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Comparative Studies of Microstructure and Fatigue Life of Selected Lead-free Alloys

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Abstract

Lead-free alloys containing various amounts of zinc (4.5%, 9%, 13%) and constant copper addition (1%) were discussed. The results of microstructure examinations carried out by light microscopy (qualitative and quantitative) and by SEM were presented. In the light microscopy, a combinatorial method was used for the quantitative evaluation of microstructure. In general, this method is based on the phase quanta theory according to which every microstructure can be treated as an arrangement of phases/structural components in the matrix material. Based on this method, selected geometrical parameters of the alloy microstructure were determined. SEM examinations were based on chemical analyses carried out in microregions by EDS technique. The aim of the analyses was to identify the intermetallic phases/compounds occurring in the examined alloys. In fatigue testing, a modified low cycle fatigue test method (MLCF) was used. Its undeniable advantage is the fact that each time, using one sample only, several mechanical parameters can be estimated. As a result of structure examinations, the effect of alloying elements on the formation of intermetallic phases and compounds identified in the examined lead-free alloys was determined. In turn, the results of mechanical tests showed the effect of intermetallic phases identified in the examined alloys on their fatigue life. Some concepts and advantages of the use of the combinatorial and MLCF methods in materials research were also presented.

Keywords: Lead-free alloys, Microstructure, Mechanical properties

1. Introduction

Following the EU Directives on the need to reduce industrial harmful materials including lead, numerous studies have been undertaken and are still continued to eliminate lead from everyday use. This is not always possible because in many solutions concerning both materials and structures the use of lead is still a must. It is particularly true in areas such as medicine, transportation, aerospace, etc. On the other hand, intensive actions could be taken in a wide range of materials used for, e.g., solder joints. Efforts were continued under successive European programs like EU COST 531, EU COST 0602, and within the framework of other similar initiatives. The aim of all these activities was to develop a composition of lead-free alloys, suitable for use in modern solder joints that meet specific performance expectations, including high temperature applications.

Until now, Sn-Ag-Cu alloys have been considered the best alternative, but their disadvantage is that they can not operate at high temperatures. In the area of lead-free alloys, the research works are continually developed in the form of various, systematically supplemented, databases [1-3] atlases of microstructures [4] and other publications, including data based on previous research carried out by the authors of this article and other researchers. In particular, studies have been focused on new chemical compositions of the alloys [5], and on the assessment of their microstructure, heat treatment parameters, mechanical properties [6] including fatigue life [7-9], corrosion characteristics, etc. Due to the fact that the problem of lead-free alloys is still very important, this article shows the results of studies based, on the one hand, on qualitative and quantitative metallographic examinations and, on the other hand, on mechanical properties.

In the authors' opinion, particular attention deserves the fact that from a methodological viewpoint the structural examinations were carried out using phase quanta theory [10], while the assessment of fatigue life was based on a modified low cycle fatigue test (MLCF) [11, 12].

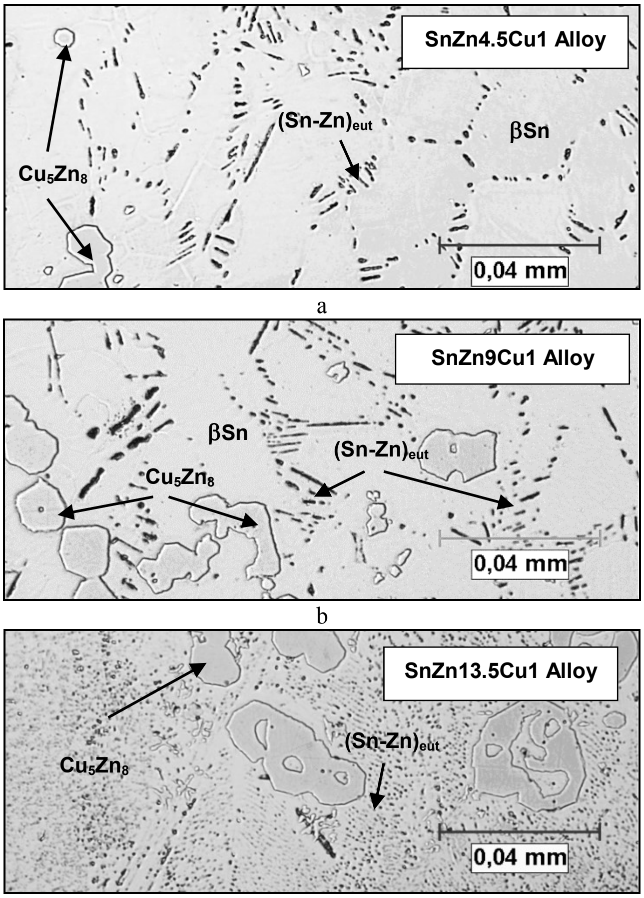
2. Test materials

The lead-free binary SnZn alloys containing 4.5%, 9% and 13.5% Zn were selected as a test material. Additionally, the chemical composition of the alloys was enriched with a constant addition of 1% Cu. As a next step, from the alloys, samples ready for mechanical tests were cast at the Foundry Research Institute in Cracow. It should be emphasized that the test alloys were prepared from metals of 99.9% purity. The metals were melted in a graphite crucible in an Ar atmosphere and then cast at a temperature exceeding by about 50°C the point of liquidus. Casting was performed into a graphite mold in such a way as to receive a ready-made samples for mechanical testing.

Then, from the shoulders of the samples, some fragments were cut off to prepare metallographic specimens and conduct qualitative and quantitative studies of the microstructure. The remaining parts of the samples were used for the mechanical tests. In order to minimize the effect of any microstructural heterogeneities, in each case the mechanical tests and studies of microstructure were carried out on the same sample.

3. Microstructure examinations

Microstructure examinations included qualitative and quantitative metallographic assessments conducted by light microscopy (LM). The results of initial microscopic observations are shown in Figure 1. The presented photographs are not representative in terms of quantity, they can only be treated as an illustration of the types of microstructure observed in the examined alloys. From the observations it follows that in alloy microstructure only the eutectic Sn-Zn precipitates of small and elongated forms, arranged in the interdendritic areas, can be identified (Fig. 1). In photographs, the primary grains of the βSn solid solution and precipitates of the Cu_5Zn_8 intermetallic compound of a nearly-spherical shape are also visible. They both appear in the photographs as brighter areas (Fig. 1).



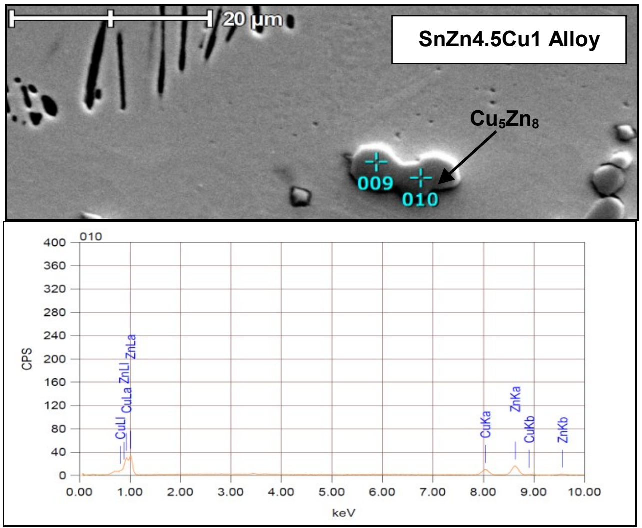
a

b

c

Fig. 1. As-cast microstructure of the examined lead-free alloys

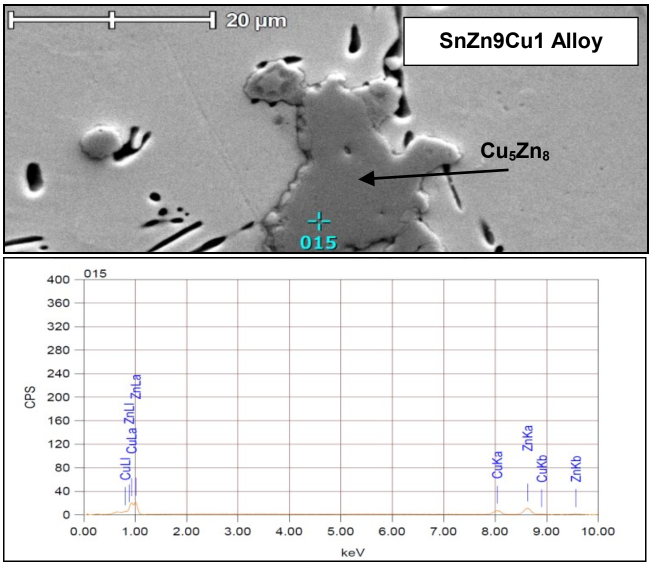
It has also been noticed that if the content of Zn in the alloy is 4.5%, the microstructure is hypoeutectic, the identified (Sn+Zn) eutectic precipitates are small in size and arranged in the interdendritic regions of βSn solid solution, while grains of this solid solution are relatively large (Fig. 1a). Moreover, due to the constant 1% Cu addition to the alloy chemical composition, zinc contained in the alloy forms with copper the Cu_5Zn_8 intermetallic compound (Fig. 1a). When the zinc content in the alloy is increased to 9%, and thereby a near-eutectic composition is achieved, the precipitates of (Sn+Zn) eutectic become much more numerous and occupy a much larger area on the metallographic cross-section. The number of the Cu_5Zn_8 intermetallic precipitates also increases, while their shape invariably remains close to the spherical one (Fig. 1b). The content of zinc in the alloy equal to 13.5% raises further the fraction of the Cu_5Zn_8 intermetallic precipitates. The remaining area of the metallographic cross-section is occupied by very small (Sn+Zn) eutectic precipitates (Fig. 1c). In this case, practically no grains of βSn solid solution are observed (Fig. 1c), contrary to the distinct areas visible for a lower Zn content in the alloy (Fig. 1a-b).



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 02992

Element	(keV)	mass %	Error %	At %
Cu K	8.040	31.72	0.35	32.34
Zn K	8.630	68.28	0.45	67.66
Total		100.00		100.00

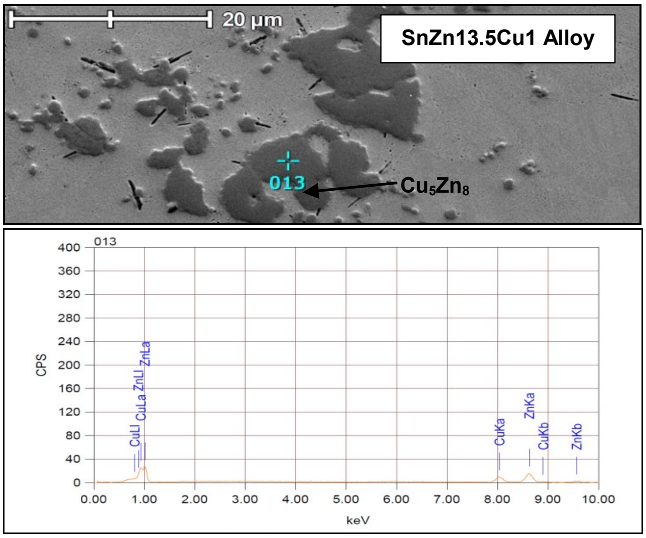
Fig. 2. The results of SEM/EDS chemical analysis carried out in microregions for SnZn4.5Cu1 alloy



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 02865

Element	(keV)	mass %	Error %	At %
Cu K	8.040	32.42	0.30	33.04
Zn K	8.630	67.58	0.38	66.96
Total		100.00		100.00

Fig. 3. The results of SEM/EDS chemical analysis carried out in microregions for SnZn9Cu1 alloy



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 02778

Element	(keV)	mass %	Error %	At %
Cu K	8.040	31.78	0.26	32.40
Zn K	8.630	68.22	0.33	67.60
Total		100.00		100.00

Fig. 4. The results of SEM/EDS chemical analysis carried out in microregions for SnZn13.5Cu1 alloy

The presence of the Cu_5Zn_8 intermetallic compound was confirmed by SEM/EDS analysis performed in microregions separately for each alloy (Figs. 2-4).

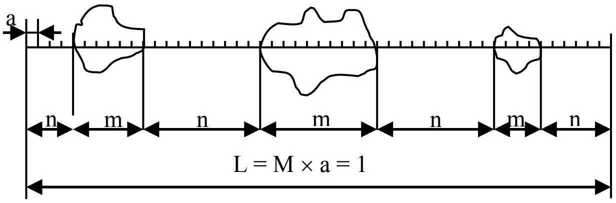
The evaluation of alloy microstructure was also based on quantitative metallographic examinations. The aim was to determine which of the microstructural geometrical parameters are important for the fatigue life of tested alloys.

The results of qualitative microscopic observations carried out by LM have led to the conclusion that the addition of 1% Cu causes large differences in the content and morphology of Cu_5Zn_8 precipitates. Thus, it has been considered that it is the morphology that will play a crucial role in the mechanical behavior of the examined alloys. For this reason, first of all, the geometrical parameters of the above mentioned intermetallic compound were determined.

It should also be emphasized that due to the addition of Cu to the chemical composition of alloys, practically total absence of the needle-like Zn-rich precipitates was achieved. This is very important remembering that these precipitates, acting as sharp microstructural notches, definitely deteriorate the mechanical properties.

Quantitative metallographic assessment was performed using combinatorial method [10] based on the phase quanta theory. According to this theory, in the quantitative metallographic analysis, the smallest measurable element of the microstructure can be treated as a phase quantum [10].

Moreover, based on this theory, every microstructure can be analyzed as an arrangement of these elements in the material matrix. Schematically, this approach to quantitative metallographic analysis is visualized in Fig. 5.



a - the measurable microstructure element (phase quantum)
m - the number of "a" phase / component elements on the M-element test line
n - the number of "a" matrix elements on the M-element test line
r - the number of segments (chords)

Fig. 5. Schematic diagram showing the principle of combinatorial method

When the combinatorial method is used in the quantitative evaluation of microstructure, the two basic estimators are determined, i.e. the estimator of volume fraction (V_V) and the estimator of the relative area (N_L) of microstructure components. Then, to determine the specific geometric parameters of microstructure, formulas [10] are used. In this study, the quantitative analysis was made for the Cu_5Zn_8 intermetallic precipitates.

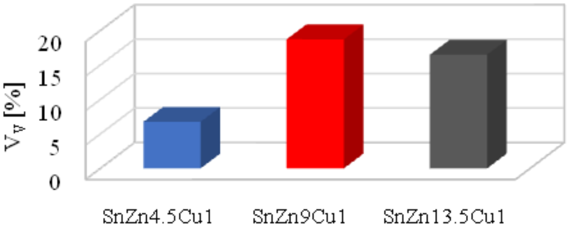


Fig. 6. Volume fraction (V_V) of Cu_5Zn_8 intermetallic precipitates in the examined alloys

Based on the obtained values of both estimators, using formulas given in [10] the volume fraction (V_V) of Cu_5Zn_8 precipitates, their number (N_A) per unit area of the cross-section, sizes defined by their mean chord (l_{avg}) and mean free distance between precipitates (λ_{avg}) were determined.

The results of quantitative metallographic analysis have confirmed the initial microscopic observations, since the volume fraction (V_V) of Cu_5Zn_8 precipitates was higher for higher Zn content in the examined SnZn9Cu1 and SnZn13.5Cu1 alloys (Fig. 6).

Moreover, for those alloys, the number of the precipitates (N_A- Fig. 7) per unit area of the cross-section as well as their sizes expressed by mean chord (l_{avg}- Fig. 8) also assumed higher values.

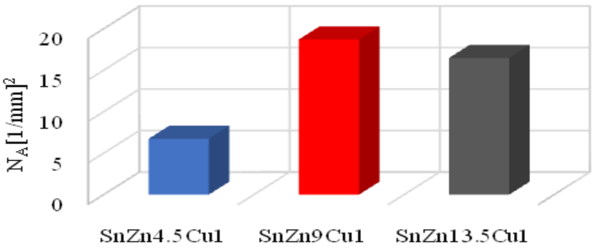


Fig. 7. Mean number (N_A) of Cu_5Zn_8 intermetallic precipitates per unit area of cross-section in the examined alloys

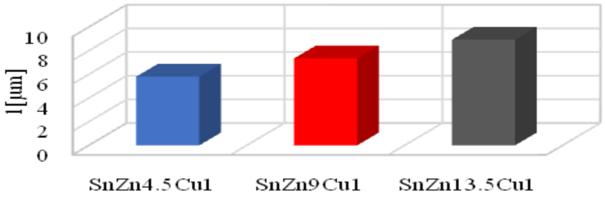


Fig. 8. Mean chord (l) of Cu_5Zn_8 intermetallic precipitates in the examined alloys

Simultaneously with the increasing number of Cu_5Zn_8 precipitates, the mean free distance (λ- Fig. 9) between them decreases.

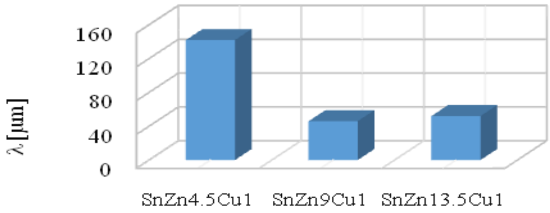


Fig. 9. Mean free distance (λ) between Cu_5Zn_8 intermetallic precipitates in the examined alloys

4. Mechanical characteristics

Mechanical characteristics, including fatigue parameters, were determined using a modified low cycle fatigue test (MLCF). The method has been successfully verified for a variety of materials including heterogenous microstructures and has already been described in detail as regards both its operating principle and measurement procedure [11, 12].

Here it should be underlined that MLCF is fast and economically viable tool to evaluate each time a dozen mechanical parameters based on the measurements made on a single sample only.

The limit of accommodation (R_a), defined as a limit stress above which the stabilization of permanent deformation occurs no longer [11, 12], was also assessed. The key parameter in MLCF method is the fatigue strength under rotary-bending conditions Z_{go}, determined from an experimental graph (Fig. 10, [11, 12]).

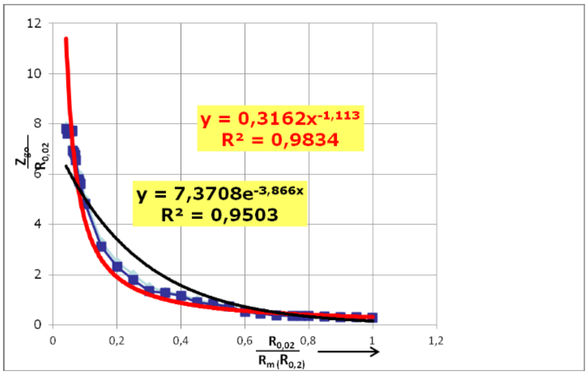


Fig. 10. Experimental curve for fatigue strength evaluation [11,12]

The parameters b, c, n', K and ε_{max} were determined based on the same methodological assumption which were adopted in [11, 12].

In order to eliminate the effect of possible microstructural heterogeneities, all the mechanical and microstructural parameters were determined on the same sample.

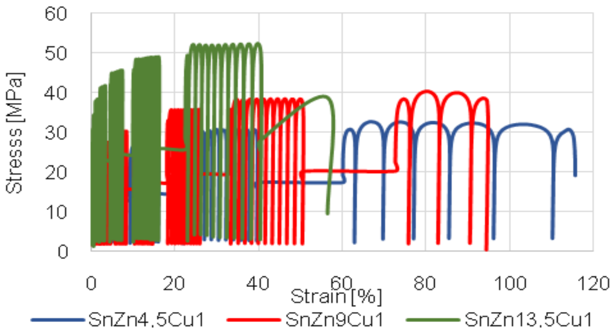


Fig. 11. A sample stress-strain diagram obtained during stress-controlled unilateral fatigue cycling of lead-free alloys

The sample stress-strain diagram in Figure 11 shows the deformation history recorded during unilateral fatigue cycling of lead-free SnZn4.5Cu1, SnZ9Cu1 and SnZn13.5Cu1 alloy samples in as-cast condition.

The stress, which controls the test, has been incremented in each consecutive set of measuring cycles.

The diagram presented in Figure 11 clearly indicates that the highest stress with some formability still preserved is achieved by the hypereutectic SnZn13.5Cu1 alloy.

The remaining alloys, i.e. the hypoeutectic SnZn4.5Cu1 and the eutectic SnZn9Cu1, show significantly higher deformability but at a much lower stress (Fig. 11). The results of the MLCF tests are presented in Figures 12-14.

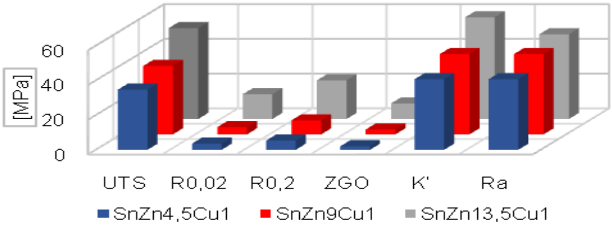


Fig. 12. Comparison of the following mechanical parameters: UTS (ultimate tensile strength), $R_{0.02}$ (elastic limit), $R_{0.2}$ (yield point), Z_{go} (assessed fatigue strength), K' (stress coefficient under cyclically varying loads) and R_a (accommodation limit) determined for the examined lead-free alloys.

Figure 12 shows a collective comparison of the mechanical parameters such as UTS, $R_{0.02}$, $R_{0.2}$, Z_{go}, K' and R_a determined for all the studied alloys. From the bars shown in Figure 10 it follows that the best results were obtained in the case of hypereutectic SnZn13.5Cu1 alloy. As regards other fatigue parameters, the results vary, the highest absolute values of c and ε_{max} parameters being obtained for hypereutectic SnZn13.5Cu1 alloy (Fig. 13). On the other hand, the highest absolute values of b and n' parameters were obtained for SnZn4.5Cu1 alloy and the lowest for SnZn13.5Cu1 alloy (Fig. 14).

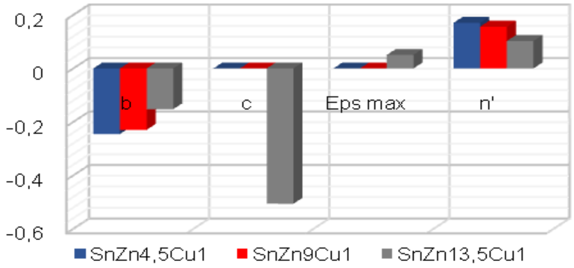


Fig. 13. Selected fatigue parameters of the examined lead-free alloys: b- Basquin's coefficient, c-fatigue ductility exponent, ε_{max} -maximum allowable strain; n′-strain hardening exponent under cyclically varying loads

Summarizing, the highest values of most of the mechanical parameters (Fig. 12, 13), including Young's modulus (E - Fig. 14) have been achieved in the case of hypereutectic alloy.

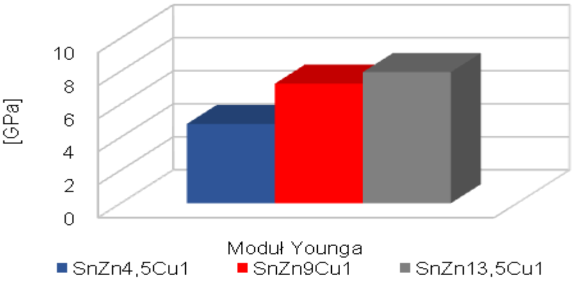


Fig. 14. Young's modulus (E) of the examined lead-free alloys

In general, it can be concluded that, as proved by both qualitative and quantitative methods, the beneficial microstructural characteristics resulting from 1% Cu addition to the binary Sn-Zn alloys composition have a positive impact on the determined mechanical characteristics of these alloys.

It should also be noted that during fatigue tests the examined material can undergo the effect of strengthening or weakening [12]. The results of fatigue testing indicate that, similar to the general tendency observed in binary Sn-Zn alloys, also the examined SnZnCu1 alloys undergo the weakening effect.

5. Conclusions

Based on the qualitative and quantitative microstructural examinations carried out by LM and SEM and on the fatigue testing by MLCF method, it is possible to formulate the following conclusions:

- the best mechanical parameters were obtained for hypereutectic SnZn13,5 alloy with 1% Cu addition introduced to its chemical composition,
- the constant addition of Cu has caused the formation of morphologically favorable Cu_5Zn_8 intermetallic precipitates replacing the too large needle-like Zn-rich precipitates occurring at a higher Zn content in binary alloys [12]. Consequently, due to the addition of 1% Cu, the microstructural notches have been significantly reduced, thus leading to an improvement of the mechanical properties,
- further improvement of the mechanical properties can be obtained with the alloy heat treatment,
- MLCF method can be considered as a fast and relatively inexpensive tool for the rapid estimation of numerous mechanical parameters.
- weakening of material is observed during fatigue cycling of SnZnCu1 alloys. The identified effect is similar to that found in binary SnZn alloys.

Acknowledgments

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