



TOHOKU  
UNIVERSITY



# Japanese-German Spring School

## on DFT Calculations for High Temperature Materials Development

March 24. and 25. 2021

Prof. Manja Krüger

Prof. Kyosuke Yoshimi

# Program

March 24, 2021

## Zoom-Meeting

<https://ovgu.zoom.us/j/99226183991>

Meeting-ID: 992 2618 3991

Code: 737071

Jap Ger

17<sup>00</sup> 09<sup>00</sup>

**Welcome notes**

17<sup>10</sup> 09<sup>10</sup>

**Rachid Stefan Touzani**

A way too short introduction to Density Functional Theory  
(key note)

17<sup>40</sup> 09<sup>40</sup>

**Janett Schmelzer**

Strengthening of additively manufactured Me-Si-B (Me = Mo, V)  
by Y<sub>2</sub>O<sub>3</sub> particles

17<sup>55</sup> 09<sup>55</sup>

**Maximilian Regenber**

A novel alloy development approach: Biomedical high-entropy  
alloys

18<sup>10</sup> 10<sup>10</sup>

**Rachid Stefan Touzani**

Site preference of V and chemical bonding in V<sub>5-y</sub>Mo<sub>y</sub>SiB<sub>2</sub> in the  
Mo-40V-9Si-8B alloy

18<sup>25</sup> 10<sup>25</sup>

**Georg Hasemann**

Novel intermetallic silicides and borides in the V-TM-Si-B system  
(TM = Ti, Cr, Nb, Mo)

18<sup>40</sup> 10<sup>40</sup>

**Discussion and Remarks**

19<sup>00</sup> 11<sup>00</sup>

**End of first Session**

# Program

March 25, 2021

## Zoom-Meeting

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**Welcome notes**

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**Takahiro Kaneko**

First-principle calculation on design of Mo-Ti based BCC solid solution

17<sup>25</sup> 09<sup>25</sup>

**Kotaro Hoshizaki**

Evaluation of composition and structure stability of mullite by First-Principles Calculation

17<sup>40</sup> 09<sup>40</sup>

**Brainstorming Session**

Discussion on joined projects to involve DFT calculations into cooperative materials development.

Identifying tasks and challenges and possible new projects.

Exchanging ideas.

18<sup>40</sup> 10<sup>40</sup>

**Final Remarks and End of Spring School**

18<sup>45</sup> 10<sup>45</sup>



**BEER**

**Online Spring School Party**

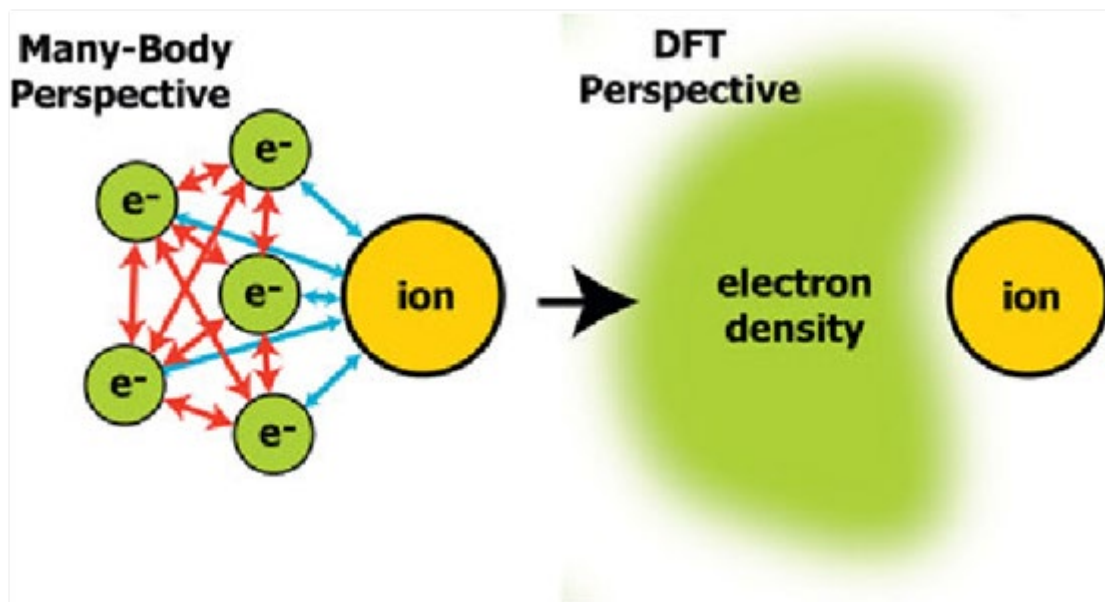
Our virtual social event.

Cheering, laughing, sharing drinks and toasts

# A way too short introduction to Density Functional Theory

Rachid Stefan Touzani

Density Functional Theory (DFT) is a well-established, ingenious approximation to the Schrödinger equation. Modern DFT is based on the ideas of Hohenberg, Kohn and Sham. DFT's fundamentals are as old as quantum mechanics itself and combine the motivation and tricks of the Hartree-Fock theory and the Thomas-Fermi density ansatz. With the help of DFT one can predict and explain experimental findings like crystal structure, site preferences, magnetism, elastic properties and thermodynamics. In this talk I will try to give a short but comprehensive introduction to DFT itself and what it is really capable of in the use to study solid state materials.



From many-body electrons to electron density [1]

[1] M.T. Lusk, A. E. Mattsson, MRS Bulletin, 2011, 36, 169-174.

# **Strengthening of additively manufactured Me-Si-B (Me = Mo, V) by Y<sub>2</sub>O<sub>3</sub> particles**

**Janett Schmelzer, Silja-Katharina Rittinghaus, Markus B. Wilms, Oliver Michael and Manja Krüger**

In the present study a new approach on strengthening of innovative high-temperature Me-Si-B (Me = Mo, V) materials by Y<sub>2</sub>O<sub>3</sub> particles is presented. This approach combines the oxide dispersed strengthening (ODS) mechanism and additive processing of innovative intermetallic materials. To this end, gas atomized powder material, suitable for additive manufacturing, was doped with Y<sub>2</sub>O<sub>3</sub> particles. Bulk materials were manufactured via direct energy deposition (DED), which is an efficient method to generate crack-free Me-Si-B alloys. The DED process further allows the homogeneous distribution of Y<sub>2</sub>O<sub>3</sub> particles in the intermetallic matrix. Hardness measurements as well as uniaxial compression tests depict the potential of novel Y<sub>2</sub>O<sub>3</sub> reinforced Me-Si-B alloys.

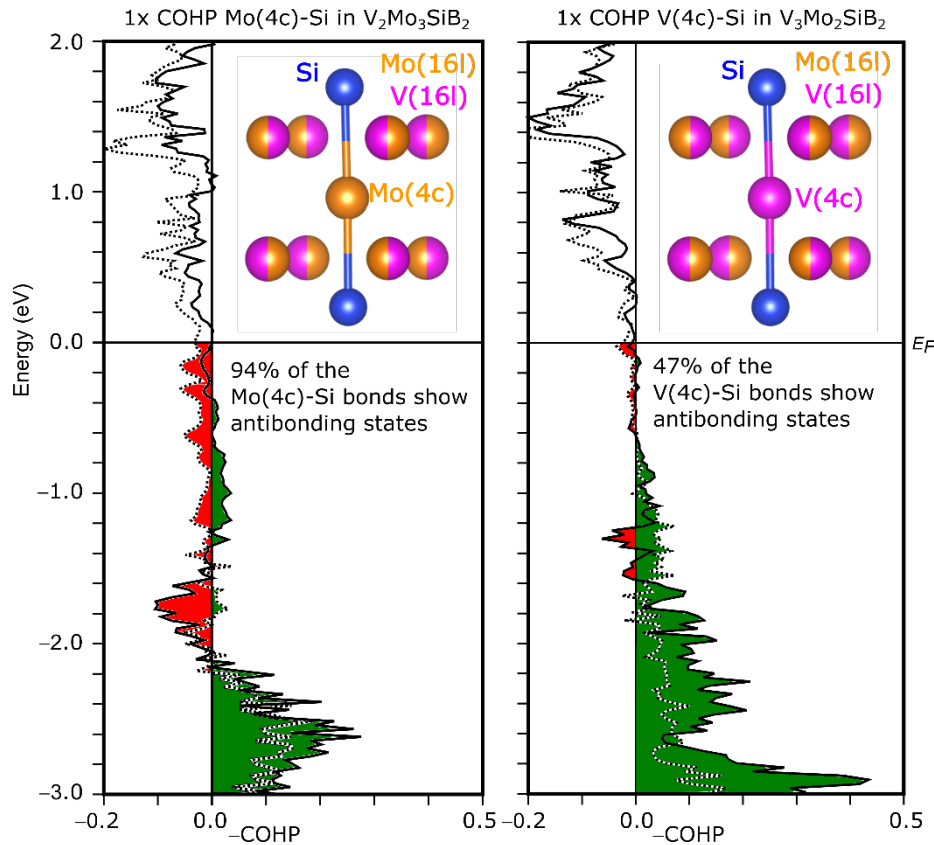
## **A novel alloy development approach: Biomedical high-entropy alloys**

**Maximilian Regenberg, Georg Hasemann and Manja Krüger**

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: The new concept of combining several elements (at least 5 principal elements with concentrations between 5 and 35 at.%) in contrast to conventional alloys, mostly containing only two or three elements. This results in a broad variety of possible combinations thus leading to completely novel alloys. Secondly, recently developed and examined 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. However, besides the outstanding mechanical properties, abrasion resistance and thermal resistance, a vast variety of chemical elements used in RHEAs also belong to the category of biocompatible elements, hence leading to potentially new biomedical materials. This whole new area of possible applications and alloy development strategies is in the focus of our current research and is reported on in the presented study.

# Site preference of V and chemical bonding in $V_{5-y}Mo_ySiB_2$ in the Mo-40V-9Si-8B alloy

Rachid Stefan Touzani, Julia Becker and Manja Krüger



-COHP-plots of the Mo-Si bond in  $V_2Mo_3SiB_2$  (left) and V-Si bond in  $V_3Mo_2SiB_2$  [1]

In the Mo-40V-9Si-8B alloys the  $T_2$  phase  $V_3Mo_2SiB_2$  shows a site preference for vanadium on the 4c Wyckoff position as reported in [2].

In our presentation we will explain this observation with the insights given by first principles density functional theory (DFT) calculations using a chemical bonding analysis.

[1] R. Touzani, J. Becker, M. Krüger, J. Alloy Comp., 2020, 819, 153041.

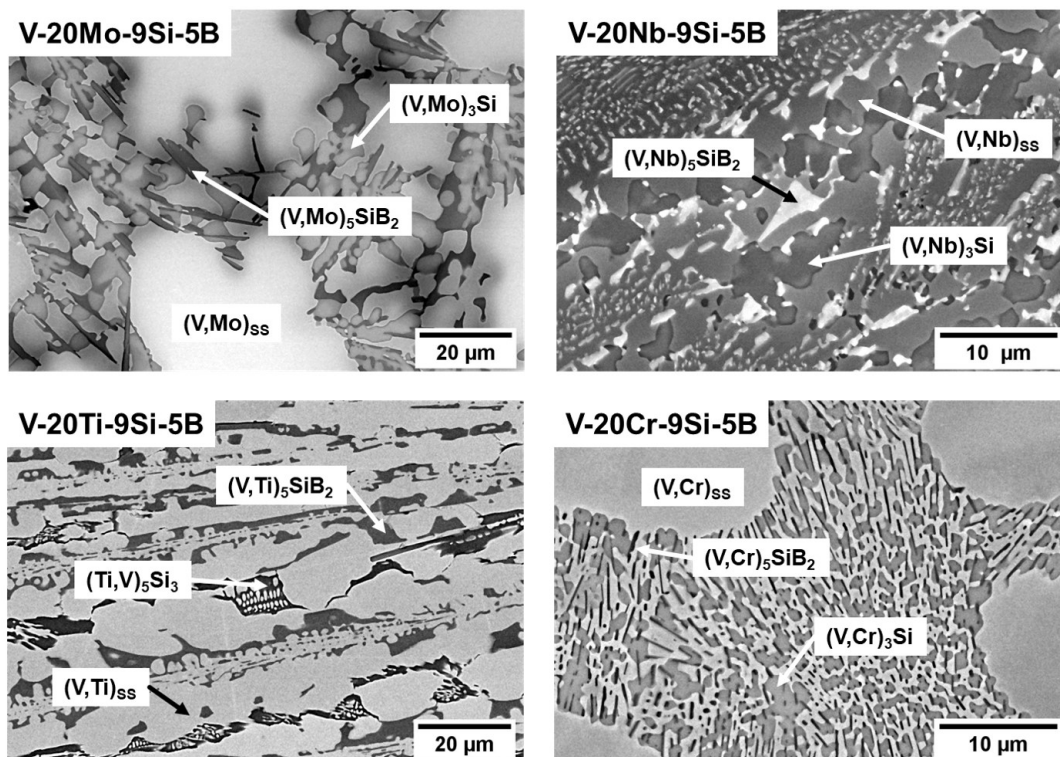
[2] J. Becker, U. Betke, M. Hoffmeister, M. Krüger, JOM, 2018, 70, 2574-2581.

# Novel intermetallic silicides and borides in the V-TM-Si-B System (TM = Ti, Cr, Nb, Mo)

Georg Hasemann and Rachid Stefan Touzani

Based on investigations and developments of the Mo-Si-B-Ti [1] and Mo-Si-Ti [2] systems, the effect of quaternary alloying elements of the V-Si-B system should be investigated. Special attention will be paid to the  $V_{ss}$ - $V_3Si$ - $V_5SiB_2$  ternary eutectic reaction and how does the additional alloying elements promote or suppress this invariant reaction. Furthermore, the chemical concentrations of the intermetallic phase should be studied and how their stability might be influenced by additional elements. Ti for example is known to destabilize the  $Mo_3Si$  phase.

DFT will help us do stable site occupations and atomic bonds in the alloyed intermetallic phases is able to predict certain mechanical properties (i.e. elastic constants, Young's modulus and hardness). Combining key experiment with ab initio DFT calculations will lead to a new materials design approach for V-based alloys.



Microstructures of quaternary hypoeutectic V-20TM-9Si-5B

[1] D. Schliephake et al., Metal Mater Trans A, 2014, 45, 1102-1111.

[2] S. Obert et al., JMR&T, 2020, 9, 8556-8567.

# First-principle calculation on design of Mo-Ti based BCC solid solution

**Takahiro Kaneko and Kyosuke Yoshimi**

MoSiBTiC [1] alloy and enriched Ti [2] one have been achieved excellent properties; ultra-high temperature strength, fracture toughness, density, and oxidation resistance. According to recent studies [2-4] these properties are achieved with Mo-Ti BCC solid solution phase. Especially, Mo:Ti ratio in the BCC solid solution phase is one of key factors on the oxidation resistance. However, the role of Ti at high concentration in the Mo-Ti BCC solid solution phase has not been clarified. In this study, structural stability, elastic modulus, and lattice parameter of the Mo-Ti BCC structure were investigated by first-principle calculation. The experimental study [2] clarified the oxidation resistance of Mo-Ti alloys is improved at a high concentration of Ti in the Mo-Ti BCC phase. However, the calculation results showed increase in Ti concentration decreases the elastic moduli of the Mo-Ti BCC phase. As an ultra-high temperature material, it is necessary to achieve both mechanical strength and oxidation resistance. In order to improve the low elastic moduli, effects of third element X was added into the Mo Ti BCC phase, and their effect on its material properties was investigated. Elastic moduli and structural stability of Mo-Ti-X BCC structures were strongly dependent on additive element, and then these values were periodically changed. Some elements increased the elastic moduli and improved the structural stability of the BCC structure as compared with Mo-Ti binary. Furthermore, it was also possible to control the lattice parameter with additive third element. In this study, the calculation results suggest that third element addition to Mo-Ti based BCC phase is the effective method to improve its performance and optimize alloy design.

[1] Shimpie Miyamoto, Kyosuke Yoshimi, Seong-Ho Ha, Takahiro Kaneko, Junya Nakamura, Tetsuya Sato, Kouichi Maruyama, Rong Tu and Takashi Goto, *Metal.Mater.Trans.A*, 45A(2014), 1112-1123.

[2] Tomotaka Hatakeyama, Shuntaro Ida, Nobuaki Sekido, Kyosuke Yoshimi, *Corrosion Sci.*, 176(2020),108937.

[3] Takahiro Moriyama, Kyosuke Yoshimi, Mi Zhao, Tiffany Masnou, Tomohiro Yokoyama, Junya Nakamura, Hirokazu Katsui, Takashi Goto, *Intermetallics*, 84(2017), 92-102.

[4] Shiho Yamamoto Kamata, Daili Kanekon, Yuanyuan Lu, Nobuaki Sekido, Koichi Maruyama, Gunther Eggeler and

Kyosuke Yoshimi, *Scientific Reports*, 8 (2018), 10487.



# Evaluation of composition and structure stability of mullite by First-Principles Calculation

Kotaro Hoshizaki and Kyosuke Yoshimi

**Introduction:** Mullite ( $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$ ,  $0.25 \leq x \leq 0.4$ ) is an aluminosilicate with a composition range of  $\text{Al}_2\text{O}_3$  from 60 to 66 mol. % and has high potential as a high-temperature material due to good oxidation resistance and better thermal shock resistance compared with  $\alpha$ - $\text{Al}_2\text{O}_3$ . However, there is still room for improvement in the high-temperature strength of mullite. Although challenges had been made by fourth element addition in previous studies, it is difficult to comprehensively evaluate their effect by means of experiments because a small amount of impurity readily changes its physical, chemical and mechanical properties. Furthermore, the site-occupation behavior of substitutional elements on the Al and Si cation sites and vacancy formation on the O anion site also change the structure stability of mullite. Therefore, in this study, the ionic-crystal structure model of mullite is constructed for first-principles calculation and the effect of fourth element on its stability is evaluated using the model in order to explore the composition of mullite with higher heat resistance.

**Computational method:** All compounds were calculated by density functional theory using the Advance/PHASE (AdvanceSoft corp.). Calculations were performed using Generalized Gradient Approximation (GGA) and the projector augmented wave (PAW-PBE) potentials,  $3 \times 6 \times 9$  k-point (Monkhorst-Pack method) and 600 eV of cut-off energy.

**Results:** In order to construct the mullite structure model, the structure of sillimanite ( $\text{Al}_2\text{SiO}_5$ ,  $\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{SiO}_2) = 0.5$ ) where the occupancy of all sites is 1, was calculated first. The mullite structure models were constructed by minimizing the formation enthalpy with the addition of  $\text{Al}_2\text{O}_3$  to the sillimanite. The calculated formation enthalpy for sillimanite and mullite at two kinds of composition are lower than the formation enthalpy line connecting between the enthalpy of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (Fig.). In addition, the formation enthalpy of mullite decreases with increasing  $\text{Al}_2\text{O}_3$ . They are in good agreement with a phase diagram [1]. Using the model, the formation enthalpy variation with a fourth element was systematically calculated and evaluated based on the periodic table.

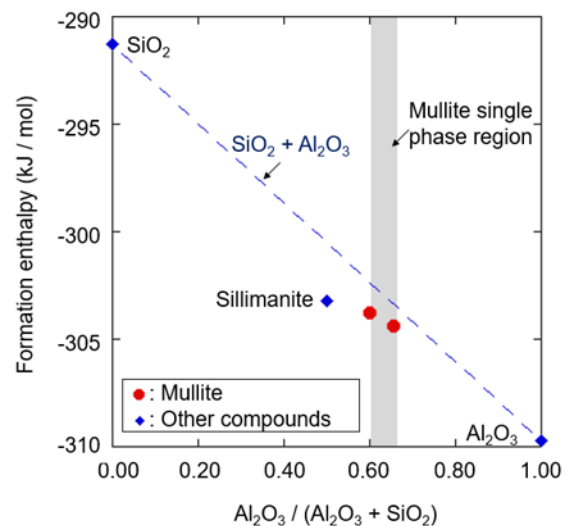


Figure: Formation enthalpy of  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  system : By increasing  $\text{Al}_2\text{O}_3$  content, formation enthalpy decreases. Both Mullite are lower than line of  $\text{SiO}_2 + \text{Al}_2\text{O}_3$ .