

The START project: Creating a sustainable supply chain for green energy harvesting products by Powder Metallurgy

Sustainable Energy Harvesting Systems Based on Innovative Mine Waste Recycling (START) is an Innovation Action project co-funded by the EU and its Horizon Europe programme. Using an advanced powder production and consolidation process, the project's aim is to create a sustainable supply chain for green energy harvesting products by transforming sulphide materials from mining waste into sustainable high-added-value Powder Metallurgy components for tellurium-free thermoelectric (TE) devices. Here, the consortium members offer a comprehensive summary of START's background, the innovative workflow developed, and its potential impact.

Launched in June 2022, the START project is formed of a consortium of fifteen institutions from eleven European countries, coordinated by LNEG - the National Laboratory of Energy and Geology of Portugal. Six research organisations with backgrounds in geology, materials science and renewable energies are represented on the consortium, as well as seven SMEs covering the entire supply chain, from production to exploitation and ecological footprint assessment, and two non-profit international associations representing a consolidated network of partners and stakeholders. START will have a duration of four years and a budget of around €9.2 million. Fig. 1 identifies the consortium partners and participating nations.

Motivation and objective

Climate change is one of humankind's greatest challenges, and fighting it depends on the rapid implementation of green technol-

ogies and business practices, known as the green transition, to which the European Union (EU) is fully committed through the European Green Deal [1]. However, this green transition is based on a shift from a fossil fuel-inten-

sive to a material-intensive energy system, increasing the need for mineral resources. The growing demand for essential minerals and declining quality of ores is substantial increasing waste volumes from mining operations.

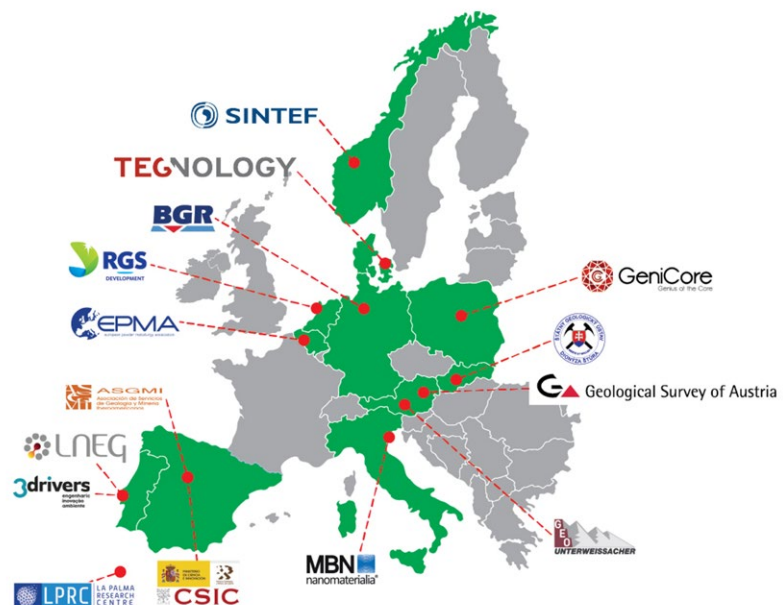


Fig. 1 START consortium members and the nations they represent

START CONCEPT

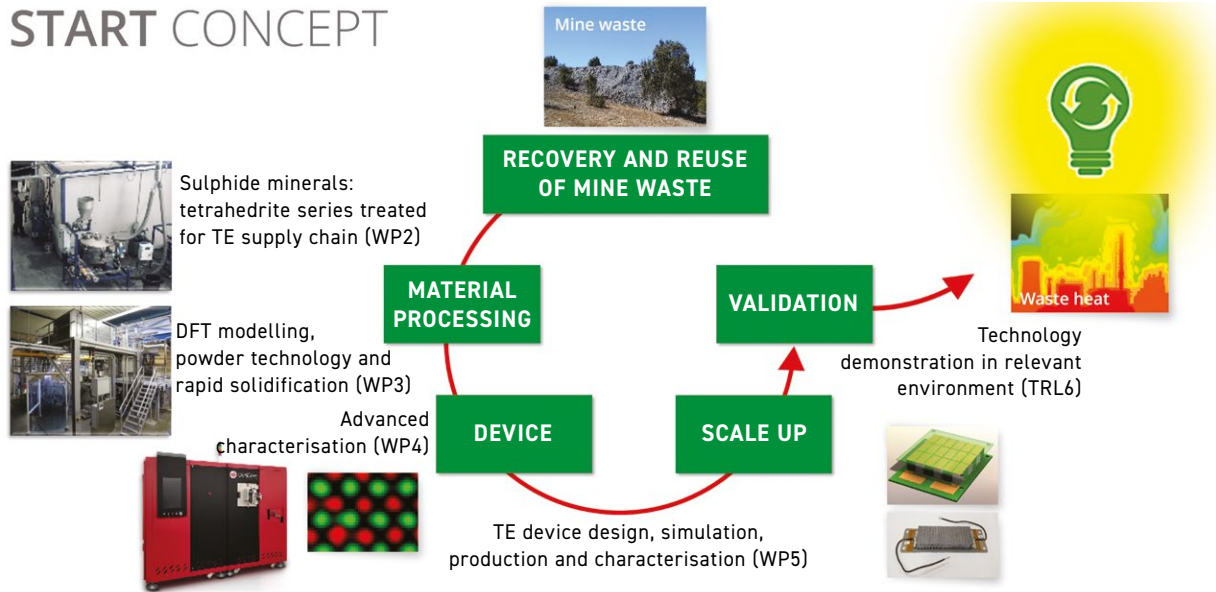


Fig. 2 The START concept is based on a 'waste material-waste heat to power' methodology

Additionally, current commercial thermoelectric (TE) generators (used to harvest waste heat from, for example, industrial processes and convert it into electric power) rely mostly on tellurium-based thermoelements [2]. Tellurium is a relatively scarce element, with a terrestrial abundance of Ca. 1 ppb. As China accounts for over 60% of its production, Europe is heavily dependent on imports [3].

The START project proposes a unique technological solution to this problem, based on a 'waste material-waste heat to power' methodology for the development of sustainable and economically viable tellurium-free TE waste heat harvesting systems (Fig. 2). This is

achieved by producing advanced sulphide p-type thermoelements that incorporate discarded sulphide minerals in mining waste, mainly of the tetrahedrite-tennantite mineral series $(\text{Cu}_6[\text{Cu}_4(\text{TM})_2](\text{Sb, As})_4\text{S}_{13})$, where TM is a transition metal) to replace the current commercial tellurium-based p-type thermoelements. The tetrahedrite-tennantite mineral series is relatively abundant in some Cu mine tailings and, at present, is an environmental hazard.

START's development of green energy harvesting devices through the incorporation of mineral-derived p-type thermoelements serves both economic and remediation purposes by reducing

mining's environmental footprint, as mining residues are converted into useful and valuable resources. This strategy is in line with the priorities set out by the European Green Deal and the EU Action Plans on Critical Raw Materials and Circular Economy [1, 4, 5].

Potential impact of the START project

Around two-thirds of the primary energy produced worldwide is lost as waste heat [6]. Using TE energy harvesting systems to capture and directly convert this waste heat into electric power has the potential to improve overall energy production efficiency and, in conserving more of the energy produced, thus preventing tens of millions of tons of CO_2 emissions.

The impact of the START project's approach towards a more sustainable and resilient EU is defined as:

1. The reduction of EU dependence on primary critical raw materials
2. The promotion of circular economy processes
3. The production of TE energy harvesting systems focused

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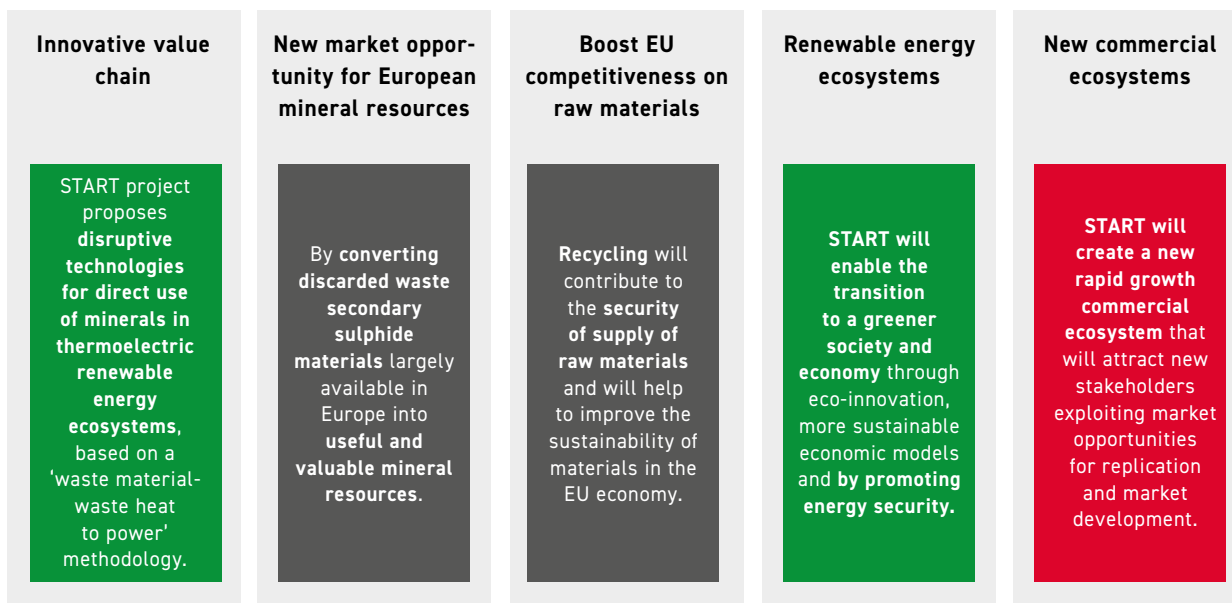


Fig. 3 The START project's main outcomes for the value chain, European mineral resources market, and green economy

on increasing the overall efficiency of energy production and consumption systems, thereby reducing greenhouse gas emissions

The main outcomes of the project are outlined in Fig 3.

Powder Metallurgy in START

Powder Metallurgy is one of the processing technologies being used to produce the mineral-derived p-type thermoelements upon which the START project's success depends. The approach followed in the START project includes three main process steps, summarised in Fig. 4.

Production of nanostructured powders by Mechanochemical Synthesis

Mechanochemical Synthesis (MCS), comprising the first process step in the START approach, is a solid-state synthesis route which uses high-energy ball mills and is already in use for large-scale nanostructured powder production by MBN [7]. The process is a suitable and fast way to produce sulphide semiconductor powders from minerals and pure elements [8, 9].

During MCS, chemical reactivity is promoted under non-equilibrium conditions, near room temperature, by unbalanced mechanical forces that transfer the mechanical energy to the powder particles. This introduces strain into the powder by generating dislocations and other defects that act as fast diffusion paths, changing the reactivity of the powders [9].

Mechanical deformation also occurs on a local basis, being mediated by dislocations and other lattice defects. As a result, the mass-transport process will be reduced relative to that of high-temperature solid-state diffusion, having a great impact on the chemical and physical behaviour of the compounds. There are several variables which influence the MCS process (e.g. type of mill, milling media, ball-to-powder ratio, filling extent of the milling chamber, milling atmosphere, milling speed, milling time, etc.) [9].

Powder consolidation by Pulse Plasma Compaction

Pulse Plasma Compaction (PPC), a method developed by GeniCore, is used to consolidate the TE materials. This technology is a modification of the conventional spark plasma sintering (SPS) process [10]. In PPC,

energy stored in a capacitor bank and charged to several kV (in the SPS process, it is typically several volts), is delivered to the powder in profoundly shorter pulses than are used in SPS technology (dozens of μs instead of a few ms) with a frequency up to 200 Hz.

Oscillating capacitor discharge is used to produce current pulses with a first half-wave amplitude of several tens of kA. The high voltage short pulses result in peak power values up to 80 MW, and field-enhanced diffusivity enables full densification at lower temperature setpoints than in conventional SPS, where low-voltage electric fields are employed [11].

SPS-based technologies have proven to be a viable consolidation technique to enable sulphide-based powders to achieve full-density compaction at temperatures considerably lower than their melting points, preserving the nanostructures developed by the MCS process [12]. Other advantages of SPS include a fast heating rate, short cycle time, accurate control of sintering energy, high reproducibility, safety and reliability.

The use of the innovative PPC device in the START approach, as

Step 1: Production of nanostructured powders from minerals and pure elements by mechanochemical synthesis

Step 2: Consolidation by pulse plasma compaction (PPC) to produce the thermoelements

Step 3: Assembly and production of the TE device

Mechanochemical synthesis is a solid-state synthesis route using high-energy ball mills.

Lab-scale production is carried out by **LNEG**, while large-scale production is carried out by **MBN Nanomaterialia**. Pilot production line is initially established, then scaled to meet the market requirement of TE at lower costs.



Courtesy MBN Nanomaterialia S.p.A., Italy

Consolidation of the TE materials by **pulse plasma compaction (PPC)**, a method developed by **GeniCore**. Sintering efficiency results from hot pressing, in which the powder is heated up using short high current impulses.



Courtesy GeniCore Sp. z o.o., Poland

Design and manufacture of TE devices incorporating the mineral-derived tetrahedrite p-type thermoelements.



Courtesy TEGnology ApS, Denmark

Fig. 4 The START process workflow. The main partners involved in these activities are nanostructured powder specialist MBN Nanomaterialia, for Step 1; material engineering company GeniCore, Step 2; and TEGnology, a leading company in TE energy harvesting, Step 3.

well as the upgraded field-assisted sintering technology (U-FAST) developed by GeniCore, is expected to enable TE materials to be produced with more appropriate densities and improved material stability, preventing thermally induced solid-state reactions in the material during service, which will enhance overall TE performance.

The production of square samples instead of traditional cylindrical compacts will also be assessed. From a technological point of view, this could represent a cost-effective solution and a huge step forward in

the consolidation of parallelepiped thermoelements required for device assembly for large-scale applications.

Mineral-derived tetrahedrite powders produced by MCS

Sulphur-based compounds are a vast class of materials, some of which are semiconductor materials with exceptional properties for energy conversion applications, either as thermoelectric materials or as photovoltaic materials [8, 12–14]. Among

these, the tetrahedrite-tennantite series offers the great advantage of being naturally occurring.

Unfortunately, the poor thermoelectric properties and low thermal stability of natural tetrahedrite-tennantite – caused by the presence of other phases (i.e., famininite) and other minerals (e.g., pyrite, chalcopyrite, and quartz) – restrict its use for commercial exploitation. The refinement of pure tetrahedrite-tennantite by conventional mining processes is not economically viable, but its direct use as a raw material in the production of modified tetrahedrite-tennantite by Powder Metallurgy is a promising route.

Tetrahedrite-tennantite powders can be produced from the elements by a relatively low-effort solid-state processing route, but a more cost-efficient approach is to start from minerals with known composition and balance them with elemental powders. Using this approach, minerals from different sites, and hence with different compositions and structures, can be processed with a dedicated material balance, targeting the same thermoelectric performance.

“The refinement of pure tetrahedrite-tennantite by conventional mining processes is not economically viable, but its direct use as a raw material in the production of modified tetrahedrite-tennantite by PM is a promising route.”

At the laboratory level, the effectiveness of processing natural and synthetic tetrahedrites has already been demonstrated in the range of grams [8]. It is now scaled by a factor of 100, approaching a relevant pilot-scale production.

Processing routes

With the support of the Lundin Mining Company, tetrahedrite-tennantite mineral from the Neves-Corvo mine (in the Portuguese sector of the Iberian Pyrite Belt) has been used. This material has been processed with purity levels of 20%, 50%, and 80% synthetic tetrahedrite (Fig. 5), via two different processing routes.

Both routes use industrial MCS apparatus, in plants designed by MBN Nanomaterialia Spa [6], which favours a direct transfer of impact energy to the processed material. The process is carried out in an argon atmosphere, with the milling chamber being cooled to operate near ambient temperature.

The first route is more conservative; the synthetic tetrahedrite is formed in a different MCS process and then added to the natural mineral for the final mixing. The second route consists of direct MCS of the natural mineral using the same composition of elemental

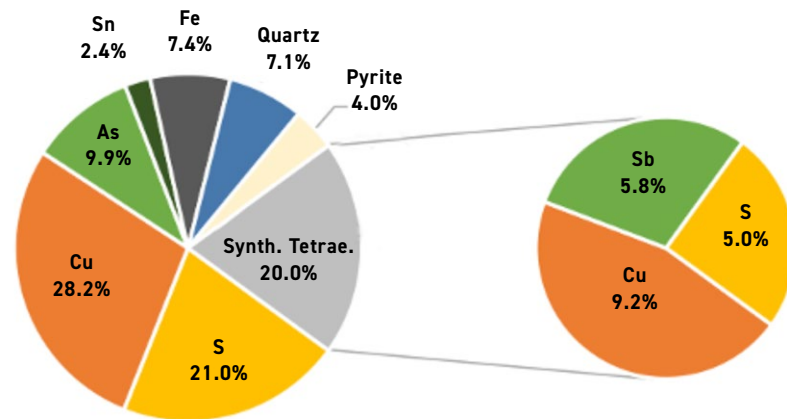


Fig. 5 Composition of the processed powder mixture with 20% of synthetic tetrahedrite

copper, antimony, and sulphur powders as was used in the first route, for consistent benchmarking.

This second route is more challenging but provides more flexibility, allowing a focus on alloying new elements into the tetrahedrite-tennantite rather than dispersing synthetic tetrahedrite into the naturally occurring one. The backscattered electron images in Fig. 6 show material obtained by both routes. The images do not reveal substantial differences between the results, even at higher magnification, regarding the distribution of pyrite (dark grey) and quartz (darker spots) distribution.

Typical X-ray diffraction (XRD) patterns for some of the processed materials are shown in Fig. 7, top. These XRD patterns confirm that the two routes are consistent with each other; a small difference appears in the famatinite peak, which is promoted when processed directly from powders mixtures containing elemental powders.

This is a positive result, since it confirms that the two routes are equally effective, and it opens the way for the direct processing via MCS of natural tetrahedrite-tennantite material with metals and sulphur powders to produce thermoelectric materials.

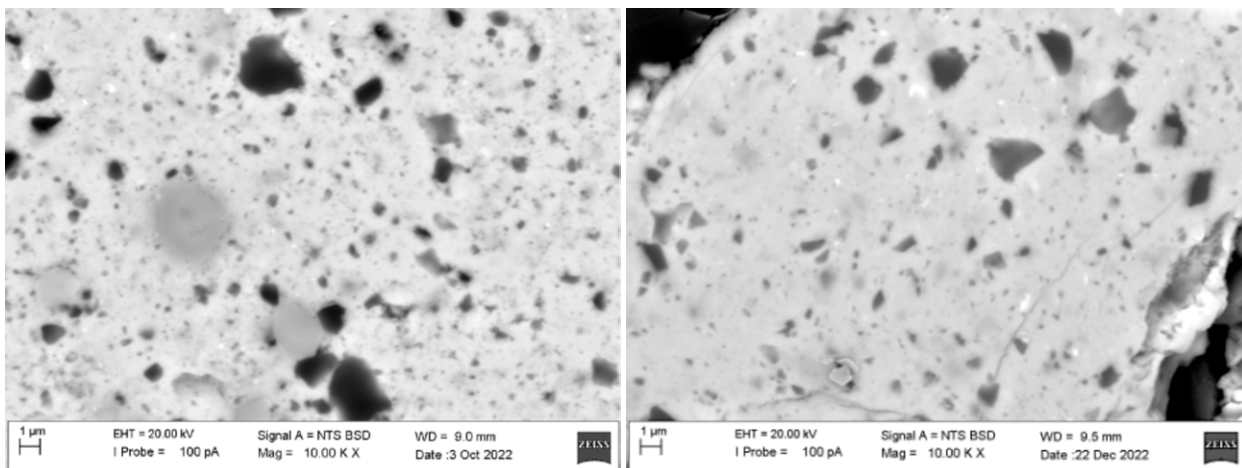


Fig. 6 Typical backscattered electron images of the processed materials when starting from powder mixtures of (a) mineral/synthetic tetrahedrite (first route), and (b) mineral/elemental powders (second route)

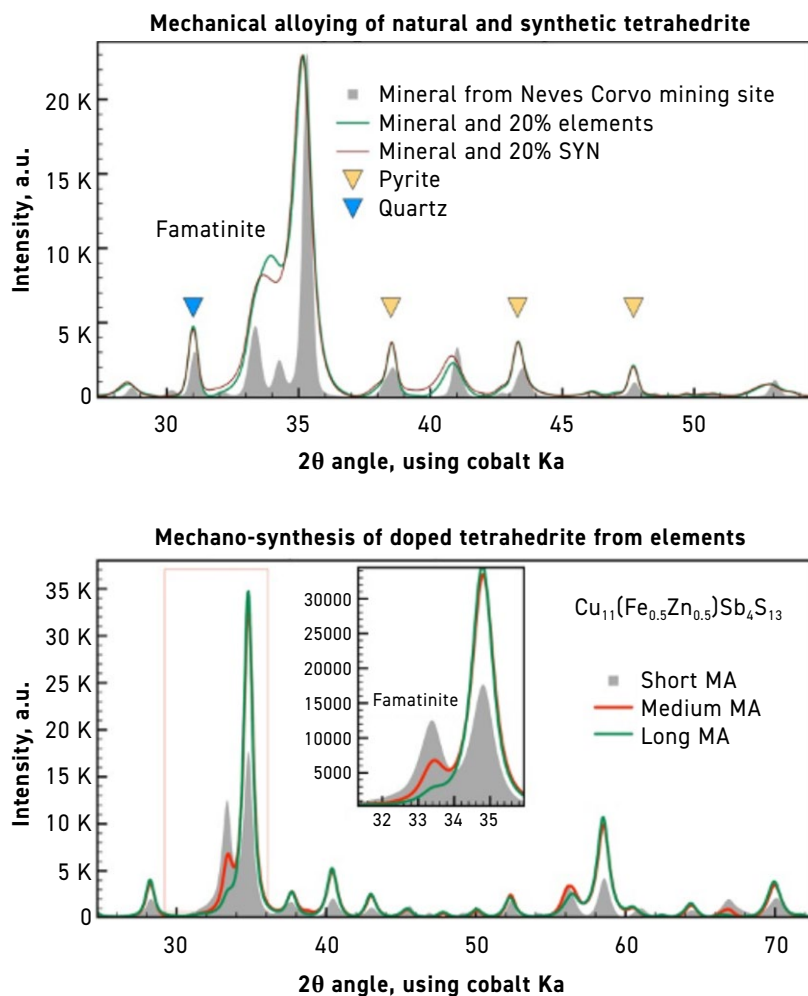


Fig. 7 Top: Typical XRD patterns of the mineral and some of the processed materials, Bottom: Typical XRD patterns for doped synthetic tetrahedrite as a function of the MCS energy level

The formation of famatinite, an unwanted phase, is due to the lack of stabilising elements such as Fe and Zn as substitutes for Cu in the synthetic tetrahedrite utilised in the experiment. The synthesis of doped tetrahedrite reduces the formation of famatinite when higher MCS energy levels are used (Fig. 7, bottom).

This synthesis has been carried out in industrial plants to validate the feasibility of the approach. The next developmental steps are related to the identification of the most effective combination of substitutional elements that will be used as a reference target in the processing of minerals with metals and sulphur powder.

This approach will enable the enhancement of naturally occurring tetrahedrite-tennantite to make it an effective thermoelectric material and has the potential to be transferred to other combinations of minerals and metals for the synthesis of functional materials.

Authors and contact

Filipe Neves, LNEG
Coordinator
filipe.neves@lneg.pt

Bruno Vicenzi, EPMA
Dissemination Manager
bv@epma.com

Alvise Bianchin,
MBN Nanomaterialia

Marcin Rosiński,
GeniCore

Hao Yin,
TEGnology

contact@start-heproject.com

Additional information

In the near future, START will organise several free webinars to provide more details on the project and offer updates on its activities. To stay informed, subscribe to the START mailing list.

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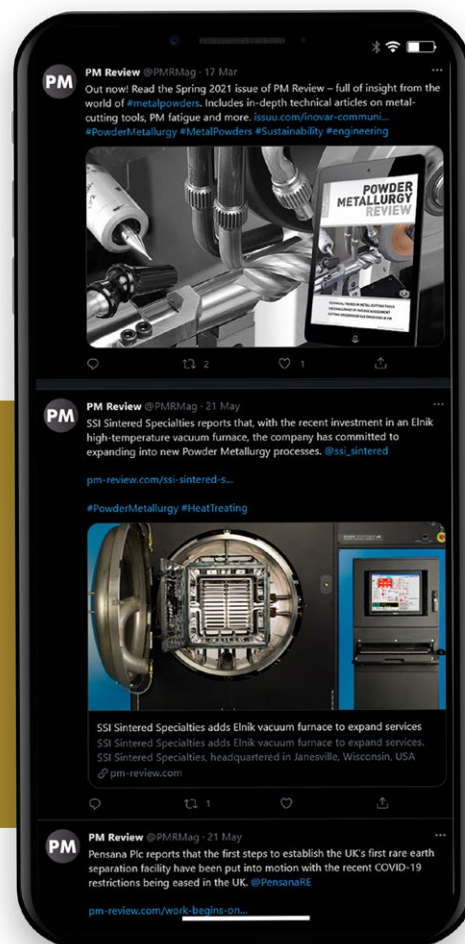


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