Ab initio study of the alloying effect of transition metals on structure, stability and ductility of CrN

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Abstract

The alloying effect on the lattice parameters, isostructural mixing enthalpies and ductility of the ternary nitride systems Cr₁₉ₓ,TMₓN (TM=Sc, Y; Ti, Zr, Hf; V, Nb, Ta; Mo, W) in the cubic B₁ structure has been investigated using first-principles calculations. Maximum mixing enthalpy due to large lattice mismatch in Cr₁₉ₓ,YₓN solid solution shows a strong preference for phase separation, while Cr₁₉ₓ,TaₓN exhibits a negative mixing enthalpy in the whole compositional range with respect to cubic B₁ structured CrN and TaN, thus being unlikely to decompose spinodally. The near-to-zero mixing enthalpies of Cr₁₉ₓ,ScₓN and Cr₁₉ₓ,VₓN are ascribed to the mutually counteracted electronic and lattice mismatch effects. Additions of small amounts of V, Nb, Ta, Mo or W into CrN coatings increase its ductility.

(Some figures may appear in colour only in the online journal)

1. Introduction

The application of transition metal nitride hard coatings to protect cutting tools and mechanical components has become a common practice in the manufacturing industry in the last two decades [1]. Conventional binary hard coatings such as TiN and CrN are often used to enhance the performance of cutting tools [2]. Due to the superior oxidation resistance of CrN when compared with TiN, CrN is one of the most important transition metal nitrides, and highly valued as a protective and anti-wear coating [3].

In order to further tune the structural, mechanical, and tribological properties, i.e., incorporation of other elements into the CrN based coating, alloying proves to be an effective concept [4–7]. Recently, various Cr₁₉ₓ,X₁N (X=Al, Ti, Ta, Zr, Mo, W and V) ternary coatings have received lots of attention due to their excellent properties [4–6, 8–16]. One of the most successful examples is the addition of Al to improve mechanical properties as well as oxidation resistance of CrN [6]. It is therefore not surprising that this system has been heavily studied both experimentally and theoretically [17–25]. Addition of V, Mo or W into CrN improves its tribological properties and toughness [11–13, 16], while thermal stability and magnetic properties of CrN can be adjusted by alloying it with TiN, hence forming a Cr₁₉ₓ,TiₓN solid solution [10]. Cr₁₉ₓ,TaₓN has enhanced simultaneously mechanical and oxidation properties with respect to CrN [5]. No experimental data are available at present for Cr₁₉ₓ,TMₓN (TM=Sc, Y and Hf), and only few studies on CrNbN have been reported in the literature [4, 26].

Apart from the experimental reports for Cr₁₉ₓ,TMₓN systems, the theoretical calculations are limited to only Cr₁₉ₓ,TiₓN [27]. Recently, plenty of examples have illustrated that a combination of theoretical studies with experimental work represent a successful approach to gain deeper understanding of the material behaviour, which can be used in, e.g., designing coatings with application tailored properties [6, 18, 19, 28]. For this reason we have carried out a systematic theoretical study of the alloying effect of transition metals (TM=Sc, Y; Ti, Zr, Hf; V, Nb, Ta; Mo, W) on CrN.
2. Calculation methods

Density functional theory (DFT) based calculations are performed using the Vienna Ab-initio Simulation Package (VASP) [29, 30]. The ion-electron interactions are described by the projector augmented wave method (PAW) [31] and the generalized gradient approximation (GGA) is employed for the exchange-correction effects, as parametrized by Perdew–Burke–Ernzerhof (PBE) [32].

In order to simulate the chemical disorder between Cr and TM atoms on the metal sublattice of the cubic B1 structure (NaCl prototype, space group \( Fm\bar{3}m \)), and also the paramagnetic state induced by Cr atoms, we use the special quasi-random structures (SQS) [33] approach as implemented in our recent study of Cr\(_{1-x}\)Al\(_x\)N system [21]. Here, the paramagnetism is modelled in a simple analogy to a chemical alloy with Cr spin up and Cr spin down being statically distributed in a disordered manner in the supercell. In a real paramagnet the direction of the local Cr moments rapidly fluctuates instead of being fixed. Hence, the lattice relaxation in static supercells always includes artificial static lattice displacements induced by the different local magnetic environment, while they are at least partially averaged out or totally suppressed in reality [34]. Recently, Alling et al demonstrated that when the magnetic induced geometry relaxations are allowed for all concentrations, the mixing enthalpies of Cr\(_{1-x}\)Al\(_x\)N based on static SQS show the best agreement with the results derived from state-of-the-art disordered local moments’ molecular dynamic (DLM-MD) method, due to an error cancelation of the spurious magnetic relaxation effect [35]. Furthermore, in our previous work [21], we have shown that using the static SQS to address chemical and magnetic disorder simultaneously has proven to be a reliable and computationally affordable approach to predict the elastic properties. In the present work, all supercells are fully relaxed to guarantee reliable results, including lattice parameters, mixing enthalpies and elastic properties. \(3 \times 3 \times 2 \) supercells (36 atoms) described in detail in [21] are used for the Cr\(_{1-x}\)TM\(_x\)N. Mixing of Cr\(^1\), Cr\(^4\) and TM atoms takes place on one sublattice while the other sublattice is fully occupied with N atoms. The short range order parameters (SROs) are optimized for pairs at least up to the fifth order. The alloying effect on the ductility has been assessed by evaluating elastic properties of Cr\(_{0.89}\)TM\(_{0.1}\)N using stress–strain method [21]. All the calculations are performed with plane wave cutoff energy of 500 eV together with \(6 \times 6 \times 9 \) Monkhorst–Pack \(k\)-point meshes, which guarantee the total energy accuracy in the order of meV per atom. To get the reference energy of N\(_2\) molecule, we put the molecule in a large box \((a = 17.1\ \text{Å})\). The calculations with 1 \(k\)-point yielded bond-length of 1.100 Å and the total energy of 8.3305 eV atom\(^{-1}\).

3. Results and discussion

3.1. Structural properties

The supercell volume and shape, as well as internal atomic positions are optimized with respect to total energy in order to obtain equilibrium properties of cubic B1 Cr\(_{1-x}\)TM\(_x\)N solid solutions using the Birch–Murnaghan equation of state [36]. The resulting lattice parameters for Cr\(_{1-x}\)TM\(_x\)N phases are shown in figure 1. Please note that figure 1 is divided into \((a), (b), (c)\) and \((d)\), according to the TM groups, IIIB, IVB, VB, and VIB, respectively. The calculated values are fitted with a quadratic polynomial:

\[
a(x) = x a_{TMN} + (1 - x) a_{GN} + b x (1 - x),
\]

where \(b\) is a bowing parameter describing the deviation from linear, Vegard’s-like behaviour [35]. The bowing parameter, \(b\), for each Cr\(_{1-x}\)TM\(_x\)N system together with the optimized lattice constants, \(a_0\), their experimental values, \(a_{exp}\), for comparison [38], and energies of formation, \(E_f\), for TMN compounds are listed in table 1. The calculated lattice parameters result in slightly larger values than the experimental ones (with the exception of VN), which is expected behaviour for DFT–GGA calculation. Good agreement with previous theoretical calculations [17, 39] is also obtained. One should notice that the experimental lattice constants of cubic B1 MoN and WN denote the lattice constants of their substoichiometric N-deficient configurations, as the stoichiometric configurations are mechanically unstable [40, 41]. Energies of formation in table 1 express the total energy difference between the binary nitride and the corresponding elements in their ground-state configurations (crystalline TM or N\(_2\) molecule). The thus obtained trends are the same as reported before by Rovere et al and Holec et al [17, 39]. \(E_f\) becomes less negative as the valence electron concentration (VEC) of TM increases. The positive energies of formation of MoN and WN further illustrate their instability.

The bowing parameters, \(b\), for the Cr\(_{1-x}\)TM\(_x\)N (TM=Y, Zr, Hf, Nb and Ta) solid solutions have positive values, which denotes a positive deviation (i.e., to large values) from Vegard’s linear interpolation. A positive deviation can be qualitatively rationalized in these cases where the lattice spacings of the constituents are very different. Compressing the larger compound is energetically more costly than to expand the smaller one, due to the anharmonicity of the binding energy curve [42]. For other Cr\(_{1-x}\)TM\(_x\)N (TM=Sc, Ti, V, Mo and W) solid solutions, the bowing parameters show small negative values. This negative deviation from Vegard’s linear interpolation is caused by the stronger interatomic bonds connected with an ordering tendency, hence decreasing the lattice parameter for the intermediate compositions. Especially, the lattice parameters of Cr\(_{1-x}\)ScN, Cr\(_{1-x}\)TiN and Cr\(_{1-x}\)VN show almost a linear behaviour, which can be ascribed to the same sp\(^3\)d\(^2\) hybridization in the 3d group TMNs, consisting of two 3d and one s electrons forming TM site and three 2p electrons donated by nitrogen atom. Comparing the calculated lattice parameters with the experimental data yields good agreement for Cr\(_{1-x}\)TM\(_x\)N (TM=Zr, Ti, Ta and Nb). In the case of Cr\(_{1-x}\)Zr\(_x\)N, the experimental data of Kim et al [8] confirm our predictions for positive bowing

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4 Powder diffraction files 00-045-0978 (ScN), 00-035-0779 (YN), 03-065-0565 (TiN), 00-035-0753 (ZrN), 00-033-0592 (HfN), 00-035-0768 (VN), 03-065-5011 (NbN), 03-065-9404 (TaN), 00-065-2899 (GN), International center for diffraction data, PDF-2/release 2007.
Figure 1. Calculated equilibrium lattice parameters in comparison with experimental results for Cr\textsubscript{1-x}TM\textsubscript{x}N (TM=Sc, Y, Zr, Hf, V, Nb, Ta, Mo and W) solid solutions as a function of TMN content. The dotted lines indicate Vegard’s linear behaviour. Open symbols correspond to the experimental data. The figure is divided into (a), (b), (c) and (d), according to the TM groups, IIIB, IVB, VB, and VIB, respectively.

of the Cr\textsubscript{1-x}Zr\textsubscript{x}N lattice parameter, although the deviation from the Vegard’s line predicted here seems to be smaller than that observed experimentally. This disagreement could be caused by residual stresses present in the thin films. The calculated lattice parameters of Cr\textsubscript{1-x}Ti\textsubscript{x}N, Cr\textsubscript{1-x}Nb\textsubscript{x}N and Cr\textsubscript{1-x}Ta\textsubscript{x}N agree well with the experimentally observed values \cite{4, 5, 10}, aside from the fact that the calculated values always show slightly larger values than the experimental ones. In addition to the overestimation of lattice constants with respect to experiment when GGA is used, substoichiometry of nitrogen reported in the experiment might be an important factor. Figure 1(d) shows the optimized lattice parameters of Cr\textsubscript{1-x}Mo\textsubscript{x}N and Cr\textsubscript{1-x}W\textsubscript{x}N solid solutions in comparison with experimental data \cite{4, 12–15}. Because of the mechanical instability of cubic B1 MoN and WN, only the calculated results for the TM content \textit{x} between 0 and 0.56 are presented. It follows that the calculated lattice parameters of Cr\textsubscript{1-x}Mo\textsubscript{x}N and Cr\textsubscript{1-x}W\textsubscript{x}N solid solutions are very close to each other. The lattice parameters near the TM-rich side agree well with experimental measurements, but the difference between theoretical and experimental results increases as TM content increases. This is more prominent for Cr\textsubscript{1-x}Mo\textsubscript{x}N. Such behaviour can be explained by large substoichiometry of nitrogen in Cr\textsubscript{1-x}Mo\textsubscript{x}N and Cr\textsubscript{1-x}W\textsubscript{x}N solid solutions as has been reported \cite{4}. Finally, no experimental data are available for the lattice parameters of ternary Cr\textsubscript{1-x}TM\textsubscript{x}N (TM=Sc, Y, Hf and V) solid solutions, which we report here for the first time. The knowledge of lattice parameters of nitrides as given in table 1 and figure 1, provides useful information for designing coatings and for interpretation of experimental results.

3.2. Phase stability

The isostructural mixing enthalpy, $H_{mix}$, as a function of TMN content in each cubic B1 Cr\textsubscript{1-x}TM\textsubscript{x}N solid solution is calculated as:

$$H_{mix} = E(Cr_{1-x}TM_{x}N) - xE(TMN) - (1-x)E(CrN) ,$$

(2)

where $E(XN)$ and $E(Cr_{1-x}TM_{x}N)$ are the total energy of binary cubic XN and ternary Cr\textsubscript{1-x}TM\textsubscript{x}N, respectively. Figure 2 summaries the calculated mixing enthalpies of the Cr\textsubscript{1-x}TM\textsubscript{x}N solid solutions. Please note that figure 2 is
divided into (a), (b), (c) and (d), according to the TM groups, IIIB, IVB, VB, and VIB, respectively. Compared with other Cr$_{1-x}$TM$_x$N solid solutions, Cr$_{1-x}$Y$_x$N displays much larger positive mixing enthalpy with a maximum value of about 0.16 eV atom$^{-1}$ at $x \approx 0.55$, indicating a thermodynamic driving force for phase separation into its binary constituents. Recently, Rovere et al. [18] reported a considerably larger maximum mixing enthalpy of 0.24 eV atom$^{-1}$, which is likely to be a supercell size effect as has been pointed out by Žukauskaitė et al. [43]. The large positive values of $H_{\text{mix}}$ are the consequence of the large lattice mismatch of YN and CrN, as shown in figure 1(a). Hence, Cr$_{1-x}$Y$_x$N will not tend to mix under realistic equilibrium conditions. On the other hand, the mixing enthalpies of Cr$_{1-x}$Sc$_x$N exhibit values close to zero. The prominently different behaviour for the mixing enthalpies between isoelectronic Cr$_{1-x}$Y$_x$N and Cr$_{1-x}$Sc$_x$N can be traced down to an interplay between lattice mismatch and the electronic effect. The bonding in the TMN can be divided into the hybridized sp$^3$d$^2$, N-p-TM-d interaction and metal–metal d–d bonding [21,44]. The stability is related to the extent of the populated nonbonding or antibonding states as reflected by the density of states (DOS) at Fermi level ($E_F$) [17,19]. High DOS at $E_F$ suggests an increasing destabilizing effect due to the population of energetically unfavourable states. In the cases of ScN [45] and YN [43] where small band gaps can be found at Fermi level ($E_F$), only negligible DOS or very small gap at $E_F$ (depending on the exchange-correlation functional [27]) is predicted in CrN, and it is ascribed to the magnetic spin polarization of spin-up and spin-down states. Hence, the addition of Y [18] and Sc into CrN has a stabilizing effect for the CrN due to depletion of non-bonding or antibonding states. This electronic stabilizing effect is compensated or overcompensated by the lattice strain in the Cr$_{1-x}$Sc$_x$N or Cr$_{1-x}$Y$_x$N, respectively, resulting in near-to-zero mixing enthalpies of Cr$_{1-x}$Sc$_x$N, and large positive mixing enthalpies in the Cr$_{1-x}$Y$_x$N solid solution.

The mixing enthalpy of Cr$_{1-x}$Zr$_x$N is much larger than that of Cr$_{1-x}$Ti$_x$N and Cr$_{1-x}$Hf$_x$N in addition to a strongly asymmetric shape, see figure 2(b). The maximum values are close to 0.08 eV atom$^{-1}$, 0.03 eV atom$^{-1}$ and 0.02 eV atom$^{-1}$ for Cr$_{1-x}$Zr$_x$N, Cr$_{1-x}$Hf$_x$N and Cr$_{1-x}$Ti$_x$N, respectively, at a TMN content around 0.6. It becomes obvious that the larger lattice mismatch between ZrN and CrN as compared with CrN–TiN and CrN–HfN is responsible for the large positive mixing enthalpies of Cr$_{1-x}$Zr$_x$N. In contrast to the electronic stabilizing effect of Sc and Y, the addition of IV, V and VIB group TM elements into CrN causes a destabilization effect due to the surplus d electrons localized at TM sites, which results in increasing DOS at $E_F$ and consequently large electronic driving force for decomposition at high TM content. Cr$_{1-x}$V$_x$N displays a similar magnitude of mixing enthalpies close to zero as one can see in figure 2(c), which is ascribed to the electronic destabilizing effect counteracted by the much smaller lattice mismatch between VN and CrN. Cr$_{1-x}$Ta$_x$N is the only system in the present study displaying negative $H_{\text{mix}}$ in the full compositional range, indicating TaN and CrN binaries are soluble. However, one should be careful about interpreting the absolute values of $H_{\text{mix}}$. The cubic B1 structures are only metastable states of NbN and TaN. When the thermodynamical ground state of TaN i.e., the hexagonal $\beta$ structure (TaN prototype, space group P6/mmm), is taken as a reference state, positive values of $H_{\text{mix}}$ are obtained also for Cr$_{1-x}$Ta$_x$N. This indicates that the system is actually thermodynamically unstable, but the decomposition is unlikely to proceed via spinodal process (i.e., decomposition into cubic Cr- and Ta-rich phases).

In the case of Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N solid solutions, only results in a limited compositional range are presented here, due to the mechanical instability of cubic B1 MoN and WN as mentioned above. As suggested by the experiments, Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N solid solutions at MoN or WN-rich side always show substoichiometry of nitrogen configurations or mixtures of cubic B1 CrN and cubic B1-like TM$_x$N (TM=Mo and W) [9]. In order to provide a deeper insight, two sets of reference states are chosen. In the first case, the mixing enthalpy of Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N is calculated with respect to cubic B1 CrN and TMN. In the second case, mixtures of cubic B1 CrN and cubic B1-like TM$_x$N are considered. In figure 2(d), the solid lines denote the mixing enthalpy with cubic B1 CrN and TMN as the reference states, while the dotted lines denote the mixing enthalpy with respect to CrN and TM$_x$N. From figure 2(d), one can see that the mixing enthalpies of Cr$_{1-x}$TM$_x$N calculated with respect to cubic B1 CrN and TMN show more negative values as TM content increases, which suggests increasing stability of these ternary alloys. However, it has been experimentally demonstrated that the deposited Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N coatings are mixtures of CrN and TM$_x$N (TM=Mo and W) [9]. In fact, substoichiometry of nitrogen is always experimentally observed in Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N solid solutions, and also the stable cubic Mo$_2$N and W$_2$N compounds can be detected in the deposited coatings. We therefore suggest that using CrN+TM$_2$N+N$_2$ as reference states is more meaningful. The mixing enthalpies of Cr$_{1-x}$Mo$_x$N and Cr$_{1-x}$W$_x$N with respect to CrN+TM$_2$N+N$_2$ have positive values (see figure 2(d)), which denotes the possibility for isostuctural decomposition, and is consistent with the experimental findings [9]. More detailed results on Cr$_{1-x}$TM$_x$N$_{1-y}$ will be presented elsewhere.

### Table 1

| Compound     | $b$ (Å) | $a_o$ (Å) | $a_{\text{exp}}$ (Å) | $E_F$ (eV atom$^{-1}$) | VEC |
|--------------|---------|-----------|----------------------|-----------------------|-----|
| ScN          | -0.018  | 4.530     | 4.440                | -1.923                | 8   |
| YN           | 0.138   | 4.921     | 4.894                | -1.698                | 8   |
| TiN          | -0.017  | 4.253     | 4.241                | -1.727                | 9   |
| ZrN          | 0.155   | 4.618     | 4.578                | -1.686                | 9   |
| HfN          | 0.152   | 4.538     | 4.525                | -1.758                | 9   |
| VN           | -0.005  | 4.127     | 4.139                | -0.983                | 10  |
| NbN          | 0.079   | 4.454     | 4.389                | -0.874                | 10  |
| TaN          | 0.110   | 4.423     | 4.358                | -0.854                | 10  |
| CrN          | 4.146   | 4.135     | -0.441               | 11                    |
| MoN          | -0.062  | 4.357     | 4.340                | 0.025                 | 11  |
| WN           | -0.024  | 4.367     | 4.250                | 0.329                 | 11  |
Figure 2. Calculated isostructural mixing enthalpy of \( \text{Cr}_{1-x}\text{TM}_x\text{N} \) (TM = Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Mo and W) solid solutions as a function of TMN content. The figure is divided into (a), (b), (c) and (d), according to the TM groups, IIB, IVB, VB and VIB, respectively. The lines denote the fits the calculated data points using third-order polynomials.

It should be noted that the strong correlation effects beyond standard DFT are not taken into account in the present work. As demonstrated in [35], GGA exchange-correlation potential over-delocalizes Cr non-bonding orbitals, resulting in over-emphasizing their stability to form metal-metal bonds. When the strong correlation effect is taken into account, mixing enthalpies of the \( \text{Cr}_{1-x}\text{TM}_x\text{N} \) systems are expected to increase.

3.3. Alloying influence on mechanical behaviour

In order to evaluate the alloying effect on the ductility, the bulk-to-shear modulus ratio, \( B/G \), and also Cauchy pressure, \( C_{12} - C_{44} \), as a function of VEC are plotted in figure 3. VEC is calculated as an average value of valence electrons per formula unit. According to Pugh [46], the higher or lower the \( B/G \) ratio is, the more ductile or brittle the material is, respectively. The critical value which separates ductile and brittle materials is approximately 1.75. Figure 3(a) demonstrates that the \( B/G \) ratio of the ternary \( \text{Cr}_{0.89}\text{TM}_{0.11}\text{N} \) solid solutions increases as the VEC increases, which has the same trend as another similar coating system TiTMN. The alloying effect is evaluated through comparing the \( B/G \) ratio of \( \text{Cr}_{0.89}\text{TM}_{0.11}\text{N} \) with that of \( \text{CrN} \). It is clear that adding small amounts of V, Nb, Ta, Mo and W into \( \text{CrN} \) coatings will increase \( B/G \) ratio above 1.75, which denotes the improved ductility. The Cauchy pressure, \( C_{12} - C_{44} \), can be used to characterize the bonding type [47]. Negative Cauchy pressure corresponds to more directional, while positive values indicate predominant metallic bonding. As the VEC is increased, Cauchy pressure values are increased, which is obviously showing the same trend as \( B/G \) ratio for the \( \text{Cr}_{0.89}\text{TM}_{0.11}\text{N} \) and suggests the gradual changes in the bonding from directional bonding towards metallic bonding type. A comparison of \( \text{CrN} \) with \( \text{Cr}_{0.89}\text{TM}_{0.11}\text{N} \) yields that alloying V, Nb, Ta, Mo and W increases the metal–metal d–d orbital hybridization, which is responsible for more ductile behavior, similarly to another system TiTMN [28]. Based on the trends for the \( B/G \) ratio and Cauchy pressure, \( C_{12} - C_{44} \), the promising candidates for improving ductility by alloying include V, Nb, Ta, Mo and W. Figure 3(c) summaries qualitatively the alloying trends on mechanical behaviour of \( \text{CrN} \), and as such can be used as a guide for tailoring the coating properties.

4. Conclusions

A systematic study of the TM-alloying effect to \( \text{CrN} \) coatings on the lattice parameters, isostructural mixing enthalpies
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