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A novel alloy development approach - biomedical high-entropy alloys

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Introduction

The modern materials class of high-entropy alloys (HEAs) gained tremendous attention in the scientific community over recent years, which can be attributed to two main reasons: Firstly, the new concept of combining several elements (at least 5 principal elements with concentrations between 5 and 35 at.% [1]) in contrast to conventional alloys, mostly containing only two or three major elements. This results in a broad variety of possible combinations thus leading to completely novel alloys with exceptional properties. Secondly, recently developed refractory metal based high-entropy alloys (RHEAs) have shown properties that are superior to the ones of current state-of-the-art alloys, which are attributed to several unique thermodynamic effects [2,3]. However, besides the outstanding mechanical properties, abrasion resistance and thermal resistance, a vast variety of chemical elements used in RHEAs also belongs to the category of biocompatible elements (exemplified in Figure 1), hence leading to potentially new biomedical materials.

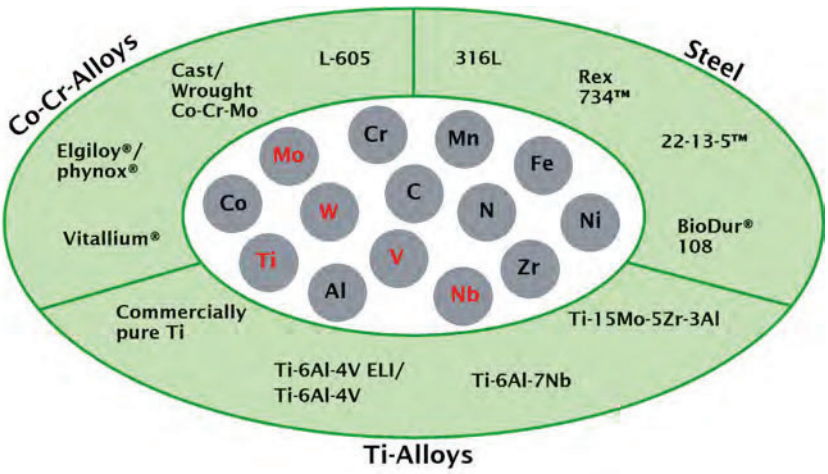

Fig. 3: Schematic representation of state-of-the-art biomaterials and the corresponding chemical elements; Refractory metals of potential interest are highlighted.

To meet the demands for biomedical applications, three main criteria must be fulfilled: Excellent mechanical properties (regarding the force transmission between implant and bone), corrosion resistance (prevention of corrosive damage to the implant) and biocompatibility (no tissue damage by the implant material or by corrosive/ abrasive particles) [4].
Our current research targets these requirements on the basis of previous investigations regarding Mo-Nb-V-W-Ti high-entropy alloys [5], which have confirmed promising mechanical properties. Furthermore, the works from Shi et al. [6] concerning the corrosive capabilities of HEAs are considered to support our theories. However, due to their good biocompatibility [7,8], we have chosen an equiatomic composition of Ta, Nb and Ti as base material for the experiments.

Materials and Methods

For sample production, high purity elemental chips or flakes of Ta (99.9 %), Nb (99.9 %) and Ti (99.6 %) were used as starting materials and were carefully weighed in. The alloying process was carried out in a conventional arc-melting device under Ar atmosphere. The sample was re-melted five times to ensure sufficient homogeneity of the alloying elements. Afterwards, the produced oblong-shaped (due to the use of an elongated mold) melted product was cut into 2 mm thick slices by means of electric discharge machining (EDM). One slice was used for microstructural analysis and thus metallographically prepared (subsequently grinded with SiC paper under flowing water and polished) afterwards. The remaining slices were cleaned from the EDM-burr and grinded to a defined grit size of 1200 under flowing water. To identify the phases present, X-ray diffraction analysis (XRD) was performed on the samples, using a X'Pert Pro (PANalytical, Almelo, Netherlands). Microstructural observations were carried out by means of scanning electron microscopy (SEM; EVO 15, Zeiss, Oberkochen, Germany), using back-scattered electron (BSE) imaging. To determine the elemental distribution and the chemical composition of the alloy, (Si(Li))-detector Energy-dispersive X-ray spectroscopy (EDS) analysis, equipped with Genesis software (EDAX, Mahwah, NJ, USA) was conducted. Furthermore, to examine and evaluate the biocompatibility of the Ta-Nb-Ti alloy produced, cell cultivation experiments were carried out on the defined surface of the specimens and compared to state-of-the-art biomaterials such as Co-28Cr-6Mo or Ti-6Al-4V, as well as to samples of pure Ta, Nb and Ti.

Results and Discussion

XRD-analysis revealed that the Ta-Nb-Ti-alloy consists of a single-phase body centered cubical (bcc) crystal structure with an Im-3m space group. However, the results of the BSE microstructural analysis (Fig. *4*) show a dendritic structure with clearly distinguished interdendritic regions (darker colored regions). EDS-analysis by means of element mappings indicated a higher fraction of high melting Ta in the dendritic crystals, whilst the lower melting Ti was enriched in the interdendritic regions. Nb exhibits an intermediate melting temperature in the alloying composition present, thus being present in the dendrites, as well as predominantly in the interdendritic regions. The observed segregation is attributed to the difference in melting temperatures of the components [5]. However, it is expected that long-term heat treatment will reduce the segregation effects [9]

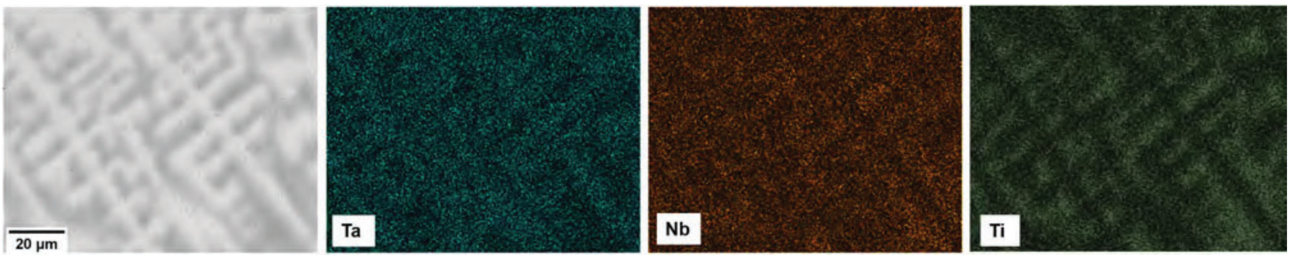

Fig. 4: EDS mappings of the Ta-Nb-Ti alloy.

In ongoing investigations, we use the as-cast alloy for cell cultivation experiments. To determine and evaluate the interaction between the material and the attached tissue (rather than the cells and different surface structures), a comparable surface grade was set on all materials tested. This was achieved by using the same size 1200 grit SiC grinding paper and different grinding times (depending on the hardness, respectively abrasion resistance of the material grinded) for all samples. The surface roughness of the different specimens is validated by using a confocal microscope, as well as a contact angle measuring device. To compare the Ta-Nb-Ti alloy to other biomaterials, osteoblasts and other cultures are then used and cultivated on the materials surfaces. The cell-growth regarding size and numbers is analyzed subsequently and compared to the publications of other working groups (f.e. Nagase et al. [10] with similar approaches to this novel topic of material development). For further investigations, results regarding the different base elements (Ta, Nb and Ti in the present study), as well as various alloying compositions (thus resulting in different microstructures) are to be examined. This helps to generate an understanding for microstructure-growth correlations in terms of f.e. preferred phases and/ or phase combinations (such as intermetallic precipitations or similar).

References

[1] M.H. Tsai, J.W. Yeh, High-entropy alloys: A critical review. Mater. Res. Lett. **2014**, *2*, 107–123.

[2] M.C. Gao, P.K. Liaw, J.W. Yeh, Y. Zhang, High-entropy alloys: Fundamentals and applications. **2016**, ISBN 9783319270135.

[3] E.P. George, W.A. Curtin, C.C. Tasan, High entropy alloys: A focused review of mechanical properties and deformation mechanisms. Acta Mater. **2020**, *188*, 435–474.

[4] S. Houis, U.a. Medizintechnik; E. Wintermantel, S.-W. Ha, Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2009**; ISBN 978-3-540-93935-1.

[5] M. Regenberg, G. Hasemann, M. Wilke, T. Halle, M. Krüger, Microstructure Evolution and Mechanical Properties of Refractory Mo-Nb-V-W-Ti High-Entropy Alloys. Metals (Basel). **2020**, *10*, 1530.

[6] Y. Shi, B. Yang, P.K. Liaw, Corrosion-resistant high-entropy alloys: A review. Metals (Basel). **2017**, *7*, 1–18.

[7] P.J. Andersen, Metals for use in medicine, Elsevier Ltd. **2017**, *1*, ISBN 9780081006924.

[8] L.T. Kuhn, Biomaterials. Introd. to Biomed. Eng. **2011**, 219–271.

[9] O.N. Senkov, D.B. Miracle, K.J. Chaput, J.P. Couzinie, Development and exploration of refractory high entropy alloys - A review. J. Mater. Res. **2018**, *33*, 3092–3128.

[10] T. Ishimoto, R. Ozasa, K. Nakano, M. Weinmann, C. Schnitter, M. Stenzel, A. Matsugaki, T. Nagase, T. Matsuzaka, M. Todai, et al. Development of TiNbTaZrMo bio-high entropy alloy (BioHEA) super-solid solution by selective laser melting, and its improved mechanical property and biocompatibility. Scr. Mater. **2021**, *194*, 2–7.