Evaluation of Hot Tearing in 925‰ Silver Alloys

Abstract

Hot tearing is the formation of a fracture in a metal casting during solidification, as a result of hindered contraction. In this study we tried to evaluate the hot tearing susceptibility of different silver alloys with 925‰ fineness. Several studies on hot tearing susceptibility of casting alloys are known, but we have not been able to find information on precious alloys. Therefore we wanted to characterize 925‰ silver alloys, that, according to our experience, are more prone to this kind of problem.

A classic 925‰ silver alloy was taken into consideration, and we evaluated the effects of additions of other elements. We compared the different behavior of binary, ternary and quaternary alloys, with and without small additions of elements such as deoxidizers or grain refiners. Besides, we carried out a metallurgical analysis on cracked areas, trying to correlate the behavior of the alloys with their microstructure.

This paper is a part of a wider research aiming to obtain silver alloys with high resistance to tarnish and a reduced tendency to hot tearing.

Introduction

Hot tearing occurs in castings when the contraction of the material is hindered during solidification. Our experience says that hot tearing during solidification occurs more frequently in silver castings than in gold alloy castings and we studied this phenomenon in sterling silver (Ag 925‰).

Hot tearing consists in the formation of macroscopic cracks in the material. These cracks are initiated above the solidus temperature of the alloy and grow with interdendritic and intergranular mechanism. Hot tearing can be ascribed to two main causes acting together during solidification. Firstly to the shrinkage of the alloy during the liquid to solid transformation. Consequently internal stresses arise that are stronger in more complicate molds (these are shrinkage – or contraction - stresses). Moreover, during solidification, the cooling rate is different in the different parts of the castings (in this case too it depends on the geometry of the casting), so the shrinkage stresses can be favored or strengthened.

Secondly, the alloying additions and the impurity elements tend to segregate, causing an increase of concentration both at microscopic and macroscopic scale. Therefore segregation causes inhomogeneity of the mechanical, physical and chemical properties of the alloy. In the last stages of solidification coalescence of the dendrites and formation of "solid bridges" among the branches of the dendrites take place. An increased concentration of low melting components in the liquid among the dendrites lowers solidification temperature and causes the formation of a mushy zone.
In the case of dendrites belonging to a single grain, the formation of interdendritic bridges takes place as soon as the branches of the dendrites come into contact, because there is no grain boundary energy to overcome. Coalescence becomes less immediate when the dendrites belong to different grains, because grain boundary energy is higher than the energy of the liquid-solid interface. Therefore more supercooling, i.e. a lower temperature, is required for the formation of interdendritic bridges. This consideration can explain why hot tearing causes intergranular fractures. The interdendritic liquid layers at the grain boundaries remain in the liquid state at lower temperature and for longer time than in the inner part of the grains. In addition to the above phenomena, we should also take into account the effect of other parameters, such as the solidification range, the temperature distribution in the castings and alloy composition. Theory shows that a wide solidification range (i.e. a marked difference between liquidus and solidus temperatures) favors the formation of shrinkage stresses for a longer time in the last solidifying zones. On the contrary, the alloys with a narrow solidification range show a lower sus-

ceptibility to hot tearing (e.g. eutectic alloys). Segregation widens the equilibrium solidification range, lengthens the permanence of a liquid layer among the dendrites and consequently increases the susceptibility to hot tearing. Therefore alloys containing a small quantity of a eutectic component should be particularly prone to hot tearing.

Longitudinal temperature gradients in the casting increase the probability of hot tearing, because they favor the occurrence of the so called “hot spots”. In the zones where the alloy stays longer in the liquid state, solidification requires a longer time to become complete. Therefore hot tearing defects are caused by a large number of interconnected factors. An alloy could show hot tearing only for some shapes of the casting and of the mold, so hot tearing occurs only for some shapes and for other shapes does not occur. Fundamentally, there are two main causes for hot tearing: the specific properties of the alloy and the characteristics of the mold.

Models and tests for studying hot tearing

The study of the resistance to hot tearing has been preceded by an evaluation of the test to be used. The development of a mathematical model describing hot tearing is very difficult, because it is necessary to know the mechanical behavior of the solid phase and the properties of the liquid ow in the interdendritic spaces. Therefore different authors based their studies on quite different parameters. We can say that the fundamental phenomena causing hot tearing are well understood on a qualitative basis, but a general quantitative criterion to evaluate the occurrence of hot tearing in the various conditions of casting has still to be found.

In this work we aim to quantify hot tearing susceptibility for different sterling silver alloys by means of laboratory tests. We need to be able to compare the behavior of different alloys, to develop a composition with reduced susceptibility to hot tearing. The ground principle for the tests is to cause shrinkage stresses, by hindering the free contraction of the castings. There are two kinds of tests for this purpose: the “dog bone test” and the “ring mold test”.

We selected the dog bone test, because it is more practical and more suitable to our goals. There are many versions for the geometry of the dog bone specimens, but all of them share the formation of a hot spot by means of an abrupt change of the cross section of the casting. For our tests we selected the model named CRC (Constrained Rod Casting) mold that has been developed by the Alcan International Ltd, Kingston Research & Development Center, with some adjustments based on our specific needs and experience.

The test specimen consists of four bars with different length, fed by a single sprue. In each bar there is a half sphere on the end near the sprue (this will form a hot spot) and a complete sphere on the far end. In this way two sudden changes of cross section hinder the free contraction of the bar during solidification. The longer bars will tend to contract more than the shorter bars, so the stresses acting on the solidification zones will be higher in the longer bars, that will crack first. The extent of cracking in each bar will be used to quantify the susceptibility to hot tearing.

Experimental tests

As said above, a dog bone test was used. Initially, we decided to use a graphite mold with the dimensions shown in Figure 1.

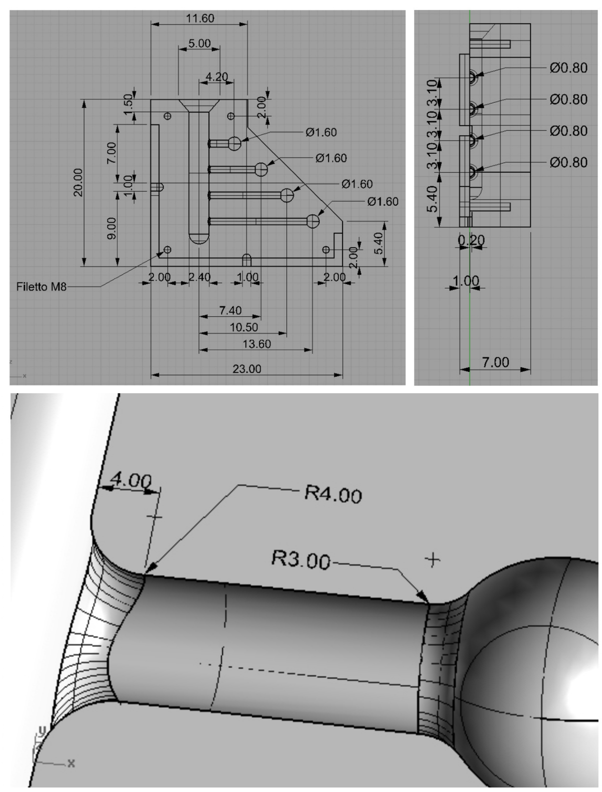
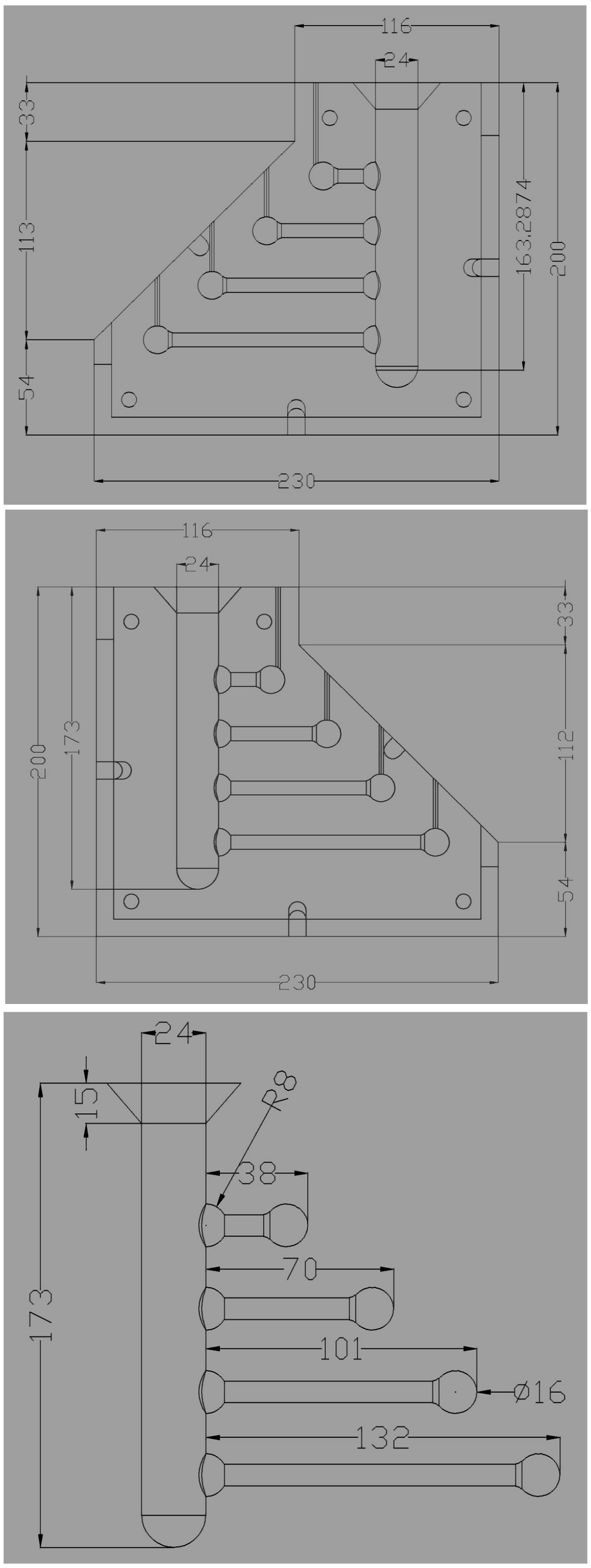


Figure 1 – Drawing of the graphite mold

The mold was heated to 300°C (572°F) in an oven. The graphite mold was used to make a set of preliminary tests aiming to find whether the selected dimensions and geometry would produce useful results. After these preliminary tests, a nodular cast iron mold was built. On the basis of the results obtained from the preliminary tests, some modifications were carried out on the cast iron mold.Namely, a hemisphere was added on the main sprue corresponding to the different bars. In our opinion, this modification facilitated the ow of the molten metal and improved the sensitivity of the test by reducing the effect of the main sprue (the cross section for stress concentration was equal to the cross section of the far end of the bar). This conclusion was reached after testing different types of fillet between the sprue and the bar. Figure 1 shows the fillet used with the graphite mold. The dimensions of the cast iron mold are given in Figure 2. The thickness of the closed mold is 100mm.



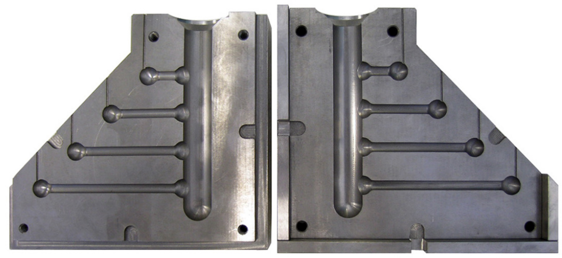


Figure 2 – Drawing of the cast iron mold

From Figure 2 it can be seen that the mold produces four cylindrical bars with different lengths. The critical zones correspond to the hemispheres present on the feeding sprue. In these critical zones a marked change of cross section can create a hot spot, and strong tensile stresses are generated by the contraction of the metal during solidification. The shorter bars only show crack evidence when cast with the alloys most prone to hot tearing.

The different alloys susceptible to hot tearing were evaluated by observing with the naked eye the size of the cracks that develop in the critical zones of the test bars. The zones near the hemisphere show the lowest loss of heat and are the last to solidify. If we also consider the change of cross section, these are the most critical zones for stress concentration and crack initiation.

Five levels of severity were set for hot tearing that are identified with numbers from 0 to 4:

- 0 corresponds to a sound, undamaged bar with no cracks
- 1 denotes a bar with small, barely visible cracks
- 2 denotes a bar with at least one well defined crack extending over about half of the circumference of the bar,
- 3 denotes a bar with a crack extending over the full circumference of the bar,
- 4 denotes a fully cracked bar, with separation of the parts.

Examples of the different cracking levels are shown in Figures 3-6.

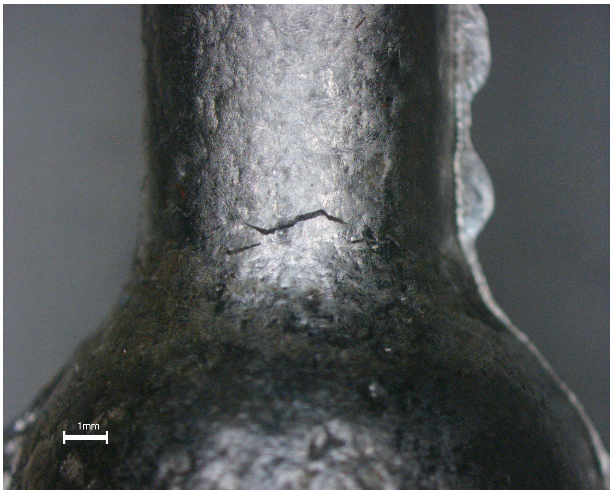


Figure 3 - Example of level 1 crack

Figure 4 - Example of level 2 crack

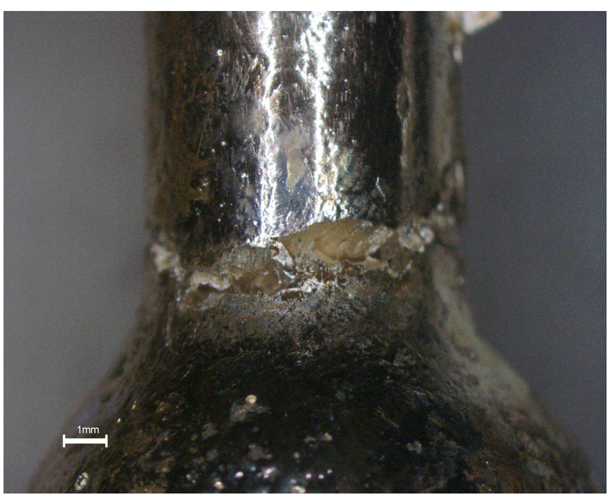


Figure 5 - Example of level 3 crack

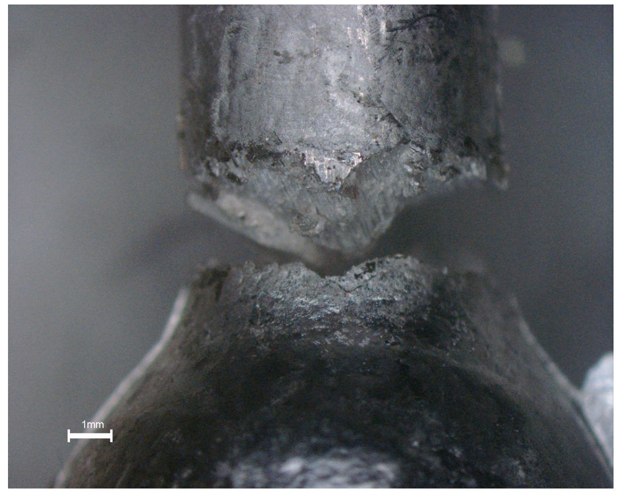


Figure 6 - Example of level 4 crack

The composition of the alloys to be tested were selected to get a detailed evaluation of the effect of some alloying elements on hot tearing, starting from the standard commercial compositions. For each composition four casting runs were carried out to also verify the consistency of the results.

Fourteen alloy compositions were cast in the first set of tests. These are ternary alloys containing silver, copper and additions of Si, Zn, Ga, In, Sn, Bi and Ge. These elements were added separately and, in the case of Si and Zn, with different concentrations. As expected, the castings showed cracks or rupture next to the hot spot, and the longest bars were the most frequently cracked.As expected, the castings showed cracks or rupture next to the hot spot and the longest bars were the most frequently cracked.

Alloy	Ag	Cu	Si	Zn	Ge	Ga	In	Sn	Bi
1	925	75							
2	925	74,9	0,1						
3	925	74,5	0,5						
4	925	74	1						
5	925	73	2						
6	925	72	3						
7	925	67,5	7,5						
8	925	70		5					
9	925	65		10					
10	925	65			10				
11	925	70				5			
12	925	70					5		
13	925	70						5	
14	925	70							5

Table 1 - Composition of the first set of alloys (‰)

Different silicon concentrations were tested, because silicon is frequently used as a deoxidizer. Also, zinc is frequently added, so different zinc concentrations were tested. Other elements used for obtaining special characteristics, such as germanium for its antitarnishing properties, were also tested.

All alloys were cast from 1050°C (1922ºF) and the mold was heated to 300°C (572ºF) in an oven. Open casting equipment was used and the melt was protected with 10% hydrogen forming gas. Pouring was carried out with the mold tilted 17.5° because results are more repeatable in this condition. A silicone non-stick product was used to facilitate the removal of the castings from the mold.

Nine hundred grams of alloy were used for each casting operation. No pre-melting was carried out because the melt was stirred with a graphite rod before pouring. This practice was considered sufficient to homogenize the melt. Graphite crucibles were used and different crucibles were used for the different alloys. The mold was opened one minute after pouring and the castings were air cooled to room temperature.

The liquid metal was not filtered or degassed because the process commonly used by silversmiths was followed. The castings were then submitted to visual evaluation and the defects were classified with the above described criteria.

The results are shown in Table 2.

Alloy	Bar 3				Bar 2				Bar 3				Bar 4			
1	4	4	4	2	3	2	2	3	0	0	1	0	0	0	0	0
2	4	4	4	4	3	3	1	3	0	2	0	1	0	0	0	0
3	4	4	4	4	4	3	4	3	0	3	2	1	0	0	0	0
4	4	4	4	4	4	3	2	4	1	3	1	1	0	0	0	0
5	4	4	4	4	4	3	3	4	1	3	1	1	0	0	0	0
6	4	4	4	4	3	3	4	4	2	3	2	2	0	0	0	0
7	4	4	4	4	4	4	4	3	3	3	3	3	0	0	0	0
8	4	4	4	4	2	2	1	1	1	1	1	1	0	0	0	0
9	2	4	4	3	1	3	2	3	1	1	1	1	0	0	0	0
10	4	4	4	4	4	4	4	4	4	4	4	4	2	3	3	4
11	4	4	4	4	4	4	4	4	1	2	1	2	0	0	0	0
12	3	4	4	4	3	3	2	4	1	1	1	3	0	0	0	0
13	4	4	4	4	3	3	2	3	1	1	1	2	0	0	0	0
14	4	4	4	4	4	4	4	4	1	3	2	3	0	0	0	0

Table 2 – Results of the tests

Bar 1 is the longest specimen while Bar 4 is the shortest one. A sketch with the denomination of the different bars and a picture of a casting are shown in Figures 7 and 8

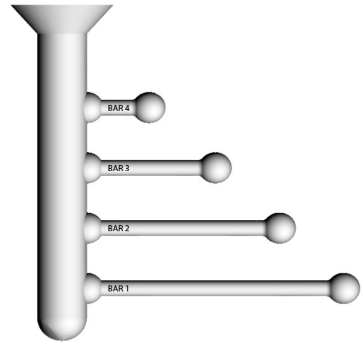


Figure 7 - Sketch with the names of the bars

Figure 8 - Picture of Alloy 1 – cast 1

It should be noted that Alloy 1 showed an anomalous behavior because in the fourth casting operation, Bar 1 (more prone to hot tearing) showed a cracking level lower than Bar 2. This is the only such case observed in this set of casting operations. For each bar type the four values of the cracking level are given, obtained with the above described criteria from four casting operations.

In the third casting operation with Alloy 1, Bar #1 (the longest) showed complete rupture and was given level 4, while Bar #2 showed a well-defined crack on approximately half the circumference and was given level 2. Bar #3 showed only some small, barely visible cracks and was given level 1. Bar #4 was sound and was given level 0.

To evaluate the hot tearing susceptibility of an alloy, an index named HTS (Hot Tearing Susceptibility) was used and was calculated with the following formula:

$$\text{HTS} = \sum_{1=4}^{4} \text{Ci} \times \text{Bi}$$

where Ci is the cracking level in the considered bar (0 to 4) and Bi is a value related to each bar type. This is 1 for Bar #1, 2 for Bar #2, 3 for Bar #3 and 4 for Bar #4.

It was decided to give the value 1 to the longest bar, which shows the minimum resistance to hot tearing and gradually higher values to the shorter bars that show higher resistance to hot tearing. Therefore, referring to the above example, i.e., the third casting operation with Alloy 1, we have:

HTS = (4 x 1) + (2 x 2) + (1 x 3) + (0 x 4) = 11

Higher values of HTS will correspond to lower resistance of the alloy to hot tearing. The values of HTS calculated for the first set of 14 alloys are given in Table 3.

Alloy	HTS values					Standard deviation
	Cast 1	Cast 2	Cast 3	Cast 4	Average	
1	10	8	11	8	9,25	1,5
2	10	16	6	13	11,25	4,27
3	12	19	18	13	15,5	3,51
4	15	19	11	15	15	3,27
5	15	19	13	15	15,5	2,52
6	16	13	18	18	16,25	2,36
7	21	21	21	19	20,5	1
8	11	11	9	9	10	1,15
9	7	13	11	12	10.75	2,63
10	32	36	36	40	36	3,27
11	15	18	15	18	16,5	1,73
12	12	13	11	21	14,25	4,57
13	13	13	11	16	13,25	2,06
14	15	21	18	21	18,75	2,87

The average values of HTS indicate that Alloy 1 (the Ag-Cu binary alloy) shows the better resistance to hot tearing. The addition of silicon lowers the resistance to hot tearing, and Si additions of 0.1% or higher cause a marked increase of HTS and a pronounced worsening of hot tearing resistance.

We could hypothesize that a high content of low-melting components could be favorable because more liquid metal in the interdendritic spaces could tend to fill and so to 'heal' the previously formed cracks. But in the case of silicon we can say that it drastically reduces the resistance to hot tearing, and the results worsen with larger silicon additions.

Also, zinc additions seem to increase HTS, even if much less drastically than silicon. Moreover, zinc concentration seems not to be proportional to the HTS increase.

Germanium seems to be a true 'poison' for silver alloys. Gallium, indium and tin show a similar behavior in increasing HTS; they give average HTS values similar to alloys with silicon additions.

Bismuth seems to increase HTS, even if less than germanium. From this first set of 14 tests we could infer that the addition of other elements to the base Ag-Cu alloy increases HTS. The results are summarized in Figure 9.

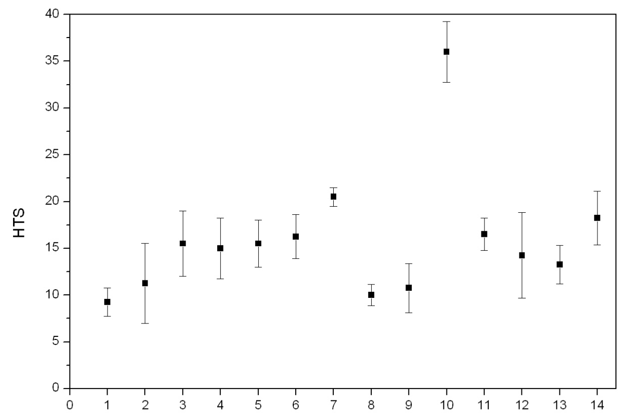


Figure 9 - HTS values for Alloys 1 to 14

These results can be ascribed to the increased grain size of the alloys, together with an increased amount of low-melting components in the interdendritic spaces. Therefore, we added 11 more alloys to our study. The compositions are shown in Table 4.

Alloy	Ag	Cu	Zn	Si	Ga	In	Sn	Bi	P
15	925	60	10		5				
16	925	60	10			5			
17	925	60	10				5		
18	925	60	10					5	
19	925	64,75	10						0,25
20	925	64	10						1
21	925	63	10						2
22	925	48	10	2	5	5	5		
23	925	48	10	2	5	5		5	
24	925	69		1	5				
25	925	55,5	16,5	3					

Table 4 - Composition of the second set of alloys (‰)

Alloys 15 to 21 aimed to study the behavior of quaternary alloys. Alloys 15 to 18 contain gallium, indium and tin in addition to zinc because such compositions are used in everyday practice. It was decided to keep zinc concentration to 10‰, because little difference has been observed between 5‰ and 10‰, and 10‰ is a commonly used zinc concentration in commercial alloys.
Alloys 19-21 were added to investigate the effect of phosphorous on HTS because phosphorous is a very good deoxidizer and can be used for removing oxygen from pure silver. Alloys 22-25 correspond to commercial alloys available from several suppliers.
The results of the cracking evaluation on the alloys of Table 4 are shown in Table 5.

Alloy	Bar 1				Bar 2				Bar 3				Bar 4			
15	4	4	4	4	3	4	3	4	0	2	1	1	0	0	0	0
16	3	4	3	4	2	4	3	3	1	3	2	2	0	0	0	0
17	4	4	4	4	4	4	3	2	1	1	3	1	0	0	0	0
18	4	4	4	4	4	4	4	4	4	3	4	3	0	0	0	0
19	4	4	4	4	4	4	4	4	2	1	2	2	0	0	0	1
20	4	4	4	4	4	4	4	4	4	4	4	4	0	0	1	1
21	4	4	4	4	4	4	4	4	4	4	4	4	1	0	1	1
22	4	4	4	4	4	4	4	3	3	2	3	2	0	0	0	0
23	4	4	4	4	4	4	4	4	4	4	2	4	0	0	0	0
24	4	4	4	4	4	4	4	4	1	3	1	2	0	0	0	0
25	4	4	4	4	4	4	4	4	3	3	4	3	1	0	0	0

Table 5 - Results of the tests

The values of HTS calculated for these alloys are shown in Table 6.

Alloy	HTS values					Standard deviation
	Cast 1	Cast 2	Cast 3	Cast 4	Average	
15	10	18	13	15	14	3,37
16	10	21	15	16	15,5	4,51
17	15	15	19	11	15	3,27
18	24	21	24	21	22,5	1,73
19	18	15	18	22	18,25	2,87
20	24	24	28	28	26	2,31
21	28	24	28	28	27	2
22	21	18	21	16	19	2,46
23	24	24	18	24	22,5	3
24	15	21	15	18	17,25	2,87
25	25	21	24	21	22,75	2,06

Table 6 - HTS values for the different alloys

Apparently the separate addition of gallium, indium, tin and bismuth along with zinc does not worsen the HTS values, which are not far from the results obtained in the absence of zinc. As far as phosphorus is concerned, we see that HTS figures increase with increasing concentration of phosphorus. Therefore, it should be necessary to add the exact stoichiometric amount of phosphorus required to remove the oxygen present in pure silver. The results of these tests show that the use of phosphorus in silver alloys should be very carefully evaluated.

The concomitant addition of silicon, gallium, indium and tin (Alloy 22) causes a marked increase in HTS when compared with the addition of the single elements. The replacement of tin with bismuth causes a further worsening of the situation, and bismuth caused a marked increase in HTS also when added alone.

Alloy 24 showed a slight increase in HTS when compared with the alloys containing the single elements separately. Alloy 25 showed a considerable increase in HTS when a high zinc concentration is used along with silicon (compare with Alloy 6). There seems to be a synergic effect between these elements, but the effect of a high zinc concentration should be more accurately investigated. Figure 10 summarizes the results obtained from Alloys 15 to 25.

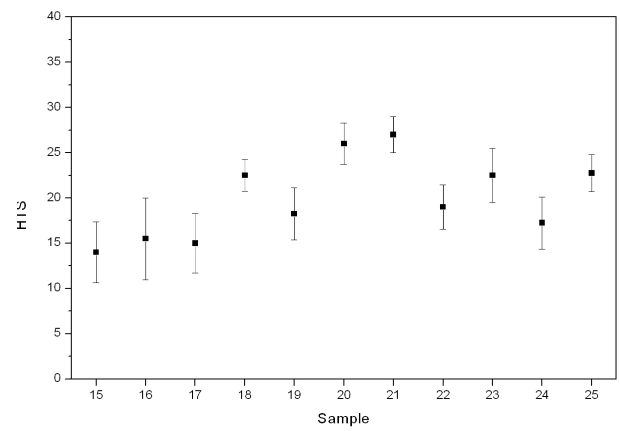


Figure 10 - HTS values for Alloys 15 to 25

In conclusion, in these 25 tests where the additional elements commonly used in silver alloys were investigated, no alloy was found showing a good resistance to hot tearing.

The study was then extended to evaluate the effect of the addition of grain refiners. Two different commercial grain refiners for sterling silver were tested. Four alloys were cast, two alloys (Alloys 26 and 27) with a grain refiner named "Refiner I" and one alloy (Alloy 28) with a refiner named "Refiner II." One more alloy without refiner addition (Alloy 29) was used as a reference for Alloy 28. No reference alloy was required for Alloys 26 and 27, whose composition was similar to some previously tested.

Tables 7-9 show the composition of the alloys, the results of the tests, and the calculated values of HTS.

Alloy	Ag	Cu	Si	Zn	Ga	GR I	GR II
26	925	64,95		10		0,05	
27	925	68,92		3	3	0,08	
28	925	64,43	0,5	10			0,07
29	925	64,5	0,5	10			

Table 7 - Composition of the third set of alloys (‰)

Alloy	Bar 1				Bar 2				Bar 3				Bar 4			
26	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
27	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
29	4	1	4	4	3	3	4	2	1	2	1	1	0	0	0	0

Table 8 - Results of the tests

Alloy	HTS					Standard deviation
	Cast 1	Cast 2	Cast 3	Cast 4	Average	
26	1	0	0	1	0,5	0,58
27	1	0	0	0	0,25	0,5
28	0	0	0	0	0	0
29	13	13	15	11	13	1,63

Table 9 - HTS values for the different alloys

The improvement obtained with the addition of grain refiners is quite evident. The grain refiners strongly reduce the problem of hot tearing and nearly eliminate it (these results could be expected from the theory and everyday practice). The explanation could be found in the deformation theory of hot tearing, where the increased number of grains more easily accommodates the stresses in the final stages of solidification.

We underline that Alloy 26 (with refiner) shows a very low value of HTS (0.5) while Alloy 9, with the same composition but without grain refiner, shows an HTS of10.75. Also, Alloy 27 shows a very low HTS value. In this case an alloy with the same composition but without grain refiner was not tested because the same results of Alloys 26 and 9 were expected. In this case the results of Alloy 15 can also be considered, even if the higher concentration of zinc and gallium makes it more prone to hot tearing.

It is also interesting to note that Alloy 28 shows an HTS of 0 while the same alloy without grain refiner shows a high HTS value. In our opinion this is the most interesting result because this grain refiner was different from the one used in Alloys 26 and 27, and above all because of the simultaneous presence of zinc and silicon. For this reason it was decided to also cast Alloy 29. It should be noted that Alloy 29 shows an HTS value lower than Alloy 3, even if the preceding observations indicate that increasing zinc concentration with constant silicon concentration could lead to higher HTS values.

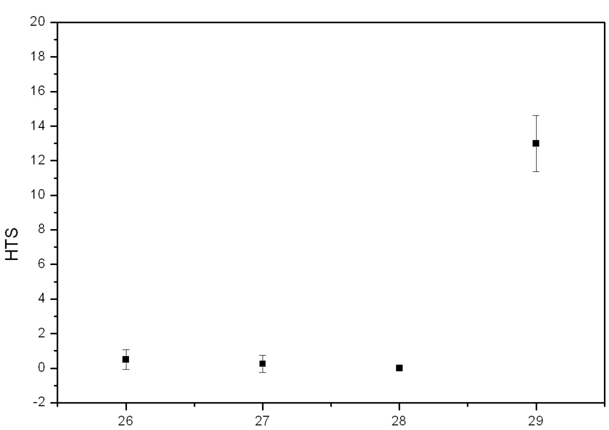


Figure 11 - HTS values for Alloys 26-29

After testing this wide range of alloys (many of them available on the market), we observed the fracture surfaces of the various cast bars under the microscope. Both an optical stereoscopic microscope and a scanning electron microscope (SEM) were used. All the fractures were of intergranular type and probably propagated along the grain boundaries because of the presence of low melting components. A detailed observation of the fractured surfaces was carried out with the SEM.

A set of SEM images of surface fractures is shown in Figures 12-23. Only a few samples are shown as examples of the surface morphology of the fractures. The aim of this work was not to understand the mechanism of hot tearing, but obviously a better understanding of the phenomenon helps to find a solution.

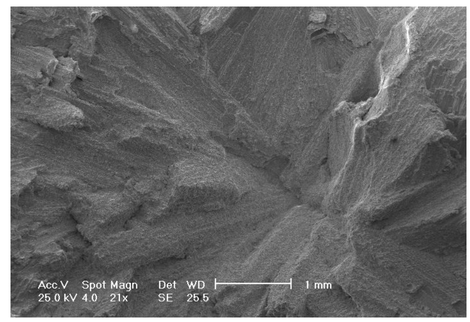


Figure 12 - Alloy 1, low magnification

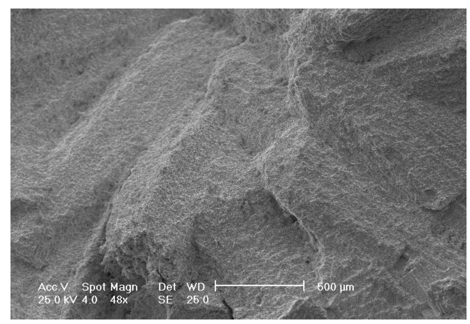


Figure 13 - Alloy 1, medium magnification

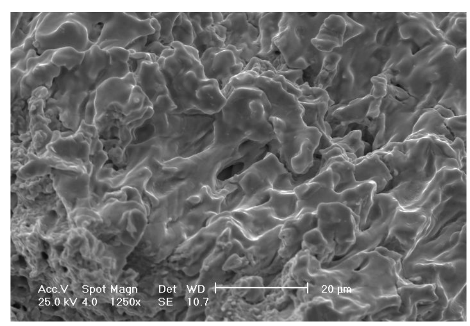


Figure 14 - Alloy 1, high magnification

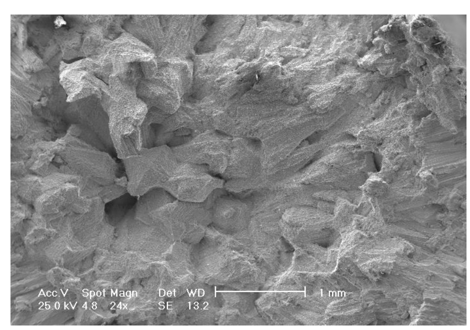


Figure 15 - Alloy 5, low magnification

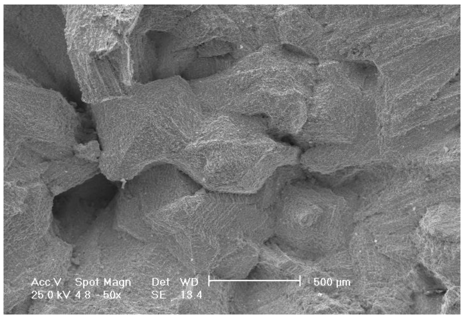


Figure 16 - Alloy 5, medium magnification

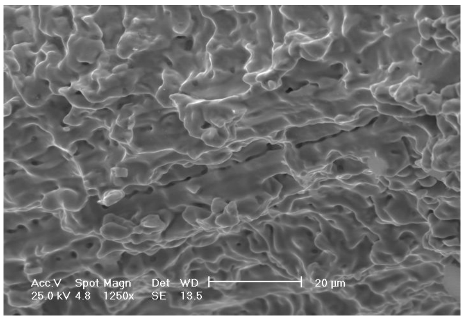


Figure 17 - Alloy 5, high magnification

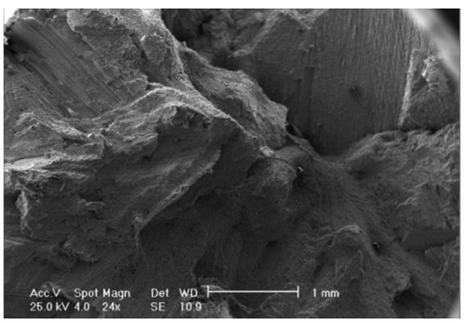


Figure 18 - Alloy 8, low magnification

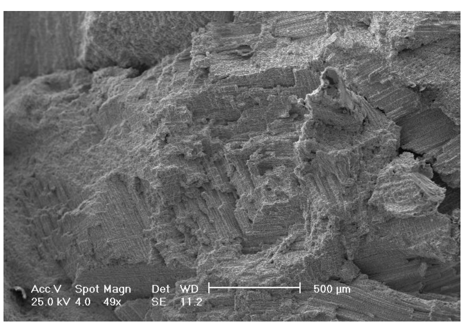


Figure 19 - Alloy 8, medium magnification

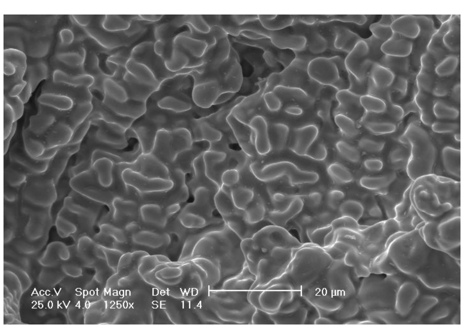


Figure 20 - Alloy 8, high magnification

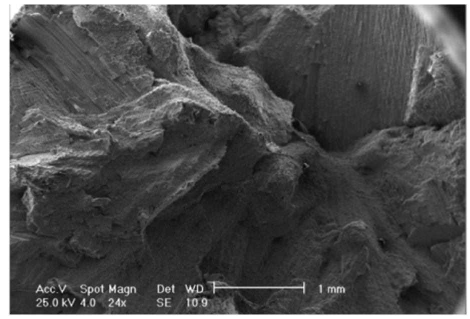


Figure 21 - Alloy 23, low magnification

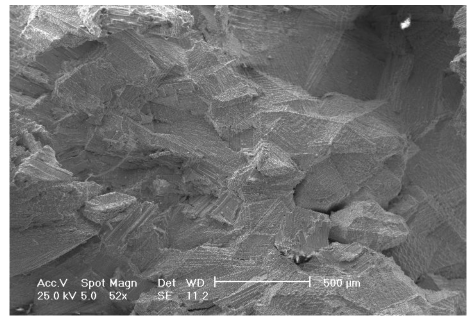


Figure 22 - Alloy 23, medium magnification

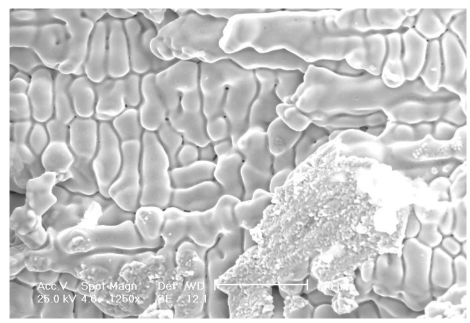


Figure 23 - Alloy 23, high magnification

SEM observations showed different types of fracture surface morphology: fracture surfaces with a coarse dendritic structure and surfaces partially covered by a eutectic phase with a dendritic structure with secondary phases. In both cases the fracture started from an interdendritic separation in the mushy zone and propagated along the grain boundaries. The dendritic structure is more evident in Alloy 8.

The presence of a marked solidification shrinkage is the more evident feature in the fracture surfaces. In all cast alloy specimens there is a notable extent of dendritic surface where regular pores (or bubbles) can frequently be seen (see the above SEM images).

This observation led us to hypothesize that other phenomena should also be taken into account in hot tearing. Some researchers correlated hot tearing with solidification shrinkage through the pressure drop in the liquid phase. These authors considered the effect of the pressure drop connected with the solidification shrinkage and with the deformation occurring in the stage near the solidification of the mushy zone. The thermal stresses cause deformations leading to hot tearing during the transition from liquid to solid state. But hot tearing is also correlated with solidification shrinkage. Both of these phenomena tend to reduce the pressure in the liquid. If this pressure lowering exceeds a critical value, hot tearing can be initiated and propagated, starting from pores or air bubbles. According to this theory, hot tearing always takes place at the grain boundaries, starting from the interdendritic liquid or from pre-existing microporosity or air bubbles generated by solidification shrinkage.

We will not delve further into theory, but we wanted only to evidence that many regularly placed pores (or air bubbles) have been observed under the SEM near the fracture surfaces. These could in some way be related to the observed fractures. More pictures taken from the alloys already observed are shown in Figures 24-27.

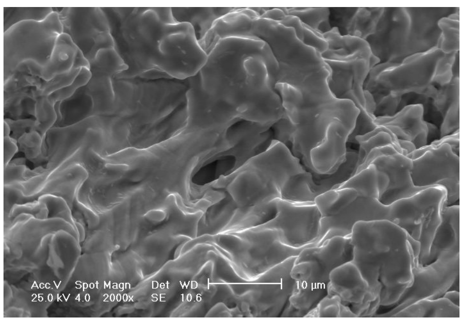


Figure 24 - Alloy 1, SEM image showing pores near the fracture surface

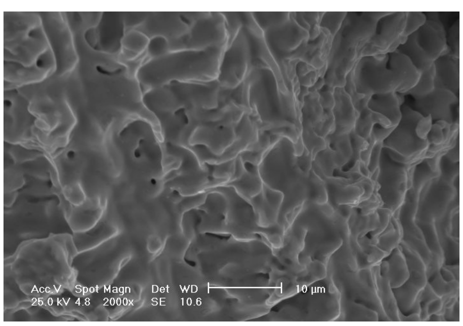


Figure 25 - Alloy 5, SEM image showing pores near the fracture surface

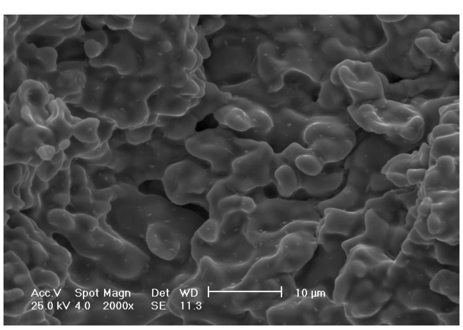


Figure 26 - Alloy 8, SEM image showing pores near the fracture surface

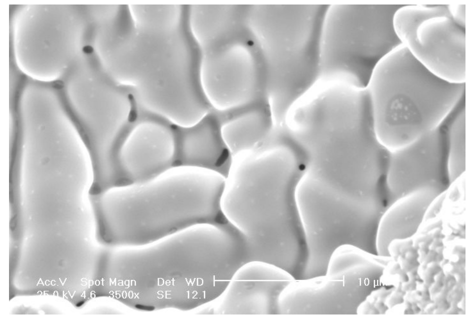


Figure 27 - Alloy 23, SEM image showing pores near the fracture surface

On the basis of the results obtained in the 29 casting tests and of the effect of the addition elements on the HTS of the 925‰ silver alloys, we tried to develop an alloy with reduced HTS without resorting to grain refiners.

We tried this approach because silver alloys should also show 'aesthetic' properties such as high resistance to hot temperature oxidation (firescale) or to tarnishing. Obtaining such properties frequently requires the addition of elements that strongly increase HTS, as shown from our tests (e.g., gallium, indium, tin, germanium, silicon). At the same time these additions are scarcely compatible with the commonly used grain refiners; they show too high affinity to grain refiners and give rise to well-known problems (hard spots).

Therefore, we tried to develop a copper-free 925‰ silver alloy since alloys showing low-melting components or a small quantity of eutectic phase are more prone to hot tearing. The silver-copper binary alloys show a eutectic so we tried to use alloys without eutectic. Therefore, we should find a suitable alloying element different from copper to which elements giving specific properties should be added. Obviously the added elements (that are always the same) increase HTS, but an element different from copper could reduce or at least not increase the adverse effects of the small additions. The ideal solution should be to use an element with complete mutual solubility with silver in the liquid and solid phase with limited tendency to generate secondary phases.

Examination of binary phase diagrams of silver showed that the only elements satisfying this condition are gold and palladium, which are too expensive, and tests have not been carried out with such elements. Therefore, we fell back on elements with good solubility in solid 925‰ silver. Tin, bismuth and zinc were found to be suitable. Gallium, indium and cadmium could also be suitable, bugallium and indium are expensive and there are toxicity problems with cadmium, so these last elements were not tested.

Three casting operations were carried out by adding tin, zinc or bismuth to the silver. The composition of the alloys and the results of the casting tests are given in Tables 10-12.

Alloy	Ag	Cu	Sn	Bi	Zn
30	925	0	75		
31	925	0		75	
32	925	0			75

Table 10 - Composition of the fourth set of alloys (‰)

Alloy	Bar 1				Bar 2				Bar 3				Bar 4			
30	0	4	2	4	1	3	0	3	4	1	0	0	0	0	0	0
31	4	4	4	4	4	4	4	4	4	4	4	4	3	1	4	2
32	3	3	3	2	2	3	2	1	1	0	2	0	0	0	0	0

Table 11 - Results of the tests

Alloy	HTS					Standard deviation
	Cast 1	Cast 2	Cast 3	Cast 4	Average	
30	14	13	2	10	9,75	5,44
31	36	28	40	32	34	5,16
32	10	9	13	4	9	3,74

Table 12 - HTS values for the different alloys

The first casting operation of Alloy 30 gave anomalous results because Bar 1 was sound, while Bar 2 showed small cracks. Alloy 32 (with zinc) gave the lowest average HTS value, followed by Alloy 30 (with tin) showing a slightly higher HTS. However, Alloy 30 gives a high standard deviation because the third casting operation gave discordant results.

The bismuth-containing alloy turned out to be very prone to hot tearing. The average HTS values of Alloys 30 and 32 are similar to the HTS values of Alloy 1 (with copper). Therefore, we decided to investigate the effect of silicon additions to the silver-tin alloy. We selected tin because we think there is a better probability of increasing the hardness of the alloy with a suitable heat treatment, even if we have no confirmation of this hypothesis.

Six alloys were cast with different additions of silicon and zinc to investigate the effect of zinc. Also a small quantity of copper was present in the alloys because a copper-silicon master alloy was added. The results are shown in Tables 13-15.

Alloy	Ag	Cu	Zn	Si	Sn
33	925	0,9		0,1	74
34	925	4,5		0,5	70
35	925	9		1	65
36	925	0,9	10	0,1	64
37	925	4,5	10	0,5	60
38	925	9	10	1	55

Table 13 - Composition of the fifth set of alloys (‰)

Alloy	Bar 1				Bar 2				Bar 3				Bar 4			
33	3	3	3	3	2	3	0	0	2	2	1	2	0	0	0	0
34	4	4	4	4	4	4	3	2	2	1	2	2	0	0	0	0
35	4	4	4	4	3	3	3	4	3	2	3	2	0	0	0	0
36	4	4	4	4	2	3	2	4	1	1	0	0	0	0	0	0
37	3	4	4	4	3	3	4	4	1	2	1	2	0	0	0	0
38	4	4	3	4	4	2	2	2	2	2	2	2	0	0	0	0

Table 14 - Results of the tests

Alloy	HTS					Standard deviation
	Cast 1	Cast 2	Cast 3	Cast 4	Average	
33	13	15	6	9	10,75	4,03
34	18	15	16	14	15,75	1,71
35	19	16	19	18	18	1,41
36	11	13	8	10	10,5	2,08
37	12	16	15	18	15,25	2,5
38	18	14	13	14	14,75	2,22

Table 15 - HTS values for the different alloys

The results are scarcely different from those of Alloys 2, 3 and 4 containing copper and the same amount of silicon. The addition of zinc to Alloys 36, 37 and 38 does not change HTS appreciably, with the exception of the alloy with the highest silicon content. These last tests seem to show that using an alloying element different from copper does not change HTS values of silver alloys when low melting components are present, namely silicon eutectics. Therefore, hot tearing can be ascribed to a low-melting, silicon-containing eutectic. The results are summarized in Figure 28.

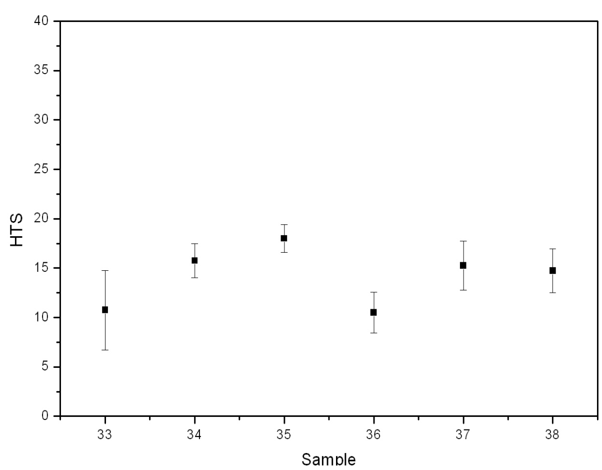


Figure 28 - HTS values for Alloys 33-38

It was planned to cast three silver-zinc alloys with three different silicon concentrations, but these tests have yet to be done.

Surface fractures of Alloys 30 and 36 were observed under the SEM, (Figures 29 to 34).

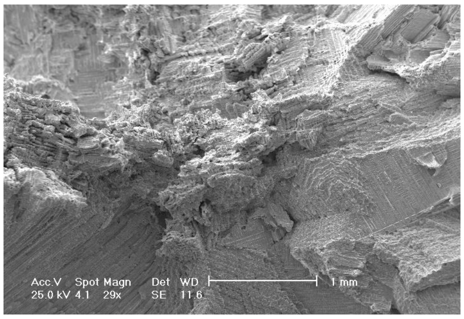


Figure 29 - Alloy 30 fracture surface, low magnification

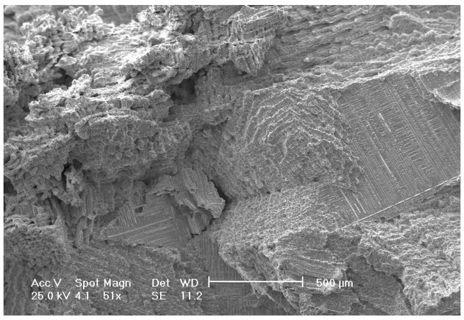


Figure 30 - Alloy 30 fracture surface, medium magnification

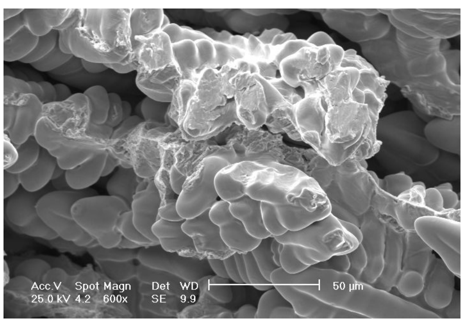


Figure 31 - Alloy 30 fracture surface, high magnification

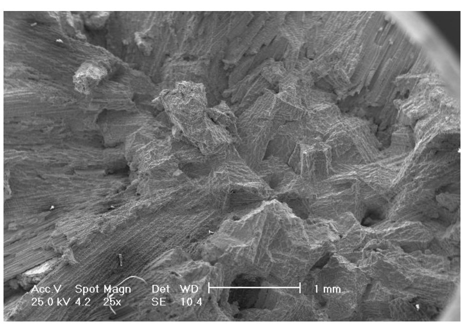


Figure 32 - Alloy 36 fracture surface, low magnification

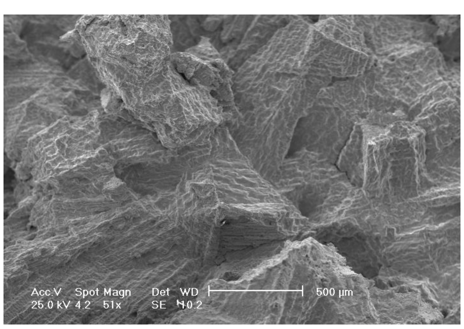


Figure 33 - Alloy 36 fracture surface, medium magnification

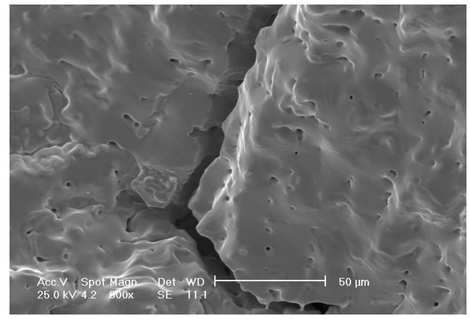


Figure 34 - Alloy 36 fracture surface, high magnification

Figures 29-34 confirm the observations made on the preceding alloys. Alloy 30 shows a larger amount of dendrites and more solidification shrinkage than alloys 33-38.

Conclusions

The evaluation of HTS for different alloys required the development of a suitable laboratory test to compare the different compositions. In our opinion, the developed test is meaningful and convenient. The observed ruptures took place in the expected places, and in some cases there were discrepancies that can be accepted in experimental tests. Moreover, both long and short bars cracked so we can assume that the size range selected for the bars was suitable for the desired aim.

Generally, the addition of alloying elements caused an increase in HTS. This can be ascribed to two different effects: the increase of grain size and the segregation of low-melting interdendritic components. The more alloying elements are added, the worse the behavior for hot tearing seems to become.

The technique of pouring the molten metal in the mold has not been investigated. An automatic pouring system should be developed to fill the mold in a consistent way.

Two different methods were followed to eliminate or mitigate hot tearing, according to the theory on this subject. The first was the addition of a grain refiner. This addition succeeded in the near elimination of hot tearing. The second was the substitution of copper with another alloying element. This method did not give acceptable results, but only a small range of compositions was investigated. It is certainly worth making a more extensive investigation.

A diagram summarizing the average HTS values calculated for all the investigated alloys is shown in Figure 35.

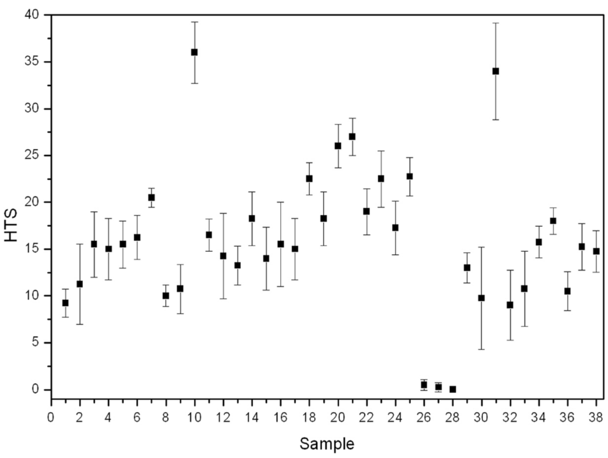


Figure 35 - Average HTS values for Alloys 1-38

The HTS values seem to allow a meaningful comparison among the different alloys. However, a more detailed comparison could be obtained by developing other types of parameters that, for example, could give the hot tearing susceptibility for each bar.

In our opinion hot tearing should be correlated with shrinkage microporosity. In all samples observed under the SEM, an appreciable shrinkage porosity has been found. Therefore, a deeper investigation of the correlation between these phenomena could be useful.

The results evidenced a considerable scattering of the experimental data (high standard deviation) for some alloys. This could depend on the fact that only four casting tests were carried out for each alloy. But maybe the importance of some variables, such as the gas content of the raw materials, could have been neglected.

Our experience says that the type of silver used for the tests could affect the end result. The equilibrium diagram says that pure silver can contain up to about 300ppm of oxygen. We presume that oxygen content could modify the end result. For the sake of precision, several grains of pure silver taken from the batches used for the experiments were subjected to ICP analysis to look for minor impurity elements. The results of ICP analysis showed that pure silver does not contain important amounts of impurity elements. The following elements were detected: Ca, Fe, Bi, Co, Ni, Pb, Mo and W, but their concentration was always below 10ppm.

Suitable gas analyzers were used for evaluating oxygen and hydrogen concentration. The results obtained with the gas analyzers were more interesting. Hydrogen was not detected, but the oxygen content changed from grain to grain In all, 16 grains were analyzed and the oxygen content varied from 222ppm to a maximum of 395ppm. The results are shown in Table 16.

	Measured O2 content [ppm]							
Ag 999,9‰	395	222	325	325	286	295	260	280
	317	318	276	252	390	321	257	307

Table 16 - Oxygen content in pure silver grains

It is advisable to evaluate the effect of oxygen content on the resistance to hot tearing. Technical papers give con icting theories. The presence of gas could be useful for pushing the residual liquid in the growing cracks, favoring the healing of the defects and increasing the resistance to hot tearing. On the other side, an excessive amount of gas could increase porosity and reduce the resistance to hot tearing.

We should try to remove oxygen completely from pure silver (e.g., argon gas could be bubbled in the liquid metal) and repeat the 38 casting operations to see if there could be a change in the already determined HTS values.

A complete study with computer simulations has not been considered. This kind of study could give useful information on the ow of the liquid metal, on the solidification process, and on stress concentration. This type of study could be done in the future.

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