improvement of depth resolution of VEPAS by simultaneous sputtering technique

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The poster shows a new method to improve the depth resolution by using Ar^+ ions to remove the surface during the measurement of the Doppler-Broadening with monoenergetic positrons. The depth resolution becomes worst with higher positron energies because of the broadening of their implantation profile. To improve the depth resolution, the sample surface is removed by sputtering with argon ions during the DB measurement.

We could show that with this sputtering technique, it is possible to investigate layer systems of different materials and make the interfaces sharply visible. Furthermore, by using this method the investigation of whole solar cells and their defect structure is possible. Finally, the identification of a depth dependent defect profile inside an implanted Si sample was demonstrated.