Japanese-German Spring School

on processing of high temperature materials

March 13th, 2023

Prof. Manja Krüger

Prof. Kyosuke Yoshimi

Program

March 13th, 2023

Zoom-Meeting

https://ovgu.zoom.us/j/61459400971

Meeting-ID: 614 5940 0971

Jap	Ger	
17^{00}	09^{00}	**Welcome notes**
17^{05}	09^{05}	**Julia Becker** Analysis of Ti modified Mo-Si-B alloys
17^{20}	09^{20}	**Dennis Zang** Alloying strategies and optimization of powder metallurgically processed Mo-V-Si-B alloys
17^{35}	09^{35}	**Shuntaro Ida** Microstructure characterization of spark-plasma sintered compacts of MoSiBTiC powder produced by gas atomization
17^{50}	09^{50}	**Hiromu Matsuura** Evaluation of physical properties of non-stoichiometric TiX_X by first-principles calculations
18^{05}	10^{05}	**Maximilian Regenberg** Further development of a novel Ta-Nb-Ti based multi-component alloy for biomedical applications
18^{20}	10^{20}	**Janett Schmelzer** Mechanical alloying of Ta-Nb-Ti powder material
18^{35}	10^{35}	**Weiguang Yang** Experimental investigation of the isothermal section of the V-rich V-Si-B system at 1400 °C
18^{50}	10^{50}	**Georg Hasemann** Microstructure and mechanical properties of V-Si-B alloys with chromium additions
19^{05}	11^{05}	**End of session**
20^{00}	12^{00}	**Online Spring School party** Discuss on our virtual social event. Cheering, laughing, sharing drinks and toasts

BEER

Analysis of Ti modified Mo-Si-B alloys

Julia Becker [1], Reshma Sonkusare[2], Torben Boll[2] and Manja Krüger [1]

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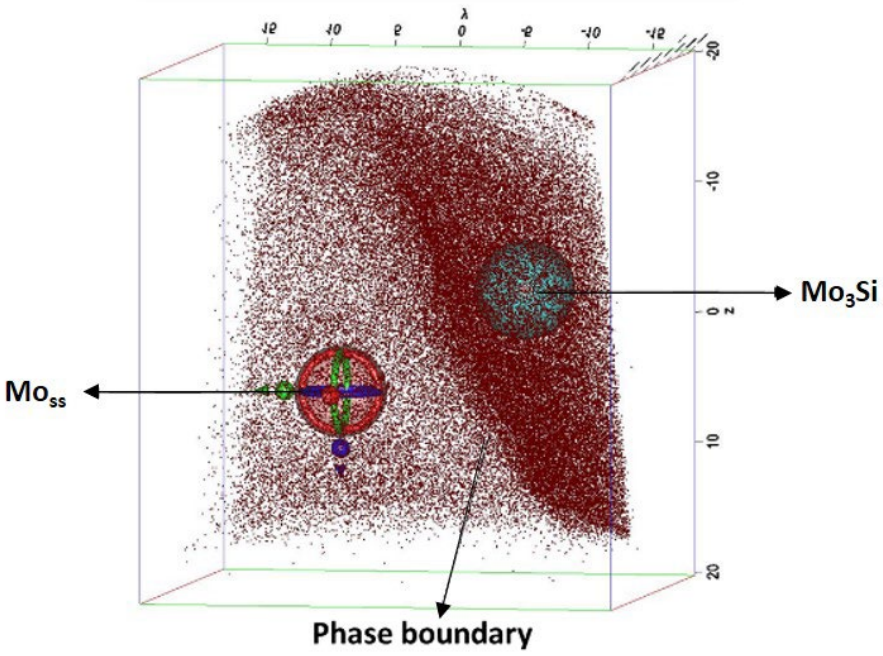
Mo-Si-B alloys are attractive high-temperature structural materials due to their high melting point (above 2000 °C), high-temperature strength, good oxidation and creep resistance. In order to reduce the density of Mo-Si-B alloys, Ti is a promising candidate for alloying. Ti additions are found to cause strengthening of the alloy at intermediate and high temperatures without decreasing the ductility at room temperature. To understand the effect of Ti on the crystal structure of the constituents, the phase fractions of the multi-phase alloy and thus the mechanical properties at a range from ambient temperatures to 1100 °C, we investigated a powder metallurgically (PM) processed Mo-Si-B-Ti alloy. The present investigations focus on the characterization of the constituents by SEM, EBSD and Atom probe tomography (APT). Based on the analyses, a conclusion can be drawn about the composition of the phases and the solubility of the elements in the phases. These in turn have an impact on the mechanical properties of the alloy, which will also be considered. For this purpose, compressive creep tests at temperatures over 1000 °C and flexural bending tests are carried out, in order to evaluate the strength and fracture toughness of the alloys.



APT tips measured in Mo-7.2Si-9.7B-1.7Ti alloy showing a phase boundary between Mo solid solution and Mo_3Si phase.

Alloying strategies and optimization of powder metallurgically processed Mo-V-Si-B alloys

Dennis Zang, Georg Hasemann and Manja Krüger

Institute of Materials and Joining Technology, Otto-von-Guericke University Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany,

The refractory metal-based Mo-Si-B alloys have long been considered as the most promising candidates for replacing nickel-based superalloys in the aerospace and energy sector, due to their outstanding mechanical properties and good oxidation characteristics of the Mo silicide phases. However, the oxidation behavior of these alloys still remains a critical issue, since catastrophic oxidation failure occurs locally at the Mo solid solution phase, especially at temperatures between 600 °C and 800 °C.

The addition of vanadium leads to a significant density reduction compared to conventional ternary Mo-Si-B alloys, which is even lower than the density of a state-of-the-art nickel-base superalloy CMSX-4. It has been found that the composition Mo-40V-9Si-8B has the best set of properties with respect to normalized mechanical strength and ductility. In this work, a milling study of mechanically alloyed Mo-40V-9Si-8B powder will be carried out first with the aim to optimize the powder metallurgical processing route. In the next step, 2 at.% titanium will be added, which improves the stress-strain properties even further. The mechanically alloyed powder obtained from the two milling studies will then be characterized as a function of milling time. Due to the high affinity of titanium for oxygen, it is believed that titanium may act as a getter for dissolved oxygen in Mo-V-Si-B alloys and thus contribute to improve ductility as well as to minimize internal oxidation. The analytical methods to determine the milling progress include SEM analysis (microstructure and EDS), XRD analysis (vanadium content of solid solution phases as well as their phase fractions, lattice constant and microstrain), oxygen measurements, microhardness measurements and laser diffraction (particle size). The aim of these studies is to obtain a better understanding of the influence of other alloying elements in powder metallurgically processed Mo-V-Si-B alloys.

Microstructure characterization of spark-plasma sintered compacts of MoSiBTiC powder produced by gas atomization

Shuntaro Ida and Kyosuke Yoshimi

The creep strength of the first-generation MoSiBTiC alloy (Mo-5Si-10B-10Ti-10C, at%) is superior to that of SiC_f/SiC composites, and the specific strength of this alloy is comparable to that of ceramics matrix composite at 1250 ºC. On the other hand, its high strength properties make hot forging and processing into complex shapes difficult. Therefore, the processing of the MoSiBTiC alloy by powder metallurgy has been investigated. In this study, the powder and sintered compact of the first-generation MoSiBTiC alloy were prepared by electrode induction gas atomization (EIGA) and spark-plasma-sintering (SPSed compact).

The spherical powder of the first-generation MoSiBTiC alloy was produced by the EIGA method. The microstructure of the powder was much more refined than that of the alloy produced by the arc-melting method (Cast sample). Interestingly, some solidification steps in the Cast sample disappeared in the powder. These differences are attributed to the rapid cooling effect of the EIGA method. Dense and sound powder compacts were successfully obtained by the SPS process. The composition of the SPS compacts was close to the nominal composition of the first-generation MoSiBTiC alloy. Therefore, it was found that there were no significant compositional changes during the powder process. The microstructure of the SPSed compact was considerably (almost one order) finer than that of the Cast sample, with random crystallographic orientation distribution and less anisotropic morphology along the solidification direction observed in the Cast sample.

Evaluation of physical properties of non-stoichiometric TiX_X by first-principles calculations

Hiromu Matsuuro, Kotaro Hoshizaki, Shuntaro Ida and Kyosuke Yoshimi

Introduction

B1-type MX ceramics are composed of transition metals (TM) in the M-site sublattice and non-metallic light elements in the X-site sublattice, and each site has the same atomic arrangement as that of FCC. B1-type MX ceramics generally have large non-stoichiometry compositions. Using non-stoichiometry compositions, each site is occupied by two or more type of atoms. Therefore, high-entropic MX ceramics can be designed. In order to predict the material properties of high-entropic MX ceramics, it is necessary to systematically study the change of material properties with non-stoichiometric composition. In a previous study, changes in material properties with changes in the ratio of transition metal at the M site ($f_{\mathrm{TM}}^{\mathrm{M}}$) and structural vacancies (Va) at the C site ($f_{\mathrm{Va}}^{\mathrm{X}}$) of MCx were calculated by first principles calculations [1]. In this study, we investigated the changes in material properties with changes in the ratio of C, N, and O atoms at the X site ($f_{\mathrm{C}}^{\mathrm{X}}, f_{\mathrm{N}}^{\mathrm{X}}, f_{\mathrm{O}}^{\mathrm{X}}$) and the ratio of structural vacancies at the X site of TiXx.

Experimental Methods

First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) based on density functional theory. k-point mesh and cutoff energy were set to $6 \times 6 \times 6$ and 600 eV, respectively. The model is a supercell with a B1-type structure doubled in the a-, b-, and c-axis directions, and the occupied atoms and structural vacancies at the X site were randomly placed using the Special Quasi-Random Structure method of the Alloy Theoretic Automated Toolkit (ATAT). The supercells were each doubled in the c-axis direction.

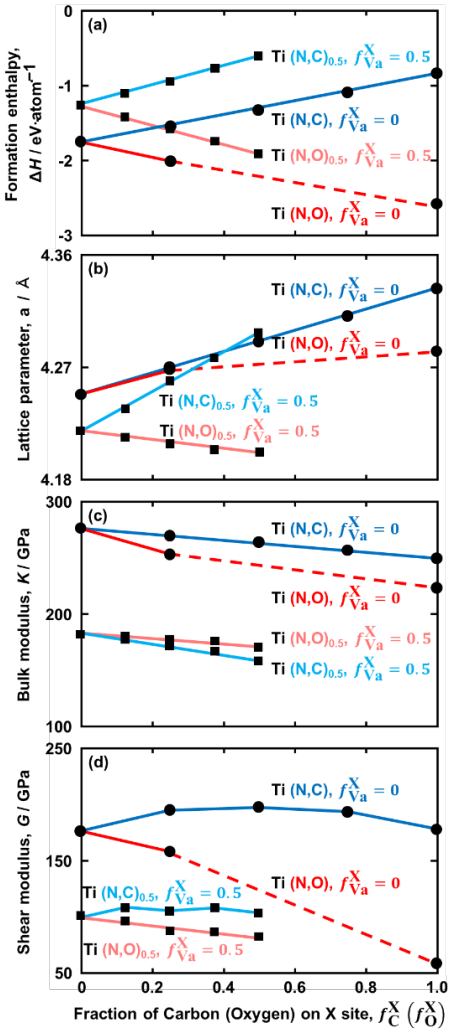


Fig.1 Change in the physical properties of TiN and $TiN_{0.5}$ with the fraction of O and C at the X site: (a) formation enthalpy (ΔH), (b) lattice parameter (c) bulk modulus (K) and (d) shear modulus (G).

Results

Stoichiometric TiN and $TiN_{0.5}$ which has structural vacancy are considered as a basis. The formation enthalpy (ΔH) of TiN and $TiN_{0.5}$ increased with increasing $f_{\mathrm{C}}^{\mathrm{X}}$ and decreased with increasing $f_{\mathrm{O}}^{\mathrm{X}}$ (Fig. 1(a)). The lattice parameter of TiN increased with increasing $f_{\mathrm{C}}^{\mathrm{X}}$ and $f_{\mathrm{O}}^{\mathrm{X}}$. However, the lattice parameter of $TiN_{0.5}$ increased with increasing $f_{\mathrm{C}}^{\mathrm{X}}$ and decreased with increasing $f_{\mathrm{O}}^{\mathrm{X}}$ (Fig. 1 (b)). The bulk modulus (K) of TiN and $TiN_{0.5}$ linearly decreased with increasing $f_{\mathrm{C}}^{\mathrm{X}}$ and $f_{\mathrm{O}}^{\mathrm{X}}$ (Fig. 1(c)). On the other hand, the shear modulus (G) of TiN and $TiN_{0.5}$ increased then decreased with $f_{\mathrm{C}}^{\mathrm{X}}$ and linearly decreased with increasing $f_{\mathrm{O}}^{\mathrm{X}}$ (Fig. 1(d)). These results indicate that each property varies systematically with the presence of structural vacancies and $f_{\mathrm{C}}^{\mathrm{X}}, f_{\mathrm{O}}^{\mathrm{X}}, f_{\mathrm{N}}^{\mathrm{X}}$.

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Further development of a novel Ta-Nb-Ti based multi-component alloy for biomedical applications

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Artificial prostheses can remain successfully implanted in the human body for many years, thereby providing enhanced mobility, vitality and overall quality of life of many patients. Due to demographic change and the associated increase in surgical interventions (implantations in particular) (cf. [1,2]), the demand for modern solutions in the filed of biomedical materials is higher than ever before. A variety of different metallic implant materials (e.g. biocompatible steels, Ti-alloys) are already in clinical use, but often show weaknesses regarding their overall properties, especially in the long term.

To meet the demands for biomedical applications, three main criteria must be met: Excellent biomechanical properties (force transmission between implant and bone, as well as abrasion resistance), corrosion resistance (prevention of corrosive damage to the implant) and biocompatibility (no tissue damage by the implant material or by abrasive particles) [3].
The modern material class of multi-component alloys, so called high-entropy alloys (HEAs) in particular, has gained tremendous interest in recent years. These materials are characterized by systems, based on multiple alloying elements in equiatomic composition, in contrast to conventional alloys, consisting of one major element and only minor additions of alloying elements. The special nature of these novel alloying systems lies within the physical and thermodynamic conditions present, leading to outstanding mechanical and corrosive properties [4–6]. However, besides these unique properties, a vast variety of chemical elements used in refractory metal based high-entropy alloys (RHEAs) also belong to the category of biocompatible elements, hence providing a perfect foundation for the development of new biomedical materials. In consideration of this background and due to the excellent biocompatibility of the constituents [7], an equiatomic composition of Ta, Nb and Ti as multi-component base alloy was chosen for the experiments.

The alloy examined was produced using an arc melting furnace under Ar atmosphere, metallographically prepared and investigated respectively. Scanning electron microscopy (SEM) analysis revealed the presence of a dendritic microstructure, with an enrichment of high-melting elements in the dendrites, as well as Ti in the interdendritic regions (verified by means of EDS mappings). Microstructure analysis by means of X-ray diffraction (XRD) showed, that there are two types of body-centered cubic (bcc) crystal structures (Im-3m I: a = 3.287 Å; Im-3m: a = 3.291 Å) present in the as-cast state. To get a better understanding of the microstructure evolution, heat-treatment experiments regarding different temperatures and times were performed and analysed subsequently. In addition, the alloying element Zirconium (Zr) was introduced to the base-alloy and the influence on the microstructure development was studied.

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Mechanical alloying of Ta-Nb-Ti powder material

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The innovative class of materials, refractory metal-based multicomponent alloys (MEAs) and high entropy alloys (HEAs), represent a unique alloy design strategy for the development of new biomedical materials. In addition to attractive mechanical properties and excellent wear or corrosion resistance, MEAs/HEAs are very promising materials in terms of biocompatibility. This is based on the fact that a large number of potential chemical elements needed to achieve the above properties belong to the category of bio-compatible materials, such as Ta, Ti, Nb, Mo, V, Zr, W, etc. For recently developed bio-HEAs described in the literature, such as Ti-Zr-Hf-Cr-Mo and Ti-Zr-Hf-Co-Cr-Mo, improved biocompatibility was demonstrated in addition to improved mechanical properties, primarily in terms of increasing mechanical hardness [1,2]. In addition to the development of novel alloy concepts for biomedical materials, research also focuses on the manufacturing of these materials. Powders are the first basis to manufacture these materials via sintering and additive manufacturing processes. To this end a very first investigation concerning mechanical alloying of an equiatomic Ta-Nb-Ti alloy was conducted and parameters for milling was determined with regard to a homogeneous distribution of the single alloying elements within the powder particles.

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Experimental investigation of the isothermal section of the V-rich V-Si-B system at 1400 °C

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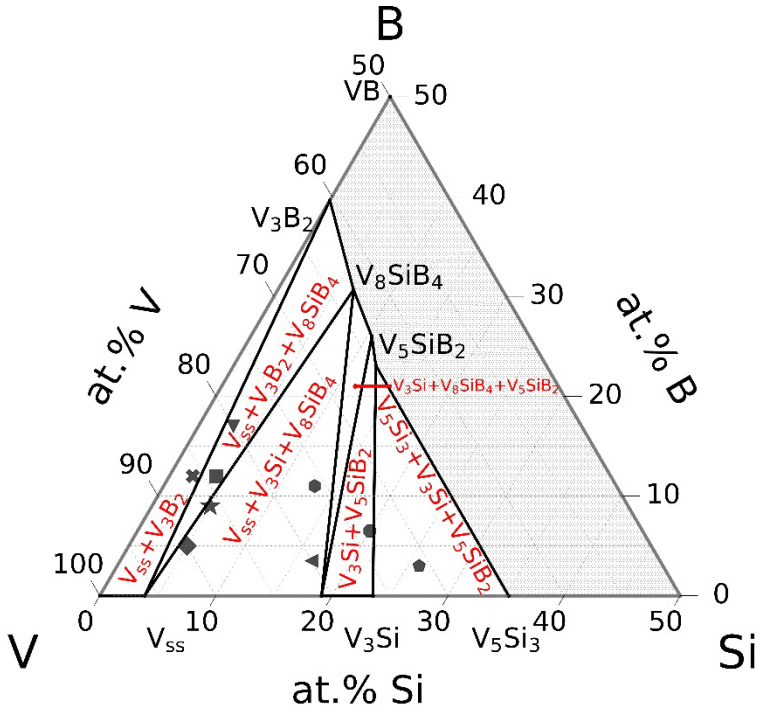
The three-phase V_{ss}-V_3Si-V_5SiB_2 alloy represents a new candidate material for high-temperature structural applications due to the high melting temperature and good creep resistance provided by the hard intermetallic phases V_3Si and V_5SiB_2. Describing the isothermal section is necessary in order to develop appropriate heat treatment and sintering processes.

In this work, eight alloy compositions were investigated to characterize the isothermal section of the V-Si-B system at 1400°C. Samples were produced via arc-melting and heat treated at 1400 °C for 100/200/300 h and furnace-cooled (within 3 h below 200 °C) in high vacuum ($1.5 \cdot 10^{-5}$ mbar). Their microstructures were characterized using scanning electron microscope, energy-dispersive X-ray spectroscopy (EDS), electron backscatter diffraction (EBSD) and X-ray diffraction (XRD). The phase area fraction determined by EBSD and the phase volume fraction, which was determined using the phase composition measured by EDS in combination with the phase molar volume measured by XRD, were used to confirm the sample equilibrium state thereby reflecting the isothermal section of the V-rich V-Si-B. Compared to the isothermal section at 1600 °C [1], the V_5SiB_2 single-phase field at 1600 °C is partially replaced by the V_8SiB_4−V_5SiB_2 coexistence line at 1400 °C. Accordingly, it divides the V_5SiB_2−V_3Si two-phase phase field at 1600 °C into the V_3Si−V_5SiB_2−V_8SiB_4 and V_3Si−V_5SiB_2 phase fields at 1400 °C. Furthermore, the V_5SiB_2 phase of the V_{ss}−V_3B_2−V_5SiB_2 and V_{ss}−V_3Si−V_5SiB_2 three-phase fields at 1600 °C is replaced by the novel V_8SiB_4 phase.



The isothermal section of the V-rich corner of the V−Si−B system at 1400 °C.

Reference

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Microstructure and mechanical properties of V-Si-B alloys with chromium additions

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The V-Si-B system has gained scientific interest as a new low-density, refractory metal-based structural intermetallic alloy system. The alloy design is strongly influenced and driven by the developments in the field of Mo-Si-B alloys and shares some interesting structural and microstructural features. Very recently, the formations of ternary eutectic V_{SS}-V_3Si-V_5SiB_2 microstructure has been reported which contains the same isomorphous phases as the ternary eutectic in the well-studied Mo-Si-B system: a refractory metal-based solid-solution phase (Mo_{SS} or V_{SS}) and the two intermetallic phases with either an A15 (Mo_3Si and V_3Si) or a $D8_l$ (Mo_5SiB_2 and V_5SiB_2) structure. However, while the Mo-Si-B-based ternary eutectic shows some oxidation resistance due to its intermetallic character, oxidation of the V-based eutectic is an even more serious issue. To address this problem, different amounts of Cr were added to an eutectic V-Si-B alloy to study the microstructural influence on the ternary eutectic reaction, the phase stability as well as the mechanical and oxidation properties as a function of Cr concentration. Alloys with Cr additions between $10 - 30$ at.% were fabricated by conventionally arc-melting and were analyzed in the as-cast state or heat-treated at 1400 °C for 100 hrs.

The present study is focused on the compressive stress-strain behavior of ternary eutectic V-Si-B alloys with 10, 20 and 30 at.% Cr additions. Compression tests were performed using an electro-mechanical universal testing machine and a constant crosshead speed corresponding to an initial (engineering) strain rate of 10^{-3} s^{-1}. The yield stresses were determined by the 0.2% offset method. The temperature dependence of its compressive yield stress between room temperature and 1000 °C was investigated in the as-cast state and compared to the Cr-free ternary eutectic alloys V-9Si-6.5B as well as V-Si-B alloys taken from the literature.