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Mechanochemical Defluorination of Polytetrafluoroethylene (PTFE) With Base Metals

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ABSTRACT

We report highly efficient mechanochemical redox reactivity between polytetrafluoroethylene (PTFE) and base metals, enabling simultaneous polymer decomposition, fluorination of metals without F_2 or HF, and mechanochemical dealloying. While milling with metals has recently emerged as a mechanochemical platform for PTFE defluorination, most such work has relied on highly reactive, air-sensitive metals, such as alkali elements. We now demonstrate a proof-of-principle for direct and efficient transformation of PTFE into a mixture of sp^2-carbon and a metal fluoride by ball-milling with stoichiometric amounts of safe-to-handle, abundant, inexpensive metals such as zinc. The reactivity is applicable to other metals, as shown by aluminum, lead and cadmium, and the process is also extendable into a two-step, one-pot mechanochemical strategy to generate NaF as a recycled fluorine source, along with a ZnO/carbon mixture which can undergo carbothermal reduction to recover zinc, suggesting an opportunity to develop a zinc-based PTFE defluorination cycle. Moreover, ball-milling with PTFE is shown to transform brass into a mixture of copper metal and ZnF_2, providing a proof-of-principle for mechanochemical dealloying of mixed-metal materials using fluoropolymer waste as a reagent. This work introduces a different, mechanochemistry-based paradigm for straightforward, atom-economic, and potentially more sustainable PTFE defluorination, presenting its valorization as a mechanochemical fluorinating agent.

1 | Introduction

Polytetrafluoroethylene (PTFE, Teflon) is a large-volume industrial polymer notable for outstanding chemical resilience to acids, bases and organic solvents, combined with thermal stability up to 400°C [1]. Applications of PTFE include nonstick coatings in cookware, packaging, textile impregnation, membranes, electrical insulators, laboratory and medical equipment, seals, lubricants, dry processed battery electrodes, and more [2]. PTFE is manufactured on a large scale, with 240,000 tons produced globally in 2023 and a market size projected to nearly $3 billion in 2033 [3, 4]. At this scale, thermal and chemical resistance of PTFE and related fluorinated molecules become an environmental challenge, earning such substances the name "forever chemicals" [5–7]. Established end-of-life disposal routes for fluoroplastics, like landfilling, energy-intensive incineration, or pyrolysis are accompanied by the release of bioaccumulative, environmentally-persistent per- and polyfluoroalkyl substances (PFAS) contaminants (Figure 1a) [8–17].

The development of methodologies to defluorinate and/or decompose such substances has attracted significant attention [18, 19], with notable advances in degradation of short-chain PFAS [20–29] and polyvinylidene fluoride (PVDF) [30–40]

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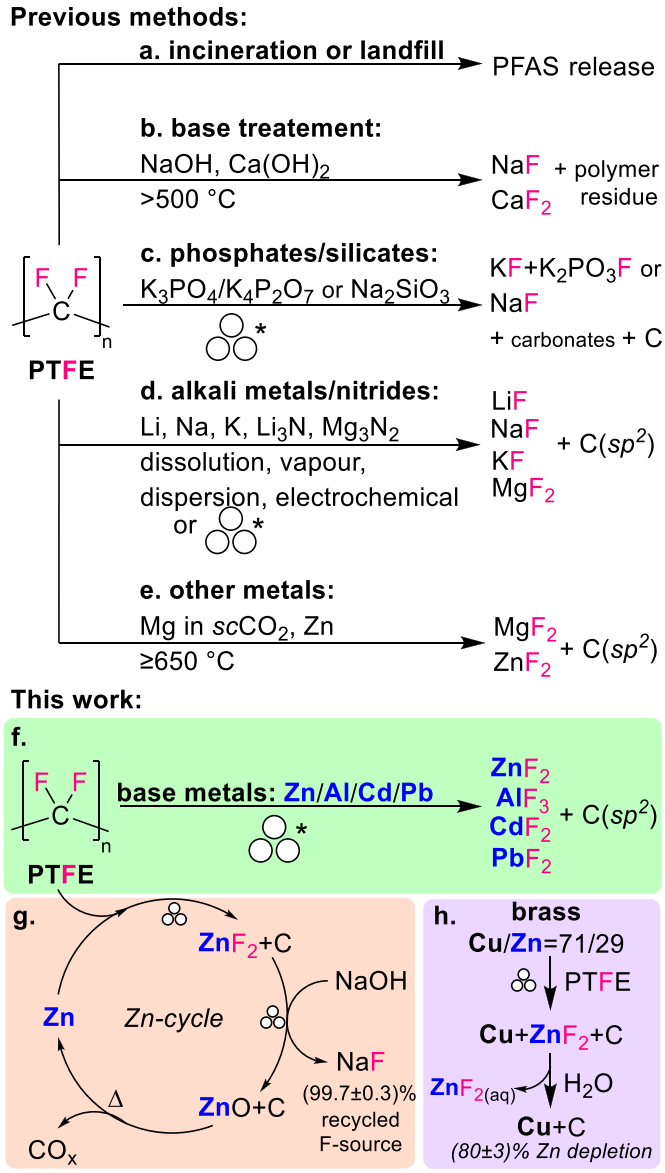

FIGURE 1 | (a–e) Examples of previously reported reactions of PTFE and approaches to its destruction and upcycling, along with mechanochemical reactivity between PTFE and base metals introduced in this work: (f) mechanochemical reductive defluorination of PTFE and direct formation of base metal fluorides, (g) extension of mechanochemical reactivity toward a closed-loop process that generates NaF and can carbothermally re-use zinc metal, and (h) a proof-of-principle route for mechanochemical dealloying with brass as a model substrate. The symbol marked with an asterisk (*) represents the use of mechanochemical methods [83].

accomplished via thermal, solvothermal, and mechanochemical routes. Such routes rely on strong bases (NaOH, KOH, potassium *t*-butoxide, potassium bis(trimethylsilyl)amide), oxides (*e.g.* Al_2O_3, CaO, SiO_2, perovskites), and are less effective for PTFE, whose destructive mineralization with NaOH [41], $Ca(OH)_2$ [42], or perovskite-type oxides [43, 44] requires temperatures >400°C (Figure 1b). Recent work has described elegant applications of low-valent magnesium complexes [45], photo- [46], and electrophoto-catalysis [47] for PTFE degradation at or below room temperature [48]. Much attention has been gathered around mechanochemical treatment [49–55], starting with the pioneering reports of the Gouverneur group on ball-milling with phosphates [56] or silicates [57] to upcycle the PTFE fluorine content to high-value chemicals (Figure 1c). Alternative mechanochemical routes have recently emerged, based on reductive milling of PTFE with alkali metals (Li, Na, K), as well as nitrides (Mg_3N_2, Li_3N) to rapidly generate carbon along with metal fluorides valued as fluorine sources in research and industry [58–60] (Figure 1d). Such emergent approaches are attractive alternatives to related solution ones, including organolithiums [61–66], metals in liquid ammonia [67, 68], and others [69–71]. The major drawback of the metal-based mechanochemical reductive approaches to PTFE defluorination, however, is the high reactivity of alkali metals and associated safety considerations related to their handling.

Here, we provide a proof-of-principle of defluorination by mechanochemical redox reactivity between PTFE and inexpensive, abundant, air-stable base metals (Figure 1f). We demonstrate rapid, high-conversion reactions with stoichiometric amounts of commercial Zn, as well as Al, Cd and Pb powders without any pretreatment, that proceed under ball-milling conditions and under air to generate metal fluorides and amorphous sp^2-carbon. The efficiency of the presented mechanochemical strategy is highlighted by the fact that metals such as Mg [72] (in supercritical CO_2) and Zn [73] were otherwise reported to react with PTFE in excess and at very high temperatures (650°C and 700°C respectively, Figure 1e), that can lead to thermite-like behaviour [74–80]. Tribochemical and theoretical studies [81, 82] have indicated surface reactivity between PTFE and diverse metals, and mechanical activation of energetic composites of Al with PTFE by high-energy ball-milling was reported to generate minor amounts of AlF_3. To the best of our knowledge, however, such reactivity has not been explored, or exploited, for controlled bulk mechanochemical defluorination.

The herein demonstrated use of Zn metal offers a potential opportunity for recycling the defluorinating reagent: further milling of the mechanochemically produced mixture of ZnF_2 and carbon with NaOH produces NaF—a known source of fluorine for synthesis—along with a mixture of ZnO and carbon, which is here shown to be amenable to carbothermal reduction to regenerate zinc metal (Figures 1g and S1). The demonstrated possibility of carbothermal recovery of zinc from this two-step mechanochemical procedure offers a proof-of-principle for a closed-loop zinc-cycle, which could serve as a stepping-stone for developing a novel, circular solventless approach for PTFE recycling. Finally, we show that mechanochemical defluorination of PTFE can also be achieved with alloys, using brass as a model (Figure 1h), selectively producing ZnF_2 to leave behind copper metal, thereby providing a proof-of-principle demonstration for a mechanochemical approach to dealloying, using waste fluoropolymer as a reagent.

2 | Results and Discussion

2.1 | Redox Reaction

Mechanochemical reductive defluorination of PTFE was recently reported using Li, Na, or K, which react cleanly by milling to yield corresponding alkali metal fluorides and sp^2-carbon [58, 59]. While efficient, such reactivity requires highly reactive

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alkali metals, inert atmosphere, and presents challenges for scale-up [57, 84]. A potential alternative could be found in certain base metals, such as Al, which exhibits both a high reduction potential (−1.66 V) [85] and air stability due to a protective surface oxide layer. As established in mechanical alloying and activation of metals [86, 87], it is reasonable to assume that mechanical stress, such as ball-milling could be used to disrupt this layer and form new surfaces, create intimate contacts between reactant particles, and activate the base metal for a reaction with PTFE, possibly following a mechanism proposed in previous studies on alkali metals, that is, by exposing the metal surface for electron transfer to the polymer backbone, weakening the C–F bonds and expelling fluoride ions [59, 70]. Indeed, the appearance of AlF_3 was noted during high-energy milling activation of energetic Al composites with PTFE, and ball-milling was previously used to activate and promote reactivity of a number of base metals with organic ligands, such as *o*-quinones, and reagents like halogenated hydrocarbons [88–93]. These considerations led us to explore the possibility of controlled mechanochemical reductive defluorination of PTFE using metals that are less reactive and easier to handle compared to the alkali elements. Specifically, we explored the reactivity of Al, Fe, Zn, Cd, Sn, and Pb powders and show that commercially available Al, Zn, Cd, or Pb powders can be used without any pretreatment for the effective defluorination of PTFE flakes. Focusing on Zn, preliminary results show that the reactivity is adaptable to gram amounts, as well as defluorination of waste PTFE swarf and other fluoropolymers.

In the interest of safety, we note that mixtures of metals with PTFE can be energetic compositions, with pyrophoric behaviour [80], as well as ignition, having been reported upon high-energy milling of Al-rich composites of aluminum and PTFE. For this reason, working with mixtures of metals and PTFE should always be performed with caution, and reactions should not be assumed to be immediately safely scalable. Ball milling of PTFE with zinc was conducted at a 30 Hz frequency, using a 10 mL zirconia milling jar charged with one zirconia ball (10 mm diameter, 3.4 g weight) mounted on a Retsch MM400 mill. In a typical reaction, 2 mmol of —CF_2— unit was milled with 2 mmol of Zn (130.8 mg), corresponding to a substrate-to-ball weight ratio of ca. 1:14. No reactions were observed after 10, 20, 30, or 40 min of milling, with resulting samples appearing as flattened PTFE flakes covered in coined metal. Analysis of the milled mixture by powder X-ray diffraction (PXRD) revealed only signals corresponding to zinc metal and PTFE (Figure S2). Analysis of the samples milled for 10 and 40 min by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) revealed an overall reduction in Zn metal particle size, from the initial range 6–66 μm to a range of 3–12 μm, with the material simultaneously appearing more homogeneous (Section S9). Longer milling times of 50 and 60 min, however, led to a reaction and complete disappearance of X-ray reflections of zinc metal along with the dominant signal of PTFE (2θ = 18.3 °, Figure 2). These observations indicate a mechanochemical reaction with an induction period, a hallmark of mechanochemical reactions whose onset is rapid and might even lead to a highly exothermic mechanically-activated self-sustained reaction (MSR), due to mechanical activation of substrate, *e.g.*, *via* introduction of lattice strain, structural defects, and/or reduction of particle size [94–98]. At the same time, PXRD patterns of the reaction mixture revealed the appearance of distinctive signals of ZnF_2 [99], accompanied by sample darkening. Due to the lack of any other additional X-ray reflections in the diffraction pattern, these observations indicate formation of amorphous carbon powder, similar to what has been observed with alkali metals [58, 59]. Indeed, the ^{13}C MAS NMR spectrum of the sample revealed a broad resonance at $\delta_C \approx 130$ ppm, corresponding to a broad distribution of sp^2-carbon environments in the material, consistent with the presence of amorphous carbon. Analysis by electron paramagnetic resonance (EPR) revealed a single resonance centered at ca. 337 mT ($g \approx 2.003$), which is reminiscent of carbon-centered radicals found in coal and disordered carbon materials in general [100, 101] (see Section S8). The SEM-EDX analysis of the produced powder revealed fine particles and a homogeneous distribution of zinc, fluorine, and carbon (Figure S17). Furthermore, quantitative solid-state ^{19}F magic-angle spinning (MAS) NMR of a sample collected after 60 min of milling revealed the complete disappearance of the PTFE CF_2 signal at $\delta_F = -122$ ppm, and the appearance of a new signal corresponding to ZnF_2 at −204 ppm (Figure 2) indicating complete mineralization of PTFE. Attempts to analyze reaction mixtures using Raman spectroscopy were not successful, with no signal visible at low laser powers, and higher powers leading to sample charring. The mechanochemically produced amorphous carbon was isolated in (87.3 ± 0.2)% yield by dissolving the ZnF_2 product in aqueous H_2SO_4 (Section S12). The NMR analysis of $CDCl_3$ solvent extracts from the samples milled for 40 min, just before the reaction onset, and for 50 min, just after the reaction took place, did not show evidence for any short-chained PFAS, indicating that the transformation of PTFE into ZnF_2 is rapid and quantitative (Section S10).

The reactions did not occur if the milling frequency was reduced to 25 or 15 Hz, or if the substrate-to-ball ratio was doubled from 1:14 to 1:7, changes which should effectively reduce energy input to the substrate (see Supporting Information) [102, 103]. These observations indicate that the reaction between Zn and PTFE depends not only on milling time but also on other factors that are related to energy supplied to the reaction mixture, which could all be relevant for process safety and future scale-up [104–106]. Because mechanical activation of metal-containing mixtures can generate pyrophoric powders, lead to self-sustained reactions, or even ignition [80], any scale-up must always be approached with caution. We have explored the reaction between PTFE flakes and zinc at scales of 10 and 20 mmol, corresponding to reaction mixture weights of 1.15 and 2.31 g, respectively, using a 25 mL stainless steel milling jar and a single stainless-steel ball of 15 mm diameter (13.5 g weight, see Section S13). While the 10 mmol reaction furnished ZnF_2 and carbon in 1 h, the 20 mmol reaction, conducted with a double substrate-to-ball weight ratio (1:6) in order to avoid unwanted thermal effects, required 2 h.

Next, the reactivity of other metals (Al, Fe, Cd, Sn, Pb) was explored using the conditions that enabled the reaction of 2 mmol of —CF_2— unit with Zn at 30 Hz for 1 h. The metals were used in stoichiometric amounts, calculated with the expectation that each of the electrons donated by the metal atom (three for Al, two for Cd, Pb, Sn, Fe) will reduce one C–F bond to generate F^-. Ball-milling of Al metal with PTFE led to the loss of Bragg reflections of reactants and the emergence of AlF_3 [107] signals in the PXRD pattern of the mixture (Figure 2). The reaction using stoichiometric amounts of Al and PTFE proceeded almost quantitatively (~97% conversion, with ~3% of

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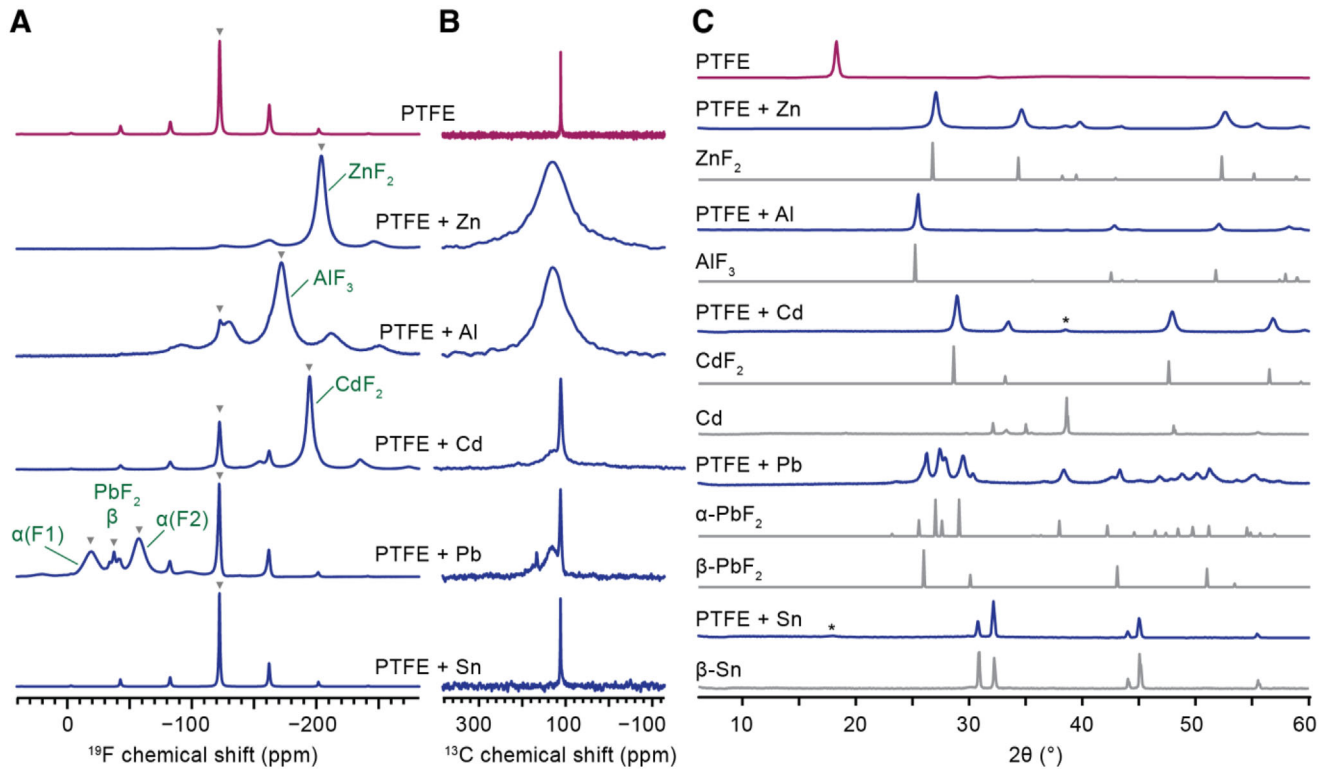

FIGURE 2 | Solid-state MAS NMR (9.4 T, room temperature) and PXRD analyses: (A) ^{19}F echo, (B) ^{13}C echo, and (C) PXRD patterns for PTFE and mixtures of PTFE with metals after 1 h of milling (1.5 h in the case of Pb). Simulated PXRD patterns for metal fluorides and experimentally measured patterns for Cd and Sn are included for reference. Grey markers in the NMR spectra indicate isotropic peaks; unmarked peaks are spinning sidebands. The X-ray reflections highlighted by the * symbol indicate residual Cd and PTFE. For further acquisition details and PXRD data on other mechanochemical experiments, see Supporting Information.

fluorine remaining as PTFE, which constitutes the total fluorine mass balance), as determined by quantitative ^{19}F MAS NMR, with the resonance at −172 ppm corresponding to solid AlF_3. In contrast, ball-milling of PTFE with Cd, Pb, Sn, and Fe did not produce similar reactivity under analogous conditions, with only low-intensity X-ray reflections corresponding to CdF_2 and PbF_2 appearing in the diffraction pattern of milled mixtures (see Supporting Information). As the reactivity of the PTFE with Zn was enhanced by longer milling times and lowering the substrate-to-ball ratio, these parameters were next employed to explore the reactivity of Cd and Pb. When the substrate-to-ball ratio of 1:10 was halved to 1:20 in the case of Cd, the intensity of the X-ray reflections of CdF_2 [108] product remained virtually unchanged. However, reducing the ratio further down to 1:40 increased their intensity, indicating improved reactivity. Quantitative ^{19}F MAS NMR analysis of the mixture revealed a signal consistent with CdF_2 at δ_F = −195 ppm, along with a signal of residual PTFE, with integrations corresponding to a conversion of 77%, with 23% PTFE remaining. With Pb as the reducing metal, a prolonged reaction time of 90 min with a substrate-to-ball ratio of 1:25 led to the formation of the α- and β-polymorphs of PbF_2 [109, 110]. Solid-state NMR analysis revealed signals at δ_F = -19 and −58 ppm, corresponding to two fluorine sites of the orthorhombic cotunnite-type α-PbF_2, a signal at −37 ppm that was split by J-coupling to ^{207}Pb, consistent with the cubic fluorite-type structure of β-PbF_2, and a signal consistent with residual PTFE [111, 112]. Quantitative ^{19}F MAS NMR analysis of these signals indicated 74% conversion to α- and β-PbF_2, while ^{13}C MAS NMR again demonstrated the formation of sp^2-carbon. Neither lowering the sample loading nor extending the reaction time has yet proven effective for inducing reactivity with Fe or Sn.

The possibility to use zinc and aluminum as sacrificial reductants for mechanochemical reductive defluorination of PTFE is attractive, considering their practicality as inexpensive, easily handled industrial metals, with global production estimated at 12 and 70 million tons, respectively. Indeed, Zn and Al are already used as sacrificial reductants for large-scale industrial processes, notably in metallurgy [113–120]. Moreover, metal fluorides generated through this reactivity are also of value in the context of industrial applications, or as materials in their own right. Specifically, AlF_3 is an important additive for electrolytic production of aluminum, a process which could also offer an opportunity to reclaim the consumed metal and design a closed-loop process for mechanochemical PTFE defluorination. The metal fluorides ZnF_2, CdF_2, and PbF_2 have attracted attention for applications in optics, electronics, synthesis and electrochemistry but, similarly to AlF_3, are generally produced by treating metals with noxious F_2 or HF [121–138]. From that perspective, the solvent-free reactions presented here, involving only stoichiometric amounts of a previously considered unreactive 'forever chemical', could represent an attractive alternative for metal fluoride synthesis. With our interest in potential future industrial application of herein reported reactivity, mechanochemical defluorination using Zn metal was also attempted on a sample of real waste industrial PTFE swarf, which readily furnished ZnF_2

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and amorphous carbon under identical conditions as commercial flakes (Section S11). Finally, preliminary tests were also performed on other commercially relevant fluoropolymers: fluorinated ethylene propylene (FEP), perfluoroalkoxy alkane (PFA), ethylene tetrafluoroethylene (ETFE), and PVDF (Section S14). The fully fluorinated polymers FEP and PFA were found to convert to ZnF_2. In contrast, no reaction was observed for PVDF and ETFE polymers that contain both hydrocarbon and perfluorocarbon groups, and that were previously found amenable to base-assisted treatment that allows the abstraction of methylene or ethylene protons, followed by elimination of fluoride [30, 31–38]. While the reason for the difference in reactivity between fluorinated and partially fluorinated polymers remains unclear, we note that a DFT study on reductive defluorination with K metal suggested that reductive abstraction of the first fluorine atom could be twice as exergonic for PTFE compared to PVDF [59].

While the application of less reactive base metals like Zn instead of alkali elements is advantageous in terms of convenience and safety, we note that intimate mixtures of PTFE and Al are considered energetic materials that can undergo ignition facilitated, or even induced by, mechanical activation [74–80]. This led us to investigate the safety of Zn/PTFE mixtures through combined thermogravimetric and differential scanning calorimetry (TG-DSC) analysis. Whereas such analyses do not reproduce the impact, friction, local heating, particle size reduction, or other aspects of ball-milling, they offer a means to evaluate important thermodynamic parameters, such as reaction enthalpy, as well as explore how mechanochemical reactivity compares to a purely thermally-activated process. TG-DSC analysis (see Supporting Information) showed that an exothermic thermal reaction will take place in a Zn and PTFE mixture, but only above the melting points of both components (*i.e.*, above 450°C). Notably, exothermic thermal behaviour was not observed for either the metal or the polymer alone and did not significantly change by conducting the experiment in a flow of air instead of nitrogen, with respective reaction enthalpies according to DSC measurements being ca. 0.7 and 1.4 kJ/g (Figures S27 and S28). While such values resemble those of moderately exothermic reactions, for example lime hydration (around 1 kJ/g) [139], and are lower than those found in energetic materials or combustion of high-energy fuels [79, 140], we also note that reported thermochemical data [141, 142] indicate that the heat released upon total defluorination of PTFE into ZnF_2 and carbon should be around 3 kJ/g. Overall, while the herein discussed mechanochemical conditions provide a straightforward route to efficiently conduct the stoichiometric reaction of Zn and PTFE at small scales, the underlying exothermicity suggests that scale-up should be approached with caution, to avoid significant thermal effects such as thermal runaway [143], or even ignition due to MSRs [98], known to take place in milling reactions of metals [144]. Notably, whereas a thermal reaction of PTFE and zinc was observed only at temperatures above 450°C, mechanical treatment was previously shown to sometimes reduce the temperature needed for thermally-driven transformations of solids [80, 145]. Therefore, it should not be assumed that herein reported conditions can be immediately scaled, and work with mixtures of fluoropolymers and metals should be approached responsibly, with consideration of released heat, possibility of MSR behavior, and other safety aspects, such as handling of fine metal powders, potential for dust ignition, or release of fluorinated compounds [146].

2.2 | Dealloying

The outlined mechanochemical reactivity of zinc is attractive compared to aluminum for several reasons. Zinc is generally less reactive, as evidenced by a less negative reduction potential of −0.76 V [85], making it, in principle, safer to handle. Moreover, upon reaction with PTFE, zinc metal yields water-soluble ZnF_2, in contrast to the poorly soluble AlF_3, which should enable simple separation from byproduct carbon. Indeed, agitation in water of the mechanochemically produced mixture of ZnF_2 and carbon, followed by filtration and evaporation, gave $ZnF_2 \cdot 4H_2O$ in a yield of (88.8 ± 1.2) % across duplicate experiments, with PXRD analysis showing traces of hydrolyzed Zn(OH)F [147] embedded within the carbon.

The observation that metals such as Zn or Al readily react by milling with PTFE, whereas some others react more slowly or apparently not at all, suggests an interesting opportunity for dealloying, that is, segregation of a valuable component from an alloy. This possibility, which would be in contrast to the well-established use of ball-milling for mechanical alloying [86, 87], was explored by ball-milling of PTFE with powdered brass of nominal composition 70% Cu and 30% Zn by weight. The composition of the alloy was also verified using ICP-OES of the digested sample, which gave a Cu:Zn weight ratio of 71:29 (see Supporting Information). The initial attempt at PTFE-based mechanochemical dealloying, using a substrate-to-ball ratio of 1:7, did not lead to any observable reaction based on PXRD analysis. However, reducing the substrate-to-ball ratio to 1:25 led to a clear visual change in the sample, with the appearance of the initially gold-colored brass turning copper-red within 90 min of milling (Figure 3). At this point, PXRD analysis revealed the disappearance of reactant X-ray reflections and the emergence of patterns corresponding to metallic Cu and ZnF_2 (Figure 3). Agitation of the reaction mixture in water and subsequent washing to remove ZnF_2 produced a solid powder which, based on PXRD analysis, contained metallic Cu and small amounts of Zn(OH)F. Notably, ICP-OES analysis of the solid residue (after digestion in *aqua regia*) indicated that the zinc in the mixture was depleted by (80.2 ± 3.3)% of its initial content (see Supporting Information). The demonstrated ability to split an alloy through selective mechanochemical reaction with PTFE, followed by aqueous leaching opens an intriguing pathway for using fluoropolymer waste as a reagent for the separation of metals from mixed metal substrates, with numerous potential applications in recycling and metallurgy.

2.3 | Zinc-Cycle

Finally, we explored how use of zinc metal as a reductant in mechanochemical defluorination might be incorporated into a closed-loop process involving PTFE destruction along with production of an industrially-relevant alkali metal fluoride. Specifically, the addition of a stoichiometric amount of NaOH to the already ball-milled reaction mixture of zinc and PTFE, followed by another milling period, was used to conduct a metathesis reaction generating a mixture of NaF, amorphous carbon and $Zn(OH)_2$, with the latter undergoing a well-documented in situ dehydration [148, 149] to form ZnO (Figure 4). Washing the mixture with water, filtration and evaporation of the filtrate led to

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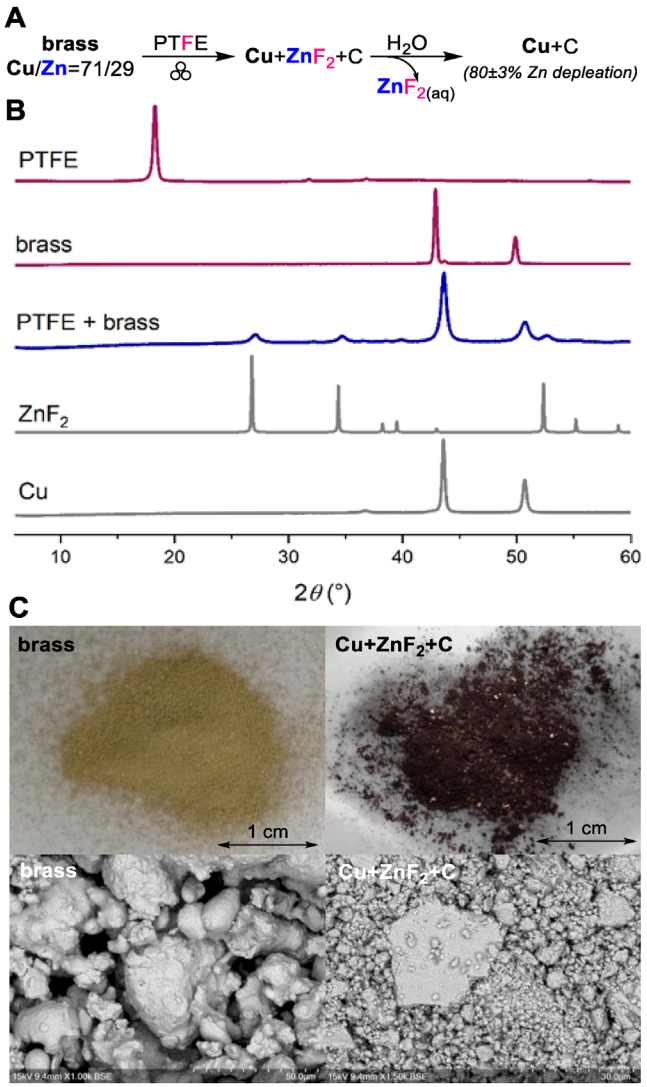

FIGURE 3 | Mechanochemical reaction of a 71/29 Cu/Zn brass alloy by ball-milling with PTFE produces Cu, ZnF_2 and carbon: (A) proposed reaction equation; (B) comparison of PXRD patterns for (top-to-bottom): PTFE and brass starting materials, reaction mixture after milling, simulated pattern for ZnF_2, and measured pattern for commercial copper metal; (C) images of: (left) brass starting material and (right) milled reaction mixture, with optical microscopy images at the top, and SEM image at the bottom. The images illustrate the change of sample appearance from gold-coloured brass powder to a dark copper-colour material, along with a change of morphology. Subsequent agitation in water and washing away of ZnF_2 depletes the mixture by (80.2 ± 3.3) % of Zn, compared to the starting brass substrate. For further experimental data, see Supporting Information.

a quantitative (99.7 ± 0.3)% gravimetrically determined recovery of NaF, a recycled fluorine feedstock that could be further applied in fluorochemicals production [30, 31, 40, 56–59, 150, 151]. The purity of recovered NaF was evidenced by sodium and fluorine being the only elements determined by SEM-EDX (Figure S20). The quantitative recovery of NaF is in agreement with ^{19}F MAS NMR evidence of complete PTFE mineralization with Zn metal.

The solid residue after filtration is expected to contain ZnO and amorphous carbon in a 1:1 stoichiometric ratio, which we note bears resemblance to the feed material mixture used in carbothermal reduction and production of Zn metal in metallurgy [152, 153]. Indeed, the ability of the mechanochemically generated mixture of ZnO and carbon to directly undergo carbothermal reduction was demonstrated in-house by heating to ca. 800°C–1200°C using a butane/propane torch in a quartz tube under nitrogen, affording metallic zinc that was then used for subsequent mechanochemical PTFE defluorination (Section S15). Considering that carbothermal reduction of ZnO is a well-established industrial process, the described qualitative demonstration of zinc recycling using carbon that constituted the waste PTFE polymer backbone (Figures S1, S14, and S22) indicates an opportunity to develop a closed-loop Zn-cycle with PTFE and NaOH as inputs, and NaF and carbon oxides as outputs (Figure 4).

3 | Conclusion

In summary, we have outlined efficient defluorination by mechanochemical reaction between bulk PTFE and base metals, offering a proof-of-concept for fluoropolymer decomposition under mild, solventless conditions, and use of waste PTFE as a reagent for industrially attractive applications, such as direct metal fluorination and dealloying. While incineration and landfill of PTFE are significant sources of toxic, and environmentally persistent PFAS, the demonstrated mechanochemical reactivity enables rapid mineralization of PTFE without external heating, using stoichiometric amounts of inexpensive, abundant, and air-stable industrial (or even waste) metals such as Zn. This approach aligns closely with sustainable development goals and could support the development of energy- and material-conserving processes.

Similarly to Zn, the metals Al, Cd, and Pb are also found to react mechanochemically with PTFE to produce industrially important fluorides under ball milling, along with amorphous sp^2-carbon byproduct, evidenced by PXRD, solid-state NMR, SEM-EDX, and EPR analyses. Fluoride salts generated by reaction with Zn are shown to be readily separable from carbon by water extraction to obtain $ZnF_2{\cdot}4H_2O$, or by subsequent mechanochemical treatment of the mixture with NaOH to quantitatively recover fluorine as NaF, along with a mixture of zinc oxide and carbon. The illustrated ability of the latter mixture to undergo a well-known carbothermal reduction reaction to furnish zinc demonstrates that the herein introduced mechanochemical reactivity is compatible with known industrial zinc recovery routes, suggesting a foundation to develop circular, zinc-based processes for degradation and upcycling of PTFE or other fluoropolymers into NaF. While carbothermal reduction is herein provided to illustrate the possibility for zinc recovery, in principle the presented mechanochemical processes could be compatible with other means of metal recycling, for example electrolytic recovery of zinc or aluminum. Furthermore, brass is here shown to undergo a mechanochemical reaction with PTFE to selectively leach ZnF_2, depleting the alloy of Zn and separating Cu metal. This process, conceptually opposite to the well-established use of ball-milling for mechanical alloying [86, 87], now offers new opportunities for recycling alloys into their component metals. While this work focuses on the recovery of fluorine in the form of metal fluorides, we are also currently exploring value-added applications of generated carbon by-product, for example, as a battery anode material.

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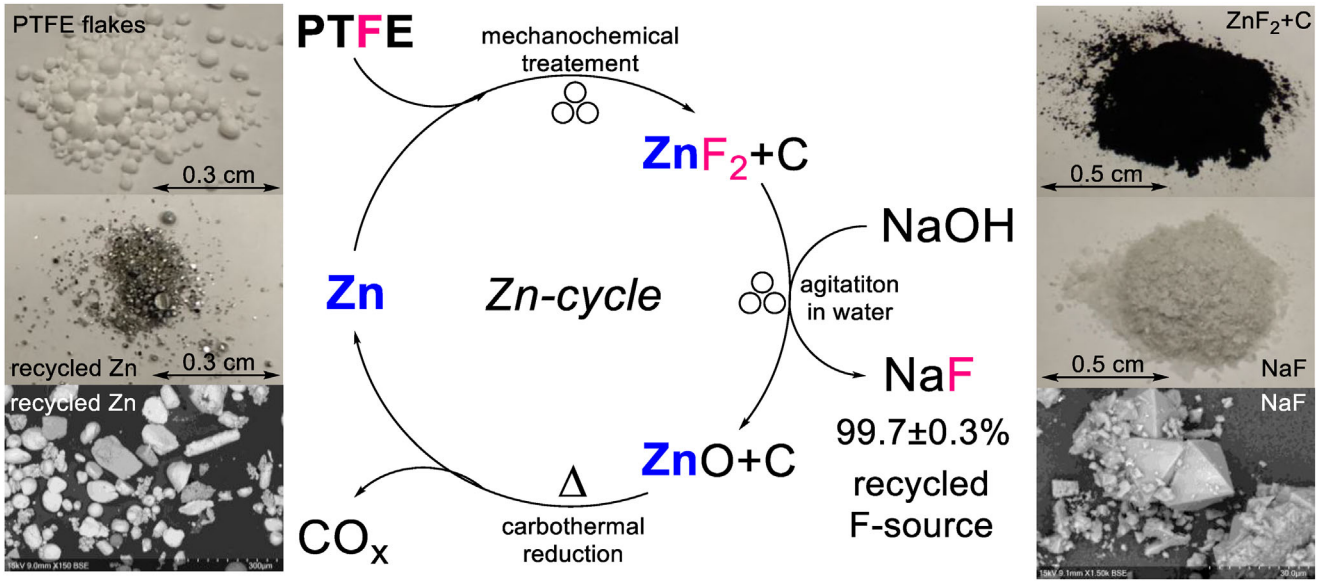

FIGURE 4 | The proof-of-principle for a proposed Zn-cycle (central image) for closed-loop treatment of PTFE, with carbon oxides as the only waste product, leading to NaF as a recycled source of fluorine. The PTFE flakes (top left) are ball-milled with zinc to produce a mixture of ZnF_2 and carbon (top right) that is further milled with NaOH to produce ZnO, carbon and NaF, which can be quantitatively extracted by agitation and washing with water (optical image shown in centre right, and a SEM image in bottom right). The residual ZnO and carbon mixture is thermally treated to produce zinc metal (optical image shown in centre left, and a SEM image in bottom left), that can be re-used in the next PTFE decomposition cycle. Further details and relevant data are found in the Supporting Information.

While the demonstrated reactivity provides an attractive alternative to using highly-reactive alkali metals, it is important to stress that mechanical activation of metal-containing mixtures could potentially generate pyrophoric powders, lead to self-sustained reactions, or even ignition. Therefore, further development of presented reactivity towards industrially-relevant processes [154] will require quantitative assessment of a number of factors, including safety design, energy consumption, CO_2 emissions and performance relative to existing PTFE destruction technologies. In that context, a comparison to existing destruction technologies is provided (Section S16), and we note that approaches for lifecycle assessment [155], technoeconomic analysis [156, 157], and scale-up engineering [158, 159] of mechanochemical processes have been reported. Preliminary results show the herein reported reactivity is applicable on gram scales, and to fully fluorinated polymers other than PTFE. Whereas the presented work demonstrated reactivity of Al, Zn, Cd, and Pb as representative base metals across different parts of the periodic table, we are currently focusing on further exploration of the underlying reaction mechanisms, as well as mechanochemical reaction parameters, such as the ball-to-sample ratio and milling assembly design, in order to achieve activation of other metals (including currently non-reactive Sn and Fe), as well as possible catalytic approaches to PTFE mineralization. Overall, the mechanochemical reactivity observed herein highlights waste PTFE as not only a socioecological burden [5–17] but also as a useful reagent with potential for direct fluorination.

Author Contributions

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Conflicts of Interest

Some of the results in this work are relevant to the UK Patent Application Number 2603927.1, filed by the authors.

Data Availability Statement

The data that support the findings of this study are included in Supporting Information and/or are available from the corresponding authors upon reasonable request. Raw solid-state NMR data can be found on Zenodo, https://zenodo.org/records/23249435.

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