Extremely hard and tough high entropy nitride ceramics

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Simultaneously hard and tough nitride ceramics open new venues for a variety of advanced applications. To produce such materials, attention is focused on the development of high-entropy ceramics, containing four or more metallic components distributed homogeneously in the metallic sublattice. While the fabrication of bulk high-entropy carbides and borides is well established, high-entropy nitrides have only been produced as thin films. Herein, we report on a new three-step process to fabricate bulk high-entropy nitrides. The high-entropy nitride phase was obtained by exothermic combustion of mechanically-activated nanostructured metallic precursors in nitrogen and consolidated by spark plasma sintering. The fabricated bulk high-entropy nitride \((\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2})\text{N}\) demonstrates outstanding hardness (up to 33 GPa) and fracture toughness (up to 5.2 MPa\(\cdot\)m\(^{1/2}\)), significantly surpassing expected values from mixture rules, as well as all other reported binary and high-entropy ceramics and can be used for super-hard coatings, structural materials, optics, and others. The obtained results illustrate the scalable method to produce bulk high-entropy nitrides with the new benchmark properties.

High-entropy (HE) ceramics are solid solutions based on interstitial phases (carbides, borides, silicides, etc.) and contain 4 or more metallic species, which endow them with unique physical and mechanical properties as a result of entropy stabilization\(^1\). HE ceramics have attracted increasing interest, as they surpass binary ceramics (such as TiC, TiN, SiC, Si3N4, ZrO2, Al2O3) in terms of hardness, fracture toughness, corrosion resistance, and high-temperature stability\(^2\). Among conventional ceramics, transition-metal nitrides (TMN) have historically been used as cutting tools and wear-resistant coatings because of their high hardness and strength, high melting points, excellent thermal conductivity, coupled with thermal and chemical stability\(^7\)-\(^10\). The hardness and toughness of TMN and related solid solutions with FCC structure are interrelated functions of electron valence. As the valence electron concentration (VEC) is minimized, the hardness is maximized (usually at VEC = 8.4); oppositely, when the valence is maximized, the toughness is minimized (at VEC ≥ 10)\(^11\),\(^12\) as the result of antibonding state occupation-induced lattice softening\(^13\),\(^14\). For example, in \(\delta\)-TiN\(_{1-x}\), the microhardness maximum occurs at \(\delta\)-TiN\(_{0.67}\), which corresponds to 7.3 valence electrons\(^14\). An increased valence electron concentration resulting from higher nitrogen content leads to a decrease in hardness. This is the reason why zirconium and titanium carbonitrides have lower hardness when carbon atoms are replaced with nitrogen\(^15\). However, for \(\delta\)-HfN\(_{1-x}\), a smooth increase in microhardness with nitrogen content is observed, due to the difference in 5f electron bonding states\(^15\). Thus, hardness and fracture toughness are inversely related in nitride ceramics, and bypassing this effect would lead to extraordinary properties and more widespread use.

Ternary nitride (TN) systems are predicted to be supertough—harder and more ductile than binary systems—due to the increased valence electron concentration\(^12\),\(^16\),\(^17\). Various research groups have studied the effect of valence electron concentration on mechanical properties for the design of advanced TMNs\(^17\). According to Balasubramanian et al.\(^12\), the optimized hardness and toughness in TMNs are expected at VEC of 9.0–9.5. A brittle-to-ductile transition is expected at a critical VEC = 10 and a transition to mechanical instability at VEC = 10.6. However, the calculated phonon dispersion curves indicate a dynamical stability-to-instability transition between VEC = 9 and 10, which is smaller than the critical VEC = 10.6 for the mechanical stability-instability transition. Overall, a narrow region between VEC = 9 and 10 is outlined for the search of phases with the highest toughness. Considering this, \(\text{T}_{1.5}\text{Ta}_{0.5}\text{N} (\text{VEC} = 9.5)\) possesses one of the highest among TMs theoretical and experimentally
Results and discussion

The convex hulls for the Hf–Nb–Ta–Ti–Zr–N system were constructed at various chemical nitrogen potentials ($\mu_N$) to estimate the range where all constituent metals could form mono-nitrides (Supplementary Table S-I in Supplementary Information). The decrease of $\mu_N$ corresponds to an increase in temperature or decrease of nitrogen partial pressure in the system. The stability range of mono-nitrides decreases in the following order: TiN (space group Fm$\overline{3}$m, stable at $-7.952 < \mu_N < -11.249$), ZrN (space group Fm$\overline{3}$m, stable at $-8.584 < \mu_N < -11.399$), HfN (space group Fm$\overline{3}$m, stable at $-9.501 < \mu_N < -11.463$), TaN (space group P6$\overline{3}$m, stable at $-9.033 < \mu_N < -10.98$), NbN (space group P6m2, stable at $-8.778 < \mu_N < -9.98$). The $\mu_N$ range in which all five mono-nitrides coexist is limited to $-9.033 < \mu_N < -9.98$. This limited stability range complicates the synthesis of bulk HENs and accounts for the lack of published reports on this topic.

The MaterialsProject database contains the data on multiple TNs: Zr$_{0.5}$Ti$_{0.5}$N, Hf$_{0.5}$Zr$_{0.5}$N, Ta$_{0.5}$Nb$_{0.5}$N, Ti$_{0.5}$Ta$_{0.5}$N, Zr$_{0.5}$Nb$_{0.5}$N, Ti$_{0.5}$Nb$_{0.5}$N, Hf$_{0.5}$Ti$_{0.5}$N, TaTi$_2$N, etc. Among them, only one TN phase Hf$_{0.5}$Zr$_{0.5}$N (space group R3m) was found to be stable in the investigated system (stability range $-9.333 < \mu_N < -11.492$). Although its energy of formation from HfN and ZrN is relatively low ($5 \text{kJ/mol}$ at $0^\circ \text{C}$), the relatively broad stability range increases the probability of formation of Hf$_{0.5}$Zr$_{0.5}$N as an intermediate phase during the employed three-step processing. This finding is consistent with the predictions of Sun et al.39, who indicated HfZrN as the only stable TN in the TM1-TM2-N systems (TM = Ta, Hf, Ti, Zr, Nb, V).

Most of the binary nitrides in TM1-TM2-N systems (TM = Ti, Zr, Hf, Ta, Nb, V) are predicted to be thermodynamically unstable yet meta-stabilizable39. In a narrow $\mu_N$ interval of $-9.333 < \mu_N < -9.033$, the Hf$_{0.5}$Zr$_{0.5}$N phase undergoes decomposition while all 5 mono-nitrides retain stability (Supplementary Table S-I). The co-existence of mono-nitride phases might be instrumental for the formation of a HEN solid solution.

The first preparation stage allowed us to make composite particles involving all five metals mixed on sub-micron sized layers of metallic constituents (Fig. 1a,g). Due to the cold-welding phenomenon during milling, thin layers of metals with a thickness of 10–100 nm formed in the bulk of each particle, providing high homogeneity for their mixing. The EDS analysis indicated that the ratio between the metals remained to be equimolar. Also, milling at relatively low speed (200 rpm) and under high pressure of pure argon allowed to produce powders with low concentrations of impurities. The XRD patterns (Fig. 1d) of thus prepared powders showed that all metals retained their crystallinity even after 10 h of mechanical treatment.

The goal of the second preparation stage is to introduce nitrogen into the system in the form of metal nitrides, as well as nitrogen solid solutions. This task was accomplished by using energy-saving combustion synthesis method31. Supplementary Table S-II demonstrates that the reactions between considered metals and nitrogen are highly exothermic with adiabatic combustion temperature well above 3000 K. The reaction between the metal composite particles and nitrogen was initiated locally by hot tungsten wire, followed by the rapid combustion front propagation along with the media. The total nitridation process duration was ~5 s. It can be seen that the combustion of such reactive metal particles in a nitrogen atmosphere leads to the formation of multiple nitride phases (Fig. 1b,e), among which there was detected the predicted Hf$_{0.5}$Zr$_{0.5}$N$_{1-x}$ TN phase. The microstructure of the inner part of the composite particles became coarser (Fig. 1b) with the grain size in the range 0.5–1 μm. A mixed hafnium-zirconium-based oxide phase was also present in the combustion products (Fig. 1h), which presumably originated due to the oxygen impurities in the initial powders and exposure of mechanically activated mixture during the pressing of green pellets for combustion synthesis.

In the third stage, the SPS of the synthesized complex metal nitride particles were used to produce bulk ceramics. After the SPS at the experimentally optimized conditions, the measured relative density of the ceramics was 96.6% of the theoretical maximum. The obtained HEN phase is characterized by narrow grain size distribution (10–16 μm) and crystals of polyhedral, mostly hexagonal, shape (Fig. 1c). Moreover, the Hf$_{0.5}$Zr$_{0.5}$N$_{1-x}$ TN phase was not found in the sintered specimens (Fig. 1f,i), indicating its successful conversion into the HEN. The lattice constant $a = 0.4443$ was calculated based on the XRD pattern of the HEN (Fig. 1f). According to the results of XRD and EDS analysis ~4.2 mol% of the (Hf,Zr)O$_2$ phase formed during the combustion synthesis, retained in the sintered ceramics (Fig. 1i). The amount of oxides is relatively small and, we suppose, could be removed by applying additional technological steps or by adjusting the technological process.

Detailed TEM investigations (Fig. 2) were performed to confirm the presence of a HEN in the sintered specimens and to define the composition of the HEN phase. HRTEM (Fig. 2a) and selected area diffraction pattern (SAED) (Fig. 2b) confirm the single-phase structure of sintered high entropy nitride. The indexed SAED pattern revealed the FCC structure of HEN with the d-spacing values $d_{020} = 0.221$ nm, $d_{130} = 0.221$ nm, $d_{120} = 0.157$ nm,
and $d_{hkl} = 0.099$ nm. The value of SAED-derived lattice constant $a = 0.443 \pm 0.001$ nm is in excellent agreement with the value calculated from XRD data. Advanced EDS mapping (Fig. 2c) demonstrates the uniform distributions of all elements along with the HEN phase. The EDS analysis of different selected areas (Supplementary Table S-III) showed the following statistically proven composition of the phase in at. %: N (28.9 ± 3.2); Hf (11.0 ± 0.4), Zr (11.0 ± 0.8); Ti (15.1 ± 0.5); Nb (15.8 ± 0.8) and Ta (18.0 ± 0.9). The lower amount of Hf and Zr in comparison with other metals could be explained by the formation of crystals of separate (Hf,Zr)Ox phase during the CS step and its recrystallization and consolidation during the SPS (Fig. 1f and Supplementary Fig. S1).

The hardness and Vickers fracture toughness of this high entropy nitride were measured at 4.9–98 N loads and compared to mono-nitrides and nitride solid solutions reported in the literature (Supplementary Table S-IV). The measured hardness $HV_{0.5}$ and elastic modulus of HEN are 32.8 ± 1.6 GPa and 352 ± 17 GPa, respectively. The elastic modulus value is comparable with the value of 360 GPa, obtained in coatings. An increase in the indentation load leads to a gradual decrease of the hardness to $HV_{10} = 22.5 \pm 1.4$ GPa (Fig. 3). However, the experimentally measured values of hardness and fracture toughness of the HEN ceramic surpass the values calculated based on the rule of the mixture on 130% and 82%, respectively ($HV_{1} = 31.2 \pm 3.6$ GPa and $K_{IC} = 5.2 \pm 0.18$ MPa are the experimental data, and $m^{1/2}ROM$ $HV_{1} = 13.6$ GPa, $K_{IC} = 2.85$ MPa$m^{1/2}$ are the calculated). It should be noticed, the measured results for our HEN are significantly higher the previously reported values for carbide, nitride, and silicide ceramics, including the HE compositions (Fig. 3). Moreover, the hardness values of
Figure 2. (a) HRTEM image of spark plasma sintered high-entropy nitride; (b) selected area electron diffraction of (HfNbTaTiZr)Nₓ taken along the [001] zone axis; (c) EDS elemental mapping of the (HfNbTaTiZr)Nₓ phase.

Figure 3. Fracture toughness versus hardness plot with measured values for high-entropy nitride and previously reported ceramics.
HEN (Hf0.2Nb0.2Ta0.2Ti0.2Zr0.2)N far surpassed the estimations for both TNs phases Ti0.5Nb0.5N (17.3 GPa) and Ti0.5Ta0.5N (17.5 GPa) by Sangiovanni17. The breakdown of the values provided in Fig. 3 can be found in Supplementary Information (Supplementary Table S-IV).

Earlier, Sarker et al.3 described an explicit strengthening effect in HE carbides. The hardness of sintered Hf6Nb4Ta4Ti4Zr4C ceramic of 32 GPa is 40% above the value calculated by the rule of mixture (23 GPa). A similar entropy-induced strengthening effect might be responsible for the increased hardness of the HEN, obtained in this work. Previously, enhancement of the mechanical performance of TMN was achieved by engineering alternating layers of TMNs and more ductile body-centered cubic metals33. Similarly, nanocomposite structures developed by Voevodin and Zabinski14 demonstrates high hardness at stresses below the elastic strength limit, while at extreme loading their mechanical behavior switches to ductile, thus preventing brittle failure. A related effect might be responsible for the increase of the fracture hardness of the HENs due to possible nanoscale precipitates of ductile elements (i.e. Ta) on the boundaries of HEN grains during the sintering.

Moreover, as the valence electron concentration of the HENs is close to the optimal value of 9.5, derived by Guo15 and Sangiovanni17, the "lattice softening" effect could also contribute to the increased fracture toughness of the HEN phase. The effect of a simultaneous considerable increase of hardness and fracture toughness in HEN warrants closer investigation and theoretical modeling. However, these results indicate that HENs have the potential to become the new benchmark ceramic for structural and machining applications since the mechanical performance of the (HfNbTaTiZr)N ceramic developed in this work is considerably superior to conventional SiC, TiC, TiN, and TiB2.

Conclusions

1. Grand potential phase diagram modeling revealed that mono-nitrides of Hf, Zr, Ta, Nb, and Ti are stable at relatively narrow nitrogen potential range $-9.033 < \mu_N < -9.98$ and that trigonal Hf6Nb4Ta4Ti4Zr4N is the only stable at $-9.333 < \mu_N < -11.492$ TN in the system. A nitrogen potential range was indicated ($-9.033 < \mu_N < -9.333$) where this trigonal phase will decompose into FCC ZrN and HfN to facilitate the formation of FCC/HEN solid solution.

2. Based on the proposed model, a three-stage synthesis protocol was developed to produce bulk HEN ceramics, including mechanical treatment of the metallic constituents in an argon atmosphere, combustion of mechanically-induced nanostructured particles in nitrogen, and spark plasma sintering of the combustion products.

3. The bulk ceramics are primarily composed of hexagonal grains (10–15 μm) of the HEN phase. The sintered HEN (Hf0.2Nb0.2Ta0.2Ti0.2Zr0.2)N demonstrates outstanding hardness (up to 33 GPa) and fracture toughness (5.2 MPa m1/2), which is significantly higher in comparison with theoretical estimations and carbide, nitride, and silicide ceramics, including TNs and other HEs.

4. The strengthening effect presumably results from entropy stabilization and optimization of valence electron concentration of the HEN phase. The obtained ceramic is a promising candidate for practical application in multiply areas, where special mechanical properties are required.

5. A scalable approach for the fabrication of bulk HEN by the complex CS-SPS consolidation of mechanically activated powders, is proposed for the first time. While the only one HEN system was studied here, countless possible other HENs can be produced using the developed technological approach.

Methods

Calculation of grand potential phase equilibria. To analyze the phase equilibria in this system, the formation enthalpies for nitride phases were calculated using mixed GGA and GGA + U (semiempirically-tuned generalized gradient approximations) frameworks, which is known for its ability to correctly predict the phase stability48. Grand potential phase diagrams at varied nitrogen potentials were calculated using PDApp software, which is integrated into Materials API37,38 and employs a database of DFT computed bulk material energies with crystal structures obtained from the Inorganic Crystal Structure Database (ICSD)39 and those generated by applying data-mined chemical substitutions40,41.

Fabrication of high-entropy ceramics. Figure 4 provides the schematic for the three-stage process employed for the synthesis of bulk high-entropy nitride ceramics. The overall processing method includes three stages: (i) preparation of the reactive nanocomposite powders by high energy ball milling (HEBM); (ii) combustion synthesis (CS) of TNs; and (iii) spark plasma sintering (SPS) of the bulk HEN ceramics.

Preparation of reactive composite powders. The metallic powders of Hf, Nb, Ta, Ti and Zr (RusRed-Met, Russia, > 99% purity) with a particle size distribution of 40–60 μm were used for preparation of a precursor mixtures. HEBM of reactive mixtures was conducted in an argon atmosphere (4 atm, 99.998%) using a double-station planetary ball mill (Activator-2s, Russia) equipped with steel mill and steel grinding medium (balls). Batches consisted of 20 g powders and were mixed in an equimolar ratio Hf: Nb: Ta: Ti: Zr = 1:1:1:1:1 using 250 ml steel jars and 6 mm steel balls. The ball to powder mixture weight ratio was 20:1. The milling speed was 200 rpm at a rotational coefficient of K = 1. The total duration of the mechanical treatment was 10 h. The goal is to produce nanostructured composite particles, which involve all five components.

Combustion synthesis. Mechanically induced nanostructured composite Hf/Nb/Ta/Ni/Zr particles were placed in a laboratory chemical reactor. Initially, the reactor was vacuumed and then filled with gaseous nitrogen.
up to 8 atm. Powder mixtures were locally preheated using a hot tungsten wire to initiate a chemical reaction with the subsequent propagation of a self-sustaining combustion front. At this stage, the metal nitrides were synthesized. The combustion products were then ball-milled for 2 h at 60 rpm using WiseMixSBML mill (DAIHAN Scientific, South Korea) equipped with 250 ml steel jars and 6 mm steel balls. The ball to powder mixture weight ratio was 6:1.

**Spark Plasma Sintering of bulk ceramics.** The synthesized powders were consolidated in an SPS system (Labox 650, SinterLand, Japan) in a nitrogen atmosphere (0.8 atm) at 2073 K. The dwell time was 20 min at a pressure of 30 MPa, the heating rate was 100 °C/min. Bulk ceramic samples in the form of disks with a diameter of 20 mm and a thickness of 5–6 mm were produced by SPS.

**Material characterization.** X-ray diffraction (XRD) was applied for the study of phase composition of the fabricated materials using DRON-4-07 (Russia) monochromatic Co-Ka radiation. The structure of the experimental materials was analyzed via scanning electron microscopy (SEM) on a Vega 3 (TESCAN, Czech Republic) and JSM-7600F (JEOL, Japan) with a microanalysis system (EDX, Oxford Instruments) and a high-resolution transmission electron microscopy (TEM) on TITAN 800-300 (Thermo Fisher Scientific, USA) equipped with an Ultim Max EDS system (Oxford Instruments).

Vickers hardness tests were used for the study of the microhardness of the synthesized materials [Emco-Test DuraScan 70 (Austria)]. The applied loads varied from 0.5 to 10 N. The fracture toughness was measured using the Vickers indentation-induced cracks corresponding to the Anstis method\(^4\). The elastic modulus was measured by Anton Paar CSM Micro Indentation Tester (Austria) under applied loads of 100 mN.

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**References**

1. Bérardan, D., Franger, S., Dragoe, D., Meena, A. K. & Dragoe, N. Colossal dielectric constant in high entropy oxides. *Phys. Status Solidi Rapid Res. Lett.* **10**, 328–333 (2016).
2. Harrington, T. J. et al. Phase stability and mechanical properties of novel high entropy transition metal carbides. *Acta Mater.* **166**, 271–280 (2019).
3. Sarker, P. et al. High-entropy high-hardness metal carbides discovered by entropy descriptors. *Nat. Commun.* **9**, 4980 (2018).
4. Zhang, Y. et al. Microstructures and properties of high-entropy alloys. *Prog. Mater. Sci.* **61**, 1–93 (2014).
5. Chang, X., Zeng, M., Liu, K. & Fu, L. Phase engineering of high-entropy alloys. *Adv. Mater.* **32**, 1907226 (2020).
6. Oses, C., Toher, C. & Curtarolo, S. High-entropy carbides. *Nat. Rev. Mater.* **5**, 295–309 (2020).
7. Hse, S.-H., Ihm, J., Louie, S. G. & Cohen, M. L. Electronic mechanism of hardness enhancement in transition-metal carbonitrides. *Nature* **399**, 132–134 (1999).
8. Aouadi, S. M. Structural and mechanical properties of TaZrN films: Experimental and ab initio studies. *J. Appl. Phys.* **99**, 053507 (2006).
9. Kim, D.-J. et al. Properties of TiN–TiC multilayer coatings using plasma-assisted chemical vapor deposition. *Surf. Coat. Technol.* **116–119**, 906–910 (1999).
10. Maerky, C., Guillon, M.-O., Henschel, J. L. & Hooper, R. M. Indentation hardness and fracture toughness in single crystal TiC0.96. *Mater. Sci. Eng. A* **209**, 329–336 (1996).

11. Richter, V., Beger, A., Drobne, J., Endler, I. & Wolf, E. Characterisation and wear behaviour of TiN- and TiC0.96-x-coated cermets. *Mater. Sci. Eng. A* **209**, 353–357 (1996).

12. Balasubramanian, K., Khare, S. V. & Gall, D. Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides. *Acta Mater.* **152**, 175–185 (2018).

13. Lengauer, W. & Ettmayer, P. Lattice parameters and thermal expansion of 8-V-N1-x from 298–1000 K. *Monatshefe fuer Chemie/Chemical Mon.* **117**, 713–719 (1986).

14. Lengauer, W. Nitrides: Transition metal solid-state chemistry. In *Encyclopedia of Inorganic and Bioinorganic Chemistry* 1–24 (Wiley, Hoboken, 2015). https://doi.org/10.1002/9781119951438.eibc0146.pub2.

15. Yang, Q., Lengauer, W., Koch, T., Scheerer, M. & Smid, I. Hardness and elastic properties of Ti(C,N)1−x, Zr(C,N)1−x and Hf(C,N)1−x. *J. Alloys Compd.* **309**, L5–L9 (2000).

16. Sangiovanni, D. G., Chirita, V. & Hultman, L. Electronic mechanism for toughness enhancement in TiM1−xN (M = Mo and W). *Phys. Rev. B* **81**, 104107 (2010).

17. Sangiovanni, D. G., Hultman, L. & Chirita, V. Supertoughening in B1 transition metal nitride alloys by increased valence electron concentration. *Acta Mater.* **59**, 2121–2134 (2011).

18. Wiemer, C., Sanjines, R. & Levy, F. Structure, stability and bonding of ternary transition metal nitrides. *Surf. Coat. Technol.* **204**, 86–87, 372–376 (1996).

19. Chang, S.-Y. et al. Improved diffusion-resistant ability of multicomponent nitride: From unitary TiN to senary high-entropy (TiTaCrZrAlRu)N. *JOM* **65**, 1790–1796 (2013).

20. Liu, L., Zhou, J. B., Hou, C., Li, J. C. & Jiang, Q. Dense and smooth amorphous films of multicomponent Fe3CoNiCuVZrAl high-entropy alloy deposited by direct current magnetron sputtering. *Mater. Des.* **46**, 675–679 (2013).

21. Yan, X. H., Li, J. S., Zhang, W. R. & Zhang, Y. A brief review of high-entropy films. *Mater. Chem. Phys.* **210**, 12–18 (2019).

22. Sobol, O. V. et al. Reproducibility of the single-phase structural state of the multielement high-entropy TiV–Zr–Nb–Hf system and related superhard nitrides formed by the vacuum-arc method. *Tech. Phys. Lett.* **38**, 616–619 (2012).

23. Pogrebnjak, A. D. et al. Influence of residual pressure and ion implantation on the structure, elemental composition, and properties of Ti(Zr,Al,Nb)N nitrides. *Tech. Phys. Lett.* **60**, 1176–1183 (2015).

24. Zhang, Y., Yan, X.-H., Liao, W.-B. & Zhao, K. Effects of nitrogen content on the structure and mechanical properties of (Al5–xFex)TiFeN2N3 high-entropy films by reactive sputtering. *Entropy* **20**, 624 (2018).

25. Sheng, W., Yang, X., Wang, C. & Zhang, Y. Nano-crystallization of high-entropy amorphous NbTiAlSiWxNy films prepared by magnetron sputtering. *Entropy* **18**, 226 (2016).

26. Matenoglou, G. M. et al. Structure, stability and bonding of ternary transition metal nitrides. *Surf. Coat. Technol.* **204**, 911–914 (2009).

27. Jin, T. et al. Mechanocochemical-assisted synthesis and bonding of ternary transition metal nitrides. *J. Mater. Chem. A* **6**, 19234–19239 (2018).

28. Abadías, G. et al. Reactive magnetron cosputtering of hard and conductive ternary nitride thin films: Ti–Zr–N and Ti–Ta–N. *J. Vac. Sci. Technol. A Vac. Surf. Film.* **28**, 541–551 (2010).

29. Weast, R. C. Handbook of chemistry and physics, 49th ed. *Am. J. Med. Sci.* **257**, 423 (1969).

30. Sun, W. et al. A map of the inorganic ternary metal nitrides. *Nat. Mater.* **18**, 732–736 (2019).

31. Mukasyan, A. S. et al. The solid flame phenomenon: A novel perspective. *Adv. Eng. Mater.* [https://doi.org/10.1002/adem.201701063] (2018).

32. Pogrebnjak, A. D. et al. Effect of the deposition parameters of nitrides of high-entropy alloys (TiZrAlYNb)N on their structure, composition, mechanical and tribological properties. *J. Superhard Mater.* **35**, 356–368 (2013).

33. Madan, A. et al. Enhanced mechanical hardness in epitaxial nonisostructural Mo/NbN and W/NbN superlattices. *J. Appl. Phys.* **84**, 776–785 (1998).

34. Voevodin, A. & Zabinski, J. Supertough wear-resistant coatings with ‘chameleon’ surface adaptation. *Thin Solid Films* **370**, 223–231 (2000).

35. Guo, X. et al. Hardness of covalent compounds: Roles of metallic component and d valence electrons. *J. Appl. Phys.* **104**, 023503 (2008).

36. Jain, A. et al. Formation enthalpies by mixing GGA and GGA + U calculations. *Phys. Rev. B* **84**, 045115 (2011).

37. Ong, S. P., Wang, L., Kang, B. & Ceder, G. Li–Fe–P–O: Phase diagram from first principles calculations. *Chem. Mater.* **20**, 1798–1807 (2008).

38. Ong, S. P., Jain, A., Hautier, G., Kang, B. & Ceder, G. Thermal stabilities of delithiated olivine MPO4 (M = Fe, Mn) cathodes investigated using first principles calculations. *Electrochem. Commun.* **12**, 427–430 (2010).

39. Belsky, A., Hellenbrandt, M., Karen, V. L. & Lükşch, P. New developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in support of materials research and design. *Acta Crystallogr. Sect. B Struct. Sci.* **58**, 364–369 (2002).

40. Ong, S. P. et al. The Materials Application Programming Interface (API): A simple, flexible and efficient API for materials data based on Representational State Transfer (REST) principles. *Comput. Mater. Sci.* **97**, 209–215 (2015).

41. Lu, Z. & Ciucci, F. Metal borohydrides as electrolytes for solid-state Li, Na, Mg, and Ca batteries: A first-principles study. *Chem. Mater.* **29**, 9308–9319 (2017).

42. Anstis, G. R., Chantikul, P., Lawn, B. R. & Marshall, D. B. A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurements. *J. Am. Ceram. Soc.* **64**, 533–538 (1981).

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Author contributions
D.M. conceived the idea and designed the experiments. V.B. and A.S. conducted the experiments. D.M. and S.V. collected all data and images presented in the paper. K.K. conducted the SEM and M.Z. conducted the HRTFM. S.V. conducted the hardness measurements. S.V. and D.M. wrote the initial version of this paper; D.M., S.V., K.K., A.K., C.S and A.M. revised the manuscript critically. All authors analyzed the data and discussed the results. D.M. supervised this study.

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