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# Stability and elasticity of metastable solid solutions and superlattices in the MoN–TaN system: First-principles calculations

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In order to develop design rules for novel nitride-based coatings, we investigate trends in thermodynamic, structural, elastic, and electronic properties of $Mo_{1-x}Ta_xN$ single-phase alloys together with $(MoN)_{1-x}/(TaN)_x$ superlattices. Our calculations predict that hexagonal $Mo_{1-x}Ta_xN$ are the overall most stable ones, followed by the disordered cubic solid solutions and superlattices. The disordered cubic systems are energetically clearly favoured over their ordered counterparts. To explain this unexpected phenomenon, we perform an in-depth structural analysis of bond-lengths and angles, revealing that the disordered phase is structurally between the NaCl-type and the hexagonal NiAs-type modifications. Similarly, the bi-axial coherency stresses in MoN/TaN break the cubic symmetry beyond simple tetragonal distortions, leading to a new tetragonal ζ-phase (P4/nmm, #129). Both ζ-MoN and ζ-TaN have lower formation energy than their cubic counterparts. Unlike the cubic TaN, the ζ-TaN is also dynamically stable. The hexagonal alloys are predicted to be extremely hard, though, much less ductile than the cubic polymorphs and superlattices.

**KEY WORDS**

MoN-TaN; phase stability; symmetry; elasticity; electronic properties

**HIGHLIGHTS**

- We present DFT calculations on $Mo_{1-x}Ta_xN$ solid solutions and $(MoN)_{1-x}/(TaN)_x$ superlattices.
- The most stable alloys crystallize with a hexagonal symmetry and exhibit high elastic moduli.
- Due to their local relaxation towards a hexagonal phase, the disordered fcc-based alloys are energetically and mechanically superior to their ordered counterparts.
- MoN/TaN interface leads to a stabilisation of novel tetragonal ζ-phases with an improved dynamical stability.
- The superlattices are predicted to be more ductile than the most stable hexagonal alloys.

## 1. INTRODUCTION

Transition metal nitrides (TMNs) represent a prominent class of materials possessing numerous outstanding physical properties, such as excellent chemical and thermal stability [1, 2], incompressibility [3, 4] and strength [5, 6], high melting point, good thermal and electric conductivity or superconductivity [7–9]. In order to enhance materials performance, considerable efforts have been devoted to investigate the possibility of fine tuning the energetic, mechanical and/or electrical properties by designing ternary or multinary (T)MN systems [10–19].

The addition of nitrogen atoms into the high-density electronic gas of transition metals together with the covalent bonding leads to extraordinary hardness [20, 21]. Specifically, the hardness of MoN and TaN ranges from 28 to 34 GPa [4, 22–24]. According to Teter's empirical law [25], hardness scales with shear modulus. Later, Chen *et al.* [26] also correlated hardness to bulk modulus. Recent systematic DFT calculations on Ta–N[27] and Mo–N[28] system suggest that the bulk modulus can reach 338 and 347 GPa for the WC-type TaN and $\delta$-$MoN_2$, respectively, which is comparable with the 370 GPa of the cubic BN[29].

TMNs often crystallise in a cubic NaCl-type structure ($Fm\bar{3}m$, #225), termed as rocksalt (rs) [30]. Despite being metastable, the cubic modifications of MoN and TaN have been synthesized using non-equilibrium growth techniques [4, 22, 31–34], e.g., reactive magnetron sputtering in high nitrogen partial pressure atmosphere, nitrogen ion implantation, or low energy ion assisted deposition. Properties of cubic MoN and TaN are comparable with, or even superior to those of the ground state phases. For example, cubic TaN prepared by shock and static compression was shown to have very good