On the ability of producing copper–silver functionally graded alloys by using an incremental melting and solidification process

L. Mazare, G. Miranda, D. Soares, F.S. Silva

Department of Mechanical Engineering, University of Minho, Azurem, 4800-058 Guimaraes, Portugal

ARTICLE INFO

Article history:
Received 16 January 2009
Received in revised form 27 May 2009
Accepted 27 May 2009

Keywords:
Functionally graded materials
Incremental melting and solidification process
Cu–Ag alloys

ABSTRACT

An incremental melting and solidification process (IMSP) has been used in order to obtain components with controlled gradient in chemical composition along one direction of the piece. The composition variation was externally induced by a sequential addition of different materials. To better assess the process of the chemical composition gradation the tests were performed in castings with and without externally induced chemical composition variation. The level of macro-segregation was also assessed in the different experiments.

Results demonstrated that a substantial gradual variation of chemical composition and metallurgical properties, along the component, may be obtained.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The IMSP is a new field of materials processing for the production of functionally graded materials and there is a substantial lack of information on this process.

As explained by Silva (2004) the operation principle can be described as follows: different materials are continuously fed to the mould and are melted by induction heating while at the bottom of the mould the materials are solidified because this mould position is water cooled. This procedure originates a gradual melting at the top of the casting, and solidification at the bottom of the casting. The IMSP proceeds from the bottom to the top of the mould by changing the relative position between the mold and the heating apparatus. Not many experiments exist on the use of this technique to produce functionally graded materials. There are, recently, some experiments on the process, made by Pinto et al. (2006) and Mazare et al. (2007). Jia et al. (1999) used the process but without chemical composition variation. He used it with a changeover in the reinforcement phase volume fraction (ceramic particles) along an homogeneous alloy. As stated by Jia et al. (1999), because of the few existing experiments with the IMSP the process is obviously not well established yet, and mainly, not well explored in different materials.

This process seems to be very promising because it allows the possibility of having local controlled properties on one single component using a casting process. It permits a new concept of materials design that may be used to respond to tailoring of complex shape components that will be exposed to different local in service demands, either mechanical or environmental, under particular applications. This may be the case of, for example, some engine components, where a component is locally at an extreme temperature and aggressive environment while the rest of the component is at a relatively lower temperature and in a completely different environment. Most of the engine components are subjected to these different in service demands. For example an intake or an exhaust valve works with substantial different temperatures and environments in the arm or in the head region of the valve. The same phenomenon exists on engine pistons, turbine blades, etc. It is common to use bi-materials in some components such as the exhaust valves or other engine components. Lee et al. (2004) used a friction welding process in order to join the dissimilar materials. According to Lee et al. (2004) the main problem on those bi-material components is the sharp transition between the dissimilar materials. This sharp transition may be the source for high thermal residual stresses and other mechanical and metallurgical detrimental features that reduce the component performance (for example the fatigue properties). Another process to produce FGMs was presented by Midson and Browne (2008). In Midson’s process, called CDC method—Cant–Decant–Cast there is a sequential addition of different alloys to the mould, with the possibility of obtaining 3D shape components. With thermal management it is possible to have some control of the transition zone. The IMSP is expected to allow the production of components with a smooth chemical transition between the dissimilar materials. This interface region might have lengths in the order of hundreds of micrometers to tens of millimeters, if necessary. The gradual transition allows for
a smoother transition in either metallurgical or mechanical properties of the materials and consequently produces components with an increased mechanical performance.

It is necessary, then, to understand how the metallurgical properties will evolve throughout the smooth chemical gradation and what properties, either chemical or metallurgical, will arise from the gradient.

This paper is concerned with the possibility of producing functionally graded Cu–Ag alloys with an extended transition region between two dissimilar materials.

Mazare et al. (in press) and Beckerman (2001) observed that an important aspect verified when using the directional solidification process is the possibility of having substantial macro-segregation effects when the cooling rates are very low. Kieback et al. (2003) showed that it is even possible to produce FGMs based macro-segregation effects. However, as reported by Mazare et al. (in press), when using the incremental melting and solidification process macro-segregation is not a desirable effect. It is important to understand if the gradient is due to an eventual macro-segregation effect or due to the incremental melting and solidification process parameters. Thus, in order to assess the influence of the cooling rate in each of the two base alloys used in this work, a series of tests was performed for each of the alloys in order to know what is the macro-segregation effect that is present with a certain mould/coil translation rate. These tests are important in order to split the effect of the IMSP and eventual macro-segregation effects in the test with sequential additions of materials.

It will be shown that the incremental melting and solidification process may be used to produce functionally gradient components with extended chemical composition gradients.

2. Materials and methods

2.1. Materials

To test the IMSP technology a simple alloy system (Fig. 1), was selected. The Ag–Cu phase diagram is constituted by an eutectic transformation and the limit solid solutions are characterized by a very low solute solubility at room temperature. No intermediate compounds (intermetallics or others) are formed in the system. Furthermore and in order to facilitate the process the pure metals do not have very different melting temperatures (Cu = 1084 °C and Ag = 981 °C).

Two base alloys (dissimilar materials) were tested: alloy A with Ag5%Cu and alloy B with Cu20%Ag (both in wt.%)(Fig. 1). It is worth to note that the two selected dissimilar alloys have substantial different 'liquidus’–'solidus' interval temperatures (alloy A has a small interval of about 50 °C while alloy B has a bigger interval of about 200 °C) (Table 1).

2.2. Methods

The materials castings were performed in an induction furnace, of 50–450 kHz, 5 kW from Ameritherm, in a mould moving inside of the induction coil (fixed) with a controlled dislocation speed as is schematically shown in Fig. 2.

The experimental technique consists in two steps: in the first step the mould is heated in a defined position inside the coil (pos. 1 in Figs. 2 and 4a) with or without the material inside; in the second step, after the mould reached a certain temperature (above liquidus temperature of the alloy inside the mould or to be added to the mould), the mould started to move downwards (the coil was fixed). During the mould movement different materials with selected chemical compositions can be added in defined moments (local specified temperatures).

The bottom of the mould is water cooled in order to promote a temperature gradient between the bottom and the top of the mould. Due to the current penetration and to the magnetic field direction (that causes liquid metal movement) differences may occur in the radial direction of the specimens. Thus, a thin specimen with a width of 6 mm (Fig. 3b) was used in order to avoid substantial differences in the radial direction. According to Davice and Simpson (1979) the current frequency should be such in order to optimize the penetration depth. The value of frequency selected in this work (Table 2) follows its optimization specifications.

The mould, made in graphite, has an external diameter of 30 mm. The obtained samples metallographic and hardness characterization were performed along the specimen’s central line.

2.2.1. Processing

Two different types of experiments were carried out:

(a) castings with sequential addition of the alloys during the casting. Alloys were sequentially added to the mould during the test, in order to generate a functionally gradient material—FGM;

(a) instant t1 and (b) instant t2.
(b) castings with homogeneous alloys (selected alloys A and B—Fig. 1). The mould was filled with the alloys (solid rod) at the beginning of the test.

The experiments with homogeneous alloys were performed in order to assess the macro-segregation effects in the alloys for different mould speeds.

Six thermocouples were placed inside the mould in order to capture the temperature profile with time along the process at six different points (see Fig. 3) from bottom to top of the specimen. The obtained specimen dimensions are shown in Fig. 3.

2.2.1.1. Incremental melting and solidification with sequential addition of dissimilar materials: from alloy B to alloy A. In this case a portion of the alloy B (5.532 g—solid state), was introduced in the mould and fully melt. Then the mould started to move downwards, at a rate of 0.1 mm/s. At a certain moment, when the lower part of the alloy was solidified and the upper part was still liquid, the alloy A was added (6.228 g—in the liquid state and at the alloy liquidus temperature) into the mould. The movement proceeded till the mould was out of the coil and then stopped (see pos. 3 in Figs. 2 and 4a). Throughout the whole process the mould was water cooled in the bottom and the induction heating power remained constant. With this procedure, at a certain moment, the temperature at the lower part of the mould is below the ‘solidus’, e.g., the material is solid, while the upper part of the mould is still at a higher temperature, still in the liquid state. The solidification is oriented from bottom to top of the casting. The obtained thermal cycles are similar to the one presented in Fig. 4 for the Ag-based alloy for a translation rate of 0.5 mm/s. Similar curves were obtained for the Ag-based alloy and for all translation rates used.

Three different mould rates were tested (0.1, 0.5 and 1.0 mm/s). Another test was performed without mould movement. This test was used for comparative terms, in order to know what could be the differences on the directional solidification effects in the samples metallurgical properties.

The obtained samples were characterized in terms of metallurgical and chemical properties, along the axial direction of the specimen. The experimental conditions are presented in Table 2.

The obtained samples were characterized in terms of chemical composition (by SEM/EDS) and microstructure (optical microscope), namely, by phase percentage quantification and secondary dendrite arm spacing (SDAS) quantification along the axial direction. Phase quantification was obtained using an image analysis technique.

2.2.1.2. Incremental solidification, with homogeneous alloys A and B, for different mould translation rates. These experiments were performed in two steps: in the first step the mould is heated in a defined position inside the coil (pos. 1 in Figs. 2 and 4a) (the alloy is inside the mould at the beginning of the test); in the second step, after the mould reached a certain temperature and the material was totally melted, the mould started to move downwards (the coil was fixed). Finally, the mould stopped when the mould was out of the coil (see pos. 3 in Figs. 2 and 4a). Throughout the whole process the mould was water cooled in the bottom and the induction heating power remained constant. With this procedure, at a certain moment, the temperature at the lower part of the mould is below the ‘solidus’, e.g., the material is solid, while the upper part of the mould is still at a higher temperature, still in the liquid state. The solidification is oriented from bottom to top of the casting. The obtained thermal cycles are similar to the one presented in Fig. 4 for the Ag-based alloy for a translation rate of 0.5 mm/s. Similar curves were obtained for the Ag-based alloy and for all translation rates used.

Another test was performed without mould movement. This test was used for comparative terms, in order to know what could be the differences on the directional solidification effects in the samples metallurgical properties.

The obtained samples were characterized in terms of metallurgical and chemical properties, along the axial direction of the specimen. The experimental conditions are presented in Table 2.

3. Results and discussion

3.1. Incremental melting and solidification with sequential addition of two different dissimilar materials: from alloy B to alloy A

In this experiment it was promoted a gradual chemical transition by a sequential addition of the two different base alloys. The obtained temperature curves are presented in Fig. 5.

The experiment started with the first material (Cu-based alloy) already inside the mould. The temperature increased until the alloy was fully liquid (Fig. 5a). The material filled only half of the mould (the related temperature positions are T5, T4, T3 and T2). The lower temperature is above the liquidus temperature of the alloy (T5 = 980 ºC) (Figs. 5 and 1). Then, after 400 s from the beginning of the test, the mould started to move downwards (at a rate of 0.1 mm/s). After some time there is a partial solidification of the Cu-based alloy inside the mould. The bottom part of the alloy, at temperature T5, is at a temperature below its solidus temperature (T5 < 780 ºC) but the top temperature of the alloy (T2) is still partially liquid (T2 in Fig. 5). The Ag-based alloy was then added in
the solid state (Fig. 5). The added Ag alloy will mix with the top part of the Cu alloy. As there is a temperature profile on the Cu-based alloy region, the mixing process should provide a gradient of chemical composition along the component. The obtained sample has a decreasing copper content from the bottom to the top part (Fig. 10b). The process proceeded till the mould was out of the coil region, with a constant mould rate (0.1 mm/s).

3.2. Incremental solidification, with homogeneous alloys, for different mould translation rates

These experiments were performed in order to assess what would be the eventual macro-segregation effects for different cooling rates (e.g., mould translation rates), on the castings. This aspect is important in order to split what are the effects of macro-segregation and what are the effects of the incremental melting process (additional material pouring). Fig. 4 presents the solidification curves and the relative position of the mould in relation to the coil for the alloy A and for a mould translation rate of 0.1 mm/s. Similar curves were obtained for the Cu-based alloy and for all translation rates.

The first part of the thermal cycle (melting of the first added alloy) is the one with the mould and coil fixed. It can be seen that, just before the mould starts moving downwards (approx. 400 s), due to the relative position of the mould in relation to the coil and to the proximity of the mould bottom (thermocouple $T_5$) to the cooling system (Figs. 3 and 4a), the temperature at the bottom of the mould is lower than the temperatures in all other positions, in about 100 °C (Fig. 4a and b). The second part of the thermal cycle is when the mould starts to move downwards. The main aspect to
highlight (Fig. 4) is that the movement has a strong influence in the temperature profile along the mould: temperatures $T_3$, $T_4$ and $T_5$ start to decrease but $T_0$, $T_1$ and $T_2$ increases for a certain period. A point to underline is that these profiles are strongly dependent on the dimensions of the coil and the mould used. In these particular experiments the height of the mould is bigger than the one of the coil (see Figs. 3 and 4). After few seconds, when $T_0$ reaches the peak temperature, all the temperatures start to decrease. It is observed that temperatures, at this moment, have a difference of about 350 $^\circ$C between the extreme positions, $T_0$ and $T_5$ (Fig. 4b) and provide a regular step among the different thermocouples between top and bottom of the mould.

It is important to highlight that the coil geometry and mould geometry, along with water cooling system and power input, are important process variables in the obtained temperature profiles. Studies with the particular influence of each of these parameters will be presented in future papers.

It can be seen in Fig. 4 (example for the alloy A) that at the end of part one of the thermal cycle (approx. 400 s) the alloy inside the mould is completely melt (all temperatures are above the alloy liquidus temperature ($920^\circ$ C)). When part two of the thermal cycle starts (at the moment when the mould starts the downwards movement) the temperatures start to decrease in positions $T_5$, $T_4$ and $T_3$ and the first solid phase is formed in the mould bottom zone (with the lower temperatures) when the temperature $T_5$ decreases below $920^\circ$C and becomes completely solid when $T_5$ reaches 870 $^\circ$C (see Figs. 1 and 4). The solidification continues gradually from bottom to top along the piece vertical axis.

It is worth to note that after temperature $T_0$ reaches the peak value, all the temperatures in different positions show a different decreasing temperature rate (see detail in Fig. 12) as well as different solidification intervals. These casting characteristics will have a substantial effect on metallurgical features.

3.3. Cooling rate

The cooling rates, during the solidification interval (from 920 to 870 $^\circ$C for alloy A and from 980 to 780 $^\circ$C for alloy B), for the different mould translation rates are presented in Table 4 and Fig. 12. In Table 4 it is possible to see the cooling rates and observe that they are similar to the ones obtained in Table 3 (for the graded alloys) for the same translation rate. Results presented in Table 4 shows that the cooling rate is higher for position $T_0$ and lower for position $T_5$. Thus, although the solidification sequence is from position $T_5$ to position $T_0$ the solidification rate follows the opposite sequence. Only for the experiments without mould movement the solidification rate is higher at the sample bottom part and solidification sequence follows from bottom to top parts. It is interesting to observe that for the each mould dislocation speed, the cooling rates are very different along the sample vertical axis.

3.4. Solidification interval

Another process variable that affects the solidification process is the solidification time interval for each experiment. Table 5 presents the solidification time interval, along the sample, for the tested mould translation rates. These values where measured as the interval time between the sample bottom and top parts reaches the solidus temperature (see Figs. 1 and 4). It is clear that, in both
alloys, the lowest solidification time interval is obtained for the test with no mould dislocation rate (0 mm/s) because the coil power is switched off after the alloy is fully melted. For the other tests the lower the mould dislocation rates the higher the solidification interval time because the coil remains switched on for a longer period. There is a huge change when the mould rate varies from 0.5 to 0.1 mm/s, which means that the period of time in which liquid and solid phases are in contact is much higher for the lower mould translation rates. This allows a higher element separation (macro-segregation) for the test bottom of the mould is also water cooled. In this test the bottom of the mould is also water cooled.

3.5. Comparative casting—homogeneous alloys without mould movement

As a comparative term, temperature profiles in tests with no movement of the mould are also provided. Fig. 6 presents temperature profiles obtained in the castings of the Ag base alloy without mould movement. Part one of the cycle (melting of alloy) is similar with the castings with mould movement but after the alloy is fully melt and the induction power is switched off the temperatures start to decrease in all positions. The obtained temperature profiles are very different from those in Fig. 5. The maximum temperature difference in the different mould positions, at the solidification interval, is less than 100°C (much lower than the obtained in Fig. 5), and the temperature decreasing rates are very similar among the different positions (Table 4).

The solidification still proceeds from bottom to top. Cooling rates between positions are now closer and, contrarily to the tests with mould movement, increase from top to bottom of the mould. In this test the bottom of the mould is also water cooled.

4. Metallurgical analysis

4.1. Incremental melting and cooling with sequential addition of two different dissimilar materials: from (Cu20%Ag) to (Ag5%Cu)

For the test with chemical composition evolution from alloy B to alloy A, imposed by two material additions, it is worth to highlight the following aspects: between the initial and final alloys chemical composition there is an eutectic transformation (Fig. 1). Thus, chemical composition of the resulting sample will start with an alloy rich in the (Cu) phase (Fig. 7a) in the bottom region. The eutectic constituent (light colour phase in Fig. 7) increases till a certain region in the middle region of the sample (Fig. 7b) and from that point on the (Ag) richer phase increases till the top region of the sample (Fig. 7c–e). The resulting chemical composition evolution along the sample is shown in Fig. 9b. It can be seen that the bottom region maintains the chemical composition of the initial alloy (Cu-based alloy), then there is a region with an evolution of chemical composition and finally there is a zone with an homogeneous chemical composition which is a mix of part of the copper alloy (the liquid part) and the added Ag-based added alloy. This result shows that it is possible to obtain a transition region of about 10–15 mm with a chemical composition gradient between initial alloys.

From the obtained result it is clear that it is possible to obtain different lengths for the transition regions. It can be obtained, for example, by using other processing parameters with different temperature gradients or adopt a procedure with more sequential additions of material. For example, after the first addition of a Cu rich alloy two or more additions of the Ag-based alloy may be used (Fig. 8).

The solidification rates along the sample vertical axis are shown in Table 3. The evolution of the SDAS along the sample vertical axis is presented in Fig. 9a. This graph shows that for higher solidification rates the SDAS is smaller. As a fact Table 3 shows that the solidification rates increases from bottom to top region of the sample (T5) and SDAS (Fig. 9a) evolves in the opposite sense (compare values of Fig. 9a with Table 3).

According to Kurz and Fisher (2005) these results, lower SDAS with higher solidification rate (lower solidification time) have a general acceptance for a wide range of different alloys.

Thus, from the previous result it is demonstrated that it is possible to obtain FGMs—functionally gradient materials by using the IMSP—incremental melting and solidification process.

However, as explained by Beckerman (2001) it is known that when using processes with directional solidification, as is the case of the IMSP, there is the possibility of having substantial macro-segregation effects mainly for low solidification rates. Thus in order to assess if the gradient is due to an eventual macro-segregation effect or due to the incremental melting and solidification process, a series of tests was performed for each of the based alloys, with different cooling rates due to different mould translation rates.

4.2. Incremental cooling, with homogeneous alloys, for different mould translation rates

Figs. 10 and 11 present, as an example, the microstructure of one series of tests (mould rate of 0.1 mm/s) for the two homogeneous
alloys. The microstructures are representative of the bottom, middle and top regions of the obtained specimens. The first aspect to highlight is that there is a gradual variation of microstructure. It is clear the difference in secondary dendrite arm spacing (SDAS), mainly for the Cu-based alloy. The SDAS decreases from bottom to top. As a fact, although the bottom region is the first to solidify the solidification rate is lower in that region (see Table 4).

These micro-structural changes can be explained by the solidification rates. In Fig. 12 are represented the solidification rates for both homogeneous alloys and in Fig. 13 is represented the SDAS along the sample vertical axis. It is clear the relationship between solidification rates and SDAS.

The cooling rates and consequently SDAS are also related to mould translation rates. Higher mould translation rates imply higher solidification rates and lower SADS values. For example for the test with 1 mm/s of mould translation rate the solidification rate increases from bottom to the top of the casting and the SDAS decreases in the same direction (Figs. 12 and 13 and Table 4). For the fastest mould translation rate (1 mm/s) the cooling rates are the highest in all positions and the SDAS values are the lowest.
For the test with ‘no mould movement’ it is observed the same logic including that there are closer solidification rates along the whole component and consequently closer SDAS values.

Regarding the chemical composition it is observed that for translation rates of 0.5 mm/s and for 1 mm/s there is no substantial change in the chemical composition along the component for both the Ag-based alloy and for the Cu-based alloy. Regarding the lower translation rate (0.1 mm/s) and for the Cu-based alloy, it is observed that although the initial alloy chemical composition was homogeneous along the component, there is a change in the copper content from 84% in the bottom to 75% (wt.%) in the top. An average percentage of 80% was expected according to the phase diagram. However, the Cu content increases at the bottom and decreases at the top.

This change in chemical composition, for low mould translation rates, is explained by the elements distribution in solid and liquid phase during the solidification interval. The first phase to solidify is much richer in (Cu) phase (95%Cu) (Fig. 1). The remaining liquid phase on the bottom region inside the mould, solute, with a higher silver content, will move to the top region of the mould and will gradually solidify in the upper zones of the mould. This is known as macro-segregation phenomena (Beckerman, 2001). Further to this the time spent on solidification (solidification interval) was much bigger for the lower translation rate (see Table 5) and there was more time for the solute to move upwards. As a fact with the increase in the mould translation rates the solidification rate also increases (Table 4), and there is no time for the liquid phase to move from the bottom to the top region of melt. Thus the distribution of (Cu) phase and eutectic constituent is more homogeneous along the sample.

While the macro-segregation occurs for the Cu-based alloy it did not occur for the Ag-based alloy. As expected, the phenomena of material transfer from bottom to top region, macro-segregation, is alloy dependent. The reason lies on the solidification interval, solute partition coefficient and on the available time for the transfer to occur. As a fact the Cu alloy has a solidification interval of about 200°C between the liquidus and solidus temperatures (Fig. 1) while in the Ag alloy it is only of about 50°C. This means that for similar solidification rates, there is much less time for the transfer to occur in the Ag alloy then in the Cu alloy. As a fact, the solidification interval time (Table 5) is lower for the Ag-based alloy and for the lower translation rate.

According to Kieback et al. (2003), macro-segregation effects have an extensive list of causes which may include microstructure, thermal gradients, applied magnetic fields, movement of solid fragments, alloy composition, purity, etc. However, in this system, the translation rate (cooling rate) of the mould and the solidification interval seem to be, according to Beckerman (2001) the fundamental variables responsible for the macro-segregation occurrence.

The previous results have shown that the IMSP—incremental melting and solidification process allows the production of FGMs—functionally graded components. It is also clear that the obtained functionally graded casting is essentially a consequence of the IMSP. In Fig. 9b it can be seen that the amount of Cu (in wt.%) changes from 80% (bottom) to about 35% (top). However, part of the gradient is also due to the macro-segregation effect. As a fact as the test was performed at a low mould translation rate there was, most probably, some macro-segregation effect on the Cu-based alloy. In Fig. 14b it can be seen that, for the mould translation rate of 0.1 mm/s the amount of Cu (wt.%) changes from 84% in the bottom to about 75% in the top.

It is expected that only by carefully coordinating the imposed temperature profiles along the piece (by changing the power input along the casting) with the characteristics of the new materials additions (chemical composition, addition time, quantity of added material and temperature of the added material (solid or liquid state)) it will be possible to control the final chemical composition gradation, phase morphology distribution and respective mechanical properties. It will be also possible to minimize the
5. Conclusions

The main conclusions of this work can be drawn as follows:

- the incremental melting and solidification process allow the production of materials with controlled graded chemical compositions;
- a smooth controlled gradient transition, in the Ag–Cu alloy system, was produced with two material additions;
- the incremental solidification process is strongly dependent on the solidification characteristics of the alloy, as imposed by the mould translation rate;
- homogeneous alloys may result in non-homogeneous castings if the solidification rates allow a macro-segregation phenomena.

References


