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ARCHIVES
of
FOUNDRY ENGINEERING

DOI: 10.1515/afe-2017-0024

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

DE GRUYTER OPEN

ISSN (2299-2944)
Volume 17
Issue 1/2017

131 – 136

Microstructural Aspects of Fatigue Parameters of Lead-Free Sn-Zn Solders with Various Zn Content

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Received 16.06.2016; accepted in revised form 29.09.2016

Abstract

The study includes the results of research conducted on selected lead-free binary solder alloys designed for operation at high temperatures. The results of qualitative and quantitative metallographic examinations of SnZn alloys with various Zn content are presented. The quantitative microstructure analysis was carried out using a combinatorial method based on phase quanta theory, per which any microstructure can be treated as an array of elements disposed in the matrix material. Fatigue tests were also performed using the capabilities of a modified version of the LCF method hereinafter referred to in short as MLCF, which is particularly useful in the estimation of mechanical parameters when there are difficulties in obtaining many samples normally required for the LCF test. The fatigue life of alloys was analyzed in the context of their microstructure. It has been shown that the mechanical properties are improved with the Zn content increasing in the alloy. However, the best properties were obtained in the alloy with a chemical composition close to the eutectic system, when the Zn-rich precipitates showed the most preferred morphological characteristics. At higher content of Zn, a strong structural notch was formed in the alloy because of the formation in the microstructure of a large amount of the needle-like Zn-rich precipitates deteriorating the mechanical characteristics. Thus, the results obtained during previous own studies, which in the field of mechanical testing were based on static tensile test only, have been confirmed. It is interesting to note that during fatigue testing, both significant strengthening and weakening of the examined material can be expected. The results of fatigue tests performed on SnZn alloys have proved that in this case the material was softened.

Keywords: Lead-free solders, Microstructure, Mechanical properties

1. Introduction

Great technical progress observed throughout the world, combined with continuous rapid growth, in addition to benefits, is also the source of many threats. Therefore, because of EU initiative, the 2002/95/EC WEE Directive (Waste from Electrical and Electronic Equipment) was developed. This legal regulation attempts to counteract the imminent risks by establishing a number of restrictions on the use of harmful materials in the industry. These also include lead which is still used in many material applications (aerospace, medical) and in the manufacture of solders. Therefore, in the years 2002-2007, research activities were undertaken under the EU COST 531 action covering several projects. The aim of this action was to study a large group of materials that could potentially replace alloys containing lead (mainly alloys included in the Sn-Pb system of nearly-eutectic chemical composition). Because of this action, a database on properties of alloys and combinations of these alloys was developed [1]. Moreover, a set of data was used to publish "Atlas of microstructures of lead-free solder alloys and solder/metal interfaces. Part 1: Optical Microscopy" [2]. Per the authors of the Atlas and its users, this publication is of great importance for both theoreticians and practitioners who want to introduce the newly developed alloys to industrial practice. At the same time, as a result of projects completed under the European COST Action 531 initiative, new alloys were proposed to replace the traditional lead-based solders. The best in the industrial soldering practice were considered the ternary Sn-Ag-Cu solder alloys. Unfortunately, these alloys are not suitable for high temperature application. Therefore, in the subsequent project executed under the next COST Action MP0602: "Advanced Solder Materials for High-Temperature Application - HISOLD", attention has been focused on the lead-free solders and their combinations designed for high temperature operation. Based on that research, the chemical compositions of binary, ternary and quaternary alloys were developed. The selected useful properties of those alloys were also examined and the results were disclosed in subsequent publications [e.g 3-5]. It should also be emphasized that progress in the studies of lead-free solders has resulted in the creation of a database of materials comprising lead-free solders and combinations thereof ([6]). This database is continuously updated with new alloys and alloy combinations, adding also their properties which are important for further practical applications.

Therefore, knowing that these problems are of vital importance all the time, it has been decided to disclose in this article the results of the qualitative and quantitative studies of the microstructure of selected lead-free solders and compare them with the results of fatigue life testing.

2. Test materials

Lead-free binary SnZn alloys with the zinc content of 4.5%, 9% and 13.5% were selected for examinations. The alloys were cast in the Foundry Research Institute in Cracow as ready-for-use tensile test pieces [3].

Pure metals of 99.9% purity were used as the starting alloy components. The alloys were manufactured by melting the starting metals in a graphite crucible in an argon atmosphere and then casting at a temperature exceeding by about 50°C the liquidus point into a graphite mould to obtain the ready-for-use tensile test pieces. From the grip section of the test pieces, the specimens for metallographic examinations were cut out and the remaining portion was used for testing of the mechanical properties. This sampling method was used to minimize the impact of possible microstructural heterogeneities.

3. Microstructure examinations

Microstructure examinations were carried out by the light microscopy, preceding the quantitative metallographic studies with preliminary qualitative research, as documented in Figure 1. It should be emphasized that the submitted photographs are of an illustrative nature only and as such cannot serve as a basis for quantitative interpretations. Rough observations have revealed that the microstructure of the examined alloys consisted of an Sn-Zn eutectic with primary precipitates of the solid β-Sn solution (bright areas) and the Zn-rich phase (dark areas).

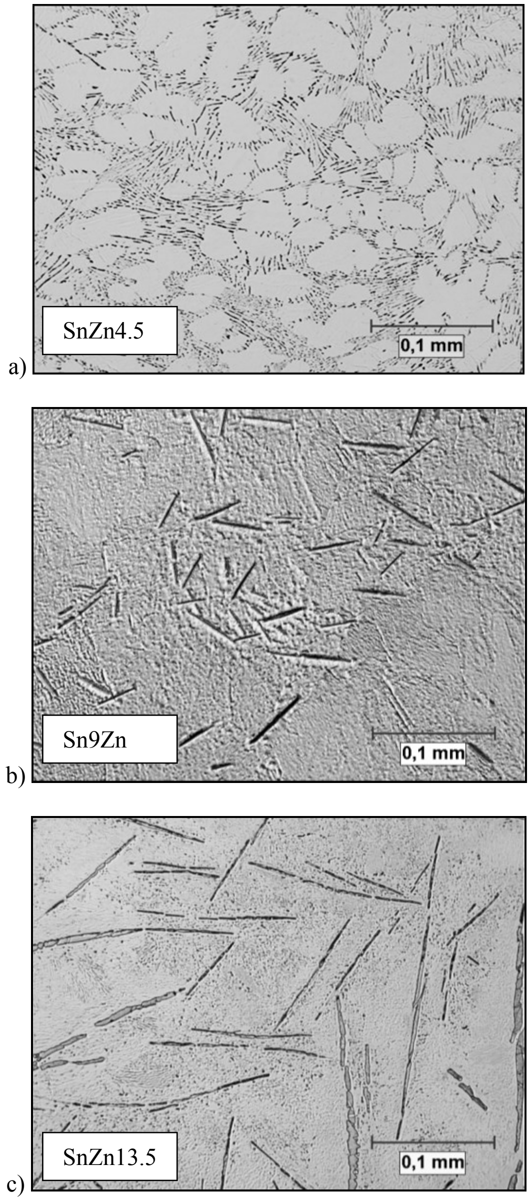
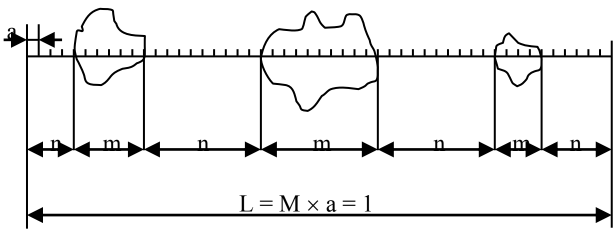


Fig. 1. Microstructure of as cast lead-free binary SnZn solders with various Zn content: a) SnZn4.5, b) SnZn9, SnZn13.5 c)

Attention also deserves the fact that at low (4.5%) Zn content in the alloy, the microstructure is hypoeutectic and the eutectic Sn-Zn precipitates are distributed in interdendritic areas located between the large grains of the Sn_{β} solid solution (Fig. 1a). In the case of an alloy containing 9% Zn, the composition of which is practically entirely eutectic, nearly all microstructure is composed of the Sn-Zn eutectic, although traces of the Zn-rich phase are also observed. In as-cast alloy, the Zn-rich precipitates occur in the form of characteristic dark needles (Fig. 1b).

On the other hand, at much higher Zn content (13.5%), the alloy is hypereutectic, and its microstructure contains eutectic Sn-Zn precipitates and large needle-like precipitates of a phase rich in Zn (Fig. 1c).

To determine whether the reported qualitative microstructural differences in the examined lead-free solders significantly affect the level of the tested mechanical properties, a quantitative assessment of the microstructure was also carried out. A combinatorial method was used to determine the geometric parameters. The method is described in detail in [7] and its general concept is illustrated by the scheme in Figure 2 [8].



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. 2. Diagram explaining the meaning of the quantities determined by combinatorial method [8]

According to this method based on the phase quanta theory [7], each microstructure can be treated as a certain array of the smallest (measurable) elements identified in the material matrix. With this approach, the measuring principle is based on the determination of only two estimators: an estimator of the volume fraction (V_V) and an estimator of the relative area of the measured objects (N_L), while other parameters are calculated from the given formulas (Table 1) [8].

In this case, it has been assumed that the most important parameters include the size of the Zn-rich precipitates (the length of the needles) and their number per 1 mm^2 of the metallographic specimen cross-section.

Table 1.
Formulas used in calculations of geometrical microstructure parameters based on combinatorial method [8]

Stereological parameter	Combinatorial parameter	Calculation formula
Relative amount of the chords N_L [mm^{-1}]	r	$N_L = r$ [mm^{-1}]
Volume fraction V_V [%]	m	$V_V = \frac{m}{M}\cdot 100\%$
Relative area S_V [mm^{-1}]	r	$S_V = 4\,r$ [mm^{-1}]
Specific surface area S_V/V_V [mm^{-1}]	$\frac{r}{m}$	$\frac{S_V}{V_V} = \frac{4r\,M}{m}$[$mm^{-1}$]
The total curvature of the relative surface K_V [mm^{-2}]	$\frac{r^2}{m}$	$K_V = 2\pi N_A = \frac{16M}{3}\cdot\frac{r^2}{m}$[$mm^{-2}$]
The average free distance between precipitates $\bar{\lambda}$ [mm]	$\frac{M-m}{M\,r}$	$\lambda = \frac{M-m}{M\,r}$[mm]
Average chord $\bar{l}$ [mm]	$\frac{m}{r}$	$\bar{l} = \frac{m}{r}a$ [mm]
The number of precipitates sections per unit area N_A [mm^{-2}]	$\frac{r^2}{m}$	$N_A = \frac{8M}{3\pi}\times\frac{r^2}{m}$[$mm^{-2}$]
The number of precipitates per unit volume N_V [mm^{-3}]	$\frac{r^3}{m^2}$	$N_V = \left(\frac{4}{3}\right)^2\frac{M^2}{\pi}\cdot\frac{r^3}{m^2}$[$mm^{-3}$]
The average diameter of the precipitate D [µm]	$\frac{m}{r}$	$D = \frac{3}{2}\cdot\frac{m}{r}\cdot\frac{10^3}{M}$[µm]

* refers to the assumed polydisperse system of spheroids

In the case of hypoeutectic solder alloy containing 4.5% Zn, due to the absence of well visible needle-like Zn-rich precipitates, the quantitative analysis of the microstructure was abandoned.

In the case of the remaining two alloys with the Zn content of 9% Zn and 13.5% Zn, which represent the eutectic and hypereutectic system, respectively, the average length (l) of the needle-like Zn-rich precipitates and their number (N_A) per 1 mm^2 of the metallographic specimen cross-section were determined by combinatorial method.

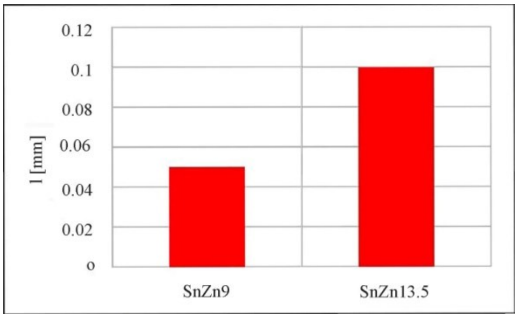


Fig. 3. Comparing the average length (l) of Zn-rich precipitates observed in eutectic SnZn9 alloy and in hypereutectic SnZn13.5 alloy

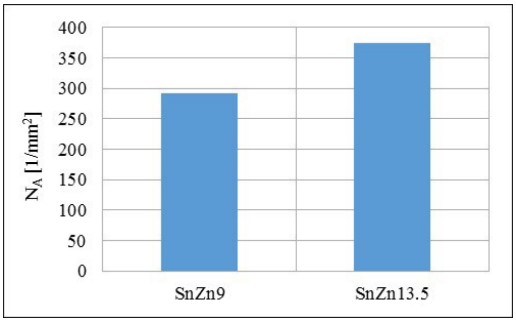


Fig. 4. Comparing the average number (N_A) of Zn-rich precipitates observed in eutectic SnZn9 alloy and in hypereutectic SnZn13.5 alloy

Based on the measurements it was found that in both alloys the needle-like Zn-rich precipitates were uniformly distributed in the matrix, but they differed in respect of both average length (l) (Fig. 3) and number (N_A) per $1mm^2$ unit area of the metallographic specimen cross-section (Fig. 4). Both these geometric parameters assume much higher values in the hypereutectic alloy (Figs. 3 and 4).

In order to determine whether the identified microstructural differences affect also the mechanical characteristics, the tests further described were carried out.

3. Mechanical characteristics

Mechanical characteristics including fatigue parameters were determined using instead of the classical low cycle fatigue method (LCF), its proprietary modified version (MLCF) [9,10]. It should be emphasized that this method has been successfully validated for many microstructurally varied materials [9, 10]. Details of both the principle and the course of measuring process are presented in [9,10].

According to the authors, the positive effects gained so far by this method [9-11] prove that the method is fast, repeatable and reproducible, and owing to this can make a reliable research tool. Consequently, the MLCF test allows obtaining all the mechanical characteristics that result from the classical low cycle test listed and defined in [9-11], and additionally also the accommodation limit (Ra) introduced to the fatigue test in [9-11] as an important mechanical parameter helpful in calculation of a limit stress, above which the stabilization of permanent deformation occurs no longer.

It is worth noting that in fatigue testing practice, difficulties such as unavailability of the necessary number of samples, costly manufacturing processes, etc. cannot be excluded. Especially in such cases, the MLCF method may be an alternative allowing for the estimation of several mechanical parameters based on the data measured on a single sample.

In the measurements taken by MLCF, parameter Z_{go} (fatigue strength under rotating and bending conditions) is the principal parameter determined from the diagram shown in Fig. 5 [9,10] plotted by the experimental method.

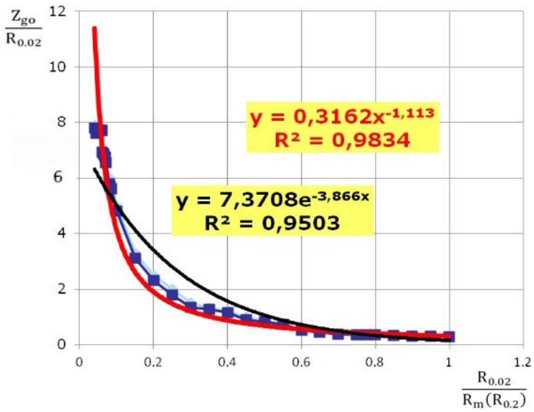
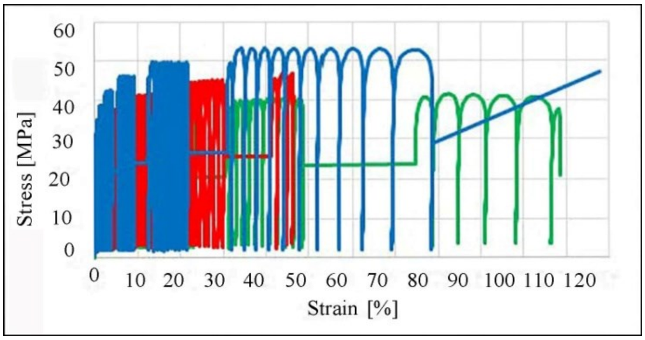


Fig. 5. Experimental curve used for fatigue strength assessment [9,10]

The diagram in Figure 5 shows the experimental curve developed for a number of metals and alloys characterized by different chemical compositions [9,10]. On the other hand, the determination of such parameters as b, c, n', K and ε_{max} was based on specific methodological assumptions identical to those adopted in [9,10,].

Mechanical tests allowed for the fact that test materials were produced by the technique of casting, and therefore microstructural heterogeneities might be expected. For this reason, also, as pointed out under section 2 of this study discussing the problem of microstructure examinations, the rule was strictly followed that all the mechanical and structural parameters should always be measured on the same single sample.

Examples of the stress-strain relationships plotted during unilateral cycling of the as cast lead-free SnZn4.5, SnZ9 and SnZn13.5 solder samples are shown in Figure 6.



SnZn4.5 SnZn9 SnZn13.5

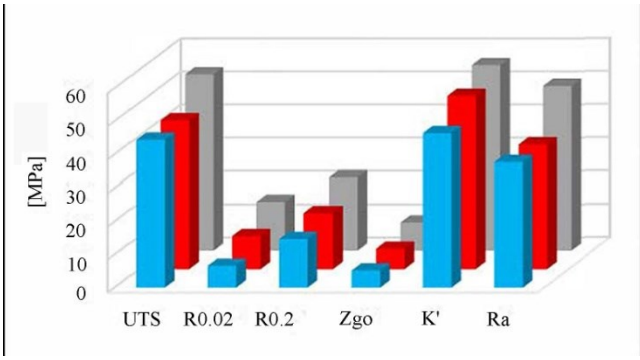
Fig. 6. Stress-strain relationship during MLCF cycling of lead

Attention deserves the fact that the test was stress-controlled, and the value of stress was increased in consecutive cycle groups.

From the presented diagrams (Fig. 6) referring to the binary lead-free alloys it follows that optimal results were obtained for the eutectic SnZn9 alloy. Hypoeutectic alloy containing 4.5% Zn was characterized by high deformability at relatively low stress values. In the case of hypereutectic alloy containing 13.5% Zn, higher stress was achieved but alloy deformability was significantly lower. Consequently, in this comparison it was the ZnSn9 alloy that achieved the preferable parameters since at the highest stress its deformability was still satisfactory.

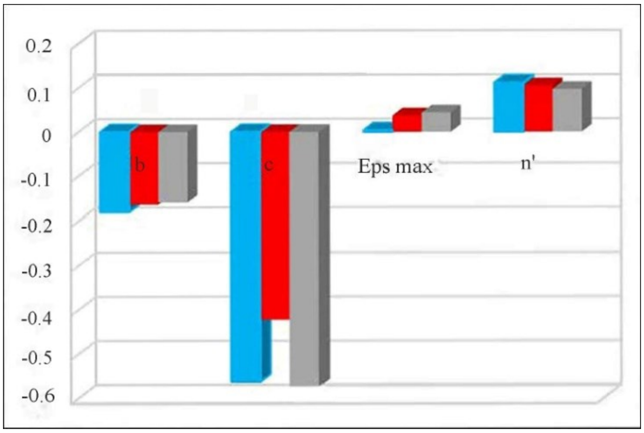
Mechanical parameters of the examined alloys determined by the MLCF test are presented in the diagrams shown in Figures 7-9.

The comparison of mechanical properties (UTS, $R_{0.02}$, $R_{0.2}$, Z_{go}, K ', and R_a) of solders with different Zn content, i.e. 4.5%, 9% and 13.5%, is presented in the form of bar diagrams in Figure 7. It shows that the best parameters were obtained in the alloy with a composition close to the eutectic one (SnZn9).



SnZn4.5 SnZn9 SnZn13.5

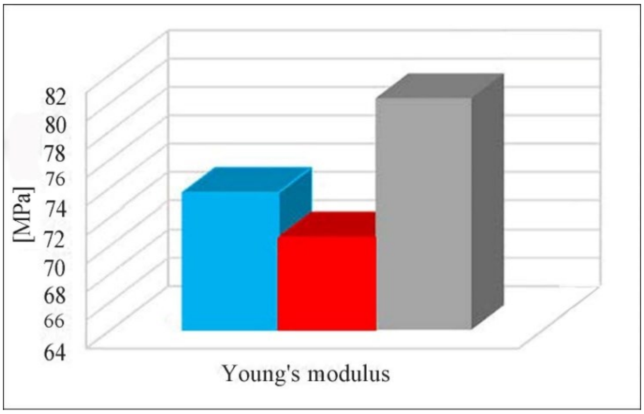
Fig. 7. Selected mechanical parameters of binary lead-free solder alloys with different Zn content: UTS-ultimate tensile strength; $R_{0,02}$-stress limit; $R_{0,2}$-yield point; Z_{go}-assessed fatigue life; R_a-accomodation limit; K'-stress coefficient under cyclically varying loads



SnZn4.5 SnZn9 SnZn13.5

Fig. 8. Selected fatigue parameters of binary lead-free solder alloys with various Zn content: b- Basquin's coefficient, c-fatigue ductility exponent, ε_{max} -maximum allowable strain; n'-strain hardening exponent under cyclically varying loads

A similar trend was observed in the case of other fatigue parameters, i.e. b, c, ε_{max} and n ' (Fig. 8) and Young's modulus (Fig. 9). These characteristics have also reached the highest values in the SnZn9 alloy with a composition close to the eutectic one.



SnZn4.5 SnZn9 SnZn13.5

Fig. 9. The values of Young's modulus (E) for alloys with various Zn content

The obtained results of mechanical tests (Figs. 7-9), analyzed in the context of changes in the microstructure of the examined alloys, indicate that the Zn-rich precipitates observed in microstructure improve the mechanical properties, but this effect has been observed only in the eutectic SnZn9 alloy.

In the as cast hypereutectic SnZn13.5 alloy, an increased number of large needle-like Zn-rich precipitates was identified. They acted as strong microstructural notches significantly deteriorating the mechanical characteristics, in this case determined by MLCF.

Thus, the results of the previously carried out own studies were confirmed. In the field of mechanical testing they included only static tensile test [3], and also according to this test, the best properties were obtained in the eutectic alloy. Studies have shown that for the same three alloys, higher values of the mechanical parameters were obtained in the static tensile test than in the fatigue test.

However, it should be noted, that during fatigue testing both hardening and softening of the alloy can occur [12]. The results of fatigue tests carried out on the SnZn alloys have shown that in this case the examined materials undergo the softening effect.

4. Conclusions

The results of the research enable formulating the following concluding remarks:

- comparison of the binary lead-free solders, i.e. hypoeutectic SnZn4.5, eutectic SnZn9 and hypereutectic SnZn13.5, shows that the best mechanical properties were obtained in the eutectic alloy,
- too coarse, needle-like Zn-rich precipitates present in a large amount in $1mm^2$ of the metallographic specimen cross-section are characteristic of the hypereutectic SnZn13.5 alloy and, by acting as strong microstructural notches, deteriorate the mechanical characteristics,
- an improvement of the mechanical properties can be obtained by heat treatment,
- using MLCF test, quick estimation of several mechanical parameters is possible,
- cycling of SnZn alloys results in material softening.

Acknowledgments

The article was in part based on research carried out in 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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