Propelling FeMnNiGeSi high-entropy alloys to new heights in magnetocalorics

Jia Yan Law[a], Victorino Franco[a]

[a] *Multidisciplinary Unit for Energy Science (MUFENS), University of Seville, Spain.*

Magnetocaloric high-entropy alloys (HEAs) is a rising subject of interest in recent years for their potential in magnetic applications due to their high configurational entropy and diverse compositional space. However, the broad compositional range complicates the search for good functional properties, and the emphasis on single-phase microstructures has limited the exploration of alternative strategies. Our work challenges this conventional focus by designing the FeMnNiGeSi HEA system, which undergoes a first-order thermomagnetic phase transition. We show that stress relaxation, rather than single-phase microstructure, is key to significantly enhancing their magnetocaloric effect (MCE). This breakthrough has propelled the FeMnNiGeSi HEA system to new heights, significantly improving its MCE and positioning it as strong candidate against established materials in the field, as well as offering a fresh perspective on the role of stress relaxation in improving magnetocaloric performance.

Keywords: Magnetocaloric effect; high-entropy alloys; third-generation; targeted property search strategy; annealing.

1. Introduction

Magnetocaloric high-entropy alloys (HEAs) have rapidly gained prominence in recent research [1-3]. By combining multiple principal elements, HEAs achieve high configurational entropy, unlocking a vast compositional space that offers exciting possibilities for discovering novel material properties. These alloys not only outperform conventional alloys in mechanical properties but also have the potential to balance both mechanical and functional properties, making them highly attractive for magnetic applications.

The vast HEA compositional space complicates the search for enhanced functional properties. Our research reveals that those centered in the multi-principal element phase diagram often exhibit subpar magnetocaloric effect (MCE). Additionally, there is a prevailing emphasis on achieving single-phase microstructures in HEAs (driven by their high configurational entropy of mixing), which has limited the exploration of strategies for improving functional properties.

In contrast, our work boldly challenges these conventional views. We adopted a focused, targeted approach and designed the FeMnNiGeSi HEA system, which undergoes a first-order thermomagnetic phase transition. Furthermore, we challenge the fixation on single-phase structures, and demonstrate that stress relaxation, not phase uniformity, significantly enhances MCE. This positions FeMnNiGeSi HEAs as strong contenders against established materials and has been recently coined as the third-generation magnetocaloric HEAs.

2. Results and discussion

The targeted-property sought FeMnNiGeSi HEAs demonstrate a substantial MCE (13 J $kg^{-1}K^{-1}$ at 2.5 T), surpassing earlier magnetocaloric HEAs, including those with rare-earth elements. These alloys feature a dual-phase microstructure, which can be transformed into a single-phase structure through high-temperature annealing. Notably, stress relaxation during low-temperature annealing significantly enhances their MCE. This breakthrough positions FeMnNiGeSi HEAs as strong candidates to established materials like La(Fe,Si)$_{13}$, Fe_2P, and $Gd_5Si_2Ge_2$. It challenges the traditional focus on single-phase microstructures in HEAs, highlighting stress relaxation as a key factor in improving magnetocaloric performance (see Figure 1).

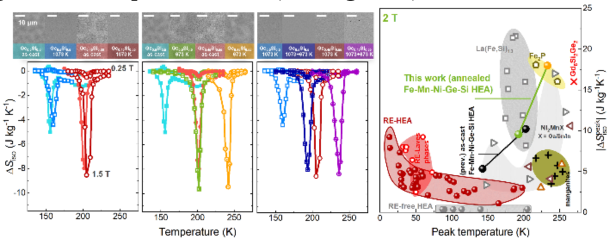

Figure 1: Microstructure and MCE of FeMnNiGeSi HEAs in as-cast and annealed states. The annealed HEAs show improved MCE, competing with La(Fe,Si)$_{13}$, Fe_2P, and $Gd_5Si_2Ge_2$ [7].

References

[1] K. Klinar, J.Y. Law, V. Franco, X. Moya, A. Kitanovski, Advanced Energy Materials **14** (2024), 2401739.
[2] C. Romero-Muñiz, J.Y. Law, J. Revuelta-Losada, L.M. Moreno-Ramírez, V. Franco, The Innovation Materials **1**(3) (2023), 100045.
[3] J.Y. Law, V. Franco, Chapter 332 in Handbook on the Physics and Chemistry of Rare Earths, Elsevier, vol. **64** (2023), 175-246. *(Commemorative volume dedicated to the memory of Prof. V.K. Pecharsky).*
[4] J.Y. Law, V. Franco, APL Materials **9** (2021), 080702.
[5] J.Y. Law, V. Franco, Journal of Materials Research **38**(1) (2023), 37-51.
[6] J.Y. Law, Á. Díaz-García, L.M. Moreno-Ramírez, V. Franco, Acta Materialia **212** (2021), 116931.
[7] Á. Díaz-García, J.Y. Law, L.M. Moreno-Ramírez, V. Franco, Scripta Materialia 258 (2025), 116492.

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