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ARCHIVES of FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 18
Issue 3/2018

31 – 36

DOI: 10.24425/123597

5/3

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Microstructure and Mechanical Characteristics of the Ternary SnZnAl Lead-Free Alloy

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Received 19.04.2018; accepted in revised form 15.06.2018

Abstract

The paper describes the studies of ternary SnZn9Al1.5 lead-free alloy from the viewpoint of its mechanical behavior as well as microstructure examined by the light and scanning electron microscopy. The authors focused their attention specifically on the fatigue parameters determined by the original modified low-cycle fatigue method (MLCF), which in a quick and economically justified way allows determination of a number of mechanical parameters based on the measurement data coming from one test sample only. The effect of the addition of 1.5% Al to the binary eutectic SnZn9 alloy on its microstructure and the obtained level of mechanical parameters was analyzed. The phases and intermetallic compounds occurring in the alloy were identified based on the chemical analysis carried out in micro-areas by the SEM/EDS technique. It was shown that the addition of 1.5% Al to the binary eutectic SnZn9 alloy resulted in a more favorable microstructure and consequently had a positive effect on the mechanical parameters of the alloy. Based on the conducted research, it was recommended to use a combinatorial method based on the phase quanta theory to quickly evaluate the microstructure and the original MLCF method to determine a number of mechanical parameters.

Keywords: Lead-free alloy, Microstructure, Mechanical properties

1. Introduction

Due to the well-known harmful effects of lead on the environment and human health, for several years studies have been focused on the possibility of introducing lead-free alloys in various fields of the economy. However, it should be remembered that in some material and construction solutions, the use of lead is still a must. This applies, first of all, to areas such as medicine, transport and aerospace.

Moreover, the applicable EU Directives require intensive efforts directed at the development of new chemical compositions of lead-free alloys characterized by satisfactory functional properties, also at high temperatures, necessary for individual material and structural solutions.

So far, studies of lead-free alloys have been intensively developed in the two subsequent international COST Actions 531 and MP062 financed by the EU.

The effects of these actions were published, among others, in the form of databases on chemical compositions, physico-chemical properties, mechanical properties, etc. [1-2].

A lot of attention is still dedicated to binary Sn-Zn lead-free alloys with the addition of a third component, including Al [3-5]. The Al addition plays a crucial role because in this way it is possible to improve such properties of lead-free binary alloys as their wettability and stress values, and reduce oxygen concentration on the surface of the alloy. All these factors play an important role in the production of soldered joints [3].

Moreover, according to [4], the Sn-Zn-Al solder exhibits the character of an ″inherent barrier″ when it is in contact with Cu. In the initial stage of liquid/solid interaction, aluminum present in the alloy tends to form a thin layer of $Al_{4.2}Cu_{3.2}Zn_{0.7}$ compound at the interface, while Cu-Zn compound is formed after long-term heating. Both compounds provide the barrier between Cu and Sn [4].

The authors of the research described in [4] also emphasize the fact that the formation of these compounds strengthens the interfacial bonding between solder and Cu substrate. Thus Sn-Zn-Al solder is the first kind of solder where Sn does not react during contact with Cu [4].

However, it should also be taken into account that the physical properties of eutectic Sn-Zn alloys with Al addition are not satisfactory [5].

Moreover, the authors of [5] found that the alloy with 91% Sn-6.5% Zn-2.5% Al has the lowest melting point. Based on the results of DTA tests and electrical resistance measurements as a function of temperature, it was determined that this composition is related with the eutectic point.

In all these cases where the melting point deterrmines the solder choice, this chemical composition may be a good option for the replacement of lead-containing solders [5].

In the Authors' opinion, another alloy composition, i.e. 25%Sn–65%Zn–10%Al, attracts attention mainly because of the low coefficient of thermal expansion, which may prove useful when temperature stability is important [5].

Many important characteristics of the ternary Al-Sn-Zn alloys known from detailed metallographic examinations have also been presented in [6].

Complex examination, including micro-hardness measurements, full chemical analysis (ICP-AES, OES) and X-ray micro-analysis by SEM and EDX were performed to determine the alloy composition and identify individual phases [6].

Due to the fact that the possibilities of replacing lead alloys with lead-free systems are still under verification, the authors of this article have decided to examine the effect of the addition of 1.5% Al to the eutectic Sn-Zn alloy on its microstructure and mechanical characteristics, including fatigue life.

It was also decided to compare present results with the results obtained previously for the binary SnZn9 [7] and SnZn9 alloy to which 1% of copper was added as a third component [8].

2. Test materials

The SnZnAl lead-free alloys containing 9% Zn and 1.5% Al were examined. The tested alloys were prepared from metals of 99.9% purity. Castings in the form of ready-for-test samples were made in the Foundry Research Institute in Cracow.

Metals were melted in a graphite crucible in an Ar atmosphere. Casting into graphite mold was performed at a temperature of about 50ºC above the liquidus line.

Next, fragments of grips of the cast samples for mechanical tests were used in the preparation of metallographic specimens for microstructure testing. In this way, each time, both mechanical properties and microstructure were examined on the same sample.

The described procedure was used to minimize the impact of possible material inhomogeneities on the test results.

The analyzes of the chemical composition were performed by X-ray microfluorescence method using the Niton XL3t XRF analyzer.

The obtained content of the basic components of the SnZn9Al1.5 alloy is confirmed in Table 1.

Table 1.
Content of the basic components in SnZn9Al1.5 alloy

Sample No.	Sn [%]	Zn [%]	Al [%]
1	87.6	9.1	1.6
2	87.5	9.1	1.9
3	87.9	9.0	1.6
4	88.0	9.1	1.5
5	87.9	9.0	1.5
6	87.8	9.0	1.9
7	87.7	9.0	1.7
8	87.7	9.0	1.9
9	88.1	9.0	1.7
10	87.0	9.0	2.1

The values compiled in Table 1 indicate the obtained stable chemical composition of the castings.

3. Microstructure examinations

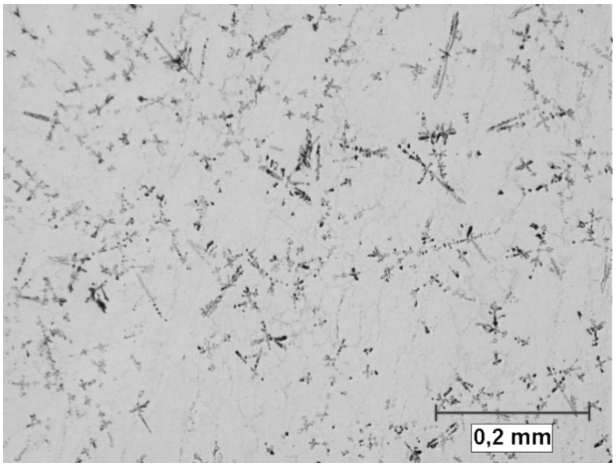
Microstructure assessment of SnZn9Al1.5 alloy was performed by both light microscopy (LM) and scanning electron microscopy (SEM). The results of microstructure examinations are shown in Figure 1.

The photographs should be treated only as an indicative classification of the microstructure type and quantitative interpretations absolutely should not be made on this basis.

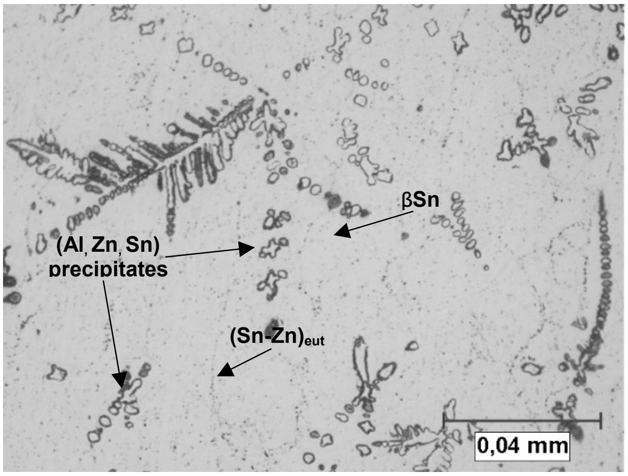
The photographs illustrate only that the microstructure of SnZn9Al1.5 alloy consists of eutectic Sn-Zn precipitates, primary grains of the solid solution βSn and (Al, Zn, Sn) precipitates of complex chemical composition. The microstructure identification was performed by SEM/EDS method.

It should also be pointed out that eutectic precipitates are very small and distributed in the interdendritic areas.

Moreover, it was noticed that (Al, Zn, Sn) precipitates are characterized by various forms (Fig. 1).



a



b

Fig. 1 Microstructure of as-cast SnZn9Al1.5 alloy: a) 100x, b) 500x

Additionally, a quantitative microstructure assessment was also carried out. Based on the observations performed by light microscopy, it has been concluded that the potential diversity of microstructure will result, first of all, from the morphological features of the (Al, Zn, Sn) precipitates.

Therefore, it was considered that the morphology of (Al, Zn, Sn) precipitates would play a crucial role in the mechanical behavior of the examined alloy and, consequently, it was decided to determine selected geometrical parameters of these precipitates.

Quantitative metallographic assessment was carried out using combinatorial method based on phase quanta theory. According to this theory, any microstructure can be described as an arrangement of the smallest measurable elements in the material matrix. In this case, the smallest measurable element of the microstructure (phase quantum) is the starting point for further quantitative analyses.

During measurement procedure the two basic estimators are determined, i.e. the estimator of volume fraction and the estimator of the relative area of microstructure elements.

Other geometrical parameters important in the researcher's opinion for the studied phenomena are determined from respective calculation formulas [9].

Based on the conducted qualitative observations, it was considered necessary to determine the following geometrical parameters of (Al, Zn, Sn) precipitates: volume fraction (V_V), estimator of relative area (N_L), mean chord (l_{avg}) and the average free distance between precipitates (λ).

Quantitative analyses were carried out on ten samples under the same measurement conditions. For each sample, 200 fields of view were analyzed at a magnification of 500x. In this way, the total area of metallographic specimens for which the analysis was carried out was equal to 5 mm^2.

The results of quantitative measurements are compared in Table 2. The presented data are mean values of the specified geometrical parameters shown separately for each sample.

In summary, the mean values of individual geometrical parameters are given for all tested samples (Table 2). The observed differences are also presented in respective diagrams (Figs. 2-4).

Table 2.
Selected geometrical parameters of (Al, Zn, Sn) precipitates in SnZn9Al1.5 alloy

Sample No.	V_V [%]	N_L [1/mm]	l_{avg} [μm]	λ [μm]
1	8.5	34.35	2	3
2	9.4	32.83	3	3
3	8.3	28.95	4	5
4	9.1	36.25	3	3
5	9.6	29.43	4	5
6	9.0	35.83	2	3
7	8.2	37.23	3	2
8	8.1	34.95	2	2
9	8.9	37.21	3	5
10	8.0	34.81	2	3
Mean value	8.7	34.18	3	3
St. Dev.	0.6	2.95	0.8	1

It should be emphasized that the volume fraction of the precipitates as well as their relative area are characterized by only small variations (Figs. 2 and 3).

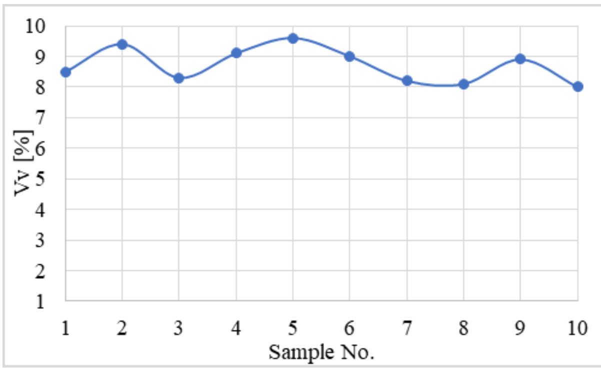


Fig. 2. Volume fraction (V_V) of (Al, Zn, Sn) precipitates in SnZn9Al1.5 alloy

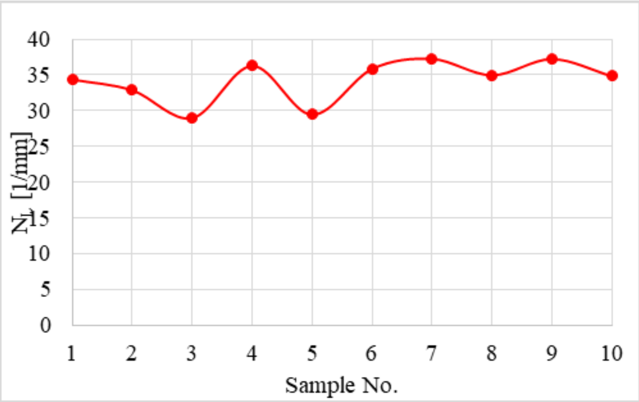


Fig. 3 Estimator of relative area (N_L) of (Al, Zn, Sn) precipitates in SnZn9Al1.5 alloy

On the other hand, the observed changes for both mean chord and mean free distance between precipitates are characterized by greater differences (Fig. 4).

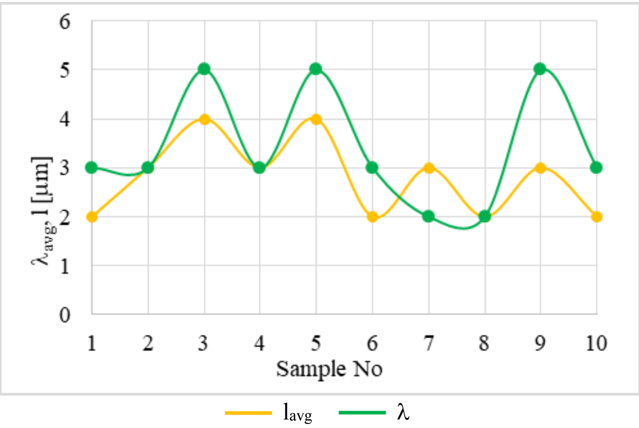


Fig. 4 Mean chord (l_{avg}) of (Al, Zn, Sn) precipitates and mean free distance (λ) between them in SnZn9Al1.5 alloy

To determine whether the observed microstructural differences can affect the mechanical behavior of the alloy, mechanical tests were also carried out.

4. Mechanical characteristics

Mechanical characteristics including fatigue parameters were determined by a modified low cycle fatigue method (MLCF). The method has been successfully verified for various materials, including heterogenous microstructures particularly characteristic of cast alloys [10].

Based on the MLCF procedure it is possible to estimate more than a dozen mechanical parameters in a quick, methodologically easy and economically justified way. At the same time, it should be clearly stated that each time the data concerning individual mechanical parameters come from a single sample.

The determination of mechanical characteristics also included the limit of accommodation (R_a). It is defined as a limit stress above which the stabilization of permanent deformations exists no longer [9].

On the other hand, the fatigue strength parameter under rotary-bending conditions (Z_{go}) was determined from an experimental graph (Fig. 5, [10]). The experimental curve presented in Figure 5 is a key element of the MLCF method.

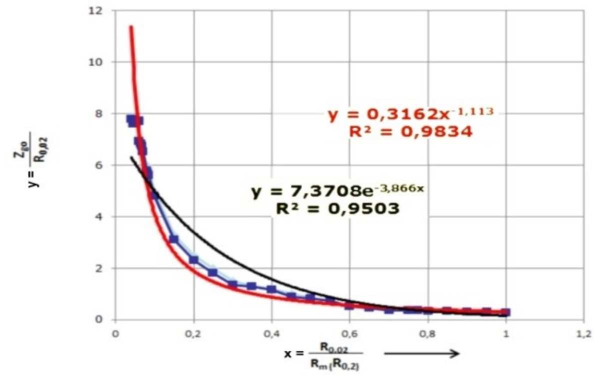


Fig. 5. Experimental curve for fatigue strength evaluation [10]: the blue line - combined experimental points, the red line - experimental curve fitting to the exponential relationship (better), the black line - the experimental curve fitting to the power dependence (worse)

The fatigue parameters such as b, c, n ', K' and ε_{max} were also determined by the MLCF method. As it was pointed out, both microstructural and mechanical tests were performed on the same sample. In this way it was possible to eliminate the effect of potential material heterogeneity.

A sample diagram of stress-strain relationship is shown in Figure 6. The course of deformation was recorded during unilateral cycling of SnZ9Al1.5 alloy.

The test was stress-controlled, increasing the stress value in subsequent groups of measurement cycles. Previous results obtained for SnZn9 [7], SnZn9Cu1 [8] alloys and for SnZn9Al1.5 alloy in this research show some differences in the influence of the third component in alloy on its deformability.

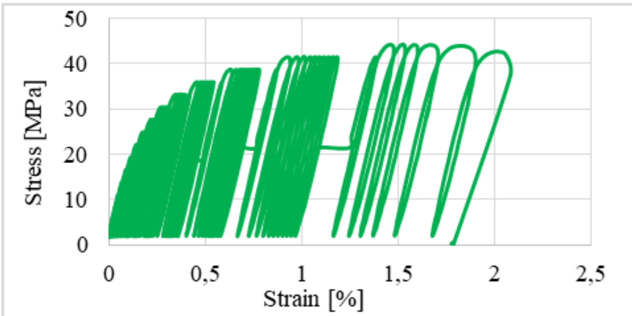


Fig. 6. Example of stress-strain diagram for unilateral cycling of SnZn9Al1.5 alloy

Significantly lower deformability was found in the SnZn9Al1.5 alloy but it was obtained at a higher stress value.

Conversely, in the case of the SnZn9Cu alloy, a much higher deformability was obtained with a lower stress value [8].

The results of tests carried out by the MLCF method are presented in Figures 7-9. The mechanical parameters UTS, $R_{0.02}$, $R_{0.2}$, Z_{go}, K' and R_a obtained for SnZn9Al1.5 alloy and also for SnZn9 [7] and SnZn9Cu1 [8] are shown in Figure 7.

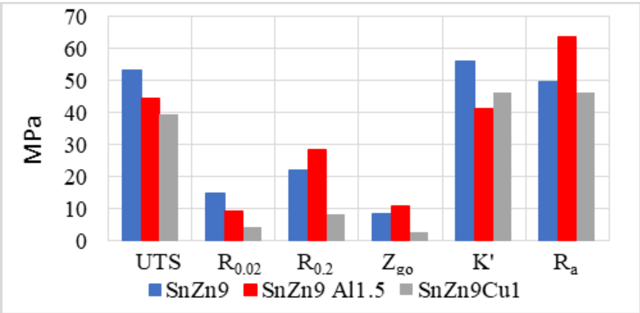


Fig. 7. Mechanical parameters: UTS, $R_{0.02}$ (elastic limit), $R_{0.2}$ (yield point), Z_{go} (assessed fatigue strength), K' (stress coefficient under cyclically varying loads) and R_a (accommodation limit) for SnZn9Al1.5, SnZn9 [7] and SnZn9Cu1 [8] alloys

Modified low cycle fatigue test (MLCF) [10] based on Manson-Coffin-Morrow dependence:

$$\sigma_a = K' (\varepsilon_p)^{n'} \quad (1)$$

$$\sigma_a = \sigma'_f (2N_f)^b \quad (2)$$

$$\varepsilon_p = \varepsilon'_f (2N_f)^c \quad (3)$$

allows you to specify the sizes b, c, n 'and K and ε_{max}, taking into account the following assumptions:

– disturbances of uniaxial stress field under compression, are eliminated by applying one-sided cycles (during tensile stress) in the fatigue test,
– dependence of permanent deformations, caused by the assumed small number of cycles (e.g. twenty cycles load - unloading) shows an analogous dependence on cycle amplitude, like deformation after sample fracture, the more so that the permanent deformation achieved after 20 cycles is already slightly changing, when enlarging number of cycles or does not change at all,
– the mechanical properties mentioned at the beginning of this chapter are determined using only one sample,
– straight courses according to equations (2) and (3), in a double logarithmic scale, are determined based on the positions of the points with coordinates: /ln 20, ln UTS/ and /ln($2N_f$), ln(Z_{go}/ in the case of the dependence (2) and /ln20, ln ε_f/ and /ln($2N_f$), ln ε_{Zgo}/ in the case of dependence (3) [10],
– the assessment of fatigue strength for rotational bending is carried out according to Figure 5.

The selected determined fatigue parameters: b - Basquin's coefficient (fatigue strength exponent), c - fatigue ductility exponent, ε_{max} - maximum allowable strain; n′ - strain hardening exponent under cyclically varying loads are presented in Figure 8.

Based on literature data [10] it can be concluded that parameters b and c obtained during the low-cycle fatigue test (LCF) should be within the following limits: b: from - 0.05 to - 0.15 and c: from - 0.5 to - 0.7.

Additionally, the fatigue strength exponent (b) decreases with a decrease in strength (its absolute value increases), while the fatigue deformation exponent decreases with the increasing plasticity of the material (its absolute value increases).

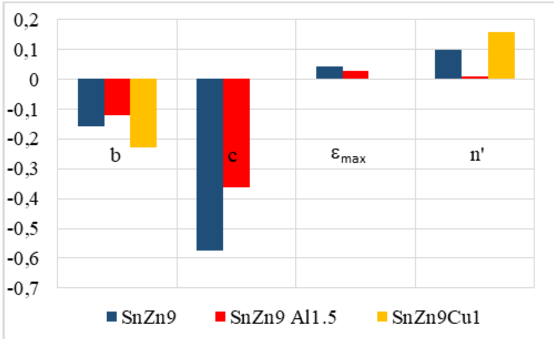


Fig. 8. Selected fatigue parameters: b- Basquin's coefficient (fatigue strength exponent), c-fatigue ductility exponent, ε_{max} - maximum allowable strain; n′-strain hardening exponent under cyclically varying loads for SnZn9Al1.5, SnZn9 [7] and SnZn9Cu1 [8] alloys

The comparison of fatigue characteristics obtained for the SnZn9 and SnZn9Cu1 alloys [7, 8] respectively with the results obtained for the ZnZn9Al1.5 alloy in the present research (Fig. 8) shows that the addition of 1.5% Al to SnZn9 alloy (SnZn9Al1.5 alloy) instead of 1% Cu (SnZn9Cu1 alloy) also contributes to obtaining better fatigue characteristics.

It was observed that for the SnZn9Al1.5 alloy the absolute value of parameter (b) is smaller than those obtained for the SnZn9 [7], SnZn9Cu1 [8] alloys, and thus, as already stated, the SnZn9Al1.5 alloy is characterized by higher fatigue strength (Zgo) (Fig. 7). Whereas, when analyzing the fatigue ductility exponent (c), its absolute value increases with the decrease of material plasticity, which means that also the strength properties of SnZn9Al1.5 alloy increase, but compared only to the SnZn9Cu1 alloy (Fig. 7) with the exception of stress coefficient under cyclically varying loads (K'). However. the maximum allowable strain ε_{max} is lower for the SnZn9Al1.5 alloy. The Young's modulus of the SnZn9Al1.5 alloy was also determined (Fig. 9) and its value was significantly higher than the value obtained for both SnZn9 and SnZn9Cu1 alloys [7, 8] respectively.

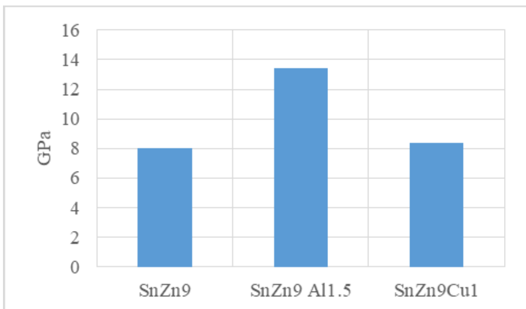


Fig. 9 Young's modulus (E) of SnZn9Al1.5, SnZn9 [7] and SnZn9Cu1 [8] alloys

In general, it can be concluded that the beneficial microstructural characteristics resulting from the addition of 1.5% Al to binary SnZn9 alloy composition instead of 1% Cu addition improve most of the determined mechanical characteristics.

It should also be noted that during fatigue tests, either the material strengthening effect or its weakening may be observed [11].

Previous studies of the effect of the addition of 1% Cu to the binary SnZn9 alloy have demonstrated the occurrence of a weakening effect [8], while current studies of the SnZn9 alloy with 1.5% Al indicate that the weakening effect is much less pronounced.

4. Conclusions

Based on the material examinations carried out, including microstructural and mechanical characteristics, the following conclusions can be formulated:

- castings from the SnZn9Al1.5 alloy examined in the form of ready-for-test samples are characterized by stable chemical composition,
- the eutectic precipitates are very small and distributed in the interdendritic areas,
- the addition of 1.5% Al to the binary SnZn9 alloy has resulted in the formation of (Al,Zn,Sn) precipitates instead of needle-like Zn-rich precipitates,
- the observed microstructural diversity characterized by the determined geometrical parameters had no adverse effect on the obtained mechanical characteristics, fatigue life included,
- compared with the results of previous tests carried out for the SnZn9Cu1 alloy [8], in the present case of the tested SnZn9Al1.5 alloy, a significant improvement was obtained in most of the determined mechanical characteristics due to the replacement of 1% Cu addition with 1.5% Al,
- further improvement of mechanical properties can be expected after alloy heat treatment,
- MLCF method can be considered a fast and relatively inexpensive way leading to the rapid estimation of many mechanical parameters,
- quantitative metallographic assessment carried out by the combinatorial method based on phase quanta theory may be treated as an easy way to determine many geometrical parameters of microstructure.

Acknowledgments

The article was in part based on research carried out within the framework of the EU COST ACTION MP0602 with financial support from the Ministry of Science and Higher Education of Poland.

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