DEVELOPMENT OF LEAD FREE COPPER ALLOY CASTINGS ; MECHANICAL PROPERTIES, CASTABILITY AND MACHINABILITY

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INTISARI

Sejak April 2003, di Jepang telah diterapkan secara ketat peraturan mengenai pengurangan kadar timbal yang mencemari lingkungan. Kadar timbal yang diperbolehkan tidak lebih dari 0.01 mg/l. Untuk memenuhi persyaratan tersebut telah dikembangkan 2 teknologi menurunkan kadar timbal yang larut di dalam air minum, yaitu : (1) penggunaan bahan paduan perunggu yang bebas timbal untuk bantalan (JIS-CAC406) dan (2) teknik pengolahan permukaan. Kedua teknologi ini telah diuji lagi. Untuk pengembangan pengecoran paduan tembaga bebas timbal telah dilakukan pengujian terhadap sifat mekanik, mampu di cor dan di mesin dari berbagai bahan cor paduan bebas timbal. Bahan paduan yang digunakan dalam percobaan-percobaan tersebut berupa bahan paduan yang telah tersedia di pasaran, yaitu perunggu bebas timbal yang mengandung unsur Bi, perunggu bebas timbal yang mengandung unsur Bi-Se, perunggu bebas timbal yang mengandung unsur Bi-Sb, dan kuningan bebas timbal yang mengandung unsur Si. Sifat-sifat mekanik paduan tergantung dari temperatur penuangan dan ketebalan penuangan, dan biasanya lebih rendah dari sifat-sifat perunggu coran (JIS-CAC406, Cu-5 wt% Sn-5 wt% Zn-5 wt% Pb). Perunggu bebas timbal yang mudah di mesin mengandung unsur Bi dan Se lebih baik bila dibandingkan dengan perunggu coran yang mengandung Bi dan Bi-Sb, tetapi standarnya masih lebih rendah, yaitu 10-15% di bawah standar JIS-CAC406. Dalam paduan bebas timbal yang diganti dengan unsur Bi telah dicoba dilakukan penyesuaian kandungan unsur-unsur timah, seng dan bismut, dan dalam sistem Bi-Se telah dicoba penyesuaian untuk kandungan bismut dan selenium, dan juga untuk kandungan timah, seng dan bismut. Saat ini sedang dikembangkan paduan logam baru yang dapat memenuhi standar JIS-CAC406.

Kata kunci - kata kunci : paduan perunggu bebas timbal, sifat mekanik, mampu di cor dan di mesin.

ABSTRACT

The regulation for the lead discharge in the environment was strengthened, in Japan, the standards 0.01 mg/l or less has been in force from April 2003. In order to meet the new standard, two technologies for reduction of lead dissolution into the drinking water have been developed in Japan; substitution of lead free copper alloys for lead bearing bronze (JIS-CAC406) and introduction of surface treatment technology. This technological trend was shortly reviewed. For development of lead free copper alloy casting, mechanical properties, castability and machinability of various lead free alloy castings were examined. Trial alloys used were commercially available ones such as the lead free bronze containing Bi, the lead free bronze containing Bi-Se, the lead free bronze containing Bi-Sb and the lead free brass containing Si. Mechanical properties of alloys were dependent on the pouring temperature and castings thickness and were generally less than those of tin bronze castings (JIS-CAC406, Cu-5 wt% Sn-5 wt% Zn-5 wt% Pb). The machinability of the lead free bronze containing Bi and Se was better than that of the lead free bronze castings containing Bi and Bi-Sb. But was still 10 to 15 % less than that of JIS-CAC406. In a lead free alloy substituted by Bi, adjustment of tin, zinc and bismuth contents was attempted and in the Bi-Se system, the adequate adjustment, for bismuth and selenium contents and also for tin, zinc and bismuth contents, was attempted. New alloy in which the mechanical properties sufficiently satisfy the standard for JIS-CAC406 is developed.

Keywords : lead free copper, mechanical properties, castability, machinability.

I. INTRODUCTION

Water supply equipments using for tap water supplement, for example, water supply valve, stop valve, fittings, water meter (meter case) and etc., have been made from leaded bronze castings for a long time because of excellent corrosion resistance, formability and cost performance. These bronze castings contain few percentage of lead. The water quality standard for lead content was revised to be 0.01 mg/l or less since April 2003 in Japan, therefore leaded bronze castings for plumbing applications have to be changed for elimination of lead dissolution into drinking water. Two ways have been exploited; replacement to lead free alloys and removal of lead from the surface by surface treatments.

As research and development for lead freeing of the copper alloy castings, this paper reports mechanical properties, castability such as fluidity and shrinkage cavity formation and machinability of various lead free alloys. This research was conducted to test and evaluate

various lead free copper alloys under the cooperative research of Japan Non-Ferrous Alloy Casting Association and Copper Alloy Committee of Japan Foundry Engineering Society^[1,2,3].

II. THEORY

2.1. Recover of Lead Particles from Surface by The Surface

The new surface treatment technology of reduction of lead and lead compounds (oxide, hydroxide) from surface layer was developed. Lead is amphoteric metal, so it can be removed by either alkali or acid. Many technologies were developed by depending on the differences between the method of removing lead and the stabilizing treatment. Representative technologies are NPb treatment^[4], PLCS treatment^[5], SLA treatment, and electrolysis treatment. Figure 1 shows a schematic illustration of the recover mechanism and the process applied.

Figure 1. Recover of lead by surface treatment; mechanism and process.

By NPb (Non Pb) treatment, lead is dissolved and removed from the surface layer by dipping into alkali or acid etching solutions. From surface layer of 5-5 μ m, lead can be

removed by dipping (See Figure 2^[4]). This technology was developed by TOTO CO., Ltd. and it was widely used by a lot of companies under the license.

PLCS treatment technology, which stands for Parker Lead Clear System, is the surface treatment based on phosphate treatment. This technology may prevent lead dissolution from

the inside by removing lead from the surface layer and being made of the phosphate skin. Nihon Parkerizing CO., Ltd. developed this technology.

Figure 2. Lead appearances around the surface by NPb treatment.

SLA treatment technology, which stands for Surface treatment for Lead reduction by Acid, is the treatment by mixed acid mainly composed by dilute nitric acid. Using this technology, it may be possible to reduce lead and lead compounds in the surface layer with

keeping copper alloy's gloss. KITZ CO., Ltd. developed this technology.

The electrolysis treatment technology, which was developed by Koei Kogyo CO., Ltd., is the reducing technology of lead compounds from surface by electrolysis.

III. EXPERIMENTAL

3.1. Melting and Casting Methods

Melting and cast conditions of various lead free alloys are shown at Table 1. Trial alloys were employed from commercialized lead free alloys available in Japan. The alloys were melted in electric and

combustion furnaces. When alloys were melted at a required temperature, molten metal treatment, mainly deoxidization was performed and then cast in various test molds at a required temperature. CAC406 (JIS-CAC406, Cu-5wt% Sn-5wt%-Zn-5wt%Pb) was also used as a comparison sample.

Table 1 Melting and casting conditions of various lead free alloys.

alloy	Bi-Se	Bi	Bi-Sb	Si
alloy base metal	safe-alloy, keepalloy	joyalloy	aquabronze	ecobrass
melting furnace	induction or combustion furnace			
melting weight	net regulated			
melting temperature	1200 to 1230 wC			not regulated
degassing processing	not regulated			
deoxidization treatment	0.2 % addition as 15 % phosphor copper			not regulated
pouring temperature	Dependent on each test ;			
tensile test mold (type A)	Green sand, shell			
step bar test mold	CO ₂ mold			
spiral fluidity test mold	Shell mold			
cylindrical test piece mold	CO ₂ mold			

3.1. Outline of Testing

3.2.1 Chemical Composition

A sample for chemical analysis was cast into the metal mold with 36 mm in diameter and 110 mm in length. The position at about 30 mm from the bottom was cut and analyzed.

3.2.2 Mechanical Properties

First, the effect of pouring temperature to mechanical properties was determined as a basic knowledge of lead free copper alloys. Melt was cast into the mold of the JIS- type A tensile test piece for lead free bronze; 1190, 1160, 1130, 1100°C and for brass; 1100, 1080, 1040, 1000°C. Tensile strength, proof stress, elongation and hardness were measured from JIS No. 4 specimen.

3.2.3 Step bar test

To know the mass effect of lead free alloys a step bar test was performed of which thickness was 10, 20, 30 and 40 mm, respectively. Melt was cast to CO₂ mold shown in Figure 3 at 1130°C. Dye penetrating inspection, macrostructure and microstructure observations were carried out. Mechanical properties of the each thickness were also measured.

Figure 3. Schematic drawings of the step bar test mold.

3.2.4 Fluidity test by the spiral mold

Fluidity was tested by using the spiral test mold (shell mold). Schematic illustration was shown in Figure 4. Flow length was measured at pouring temperature of 1190, 1160, 1130 and 1100°C.

Figure 4. Cross section of fluidity test mold.

3.2.5 Machinability

Machinability was compared between each lead free alloy to measure the cutting resistance of the chip attached on the lathe. Cutting resistance, P , was calculated from three measured component forces as $P = \sqrt{P_1^2 + P_2^2 + P_3^2}$, where P_1 , principal force, P_2 , feeding force and P_3 , vertical force. Test piece was made from the cylinder castings (CO₂ mold, 30 mm in diameter and 150 mm in length) at pouring temperature 1130°C. The cutting rating was evaluated as ratio of measured cutting resistance to one of free cutting brass or JIS-CAC406. The outline of the test method and test condition is shown in Figure 5 and Table 2.

Table 2. The cutting condition.

Cutting speed	100 m/min
Feed per revolution	0.1 mm/rev
Cutting depth	1 mm
Chip	TNMG 160404 (TOSHIBA)

Figure 5. Schematic drawings of test method.

IV. RESULTS

4.1 Mechanical properties

4.1.1 Lead free bronze

Figure 6 shows the relationship between tensile strength and elongation of various lead free bronzes obtained from type A test pieces and of Bi-bronze obtained from type E test pieces.

Figure 6. Relationship between tensile strength and elongation of lead free bronzes.

Generally speaking data obtained were scattered among charging companies mainly owing to difference between melting furnaces and liquid metal treatment. Dependencies of mechanical properties on pouring temperature and casting thickness were different from one company to another. Some data showed much lower properties than typical ones which are cited by the brochure of alloy developed companies. Many alloy systems, especially one containing Bi, took lower values than requested ones of CAC406 (tensile strength ≥ 195 MPa, elongation $\geq 15\%$). Lead free bronze is expected to show the same or larger values of the CAC406 Standard. Therefore these lead free materials developed to 2002 mainly overseas are unsuitable for water supply equipments in Japan.

Dye penetration test and microstructure observation elucidated that micro shrinkage cavity appears more remarkably as the casting thickness becomes larger. Decrease in Bi content has proven to reduce micro shrinkage cavity and to result in better mechanical properties. Newly developed lead free bronzes in Japan have become reducing Bi content for any alloy system, and for Bi-Se lead free bronze alloys with lower content in Se, together with reducing Bi content, has been developed. Adjustment of another element, in general terms, was made by increasing Sn and decreasing Zn contents as compared with previously developed alloys.

Exploit by these trials produced the new alloys shown in Table 3. From Table 3 and Figure 7, these materials have mechanical properties as same level as JIS-CAC406. and improve mass effect. Decrease in bismuth content, generally, results in improving the

prevention of micro shrinkage cavity formation and in worse machinability. Therefore bismuth content is a trade off between shrinkage cavity formation and machinability and is determined to balance them.

Table 3 Chemical compositions newly developed in Japan.

	Cu	Sn	Zn	Bi	Se	Pb	Sb	Si	P
LF-4A	82.0-87.0	3.5-5.5	5.0-9.0	1.5-4.0		<0.2	<0.25		
AQ-30		3.0-6.0	5.0-9.0	1.5-6.0		<0.2	0.05-0.5		
AQ-N20		4.0-5.0	4.0-5.6	1.7-2.2		<0.2	0.15-0.3		
ARA-2AD	86.0-88.0	5.0-6.0	5.5-6.6	≤ 0.49		<0.2	<0.25		
NEW Keepalloy	84.0-89.0	3.5-6.0	4.0-9.0	0.8-2.5	0.1-0.95	<0.2			
Safe-alloy	85.0-89.0	4.0-6.0	4.0-7.0	1.5-3.0	0.1-0.3	<0.25	<0.2		
Ecobrass	74.0-78.0		Rem.			<0.1		2.7-3.4	0.05-0.2

Figure 7. Mechanical property of lead free materials newly developed.

4.2.2 Lead free brass containing Si

Effect of pouring temperature on mechanical properties tested on type A test piece is that pouring of higher temperature more than 1160°C happens, in some cases, a lower elongation. Therefore it can be said pouring less than 1140°C is recommended. Generally strength much higher than that of CAC406 is achieved tensile strength and elongation are 400 MPa and 20%, respectively. Mass effect is said to be small.

4.3 Fluidity

The relationship between pouring temperature and the flow length, fluidity, is shown in Figure 8. Fluidity is increasing as pouring temperature is increasing for each alloy. Bronze type lead free copper alloys showed almost same as CAC406 alloy. The fluidity of Si containing brass is much better than that of CAC406.

Figure 8. Relationship between flow length and pouring temperature.

4.4 Machinability

Table 4 shows cutting resistance and machinability rating compared with free cutting brass and JIS-CAC406. Machinability

rating is the order of Bi-Se, Bi-Sb, Bi bronzes and Si contained brass, however, best Bi-Se bronze is still interior to JIS-CAC406.

Table 4 Cutting resistance and machinability rating

alloy	Charge company	Cutting resistance	Machinability rating	Contrast with JIS-CAC406
Bi-Se	A	127	80	92
	B	129	79	90
	D	137	74	85
Bi	E	139	73	84
	F	134	76	87
Bi-Sb	H	133	76	87
	I	134	76	87
Si	J	138	74	87
	K	139	73	84
contrast	CAC406	117	87	100

V. CONCLUSIONS

Mechanical properties, castability and machinability of various lead free alloys of lead free bronze containing Bi, Bi-Sb and Bi-Se, and lead free brass containing Si were examined. Main results obtained were as follows.

1. All tested lead free bronze castings including Bi have inferior mechanical properties to that of JIS CAC406. Lead free brass including Si has superior mechanical properties to JIS CAC406.
2. Mass effect as severe for all tested lead free bronzes because micro-shrinkage information is easily formed at heavier section. Lead free brass shows little mass effect.
3. The fluidity of lead free bronze is almost equivalent to that of JIS-CAC406. Lead free brass as an excellent fluidity.
4. Machinability of lead free bronze and lead free brass is 8-13% less and 17 % less, respectively, than that of CAC406. Among them Bi-Se bronze showed better machinability.
5. Mechanical properties, especially, elongation, were improved by reducing Bi content for very lead free bronze and also by reducing Se content for Bi-Se bronze.

This is caused with reducing micro-shrinkage cavity.

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