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Atomization of the Fe-rich MnNiCoCr high-entropy alloy for spherical powder production

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ABSTRACT

This paper explores the innovative technology of ultrasonic atomization by employing metal powder-cored wire as a filament to fabricate spherical powders. The method demonstrates a novel approach to generate uniform size distributions of spherical-shaped powders in the range of 30–60 µm, characterized by a homogeneous high-entropy composition. This technique's significance lies in its ability to efficiently produce High Entropy Alloy (HEA) powder, marking a substantial stride toward energy-efficient routes in material fabrication. The implications extend across multiple industrial sectors, promising new way for advanced materials synthesis and manufacturing processes.

1. Introduction

In the field of materials science and engineering, the pursuit of novel materials has led to the exploration of high entropy alloys (HEAs) as a promising route to yield systems with exceptional properties [1,2]. The HEAs, characterized by the simultaneous presence of multiple principal elements in equiatomic or near-equimolar proportions, have garnered significant attention due to their potential to exhibit extraordinary mechanical, thermal, and corrosion-resistant properties [3]. The fabrication of HEAs in the form of spherical powders through atomization techniques has emerged as a crucial area of study, driven by the increasing demand for advanced materials in industries ranging from aerospace, and energy to additive manufacturing.

Powder atomization is a process used to produce high entropy alloy (HEA) powders. In this process, a stream of molten metal is atomized into small droplets using a gas jet, following by a solidification into spherical powders as they fall through the gas stream. Several studies have investigated the fabrication of HEA powders by gas atomization, including Al0.5CoCrFeMnNi, AlCoCrFeNi, AlCoCrCuFeNiSi [4], and AlCrCoNiCu [5]. The resulting powders have been found to be spherical in shape and composed of a single FCC phase with uniform composition. The use of powder from Metal Powder Cored Wire (MPCW) [6,7] as a feedstock for additive manufacturing (AM) powder bed fusion, along with the characterization of the final spherical powders, represents an innovative approach to ensure the quality and suitability of metal powders for additive manufacturing. The research and development of this process is crucial for advancing the capabilities and applications of AM technology.

2. Experimental

2.1. Powder atomization

The atomization process relies on utilizing ultrasonic vibrations to atomize liquid metal, creating spherical particles. For testing alloys, the molten state is achieved either directly via plasma or through induction

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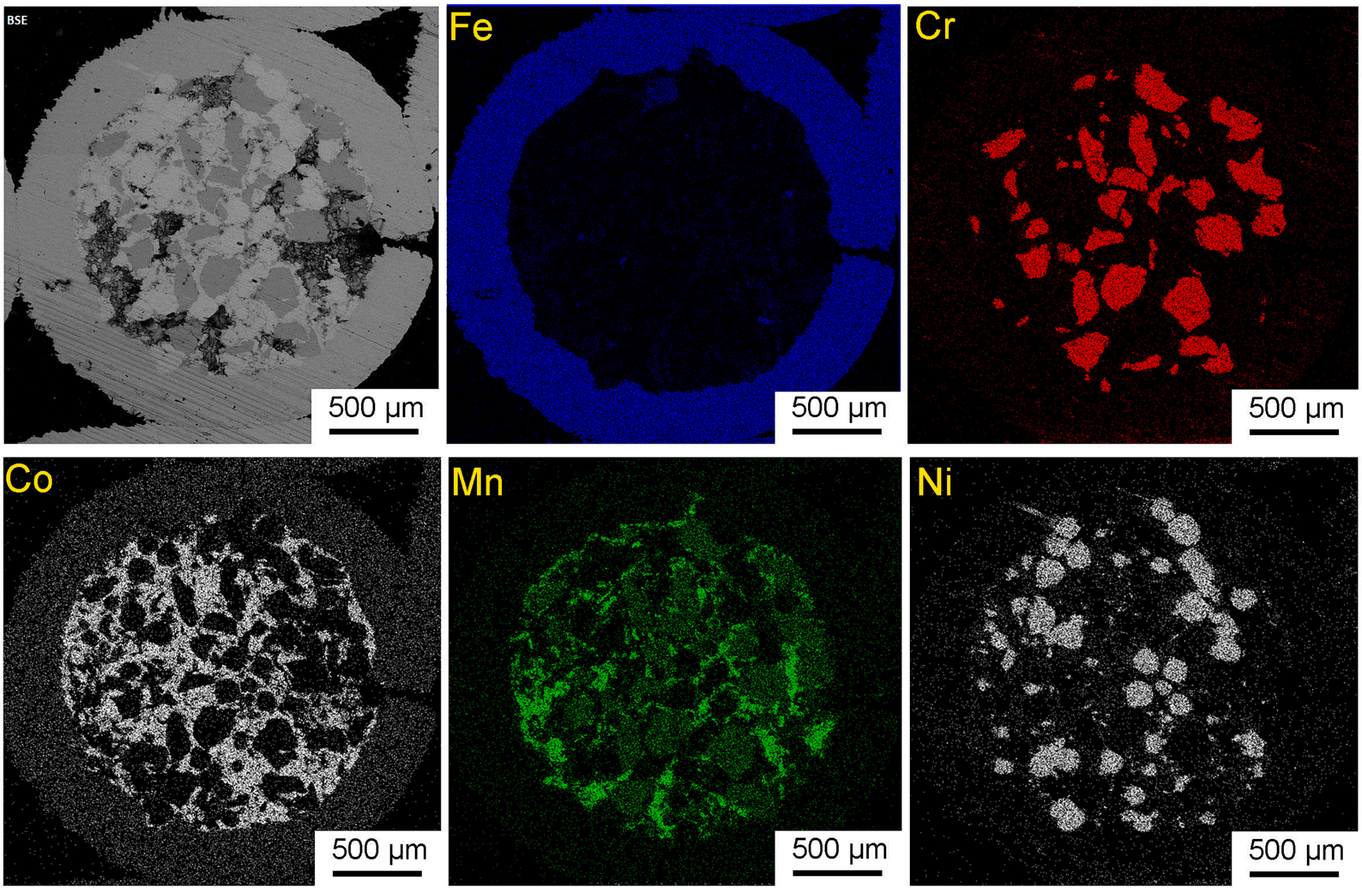

Fig. 1. MPCW cross section EDS maps [6].

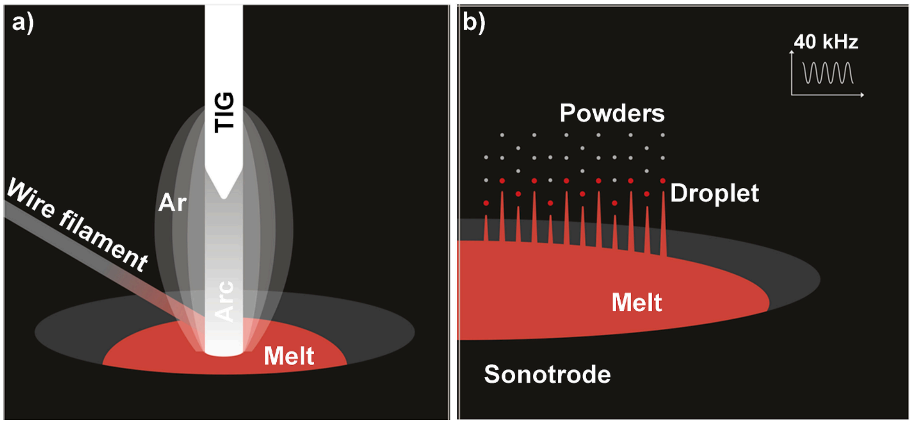

Fig. 2. Scheme of the HEAs atomization: a – melting scheme, b – droplets formation scheme.

melting in a crucible [8]. In the case of the FeMnNiCoCr High Entropy Alloy (HEA), the anticipated high melting point requires using a Tungsten Inert Gas (TIG) power source. For high entropy alloy filament is used metal powder cored wire, which was previously designed by authors [6,7]. It presents a Ferrum tube filled with a mixture of pure powders of Co, Ni, Cr and Mn (see EDS maps Fig. 1.).

The material was sprayed using an ultrasonic element known as a sonotrode (Fig. 2). A full description of the experimental setup is presented in our previous work [8]. Here is shown the schematic overview of the atomization process (Fag 2). Namely, wire filament feeds into the TIG arc zone with Ar shielded gas (Fig. 2.a). Melt pool forms in sonotrode vibrating with 40 kHz frequency (Fig. 2b). After the melt reaches the critical amplitude value, small droplets are ejected from the melt and solidified in a free flow forming highly spherical powder. The volume of the working chamber is 50 L. Atomization process occurred in an Argon 5.0 environment with an oxygen content below 100 parts per million (ppm), assessing the feasibility of directly molten with plasma. All equipment was thoroughly cleaned the day before the process, and the chamber was maintained in an argon environment until the beginning of the procedure, ensuring oxygen levels remained below 100 parts per million (ppm).

Argon, supplied at a flow rate of 7 L/min from the TIG source, served as the inert gas. Occasionally, the Argon flow was maintained below 7 L/min as atomization of the alloy required high currents. A higher Argon

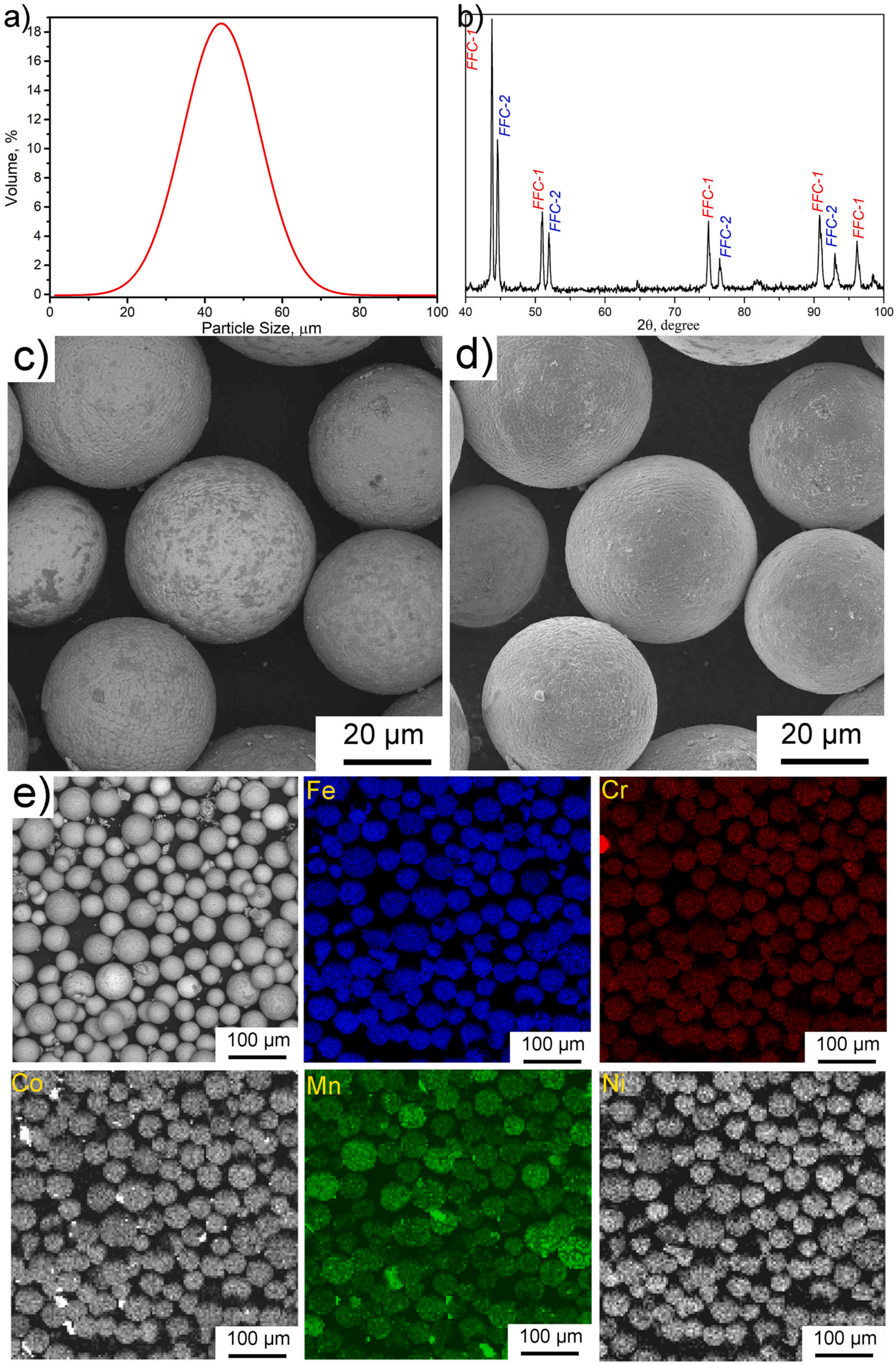

Fig. 3. HEAs spherical powders characterization: a – size distribution, b – X-ray diffraction, c – SEM BSE contrast, d – SEM – SE contrast, e – EDX X-Ray maps.

Table 1
Characterization of the chemical composition, at.%.

	Fe	Cr	Mn	Co	Ni
MPCW*	49.87	11.60	12.26	13.16	13.10
Mn enriched (FCC2)	51.02	12.74	9.61	10.45	16.17
Mn depleted (FCC1)	50.13	13.81	5.58	11.54	18.93

* programmed chemical composition calculated from the raw wire.

flow resulted in the cooling of the feedstock, halting atomization. To understand the material behavior at varying temperatures, different current settings were initially tested. Although the FeMnNiCoCr alloy could be atomized at a 220A current, the optimal solution was based on a current of 245A to ensure high wettability of molten material on the sonotrode. In addition to this, creating wide arc area is better to atomize this alloy. In the case when the feedstock is focused by a small area, it was observed that wetting did not start. Another, creating a wider arc area directly starts wetting of the surface, immediately after atomization. Under the mentioned parameters, there is less scrap formation and continuous atomization. The productivity of the suggested technology is reached up to 1 kg of wire filament to be atomized per 1 h.

2.2. Powder characterization

The equilibrium state of the atomized powders was assessed using X-ray analysis, which determined the angular position of diffraction peaks on the "θ-2θ" X-ray pattern. This analysis was conducted utilizing the DRON-3 M equipment with $Cu_{K\alpha}$ radiation in automatic mode.

Particle size measurements were performed using laser diffractometry on a Mastersizer 2000 instrument (Malvern) equipped with a HydroMu dispersing unit (Malvern). These measurements were conducted within the range of 0.1 to 1000 μm under specific conditions: particle refractive index set at 0.54, particle absorption coefficient at 4, water refractive index at 1.33, and utilizing a general calculation model for irregular particles.

A scanning electron microscope (SEM), Tescan Mira 3 LMU, was utilized for detailed analysis. The chemical composition of the structural components was determined through Energy-Dispersive X-ray Spectroscopy (EDS) facilitated by Oxford Instruments.

3. Results and discussion

Uniformity and good spherical shape of the powder are crucial factors for ensuring the quality of the powder for further processing in additive manufacturing (AM). The spherical shape of the powder ensures good flow, close packing of particles, and consistent and predictable powder dosing and layer formation. The uniform particle size distribution is also important for ensuring the quality of the final part. The results show that the as-manufactured powders from MPCW using gas atomization methods are uniform in size in the 30–60 μm range (Fig. 3a), with a clear FCC (Face-Centered Cubic) crystal lattice (Fig. 3b) and spherical shape (Fig. 3c–e). In essence, achieving a consistently uniform and spherical shape for the powder, coupled with a uniform particle size distribution, is pivotal in ensuring high-quality powder suitable for subsequent processing in additive manufacturing. Research findings indicate that employing sonotrode gas atomization methods and utilizing MPCW as a feedstock can yield to spherical powders with uniform element distribution (Fig. 3e), forming a solid solution for high entropy alloy within the powder. However, analysis of the final spherical powders derived from the MPCW feedstock via X-ray data reveals the presence of two distinct FCC phases.

A closer consideration of this effect could be explained by local segregation during the solidification of the droplets. Considering the SEM image of the powder in phase contrast mode (Fig. 3c.) is seen some difference. Visualization by X-ray mapping has shown the presence of Mn micro-segregation, correlated with nickel and ferrum. The other components of chromium and cobalt distribute rather uniformly. Namely, bigger powders are enriched with Mn while smaller ones are depleted. As Mn belongs to a volatile element its evaporation is more intense in smaller particles owing to the bigger specific surface of the last (Table 1). The increasing concentration of manganese in solid solution leads to shifts of the x-ray peaks toward higher angles. Thus, the enriched with Mn phase attributed to FCC1 while depleted to FCC2. This effect is eliminated in further 3Dprinting, due to averaging of the alloy composition in the process of consequent remelting.

4. Conclusion

The innovative application of re-powder technology, incorporating metal powder cored wire (MPCW) as feedstock, presents a transformative methodology for the fabrication of spherical powders. This technique yields powders with a consistent size distribution, spherical morphology, and a homogeneously composed high-entropy structure. This breakthrough approach not only enables the efficient production of a diverse array of High Entropy Alloy (HEA) powders but also signifies a pivotal advancement in energy-efficient routes for obtaining these crucial materials. Its potential implications span across various industrial sectors, promising novel avenues for advanced materials synthesis and manufacturing processes.

CRediT authorship contribution statement

Anatoliy Zavdoveev: Supervision, Data curation, Conceptualization. **Łukasz Zrodowski:** Writing – review & editing, Methodology, Conceptualization. **Dmytro Vedel:** Writing – original draft, Methodology, Data curation. **Pedro Cortes:** Writing – review & editing, Supervision. **Tomasz Choma:** Writing – original draft, Data curation, Conceptualization. **Mateusz Ostrysz:** Data curation, Conceptualization. **Oleksandr Stasiuk:** Methodology, Data curation. **Thierry Baudin:** Writing – review & editing, Supervision. **Andrey Klapatyuk:** Methodology, Data curation. **Aleksandr Gaivoronskiy:** Methodology, Data curation. **Vitaliy Bevz:** Methodology, Data curation, Conceptualization. **Elena Pashinska:** Writing – review & editing, Data curation, Conceptualization. **Mykola Skoryk:** Writing – review & editing, Methodology, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] L. Ladani, M. Sadeghilaridjani, Review of powder bed fusion additive manufacturing for metals, Met. 11 (2021), https://doi.org/10.3390/met11091391.

[2] E.P. George, D. Raabe, R.O. Ritchie, High-entropy alloys, Nat. Rev. Mater. 4 (2019) 515–534, https://doi.org/10.1038/s41578-019-0121-4.

[3] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. a. 375–377 (2004) 213–218, https://doi.org/10.1016/j.msea.2003.10.257.

[4] C.-C. Yang, J.L. Hang Chau, C.-J. Weng, C.-S. Chen, Y.-H. Chou, Preparation of high-entropy AlCoCrCuFeNiSi alloy powders by gas atomization process, Mater. Chem. Phys. 202 (2017) 151–158, https://doi.org/10.1016/j.matchemphys.2017.09.014.

[5] Z. Ren, S. Zhu, X. Wang, Y. Zhao, G. Han, K. Zhou, W. Wang, G. Tian, Preparation and microstructure of multi-component high entropy alloy powders fabricated by gas atomization method, Metals (basel). 13 (2023), https://doi.org/10.3390/met13020432.

[6] A. Zavdoveev, A. Klapatyuk, T. Baudin, E. MacDonald, D. Mohan, J. Oliveira, A. Gajvoronskiy, V. Poznyakov, H.S. Kim, F. Brisset, M. Khokhlov, M. Heaton, M. Rogante, M. Skoryk, D. Vedel, R. Kozin, I. Klochkov, S. Motrunich, Non-equimolar cantor high entropy alloy fabrication using metal powder cored wire arc additive manufacturing, Addit. Manuf. Lett. (2023) 100124, https://doi.org/10.1016/j.addlet.2023.100124.

[7] A. Zavdoveev, H. Seop Kim, Y.-U. Heo, T. Baudin, P. Cortes, F. Brisset, D.-H. Kim, D. Vedel, A. Klapatyuk, A. Gajvoronskiy, V. Poznyakov, E. Pashinska, S. Motrunich, Microstructure and properties of HEA fabricated through metal powder wire ARC additive manufacturing, Mater. Lett. (2023) 135726, https://doi.org/10.1016/j.matlet.2023.135726.

[8] Ł. Żrodowski, R. Wróblewski, T. Choma, B. Morończyk, M. Ostrysz, M. Leonowicz, W. Łacisz, P. Błyskun, J.S. Wróbel, G. Cieślak, B. Wysocki, C. Żrodowski, K. Pomian, Novel cold crucible ultrasonic atomization powder production method for 3D printing, Mater. (basel). 14 (2021), https://doi.org/10.3390/ma14102541.