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FACULTY OF MATHEMATICS AND PHYSICS
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Miscibility gap in tungsten-based alloys

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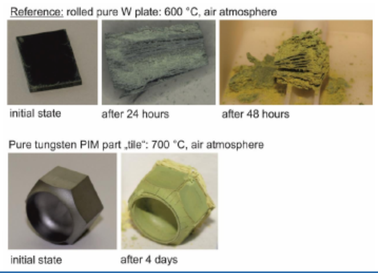


Thermonuclear reactors

clean energy	⇔	novel **fusion** reactors
D + T	$\xrightarrow{fusion}$	He^4 + n + energy
plasma	$\xrightarrow{heat}$	**wall**
wall	$\xrightarrow{heat}$	water
hot water	$\xrightarrow{turbine}$	electricity

extreme conditions (plasma ∼100 000 000°C in 5T)
→ new **materials** on the **wall**
→ **material design** of tungsten (second hardest element) based alloys

Methods - Computation details

Electronic structure calculations

- Density Functional theory[1](DFT) based electronic structure calculations using VASP code[2; 3]
- projector-augmented wave (PAW) pseudopotentials of Perdew-Burke-Ernzerhof type[4]
- Γ-centered k-point mesh of 4×4×4 used for the supercell(see below)
- Kinetic (cut-off) energy of 320eV
- Valence states of 6*e*, *i.e.* $5d^46s^2$, $4d^55s^1$, $3d^54s^1$, for W, Mo, Cr, 5*e*, $5d^36s^2$ for Ta and 4*e*, $5d^26s^2$ for Hf, respectively.

Gibbs energy evaluation:

- Phononic spectra within 90-110% volume obtain within quasi-harmonic approximation[5] employing Phonopy code[6]
- Supercell of 3×3×3
- Frozen ion calculations displacement of 0.01Å
- Thermodynamical properties evaluated up to 3000K with step of 1K on fine q-mesh 69×69×69
- $S(T) = S_{configuration} + S_{electronic(T)} + S_{phononic(T)}$, $S_{configuration} = -k_B\Sigma_i x_i log(x_i)$ for alloy $A_{x_1}B_{x_2}C_{x_3}...(\Sigma_i x_i = 1)$
- Gibbs energy of formation $\Delta G_{A_x,B_y,C_z} = G_{A_x,B_y,C_z} - xG_A - yG_B - zG_C$, where $x+y+z=1$, and $G_A = G_A(T,P), G_B(T,P), G_C(T,P)$ are Gibbs energy of pure systems.

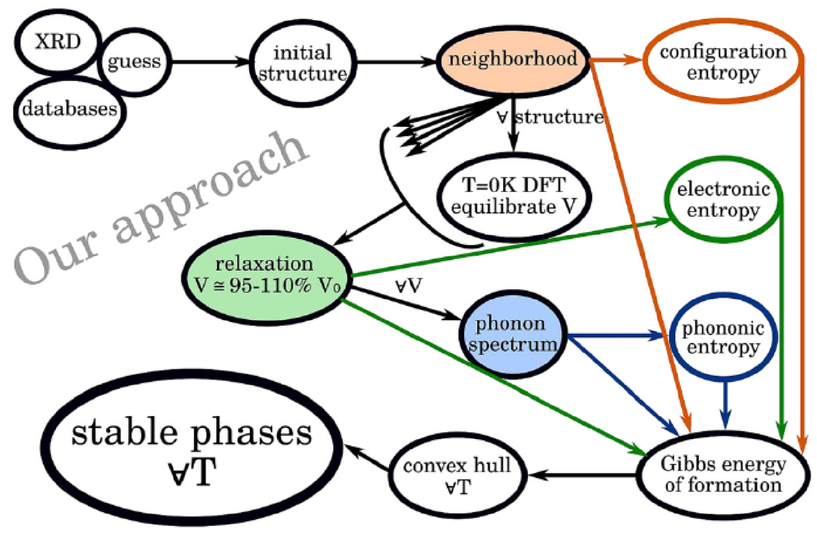
Special quasirandom structures (SQS) generation:

- SQS - originally developed in 90's of 20^{th} century[7], starting from 1.P1 symmetry group
- Error function optimized by Metropolis-Hastings algorithm[8; 9]
- Our approach much faster: (*i*) Body-centered cubic (BCC) based structure alloys of N-size, (*ii*) random change of $n << N$ on BCC lattice, (*iii*) analysis of symmetry to remove redundant and the ones with lowest symmetry (1.P1), (*iv*) calculate error function for each surviving structures with probability $P_i = \frac{\zeta_0}{\zeta_i}$, (*v*) if not desired concentration achieved we create a new set of of best surviving structures inserting into (*ii*).

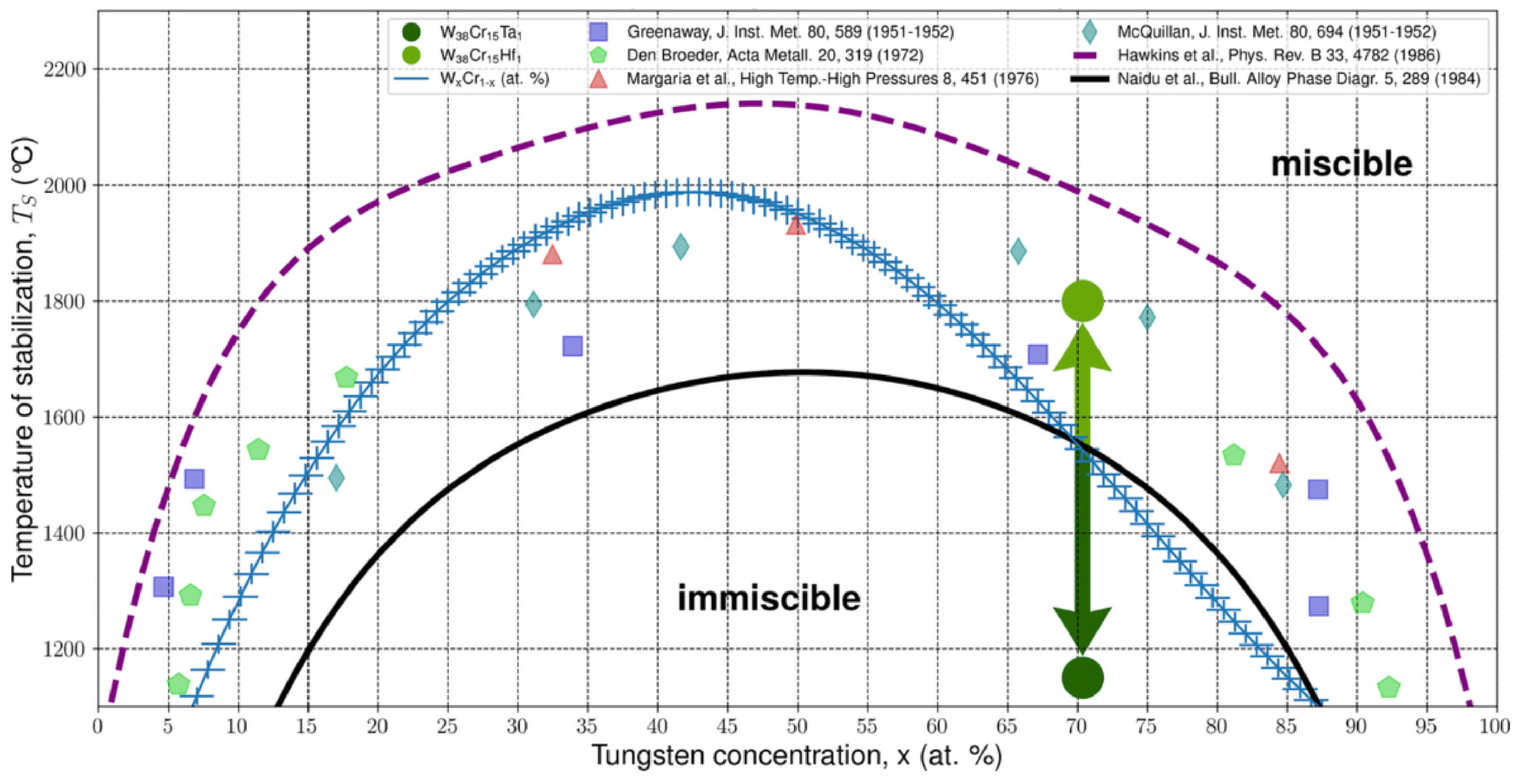
More details in Ref.[10] and references therein.

Abstract

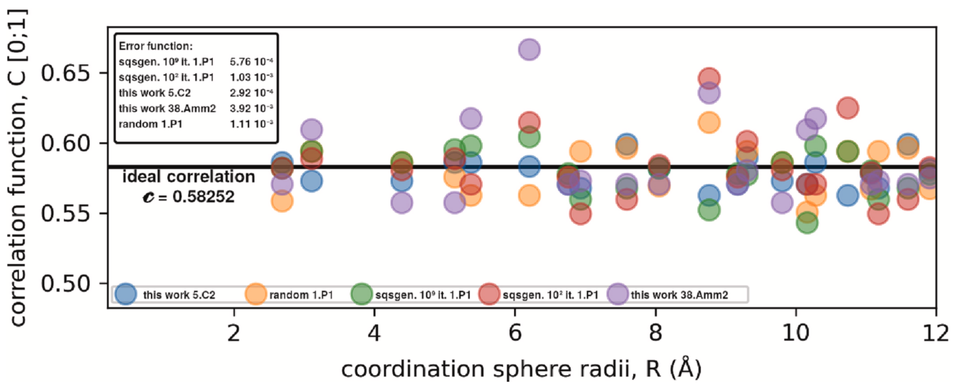
We establish an approach to model miscibility gaps of alloys using statistical physics, lattice dynamics from first-principles calculations. We carefully calculate the entropy to include all processes introducing disorder to the system, i.e., combining the electronic, phononic, and configuration entropies. Furthermore we present our algorithm for generating Special Quasirandom Structures (SQS). We model the miscibility gap in tungsten - chromium and tungsten - molybdenum systems, obtaining the agreement with the experimental data. Furthermore, we propose an enhancement for the tungsten-chromium $W_{70}Cr_{30}$ alloy with tantalum and hafnium, leading to the modified stabilization temperatures T_S, where the solid solution is miscible. **The work is published in Ref.[10]**



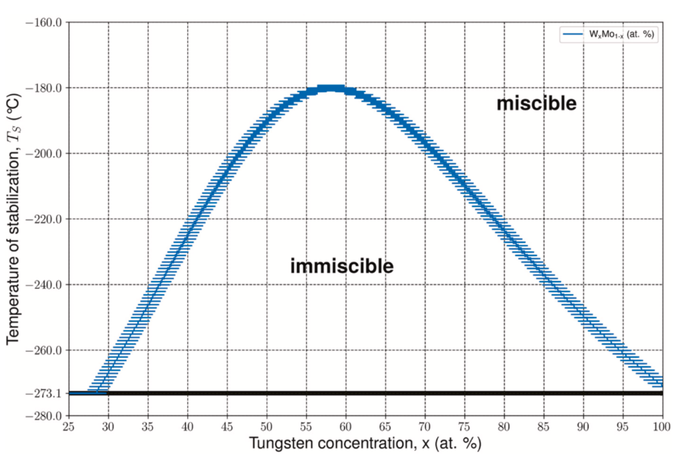
RESULTS: Miscibility gap in Tungsten-Chromium alloys



SQS - Generated structures - correlation function



Miscibility gap in Tungsten-Molybdenum alloys



Conclusion

- We are able to compute miscibility gap for any kind of alloys without any empirical parameter, just based on electronic structure method (DFT), see the blue crosses in W-Cr and W-Mo phase diagrams.
- In contrast, until now only empirical and parameter-based calculations[11; 12] (solid black line and dashed purple line) model the phase diagrams for high temperatures, however, with very small accuracy.
- We determine the modification of the miscibility temperature of the system by adding ternary element Ta (decrease) and Hf (increase) according to recent experimental study.[13]

References

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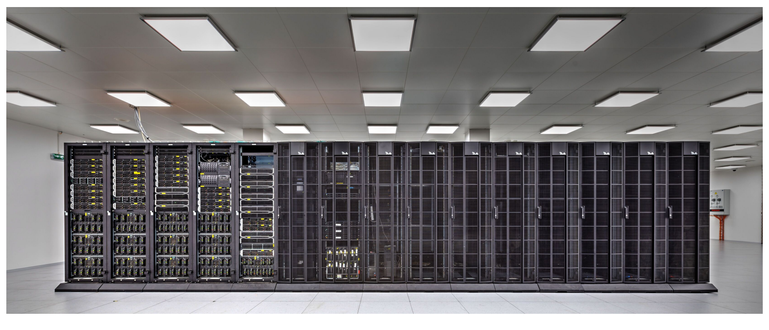
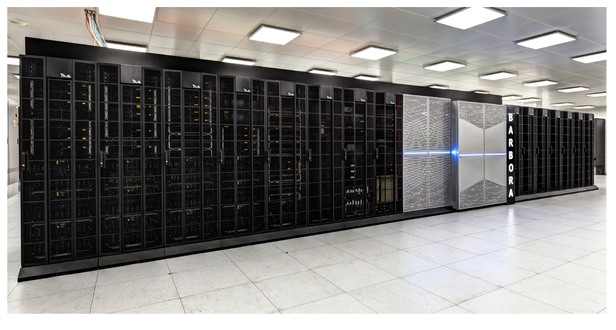
IT4INNOVATIONS - Czech National Supercomputing Centre - ”Equipment” for our calculations





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