STABILITY AND ELASTICITY OF THE MoN–TaN SYSTEM: AN ATOMISTIC INSIGHT

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Transition metal nitrides (TMNs) represent a prominent class of materials possessing numerous outstanding physical properties, such as excellent chemical and thermal stability, incompressibility and strength, high melting point and good thermal and electronic conductivity or superconductivity. Therefore, considerable efforts have been devoted to investigate the possibility of enhancing performance of exceptional TMNs by designing ternary or multinary TMN systems. MoN and TaN have attracted significant attention owing to their beneficial properties in functional thin film applications spanning from electronics to protective coatings. Up to date, however, there has been only one first-principles study [1] on the MoN–TaN ternary system.

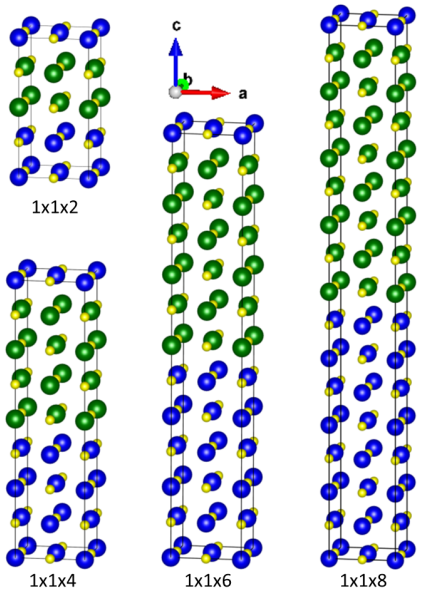

Figure 1: Computational models for MoN/TaN superlattices.

To gain a deep insight into chemical, mechanical, and dynamical stability of MoN–TaN, it is desirable to employ density functional theory (DFT), as a state-of-the-art method of quantum-mechanical modelling. Thanks to its high reliability, DFT has become a powerful tool of computational materials science and an important counterpart to experiment. In the present study, the $Mo_{1-x}Ta_xN$ solid solutions are assumed to adopt the cubic structure with NaCl prototype ($Fm\bar{3}m$, #225, B1-type), often referred to as rocksalt (rs) structure, and the hexagonal structures with NiAs ($P6_3/mmc$, #194), WC ($P\bar{6}m2$, #187), and TaN ($P\bar{6}2m$, #189) prototypes, respectively. Besides, we consider cubic-like MoN/TaN superlattices, as another materials design concept (Fig. 1).

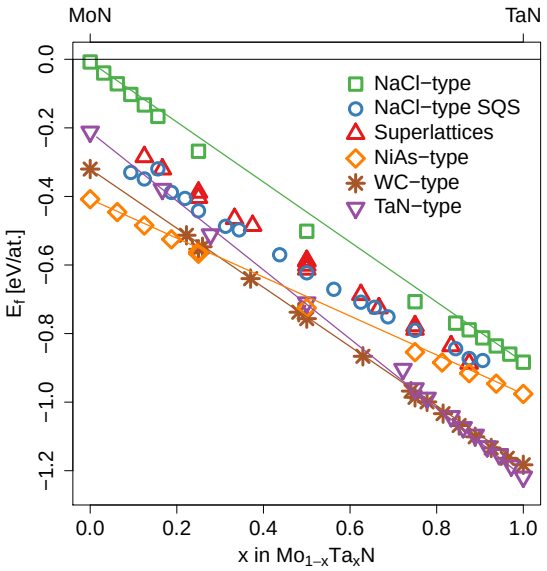

Figure 2: Energy of formation, E_f, of various $Mo_{1-x}Ta_xN$ systems as a function of Ta content.

Our calculations (Fig. 2) clearly demonstrate that hexagonal-type $Mo_{1-x}Ta_xN$ solid solutions based on low-energy modifications of MoN and TaN are the most stable over the whole compositional

range. Despite being metastable, the disordered cubic polymorphs are energetically significantly preferred over their ordered counterparts. An in-depth analysis of atomic environments in terms of bond lengths and angles (Fig. 3) reveals that the chemical disorder results in (partially) broken symmetry, i.e., the disordered cubic structure relaxes towards a hexagonal NiAs-type phase, the ground state of MoN.

Surprisingly, superlattice architecture is also clearly favored over the ordered cubic solid solution. We show that the bi-axial coherency stresses in superlattices break the cubic symmetry beyond simple tetragonal distortions and lead to a new tetragonal ζ-phases (P4/nmm, #129) exhibiting a lower formation energy than the symmetry-stabilized cubic structures of MoN and TaN. Unlike the cubic TaN, the ζ-TaN is predicted elastically and vibrationally stable, while the ζ-MoN is stabilized only by the superlattice structure.

To analyse compositional trends in the elastic response of various $Mo_{1-x}Ta_xN$ systems, we establish their mechanical stability and find the closest high-symmetry approximants of the elastic tensors. The disordered cubic and all the hexagonal systems are mechanically stable (though the TaN-type MoN is nearly unstable); on the contrary, the ordered cubic systems and superlattices are stabilized only above some critical Ta content of $\sim 25\%$ and $\sim 50\%$, respectively. The estimated polycrystalline elastic moduli shown in Fig. 4 suggest than the hexagonal NiAs- and WC-phases of $Mo_{1-x}Ta_xN$ are significantly harder that the other modifications. According to the Pugh's criterion and Poisson's ratio, the cubic polymorphs and the sublattices are predicted to be ductile. The trends in stability based on energetics and elasticity are corroborated by density of electronic states.

Finally, our systematic and in-depth study provides information on stable and metastable phases in quasi-binary MoN–TaN system, and as such can guide experimental search for functional thin films with complex chemistry and/or architecture.

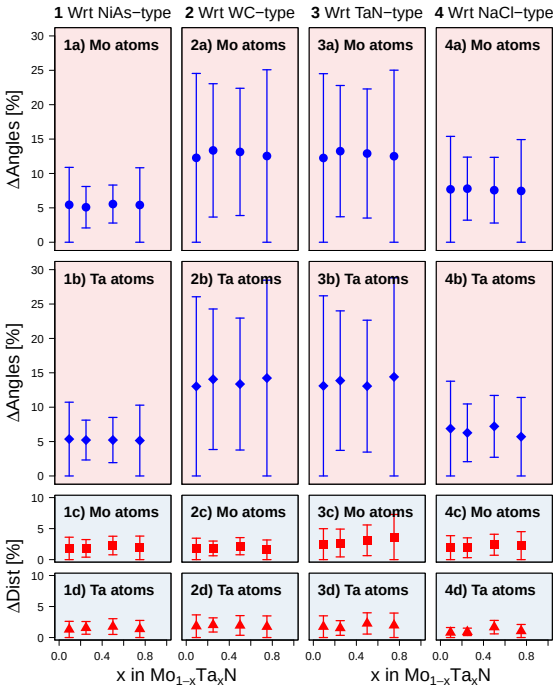

Figure 3: Analysis of local environments in disordered $Mo_{1-x}Ta_xN$ systems.

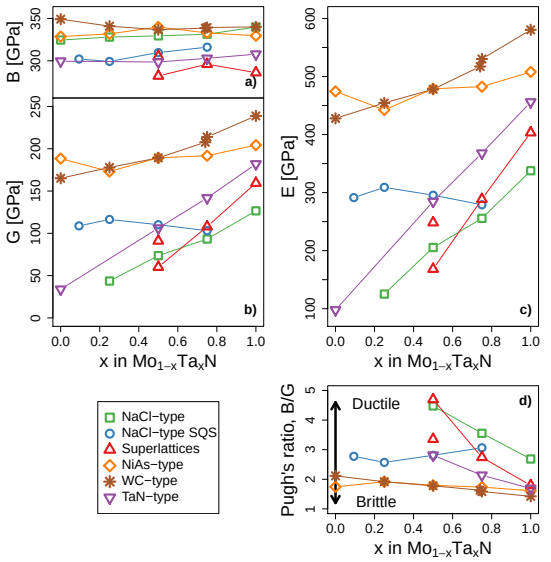

Figure 4: (a) Bulk modulus, (b) shear modulus, (c) Young's modulus, and (d) Pugh's ratio of various $Mo_{1-x}Ta_xN$ systems.

REFERENCES

[1] K. Bouamama, P. Djemia, and M. Benhamida, Journal of Physics: Conference Series **640** (2015) 012022.