საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 20(194), №1, 2026
BULLETIN OF THE NATIONAL ACADEMY OF SCIENCES OF GEORGIA, vol. 20(194), no. 1, 2026

Materials Science

The Study of the Effect of Mechanical Activation of the Initial Powders of the Fe-Cu-Ni-Sn Alloy on the Shrinkage Kinetics during Sintering under Hot Pressing Conditions

Nikoloz Loladze[*], Nikoloz Chikhradze[**], Mikheil Tabatadze[*], Medea Tserodze[*], Zurab Avalishvili[*], Nana Tserodze[§]

[*] *Scientific Center "Diamonds & Composite Materials, Georgian Technical University, Tbilisi, Georgia*
[**] *Academy Member, G. Tsulukidze Mining Institute, Tbilisi, Georgia*
[§] *P. Melikishvili Institute of Physical and Organic Chemistry, Ivane Javakhishvili Tbilisi State University, Georgia*

Abstract. This paper examines the influence of mechanical activation of the initial metal powders on the hot-pressing sintering process in metal system Fe-Cu-Ni-Sn. In order to understand the influence of activation on the sintering mechanisms of the densification in Fe-Cu-Ni-Sn compacts, the kinetics of linear shrinkage were evaluated. In one case the initial charge was represented as independent Cu, Fe, Sn and Ni powder mixture and in the second case, the same powder mixture was used after mechanical activation. Obtaining kinetic curves in the temperature range of 600-800°C and P = 20 MPa made it possible to determine the activation energy for different stages of densification: I – 87%, II – 93%, and III – 95-96%. Calculated kinetic values (E act) showed that activation of the initial powders charge contributes to the intensification of the sintering process and a decrease in (E act), especially in the final stages of the process from 58 kJ/mol to 25 kJ/mol. © *2026 Bull. Natl. Acad. Sci. Georg.*

Keywords: sintering kinetics, hot pressing, mechanical activation

Introduction

Superhard composite diamond-containing materials are manufactured mainly by powder metallurgy methods, which differ from each other by the time and temperature of sintering process and by the pressure value. Among various technological ways of DCM sintering the most popular ones are vacuum sintering, electro discharge and hot pressing. Currently, hot pressing is one of the main methods for producing DCM with metal binder (Borowiecka-Jamrozek & Lachowski, 2017; Maistrenko et al., 2000; Liyong et al., 2021).

During the sintering process, two or more sintering mechanisms often occur simultaneously. So a single sintering theory cannot fully reflect the nature of sintering. Understanding the dependence of the structural features (dispersity, morphology, disorder of the crystalline structure) of the original metal powders (binder) on the densification mechanism of DCM, is the key to achieve optimal

© 2026 Bull. Natl. Acad. Sci. Georg.

properties of the DCM binder under certain P – T – τ conditions.

The objectives of this study was to identify and study the influence of the physical and physicochemical properties of the initial metal powders on the kinetics of their sintering process, as well as the properties of the resulting sintered materials under hot pressing conditions.

The object of study was a metal composition of Fe – Cu – Sn – Ni, which is widely used as a binder in the production of diamond composite materials (Mechnik, 2014; Zaitsev et al., 2012).

Powders of irons PJI MZ, copper MPS-1 (99,5-Cu), nickel PNE-1, tin PO-1 (metals powders grade in Russian) were used at starting materials to manufacture metal compositions for sintering. Powder of the composition under study Fe – Cu – Sn – Ni (47 – 32 – 8 and 13%, respectively) was used. Powder dispersion <63 μm. Metal powders were mixed for 30 min in industrial mixer. Afterwards, part of the powder mixture was subjected to mechanical activation. The powders were subjected to mechanical treatment in a stainless steel ball mill using alloy steel grinding balls with 12 mm in diameter.

The sintering process in both cases (initial powder mixture and powders mixed after activation) was performed in cylindrical molds by hot pressing. The developed sample was about 20 mm in diameter and 8 mm in height. Graphite CPV 14814000 was used as the hot pressing mold material. The process was conducted on hot-pressing equipment in pressure conditions of 20 MPa, holding time of 2 min, and temperature up to 830°C, each sample mass was 20 g.

The heating rate was 150°C/min up to 600°C. At 600°C, the sample was held until complete shrinkage stabilization (2-3 min). Afterwards, with the temperature increasing at a rate of 40°C/min, the linear shrinkage of the sample was recorded as a function of the process temperature using a built-in displacement sensor (micrometer) with an accuracy of 0.01 mm. The linear shrinkage and subsequently density of the sintering billet changed during the same step. So the obtained data of $\Delta L/L_0$ were used to calculate the relative density using the equation (An, 2011; Hao-Jun Zhou et al., 2020; Shao et al., 2008):

$$\rho = \frac{\rho_g}{\left(1-\frac{dL}{L_0}\right)^3}\cdot\frac{1}{\rho_0},$$

where ρ_g is the greendensity (density of sinter at 600°C), ρ_0 is the theoretical density, L_0 is the initial height of compact at 600°C, and dL/L_0 is the instantaneous linear shrinkage. Density calculation of sintered alloy composites was performed according to the formula:

$$\gamma = m_1 \cdot y_{water} / m_1 - m_2,$$

where m_1 is the mass of the sample in air g; m_2 is the sample in water, g; y is the density of water at the measurement temperature, g/mc^3. The mass was measured with an accuracy of $10^{-4}g$. Also, the hardness of sintered samples was characterized according to the Rockwell B scale.

In order to more deeply study and reveal the physicochemical processes occurring in the Fe-Cu-Ni-Sn system during hot pressing, we studied the kinetics of consolidation processes occurring under P–T conditions. (Figs. 1; 2) The kinetic curves of the consolidation process occurring at different temperatures of the Fe-Cu-Ni-Sn composition are given, when the grain size of the initial components is ≤63 μm. (Fig. 1). The same dependence curves are given when the initial components are activated (Fig. 2). Such kinetic curves during the hot pressing process allowed determining the activation energy of the ongoing process.

It is noteworthy that the mechanical activation of powders in given regimes significantly changes the morphology and structure of powder particles, while their physical-chemical parameters such as specific surface area (σ m2/g), granulometry, such as the minimum and maximum grain size, are changed insignificantly (Tabatadze, 2023).

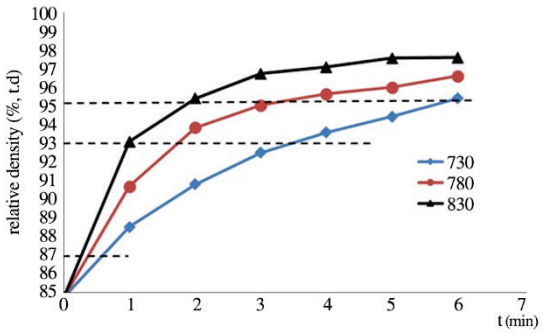

Fig. 1. Kinetic curves of the temperature dependence of the densification of the Fe-Cu-Ni-Sn composition under conditions of P=20 MPa, when the grain size of the initial component is -63 μm.

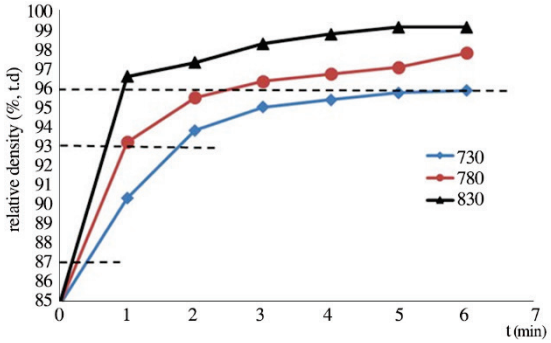

Fig. 2. Kinetic curves of the temperature dependence of the densification of the Fe-Cu-Ni-Sn composition under conditions of P= 20 MPa, when the initial component is mechanized.

It should be noted that the hot pressing process is quite dynamic and the mechanism determining the process itself can change rapidly during the sintering process. Given this, it was of interest to determine the kinetic characteristic (activation energy Es) for different stages of the sintering process.

The obtained kinetic curves allowed determining the activation energy values at different stages of the process in the temperature range 700-820°C. To investigate the activation energy, we used the well-known expression (Elyutin et al., 1976): $dlnV/dT = E/RT^2$ and the well-known equation obtained as a result of simplification: E=4,575 tgα, where $tg\alpha = lgV/\frac{1}{T}$, lgV – is the rate of densification of the composition, and 1/T is the reverse of the process temperature.

For a better understanding of the essence of the sintering process when using activated initial charge calculations were made for different stages of the process: as for the initial stage τ = 10 - 40 s, when the degree of densification α is equal to 87%, for the intermediate stage τ = 60 - 220 s, when the degree of densification α is equal to 93%, and for the late stage of the process τ = 50 - 300 s, when the degree of densification α is equal to 95-96%.

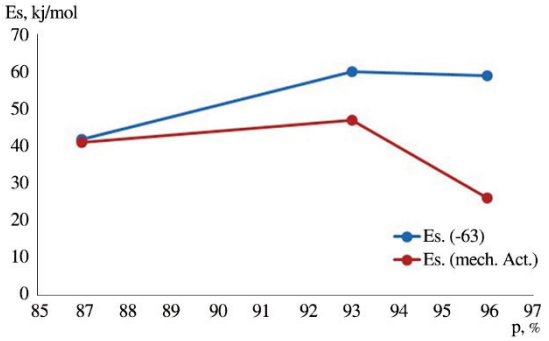

Fig. 3. Calculations of the change in activation energies (kJ/mol) of the sintering process of Fe-Cu-Sn-Ni powders in relation to the degree of densification of the samples.

Fig. 3 shows the calculated changes in the activation energies of the sintering process of Fe-Cu-Sn-Ni powders in relation to the degree of compaction of the samples. Data analysis shows that during hot pressing at a pressure of P=20 MPa at the first stage of sintering, which is mainly controlled by the viscous flow of the solid body and is also facilitated by the pressure factor, the process proceeds at quite high speeds and is characterized by relatively low values of activation energies - 42 kJ/mol and 41 kJ/mol, respectively. At the late stage of sintering, the dynamic of the processes are mainly determined by the grain boundary diffusion and volume diffusion, which are characterized by high activation energy values, especially volume diffusion. At this stage, the same level of activation energy is maintained for activated powder, while for untreated powder it has become 60 kJ/mol. There is a significant difference in the kinetic characteristics of the final stage of the sintering process. When using untreated powders, the final stage of sintering is characterized by practically the same value of activation energy of 58 kJ/mol, while

when using activated powder, the value of activation energy is significantly reduced and reaches a minimum value of 25 kJ/mol. This is due to the fact that the process is practically completed for specific P-T-τ conditions. The nature of the obtained kinetic curves is in good agreement with the data obtained in similar works (Pouchly et al., 2016; Shao et al., 2008). The obtained results show that the activation of powders significantly stimulates the process and allows the prospect of obtaining composites with high performance under given P-T-τ thermodynamic conditions.

მასალათმცოდნეობა

Fe-Cu-Ni-Sn შენადნობის ცხელი დაწნეხვის პირობებში შეცხობისას საწყისი ფხვნილების მექანიკური აქტივაციის გავლენის შესწავლა შემკვრივების კინეტიკაზე

ნ. ლოლაძე*, ნ. ჩიხრაძე**, მ. ტაბატაძე*, მ. წეროძე*, ზ. ავალიშვილი*, ნ. წეროძე§

** საქართველოს ტექნიკური უნივერსიტეტი, ალმასებისა და კომპოზიციური მასალების სამეცნიერო ცენტრი, თბილისი, საქართველო*
*** აკადემიის წევრი, გ. წულუკიძის სახელობის სამთო ინსტიტუტი, თბილისი, საქართველო*
§ ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პ. მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, საქართველო

ნაშრომში განხილულია საწყისი ლითონური ფხვნილების მექანოლეგირების გავლენა ცხელი დაწნეხვის შეცხობის პროცესზე, სისტემაში Fe-Cu-Ni-Sn. მექანოლეგირების გავლენის დასადგენად Fe-Cu-Ni-Sn ნამზადებში შემკვრივების კინეტიკაზე მოხდა ხაზოვანი ჩაჯდომის სიდიდის განსაზღვრა. ერთ შემთხვევაში საწყისი ფხვნილი წარმოდგენილი იყო ცალკეული Cu, Fe, Sn და Ni კომპონენტების სახით, ხოლო მეორე შემთხვევაში – მექანიკური გააქტიურების შემდეგ გამოყენებულ იქნა იმავე ფხვნილების ნარევი. კინეტიკური მრუდების მიღებამ 600-800°C ტემპერატურის დიაპაზონში და P = 20 მპა-ში შესაძლებელი გახადა შემკვრივების სხვადასხვა ეტაპისთვის აქტივაციის ენერგიის განსაზღვრა: I-87%, II-93% და III-95-96%. გამოთვლილმა კინეტიკურმა მნიშვნელობებმა ($E_{აქტ}$) აჩვენა, რომ საწყისი ფხვნილების გააქტიურება ხელს უწყობს შეცხობის პროცესის ინტენსიფიკაციას და ($E_{აქტ}$)-ის შემცირებას, განსაკუთრებით, პროცესის ბოლო ეტაპებზე 58 კჯ/მოლ-დან 25კჯ/მოლ-მდე.

REFERENCES

An, K. J. (2011). Modeling of densification during hot pressing of Fe–Cu–Co–Ni–W–Sn powder mixture. *Materials Transactions, 52,* 6, 1334-1337.

Borowiecka-Jamrozek, J., & Lachowski, J**.** (2017). The effect of the properties of the metal matrix on the retention of a diamond particle. *Metallurgija, 56,* 83-86. https://hrcak.srce.hr/16889

Elyutin, V. P., Pavlov, Yu. A., Polyakov, V. P., & Sheboldaev, S. B. (1976). Vzaimodeistvie okislov metallov s uglerodom [Interaction of metal oxides with carbon]. Metallurgiia.

Hao-Jun Zhou, H., Huang, M.-C., Yang, H., Tao, H.-L., Yin, Y.-H., & Luo, F.-H. (2020). Densification kinetics and sintering behaviour of a Ti(C0.7N0.3)-WC-Mo2C–NbC-(Co,Ni) compact. *Journal of Alloys and Compounds,* 843, 156072. https://doi.org/10.1016/j.jallcom.2020.156072

Liyong, M., Ziyong, Z., Bao, M., & Min, W. (2021). Effect of pressure and temperature on densification in electric field-assisted sintering of Inconel 718 super alloy. *Materials,* 14, 25-46. https://doi.org/10.3390/ma14102546

Maistrenko, A. L., Ivanov, S. A., Pereyaslov, V. P., & Voloshin, M. N. (2000). Intensive electrosintering of diamond-containing composite materials. *Superhard Materials,* 5, 39-45.

Mechnik, V. A. (2014). Production of diamond–(Fe–Cu–Ni–Sn) composites with high wear resistance. *Powder Metallurgy and Metal Ceramics, 52*(9), 577-587.

Pouchly, V., Hruby, J., & Maca, K. (2016). A practical approach for the calculation of the activation energy of sintering. *Science of Sintering,* 48, 317-324.

Shao, W. Q., Chen, S. O., Li, D., Cao, H. S., Zhang, Y. C., & Zhang, S. S. (2008). Apparent activation energy for densification of α-Al_2O_3 powder at constant heating-rate sintering. *Bulletin of Materials Science, 31*(6), 903-906.

Tabatadze, M. (2023). *The influence of some chemical properties of the starting components on the formation of the structure of a composite material* [Master's thesis, 77 p.].

Zaitsev, A. A., Sidorenko, D. A., Levashov, E. A., Kurbatkina, V. V., Rupasov, S. I., Andreyev, V. A., & Sevast'yanov, P. V. (2012). Development and application of dispersion-hardened binder based on Cu–Ni–Fe–Sn alloy for cutting tools from superhard materials. *Superhard Materials,* 2, 75-88.

Received December, 2025