Applicability of Permanent Mold Casting for Lead Free Bronze with Sulfide Dispersion

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ABSTRACT

The leaded bronze, the leaded brass, the lead free bronze including bismuth and the lead free bronze with sulfide dispersion were cast into the permanent mold for the solidification cracking test. The applicability of the permanent mold casting process for bronzes was evaluated with comparison of the range of the solidification temperature.

The lead free bronze with sulfide dispersion was more unbreakable than the other copper alloys. There were differences of the dendrite form near by the fracture and the distribution of the residual melt segregated at a part of the end of the solidification. The lead free bronze with sulfide dispersion may have a solidification form being unlikely to crack. It dispersion is possible to apply the permanent mold castings process rather than the other copper alloys, and the applicability is almost same as brass castings.

Keywords: copper, alloy, permanent mold, casting, lead free bronze, solidification cracking, sulfide, dispersion

INTRODUCTION

The conventional leaded bronze casting (CuSn5Zn5Pb5) used for a valve and a water joint is produced by the sand mold casting process. On the other hand, the permanent mold casting for the conventional leaded bronze casting has not been researched very much because it has been reported that the conventional leaded bronze is not suitable for the permanent mold casting process due to cracking and the outside shrinkage[1].

Nevertheless, the permanent mold casting process for the bronze has been required for an improvement in productivity of bronze castings because the sand mold casting process has low productivity and makes a foundry dirty.

Therefore the permanent mold casting process for the lead free bronze has been required more than for the conventional leaded bronze because lead is harmful element and the use of lead has been restricted in the world[2-5].

Bi and Se are added to the lead free bronze developed until now. However, Bi and Se have difficulty in ensuring a stable supply and cost because they are scarce elements and Bi is produced from a byproduct of lead refinement.

Therefore we took sulfide into account as a substitute of lead and developed the lead free bronze with sulfide dispersion (Cu-Sn-Zn-Ni-S alloy). The alloy decreases porosity by sulfide formation at part of final solidification[6], and the sulfide has solid lubricity as lead and become chip breaker during cutting[7]. The alloy was certified as Japanese Industrial Standards (JIS) and is expected to be increasingly used.

The lead free bronze with sulfide dispersion is expected to have possibility of the permanent mold castings process because the alloy is expected not to cause the solidification cracking due to more narrow range of the solidification temperature than those of the conventional leaded bronze and other lead free bronzes[8].

However, the permanent mold casting process for the lead free bronze has not been researched. Therefore, we research on the applicability of the permanent mold casting process, especially occurrence of solidification cracking.

EXPERIMENTAL PROCEDURE

The nominal compositions and casting temperatures of the alloys are given in Table 1. There are 4 types of alloy; the lead free bronze with sulfide dispersion (BWL), the conventional leaded bronze (Pb bronze), the lead free bronze including Bismuth (Bi bronze), the bronze not including lead and sulfur (S free BWL) and the leaded brass (Brass). The amount of each alloy was 3.5kg. Raw materials were ingots, pure metals and a Cu-P alloy for deoxidation. The alloys were melted in a graphite crucible lined by alumina cement in a high-frequency induction furnace (30kVA). The alloys were poured into a permanent mold for solidification cracking test and the mullite wool mold for thermal analysis.

Table 1 The nominal compositions and casting temperatures of the alloys.

Sample	Nominal composition (mass%)									Casting temp. /K
	Cu	Sn	Zn	Ni	Fe	S	Pb	Bi	P	
BWL	Bal.	4.0	2.5	0.5	<0.5	0.58	—	—	0.05	1473
Pb bronze	Bal.	5.0	5.0	<1.0	<0.3	—	5.0	—	0.05	1443
Bi bronze	Bal.	5.0	6.5	—	—	—	—	1.5	0.05	1423
S free BWL	Bal.	5.0	2.5	0.5	—	—	—	—	0.05	1473
Brass	Bal.	—	31.0	—	—	—	2.0	—	0.05	1373

The shape and size of the permanent mold for solidification cracking test[9] is shown Fig. 1. Tensile stress is generated in the linear part of the casting because both ends of casting are fixed by flanges of the permanent mold. The solidification crackability of the alloys was evaluated by changing the distance between flanges, L. Table 2 shows the distance between flanges of the permanent mold for the solidification cracking test and the length of the insulator. The linear part of the permanent mold was insulated with the insulator for ease of occurrence of the solidification cracking at the center of castings. Hence, the length of the insulator was smaller than the distance between flanges. The permanent mold was lined by acetylene smog and preheated at 393K.

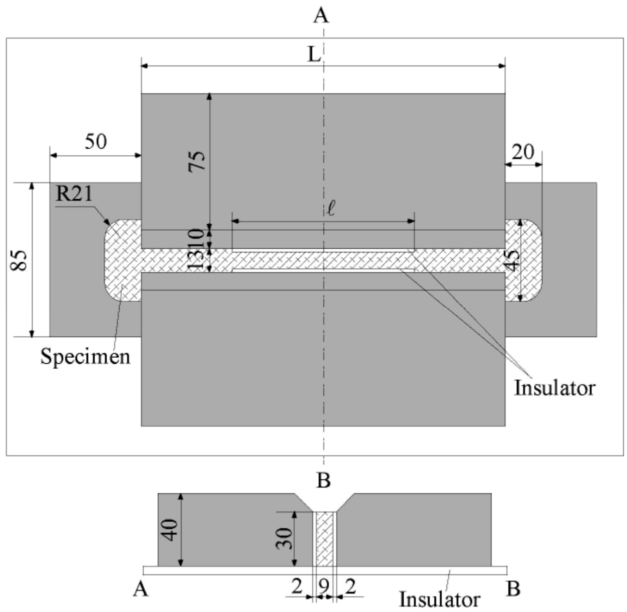

Fig. 1 The shape and size of the permanent mold for solidification cracking test[9].

Table 2 The distance between flanges of the permanent mold for the solidification cracking test and the length of the insulator.

Distance of flanges, L /mm	Length of insulator, ℓ /mm
30	28
50	45
70	60
100	70
200	100

The shape and size of the mullite wool mold for thermal analysis is shown Fig. 2. Almel-chlomel thermocouple was inserted into the mullite wool mold to measure the solidification temperature of castings.

Appearance, fracture and microstructure on the samples were observed.

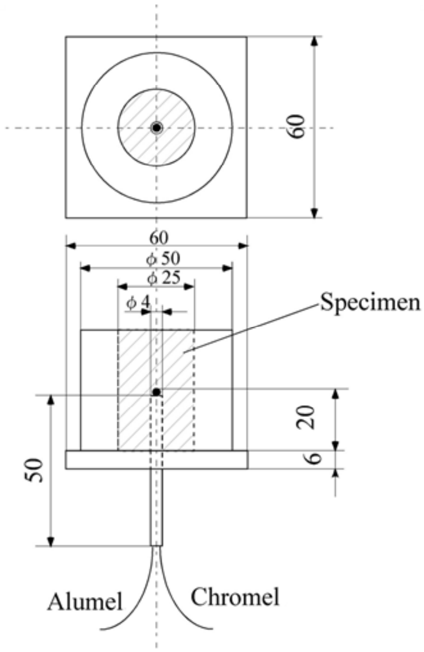

Fig. 2 The shape and size of the mullite wool mold for thermal analysis.

RESULTS AND DISCUSSION

Fig. 3 shows the appearance of various Cu alloy castings on the permanent mold for the solidification cracking test. The appearance of castings was observed to evaluate degree of the solidification cracking of alloys. The degree is classified into three types. If there is no crack on the sample, the degree is defined as "No cracking". If there is crack on the sample without separation, the degree is defined as "Partial cracking". If the sample is fractured completely, the degree is defined as "Complete cracking".

There is one crack on samples having "Complete cracking", whereas there are some cracks on samples having "Partial cracking". Pattern of the cracking didn't depend on composition of alloys and the distance between flanges. It is considered that the solidification cracking formed near by a part of the final solidification because it has the weakest strength in castings. From these appearances, it is difficult to estimate where the initial point of the solidification cracking is. It is difficult to know the direction of the solidification because three sides of the mold are covered by insulator. Therefore, it's necessary to find out how melt solidifies, for example, temperature profile in castings.

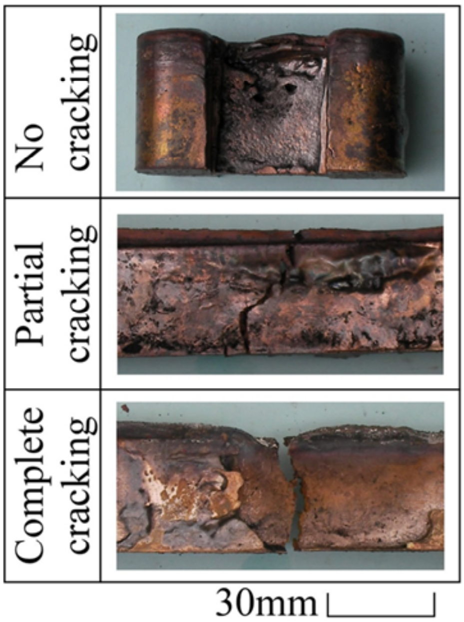

Fig. 3 The appearance of various Cu alloy castings on the permanent mold for the solidification cracking test.

Fig. 4 shows relation between the range of the solidification temperature and the degree of the solidification cracking in the distance between flanges on various Cu alloy castings on the permanent mold for the solidification cracking test. In the lead free bronze with sulfide dispersion (BWL), "No cracking" occurred on 30mm of the distance and "Partial cracking" occurred on longer than 50mm of the distance. In the conventional leaded bronze (Pb bronze) and the lead free bronze including Bi (Bi bronze), "Partial cracking" occurred on smaller than 100mm of the distance and "Complete cracking" occurred on longer 200mm of the distance. In the bronze not including lead and sulfur (S free BWL) and the leaded brass (Brass), "Partial cracking" occurred from 30mm to 200mm of the distance.

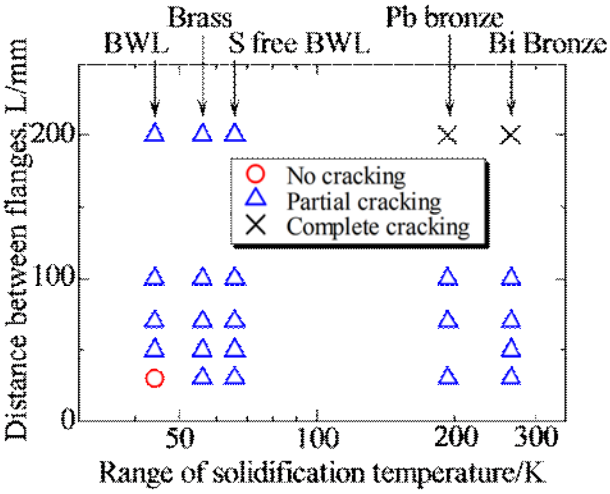

Fig. 4 Relation between the range of the solidification temperature and the degree of solidification cracking in the distance between flanges on various Cu alloy castings on the permanent mold for solidification cracking test.

The larger the distance between flanges, the easier to create the solidification cracking in samples. The tensile stress is caused by the solidification shrinkage because castings were restricted with the permanent mold. The tensile strength of castings does not change even if the solidification shrinkage increases with increasing the distance between the flanges. Therefore, the solidification cracking occurs when the tensile stress due to the solidification shrinkage exceeds the tensile strength of the casting. The longer the maximum distance between flanges when "No cracking", the more difficult to create the solidification cracking. The lead free bronze with sulfide is the most difficult to create the solidification cracking. The maximum distance between the flanges, without the solidification cracking, decreases with increasing the range of the solidification temperature. With increasing the range of the solidification temperature, the solidification type changes from skin formation type to mushy type. If the alloy has wide range of the solidification temperature, the residual melts at interdendrites are separated at a part of the final solidification.

In beginning of the solidification, the cracking part due to the solidification shrinkage can be healed by filling the melts into the cracking part. However, it's especially difficult to heal the cracking when the residual melts are separated.

When the tensile stress occurring by the solidification shrinkage exceeds the strength at solid-liquid mixture during the solidification, the solidification cracking occurs. Therefore, the larger the range of the solidification temperature, the easier the solidification cracking occurs. Fig. 4 shows castings with narrow range of the solidification temperature tend not to form the solidification cracking. There is no difference when the range of the solidification temperature is larger than 200K.

Fig. 5 shows the appearances of the fracture of various Cu alloy castings on the permanent mold with 200mm of the distance between the flanges. Samples of the lead free bronze with sulfide dispersion (BWL) and the bronze not including lead and sulfur (S free BWL) were broken for observation of the fracture because they were not broken due to "Partial cracking". In all samples, the fracture was oxidized and have very uneven surface.

Fig. 6 shows secondary electron images (SEI) and element distributions by EDX analysis on the fracture of various Cu alloy castings on the permanent mold for the solidification cracking test. In all samples, especially the lead free bronze including Bi (Bi bronze) and the bronze not including lead and sulfur (S free BWL), the structure of fracture was formed into the shape of the dendrite and smooth. Oxygen was detected on the fractures overall. It is confirmed that the solidification cracking occurred in all samples during the solidification. In the conventional leaded bronze (Pb bronze), the lead free bronze including Bi (Bi bronze) and the leaded brass (Brass), there are a lot of part with Pb-rich or Bi-rich on dendrite. On the other hand, in the lead free bronze with sulfide dispersion (BWL), a number of S-rich parts on dendrite is smaller, and a size of S-rich part is larger than that in the cases of Pb and Bi.

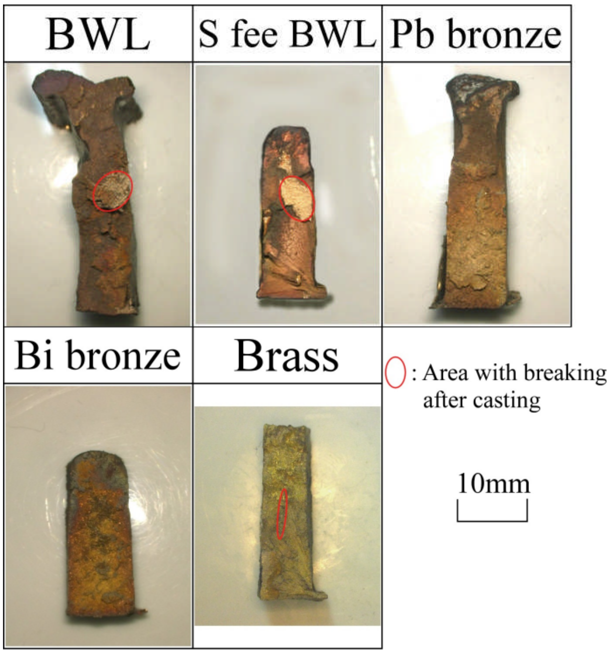

Fig. 5 The appearances of the fracture of various Cu alloy castings on the permanent mold with 200mm of the distance between flanges.

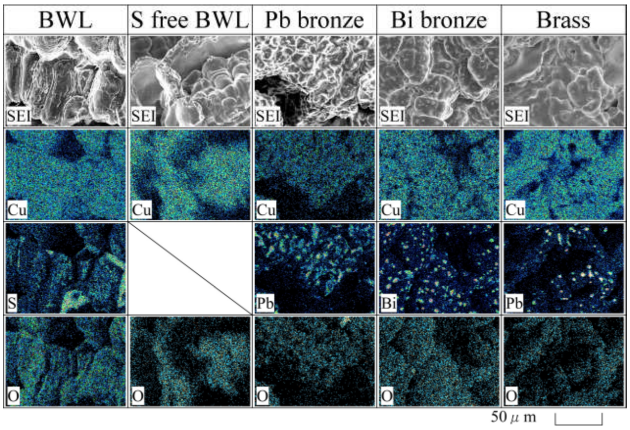

Fig. 6 Secondary electron images (SEI) and element distributions by EDX analysis on the fracture of various Cu alloy castings on the permanent mold for the solidification cracking test.

When the solidification cracking occurred, Pb-rich, Bi-rich or S-rich liquid phase may exist because the solidification cracking occurs at solid-liquid mixture. These element distributions might be formed after the solidification cracking, however, if these elemental distributions are caused by elemental segregation in the residual melts before the solidification cracking, at the part of the final solidification, S-rich phase in the lead free bronze with sulfide dispersion (BWL) exists in small number and in large size and Pb-rich and Bi-rich phase in the alloys including Pb and Bi, respectively, exist in large number and in small size.

Fig. 7 shows microstructure near by the fracture of various Cu alloy castings on the permanent mold for the solidification cracking test. The fracture is to the left of picture in all samples. In the lead free bronze with sulfide dispersion (BWL), the part of light gray and the dark gray is Cu sulfide and Zn sulfide, respectively, and the part of black is porosity. In the conventional leaded bronze (Pb bronze), the part of black is Pb and porosity. In the lead free bronze including Bi (Bi bronze), part of metallic luster is Bi, the part of white is Sn-rich phase, and the part of black is porosity. In the bronze not including lead and sulfur (S free BWL), the part of black is porosity. In the leaded brass (Brass), part of black is Pb and porosity. In all samples, the structure of fracture was dendritic. At interdendrite, there is sulfide in the lead free bronze with sulfide dispersion (BWL), Bi in the lead free bronze including Bi (Bi bronze), and Pb in the conventional leaded bronze (Pb bronze) and the leaded brass (Brass). In addition, these phases at interdendrite exist with porosity. Therefore, it is considered that the solidification cracking occurred before the end of the solidification.

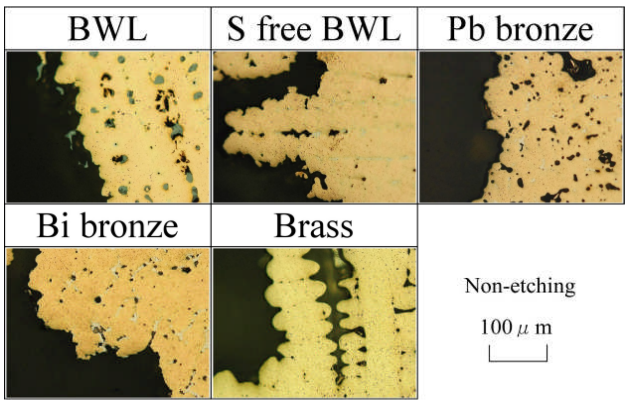

Fig. 7 Microstructure near by the fracture of various Cu alloy castings on the permanent mold for solidification cracking test.

There is, at interdendrite, Sn-rich phase contacted with Bi phase near by the fracture. Therefore, the residual melts which is Sn and Bi-rich may be linked through interdendrite until the end of the solidification.

As the results from Fig. 4 to Fig. 7, it is considered that the growth of solidifying phase in the final solidification affects the solidification cracking. In comparison between the lead free bronze with sulfide dispersion (BWL) and the conventional leaded bronze (Pb bronze) having monotectic reaction, there is difference between the distributions of S-rich and Pb-rich phase. Therefore, the structure of α-Cu phase solidified by the monotectic reaction may be different between the lead free bronze with sulfide dispersion (BWL) and the conventional leaded bronze (Pb bronze), because the distribution of the monotectic liquid phase effects the structure of the monotectic solid phase just before the occurrence of the solidification cracking. The surface area contacted between dendrites in the lead free bronze with sulfide dispersion (BWL) may be larger than that in the conventional leaded bronze (Pb bronze) because the range of the solidification temperature of the lead free bronze with sulfide dispersion (BWL) is smaller than that of the conventional leaded bronze (Pb bronze).

As the results, the conventional leaded bronze (Pb bronze) castings have possibilities for the solidification cracking because there is the locally weak point due to very small bonding area, and the solidification cracking is initiated and/or grows at the locally weak point.

In the lead free bronze including Bi (Bi bronze), the leaded brass (Brass) and the bronze not including lead and sulfur (S free BWL), the fracture had very smooth surface shaped into dendrite shaped. Primary α-Cu dendrite in these alloys was growing and becoming thick without the monotectic reaction. Therefore, it is considered that the interdendrite can only have weak bonding until finishing the solidification, as the result, the solidification cracking occurred easily at the interdendrite.

CONCLUSIONS

The applicability of the permanent mold casting process, especially occurrence of solidification cracking for bronzes and the brass was evaluated.

1) The solidification cracking occurred during the solidification in the leaded bronze, the lead free bronze including Bi, the lead free bronze with sulfide dispersion, the bronze not including lead and sulfur, and the leaded brass in the solidification cracking test.

2) The lead free bronze with sulfide dispersion is possible to apply the permanent mold castings process rather than the other copper alloys, and the applicability is almost same as brass castings.

3) The growth of solidifying phase in the final solidification affects the solidification cracking.

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