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**Effects of atomic ordering on the elastic properties of
TiN- and VN-based ternary alloys**

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Abstract

Improved toughness is one of the central goals in the development of wear-resistant coatings. Previous studies of toughness in transition metal nitride alloys have addressed the effects of chemical composition in these compounds. Herein, we use density functional theory to study the effects of various metal sublattice configurations, ranging from fully ordered to fully disordered, on the mechanical properties of VM₂N and TiM₂N (M₂ = W, Mo) ternary alloys. Results show that all alloys display high incompressibility, indicating strong Me-N bonds. Disordered atomic arrangements yield lower values of bulk moduli and C₁₁ elastic constants, as well as higher values of C₄₄ elastic constants, compared to ordered structures. We attribute the low C₄₄ values of ordered structures to the formation of fully-bonding states perpendicular to the applied stress. We find that the ductility of these compounds is primarily an effect of the increased valence electron concentration induced upon alloying.

Keywords: Nitrides, density functional theory, elastic properties, ductility, toughness

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1. Introduction

Transition metal nitrides are commonly employed as protective coatings in the cutting tool industry due to their excellent properties, such as high hardness and wear resistance, high melting temperature, and chemical inertness [1–3]. In particular, hard coatings prevent the surfaces of the components from being scratched and worn at extreme working pressures, thus significantly enhancing the lifetime of tools and reducing costs.

During the past two decades, development of coating materials with increasingly higher hardness has been one of the major focus areas of materials science. Great success has been achieved using a variety of experimental approaches, which generally aim to enhance hardness by reducing the mobility of dislocations. These include, for instance, synthesis of nano-scale composites [4,5] and vacancy-induced hardening [6–8]. Hardness may also be improved by tuning the material valence electron concentration (VEC). Jhi et al. [9] demonstrated that a VEC of 8.4 yields maximum hardness in cubic transition metal nitride and carbide alloys, as shear resistant metal-N/C d-p electronic states are fully occupied, while metallic d-d states remain empty. Hugosson et al. [10,11] employed VEC-tuning to set the cubic and hexagonal structures of transition metal nitride and carbide alloys to equal energy, thus promoting the formation of stacking faults, which increases hardness by hindering slip across the faults.

Hard materials are less responsive to plastic deformations. This limits their ability to dissipate stresses by plastic flow, and results in crack formation and

propagation leading to brittle failure. Ceramics, such as transition metal nitrides, are inherently brittle [12,13], and consequently, modern hard ceramic thin film coatings are prone to brittle failure, especially during in-use conditions [14,15], for example in cutting tool applications. It is thus a priority to design coating materials which, aside from being hard, are also ductile. The combination of hardness and ductility in a material is referred to as high toughness.

In previous studies [16,17], we predicted that ordered cubic $\text{Ti}_{0.5}\text{Mo}_{0.5}\text{N}$, $\text{Ti}_{0.5}\text{W}_{0.5}\text{N}$, $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}$, and $\text{V}_{0.5}\text{W}_{0.5}\text{N}$ alloys are not only harder, but also significantly more ductile than their parent binaries TiN and VN. The enhanced toughness in these ternary alloys was shown to be induced by the increased occupation of the metallic states at the Fermi level, due to the higher VEC obtained upon the substitution of Ti/V with Mo/W atoms on the metallic (*Me*) sublattice. The higher VEC not only preserves the typically strong *Me*-N bonds found in binaries, but enables the formation of stronger *Me-Me* bonds compared to TiN and VN. Overall, high VEC lowers the shear resistance and energetically promotes dislocation glide, thus leading to increased ductility.

Experimental verification of these predictions was recently provided by the synthesis and testing of cubic single-crystal $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_x$ ($0.55 < x < 1$) thin films [18,19]. Stoichiometric VMoN alloys are harder than VN [18], and the hardness of VMoN_x films increases with the addition of N vacancies [19]. Moreover, nanoindentation experiments conducted at constant penetration show that, while VN and TiN films systematically crack, $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}$ films never exhibit crack formation [18,19]. In contrast, the alloy samples display material pile-up, due to plastic flow, in the regions adjacent to the indented area, which is characteristic of ductile materials.

The deposited VMoN films, however, show no evidence of ordering on the metal sublattice.

Single-crystal cubic-B1 $V_{1-x}W_xN$ thin films, which is another ternary alloy we predicted to possess enhanced toughness, have also been recently synthesized in the compositional range $0 < x < 0.60$ [20,21]. These films exhibit a monotonic increase in hardness with x , of up to 55%, at $x = 0.60$, as well as reduced elastic modulus and increased Cauchy pressures ($C_{12} - C_{44}$), both of which are indicative of enhanced toughness. We note that alloying TiAlN with WN has a similar effect on the hardness of TiAlWN thin films [22], in agreement with our predictions for TiAlN-based quaternaries [23]. Local [111] ordering has been observed in $V_{0.6}W_{0.4}N$ films deposited at 600 - 700 °C [20], while films grown at higher temperatures showed no evidence of ordering. Long-range CuPt ordering on the metal sublattice was observed in $Ti_{0.5}W_{0.5}N$ thin films grown on MgO(001) substrates at 500 °C [24].

Our previous theoretical predictions of toughness enhancements in $MI_{0.5}M2_{0.5}N$ ($M1 = Ti, V$; $M2 = Mo, W$) alloys [16,17], were based on calculations carried out on structures with long-range order, closely resembling the ideal CuPt arrangement observed in $Ti_{0.5}W_{0.5}N$ thin films [24]. However, the experimental results show that as-deposited cubic $MI_{0.5}M2_{0.5}N$ films are solid solutions in most cases. To date, the effect of ordering on the metallic sublattice, on the elastic properties of these ceramics, has not been investigated. In this paper, we use density functional theory (DFT) calculations to assess the effects of varying the metal sublattice atomic arrangement, from highly ordered to fully disordered, on the formation energies and the mechanical properties of $MI_{0.5}M2_{0.5}N$ alloys. Our results show that while the elastic properties of these alloys vary, and thus depend on the degree of order on the cation

sublattice, the enhanced toughness of these compounds, as demonstrated experimentally, remains primarily a VEC effect.

2. Computational details

We use the Vienna ab initio simulation package (VASP) [25] to perform DFT calculations in the generalized gradient approximation of Perdew-Wang (GGA-PW91) [26]. Electron-ion interactions are described using projector augmented wave potentials (PAW) [27]. Total energies are minimized to converge within 10^{-5} eV using an energy cut-off of 500 eV for the plane wave basis set. For each alloy, we investigate the physical properties of five different atomic arrangements, as shown in Fig. 1: ordered C#1, C#3, and CuPt, a purely random arrangement, and a special quasirandom structure (SQS) [28].

Figure 1: Atomic arrangements on the metallic sublattice. (a) C#1 structure. (b) C#3 structure. (c) CuPt structure. (d) Intermediately disordered, Random structure. (e) Fully-disordered, 128-atom SQS structure.

The SQS structure is constructed in supercells with 128 atoms to better model a disordered system. Supercells of all other atomic configurations contain 64 atoms. Structure optimizations are carried out by relaxing supercell volumes, shapes, and atomic positions, using the conjugate gradient algorithm. The Brillouin zone is scanned via the Monkhorst-Pack scheme [29], on $4 \times 4 \times 4$ and $6 \times 6 \times 6$ $\mathbf{k}$ -point grids, for the 128-, respectively 64-atoms, supercells. For all charge density calculations we use $8 \times 8 \times 8$ $\mathbf{k}$ -

point grids. Charge transfer maps are obtained by subtracting superimposed atomic wave function charge densities from calculated alloy charge densities. Figures of charge density maps and charge transfer maps are produced using the VESTA [30] and the STRender codes.

The C#1 structure is the $L1_0$ variant of the rocksalt structure, as it contains alternating $M1/N$ and $M2/N$ (001) planes (Fig. 1a), and has tetragonal symmetry. The C#3 structure, used in our previous studies [16,17] consists of alternating (111) planes containing 75/25%, respectively 25/75%, $M1/M2$ ratios (Fig. 1b). The C#3 structure is closely related to the CuPt arrangement (Fig. 1c), which consists of alternating (111) planes containing 100% $M1$ or $M2$ atoms, respectively. We note that while the C#3 structure has cubic symmetry, the CuPt structure, which corresponds to $L1_1$ ordering, is rhombohedral. From the CuPt structure, the C#3 structure can be formed by rotating every other (001) plane by 90° . The atomic configuration shown in Fig. 1d, which mimics an intermediate level of short-range disorder in the crystal, is obtained by arbitrarily placing $M1/M2$ atoms on the metallic sublattice, and is referred to herein as the Random structure. The SQS-structure supercell is formed by inter-penetrating 64-fcc-sites Me and N sublattices (Fig. 1e), and has non-orthogonal primitive vectors, in order to minimize $Me-Me$ correlations on neighboring shells. This procedure allows for the simulation of fully disordered solid solutions.

To assess the degree of short-range order (SRO) in our alloys we use the Warren-Cowley α parameter [31]. For pseudo-binaries $M1_{1-x}M2_xN$, this is defined as $\alpha_n = 1 - P_{M2}(R_n)/x$, where $P_{M2}(R_n)$ is the probability of finding an atom $M2$ on the n^{th} neighboring shell, at a distance R , from a $M1$ atom. Ideal solid solutions will thus have α values close to zero on all neighboring shells. Negative α values on any neighboring

shell are indicative of ordering. This means that the probability of finding *M1* atoms, on spheres of radii R_n centered on *M2* atoms, is larger than the average *M1* concentration on the metallic sublattice. Positive α values, instead, are indicative of clustering, i.e. the probability of finding *M1* atoms on neighboring shells centered on *M1* atoms is larger than the average *M1* concentration on the metallic sublattice. Thus, both positive and negative α values, with extremes +1 and -1, are indicative of highly correlated atomic positions on neighboring spherical shells.

In figure 2 we plot the values of the Warren-Cowley α parameter obtained for the five structures studied herein, as calculated on neighboring spherical shells extending up to ten interatomic distances ($10 \times d_{NN} \sim 2$ nm). As expected, the C#1, C#3, and CuPt structures are highly ordered within both short and long interatomic-distance intervals. The degree of disorder is clearly higher in the Random structure, compared to the C#1, C#3 or CuPt configurations, while the SQS arrangement is close to an ideal solid solution, and has the highest degree of disorder over the entire interatomic-distance range.

Figure 2: Warren-Cowley short range order parameters, plotted as a function of interatomic-distance, for the studied atomic configurations.

For each alloy and atomic configuration, we calculate formation energies ΔE , lattice constants a , bulk moduli B , elastic constants C_{11} , C_{12} and C_{44} , Young's and shear moduli E and G , Poisson's ratios ν , and anisotropy factors A . From total energies $E_{M1_{0.5}M2_{0.5}N}$ of equilibrium structures, we estimate alloy formation energies ΔE according to:

$$\Delta E = E_{M1_{0.5}M2_{0.5}N} - 0.5E_{cubic\ M1N} - 0.5E_{cubic/hexagonal\ M2N}. \quad (1)$$

The total energies of cubic and hexagonal (hex-WC) reference binaries $M1N$ and $M2N$ structures are calculated separately using $6 \times 6 \times 6$ and $7 \times 7 \times 7$ $\mathbf{k}$ -point grids, respectively.

Average lattice constants a are obtained from $a = V^{1/3}$, where V is the unit cell equilibrium volume. The bulk modulus is calculated by fitting the energy-volume curve

to the Birch-Murnaghan equation of state [32]. Cubic systems exhibit three independent elastic constants, namely C_{11} , C_{12} and C_{44} . With the exception of C#3 lattices, the supercells used in the present study do not possess cubic point-group symmetries. However, by using a symmetry-based projection technique it is possible to find the closest elastic tensor with cubic symmetry [33,34]. The projected cubic elastic constants are found as averages according to

$$\bar{C}_{11} = \frac{C_{11} + C_{22} + C_{33}}{3}, \quad (2)$$

$$\bar{C}_{12} = \frac{C_{12} + C_{13} + C_{23}}{3}, \quad (3)$$

$$\bar{C}_{44} = \frac{C_{44} + C_{55} + C_{66}}{3}. \quad (4)$$

The elastic constants are calculated by fitting energy versus strain. We use a strain of $|\delta| \leq 0.005$. Anisotropy factors A are then determined from the expression

$$A = \frac{2\bar{C}_{44}}{\bar{C}_{11} - \bar{C}_{12}}. \quad (5)$$

Elastic moduli E , G , and Poisson's ratios ν are determined by means of the Voigt (V), Reuss (R), and Hill (H) expressions:

$$G_V = \frac{3\bar{C}_{44} + \bar{C}_{11} - \bar{C}_{12}}{5}, \quad (6)$$

$$G_R = \frac{5\bar{C}_{44}(\bar{C}_{11} - \bar{C}_{12})}{3(\bar{C}_{11} - \bar{C}_{12}) + 4\bar{C}_{44}}, \quad (7)$$

$$G_H = \frac{G_V + G_R}{2}, \quad (8)$$

$$E_{V,R,H} = \frac{9BG_{V,R,H}}{3B + G_{V,R,H}}, \quad (9)$$

$$\nu_{V,R,H} = \frac{3B - G_{V,R,H}}{2(3B + G_{V,R,H})}. \quad (10)$$

The use of the expressions (6)-(10) for the estimation of elastic moduli allows for direct comparison with nanoindentation measurements [35].

3. Results and discussion

Table 1 shows the calculated formation energies ΔE for each alloy and atomic configuration, as well as corresponding calculated and experimental lattice constants. The values for energy per atom of the reference binaries are provided in Table 2. A clear trend in formation energy of cubic phases, as a function of the degree of order on the metallic sublattice, is immediately observed for all alloys. In each case, the disordered SQS arrangement, followed by the Random configuration, are the most energetically favored structures at 0 K. Temperature will further promote disorder on the cation sublattice, due to increasingly larger contributions of the configurational entropy to the free energy. The positive ΔE values obtained for B1-*M*IN/h-*M*2N mixing suggest that the studied alloys are metastable with respect to separation in the B1 and hexagonal phases. However, as demonstrated experimentally, these thin films can be synthesized in the B1 structure [19,21,24,36].

As expected, the CuPt and C#3 structures are found to have similar formation energies, with the CuPt slightly more stable. The difference in energy between ordered CuPt and disordered SQS structures, 100-130 meV/atom for VM2N and 50-60 meV/atom for TiM2N alloys, suggests that $\langle 111 \rangle$ atomic ordering is less likely to be achieved in the studied VN-based compared to TiN-based alloy thin films. Crystal

growth by sputtering, however, is a non-equilibrium process; suitable deposition parameters can promote the formation of short-range [20] or long-range [24] $\langle 111 \rangle$ ordered transition metal nitride layers. The C#1 structure is the least stable in all cases, even displaying positive formation energies for the VMoN alloy. This indicates the L1₀ ordering of $M1/M2$ atoms on the cation sublattice is energetically unfavored.

Calculated average lattice constants (Table 1) are not significantly affected by the degree of configurational order on the metallic sublattice for any of the studied alloys. The theoretical results are in good agreement with experimental measurements [19,21,24,37,38]. Calculated lattice parameters are approximately equal to 4.3 Å for TiMoN and TiWN, and 4.25 Å for VMoN and VWN. The discrepancy, ~1%, is within the error of DFT+GGA, which tends to overestimate lattice parameters [39]. Due to the point group symmetry reduction, from a cubic solid solution to CuPt, the Ti_{1-x}W_xN(001) thin film out-of-plane lattice parameter $a_{\perp}$ relaxes from 4.251 to ~4.226 Å for W concentrations $x = 0.5$ [24]. The measured $a_{\perp}$ relaxation translates into a corresponding decrease in the relaxed average Ti_{0.5}W_{0.5}N lattice parameter a_0 [21], which is obtained from the expression

$$\Delta a_0 = 1 - \frac{a_0^{cubic}}{a_0^{CuPt}}, \quad (11)$$

for which

$$a_0 = \frac{a_{\perp}(1 - \nu) + 2\nu a_{\parallel}}{1 + \nu} \quad (12)$$

where ν is the Ti_{0.5}W_{0.5}N Poisson's ratio (0.384) obtained from present DFT calculations, and $a_{\parallel}$ is the in-plane Ti_{0.5}W_{0.5}N(001) lattice parameter. Regardless of the magnitude of $a_{\parallel}$ (not reported in [24]) the TiWN thin film relaxation along the [001]

growth direction corresponds to a a_0 decrease of $\sim 0.25\%$, in good agreement with our calculations which estimate a reduction in a_0 due to change of symmetry from cubic solid solution ($a_{\text{SQS}} = 4.307 \text{ \AA}$) to CuPt ($a_{\text{CuPt}} = 4.299 \text{ \AA}$) of $\sim 0.19\%$.

Calculated elastic properties for VWN, VMoN, TiWN, and TiMoN are found in Tables 3 to 6. Elastic properties for the parent binaries VN [17] and TiN [16] are included for reference. The indexes v, r, and h correspond to Voigt, Reuss, and Hill averages, respectively. As can be seen from Table 3, alloying VN with WN has little effect on the bulk modulus as compared to the parent VN binary. A small increase in B can be seen for the ordered alloys, of the order of 10%. In the fully-disordered SQS and Random alloys, instead, there is a 2% decrease of B. For all structures, however, W substitutions induce significant Young's and shear moduli reductions; 31% – 40% for E_h , and 35% – 45% for G_h . Similar effects are seen in the VMoN alloys (Table 4) for all calculated elastic moduli. In this case, B increases for the highly ordered structures by $\sim 4\%$, and decreases by 6-7% for the fully-disordered SQS and Random structures. Likewise, E_h and G_h for VMoN decrease by 30 – 55% compared to VN values. We note that there is no clear dependence between the decreases observed in either E or G, and the degree of disorder in either alloy. For example, the VMoN structure with smallest E_h is the CuPt, while for VWN it is the C#1.

The significant trend, however, is that regardless of the atomic arrangement on the metallic sublattice, alloying VN with WN or MoN significantly reduces the $\bar{C}_{44}$ elastic constant in each case. The $\bar{C}_{44}$ values of ordered configurations for VWN alloys decrease by as much as 56%, and those of VMoN alloys by 69%, compared to the $\bar{C}_{44}$ value of pure VN. For the Random and the SQS structures, the $\bar{C}_{44}$ reductions are smaller, but nevertheless still considerable, 32% and 35%, for VWN and VMoN alloys,

respectively. A similar, general decrease, though not of the same magnitude, can be observed for the $\bar{C}_{11}$ elastic constant values, indicating lower resistance to tensile $\langle 100 \rangle$ -deformation, in both VWN and VMoN ternaries. In this case, however, the largest $\bar{C}_{11}$ reduction is obtained for disordered structures. In summary, all VN-based alloys studied herein, regardless of the degree of order on the metal sublattice, exhibit small changes in B, and significantly lower E, G, $\bar{C}_{44}$, and $\bar{C}_{11}$ values, compared to the parent VN binary. The largest reductions in $\bar{C}_{44}$ values are obtained for ordered structures, respectively in disordered configurations for $\bar{C}_{11}$ values. Overall, these results indicate that replacing V with W or Mo atoms on the VN metal sublattice reduces both the shear ($\bar{C}_{44}$ and G) and tensile ($\bar{C}_{11}$) resistance to deformation, while preserving high incompressibility ($B > \sim 300$ GPa).

For TiN-based ternaries, results show that upon alloying TiN with either WN or MoN, and regardless of the degree of order on the metal sublattice, the formed alloys possess increased bulk moduli, primarily for ordered structures (Table 5 and Table 6). At the same time, as observed for VN-based ternaries, E_h and G_h are reduced, for both TiWN and TiMoN alloys, by up to 33%. In this case, however, the largest reductions are observed in disordered configurations. Furthermore, regardless of the degree of order on the metallic sublattice, the $\bar{C}_{44}$ elastic constant is reduced, as compared to the parent binary TiN, in both TiWN and TiMoN alloys. The $\bar{C}_{44}$ values of TiWN alloys decrease by up to 52% (Table 5), while those of TiMoN alloys by up to 43% (Table 6), and in both cases, the largest reductions in $\bar{C}_{44}$ are observed for ordered structures. In terms of $\bar{C}_{11}$ elastic constant values, the trend in TiN-based alloys is somewhat different to that observed in VN-based alloys, in the sense that for both TiWN and TiMoN alloys, we obtain marginally higher $\bar{C}_{11}$ values for ordered structures, and lower $\bar{C}_{11}$ values in

disordered configurations, compared to the $\bar{C}_{11}$ value of the TiN parent binary. Overall, the elastic properties dependence on the degree of order, is similar for both VN- and TiN-based alloys, as the lowest $\bar{C}_{44}$ and $\bar{C}_{11}$ values are found for ordered, and disordered structures, respectively.

With respect to comparing our calculations to experiments, we note that the elastic constants of VN- and TiN-based alloys have not been yet measured experimentally. However, our calculated Young's moduli E values are consistent with the results of indentation measurements conducted on samples with chemical compositions similar to those used in the present study. This can be seen in Table 7, in which the Young moduli values predicted with DFT, and the corresponding experimental values [19,21,36,40], are presented. It should be noted that due to effects of anisotropy during nanoindentation, the experimental Young's moduli do not directly correspond to the calculated Young moduli. Nevertheless, there is qualitative agreement between the experimental and calculated values.

Naturally, the changes in bulk moduli and elastic constants reported above reflect upon a number of other alloy properties, such as the G/B and Poisson ratios, and the Cauchy pressure, which are typically used to estimate the trend of ductility in materials [41]. According to the Pugh [42] and Pettifor [43] criteria, which reflect the phenomenological relationship between the elastic constants and the covalent/metallic character in chemical bonds, ductility is associated with $G/B < 0.5$ and positive Cauchy pressures ($C_{12} - C_{44}$). Based on these criteria, our results clearly show that both VN- and TiN-based alloys, regardless of the degree of order on the metallic sublattice, are significantly more ductile than the parent VN and TiN binaries. For VN-based alloys (Table 3 and Table 4), Cauchy pressures lie in the interval [108, 165] GPa, significantly

above the VN value (1 GPa), and the G_h/B ratios, within the interval [0.245, 0.377], are drastically smaller than the value of 0.569 of the parent binary. Likewise, compared with TiN, which has a Cauchy pressure of -44 GPa and a G_h/B ratio of 0.671, we find TiN-based alloys to have positive Cauchy pressures, in the [61, 110] GPa interval, and G_h/B ratios between 0.384 and 0.448.

The ductility trends for VN- and TiN-based alloys are illustrated in the maps shown in Figs. 3a, 3b, and 3c. The corresponding values of the parent VN and TiN binaries are also included in the panels for comparison. As can be seen in Fig. 3a, TiN-based alloys exhibit higher G_h/B ratios and lower Cauchy pressures, up to 110 GPa, compared to the VN-based alloys, here predicted to be the most ductile. This observation is consistent with the findings of our previous theoretical investigations [16,17], confined to the analysis of mechanical and electronic properties for alloys with highly-ordered metallic sublattices. At the same time, from Figs. 3b and 3c, it is evident that for each ternary alloy, the Cauchy pressure and G/B data set span a wide interval on the ductility maps. This is clearly a lattice configuration effect.

Figure 3: (a) Ductility map of VN- and TiN-based alloys. Reference binaries are included for comparison. (b) Ductility trends in VMoN and VWN alloys. (c) Ductility trends in TiMoN and TiWN alloys. Red symbols indicate $M2=W$, cyan symbols indicate $M2=Mo$. The shapes of the symbols indicate the different arrangements on the metallic sublattice.

The VN-based and TiN-based ductility trends are shown in Fig. 3b and Fig. 3c, respectively. As can be seen, the different atomic arrangements yield significant differences in the elastic properties of each ternary compound. However, no clear trend of ductility vs. order on the metallic sublattice is observable for the studied ternaries. For example, for VN-based alloys, the highly ordered structures, C#1 and CuPt, are the most ductile, while for the TiN-based alloys, the highest ductility is obtained for the fully-disordered (SQS) and the intermediately-disordered (Random) configurations. It is also clear that the VM_2N alloys and the TiM_2N alloys occupy distinct regions on the ductility map, with the VN-based alloys predicted to be the most ductile. Yet, it is important to note that the least ductile configurations for VM_2N alloys, and the most ductile configurations for TiM_2N alloys, overlap on the ductility map, a clear effect of the degree of configurational order/disorder (see also Fig. 3a). The fact that all alloy configurations, with such diverse atomic arrangements on the metallic sublattice, span only the ductile region of the map, demonstrates that although ordering affects the mechanical properties of TiM_2N and VM_2N alloys, leading even to the overlap in ductility trends mentioned above, compared to the parent binaries, their enhanced ductility, and toughness, is primarily a VEC effect.

To further investigate the effect of ordering on the metallic sublattice on the mechanical properties of these alloys, we carry out a thorough electronic structure analysis. We choose for this purpose $V_{0.5}Mo_{0.5}N$ alloys, in all ordering configurations considered herein, as for these films, recently synthesized, the toughness enhancements were confirmed in severe nanoindentation tests [18,19]. The description of the electronic structure, reported below for VMoN alloys, applies to all presently studied ternaries.

In Fig. 4, we plot the (001)-plane charge-density maps, including contour lines, of unstrained $V_{0.5}Mo_{0.5}N$ crystal lattices. For the C#1 configuration (Fig. 4a), the electron density cut is on the (001) plane containing only Mo atoms. As can be seen in all panels (Figs. 5a – 5e), V and Mo atoms are easily distinguished by the shape of the electron distribution in their vicinity; the concentric contour lines show that the electrons are localized on V atoms, whereas the charge around Mo atoms is more delocalized. The charge distributions in all ordered configurations, C#1 (Fig. 4a), C#3 (Fig. 4b), and CuPt (Fig. 4c) are very similar, as ionic-covalent bonds are formed exclusively between *Me* and N atoms. For the intermediately-ordered Random structure (Fig. 4d), one can observe a more irregular charge distribution and, consequently, the formation of randomly distributed *Me-Me* bonds. Similarly, for the SQS configuration (Fig. 4e), the fully disordered atomic arrangement results in more *Me-Me* bonds being formed between *Me* pairs along the [110] direction.

Figure 4: Charge densities of unstrained VMoN alloys with the following structures: (a) C#1, (b) C#3, (c) CuPt, (d) Random, (e) SQS. The cut for C#1 is along the (001) plane containing only Mo metal atoms. The cuts for the C#3, CuPt, Random and SQS structures are along (001) planes. The color scale is expressed in electrons/ $\text{\AA}^3$.

To complete the analysis, one needs to examine the chemical bond response to applied stresses. Fig. 5 illustrates the charge-density maps obtained for VMoN sheared structures; a trigonal strain of 10% is applied along the $[111]$ direction. The five panels (Figs. 5a – 5e) depict the charge distributions on the same cuts used for the unstrained configurations. As can be seen, upon shearing the C#1 structure (Fig. 5a), second-nearest neighbor Mo-Mo bonds are formed along the strain orthogonal direction. As expected, in the C#3 (Fig. 5b) and the CuPt (Fig. 5c) arrangements, one can observe the formation of layered electronic structures, consisting of alternating high/low charge density regions, along the $[1\bar{1}0]$ -oriented Mo and V atomic rows, as previously shown [16,17].

Figure 5: Charge densities of strained VMoN alloys (10% trigonal strain), with the following structures: (a) C#1, (b) C#3, (c) CuPt, (d) Random, (e) SQS. The cut for C#1 is along the (001) plane containing only Mo metal atoms. The cuts for the C#3, CuPt, Random and SQS structures are along (001) planes. The color scale is expressed in electrons/ $\text{\AA}^3$.

Charge layers are also visible in the density map of the sheared Random structure (Fig. 5d). Clearly, the formation of $\langle 110 \rangle$ -layered electron distributions upon shearing is a lattice ordering effect. Due to the trigonal deformation, for atomic rows comprised exclusively of Mo atoms, the shortening of Mo – Mo interatomic distances results in a marked electron delocalization. This indicates the formation of strong d-d metallic bonds. In contrast, the electron charge remains localized onto their nuclei for closely interacting V atoms. In the case in which V and Mo atoms are nearest neighbors, shearing results in charge accumulation between the nuclei, indicating strong V – Mo bonds. In the sheared SQS structure (Fig. 5e) one can still observe the electron-rich areas between *Me-Me* atoms, as for the unstrained configuration (Fig. 4e). Due to

shearing, however, the *Me-Me* bonding pairs are formed along the $[1\bar{1}0]$ direction, i.e. perpendicular to the applied stress. This is the same direction along which the high/low charge layers, formed upon shearing, are aligned in the ordered structures (see Figs. 5a – 5c). Generally, for the disordered SQS configuration, cuts along different planes will yield, as expected, different electron distributions. We observe the formation of pairs of *Me-Me* bonds along the $[1\bar{1}0]$ direction in most (001) charge-density maps.

The formation of metallic bonds upon shearing is best illustrated in Fig. 6, which shows the charge-transfer maps of VMoN alloys with the CuPt (Fig. 6a) and SQS (Fig. 6b) arrangements under 10% $[111]$ trigonal strain. As can be seen, in the highly ordered CuPt configuration, shearing induces a systematic accumulation of electrons between Mo-Mo atoms along the $[1\bar{1}0]$ direction, i.e. the formation of *fully-bonding* electronic states, which stems from a chain of constructively interfering Mo 5d-waves.

Figure 6: Charge transfer maps of sheared VMoN alloys: (a) ordered CuPt; (b) fully-disordered SQS. Corresponding overlap of d-orbitals is shown in (c) for CuPt and (d) for SQS. The color scale is expressed in electrons/ $\text{\AA}^3$.

The chain of d-orbitals overlapping in phase, Fig. 6c, schematically represents such a fully-bonding electronic state. In the sheared disordered SQS configuration (Fig. 6b), the formation of metallic bonds in the strain orthogonal direction occurs only between every second *Me-Me* pair. This phenomenon can be illustrated by a sequence of alternated in-phase/out-of-phase d orbitals (Fig. 6d), which give rise to electron-accumulation/electron-depletion centers located between Me atoms; this is a partially bonding metallic state. As demonstrated experimentally for disordered VMoN solid solutions [18], the alloy ability to form partially-bonding d-states upon mechanical

deformation is sufficient to enhance ductility and toughness. This fact is reflected in significantly reduced shear resistance, as well as preserved strong interatomic bonds (see high bulk moduli, Tables 3-6). Summarizing, alloys with disordered structures are compliant to shearing due to an electronic mechanism which is similar to that found for ordered structures, i.e. ability to dissipate high mechanical stresses by forming metallic bonds. Ordering on the metal sublattice produces the highest tensile resistances as well as the lowest shear resistances. The enhanced toughness of VN- and TiN-based ternaries, however, primarily stems from the increased VEC induced by alloying.

4. Conclusions

We calculate the elastic properties of $V_{0.5}W_{0.5}N$, $V_{0.5}Mo_{0.5}N$, $Ti_{0.5}W_{0.5}N$, and $Ti_{0.5}Mo_{0.5}N$ alloys with various degrees of order/disorder on the metallic sublattice. Results show that regardless of the atomic arrangement, all alloys exhibit high incompressibility ($B > \sim 300$ GPa), indicating the presence of strong *Me*-N bonds, comparable to those of TiN and VN parent binaries. The fully-disordered and intermediately-ordered structures consistently exhibit lower values of bulk modulus and $\bar{C}_{11}$, as well as higher values of $\bar{C}_{44}$ compared to ordered structures. The small (< 100 GPa) $\bar{C}_{44}$ values obtained for the highly-ordered alloys are attributed to the formation, upon the application of trigonal stresses, of fully-bonding metallic states perpendicular to the direction of the applied stress. Even though reduced, a similar effect is observed in disordered structures, as evidenced by the formation of alternating pairs of strong *Me*-*Me* bonds upon shearing, which explains their increased compliance to this type of stresses, compared to the reference binaries. The ductility of the VN- and TiN-based alloys studied herein, while clearly affected by the degree of disorder on their metallic sublattice, is shown to be superior to that of reference binaries. Present calculations

demonstrate that the experimentally verified toughness enhancements in these alloys are primarily an effect of increased VEC, induced upon alloying.

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Table 1. Calculated formation energies and lattice constants of studied structures. Experimental lattice constants are included for comparison.

	Formation energy (eV/atom)		Average lattice constant a (Å)
	B1 Ti(V)N – B1 W(Mo)N	B1 Ti(V)N – hex W(Mo)N	
$V_{0.5}W_{0.5}N$			
C#1	-0.042	0.162	4.254
C#3	-0.051	0.152	4.247
CuPt	-0.062	0.141	4.242
Random	-0.184	0.019	4.253
SQS	-0.193	0.010	4.259
Experiments	-	-	4.19 – 4.21 ^a
$V_{0.5}Mo_{0.5}N$			
C#1	0.021	0.179	4.253
C#3	-0.015	0.143	4.241
CuPt	-0.019	0.139	4.240
Random	-0.113	0.045	4.247
SQS	-0.122	0.037	4.252
Experiments	-	-	4.18 – 4.20 ^b
$Ti_{0.5}W_{0.5}N$			
C#1	-0.074	0.130	4.295
C#3	-0.096	0.107	4.294
CuPt	-0.099	0.105	4.299
Random	-0.157	0.047	4.306
SQS	-0.159	0.044	4.307
Experiments	-	-	4.25 ^c , 4.28 ^d
$Ti_{0.5}Mo_{0.5}N$			
C#1	-0.025	0.133	4.296
C#3	-0.053	0.105	4.292
CuPt	-0.057	0.102	4.298
Random	-0.099	0.059	4.304
SQS	-0.104	0.054	4.307
Experiments	-	-	4.25 ^e , 4.33 ^d

^aRef. [21]

^bRef. [19]

^cRef. [24]

^dRef. [37]

^eRef. [38]

Table 2. Calculated energy per atom of reference binaries.

	Energy/atom (eV/atom)	
	B1	Hexagonal (WC structure)
VN	-9.620	-
TiN	-9.763	-
MoN	-9.651	-9.968
WN	-10.367	-10.774

Table 3. Calculated elastic properties of VWN alloys.

	Atomic arrangement	B (GPa)	E (GPa)			G (GPa)			ν			$\bar{C}_{44}$ (GPa)	$\bar{C}_{11}$ (GPa)	$\bar{C}_{12}$ (GPa)	$\bar{C}_{12} - \bar{C}_{44}$ (GPa)	G_h/B	A
			E_v	E_r	E_h	G_v	G_r	G_h	ν_v	ν_r	ν_h						
VN	B1	320	479	439	459	191	172	182	0.334	0.348	0.341	139	680	140	1	0.569	0.515
V ₁₆ W ₁₆ N ₃₂	C#1	354	308	242	275	114	87	100	0.403	0.424	0.414	64	604	229	165	0.284	0.266
V ₁₆ W ₁₆ N ₃₂	C#3	338	342	239	290	128	86	107	0.388	0.422	0.405	61	644	185	124	0.318	0.343
V ₁₆ W ₁₆ N ₃₂	CuPt	348	380	259	319	144	94	119	0.379	0.417	0.398	66	696	174	108	0.342	0.253
V ₁₆ W ₁₆ N ₃₂	Random	315	305	294	300	114	110	112	0.392	0.396	0.394	95	506	220	125	0.355	0.661
V ₃₂ W ₃₂ N ₆₄	SQS	313	323	306	315	122	115	118	0.385	0.391	0.388	96	526	207	110	0.377	0.603

Table 4. Calculated elastic properties of VMoN alloys.

	Atomic arrangement	B (GPa)	E (GPa)			G (GPa)			ν			$\bar{C}_{44}$ (GPa)	$\bar{C}_{11}$ (GPa)	$\bar{C}_{12}$ (GPa)	$\bar{C}_{12} - \bar{C}_{44}$ (GPa)	G_h/B	A
			E_v	E_r	E_h	G_v	G_r	G_h	ν_v	ν_r	ν_h						
VN	B1	320	479	439	459	191	172	182	0.334	0.348	0.341	139	680	140	1	0.569	0.515
V ₁₆ Mo ₁₆ N ₃₂	C#1	334	290	254	272	107	92	100	0.404	0.416	0.410	72	546	228	156	0.299	0.455
V ₁₆ Mo ₁₆ N ₃₂	C#3	335	352	270	311	133	99	116	0.383	0.410	0.397	72	634	185	113	0.346	0.321
V ₁₆ Mo ₁₆ N ₃₂	CuPt	335	277	176	227	102	62	82	0.408	0.442	0.425	43	588	208	165	0.245	0.226
V ₁₆ Mo ₁₆ N ₃₂	Random	300	301	292	296	113	109	111	0.389	0.392	0.390	95	485	207	112	0.370	0.686
V ₃₂ Mo ₃₂ N ₆₄	SQS	296	281	274	278	105	102	103	0.394	0.397	0.396	90	465	212	121	0.349	0.714

Table 5. Calculated elastic properties of TiWN alloys.

	Atomic arrangement	B (GPa)	E (GPa)			G (GPa)			ν			$\bar{C}_{44}$ (GPa)	$\bar{C}_{11}$ (GPa)	$\bar{C}_{12}$ (GPa)	$\bar{C}_{12} - \bar{C}_{44}$ (GPa)	G_h/B	A
			E_v	E_r	E_h	G_v	G_r	G_h	ν_v	ν_r	ν_h						
TiN	B1	290	489	465	477	200	189	195	0.313	0.322	0.317	159	640	115	-44	0.671	0.606
Ti ₁₆ W ₁₆ N ₃₂	C#1	343	431	329	380	167	123	145	0.361	0.393	0.377	89	721	154	65	0.422	0.314
Ti ₁₆ W ₁₆ N ₃₂	C#3	338	407	291	349	157	107	132	0.366	0.404	0.385	76	708	153	77	0.390	0.274
Ti ₁₆ W ₁₆ N ₃₂	CuPt	332	395	296	345	152	110	131	0.368	0.401	0.384	79	679	158	79	0.393	0.303
Ti ₁₆ W ₁₆ N ₃₂	Random	319	332	319	325	125	120	122	0.384	0.389	0.387	103	531	213	110	0.384	0.646
Ti ₃₂ W ₃₂ N ₆	SQS	315	336	320	328	127	120	124	0.382	0.387	0.384	102	534	206	103	0.393	0.624

Table 6. Calculated elastic properties of TiMoN alloys.

	Atomic arrangement	B (GPa)	E (GPa)			G (GPa)			ν			$\bar{C}_{44}$ (GPa)	$\bar{C}_{11}$ (GPa)	$\bar{C}_{12}$ (GPa)	$\bar{C}_{12} - \bar{C}_{44}$ (GPa)	G_h/B	A
			E_v	E_r	E_h	G_v	G_r	G_h	ν_v	ν_r	ν_h						
TiN	B1	290	489	465	477	200	189	195	0.313	0.322	0.317	159	640	115	-44	0.671	0.606
Ti ₁₆ Mo ₁₆ N ₃₂	C#1	326	410	332	371	159	125	142	0.360	0.387	0.373	93	670	154	61	0.435	0.361
Ti ₁₆ Mo ₁₆ N ₃₂	C#3	327	397	323	360	153	121	137	0.365	0.390	0.378	90	657	162	72	0.419	0.364
Ti ₁₆ Mo ₁₆ N ₃₂	CuPt	322	406	346	376	158	131	144	0.360	0.381	0.370	100	647	159	59	0.448	0.410
Ti ₁₆ Mo ₁₆ N ₃₂	Random	299	354	337	346	136	128	132	0.368	0.375	0.372	109	535	181	72	0.442	0.615
Ti ₃₂ Mo ₃₂ N ₆₄	SQS	301	353	334	343	135	127	131	0.370	0.377	0.373	106	539	182	76	0.435	0.595

Table 7. Comparison of calculated Young's moduli values with experimental results from alloys of similar composition. Calculated values span Reuss, Voigt and Hill averages.

	Young's modulus E (GPa)	
	calculated	experimental
V _{0.5} W _{0.5} N	239 – 380	353 – 376 ^a
V _{0.5} Mo _{0.5} N	176 – 352	265 – 370 ^b
Ti _{0.5} W _{0.5} N	291 – 431	293 – 384 ^c
Ti _{0.5} Mo _{0.5} N	323 – 410	332 – 344 ^d

^aRef 21

^bRef 19

^cRef 40

^dRef 36