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Microstructural Aspects of Fatigue Life of Sn-Zn Lead-free Solders with 1% of Ag Addition

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Abstract

The article presents the study results of Sn-Zn lead-free solders with the various Zn content. The results concern the hypoeutectic, eutectic and hypereutectic alloys containing respectively 4.5% Zn, 9% Zn and 13.5% Zn. Moreover, these alloys contain the constant Ag (1%) addition. The aim of the study was to determine the microstructural conditionings of their fatigue life. In particular it was focused on answer the question what meaning can be assigned to the Ag addition in the chemical composition of binary Sn-Zn alloys. The research includes a qualitative and quantitative assessments of the alloy microstructures, that have been carried out in the field of light microscopy (LM). In order to determine some geometrical parameters of the microstructure of alloys the combinatorial method based on the phase quanta theory was applied. Moreover, for the identification necessities the chemical analyses in the micro-areas by SEM/EDS technics were also performed. Based on the SEM/EDS results the phases and intermetallic compounds existing in the examined lead-free solders were identified. The mechanical characteristics were determined by means of the modified low cycle test (MLCF). Based on this method and on the results obtained every time from only one sample the dozen of essential mechanical parameters were evaluated. The research results were the basis of analyzes concerning the effects of microstructural geometrical parameters of lead-free alloys studied on their fatigue life at ambient temperature.

Key words: Lead-free solders, Microstructure, Mechanical properties

1. Introduction

The paper presents the microstructure conditionings of the fatigue life of lead-free Sn-Zn solder alloys with differing Zn content in alloy and constant 1% Ag addition.

Sn-Zn lead-free alloys are considered attractive for solder joint applications because they can replace conventional eutectic solder Sn-Pb without the need to increase soldering temperatures [1].

However, these alloys show a low resistance to oxidation and are characterized by high embrittlement [1]. Various additives such as rare earth metals, Bi, Ag, Al, Ga, In, Cr, Cu, Sb, Ni, Ge are added to these alloys to obtain better utility characteristics. These additions can improve wettability, mechanical properties, oxidation resistance and creep resistance [1].

Much attention is paid to the melting point of alloys, which determines the maximum and minimum of system operating temperature at which the components should survive [1].

Results of the DSC curves in Sn-9Zn-xAg alloys indicate the unequivocal effect of Ag addition on the solidus temperature of these alloys [1]. At the same time, the addition of Ag to the eutectic SnZn9 alloy, depending on the size of the additive, improves the specific properties of the alloy.

The content for example, of the 0. 3% Ag in the alloy allows to obtain the smallest angle of wetting, the content of the 2.0% Ag results in an increase in the strength of the solder connections, and content of 3.0% Ag allows to achieve the improvement of wettability, resistance to oxidation and extension of the wetting time [2].

These effects are mainly related to the formation of Ag_3Zn, $AgZn_3$, Ag_5Zn_8 intermetallic compounds. Stoichiometric form of those depend on the amount of Ag additions respectively 2% Ag or 3% Ag to the eutectic SnZn9 alloy [2].

Microstructural characteristics and their effect on the strength properties of the eutectic Sn-Zn alloy with different Ag content were also analyzed in [3]. Based on the results obtained, the authors concluded that the main effects of Ag additives were lowering strength and increasing the ductility of the alloy. It was ascertained that this was due to differences in the morphology and distribution of the secondary phases. It has also been found that microstructure modifiable due to rapid solidification results in better strength properties.

This article, as mentioned, is related to the structural conditionings of fatigue life of lead-free Sn-Zn solder alloys with differentiated Zn content and constant 1% of Ag additive to the chemical composition of the tested alloys.

Up to now, in the range of previous studies the SnZn4.5, SnZn9, SnZn13.5 alloys as cast [4] and the same alloys also as cast but containing 1% Cu were analyzed from their fatigue life view point [5].

As a result of the research carried out, defined regularities and microstructural causes of the existing differences in mechanical characteristics have been identified and they have been presented in detail [4, 5].

Therefore, it was considered that this study direction should be continue for the other chemical compositions of lead-free solder alloys.

According to the authors opinion, it should be underlined that up to now realized studies and planned in the future analogous test cycles for the other chemical composition are based on two original research methods.

In the field of mechanical research, the authors use a modified low cycle fatigue method hereinafter referred to as MLCF and in the metallographic studies a combinatorial method based on the phase quanta theory. The both methods present a different approach than commonly used. Their advantages have already been described in detail in [6, 7].

2. Materials

The SnZn alloys with varying zinc contents of 4.5%, 9% and 13.5%, respectively, in each case with an addition of 1% Ag were subjected to examination. These alloys were gravity cast, thus obtaining ready strength specimens.

It should be emphasized that 99.9% pure metals were used to obtain the ready casts. The procedure is described in detail in [4].

In order to eliminate the influence of possible microstructural heterogeneities on the interpretation concerning the interrelations between microstructure and the mechanical characteristics of alloys, the samples required for microstructural testing were taken from the handle parts of individual strength samples.

3. Microstructure of examined alloys

In order to determine the microstructures of the investigated alloys and to assess their possible variations, qualitative microscopic assessment in light microscopy (LM) field was performed, quantitative metallographic studies to determine the geometric parameters of the microstructure were conducted as well as quantitative chemical analyzes in micro areas by SEM/EDS were carried out.

The determination whether and if so which microstructural factors play an important role in the fatigue life of the tested materials was the aim of this part of the research.

The results of conducted observations in the field of the LM are shown in Fig. 1-3.

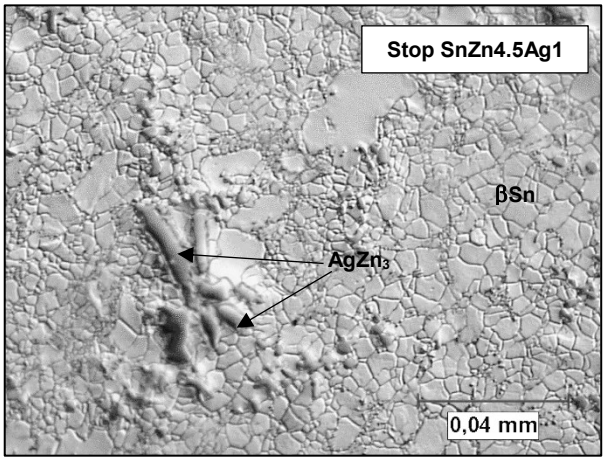


Fig. 1. Microstructure lead-free SnZn4.5Ag1 solder alloy as cast

It has been found that depending on the Zn content in the tested alloys their microstructure shows some variation.

In the case of hypoeutectic SnZn4.5 alloy containing 1% Ag, is visible the βSn solid solution in alloy microstructure as well as a small amounts of precipitates (Fig. 1), which were identified by the SEM/EDS method (Fig. 4) as the AgZn3 intermetallic compound.

The shapes of these precipitates are different because they can be seen as elongated or as of practically spherical form.

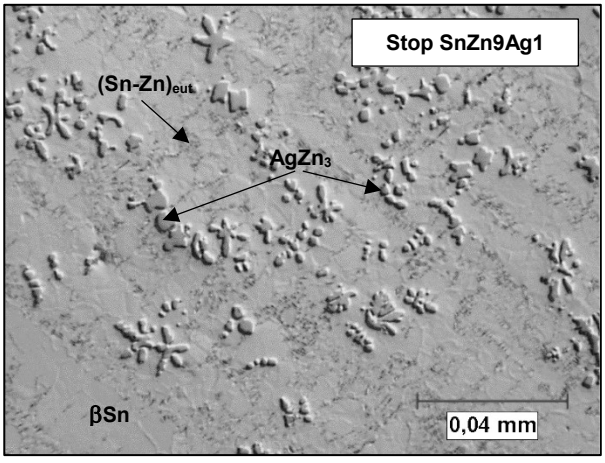


Fig. 2. Microstructure lead-free SnZn9Ag1 solder alloy as cast

Whereas, with larger Zn contents of 9% and 13.5% in alloys, their microstructure, besides βSn solid solution, contains also the interdendritic eutectic areas (Sn + Zn), which are however very fine (Fig. 2, 3).

Moreover, considerably larger amounts of $AgZn_3$ precipitates (Fig. 2, 3) are observed in these alloys if to compare them to the hypoeutectic alloy.

At the same time, the alloy with the highest Zn content of 13.5% contains the largest $AgZn_3$ precipitates (Fig. 3).

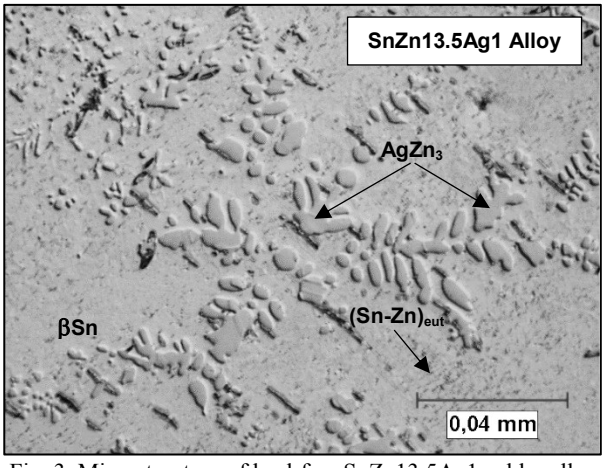
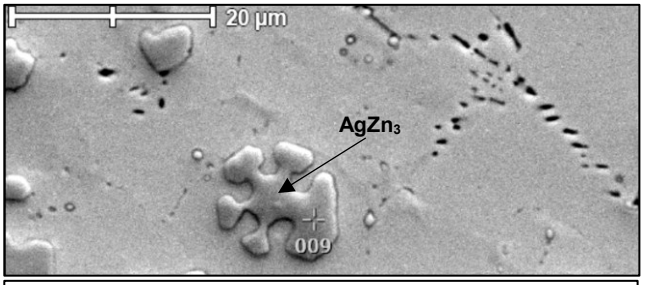
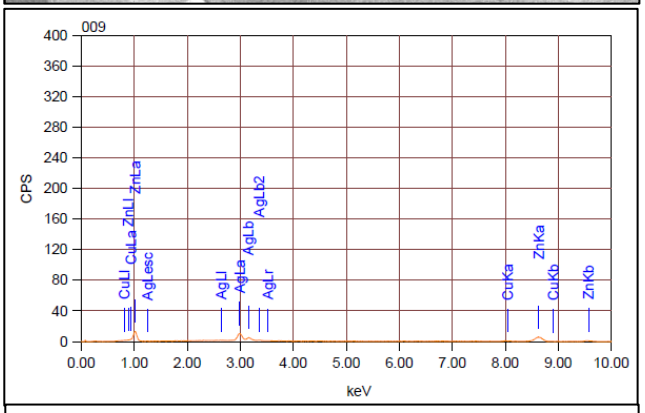


Fig. 3. Microstructure of lead-free SnZn13.5Ag1 solder alloy as cast

As already mentioned, the occurrence of $AgZn_3$ precipitates has been confirmed by the quantitative chemical analysis in micro-areas using SEM/EDS technique.





ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.3648

Element	(keV)	mass %	Error %	At %
Cu K	8.040	3.04	0.69	3.63
Zn K	8.630	61.58	0.88	71.48
Ag L	2.983	35.38	0.33	24.88
Total		100.00		100.00

Fig. 4. Results of chemical analysis performed in micro-areas by SEM/EDS method

In order to determine how much differences observed affect the mechanical characteristics of the tested alloys, quantitative metallographic studies were performed.

Due to the fact that tested eutectic and hypereutectic alloys contain very fine and regular distributed (Sn-Zn) eutectic areas and because in their microstructure cannot be seen the needle-like Zn-rich precipitates, it was recognized that the content and morphology of $AgZn_3$ precipitates play an important role in the mechanical behavior of the alloys studied.

Therefore, the geometric parameters of $AgZn_3$ precipitates such as volume fraction (V_V [%]), number of precipitations per 1mm^2 of metallographic cross section (N_A [1/mm^2]), mean size of chord ([µm]) and number of chords per 1mm of the test line (N_L [1/mm]) as a parameter necessary to determine the distribution of precipitates (λ [µm]) were determined. Quantitative metallographic studies were carried out using the combinatorial method [7], based on the phase quanta theory.

The idea of the method and the way of determining the geometrical parameters of the microstructure is presented in detail in [7].

In this method, only the estimators of volume fraction (V_V) and relative area (N_L) of the specified phases/microstructure components are determined.

Then, based on these estimators and using the formulas included in [7], the geometric parameters of the microstructure for further analyzes and interpretations are calculated. The influence of geometric parameters of $AgZn_3$ precipitates on the obtained mechanical characteristics was analyzed.

The results of the quantitative studies are shown in the graphs (Fig. 5-8).

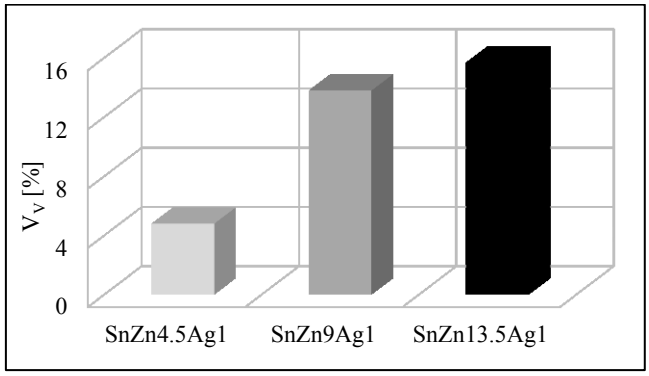


Fig. 5. Volume fraction (V_V) of $AgZn_3$ precipitates in: SnZn4.5Ag1, SnZn9Ag1 and SnZn13.5Ag1 alloys

Based on the quantitative analysis it was found that with the increase of the Zn content in the alloy only the parameter λ is significantly reduced (Fig. 8). On the other hand, the values of other geometric parameters such as V_V, N_A and l_{avg} increase with increasing Zn content in the alloy (Fig. 5-7).

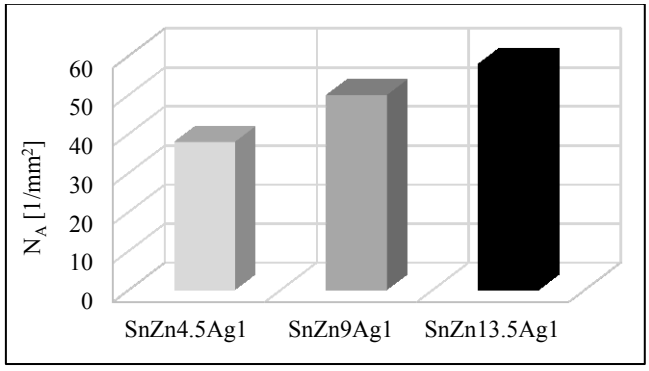


Fig. 6. Average number (N_A) of $AgZn_3$ precipitates in the alloys: SnZn4.5Ag1, SnZn9Ag1 and SnZn13.5Ag1

The results of both initial observations and quantitative analyzes indicate that the modification of the chemical composition of binary Sn-Zn alloys with the addition of 1% Ag to these alloys results in the removal of significant structural notch.

This is due to the formation of morphologically advantageous $AgZn_3$ precipitates of the intermetallic compound instead the needle-like Zn-rich precipitates.

Moreover, as already was noted, as the Zn content in the alloy increases, the free distance between the $AgZn_3$ precipitates decreases. With the simultaneous increase of their volume fraction (V_V), sizes (l_{avg}) and number precipitates (N_A) per 1mm^2 of metallographic cross section, it also means achieving greater microstructure homogeneity.

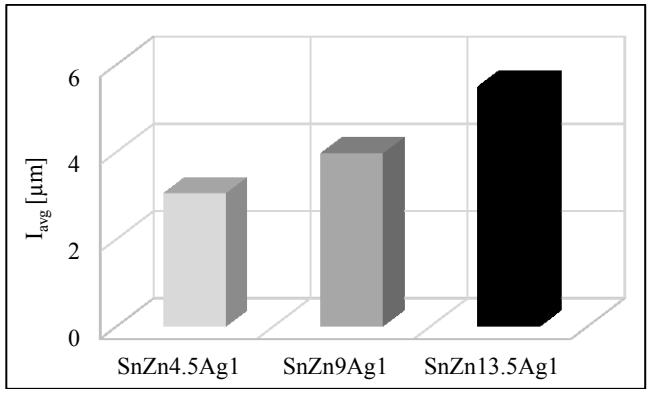


Fig. 7. Average chord (l_{avg}) of $AgZn_3$ precipitates in: SnZn4.5Ag1, SnZn9Ag1 and SnZn13.5Ag1 alloys

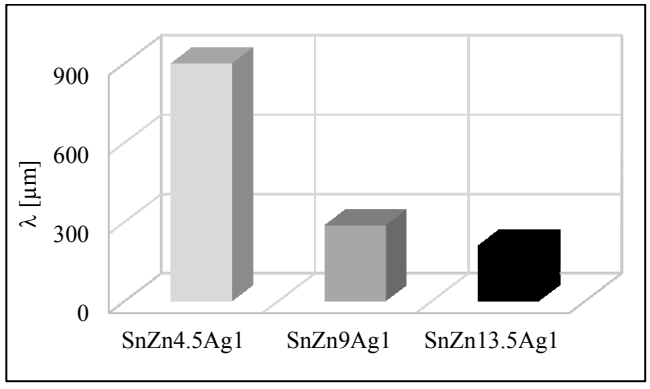


Fig. 8. Mean free path ($\lambda_{avg.}$) between $AgZn_3$ precipitates in: SnZn4.5Ag1, SnZn9Ag1, SnZn13.5Ag1

The similar microstructural effects were obtained in previous own studies concerning the same Sn-Zn binary alloys, but whose chemical composition was modified with the addition of 1% Cu [5].

4. Mechanical properties

The modified Low Cycle Fatigue Test (MLCF) was used to evaluate the fatigue life. Authors repeatedly demonstrated its advantages especially when the significant microstructural heterogeneities are observed. Based on the MLCF tests, several mechanical parameters, including the accommodation limit (Ra), can be estimated in a quick and relatively inexpensive way [7].

The results obtained by this method are consistent with those obtained using the classical LCF method.

Based on the representative results obtained for a variety of materials, such as metals and their alloys, an experimental curve for determination of fatigue strength has been developed [9].

From the material viewpoint, the developed curve has been verified for a number of ferrous and nonferrous metals and their alloys. Whereas, from a technological point of view, a positive verification was obtained for both metals obtained by metallurgical methods and foundry techniques. This is important

because in particular when using foundry techniques the significant heterogeneous microstructures can be observed.

For the purpose of this study, the MLCF method was considered to be very useful because both the mechanical parameters and the geometrical parameters of the microstructure could be obtained on the basis of measurements carried out on a single sample. This fact significantly eliminates the possible heterogeneity factor.

In the case of SnZn lead-free solders with different Zn and the constant 1% Ag addition using the MLCF method, the following mechanical parameters were determined: UTS-tensile strength, $R_{0.02}$- elastic limit, $R_{0,2}$-Yield Point, R_a-limit of accommodation, as a limit stress above which there is no longer stabilize the permanent deformation [6] and K'- stress coefficient under cyclically varying loads. In addition, the same assumptions as in [6] were used for determining the following mechanical parameters: b, c, n 'and K and ε_{max}. In mechanical tests, the stress was increased in successive measurement cycles.

An exemplary graph showing the dependence of the strain on the deformation recorded during one-sided cycling samples of SnZn4.5Ag1, SnZ9Ag1 and SnZn13.5Ag1 lead-free solders as cast is illustrated in Fig. 9.

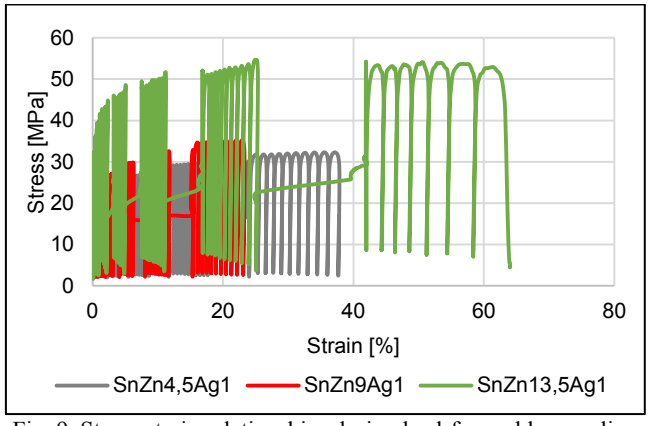


Fig. 9. Stress-strain relationships during lead-free solders cycling according to MLCF test

The presented course of the graphs clearly indicates that both the highest stress and the greatest deformability of the SnZn13.5Ag1 alloy are observed (Fig. 9).

On the other hand, for both the SnZn4.5Ag1 and eutectic SnZn9Ag1 alloys nearly twice the lower stress values (Fig. 9) were recorded and at the same time the lowest deformability of hypoeutectic SnZn4.5Ag1 alloy was identified (Fig. 9).

The values of the determined mechanical parameters are shown in the form of bar graphs (Fig. 10-12).

The summarized comparison between the determined mechanical parameters UTS, $R_{0.02}$, $R_{0.2}$, Z_{go}, K 'and R_a for the individual alloys is shown in Fig. 10.

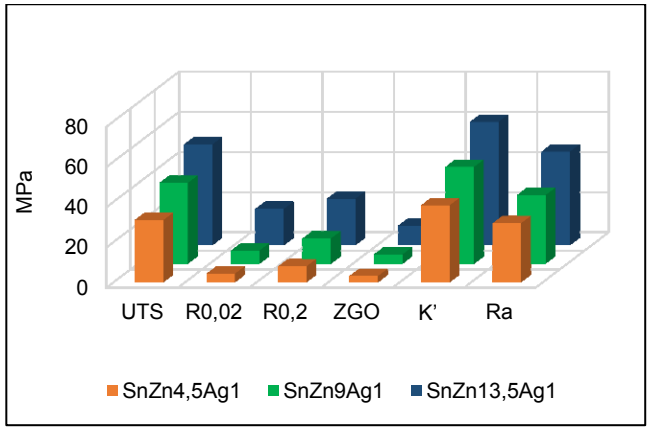


Fig. 10. Mechanical parameters of examined lead-free solders: UTS-ultimate tensile strength; $R_{0,02}$-stress limit; $R_{0,2}$-Yield Point; Z_{go}-assessed fatigue life; R_a-accomodation limit; K'-stress coefficient under cyclically varying loads

Based on the summarized comparison (Fig. 10), it can be stated that the best parameters were obtained for the hypereutectic SnZn13.5Ag1 alloy and the worst for the hypoeutectic SnZn4.5Ag1 alloy.

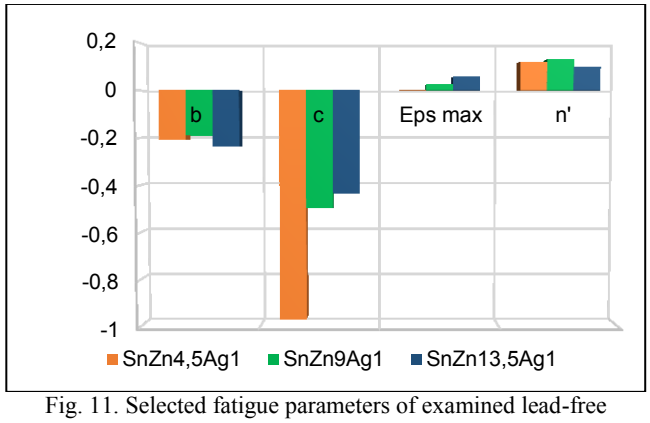


Fig. 11. Selected fatigue parameters of examined lead-free solders: b- Basquin's coefficient, c-fatigue ductility exponent, ε_{max} -maximum allowable strain; n'-strain hardening exponent under cyclically varying loads

For other mechanical parameters (Fig. 11), no uniform trend was obtained. It turned out that the highest absolute value of the c parameter was obtained for the hypoeutectic SnZn4.5Ag1 alloy (Fig. 11), which, according to Fig. 9, was also the most deformable at the same time as the highest stress was achieved.

The biggest absolute values of the parameters b and ε_{max} were obtained for the hypereutectic SnZn13.5Ag1 alloy and the highest value of the parameter n' was recorded for the eutectic alloy SnZn9Ag1 (Fig. 11).

The very high absolute value of the parameter c achieved for the hypoeutectic SnZn4.5Ag1 alloy demonstrates the presence of significant material weakness because the exponent c decreases generally with increased plasticity.

During fatigue tests, both the strengthening and weakening of the material may occur [8]. So in a given case there is a weakening effect.

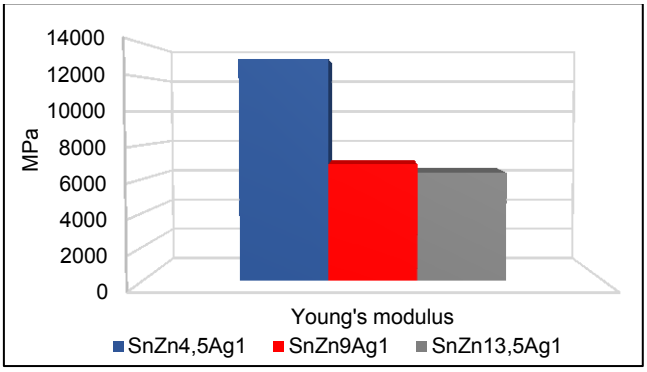


Fig. 12. Values of Young's modulus (E) for examined lead-free solders

On the basis of the tests, it was also found that the largest value of Young's modulus (E) was obtained for the hypoeutectic SnZn4.5Ag1 alloy and the lowest for the hypereutectic SnZn13.5Ag1 alloy (Fig. 12).

In conclusion, it can be stated that the favorable microstructural characteristics resulting from the addition of 1% Ag to binary Sn-Zn alloys had a positive effect on the determined mechanical characteristics of the tested alloys.

5. Conclusions

Based on the conducted studies on the microstructure in the LM and SEM fields and also performed mechanical tests using the modified MLCF low-cycle test, the following final conclusions were formulated:

- the best mechanical parameters determined on the basis of the MLCF method were obtained for the SnZn13.5Ag1 alloy,
- the constant Ag addition resulted in the formation of $AgZn_3$ precipitates morphologically beneficial instead of too large Zn-rich needle-like precipitates occurring at higher Zn content in binary SnZn alloys [4],
- with the addition of 1% Ag, a significant reduction in microstructure notches has been achieved, resulting in improved mechanical characteristics,
- the heat treatment of alloys should be applied, to further improve the mechanical characteristics,
- as a result of cycling the SnZnAg1 solders with different Zn content, there is a material weakening effect similar to that observed for SnZn alloys [4], or alloys containing 1% Cu additionally [5].
- the combinatorial method applied in quantitative microstructure assessment is very useful because of both ease of testing and the ability to increase the number of geometric parameters without the need for new measurements.
- the MLCF method is a fast and relatively inexpensive alternative when it comes to the rapid estimation of many mechanical parameters,
- the MLCF method is particularly useful for non-homogeneous materials, which are costly to produce both from the technological view point and preparing the strength specimens.

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