# Phenomena during liquid-phase assisted sintering in High-Entropy Ceramics with a Ni binder

Humeniak Mykola[1], Vedel Dmytro[1,2], Vronska Yuliia.[1], Zatsarna Oleksandra[1], Taran Serhii[3], Stasiuk Oleksandr.[1]

[1] G. V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine
[2]Frantsevich Institute for Problems in Materials Science, 3 Krzhizhanovsky St., 03142 Kyiv, Ukraine
[3]Interregional academy of personal management, Kyiv, Ukraine

E-mail: olek.stasiuk@gmail.com

***Abstract:*** *This study investigates the mechanisms of liquid-phase assisted sintering in high-entropy ceramics (HECs) using a nickel binder. The research focuses on the densification process of (Ti, Zr, Hf, Nb, Ta)C-based cermets with 10 vol% Ni, and how pressure influence liquid-phase extraction. Results show that eutectic reactions between Ni and carbide phases was observed during liquid formation below 1400°C. Microstructural analysis reveals a nickel-rich matrix, solid solutions, and NbC-based carbide inclusions in the extracted drop. These findings provide insights into optimizing processing parameters for advanced HEC-based composites.*

**Keywords:** CERMETS, MICROSTRUCTURE, HIGH-ENTROPY CERAMICS, LIQUID-PHASE ASSISTED SINTERING

## *Introduction.*

High-entropy ceramics (HECs) offer an excellent combination of hardness, wear resistance, and oxidation resistance compared to conventional single-phase ceramics. HECs can be classified into several categories, including high-entropy carbides, borides, oxides, and silicides [1-20]. The base line high-entropy carbide is (Ti, Zr, Hf, Nb, Ta)C, which have high mechanical properties at both room and elevated temperatures compared to single-phase carbides. Achieving full densification of HECs typically requires high sintering temperatures, around 2100–2300°C. However, two main approaches can be used to decrease the densification temperature: (i) the addition of refractory compounds such as SiC, and (ii) the indroduction of metals like Co, Ni, or their combinations.

The development of cermets with a hard HEC phase have several advantages, most notably a significant reduction in the densification temperature while retaining high mechanical properties. Nevertheless, due to the high contact angle between HECs and Fe, Co, or Ni, additional pressure is required to achieve a fully dense composite. Our previous work [21] has shown that applying a relatively low pressure (~10 MPa) can substantially increase the density of HEC cermets, whereas higher pressures (e.g., 15 MPa) may result in the extraction of liquid from the cermet. This liquid phase led to densification of the ceramics.

The aim of the present study is to investigate the nature of the liquid phase extracted during the densification of cermets based on (TiZrHfNbTa)C with a 10 vol% Ni binder, in order to better understand the phenomena occurring during liquid-phase assisted sintering.

## *Materials and experimental procedure.*

The carbides powders were weighted in an equiatomic ratio and then mixed in acetone for 5 h by using the planetary mill. The (Ti, Zr, Hf, Nb, Ta)C powders were heating with heating rate 100 o C/min to 1800 o C in a vacuum and held 1 hour in heat resistance graphite furnace SSHVL-10 (IPMS, Ukraine). After first synthesis powders were ground and sifted through a sieve and mixed in acetone for 5 h by using the planetary mill. The second synthesis was carried out in the same condition. The powder size after second synthesis and grounding was ~ 2-4 mm.

The powder of HEC and metals were weighted in ratio 90 vol% HEC and 10 vol% Ni The powders were mixed in acetone during 5 h to obtain homogenous mixture.

Disk with a diameter of 30 mm was placed in a graphite die pre-coated with boron nitride for protection of the materials from direct interaction with the tools. Hot pressing was carried out in an SPD-120 apparatus (Frantsevich Institute for Problems in Materials Sciences, Ukraine (IPMS)). An induction-heating with heat rate 100°C/ min was set to achieve temperature of 1400-1550°C according to the piston movement during shrinkage. The initial load was 7 MPa and, once achieved the peak temperature, the load was increased to 5 or 30 MPa. The dwell at the maximum temperature was 15 min, the furnace was slowly cooled down to 1200°C to avoid crack formation.

The microstructure of the drop was investigated by scanning electron microscopy (SEM) on a MIRA 3 microscope (Tescan Co., Czech Republic) equipped with an energy diffraction spectroscope (EDS) (INCA X- Max, Oxford Instruments, Abingdon-on-Thames, UK).

## *Results and discussion.*

The liquid phase sintering was the main mechanism of densification in cermets. It should be noted that there is melting in binary Ni-Single phase carbide system: (Ni-TaC)eutectic (Te=1340°C), (Ni-NbC) eutectic (Te=1320°C) , (Ni-HfC)eutectic (Te=1310°C), (Ni-WC)eutectic (Te=1300°C), (Ni-ZrC)eutectic (Te=1290°C), (Ni-TiC)eutectic (Te=1260°C).

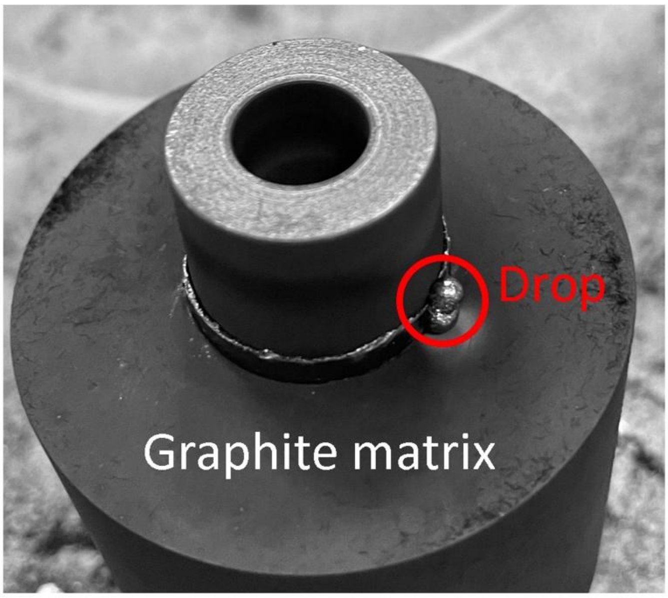


***Fig. 1*** *– The general view of the graphite matrix after densification of HEC-10 vol. % Ni system*

From this perspective, in the Ni/HEC (high-entropy ceramic) system, the formation of a liquid phase can be observed at temperatures below 1400°C. This is due to the eutectic reactions between nickel and the various carbide components, which lower the melting point compared to the individual components.

The careful optimization of both temperature and pressure is necessary for achieving fully dense composite densification by hot pressing liquid-phase assistant sintering. Because these parameters critically influence the microstructure and properties of the final composite.

Among these factors, pressure stands out as one of the most significant variables affecting the microstructure. At low to medium pressures (5–10 MPa), the generated liquid phase tends to remain within the cermet matrix, increasing the densification rate.

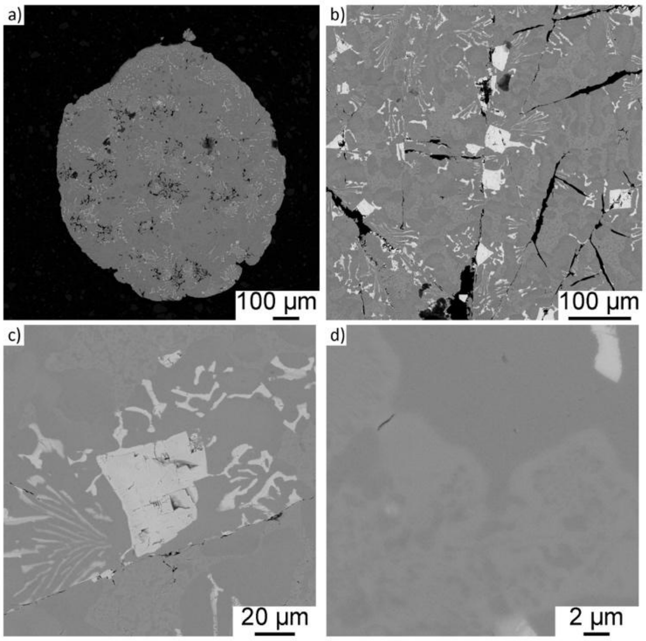


*Fig. 2 – The cross section of the drop that extract after densification in HEC-10 vol. % Ni system: general view (a), microstructure of the eutectics (b), microstructure of the NbC based and lamellar ZrC based crystal (c), microstructure of the Ni and Ni solid solution (d)*

However, as the pressure increases to around 15 MPa, the liquid phase begins to be expelled from the cermet, and at even higher pressures (30 MPa), it is completely extracted from the graphite die. This extraction process can alter the distribution of phases and may impact the overall mechanical properties of the material.

Simultaneously, overheating of the material during hot pressing can lead to pronounced grain growth. While the microstructure may remain homogeneous, the increase in grain size can negatively affect certain mechanical properties, such as hardness and toughness.

A cross-sectional analysis of a drop extracted after hot pressing in the HEC-Ni system (Fig. 2) reveals a complex phase composition. The droplet consists of pure nickel, a nickel solid solution with dissolved elements such as Zr, Ti, Hf, Nb, and Ta (Fig. 3), and various carbide phases. In the droplet, the metal and carbide phases form a eutectic microstructure, confirming the occurrence of eutectic reactions in the HEC-Ni system (Fig. 2b). The matrix is primarily composed of nickel and nickel-based solid solutions, while the carbide inclusions exhibit both lamellar and faceted morphologies.

Notably, the main carbide phase is based on NbC, which forms as a result of liquid-phase interactions during the crystallization process. The thin, lamellar crystals are enriched with Zr, Hf, and Nb. It is inferred that at approximately 1298°C, the liquid phase forms, and when a high additional load is applied, this liquid is forced through the powder compact and graphite die.

This liquid wets the powder surface and leads to its densification. The euctic nature of the droplet indicates that the initial stage of sintering involves the dissolution of carbide elements in the nickel, followed by their reprecipitation through the liquid phase.

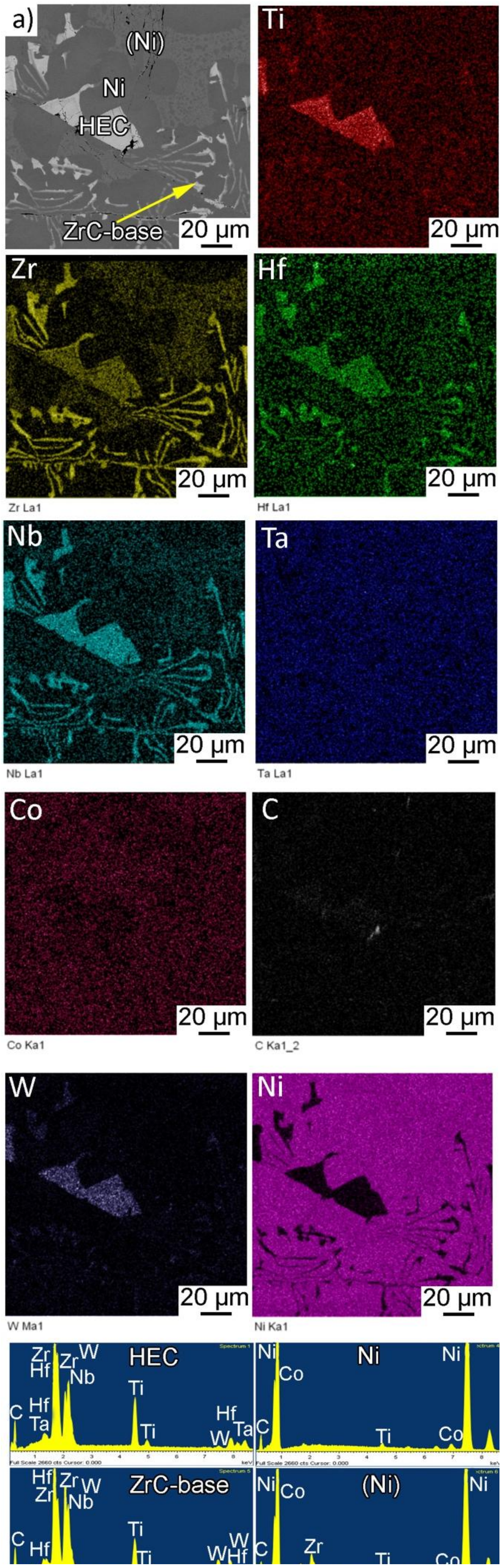


***Fig. 3** – The microstructure of the drop at high magnification with EDS map analysis and EDS spectrum of the separate phase*

The extracted liquid dissolves carbides, resulting in a supersaturated melt of these elements, which subsequently crystallizes to form a skeleton of carbide phases. This process significantly influences the thermal and chemical behavior of the material, as well as its final microstructure and properties.

## Conclusions

1. Eutectic reactions between nickel and carbide phases in the Ni/HEC system was observed during HP sintering by investigation of the drop that extract.
2. The formed liquid wets the surfaces of the particle that increase the densification rate.
3. The liquid phase promotes the formation of a nickel-rich matrix, solid solutions, and NbC-based carbide inclusions. Careful control of temperature and pressure is essential for optimizing the microstructure and mechanical properties of advanced HEC-based composites.

## References.

[1] P. Sarker et al., “High-entropy high-hardness metal carbides discovered by entropy descriptors,” Nat Commun, vol. 9, no. 1, pp. 1–10, 2018, doi: 10.1038/s41467-018-07160-7.

[2] A. Sarkar, B. Breitung, and H. Hahn, “High entropy oxides: The role of entropy, enthalpy and synergy,” Scr Mater, vol. 187, pp. 43–48, 2020, doi: 10.1016/j.scriptamat.2020.05.019.

[3] H.-R. Mao, E.-T. Dong, S.-B. Jin, X.-M. Qiu, and P. Shen, “Ultrafast high-temperature synthesis and densification of high-entropy carbides,” J Eur Ceram Soc, vol. 42, no. 10, pp. 4053–4065, 2022, doi: https://doi.org/10.1016/j.jeurceramsoc.2022.03.054.

[4] J. Gild et al., “A high-entropy silicide: (Mo0.2Nb0.2Ta0.2Ti0.2W0.2)Si2,” Journal of Materiomics, vol. 5, no. 3, pp. 337–343, 2019, doi: 10.1016/j.jmat.2019.03.002.

[5] M. H. Tsai and J. W. Yeh, “High-entropy alloys: A critical review,” Mater Res Lett, vol. 2, no. 3, pp. 107–123, 2014, doi: 10.1080/21663831.2014.912690.

[6] Y. Zhang et al., “Fabrication of textured (Hf0.2Zr0.2Ta0.2Cr0.2Ti0.2)B2 high-entropy ceramics,” J Eur Ceram Soc, vol. 41, no. 1, pp. 1015–1019, 2021, doi: 10.1016/j.jeurceramsoc.2020.08.071.

[7] J. Gild et al., “High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics,” Sci Rep, vol. 6, no. October, pp. 2–11, 2016, doi: 10.1038/srep37946.

[8] E. Castle, T. Csanádi, S. Grasso, J. Dusza, and M. Reece, “Processing and Properties of High-Entropy Ultra-High Temperature Carbides,” Sci Rep, vol. 8, no. 1, Dec. 2018, doi: 10.1038/s41598-018-26827-1.

[9] L. Feng, W. G. Fahrenholtz, G. E. Hilmas, and Y. Zhou, “Synthesis of single-phase high-entropy carbide powders,” Scr Mater, vol. 162, pp. 90–93, 2019, doi: 10.1016/j.scriptamat.2018.10.049.

[10] Y. Zhang et al., “Dense high-entropy boride ceramics with ultra-high hardness,” Scr Mater, vol. 164, pp. 135–139, 2019, doi: 10.1016/j.scriptamat.2019.01.021.

[11] Y. Zhang et al., “Microstructure and mechanical properties of high-entropy borides derived from boro/carbothermal reduction,” J Eur Ceram Soc, vol. 39, no. 13, pp. 3920–3924, 2019, doi: 10.1016/j.jeurceramsoc.2019.05.017.

[12] L. Feng, F. Monteverde, W. G. Fahrenholtz, and G. E. Hilmas, “Superhard high-entropy AlB2-type diboride ceramics,” Scr Mater, vol. 199, p. 113855, 2021, doi: 10.1016/j.scriptamat.2021.113855.

[13] S. Failla, P. Galizia, S. Fu, S. Grasso, and D. Sciti, “Formation of high entropy metal diborides using arc-melting and combinatorial approach to study quinary and quaternary solid solutions,” J Eur Ceram Soc, vol. 40, no. 3, pp. 588–593, 2020, doi: 10.1016/j.jeurceramsoc.2019.10.051.

[14] A. Sarkar et al., “High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties,” Advanced Materials, vol. 31, no. 26, 2019, doi: 10.1002/adma.201806236.

[15] Y. Qin et al., “High-entropy silicide ceramics developed from (TiZrNbMoW)Si2 formulation doped with aluminum,” J Eur Ceram Soc, vol. 40, no. 8, pp. 2752–2759, 2020, doi: 10.1016/j.jeurceramsoc.2020.02.059.

[19] D. V. Vedel, P. V. Mazur, O. M. Grigoriev, L. M. Melakh, M. D. Bega, and Kozak I.V, “Obtaining and mechanical properties of high-entropy ceramics (TiZrHfNbTa)C (in Ukraine),” Journal of Superhard materials, vol. 5, pp. 1–10, 2022.

[20] L. Dakova et al., “Processing and Mechanical Properties of (Hf-Ta-Zr-Nb-Ti)C,” Materials Science Forum, vol. 1082, pp. 84–89, Oct. 2023, doi: 10.4028/p-s8gm7c.

[30] Dmytro Vedel, Tamás Csanádi, Petro Mazur, Anton Osipov, Juraj Szabó, Vladyslav Shyvaniuk, Richard Sedlák, Oleksandr Stasiuk, Veronika Kuchárová, Oleg Grigoriev Effect of densification technology on the microstructure and mechanical properties of high-entropy (Ti, Zr, Hf, Nb, Ta) C ceramic-based cermets. Open Ceramics. Volume 19,2024