

Investigations of Possibilities for Cleaning of Aluminium Bronze for the Recycling of Cast Alloys

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For the production of large ship propellers mainly aluminium bronze cast alloys are used. This material is highly resistant against sea water and it also offers all other necessary physical properties. In a cooperative project, which was sponsored by the German Federal Ministry of Education and Research (BMBF), methods and procedures for the selective removal of impurities from aluminium bronze have been developed.

The technology for cleaning of the dust after grinding have been improved and prepared for the implementation into the industry. The re-melting processes of this kind of material have been investigated and optimized.

By increasing the usage of scrap for the alloying of aluminium bronze in cast shops the expensive use of primary metals or alloys can be reduced.

In the beginning thermo-dynamical calculations were performed to pre-estimate which impurities are capable for a removal by chemical/metallurgical reactions. Both, selective oxidation and selective chloride and nitride formation were examined experimentally. Other methods to refine aluminium bronze are the evaporation of volatile elements or the application of refining salts.

The investigations showed that refining salts and the evaporation of volatile components gave the best effects for cleaning and recycling. Except of silicon nearly all potential impurities of aluminium and copper scrap can be removed.

Within the project, supported by BMBF, procedures and methods for selective extraction of disturbing impurities from copper casting alloys had to be developed, particularly from aluminium containing bronze [1]. Moreover, metallic waste products that are a side effect of the production of propellers, e.g. dusts, are to be included into the refining technology that had to be developed (scrap cleaning). Copper alloys with less than 15 wt.-% aluminium are called aluminium bronze. Excellent mechanical and physical properties are obtained by

further addition of up to 5 wt. % iron and nickel. This particular kind of alloy is used e.g. for the casting of ship propellers.

The foundry industry uses the alloy CuAl10Mn5FeNi to produce the ship propellers and other elements for marine use. One of the operations is to grind the cast propellers with the polishing papers, mechanical tools for example, to produce the expected surface (Fig.1). The dust after the polishing is collected and sporadically reused within the foundry. Due to the high aluminum concentration in the alloy one of the problems was the in house re-melting of the dust in the foundry. Before the project the material was sent to a copper plant for recycling

to produce the pure copper. During the refining process, all elements, except of copper, were reduced and removed with the slag. More than 20 wt.-% of the sent material was slagged - even such expensive metals like Manganese. In opposite, the in house recycling gives the possibility to save all elements of the alloy with lower waste level and costs of the energy to protect the environment. Costs of the transport can be also reduced. There is the presentation of the closing the material flow for recycling within the foundry using the internal recycling ways of

the preparation of the dust before the re-melting, additionally re-melting under usage of new types of refining-salts to keep the homogeneity of the melted metal in the furnace for good quality of the castings is presented.



Fig. 1: Grinding of the propeller

Aluminium bronze dust

There were 3 different samples of the aluminum bronze dust taken for analysis. All fractions were separately collected within the industry. The first step of the investigations was to analyze the chemical composition of all three samples with the Atomic Absorption Spectrometer (AAS). The chemical composition was determined (Tab.1) by dissolving of 10 g of each sample in hot diluted nitric acid and the indissoluble residues were separated by membrane filtration PTFE (1.2 µm). The residues were washed with hot water, dried and weighed. Therefore, the sum of analyzed elements did not reach 100 %, regarding silicon and aluminum in the residue. Silicon as an alloying element can also be found in the dust. However, it is also a main component of the ceramics for grinding and polishing. Silicon is used there in the form of indissoluble SiO₂ which is removed almost as residue in the analyses. The same problem occurs with the aluminium concentration, where aluminum on the one hand is a main part of the

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Element	Sample 1	Sample 2	Sample 3
Cu	78,91	74,74	63,92
Al	8,27	7,558	7,06
Ni	4,58	4,335	3,96
Fe	3,83	3,664	3,89
Mn	0,63	0,613	0,41
Zn	0,095	0,109	0,003
Pb	0,015	0,025	0,0001
Na	0,080	0,116	0,013
Si	0,31	0,61	0,67
Sn	0,01	0,01	0,10

Tab. 1: Chemical composition of the dust samples in wt-%

alloy, on the other hand it is used as Al₂O₃ in the abrasive. Because of the higher concentrations of this element in the alloy the influence of the impurities (i.e. form abrasive) on the final result is much smaller compared to silicon.

The grain-size distribution in all three samples was carried out with the Particle analyzer Sympatec Helos and a grain-size spectrum can be determined in the area from 0.5 to 1200 µm. For the investigations the samples were supplied to the analyzer and there the grain-size distribution was determined by a laser-optical system. In Tab. 2 the grain-size distributions of 3 examined samples are shown. However, during the investigations sometimes material was blocking the analyzer and therefore disturbed the measurement. With these investigations no fine fraction <10 µm could be determined in sample 1. Only 10% of the material had a grain-size <70 µm, the average grain-size was found to be approx. 200 µm. 90% of the material had a grain-size

Sample	Particle size [µm]		
	10 %	50 %	90 %
Sample 1	< 70	200	< 420
Sample 2	< 30	100	< 320
Sample 3	< 41	122	< 350

Tab. 2 Fractions of aluminum bronze dust particles

<420 µm. Sample 2 is much finer in comparison to sample 1. The fine fraction <10 µm was determined to 1.4% and to the average grain-size to approx. 100 µm. Sample 3 is finer in comparison to sample 1, too. The average grain-size is approx. 120 µm and 90% of the material is smaller than 350 µm. However, the size also shows that the sample 3 is a mixture of a gross and a fine dust. It indicates that this material is collected without previous separation of factions.

Magnetic cleaning of the aluminium bronze dust

The analyses have shown that it is possible to use the dust as a valuable material if it can be separated from impurities like silicon. To analyze possibilities for separation the susceptibilities of the different materials like alloy and oxides were compared by with those of silicon and his possible compounds. The aluminum bronze with 2.5% - 3.5% of iron (propeller alloys) shows relatively high magnetic susceptibility. Therefore the possibility to separate both fractions in the magnetic field was suggested. The magnetic separation should offer the chance to clean the dust from silicon and silicon compounds without any chemical treatment and to melt it in the original physical form. A Rotating Drum Magnetic Separator 9630\110 was chosen with changeable poles (Fig. 2). The investigations have been realized for all 3 samples separately. After the sieves have been cleaned approx. 2 kg of sample 1 was treated with the magnetic separator. In Fig. 3 the investigation steps are given. 82.17% of the material could be separated as magnetic sample. The unwanted non-magnetic sample was lower than 5 % of the incoming material. Tab. 3 presents the silicon concentration in all cleaned fractions. The concentration was reduced from 0,18 wt-% to 0,03 wt-% in the magnetic fraction. The fine fraction of the dust was for experimental purpose re-melted in the casting shop. To check the re-melting possibility of 360 kg of dust, sample 2 was sieved and magneti-



Fig. 2: Rotating drum magnetic separator

cally cleaned. To find the optimal parameters and to minimize the non-magnetic residue, the paramagnetic sample from the first cleaning step was cleaned again with the same equipment. Fig. 4 presents the results of the experiment and the weights of each fraction. The silicon concentration in the dust after the first cleaning is presented in the Tab. 4. By sieving all particles >1 mm were separated. This fraction was found to be 1 wt-% of the incoming sample 2. The sieved 99 wt-% was magnetically cleaned. 79.9 wt-% could be transferred into the magnetic product. By the process the silicon concentration was reduced from 0.07 wt-% to 0.025 wt-%. After the second cleaning step of the paramagnetic fraction the magnetic fraction of sample 2 has a concentration of 0.1 wt-% silicon.

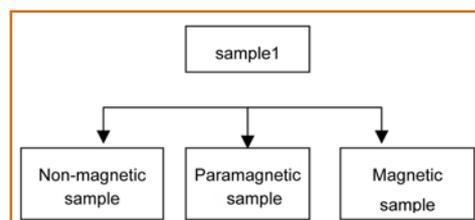


Fig. 3: Schematic presentation of the separation process for aluminium bronze dust - sample 1

Sample	Magnetic	Para-magnetic	Non-magnetic
1	0.03 % Si	0.13 % Si	0.51 % Si
2	0.02 % Si	0.18 % Si	0.42 % Si
3	0.03 % Si	0.32 % Si	0.68 % Si

Tab. 3: Silicon concentrations in all cleaned samples in three different products of the separation

Sample	Magnetic	Para-magnetic	Non-magnetic
2	0.1	0.07	0.33

Tab. 4: Silicon concentration after the second cleaning of the paramagnetic fraction [wt-%]

Scrap cleaning

Included in the project technologies and methods for selective extraction of contaminating impurities from copper casting alloys had to be deve-

Element	Cu	Al	Ni	Fe	Mn	Mg	Pb	Si	Sn	Zn
Aluminium-bronze	-	-	-	-	2%	-	8%	32%	-	28%

Tab. 5: Amount of additions in scraps' supply for aluminium alloys (period: from September 1999 until September 2001)

loped, particularly from aluminium containing bronze.

The Mecklenburger Metallguss GmbH already utilises at limited extent copper and aluminium scraps beside pure metals for production of propellers. The scraps are characterized by chemical composition, metal content, humidity and size of the particular piece. Having made research of scraps' supply for production of aluminium bronze, we received the results in tab. 5.

Because more than 30 % of the usage of the supplied scraps has been due to high silicon and zinc concentrations, the possibility of reducing the con-

tent of these elements in the casting process has to be examined. Starting from the alloys' elements and from the impurities of the aluminium casting, we can break down the data into groups specified in table 6.

In literature mostly the recovery of copper from scraps from electronic equipment is discussed in addition to the concerning technology [2] und [3]. The usage of refining-salts in order to prevent oxidation of metals and to absorb impurities is known from gaining and production of aluminium [4]. Refining procedures of copper casting alloys are not included in the literature. To what extent selective

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Group	Element	Description
Group 1	Copper, aluminium, nickel, manganese, iron	Casting metals of aluminium bronze alloys
Group 2	Oxides (primarily Al ₂ O ₃)	Composition is to be prevented by smelting; already existing oxide has to be removed
Group 3	Silicon and lead	Both kinds of impurities negatively influence the propeller alloys and are to be removed
Group 4	Magnesium	This metal decreases the refining ability of the salts
Group 5	Primarily gases, such as H ₂ , N ₂ and other	Have a negative influence on quality of propellers' casts and therefore also have to be removed
Group 6	Zinc, tin	Are accepted in the propellers' casts to limited concentrations

Tab. 6: Classifications in groups of substance concerning content in the aluminium bronze alloy

refining procedures including the use of refining-salts can remove contaminating impurities had to be explained by thermo-dynamical investigations.

Thermo-dynamical investigations

With the help of thermo-dynamical analyses it had to be estimated, which impurities in the aluminium bronze could be removed by chemical reactions. By comparison of the figures of Gibbs free energy of oxide formation it could be determined, which element can be refined by a selective oxidation. With help of thermo-dynamical analyses of the systems copper – impurities and aluminium – impurities it is generally possible to receive information on the refining ability of these contaminations. Analogical the partial pressure of the

single components of the aluminium bronze can be considered.

In Table 7 the partial pressures of metals and oxides are given as well as free energy of the oxide formation of the metals included in the aluminium bronze at 1200 °C.

Oxygen or air treatment of aluminium bronze at first leads to the formation of alumina. Therefore refining by oxidation is possible only for aluminium free copper scraps.

Similar calculations have been made for selective formation of nitrides and chlorides of the impurities and alloying elements. By selective formation of nitrides or chlorides as well as by evaporation, tin, lead and zinc should be removable from the liquid aluminium melt and respectively from the aluminium bronze melt.

From literature it is also known that further examinations concerning

Element	Partial-pressure [atm] 1200°C	Reaction of the oxidation	ΔG^0 , [kJ/mol O ₂] at 1200°C
Zn	$1 \cdot 10^1$	$2 \text{ Zn} + \text{O}_2 = 2 \text{ ZnO}$	$-3.9 \cdot 10^5$
Sn	$7 \cdot 10^{-6}$	$\text{Sn} + \text{O}_2 = \text{SnO}_2$	$-2.7 \cdot 10^5$
Pb	$2 \cdot 10^{-2}$	$2 \text{ Pb} + \text{O}_2 = 2 \text{ PbO}$	$-1.6 \cdot 10^5$
Al	$1 \cdot 10^{-5}$	$4/3 \text{ Al} + \text{O}_2 = 2/3 \text{ Al}_2\text{O}_3$	$-7.8 \cdot 10^5$
Si	n. g.	$\text{Si} + \text{O}_2 = \text{SiO}_2$	$-6.5 \cdot 10^5$
Cu	$4 \cdot 10^{-6}$	$4 \text{ Cu} + \text{O}_2 = 2 \text{ Cu}_2\text{O}$	$-1.2 \cdot 10^5$
Fe	$1 \cdot 10^{-7}$	$2 \text{ Fe} + \text{O}_2 = 2 \text{ FeO}$	$-3.4 \cdot 10^5$
Ni	$2 \cdot 10^{-10}$	$2 \text{ Ni} + \text{O}_2 = 2 \text{ NiO}$	$-2.2 \cdot 10^5$

Tab. 7: Partial pressure and free energy of oxidation of selected metals

vacuum refining of aluminium and copper alloys have been made. This way, tin, lead and zinc concentration could be reduced, however, not the concentration of silicon. Introducing this vacuum technology into a casting shop could not be the economic way because of high investment cost and nevertheless no reduction of the silicon concentration in the melt. Hence this kind of technology has not been investigated and research has been concentrated on following refining procedures:

- gas treatment of the melt,
- salt refining of the melt.

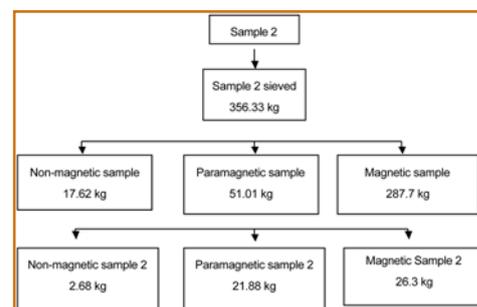


Fig. 4: Schematic presentation of the separation process of the aluminum bronze dust - sample 2

Experiments

Gas Refining

According to thermo-dynamical calculations with the HSC - Chemistry 5.1 program [5] the theoretical possibilities for removing of impurities from copper alloys with means of miscellaneous reaction gases can be shown.

According to Fig. 5 the formation of Si₃N₄ should be possible by the reaction of silicon with ammonia at simultaneous release of hydrogen. With increasing temperature the stability of this compound is increasing. Therefore this reaction should be examined in a temperature range of 1300 °C to 1500 °C. Primarily, the nitrogen in ammonia can get in touch with the silicon in the melt and thereby form silicon nitride (Si₃N₄). This process, like all heterogeneous reactions is strongly affected by the convection in the melt. At high temperatures the for-

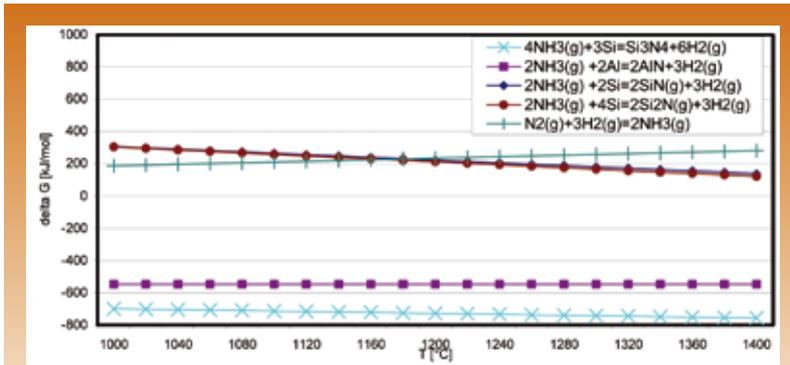


Fig. 5: Schematic illustration of temperature dependency on calculated DG0 value in the temperature range 1000 °C – 1400 °C for reactions of Si and Al with ammonia in aluminium bronze

mation of aluminium nitride is possible as well.

Gas refining was examined from 1300 °C to 1500 °C in a Tamman furnace. During refining the temperature continuously was controlled with a thermocouple Ni–CrNi. Gas was injected centric into the melt through the graphite lance with a 3 mm open

diameter. To prevent the oxidation of the melt, always 5% of refining-salts were added to the melt in the crucible. Refining time was 30 minutes.

As can be seen from Fig. 6 concentrations of the impurities Pb, Sn and Zn can be decreased during refining. The removal rates depend on the temperature of the melt. After 30 min of

treatment the zinc concentration was reduced from 0.12 or 0.14 wt.-% to 0.001 wt.-%. The content of lead and tin in the melt could only be decreased less. On the other side, silicon concentration increases significantly from under 0.1% to 0.14% at 1300 °C and up to 0.16 % at 1500 °C. The reason for this increasing Si-concentration can be the reduction of silicon dioxide to silicon from the graphite crucible or/and the loss of zinc by evapora-

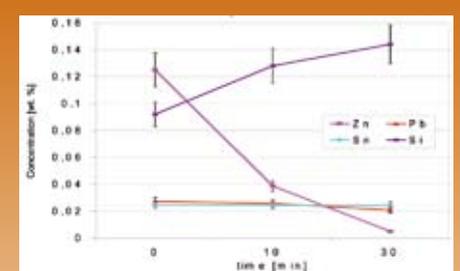


Fig. 6: Behaviour of impurities during the refining of aluminium bronze with nitrogen at 1300°C

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Element	before refining [wt. %]	after 10 min.[wt. %]	after 30 min. [wt. %]
Zn	0.18	0.13	0.03
Pb	0.02	0.02	0.02
Sn	0.02	0.02	0.02
Si	0.11	0.11	0.11
Mn	1.18	1.19	1.13
Fe	4.67	4.64	4.69
Ni	4.4	4.4	4.56
Al	8.46	8.33	8.02
Cu	80.9	81.11	81.37

Tab. 8: Results of the gas refining of aluminium bronze with nitrogen and 10% of ammonia at 1300 °C

tion from the melt. The reduction of SiO₂ from the grid of the crucible can happen by the intensive convection of the liquid melt by means of molten salts. SiO₂ further is reduced by Al and dissolved in the melt.

Having made the experiments with pure gases, one can assume that refining efficiency of nitrogen and argon on aluminium bronze melt is limited. Hence further experiments have been conducted with addition of reactive gases, e.g. chlorine or ammonia with concentrations of 10 % and 20 % in the gas mixture.

The thermal decomposition of NH₃ in H and N atoms in the melt can lead to the reaction of these reactive atoms with components of the alloy. During the refining, significant loss on aluminium occurs, even up to 10 % of the initial content. Thus the concentration of copper as main component of the alloy increases significantly (Tab. 8). Same happens to the others alloying components and trace elements.

Behaviour of main alloying components prove that the metals like copper or nickel do not react with ammonia. The relative increase of contents can be explained with losses on aluminium from the alloy by oxidation. Gas handling of aluminium bronze with ammonia at 1300 °C also evaporates zinc. Tin and lead contents remain on the same level, because they do not form nitrides nor can be evaporated. The results of gas treatment of aluminium bronze with argon and ammonia show that only zinc has been removed with simultaneous loss of aluminium from the liquid melt.

Therefore gas refining with ammonia does not result in the desired goal – a significant reduction of impurity concentrations of tin, lead and silicon.

Hence injection of chlorine to the alloy liquid melt has been investigated as an alternative gas refining possibility. The influence of chlorine on the melt leads to a direct reaction of aluminium with chlorine with simultaneous formation of AlCl₃. This compound separates from the metallic melt to the surface forming a salt slag. On its way to the surface it can agglomerate with oxide particles and other contaminations incorporating them into the slag.

The injection of chlorine gas (with a content of 10 vol. % and 20 vol. %) has been made by means of gas carrier nitrogen and argon at 1300 °C.

The results in Fig. 7 show a 400 % increase of the silicon concentration. This proves that SiO₂ from the crucible is attacked with chlorine and dissolved

into the melt after reduction with aluminium from the alloy. Due to strong reaction of chlorine with aluminium in the sense of oxidation and the reaction with SiO₂ from the crucible, this gas is not appropriate for the refining of aluminium bronze.

In general one may express, that complete removal of zinc is possible with every reaction gas by evaporation. The fastest result is obtained at higher temperatures. Silicon contents can not be reduced by gas refining, but in contrary can be increased by reactions of SiO₂ from the crucible. The contents of trace elements such as Cr, As or P are not reduced by gas refining. The contents of major elements of the alloy such as Cu, Mn, Ni, Al, and Fe are kept constant on the same level at 1300 °C. At 1500 °C injection temperature the losses on aluminium from the melt increases further more.

Refining of Aluminium Bronze with Molten Salts

Goal of these investigations was to develop new, high effective salt compositions, which react selectively with impurities and protect the surface of the alloy from oxidation.

Fluoride containing salts promised best results for the application with aluminium bronze, because they are able to bind oxides such as e.g. Al₂O₃ and thus they show an influence on the refining. A technically used salt must smelt rapidly during handling and must be chemical reactive, so that

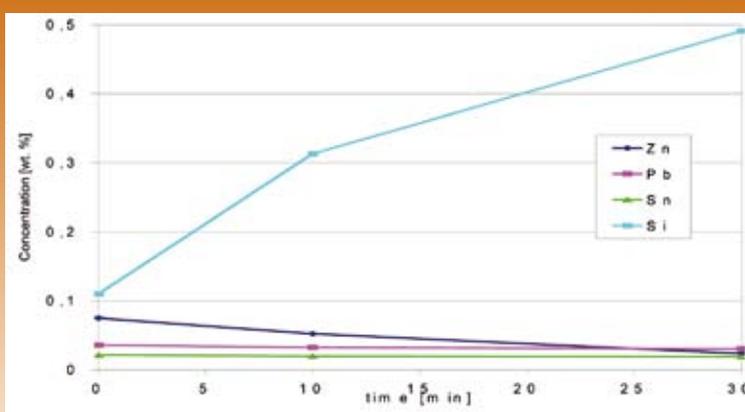


Fig. 7: Behaviour of impurity elements during treatment of aluminium bronze with argon and 10 % of chlorine at 1300 °C

Refining-salt	Silicon concentration in the alloy [wt. %]		Aluminium concentration in the alloy [wt. %]		Copper concentr. in the slag [wt. %]
	before refining	after refining	before refining	after refining	after refining
Flux 6	0.108	0.092	8.90	9.04	12.23
Flux 7	0.101	0.126	8.84	8.81	24.31
Flux 8	0.110	0.111	9.22	9.04	14.03
Flux 9	0.157	0.129	7.94	8.37	8.99
Flux 10	0.116	0.113	8.70	8.76	2.48
Flux 11	0.106	0.113	8.18	8.55	16.86

Tab. 9: Aluminium- and silicon concentrations in the melt before and after salt refining, copper concentrations in slag after salt refining of aluminium bronze

fluoride components can react with the oxide impurities. The resulting salt mixture, that has significantly lower density than the melt, covers the surface of the melt and can be removed after the reaction as a slag.

Thus systematic investigations on the evaporating and decomposition behaviour of different fluorides lead to a few thermally stable compounds in the interesting system.

Using thermal stable fluoride compounds and corresponding salt mixtures the compositions marked as Flux 6 to Flux 11 were created [6].

The smelting investigations have been made in an 8000 Hz middle frequent laboratory inductive furnace. Primarily 2 kg bronze alloy was smelted in a graphite crucible and a sample was taken. Later on a mixture of swarf and refining-salt (5 wt. % of total mass of the melt and swarf) has been added. The molten material was treated in the furnace for further 5 min at 1200 °C. Thereafter a second sample was taken for the analysis of the aluminium and silicon content. The results of these experiments using the salt mixtures Flux 6 – Flux 11 are shown in Tab. 9. Simultaneously another sample was taken from the solidified refining-salt in order to determine the copper concentrations in the salt slag as a rate of copper loss (Tab. 9). The new refining-salts can cover and wet the melt very well, so that losses on aluminium are minimized. The increase of the Al-content in the melt in some cases is due to melted swarf that does not have really constant Al-content (Tab. 9).

These results indicate that the new developed refining-salts are able to protect the melt of the alloy better from oxidation rather than the common salt mixtures known before. From the characteristics of refining-salt behaviour during the process one can say that evaporating of components was on a very low level. The swarf is melted successfully with every salt mixture used in the tests. Oxide layers were removed fast, so that the alloy obtained a homogeneous and compact structure after the process by solidification. In contrary concentrations of copper in the slag are relatively high after the refining. This reveals that copper rich swarf particles are left un-reacted in the slag. This could be explained with a low convection in the crucible during laboratory tests.

The investigated refining-salts lead only to a small increase of the silicon content in the melt. They are less aggressive against the crucible material, what is proved by the silicon concentrations in Table 9. Having made laboratory investigations, the new developed salt mixtures where tested in the industrial scale. It has been revealed that by simple addition of the refining-salts to the alloy and the following addition of swarf it is possible to smelt the mixture with minimal losses of the original alloy.

Summary

Within this project supported by BMBF procedures and methods for selective refining of aluminium bron-

ze were developed with the goal to eliminate harmful impurities from the cast alloys.

Concluding the results of the experimental investigations the most effective refining procedure for the interesting type of alloy can be formulated as: removing of elements that can easily be evaporated at high temperatures and additionally covering the melt as protection for oxidation with the refining-salt. Apart from silicon, all potentially impurities in copper- and aluminium-scrap can be removed by using these methods for refining when secondary material is added to melts of aluminium bronze in a casting shop.

By conducting laboratory investigations with parallel industry examinations together with Schäfer Chemische Fabrik GmbH refining-salts have been developed which show good refining effects on aluminium bronze alloys. These salts have good wet ability by smelting of metallic swarfs and can be classified as non-toxic.

Due to the investigations it is possible to utilise more aluminium- and copper-scrap for production of this type of bronze. However, one should pay attention to silicon content, because a refining of this element is not possible in principle until now.

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