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Strong yet Ductile High Entropy Alloy Derived Nanostructured Cermet

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ermet is a hybrid/composite material made up of \checkmark ceramics and metals.¹⁻⁴ To fabricate cermets, brittle and hard ceramics, such as carbides (e.g., WC, TiC) and nitrides (e.g., TiN), are usually mixed with malleable and soft metals, such as Fe, Co, Ni, and Mo via powder consolidation techniques.¹ As a result of the mixed ceramic-metallic bonding, cermets usually exhibit superb hardness (15-35 GPa),^{2,3} remarkable wear/oxidation resistance,^{5,6} and excellent chemical/thermal stability.^{2,7,8} Despite this unique combination of physical properties, the Achilles' heel of cermets is their lack of ductility and poor room-temperature toughness (e.g., 5-25 MPam^{1/2}).^{2,3,9,10} Therefore, people have made tremendous effort over the past years in the compositional and microstructural design of cermets in order to improve their toughness/ductility.^{2,3,10-13} At the current moment, fabrication of cermets is mainly based on a variety of ex situ methods derived from powder metallurgy.²⁻¹² While these fabrication methods have been widely adopted, fine-tuning of the fabrication parameters, such as sintering temperature⁸ and sintering cycling,¹¹ is necessary to improve their toughness/ ductility. Unfortunately, despite these prior efforts, cermets are still plagued by the lack of ductility, which may be attributed to the inherent brittleness of ceramics.^{2,3} Therefore, to the best of our knowledge, no ductility in cermets has been ever reported yet. Even though cermets are generally brittle, some cermets are very attractive because of their excellent functional properties, which have already found applications in energy related devices, 4,14,15 such as the Ni/Y₂O₃-ZrO₂ cermet as an anode in solid oxide fuel cells¹⁴ and the Cr₂O₃-Cr and Al₂O₃-

Ni cermets as solar absorbers in solar energy harvesting.¹⁵ These functional applications of cermets were usually based on coatings or thin films.⁴ Interestingly, it was found that the physical properties of the cermet films can be improved as their thickness reduces.⁴ This behavior is intriguing, which suggests that ultrathin cermets might overcome the issues facing bulk cermets, such as ductility. Unfortunately, this issue still remains open to date.

Following the polymer surface buckling enabled exfoliation (PSBEE),^{16,17} we synthesized freestanding ultrathin cermet nanosheets by depositing a precursory high entropy alloy (HEA) via magnetron sputtering onto a poly(vinyl alcohol) (PVA) thin film supported by substrates (please see Video S1 and Methods in the Supporting Information). In this work, we selected a prototypical HEA with the nominal composition of FeCoNiCrCu as the target material. According to the thermodynamics,¹⁸ it is energetically favorable for this precursory HEA to be deposited in the form of nanocrystals, as illustrated in Figure 1 and shown in Figure S1. By tuning the sputtering time, we synthesized the freestanding FeCoNiCrCu

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Figure 1. Synthesis and structural characterization of the freestanding cermet nanosheet. (a) The schematic illustrations of the formation of freestanding ultrathin nanosheet. (b) Low-magnification TEM image of the 20 nm-thick freestanding cermet nanosheet. The inset shows the corresponding SADP. (c) HRTEM image of the 20 nm-thick freestanding cermet nanosheet. Nanocrystals are highlighted by the yellow dash circles. (d1-d4) are the local HRTEM image and the corresponding FFT images of the amorphous regions that contain various degrees of ordering. (e) HAADF-STEM image of the 20 nm-thick freestanding cermet nanosheet showing the nanocrystal phase (bright region) and amorphous phase (dark region). (f) Size distribution of the nanocrystals. (g) Radially integrated intensity of the diffraction patterns of the freestanding cermets with various thicknesses, in comparison with that of the single-phase FCC FeCoNiCrCu film deposited on Si. The indexed FCC crystallographic directions and amorphous "humps" are indicated by the dash lines and ribbons, respectively.

based nanosheets with different thicknesses, ranging from 12 to 85 nm (Figure S2).

Figure 1b shows the transmission electron microscopy (TEM) image of the 20 nm-thick freestanding nanosheet. Evidently, the nanosheet comprises individual nanocrystals separated by interphase with nanoscale thickness. This finding verifies that the deposition of FeCoNiCrCu should occur via atomic clusters. Figure 1c shows the high-resolution TEM (HRTEM) image of the nanocrystals (highlighted by yellow dash circles) and the interphase, the latter of which appears to be amorphous as seen in Figure 1d2,d4. The presence of both crystalline and amorphous phases can be also confirmed by the corresponding selected area diffraction pattern (SADP) in the inset of Figure 1b. Furthermore, we examined the nanostructure by high-angle annular dark-field scanning TEM (HAADF-STEM) experiments. As shown in Figure 1e, the bright Z contrast of the nanocrystals indicates that they mainly contain metallic elements, and in comparison, the dark Z contrast of the amorphous interphase can be attributed to a relatively high concentration of light elements (e.g., C, O etc.) resulting from the hydrogels or native oxides. Figure 1f plots the size distribution of these nanocrystals, which obtains an averages size of 5 ± 1.5 nm. By comparison, the width of the amorphous interphase ranges from 1 to 5 nm. Figure 1g shows the 1D intensity curves for our nanosheets with different thicknesses by integrating the SADPs (see Methods in the Supporting Information). We can identify a set of FCC diffraction peaks that can be keyed to the nanocrystals, which become broader as the nanosheet thickness diminishes, thereby implying that the FCC nanocrystals become more defected in the thinner nanosheet. In contrast, we can also identify a number of diffraction humps that can be attributed to the amorphous interphase, the intensity of which becomes stronger with the decreasing nanosheet thickness (Figure 1g and Figure S3). Compared to the 1D diffraction intensity curve of the singlephase FCC FeCoNiCrCu film deposited on a silicon

substrate,¹⁹ it is clear that the nanocrystals in our freestanding nanosheets exhibit a similar FCC structure as the regular single phase FCC FeCoNiCrCu film.

Subsequently, we examined the chemical distribution in the freestanding nanosheet by energy-dispersive X-ray spectroscopy (EDX) equipped with STEM. As seen in Figure 2a-h, we identified the metallic elements (e.g., Fe, Co, Ni, Cu, and Cr) and nonmetals (O and C) inside the nanosheet (Figure S4). We performed EDX line scanning across several nanocrystals and amorphous interphase (Figure 2i), and it is evident that the distributions of the identified elements fluctuate in space, indicating a rather complex chemical heterogeneity. Specifi-



Figure 2. The chemical characterization of the 20 nm-thick freestanding cermet nanosheet. (a-h) HAADF-STEM image and corresponding EDX maps of Fe, Co, Ni, Cu, Cr, O, and C. (i) The line scan profiles across several amorphous-crystal interfaces.



Figure 3. XPS depth profile analysis of the 20 nm-thick cermet nanosheet. (a-g) The narrow scan XPS spectra with increasing etching time for (a) C 1s, (b) O 1s, (c) Fe 2p, (d) Co 2, (e) Ni 2p, (f) Cu 2p, and (g) Cr 2p, respectively. (h) The quantitative analysis of the concentrations of different chemical species at different etching time. (i) The schematic illustration showing the heterophased structure of the cermet.

cally, the fluctuations of Fe, Co, Ni, and Cu are generally in phase with each other, while out of phase with those of Cr and O. We note that Fe, Co, Ni, and Cu are mainly distributed in the nanocrystals (region I in Figure 2i), while Cr and O are in the amorphous interphase (region II). Considering the limitation of the STEM-EDX technique,²⁰ we can only obtain the concentration of metallic elements in the nanocrystals and amorphous interphase. As seen in Figure S5 and Table S2, the nanocrystals contain $19 \pm 2.2\%$ Fe, $19 \pm 3.7\%$ Co, $20 \pm 2.5\%$ Ni, $23 \pm 2.9\%$ Cu, and $20 \pm 1.99\%$ Cr (in atomic percentage), while the amorphous interphase contains $22 \pm 4.7\%$ Fe, $11 \pm 4.4\%$ Co, $11 \pm 3.4\%$ Ni, $8 \pm 2.1\%$ Cu, and $49 \pm 6.3\%$ Cr.

As a supplement to EDX analyses, we performed extensive X-ray photoelectron spectroscopy (XPS) depth profile analyses on our 20 nm-thick nanosheets. Figure 3a-g presents the narrow-scan profiles of C 1s, O 1s, Fe 2p, Co 2p, Ni 2p, Cu 2p, and Cr 2p obtained for different etching time. As shown in Figure 3a, the C 1s spectra comprises three peaks with distinct

binding energies, which can be keyed to metallic carbide at 283.2 ± 0.34 eV, C-C/C-H at 284.8 eV, and C-O at 286.2 \pm 0.03 eV. Likewise, the O 1s spectra exhibits the peaks of C-O-H/C-O at 532.2 \pm 0.18 eV and metallic oxide at 530.3 \pm 0.45 eV (Figure 3b). With increasing etching time or depth, the presence of C in the nanosheet is manifested mainly as C-C/C-H and metallic carbides, while that of O is mainly via metallic oxides. By comparison, the metallic elements exist primarily in their metallic and oxide forms in the nanosheet (Figure 3c-g), with only a slight amount of iron carbide being detected (Figure 2c). At etching time = 0 s, the XPS spectrum clearly shows the presence of metallic oxides and adventitious carbon (Figure S6), which may result from ambient oxidiation and/or surface contaminations.²¹ However, at etching time \geq 600 s, the signals of metallic oxides diminish and those of pure metals become dominant, as shown in Figure 3c-g. Through data fitting (Figure S6 and Table S3), we obtained the molar fraction of different chemical species, including C-



Figure 4. Mechanical and thermal behavior of the freestanding cermet nanosheet. (a) The experimental force-displacement curve of a 20 nm-thick cermet nanosheet under AFM indentation in comparison with the FEA simulations. (b, c) AFM scanning images of the suspended cermet nanosheet before indentation (b) and after fracture (c). (d) The plot of yield strength versus ductility for our HEA derived cermet in comparison with other metals and cermets. (e) TEM image of the arrested crack in the 20 nm-thick cermet nanosheet. (f) The enlarged view of the fracture process zone, as indicated by the red box in (e). (g1, g2) The HRTEM image and corresponding FFT image of the highly deformed amorphous ceramic interphase. (h) The HRTEM image of the amorphous ceramic interphase being stretched by ~500%. Note this image is a montage of two HRTEM images. (i) The F-DSC curves of the 20 nm-thick cermet nanosheet obtained at different heating rates. The inset shows a photo of a nanosheet sample on a chip sensor before testing.

C/C-H, C-O, C-O-H/C-O, metallic carbides, metallic oxides, and pure metals, as displayed in Figure 3h. As etching time increased to 900 and 1200 s, we reached the inner part of the nanosheet, which contained \sim 30% of pure metals, \sim 45% of metallic oxides, and a fraction (13-17%) of C-C/C-H and C-O/C-O-H resulting from residuals of the decomposed PVA²¹ (Figure S6). It is worth mentioning that the Fourier transform infrared (FTIR) spectra also indicate no PVAs inside our cermets (Figure S7). Finally, at the etching time of 1500 s, we approached the other surface of the nanosheet that was attached to the PVA before exfoliation. The variation of concentrations of different chemical species with increasing etching time is given in Figure 3h. Here, we note that the molar fraction of metallic carbides is consistently low (<8%) across the nanosheet thickness. Based on the above findings, we conclude that the nanocrystals in the nanosheet are made up of metals with a composition of near-equimolar FeCoNiCrCu, while the amorphous interphase is mainly metallic oxides. In other words, the nanosheet is a chemically complex nanostructured cermet that contains metallic nanocrystals surrounded by amorphous oxides in the presence of some residuals of the decomposed PVA, as sketched in Figure 3i.

Following the previous approach,^{22,23} we measured the mechanical properties of our freestanding cermet nanosheets through atomic force microscopy (AFM) indentation

(Methods and Figures S8 and S9). Figure 4a shows a typical force-displacement curve obtained from the 20 nm-thick cermet nanosheet, which can be keyed to the AFM images of the intact nanosheet before indentation (Figure 4b) and of the partially fractured nanosheet after indentation (Figure 4c). Furthermore, we performed finite element analysis (FEA) to fit our AFM data (Methods in the Supporting Information). Through data fitting, we obtain a yield strength of 3.2 ± 0.73 GPa and an elastic modulus of 177 ± 27.9 GPa for the cermet nanosheets with a strain hardening modulus of 0.01 GPa. Interestingly, the force-displacement curve (Figure 4a) indicates that our cermet nanosheet deformed plastically, which also was confirmed by the sequential loading-unloading curves (Figure S9). According to our FEA analyses, our cermet nanosheet can withstand a large plastic strain after yielding, which can reach 53 \pm 17.1% in terms of von Mises strain before mechanical softening (Figure S9). Here, we emphasize that we repeated the same AFM indentation experiments on more than 15 suspended nanosheet samples, and the results were consistent. According to the literature,^{2,3,11-13,24-26} such a strength-ductility synergy is rare in cermets (Table S4). Figure 4d compares our cermet nanosheets with their constituent elemental metals, bulk HEAs, and conventional cermets with respect to their strength and ductility. Evidently, our cermet nanosheets outperform all the above-mentioned metals and cermets for both high strength and high ductility.



Figure 5. MD simulations on the mechanisms of plasticity in the HEA derived cermet. (a) The representative cermet nanostructure in our MD simulations. (b) Strain-stress curves of the pure crystalline and cermets models with different O concentrations in the amorphous ceramic interphase, nanocrystal size = 5 nm. (c) Variation of the calculated strength and uniform strain with the O concentration. Inset shows the percolation network of O atoms. (d-f) The mappings of local atomic packing, von Mises strain, and atomic-level stress along the loading direction at different applied strains. Note that these mappings were obtained from the atomic model with the O concentration of 30% and the nanocrystal size of 5 nm. (g) Histogram of atomic-level stress along the transverse direction or the y direction at different applied strains.

Afterward, we also examined the atomic structure of the partially fractured cermet nanosheet (Figure 4c). Figure 4e shows the arrested main crack in the cermet nanosheet; the crack bridging, crack tip blunting, and deflection indicates ductile fracture. Given a crack-tip opening displacement of >15 nm, we estimate the fracture toughness of our cermet to be $>50 \text{ J/m}^2$ following the prior work.²⁷ Considering the ultrathin thickness of our nanosheet (20-30 nm), this toughness is very impressive, which is higher than that of 100 nm-thick Cu nanosheet ($\sim 40 \text{ J/m}^2$),²⁸ 60 nm-thick Au nanosheet ($\sim 20 \text{ J/m}^2$) m^2),²⁹ and single atomic layer graphene (~16 J/m²).³⁰ Figure 4f displays the enlarged view of the fracture process zone. It is evident that cracking occurred mainly through the amorphous interphase, while the nanocrystals remained almost undeformed even along the crack wake (Figure S10). To bridge the crack, the nanosized amorphous interphase is stretched by 100% to 500% despite its oxide nature (Figures 4f-h). This superstretchability is surprising and resembles the liquid-like

behavior of nanoscale metallic glasses (MGs) observed in in situ TEM experiments.³¹ To characterize the thermal properties of our nanostructured cermet, we carried out flash differential scanning calorimetry (F-DSC) experiments (Methods in the Supporting Information). As shown in Figure 4i, we can only identify a pronounced glass transition between 600 and 720 K as the heating rate (ϕ) was increased from 500 to 10000 K/s, which can be keyed to the amorphous interphase. As a result, we obtained a series of rate-dependent glass transition temperatures (T_g) . After the Vogel-Fulcher-Tammann fitting (Figure S11), we can extrapolate $T_g = 553$ K for the amorphous interphase for $\phi = 10$ K/min. Here, it is worth noting that our measured T_g is much lower than those of ordinary amorphous ceramics seen in conventional cermets, such as 1475K for SiO₂,³² 1723 K for SiCN,³³ and 1800 K for Fe₂O₃;³⁴ however, it is comparable to soft yet plastic MGs, such as rare-earth-based MGs.³⁵ Therefore, the observation of superstretchability or superplasticity (Figures 4f-h) is

consistent with the low T_g measured through F-DSC relative to the room temperature T_R , which leads to a high homologous temperature, $T_R/T_g = 0.54$. According to ref.,³⁶ glasses tend to behave in a plastic manner for $T_R/T_g > 0.5$. Here, it may be worth mentioning that the PVA used in the current study has a very low modulus (535 ± 79.3 MPa) and low glass transition temperature (312 K) (Figure S12). Therefore, the effect of the decomposed PVAs on the mechanical properties of our cermet is negligible.

To gain insights into the atomic origin of plasticity in our cermet, we performed extensive molecular dynamics (MD) simulations (Methods in the Supporting Information). Figure 5a displays a perspective view of a representative volume in the atomic model, which comprises only half of a HEA nanocrystal and its surrounding amorphous ceramic interphase (see Figure S13 for full model). As the first attempt, we varied the O concentration in the amorphous interphase between 5% and 60% for a comprehensive study and fixed the size of the HEA nanocrystal at 5 nm (Figure S13). We also built a nanograined crystalline HEA atomic model with the grain size of 5 nm as the control. Figure 5b shows the strain-stress curves with varying O concentrations. These strain-stress curves are plotted up to the maximum uniform strain attainable in our MD simulations. Evidently, the nanograined HEA crystal is strong (strength ~4 GPa) but appears brittle, which generally agrees with our previous findings.¹⁹ By comparison, the presence of the amorphous ceramic interphase leads to strength reduction but imparts ductility (Figure 5b). For a quantitative study, we extracted the yield strength and ductility of the model cermet, as displayed in Figure 5c. We note that both yield strength and ductility increase with the O concentration but start to drop when the O concentration reaches a threshold that leads to O percolation in the nanostructure (inset in Figure 5c). In experiment, the amorphous ceramic interphase contains 40%-50% O, which already bypasses the percolation threshold according to the MD simulations. Despite that, the corresponding strength of the atomic model is still as high as 2 GPa with a uniform strain of >7%. Given the spatial and temporal limitations of the MD simulations, we consider that the current results are reasonable, which is consistent with the trend observed in our experiments. In addition, the simulation results are similar as the HEA nanocrystal size is varied between 3 and 7 nm (Figure S14).

Without the loss of generality, we studied the evolution of local atomic packing, von Mises strain, and atomic-level stress³⁷ in our atomic model with the O concentration of 30%. Figure 5d-f shows their typical mappings around a 5 nm HEA nanocrystal at the applied strain $\varepsilon_{\rm app}$ of 0%, 8%, and 15%. Prior to deformation ($\varepsilon_{app} = 0\%$), we can see that the amorphouscrystal interface is diffusive with a transition layer about one atom size (Figure 5 d1). When ε_{app} increases to 8% and 15%, local structural rearrangements become evident around the diffusive interface, leading to the reshuffle of atoms that resembles local order-disorder transition and hence local boundary migrations into the nanocrystal, as seen in Figure 5 d2,d3. Figure 5e1–e3 shows the mappings of von Mises strains at different ε_{app} . Clearly, deformation is mainly accommodated in the amorphous interphase, being consistent with our TEM observations (Figures 4f-h). In contrast, deformation in the nanocrystal is only concentrated around its boundary where local atom reshuffle occurs (Figure 5e2,e3). A similar behavior is observed in other amorphous-crystal interface^{38,39} which leads to deformation compatibility (or codeformation)³⁸ and

promotes ductility.³⁹ However, we note that this codeformation mechanism starts to fail somewhere else in the model cermet at $\varepsilon_{app} = 8\%$, leading to void nucleation (Figure S15). Throughout the deformation, the overall local short-range order (e.g., crystal-like order) in the amorphous interphase, however, remains almost invariant with the applied strain (Figure S16).

Figure 5f2,f3 displays the mappings of the atomic-level stress in the x direction. It is intriguing that no stress concentration can be observed around the amorphous-crystal interface even after by passing the uniform strain limit $\varepsilon_{\rm app}$ = 8%. This behavior suggests that the amorphous interphase is fluid-like, which can quickly relax local high stresses.³¹ We note that the atomic stress fluctuates in the amorphous interphase, which may be attributed to the structural heterogeneity inherent to glasses.⁴⁰ Aside from the atomic stress in the loading direction, we also calculated the atomic stress in the amorphous interphase in the y direction. As shown in Figure 5g, there are large compressive atomic stresses, indicating strong elastic confinements against the flowing amorphous interphase from sideways when the model cermet is pulled. A similar phenomenon was observed when viscous metallic liquids were pulled through narrow confinements.⁴¹ Based on the atomistic simulations, we conclude that plasticity in our cermet is mainly accommodated by the amorphous interphase, and the atomic reshuffles around the nanocrystal boundaries as well as the elastic confinements in the unique nanostructure contribute to strain hardening, which is required for the uniform strain, or the ductility measured for our cermet (Figure 4d).

Compared to conventional bulk and thin film cermets, our large-sized HEA derived ultrathin cermet is not only strong (strength = 3.2 ± 0.73 GPa) but also highly deformable at the ambient temperature (ductility = $53 \pm 17.1\%$), which endows them with the quintessential properties for the development of next-generation conformable body electronics.⁴² Therefore, we also measured the sheet resistance of our cermet (Methods and Figure S17). The electrical resistivity is ~80 m Ω ·cm, which is comparable to those of many HEAs.^{43,44} Apart from that, the extremely high aspect ratio $(10^4 - 10^6)$ also makes our ultrathin cermet an ideal candidate material for nanomechanical resonators.⁴⁵ In addition, the PSBEE method we used to fabricate the ultrathin cermet is facile, scalable, and of low cost,^{17,22,46} which enables mass production and industrial applications of this material in coming years. Although our HEA derived cermet is currently of a thin sheet, we emphasize that it is feasible to stack or assemble these nanosheets into a bulk layered structure with the bottom-up fabrication methods well established for other 2D materials, such as polymerassisted assemble⁴⁷ and low-temperature ultrasonic welding,⁴⁸ which are the ongoing research efforts in our group.

In summary, we develop a strong yet ductile ultrathin cermet through the reaction of HEA nanocrystals with hydrogels. The HEA derived cermet is made up of 5 nm-sized HEA metallic nanocrystals bonded with chemically complex amorphous ceramic interphase. Such a unique nanostructure leads to an excellent combination of strength (3.2 GPa) and ductility (>50%), which outperforms bulk cermets and thin-film cermets reported in the literature as of today. Compared to conventional ceramics, the nanostructured complex amorphous ceramic interphase has a rather low glass transition point T_{g} , which renders it with a high stretchability unmatched by conventional ceramics. Atomistic simulations reveal that ductility could originate from codeformation at the amorphous-crystal interface and the elastic confinements imposed by the nanostructure on the amorphous interphase. These excellent mechanical properties, ultrathin thickness, and high aspect ratio make our HEA derived cermet an excellent candidate material for next-generation nanomechanical resonators and conformable flexible electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c02097.

Synthesis of cermet nanosheets, thermodynamics of atomic cluster formation, structural and chemical characterization, mechanical property measurement and finite element analysis, thermal properties characterization, sheet resistance measurement, molecular dynamics simulations, supplementary figures and tables (PDF)

Video S1: Synthesis of freestanding ultrathin cermet nanosheets (MP4)

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Author Contributions

J.Z., Q.Y., and Q.W. contributed equally. Y.Y. and Q.Z., and Q.F. supervised the project. Y.Y. and J.Z. conceived the idea. Z.J. synthesized the material and carried out the TEM observation. Q.Y. performed the XPS, AFM, and resistance characterizations and assisted the corresponding data analysis. Q.W. performed the Cs-TEM characterizations and assisted the corresponding data analysis. J.L. carried out the MD simulation. Z.Z. conducted the F-DSC experiment. T.W. developed the synthesis method and the FEA model. S.S. assisted the XPS data analysis. Z.J. carried out the data analysis. Z.J. and Y.Y. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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