

The role of eutectic colonies in the tensile properties of a Sn–Zn eutectic solder alloy

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ABSTRACT

The growth of eutectic colonies in Sn–Cu, Sn–Zn and Sn–Ag–Cu eutectic alloys has already been reported in the literature. However, relationships between this kind of microstructure and mechanical properties remain undetermined for solders. The use of water-cooled copper (Cu) and AISI 1020 low-C steel molds and the eutectic Sn–9 wt.%Zn alloy make it possible to address this matter. The samples grown in the Cu mold demonstrated higher solidification rates than those developed in the low-C steel mold. Overall, the microstructure is constituted by Zn-lamellae embedded in a Sn-rich matrix. The Zn lamellae are not only uneven in thickness but also irregularly perforated. Due to Cu dissolution into the alloy, a small fraction of Cu₅Zn₈ intermetallic particles formed during solidification of the Sn–9 wt.%Zn alloy in the Cu mold. The contamination with Cu appears to be responsible for the improvement in the distribution of Zn-lamellae. The decrease in spacing between broken lamellae measured from SEM images, as well as a higher number of Zn particles per area, explain such occurrence. Ductility and tensile strength of different samples could allow the establishment of relationships among properties vs. eutectic colony spacing. For the Cu mold, the motion of Cu towards the alloy as well as higher solidification rates, allowed microstructures to be formed combining 60% of strain to fracture and 52 MPa of ultimate tensile strength. These achievements are mainly due to the finest spacings of both the eutectic colony ($\lambda_c = 36 \mu\text{m}$) and the Zn lamellae ($\lambda_L = 0.9 \mu\text{m}$), besides homogeneous distribution of Cu across the resulting microstructure.

1. Introduction

Soldering is a process utilized to interconnect electronic components in which a solder alloy operates as a filler material. Solder firstly melts, then adheres and finally connects the components together after cooling [1]. Various properties and prerequisites may characterize good solder materials, such as low melting point, low cost, suitable wettability, mechanical reliability, and favorable electrical and thermal characteristics [2–4].

Even though Sn–Pb alloys encompass the aforementioned features, US and European legislations restricting the use of lead (Pb) highly inhibit the use of these alloys [5,6]. The restriction became effective since, in the US, manufacturers may receive tax benefits by reducing/ending the use of lead-based solders. Such conditions have driven the advent of lead-free solders in the course of the last 15 years, which

are the materials almost exclusively used today in consumer electronics [7].

One of the alternative lead-free solders in recent years is the Sn–Zn eutectic. It is as a possible substitute in the replacement of the Sn–Pb eutectic without rising either cost or melting temperature [8,9]. Off-eutectic alloys, in their turn, have different *liquidus* and *solidus* temperatures. The mushy state attained between the aforementioned temperatures is considered a drawback for cases in which a joint is disturbed before solidification is completed. A poor electrical connection may result from that occurrence, which indicates that eutectic proportions must be targeted. Another point is that fluidity tends to decrease due to the mixture of solid particles with molten eutectic in the case of non-eutectic chemistries.

On the other hand, other available eutectics such as Sn–Ni and Sn–Cu have higher melting points of 231 °C and 227 °C, respectively, as

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Table 1

Chemical compositions (wt.%) of metals used to prepare the Sn-9 wt.%Zn alloy.

Element	Pb	Fe	Sb	Sn	Cd	Ni	Cu	Bi	Zn
Sn	0.025	0.003	0.003	99.96	0.002	<0.001	<0.001	0.005	<0.001
Zn	0.0026	0.0001	–	0.0001	0.0006	–	0.0002	–	99.997

compared to the melting temperature of the Sn–Zn eutectic of 198 °C [10]. Even if the Sn–Ni and Sn–Cu eutectic alloys become attractive materials for solders, their high melting temperatures remain an important drawback for wide application as solders.

The Sn–Zn eutectic shows excellent plasticity due to the absence of brittle intermetallic particles in the whole Sn–Zn phase diagram, in which only β -Sn and α -Zn phases form during cooling. Once this condition is assured, it is very reasonable to conceive that the proportions, distributions, sizes, length-scales and morphologies of the phases constituting the microstructure are of utmost importance in defining the range of application properties of a particular Sn–Zn alloy composition. Such features may be affected by the solidification kinetics. Cooling thermal parameters during processing, such as the solidification cooling rate (K/s) and solidification velocity (mm/s) are fundamental in the control of the resulting eutectic arrangement [11]. And in turn, the final properties and pre-requisites of as-soldered fillets are mainly connected to the as-solidified microstructures. Attempts to better investigate the role of eutectic array features of the Sn–Zn eutectic are essential for the improvement of quality of the produced solder joints.

One of the goals is to interpret the composite microstructures formed by two solid phases growing simultaneously from the melt. This is explained due to the improved properties that can be obtained depending on the combination of the phases constituting the eutectic. The eutectic pattern is typically about one order of magnitude smaller in size than that found in dendritic alloys, which is a clear benefit to achieve optimized properties [12].

Amplification of cooling rates may allow several non-conventional morphologies to take place in eutectic or near eutectic alloys, such as degenerated eutectics, banded structures or even amorphous structures [13–16]. One of these non-conventional formations refers to the growth of eutectic colonies.

Despite its importance as a particular eutectic morphology, the growth of eutectic colonies is barely reported for the Sn–Zn eutectic. Wu et al. [17] and Suganuma and Niiara [18] limited to describe microstructures having large Sn grains with a fine uniform two-phase eutectic colony. To the author's knowledge, this peculiar microstructure has not been deeply demonstrated in the Sn–Zn eutectic. Chen et al. [19], in an attempt to improve the melting temperature, wettability and mechanical properties, added silver (Ag) and gallium (Ga) to the Sn–Zn eutectic alloy. It was described that both ternary and quaternary alloys' microstructures exhibited the two-phase colony structure, despite the increased fraction of the primary β -Sn phase in the Ga-containing alloy.

Recent studies have also focused on the selection of 3rd element additions to the Sn–Zn eutectic with a view to providing better properties [20–24]. In the case of Cu addition, for instance, increase in mechanical strength is generally associated with the formation of additional phases such as Cu_6Sn_5 , $\epsilon\text{-CuZn}_5$ and/or $\gamma\text{-Cu}_3\text{Zn}_5$.

Cu is a very common material in electronics. For example, it is frequently employed in printed wiring boards (PWBs) being exposed to Sn-based alloys during soldering operations. A further characteristic of the new alloys of interest is the higher tin compositions (at least 90%) as compared to that of the Sn–Pb eutectic. Higher Sn contents favor the risk of damage copper dissolution. Therefore, the microstructures and properties of solders may or may not change due to the presence of remaining impurities. Only few reports deal with the influence of a minor Cu content on the microstructure of the Sn–Zn eutectic [24]. Pandey et al. [24] demonstrated that the average spacing between broken Zn-lamellae shifted from 3.0 μm to 8.0 μm with the increase in Cu content from 0 to 1.3 at.% Cu in the Sn–Zn eutectic. Further Cu

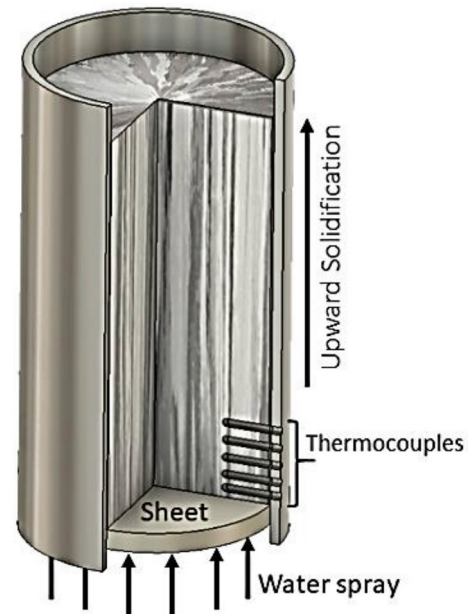


Fig. 1. Representative draw of the cylindrical split container designed to permit upward directional solidification of the Sn-9 wt.%Zn alloy. This system permits the use of bottom sheet molds of different materials.

increase provoked decrease in the spacing. Pandey et al. [24] did not consider possible variations in the solidification velocity in their analysis.

The present study is a continuation of an investigation by these researchers with a Sn-2 wt.%Sb alloy [25], which has advanced our understanding of the role of microstructure on Sn-based solder alloys. In the present investigation, the effect of different mold materials on the solidification rate of the Sn–Zn eutectic is compared, and eutectic colonies features as well as the influence of Cu presence on the formation of microstructures of a eutectic Sn–Zn/Cu couple are investigated. Relationships of tensile properties such as the ultimate tensile strength and the strain to fracture vs. eutectic colony spacings are established. Finally, we give insight into the thermal and microstructural conditions that may contribute to the increase in the ductility of the Sn–Zn eutectic.

2. Experimental procedure

The compositions of Sn and Zn used to prepare the Sn-9 wt.% Zn eutectic alloy are shown in Table 1. An upward vertical solidification device was used to promote directional solidification of castings in the unsteady state regime, as can be seen in Fig. 1 [26–28]. The device consists of the following main parts: refractory material to minimize heat losses; controlled electrical resistances to provide the desired melt superheat (30 °C above the eutectic temperature); a cylindrical stainless steel split mold having an internal diameter of 60 mm, a height of 157 mm, and a wall thickness of 5 mm; interchangeable sheets made of different materials (carbon steel and copper) with a thickness of 3 mm and active surface ground by a #1200 grinding wheel coupled to the bottom part of the mold; a coating having a 2 mm-thick of insulating silica-alumina applied into the inner stainless steel mold surface; a water spray system providing cooling at the sheet when the molten alloy

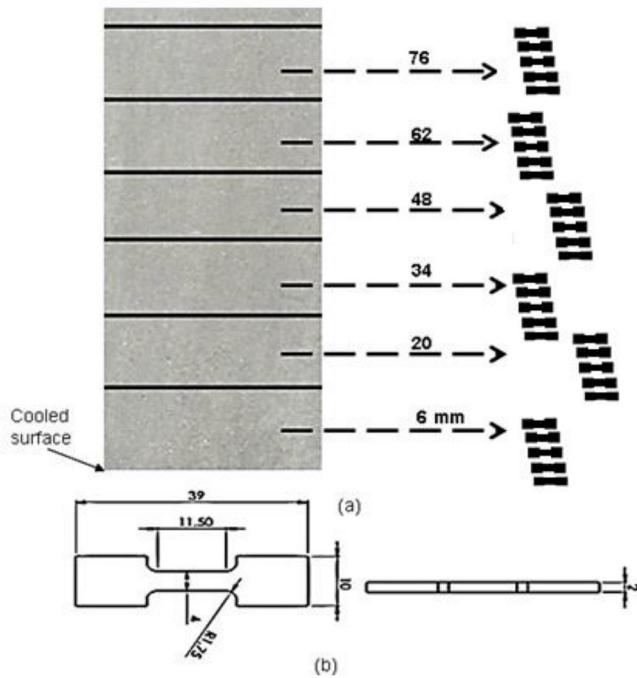


Fig. 2. Tensile tests: (a) sampling positions along the length of the DS casting; and (b) geometry and dimensions of tensile specimens.

achieves the superheat and at the same time the electrical resistances are switched off.

The temperatures of the castings during solidification were monitored by a set of J type thermocouples, located at different positions (P) along the length of the castings, from the heat-extracting surface. The chosen positions for the present investigation in the case of both produced castings were 5, 10, 15, 20, 25, 45, 70 and 90 mm. The temperature data were acquired automatically, at the frequency of 5 Hz, through a data logger system connected to the thermocouples. Two directionally solidified (DS) castings were generated: using the Sn–Zn/steel and the Sn–Zn/Cu setups. Samples extracted from different positions along the length of the DS castings were polished and etched (with a solution of 92 mL of CH_3OH , 5 mL of HNO_3 and 3 mL of HCl) for metallography.

Firstly, micrographs of samples extracted from various positions along the length of both DS Sn–Zn alloy castings were examined by using a Nikon optical microscope (model Eclipse MA2000). Such examination allowed the eutectic colonies to be typified. Several optical images were collected so that the eutectic colony spacing could be measured in all distinct slices removed from the DS castings. The spacing between the colonies, λ_c , was established based on the well-known methods to determine cellular spacings [29]. With this aim, various selected transverse samples were considered along the length of the DS castings, i.e., positions at 5, 10, 15, 20, 30, 50, 70 and 90 mm from the cooled surface.

Secondly, the spacing between broken Zn-lamellae was measured from images generated by a Scanning Electron Microscope (SEM) from Zeiss (Oberkochen, Germany, Auriga 40 model). SEM images were obtained from transverse samples (perpendicular to the growth direction) of the DS Sn–9 wt.%Zn alloy castings. In this case, five (5) positions were examined along the length of each of the tested DS castings, which were: 5, 20, 50, 70 and 90 mm. These samples were polished, firstly, with a solution of 1 μm alumina and secondly, using 0.06 μm colloidal silica. The line intercept method [30] was applied for measuring the lamellar spacing of Zn, λ_L , either within the fine-scale central region of the colonies or in the coarse lamellar zone at the boundaries.

Samples associated with very distinct solidification cooling rates (K/s) were chosen for the x-ray diffraction analyses of the two Sn–Zn/steel

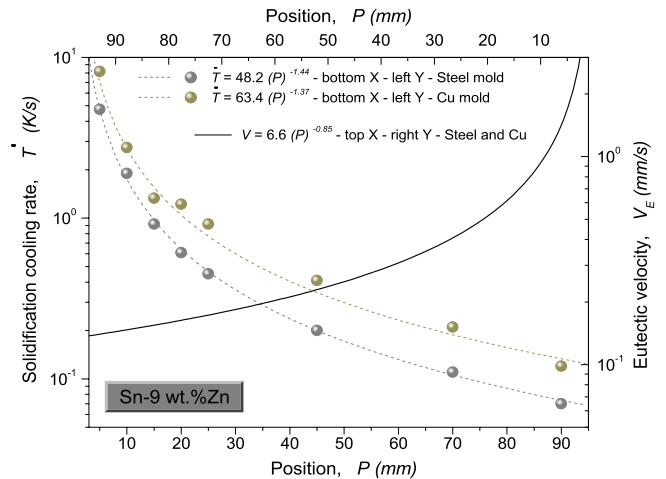


Fig. 3. Variations of solidification cooling rate and eutectic velocity along the length of the DS Sn–9 wt.%Zn alloy castings both for copper and steel molds.

and Sn–Zn/Cu DS castings. A Shimadzu diffractometer (Kyoto, Japan) was employed to obtain the x-ray diffraction patterns under the 2θ range from 25° to 80° using Cu–K α radiation with a wavelength of 0.15406 nm.

In order to assess both area distribution and size of Zn particles upon the two established conditions of this investigation, a more detailed analysis of the SEM micrographs of each ensemble of images has been performed using the processing software (Image J). This software is an open source Java image processing program inspired by NIH Image [31]. The number and average size of Zn particles have been determined for images associated with four (4) different positions examined in each of the generated castings. The positions of interest were established so that slices related to distinct cooling rates could be examined for each casting. The computation of these numbers was possible thanks to the computation of the dark areas in the corresponding SEM micrographs.

Samples of different positions along the length of the DS castings were extracted so that specimens could be machined for tensile testing according to specifications of ASTM Standard E 8 M. The tests were performed at a strain rate of about $3 \times 10^{-3} \text{ s}^{-1}$ [26]. Four to five specimens were tested for each selected position along the length of each casting. The following tensile properties were correlated with a variety of microstructures: ultimate tensile strength (σ_u), yield tensile strength (σ_y) and elongation (δ). Fig. 2(a) shows a scheme explaining the removal positions for the tensile tests taken the cooled surface of a Sn–Zn alloy casting as a reference. Furthermore, the geometry and dimensions (in mm) of the tensile specimens can be found in Fig. 2(b).

3. Results and discussions

Fig. 3 shows the experimental variations of the solidification thermal parameters along the length of the DS Sn–Zn eutectic castings. The profiles are associated with data in both Cu and steel mold sheets. Experimental solidification cooling rates are taken as the time derivative of the thermal profiles provided by the thermocouples (slope of the cooling curve) at the eutectic temperature. Couples of values of position (P), from the sheet surface, and related time (t_E) of the eutectic front generated an experimental function $P=f(t_E)$. Moreover, this function is derived with respect to time so that the eutectic velocities (V_E) could be rated.

The particular positions near to the metal/bottom-sheet region are those of more interest in solders. This is because in industrial environments any thermal instrumentation based on contact would be highly disturbing due to the small volumes involved, as those of soldering balls, for instance. Nevertheless, approaches like those in the present study come to light as a useful tool to provide a view of scale at which the solidification rates develop in a specific solder material.

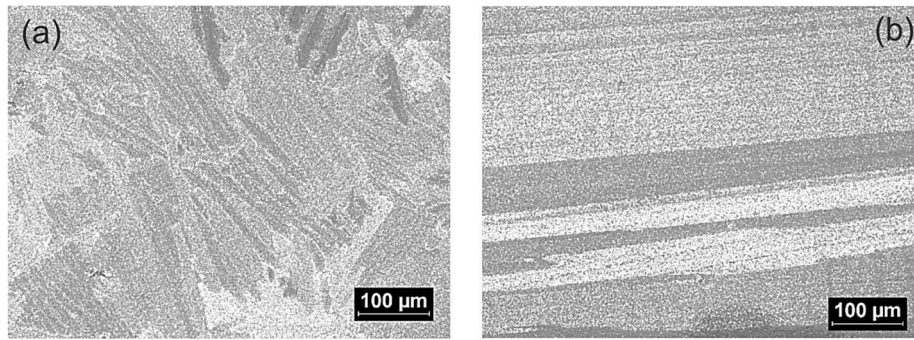


Fig. 4. Micrographs showing the eutectic cells' morphology visualized either in (a) transverse or in (b) longitudinal sections (Sn-9 wt.%Zn samples cooled at 4.7 K/s in low carbon steel mold).

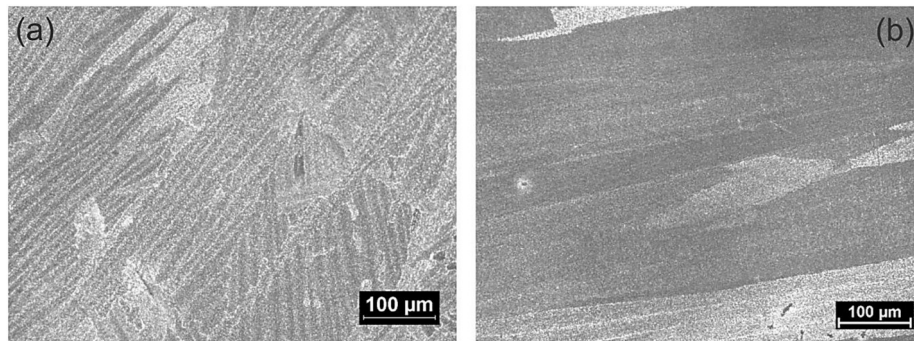


Fig. 5. Micrographs showing the eutectic cells' morphology visualized either in (a) transverse or in (b) longitudinal sections (Sn-9 wt.%Zn samples cooled at 8.2 K/s in copper mold).

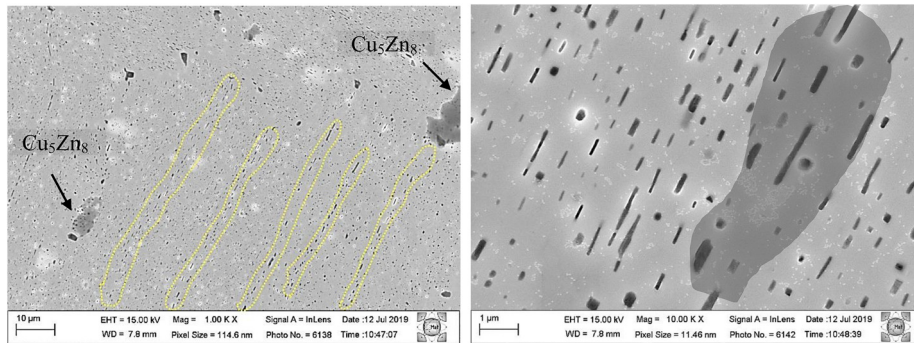


Fig. 6. (a) Boundaries characterizing the formation of colonies and (b) details of the morphology of lamellae in the eutectic regions of the DS Sn–Zn eutectic samples cooled at 8.2 K/s.

It is possible to affirm that solidification cooling rates from 0.5 K/s to 8.2 K/s are reached for the cases of solidification against Cu and steel molds. A single trend (solid line) encompassed both conditions regarding the solidification velocity. As the eutectic front advances from the bottom to the top, thicker solid forms and consequently both thermal parameters tend to decrease since the solid thermal resistance tends to increase. According to reference [32], Cu's and steel's thermal conductivities are $385 \text{ W m}^{-1} \text{ K}^{-1}$ and $25 \text{ W m}^{-1} \text{ K}^{-1}$ respectively. Therefore, the Cu mold is associated with a higher heat extraction capability than the steel one. This is possibly a factor explaining the higher solidification cooling rates related to the Sn–Zn/Cu couple.

The experimental points and trends observed in Fig. 3 were used as a map of the thermal parameters associated with each of the metallographic prepared samples, as will be seen later.

Fig. 4 and Fig. 5 show typical examples of the transverse and longitudinal views of the eutectic colonies in the Sn–Zn eutectic. The

revelations are very similar to each other when the Sn–Zn/Cu and Sn–Zn/Steel results are compared. The left side transverse section images (Figs. 4(a) and Fig. 5(a)) were those considered to perform the line intercept method for determining the colony spacings.

The boundaries of the developed colonies observed in the Sn–Zn eutectic alloy are very thin as compared to those found, for instance, in Sn–Cu alloys [10]. In spite of this, all characteristics typifying a colony are offered as following: alignment of two-phase cells with the thermal gradient, alternation of fine and coarse structures, finer lamellar eutectic grown in the center zone of the cells while coarser eutectic at the boundaries. These features can be clearly observed in Fig. 6, in which the borders have been outlined.

All phases identified by x-ray diffraction analyses constituting the bulk DS alloy of the Sn–Zn/steel and Sn–Zn/Cu couples can be seen in Fig. 7 (a). These analyzes have been performed in different slices corresponding to different solidification cooling rates to give an idea on

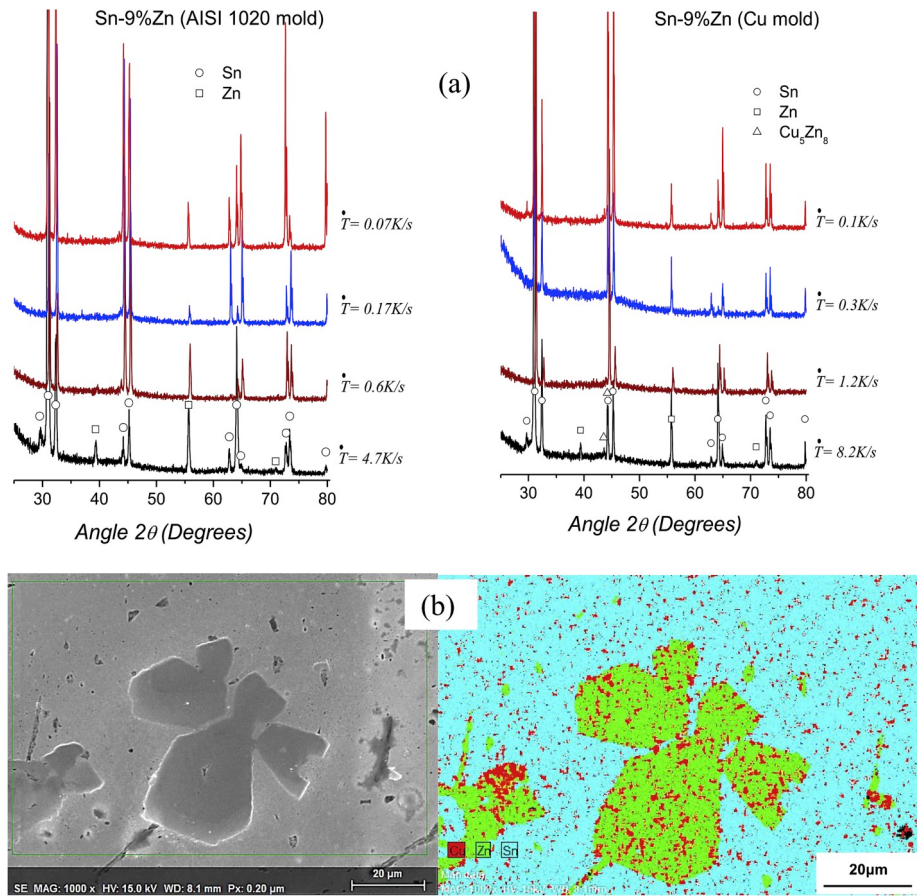


Fig. 7. (a) X-ray diffraction spectra for the Sn-9 wt.%Zn samples cooled against steel and copper molds as well as the respective solidification cooling rates; and (b) SEM-EDS images demonstrating the growth of the Cu_5Zn_8 phase due to dissolution of Cu in the case of the Cu mold. The corresponding cooling rate of this sample was 8.2 K/s.

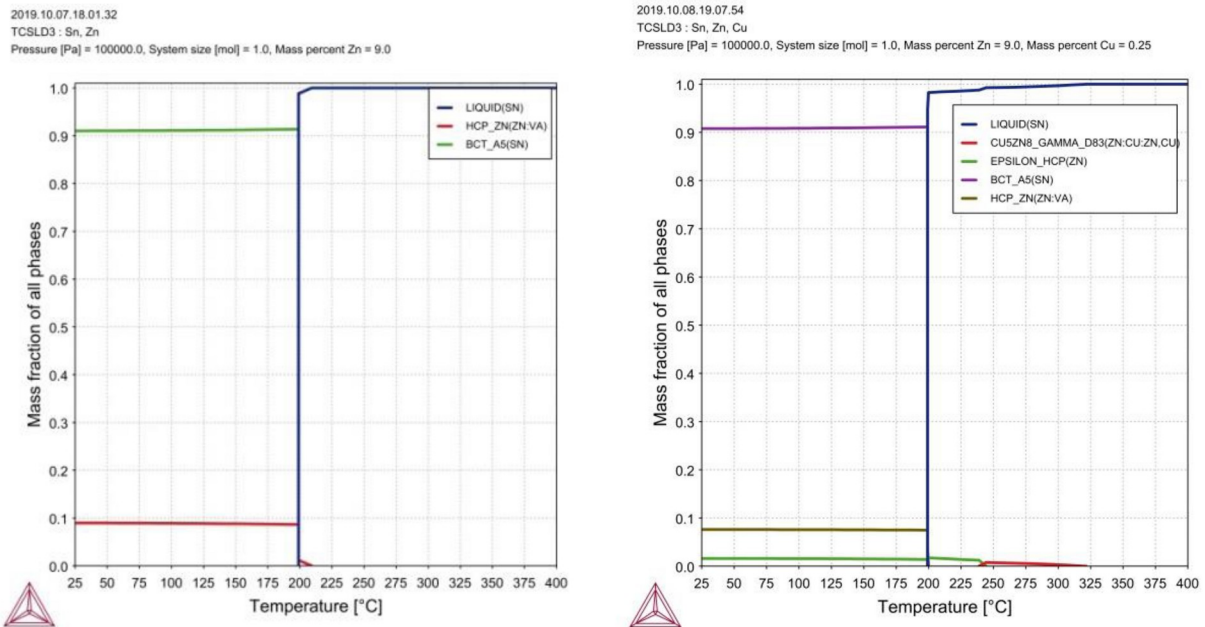


Fig. 8. Equilibrium phase fractions of (a) Sn-9 wt.%Zn and (b) Sn-9 wt.%Zn-0.25 wt.%Cu alloys as a function of the temperature, computed using TCSD3 database of the Thermo-Calc (TC) software.

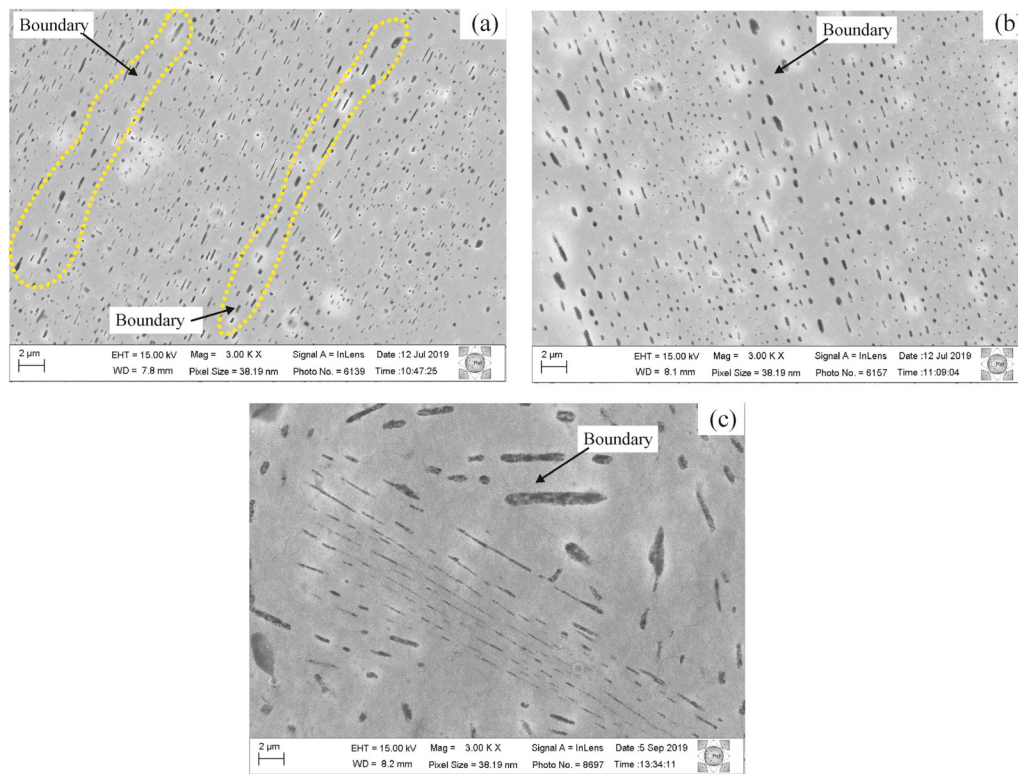


Fig. 9. SEM microstructures of the DS Sn-Zn eutectic samples showing the broken-lamellar structures formed either at the center or at boundaries of the eutectic colonies: for samples cooled at (a) 4.7 K/s, (b) 0.61 K/s and (c) 0.11 K/s in AISI 1020 steel mold.

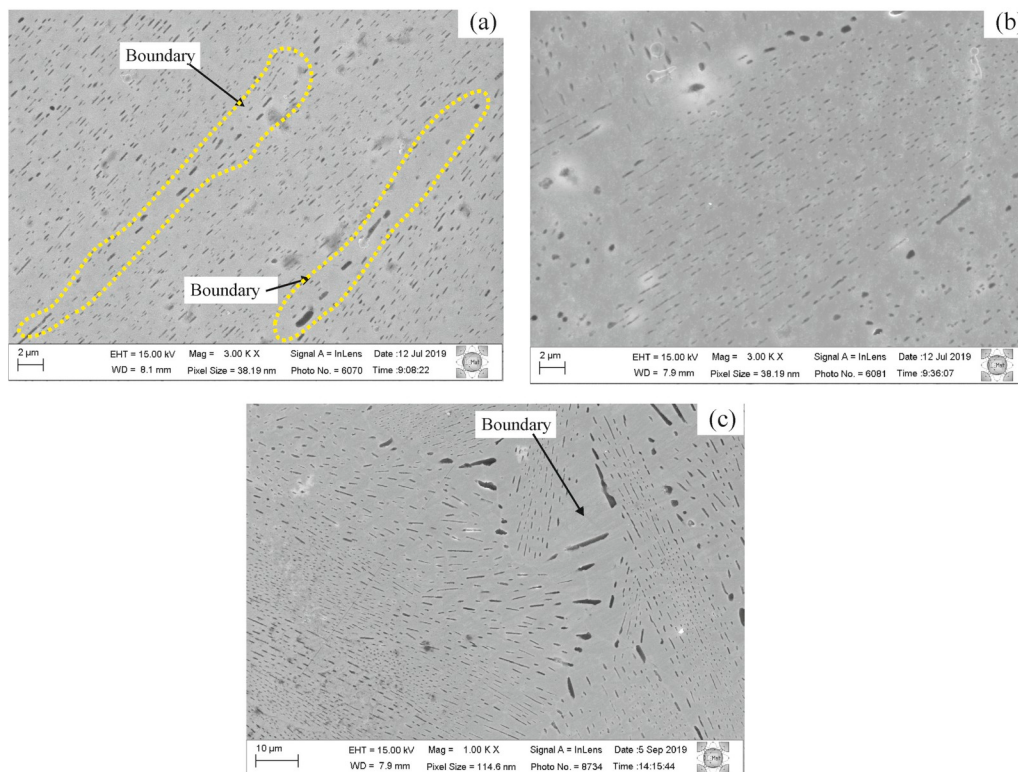


Fig. 10. SEM microstructures of the directionally solidified Sn-Zn eutectic samples showing the broken-lamellar structures formed either at the center or at boundaries of the eutectic colonies: for samples cooled at (a) 8.2 K/s, (b) 1.2 K/s and (c) 0.12 K/s in copper mold.

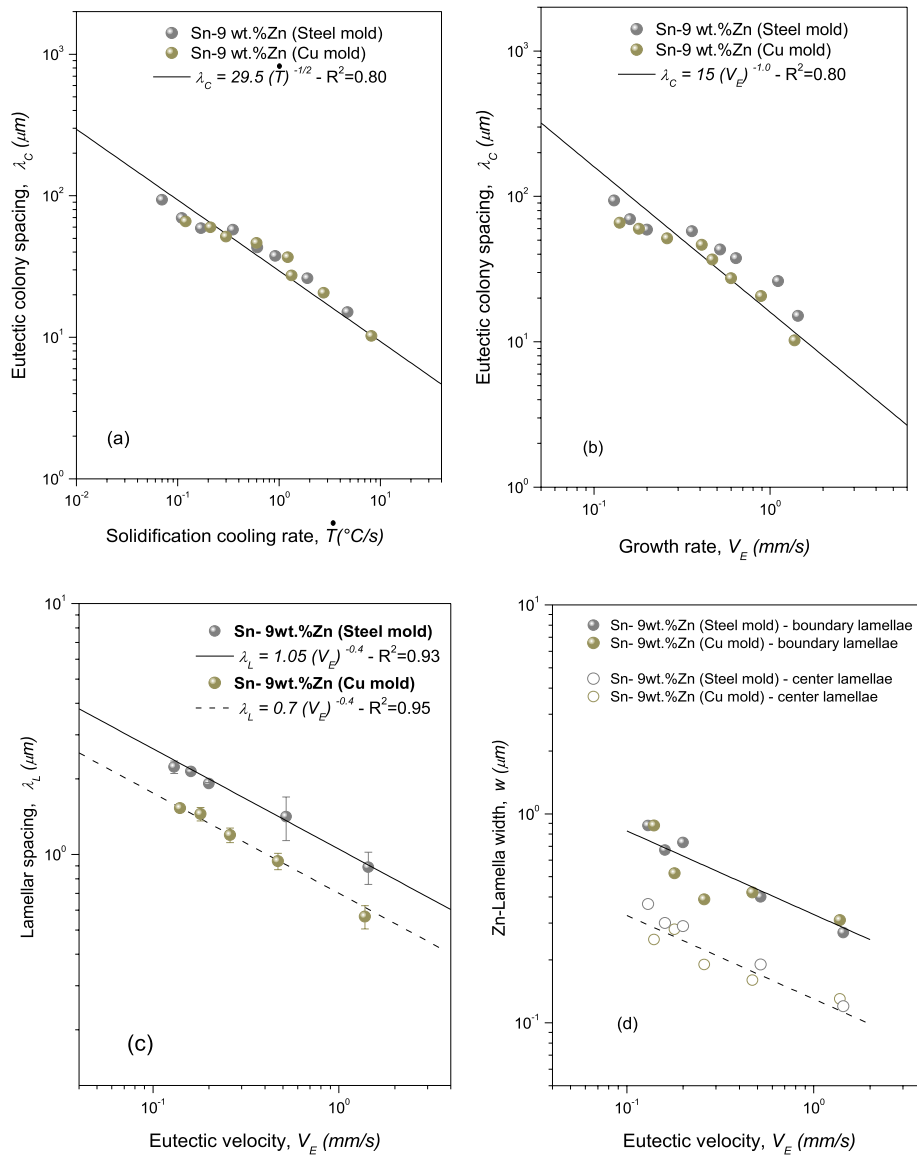


Fig. 11. Determined relationships for the eutectic growth of the DS Sn-9 wt.%Zn alloys castings: (a, b) eutectic colony spacing, λ_c ; (c) perforated lamellar spacing, λ_L , and (d) Zn lamella width, w , vs. solidification cooling rate and eutectic velocity.

how the phases develop having as reference the sheet surface. Overall, the x-ray diffraction patterns recorded from the alloy solidified against the steel sheet shows peaks related to β -Sn and α -Zn phases. In contrast, besides these phases, the patterns associated with the alloy solidified in the Cu mold show the presence of two peaks corresponding to the γ -Cu₅Zn₈ phase. The reason behind this is the presence of Cu dissolved into the alloy. The Energy Dispersive x-Ray Spectroscopy (EDS) map analysis has found a Cu content in the alloy of about ~ 0.25 wt.%. Another point worth noting is that the driving force for formation of intermetallics between Cu and Zn, namely ϵ -CuZn₅ and γ -Cu₅Zn₈, is higher than that for CuSn intermetallics [33].

The detailed SEM-EDS analysis in Fig. 7(b) further supports the x-ray diffraction patterns findings under such conditions. The identified β -Sn, α -Zn and γ -Cu₅Zn₈ phases can be clearly seen in Fig. 7(b) besides a significant presence of Cu in solid solution within the β -Sn matrix. The Cu content is rather small, being more intense in the regions closer to the heat extracting surface, which is the source of the contamination with Cu. This explains why the XRD spectrum associated with closest position of analysis at $P = 5$ mm (i.e., 8.2 K/s) barely revealed the occurrence of the Cu₅Zn₈ phase. However, the occurrence of this phase (tracked by

SEM micrographs) was found for all examined positions in the casting.

Pandey and co-authors [24] demonstrated that depending on the Cu alloying in the Sn-Zn eutectic both ϵ -CuZn₅ and γ -Cu₅Zn₈ could coexist dispersed within the β -Sn + α -Zn composite. With this in mind, Thermo-Calc [34] plots in Fig. 8 were computed so that the predicted phases could be faced with those supported by the x-ray diffraction patterns. It was considered that 0.25 wt.% Cu was dissolved and joined the alloy composition. According to the evolution of the phase fractions in equilibrium conditions observed in Fig. 8 (b), the γ -Cu₅Zn₈ (red line) forms first and then gives rise to the ϵ -CuZn₅ phase (green line) at lower temperatures, as a result of a peritectic reaction. Nevertheless, it appears that such reaction may not be possible in the present results since the cooling conditions are far from equilibrium. Therefore, the γ -Cu₅Zn₈ phase could sustain in the liquid until solidification is completed. Another factor to consider is the morphology of the phase. Flower-shaped Cu₅Zn₈ has already been reported by a previous article [22].

As can be seen in Fig. 9 and Fig. 10, oriented Zn-lamellae form cells, or colonies, divided by coarsened colony boundaries. Some number of Zn-lamellae appears in the boundary of the envelopes while the size of

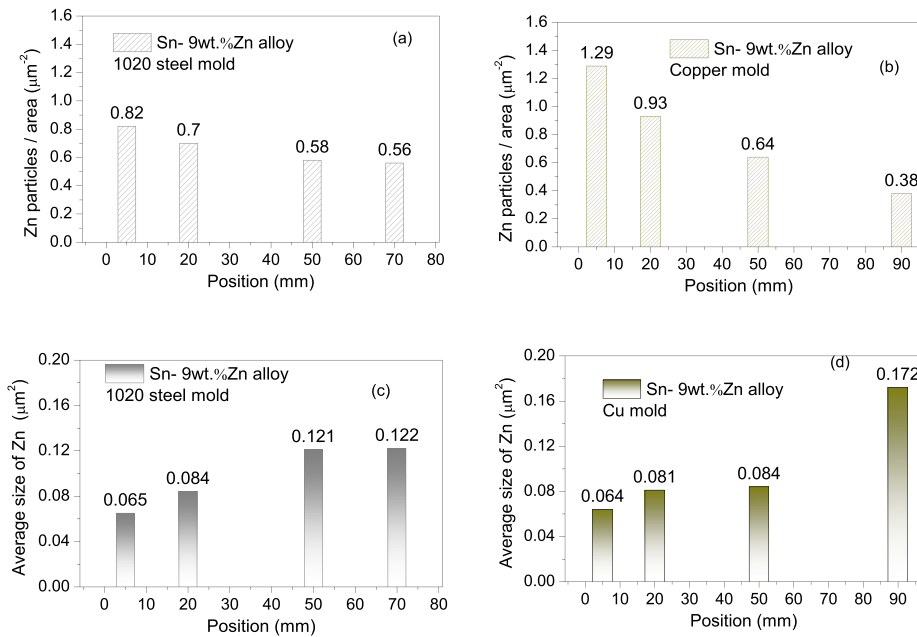


Fig. 12. (a, b) Number of Zn particles and (c, d) Zn average size for various relative positions within the DS Sn-9 wt.%Zn alloys castings cooled in both mold materials, i.e., low-C steel and Cu molds.

the Zn-rich phase in the central areas of the eutectic colony gets finer. The coarsening mechanisms at the boundaries are mainly related to the concentration/level of strain at these regions during cooling. This may cause the phases at the boundaries to further coarsen. This feature is highlighted in yellow/dot area marks in both Figs. 9 and 10. According to Crocker et al. [35] and Vnuk et al. [8], the Sn–Zn eutectic may grow as “broken-lamellae”, with the lamellar Zn phase growing in a faceted manner while the other phase as non-faceted (β -Sn). The SEM images related to both setups (i.e., Sn–Zn/steel and Sn–Zn/Cu) show similar overall features when compared to each other, as shown in Figs. 9 and 10. In this context, quantification of spacing and number of Zn-particles is necessary in order to certify some concluding difference or not between both tested conditions.

The experimental values of the eutectic colony spacing and lamellar spacing were determined for each sliced sample extracted along the length of each of the DS castings. Considering that the thermal parameters of each measured sample were already known, Fig. 11 plots the relationships: microstructural spacing vs. solidification cooling rate and solidification velocity. These plots result in a clear observation of the effects of the solidification kinetics in the spacings. Higher V_E and $\bar{T}$ are associated with smaller λ .

For the growth of colonies in the Sn–Zn eutectic, single relationships following $-1/2$ and -1.0 power function exponents for solidification cooling rate and eutectic velocity, respectively, are appropriate to represent the data generated in both Cu and steel sheets, as can be seen in Fig. 11(a) and (b).

Previous studies focusing on the growth of monophasic cells demonstrated that -0.55 and -1.1 exponents are effective in representing the variation of cell spacing against solidification cooling rate and solidification velocity, respectively [36,37]. The exponents derived based on the present results are quite similar to those reported in the literature. It appears that the eutectic cells kinetically behave in a similar fashion with the monophasic ones.

Very few studies proposed experimental correlations between eutectic colony spacing and solidification thermal parameters. One can cite the available researches as those developed by Han [38] and by Farag and Taha [39]. Despite not specifically devoted to Sn–Zn eutectic, both studies demonstrated that the variations in spacing between the eutectic colonies with the imposed growth velocities may be governed

by power growth expressions, whose exponents were demonstrated to be $-1/4$ or $-1/3$. In contrast with the present results, the line in Fig. 11 (b) is associated with an exponent of -1.0 . Therefore, the transient growth of eutectic colonies in the Sn–Zn eutectic alloy observed in the present contribution remains more sensitive to the variations in the growth velocity as compared to the previous results in the literature.

The Sn + Zn eutectic structures inside the colonies were also evaluated. The scaling laws were characterized by a -0.4 power function exponent for the lamellar spacing scatters of the Sn–Zn eutectic solidified both in steel and Cu sheets. This slope is also reported by Vnuk et al. [8] for velocities varying from $1.42 \mu\text{m/s}$ to $1100 \mu\text{m/s}$ during the growth of the Sn–Zn eutectic. The eutectic Zn-spacing scales of the castings solidified in steel and Cu may be directly compared using the multipliers derived by the power functions inside Fig. 11(c). The lamellar spacing of the alloy solidified against Cu is 50% lower than the other examined condition. Cu appears to be a substrate to boost the nucleation rate of Zn particles during cooling. The experimental variations of lamella width are plotted as a function of the eutectic velocity in Fig. 11(d). These measurements were considered either in the middles or in the boundaries of the colonies. It is worth noting that values at the boundaries roughly changed from $0.75 \mu\text{m}$ to $0.28 \mu\text{m}$ while at the middles from $0.30 \mu\text{m}$ to $0.12 \mu\text{m}$.

Fig. 12 plots the number of Zn particles and the average size of Zn as a function of position (distance from the mold sheet). It compares these indicators for both conditions tested here, i.e., the Sn–Zn/Steel and Sn–Zn/Cu setups. It can be noted that a higher density of particles appears in the first positions of the alloy casting solidified in the Cu mold. Moreover, the average size of Zn does not change significantly when both tested conditions are compared. Zn-lamellae are better distributed in the case of the alloys solidified in the Cu mold. The reasons behind this are the higher solidification cooling rates as well as the presence of Cu in the molten alloy stage.

Samples at high cooling rates are also followed by high growth velocities as can be seen in Fig. 3. It is well known that large eutectic undercoolings may happen for higher growth velocities. Bearing in mind the general theory for the growth of eutectics by Jackson and Hunt [40], the relation between the eutectic undercooling ΔT at the solid-liquid interface and the eutectic spacing λ at a certain velocity V is given by: $\Delta T = K_1 \lambda V + K_2 / \lambda$, where K_1 and K_2 are material's constants. As a

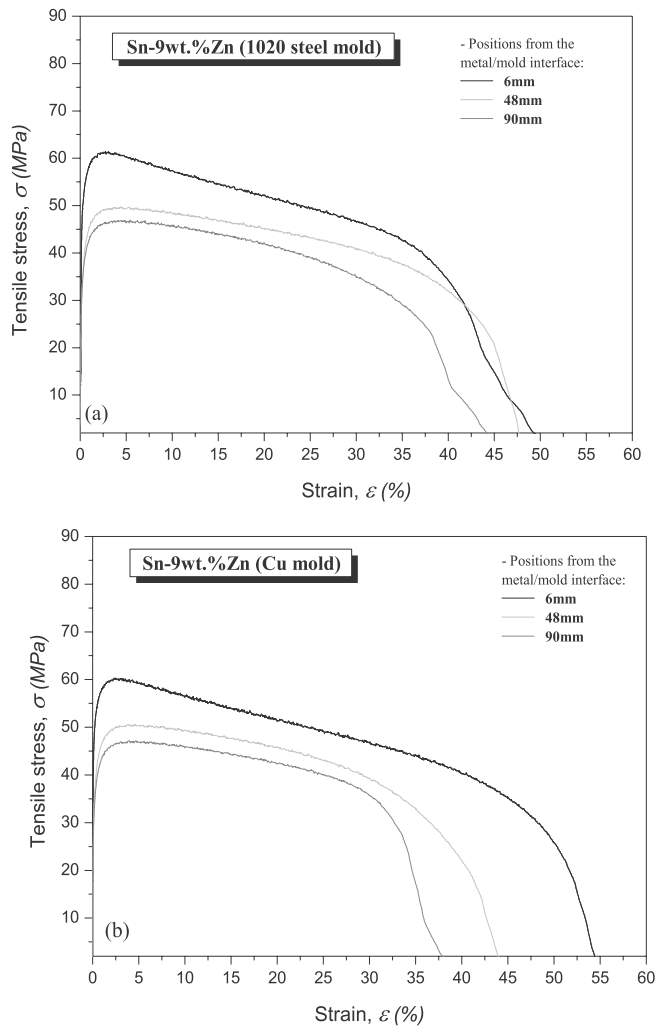


Fig. 13. Tensile stress-strain curves corresponding to the specimens extracted at the positions 6 mm, 48 mm and 90 mm from the cooled surface of the Sn-9 wt.%Zn alloys castings: (a) low-C steel and (b) Cu molds.

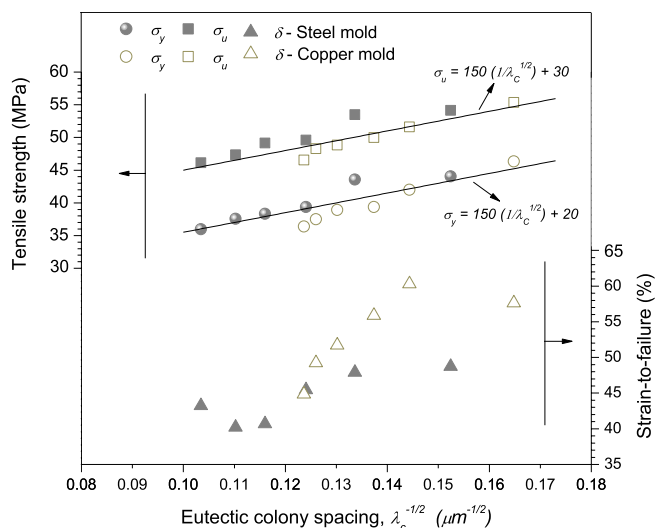


Fig. 14. Relationships established for tensile properties affected by the colony spacing for DS Sn-9 wt.%Zn alloy castings under two conditions, i.e., solidified against copper and low-C steel molds.

consequence, smaller Zn particles characterize the samples closer to the heat extracting surface as can be seen in Fig. 12.

Fig. 13 depicts some representative stress-strain curves of the DS Sn-Zn eutectic alloy specimens as registered for three different positions along the casting length (i.e.: P = 6 mm, P = 48 mm and P = 90 mm from the bottom surface of the DS casting), considering both mold materials, i.e., low-C steel and Cu molds.

As can be seen in Fig. 14, the ultimate (σ_u) and yield (σ_y) tensile strengths slightly change for samples along the length of the DS Sn-Zn eutectic castings. As mentioned before, the values quantifying the microstructure are associated with various solidification cooling rates and eutectic velocities. Fig. 14 reveals if these quantified aspects affect the tensile strength and ductility.

Taking into consideration that the eutectic colony spacing has a scale that is larger than that of the lamellar spacing, λ_c is the first microstructural characteristic to be taken into account. A method was adopted using “Hall-Petch” relationships to compare the strengths of the two tested conditions. This kind of approach was also demonstrated elsewhere [41,42]. This approach establishes the alloy tensile strength as a function of a representative microstructural spacing instead of comparing the strength to the grain size.

It can be seen in Fig. 14 that single Hall-Petch type trends may represent either σ_u or σ_y variations with the λ_c length scale. The fraction of hard CuZn intermetallic particles, which resulted from solidification in the Cu mold, appears to be not enough to improve the strength of the alloy.

A higher variation in ductility can be observed in Fig. 14 for the alloy samples solidified in the Cu mold. On the other hand, δ values associated with the samples of the Sn-Zn/Steel setup barely varied. The positive effect of Cu contamination of the alloy in the present investigation is very clear if one compares the ductility plots in Fig. 11. For the casting solidified in the Cu mold, for those samples closer to the sheet surface ($\lambda_c^{-1/2}$ varying from 0.140 to 0.165 $\mu\text{m}^{-1/2}$) a higher level of Cu is expected to occur and at these conditions the ductility is roughly 20% higher than the values found in the other setup (i.e., steel mold). The reasons for that are the increase in the number of Zn particles and the presence of Cu in solid solution.

The ductility of the Sn-Zn eutectic attained values very close to those recently found in our research regarding the Sn-2 wt.%Sb alloy [25]. Of particular note, changing solute from Sb to Zn allowed increasing the alloy strength by two-fold.

The combination of higher strain-to-failure maintaining suitable tensile strengths is associated with fine microstructural spacings ($\lambda_c=36 \mu\text{m}$ and $\lambda_L=0.9 \mu\text{m}$), while the number of Zn particles per area is 0.93 μm^{-2} or higher. In order to achieve optimized ductility for the Sn-Zn eutectic with dissolved Cu from the mold, eutectic velocities as high as 0.6 mm/s or higher and solidification cooling rates of 1.2 K/s or higher may be required.

4. Conclusions

Two fronts of investigation were accomplished with the Sn-Zn eutectic solder. Both microstructure and mechanical behavior aspects have been focused on. The microstructure of the Sn-9 wt.%Zn alloy was formed by eutectic colonies. This is mainly constituted by the Sn-Zn eutectic mixture of β -Sn and α -Zn phases. Oriented Zn-lamellae formed colonies divided by coarse colony boundaries. Some number of Zn-lamellae appears in the boundary of the envelopes while a finer Zn-rich phase appears in the central areas of the eutectic colony as observed in both Sn-Zn/Cu mold and Sn-Zn/steel mold results.

The alloy solidified in the Cu mold was shown to have also the presence of the $\gamma\text{-Cu}_5\text{Zn}_8$ phase, caused by Cu dissolved into the alloy. This phase was the unexpected one according to thermodynamic calculations. However, the growth of the $\epsilon\text{-CuZn}_5$ phase was avoided due to the conditions far from equilibrium during solidification. As a result of the evaluation of the Sn + Zn eutectic microstructures, it was possible to

characterize the growth of the lamellar spacing, which was related to the eutectic velocity by a -0.4 power function exponent. Both higher solidification cooling rates and the presence of Cu in the molten alloy stage caused a better distribution of the Zn-lamellae.

The relatively small fraction of hard CuZn intermetallic particles, which resulted from solidification in the Cu mold, appears to be not enough to improve the tensile strength of the alloy. In contrast, a higher variation in ductility was shown to occur for the alloy samples solidified in the Cu mold. The combination of higher ductility and suitable tensile strength was shown to be associated with fine microstructural spacings ($\lambda_c=36\text{ }\mu\text{m}$ and $\lambda_L=0.9\text{ }\mu\text{m}$), and a number of Zn particles per area of $0.93\text{ }\mu\text{m}^{-2}$ or higher. This is thanks to solidification cooling rates higher than 1.2 K/s .

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Lidiane Silva Ramos: Data curation, Formal analysis. **Rodrigo Valenzuela Reyes:** Data curation, Formal analysis. **Leonardo Fernandes Gomes:** Data curation, Formal analysis. **Amauri Garcia:** Writing - review & editing. **José Eduardo Spinelli:** Funding acquisition, Writing - original draft. **Bismarck Luiz Silva:** Supervision, Writing - original draft.

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