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SPECIFIC BEHAVIOUR OF Sn-9Zn LOW FUSION ALLOY USED AS MATERIAL FOR FILAMENT DEDICATED TO FDM PRINTING PROCESS

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Abstract: FDM printing process uses filaments made of polymers. The paper aims to analyze the behaviors of Sn-9Zn low fusion alloy as potential material for elaboration of metallic filaments for FDM process. Sn-9Zn has low melting point, which is below the maximum temperature reached by all common FDM printers. No alterations of the heater component of a printer are required when replace the polymeric filaments with Sn-9Zn filament. Different from ABS and PLA, Sn-9Zn is softer and has lower stiffness. Lower stiffness proved to involve difficulties in the transfer of the filament from the spool to the hot-end. Inside the hot-end the material is very fluid and, due to its transfer speed, the filament fills the heating chamber and the nozzle. That creates a resistance to the transfer process and the filament suffers deformation and even blockages. Specific correlation of the nozzle diameter with the heating temperature and the transfer speed was considered. Increasing of the nozzle diameter from 0.4 to 1.8 mm was necessary to maintain appropriate flow of the molten metal. Filament continued to experience deformations during transfer, but the transfer became possible.

Key words: low fusion metal, metallic filament, FDM printing process, stiffness, heating of filament, flowing of molten filament, metal deposition.

1. INTRODUCTION

FDM process is an additive technology process [1,2], a 3D printing process, which uses polymeric filaments [2-5] for the deposition of successive layers [2-6], in order to build specific shapes and volumes [2,4,7,8]. In specific applications, the physical and electrical and mechanical properties of the used polymers assure partially, only, the characteristics required for the built product [3-6]. For instance, polymers are electrical insulators [5] and they give no possibility to build components for electrical contacts [3,4]. Other applications request soft but elastic behaviour of the used material, and the deposited polymers by FDM printing process cannot fill such requirement [2-4]. To apply surfacing processes [9] in order to improve different characteristics is possible, but the entire fabrication becomes too expensive. Due to that, replacing the polymers with metals

is an option to consider, when develop new versions of the FDM process [5].

Replacing the polymer filament with metal filament involves two possible interventions, or a mixing of the two: the modification of the 3D FDM printer in order to be able to melt the metallic filament, on one hand, or to use a low fusion metal, on the other hand. The first intervention is an expensive one, since the use of a low fusion metal is facile, cheap and improves different characteristics of the printed product. The second intervention is approached and several preliminary tests are presented in this paper.

2. MATERIALS AND METHODS

One of the lead-free low fusion alloy systems, successfully used by electronics as a soldering alloy, is the Sn-Zn system. Both Sn and Zn have relatively low melting points as chemical

elements: Sn - 231.97 °C and Zn - 419.58 °C. The system knows the eutectic composition of 85.1 % Sn, having its melting point at 198.5 °C. Analysing the Sn-Zn binary system [10,11], it can be observed that the near-eutectic alloys, in a range of ± 3 %Zn, the alloys maintain their melting point below 220 °C. That means that exists a domain of alloys possible to be used in FDM 3D printing process, without any change of the heating system [14,19].

The alloy Sn-9Zn is one of the most used Sn-Zn alloys by the electronic industry because its melting point is below 240 °C, which is a critical temperature for the components of a printed circuit board [12,19]. Due to that, it has been decided to be used as material for the FDM filament. A commercial solder was considered for experimental program and its melting point has been determined by using differential thermal analysis test (DTA) during heating. Based on previous expertise [6] the test has been performed with common heating rate of 10°C/min, and the obtained melting temperature was 200.9 °C (figure 1). That means that the impurities contained by the solder increased the melting temperature with 1 °C. Analysing the curve, it can be observed that, during the applied heating for testing, the material presented an endothermic melting (range: 198.9-213.6°C), according to figure 1.

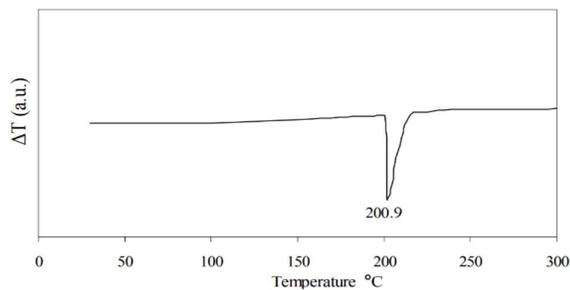


Fig. 1. The DSC test indication for the melting point of Sn-9Zn

The melting was initiated very fast, and the entire melting happened in 1 °C, only. Different from that fast behaviour, the consumption of heat continued for about other 13 °C, which means a real large range of temperatures and time. The vertical segment of curve reveals a high chemical homogeneity of the tested material, characteristic which is visible in the

XRD patterns. DTA was used to build the XRD patterns of Sn-9Zn tested sample, and the figure 2 shows the patterns and the marked peaks are Zn peaks. They were identified by converting the observed peak positions, $^{\circ}2\theta$, into $dhkl$ values using Bragg's Law.

The presence of Zn in very large range of $^{\circ}2\theta$ angle confirms the high homogeneity of the chemical composition.

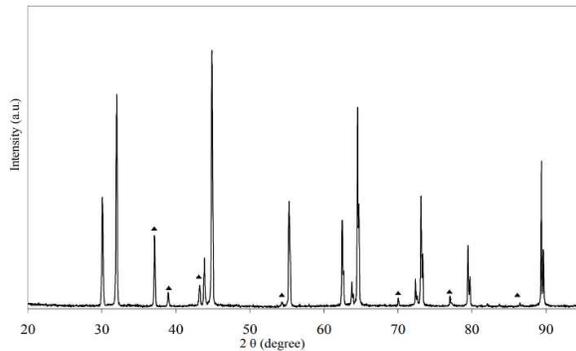


Fig. 2. XRD patterns of Sn-9Zn with the Zn peaks marked on

Taking account of the low value of the melting point (200.9 °C), it can be concluded that Sn-9Zn alloy can be used as material for FDM filament, because all commercial FDM 3D printers are able to assure heating up to 240°C, at least.

Another characteristic should be checked before the introducing of the new filament: the stiffness of the filament at its diameter. The stiffness of a low fusion metal is, usually, lower than the stiffness of the PLA and ABS polymers [3,10,11], which are often used in FDM process as filaments. Taking account of the specificity of the FDM process, in which the filament is transferred from a spool to the hot-end [2-4], the stiffness becomes an important factor of influence for the transfer of filament.

The stiffness depends on the elastic modulus of the material and on the transversal surface of the filament, while the elastic modulus depends on the temperature, as many researchers reported [19]. There are conventional methods used for the mechanical characterization of the alloys, and they include tensile and compressive tests, nanoindentation test, acoustic wave propagation test, and dynamic analysis. Most of the authors prefer to use nanoindentation to

determine different mechanical properties, but that test could return errors, because the values are specific to the existent individual phases, which is different from the values of the real bulk material. Using the traditional method, it was determined the elastic modulus, by direct tensile test applied at different temperatures: 20 – 40 – 60 – 80 – 100 °C (figure 3). The test has been performed by using universal testing machine returning the deformation curve (figure 4).

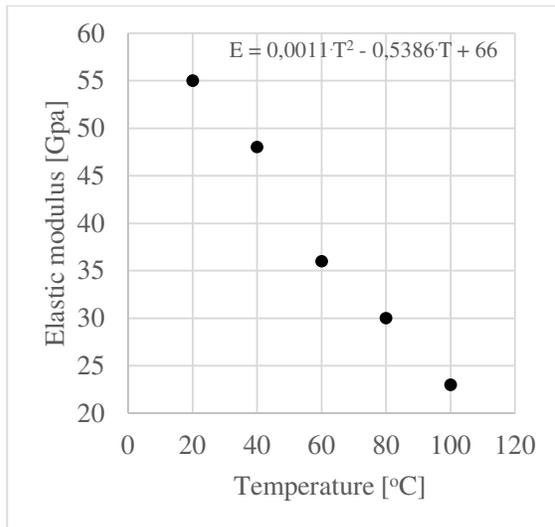


Fig. 3. Recorded values for the elastic modulus during the tensile test

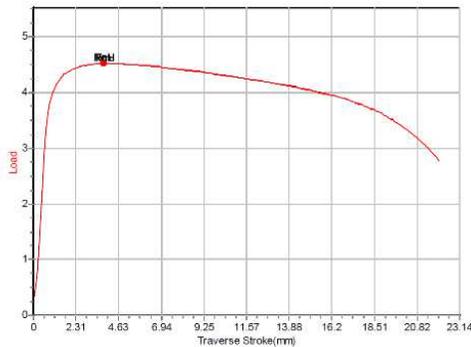


Fig. 4. Tensile test equipment and example of obtained stress-deformation curve

The material proved almost linear evolution of the elastic modulus, because the coefficient of the parabolic component is 0.001. Taking account of potential measurement errors, it can be accepted that the curve has linear evolution. In that case is simple to predict the behaviour of the material during heating before the extrusion

and to propose constructive measures in order to maintain minimal required elasticity of the filament up to high temperatures.

During the process, the filament is heated to melting temperature and is forced to decrease from 1.75 mm diameter (which is the most used value for PLA and ABS filaments [20]) to the diameter of the extrusion nozzle, which is 5-6 times lower. That produces a blockage of the filament and the low stiffness results in important deformations, and failures of the transfer process.

To analyse the evolution of the stiffness, and subsequently the behaviour of the filament, the heating process in time and space of the filament is required.

The differential equation of thermal conductivity, in the case of a solid cylinder (metallic filament), having radius r , when the temperature varies with time, is:

$$\frac{\delta T}{\delta t} = a \cdot \left(\frac{\delta^2 T}{\delta r^2} + \frac{1}{r} \cdot \frac{\delta T}{\delta r} \right) \quad (1)$$

in which $\frac{\delta T}{\delta t}$ is the variation of temperature with time and $\frac{\delta T}{\delta r}$ is the variation of temperature from the surface of the cylinder to the core.

The equation is known to have the particular of:

$$\frac{\delta T}{\delta t} = a \cdot e^{-2x} \cdot \frac{\delta^2 T}{\delta x^2} \quad (2)$$

when $r = e^x$. The new form results in:

$$\frac{\delta T}{\delta t} = \frac{a}{r^2} \cdot \frac{\delta^2 T}{\delta x^2} \quad (3)$$

Turning to finite differences, the equation (3) turns to:

$$\frac{\Delta_t T}{\Delta t} = \frac{a}{r^2} \cdot \frac{\Delta_x^2 T}{(\Delta x)^2} \quad (4)$$

which gives:

$$\Delta_t T = \frac{1}{r^2} \cdot \Delta_x^2 T \quad (5)$$

And that helps to determine the evolution of the temperature inside the filament. The geometrical model and the effect of the heating process are presented in figure 5.

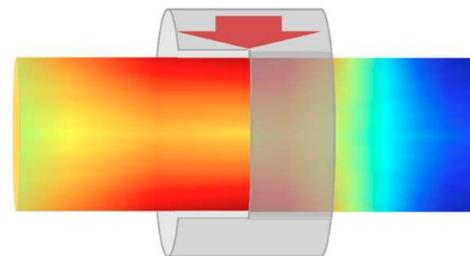


Fig. 5. Tensile test equipment

The calculated thermal field is shown in figure 6a and 6b with a difference of 0.5 s in time.

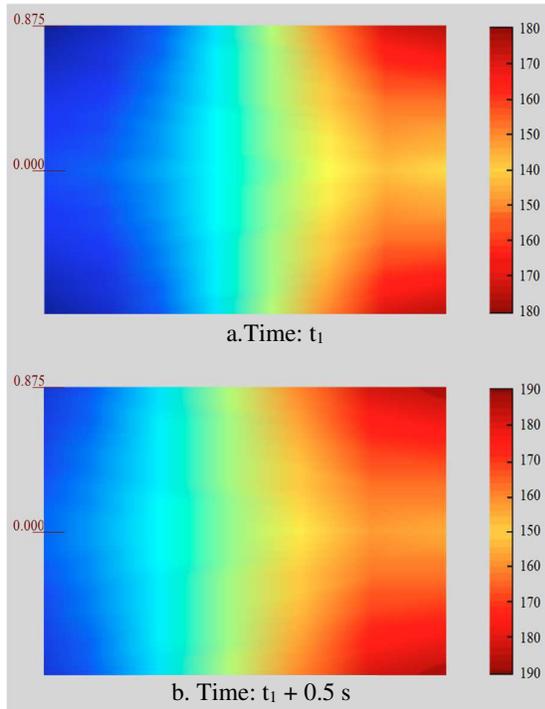


Fig. 6. Thermal field on the surface of the filament in a point at the middle of the heater and after 0.5s

Time t_1 is the moment for which a transverse section is in the middle of the heater and the temperature is 20 °C below the melting point. After 0.5 s, the same section increased in temperature with about 10 °C. Important is to observe that the core of the filament is 40 °C colder and, taking account of the filament transfer speed, it is confirmed that it remains a very thin core which is not reaching the melting point, when exit the heater. It is important to observe that the shape of the thermal field is maintained, and the core of the filament is kept at lower temperature than the surface. The melting of the core-line will be reached within the chamber before the extrusion nozzle, where a pool having 2.5 mm diameter (which is the inner diameter of the chamber) is created. From here the pool is constricted to the diameter of the extrusion nozzle, which usually is 0.3-0.4 mm (figure 7).

The constriction creates a resistance to the filament transfer and part of the molten metal

trends to return from the conical area of the nozzle, back to the heating area.

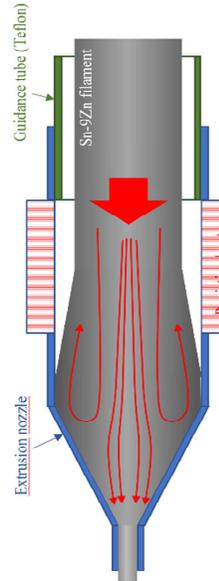
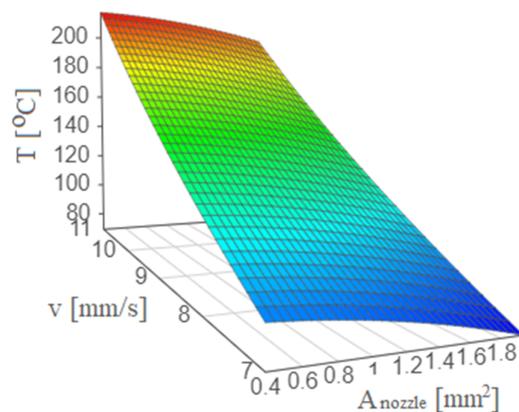
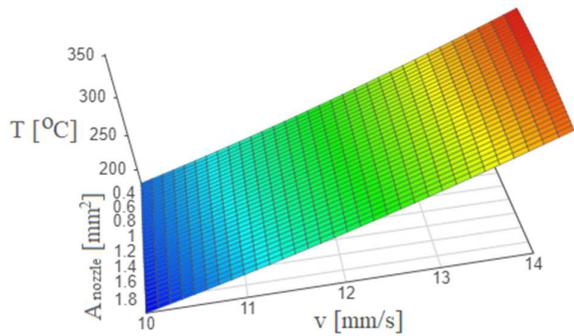


Fig. 7. Sketch of the hot-end used for experiments and the flowing of the molten volume of filament

Based on the experimental results, it has been concluded that a specific correlation of the extrusion nozzle diameter with the heating temperature and the speed of the filament transfer is required. Modifying the diameter of the nozzle in the range of 0.4-1.8 mm, and the transfer speed in two types of ranges, „normal” and „high productivity”, for temperatures applicable with a commercial FDM 3D printer, it was possible to establish a correlation in order to obtain appropriate behaviour of the molten metal inside the heater and extrusion nozzle. Fig. 8 a and b show the developed correlations.



a. A_{nozzle} : 0.4-1.8 mm, $v_{filament}$: 7-11 mm/s



b. A_{nozzle} : 0.4-1.8 mm, v_{filament} : 10-14 mm/s

Fig. 8. Empiric correlation of the parameters

4. CONCLUSION

FDM printing process uses polymers but the requirements regarding the mechanical and electrical characteristics of specific products involve the necessity to replace the polymers with metals. Sn-9Zn is metal used as solder in electronics, mainly, and its properties give possibility to be used as filament without modifying a common FDM 3D printer. Comparing to polymeric filaments, Sn-9Zn has lower stiffness. Lower stiffness and that involves difficulties in the transfer of filament. Inside the heating chamber and extrusion nozzle the material is very fluid and, due to its transfer speed, the filament fills the entire inner volume. Due to that the metal trends to flow back from nozzle to heater. To avoid or diminish the flowing back, a correct correlation between the nozzle diameter, the heating temperature, and the transfer speed should be respected. Best results, regarding the flow of the molten metal, were obtained for 1.8 mm nozzle diameter.

5. ACKNOWLEDGEMNT

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6. REFERENCES

- [1] Campbell I, Bourell D, Gibson I (2012) Additive manufacturing: rapid prototyping comes of age. *Rapid Prototyp J* 18:225–258

- [2] Monzón, M. D., et al., *Standardization in additive manufacturing: activities carried out by international organizations and projects*, *Int J Adv Manuf Technol* (2015) 76: 1111. <https://doi.org/10.1007/s00170-014-6334-1>
- [3] Durgun I., Ertan R., *Experimental investigation of FDM process for improvement of mechanical properties and production cost*, *Rapid Prototyping Journal* 20.3, 2014, pp. 228–235
- [4] Shahrubudin, N., Lee, T.C., Ramlan, R., *An Overview on 3D Printing Technology: Technological, Materials, and Applications*, *Procedia Manufacturing* 35 (2019) 1286–1296
- [5] Savu, I.D., Savu, S.V., Simion, D., Sîrbu, A.N., Ciornei, M., Rațiu, S.A., *PP in 3D Printing – Technical and Economic Aspects*, *Materiale Plastice*, 56, no. 4, 2019, pp 931-936
- [6] Turner B. N., Strong R., Gold S. A., *A review of melt extrusion additive manufacturing processes: I. Process design and modeling*, *Rapid Prototyping Journal* 20.3, 2014, pp. 192–204
- [7] Berger A., Sharon Y., Ashkenazi D., Stern A., *Test artifact for additive manufacturing technology: FDM and SLM preliminary results*, *The Annals of “Dunarea De Jos” University of Galati Fascicle XII, Welding Equipment and Technology* 27, 2016, pp. 29–37
- [8] Finnes, T., *High-Definition 3D Printing – Comparing SLA and FDM Printing Technologies*, *The Journal of Undergraduate Research: Vol. 13, Article 3*. Available at: <http://openprairie.sdstate.edu/jur/vol13/iss1/3>, 2015
- [9] Savu S. V., Savu I. D., Benga G. C., Ciupitu I., *Improving functionality of Ti₆Al₄V by laser technology surfacing*, *Optoelectronics and Advanced Materials, Rapid Communications*, 2016
- [10] Aindow, J., Yu, H., Bellinger, M.A., Aindow, M., *Eutectic Solidification in Zn-Sn Binary Alloys: An Experiment for High Schools*, *Microsc. Microanal.* 23 (Suppl 1), 2304-2305, 2017, doi:10.1017/S14319276 17012181
- [11] Okamoto, H., Schlesinger, M.E., Mueller, E.M. (Editors), *ASM Handbook Vol. 3: Alloy Phase Diagrams*, ISBN: 978-1-62708-070-5
- [12] Savu, S.V., Savu, I.D., *Influence of the ultrasonic activation on the wetting process and on the Ag₃Sn needles evolution in the soldering process of copper by using Sn-Ag3.5% solder*, *U.P.B. Sci. Bull., Series B, Vol.81,Iss.2,2019*, ISSN1454-2331, 155-170
- [13] Savu, S.V., Savu, I.D., *Intermetallic behaviour in ultrasonic activation of the Sn-Ag-Cu solder during eutectic soldering process*, *U.P.B. Sci.*

- Bull., Series B, Vol. 80, Iss., 2, 2018, ISSN 1454-2331, 193-212
- [14] Gancarz, T., *Physical, Thermal, Mechanical Properties, and Microstructural Characterization of Sn-9Zn-XGa Alloys*, Metallurgical and materials transactions, vol. 46A, 2016
- [15] Hammam, M., Allah, F.S., Gouda, E.S., Gendy, Y.E., Aziz, H.A., *Structure and Properties of Sn9Zn Lead-Free Solder Alloy with Heat Treatment*, Engineering, 2010, 2, 172-178, 2010
- [16] Lee, J.E., Kim, K.S., Suganuma, K., Inoue, M., Izuta, G., *Thermal Properties and Phase Stability of Zn-Sn and Zn-In Alloys as High Temperature Lead-Free Solder*, Materials Transactions, Vol. 48, No. 3, 584-593, 2007
- [17] Ren, G., Collins, M.N., *Improved Reliability and Mechanical Performance of Ag Microalloyed Sn58Bi Solder Alloys*, Metals, 9, 462; 2019
- [18] Nguyen, T.T., Yu, D., Park, S.B., *Characterizing the Mechanical Properties of Actual SAC105, SAC305, and SAC405 Solder Joints by Digital Image Correlation*, Journal of Electronic Materials, Vol. 40, No. 6, 2011
- [19] Liao, Y., et.al., *Effect of Porosity and Crystallinity on 3D Printed PLA Properties*, Polymers 2019, 11(9), 1487
- [20] Tarnita, D., Berceanu, C., Tarnita, C., *The three-dimensional printing—a modern technology used for biomedical prototypes*, Materiale plastice, no.47, nr.3, pp 328-334, 2010,

Comportamentul specific al aliajului ușor fuzibil Sn-9Zn utilizat ca filament de depunere pentru procesele de imprimare FDM

Rezumat: Procesul de imprimare FDM utilizează filamente confecționate din anumite tipuri de polimeri. Lucrarea își propune să analizeze aspectele comportamentale ale aliajului ușor fuzibil Sn-9Zn, aliaj cu potențial în elaborarea de filamente metalice pentru procesul FDM. Sn-9Zn are un punct de topire scăzut, care este sub temperatura maximă atinsă de imprimantele FDM comerciale, astfel că, înlocuind filamentele polimerice cu un filament din Sn-9Zn nu este necesară nicio modificare a sistemului de încălzire al imprimantei. Diferit de ABS și PLA, Sn-9Zn are o rigiditate mai mică. Experimentările efectuate au demonstrat că rigiditatea mai mică a Sn-9Zn a produs o serie de dificultăți în transferul filamentului de la bobină către sistemul de încălzire. În interiorul sistemului de încălzire materialul este foarte fluid și, datorită vitezei sale de transfer, filamentul umple camera de încălzire și duza de extrudare. Acest fenomen creează o rezistență la procesul de transfer al filamentului, iar filamentul suferă deformări și chiar blocaje. În urma observațiilor efectuate s-a concluzionat că este necesară o corelare specifică a trei parametri: diametrul duzei, temperatura de încălzire și viteza de transfer. Pentru a menține fluxul adecvat de metal topit a fost necesară creșterea diametrului duzei de la 0,3 la 1,0 mm. Filamentul a continuat să experimenteze deformări în timpul transferului, dar transferul a devenit posibil.

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