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SOME ERRORS IN THE DETERMINATION OF CHROMIUM IN Cu-Cr-Ni-Si ALLOYS USING ATOMIC ABSORPTION SPECTROMETRY TECHNIQUE

NIEKTÓRE ŹRÓDŁA BŁĘDÓW W OZNACZANIU CHROMU W STOPACH Cu-Cr-Ni-Si TECHNIKĄ ATOMOWEJ SPEKTROMETRII ABSORPCYJNEJ

***Summary**: Copper alloys with chromium commonly called chromium bronzes still play an essential role as alloys of good conductivities and mechanical properties. Cu-Ni-Si-Cr alloys are a full-value substitute for beryllium bronzes in the machine, mining, chemical and electrical industries. They do not contain toxic beryllium, which means there are no problems with scrap and waste disposal, as well as with strict health and safety regulations. Regardless of the type of metallurgical technology used, the main technological problem during the smelting of copper alloys with chromium and other components is to obtain the intended chromium content in the final product. This situation indicates the need for exceptionally careful compliance with the individual technological parameters of smelting these alloys. The melting and casting processes of the described alloys are presented. Of particular importance are such parameters as: temperature and time of smelting, size of chromium pieces and oxygen content in the bath, at the same time indicating these factors as sources of errors in determining the chromium content in these alloys. The flame atomic absorption spectrometry (FAAS) technique was used to determine the content of chromium, as well as nickel and silicon. The relative standard deviations of the obtained results of the chemical analysis of these alloys using the AAS technique were: Cr – 1.4%, Ni – 1.0% and Si – 1.6%, respectively.*

***Keywords**: Cu-Cr-Ni-Si alloys, determination of Cr, Ni and Si, sources of errors in the determination of Cr, AAS technique*

Streszczenie: Stopy miedzi z chromem nazywane popularnie brązami chromowymi odgrywają nadal istotną rolę jako stopy o dobrej konduktywności i właściwościach mechanicznych. Stopy Cu-Ni-Si-Cr stanowią pełnowartościowy zamiennik brązów berylowych w przemyśle maszynowym, wydobywczym, chemicznym i elektrotechnice. Nie zawierają toksycznego berylu w związku z czym nie występują problemy z utylizacją złomu i odpadów, a także z rygorystycznymi przepisami bhp. Bez względu na rodzaj stosowanych technologii metalurgicznych, głównym problemem technologicznym podczas wytapiania stopów miedzi z chromem i innymi składnikami, jest uzyskanie w wyrobie końcowym założonej zawartości chromu. Ta sytuacji świadczy o konieczności wyjątkowo starannego przestrzegania poszczególnych parametrów technologicznych wytapiania tych stopów. Przedstawiono procesy topienia i odlewania opisywanych stopów. Szczególne znaczenie odgrywają takie parametry, jak: temperatura i czas wytapiania, wielkość kawałków chromu i zawartość tlenu w kąpieli, wskazując jednocześnie te czynniki jako źródła błędów w oznaczaniu zawartości chromu w tych stopach. Do oznaczania zawartości chromu, a także niklu i krzemu zastosowano płomieniową technikę atomowej spektrometrii absorpcyjnej (AAS). Względne odchylenia standardowe uzyskanych wyników analizy chemicznej tych stopów techniką AAS wynosiły odpowiednio: Cr – 1,4%, Ni – 1,0% i Si – 1,6%.

Słowa kluczowe: stopy Cu-Cr-Ni-Si, oznaczanie zawartości Cr, Ni i Si, źródła błędów w oznaczaniu Cr, technika AAS

Introduction

Copper alloys containing chromium and other components (*inter alia*, Ag, Zr, Co, Be, Ni, Si, B, Cd) in the quantities, not exceeding, as a rule, 5% in total, are characterized by as high hardness and electric and thermal conductivity. They are employed as materials for tools intended for resistance welding and electric spark machining, non-sparking elements, crystallisers for continuous casting, coolers, trusses (lattice frame elements), parts of chemical equipment and, also, other parts of machines, equipment and electric current or heat-transferring installations [1–8].

A process of melting the discussed alloys may be implemented in open furnaces, under the coverage or protective slag. In such case, copper-based alloys, containing the required alloy additives are employed as the components. The alternative includes melting of the alloys in the closed induction furnaces, under vacuum or at the protective atmosphere, mainly argon. It is then possible to use pure metals as the charge components instead of alloys. Irrespectively of the type of the employed foundry technologies, the main technical problem during smelting of copper alloys, containing chromium and other components, is obtaining of the assumed content of chromium in a final product. The process of dissolving of the discussed metal in copper is difficult and time consuming and its final content is dependent, *inter alia*, on the content of oxygen in the liquid copper, time and temperature of melting, size of the pieces of the charged substance (chromium) and the content in the liquid solution of other alloy additives [1, 3–5].

As it was revealed in the studies, the increase of oxygen in copper from 0.001% to 0.01% causes the decrease of the amount of dissolved chromium form 60% to 40% [4]. It was also found that the surface-oxidized pieces of chromium were not dissolved in the liquid solution on basis of copper [3].

Within the frames of the present study, when stressing the role of technological factors (time and temperature of melting, the content of nickel and silicone in the liquid solution), several alloys of Cu-Cr-Ni-Si type were analysed; the final chemical composition of the basis of copper, containing, apart from chromium, nickel and silicone, was determined [3, 7, 8]. The determination of chemical composition of the discussed alloys was carried out with the application of flame absorption atomic spectrometry (FAAS), using spectrometer model 503 by Perkin-Elmer company. The conducted chemical analysis of the samples. which were sent to specialistic laboratories for determination of the contents of alloy components, especially of chromium, recorded big differences in the content of the mentioned element in final products in the case of some alloys. When taking the indicated technological factors into consideration, their role in the manufacturing process of the discussed alloys was confirmed, especially in respect of obtaining the assumed content of chromium in the mentioned alloys. Another aim of the present study was to investigate the situation and find out the reasons for differences in the chromium content in the studied alloys, while indicating simultaneously the source of the errors.

The experimental

To study the process of dissolving chromium in copper and in liquid solutions of Cu-Ni and Cu-Si, the cycle of casts in the vacuum induction furnace IS 5/III by Leybold-Heraeus was carried out. The experiment was conducted in silicon carbide crucible, under the vacuum of 0.1Pa order. Melting temperature was equal to 1573 20 K. The tests covered alloys of Cu-Ni-Si-Cr with the following basic composition: Cr 1%, Ni 2.4% and Si 0.6% [3].

During the first few melts, there was employed chromium (1% weight in relation to the weight of charge equal to 5 kg) in pieces with the differentiated dimensions (0.1÷1.5 mm). In effect, after melting for ca. 1200 s, there was obtained the content of chromium in copper at the level of 0.35–0.40 by weight. The reason for a low level of chromium was its non-uniform dissolving and evaporation – the pieces with the smaller dimensions were dissolved at the initial period of melting and then, they successively were evaporated, decreasing the final content of the discussed element in the alloy. On the other hand, the pieces of the greatest size were not dissolved after 1200 seconds of melting what is manifested by the image of macrostructure of the ingot, containing a visible, big, non-dissolved piece of chromium [Fig. 1a].

The mentioned situation is an evidence of the necessity of extremely careful observing the particular technological parameters of melting the mentioned alloys. Especial role is also played by such parameters as temperature and time of melting, size of the chromium pieces and oxygen content in the bath. When basing upon the results of the conducted studies as well as earlier experiments [2, 3] during melting of Cu-Ni-Si-Cr alloys, there was developed the optimal arrangement of technological parameters

Fig.1. Macrostructure of the Cu-Cr-Ni-Si alloy
A) Toos short time or too low melting temperature (large undissolved pieces of chromium visible)
B) Optimal melting time and temperature (structure after etching)

Table 1. Operating parameters for the determination of Cr, Ni and Si

Element	Analytical line (nm)	Slit (nm)	Flame	Type of flame1)	Burner height (cm)	Integration period (s)	Linear working range (µg/ml)
Cr	357,9	0,7	C_2H_2-N_2O	R	9	10	10
Ni	232,0 341,5	0,2 0,2	C_2H_2-air	O	7	3	10 25
Si	251,6	0,2	C_2H_2-N_2O	R	8	3	100

1) R – reducing, O – oxidizing

including temperature of melting equal to 1300°C, time of melting 15 minutes and size of the charge within the dimensions from 8 to 10 mm. It allows eliminating the unfavourable events in the processes of dissolving and evaporation of chromium pieces which differ considerable in their dimensions. The mentioned set of technological parameters facilitated obtaining the final chromium content in the alloys at the level of ca. 75% in a form of solid solution and intermetallic phases of Cr_3Si and $Ni_{16}Cr_6Si_7$ type, that is, the structures with optimal physical-mechanical properties [Fig. 1b; 3, 7, 8].

To determine the content of chromium, nickel and silicone in the discussed alloys, the method of atomic absorption spectrometry and, to a limited extent, the selected chemical methods [3, 8–13] were employed. The studies on the chemical composition of metal alloys and of the isolated phases were carried out with the application of FAAS spectrometer with the devices able to work in flame acetylene – air as well as acetylene – nitrous oxide. The initial pressures and gas flows were employed in conformity with the instruction of the equipment producer; however, each time the mentioned flows were so regulated as to obtain the maximum stable readouts of absorbance of the analysed elements. The earlier development [3] was employed in setting the optimal measuring heights (height of burner in relation to spectrum of radiation). The detailed measuring parameters of the elements determined in the tested alloys have been given in Table 1. In each analytical operation, a redistilled water was used. To eliminate the inter-elementary effects, own (internal) specific models were applied, with the chemical composition similar as that one of the analysed samples [4]. The obtained solutions of the samples and models were stored in the hermetically closed polyethylene containers. The comprehensive analytical diagram for determination of Cr-Ni-Si in Cu-Cr-Ni-Si alloys by AAS technique was presented in Fig. 2. We wish once again stress the role of technological parameters in the process of chromium dissolving in copper alloys: the samples sent to laboratory for determination of chemical composition may also contain such ones which contain small, undissolved pieces of chromium; it constitutes simultaneously the source of errors in determination of chromium level. It was also confirmed by the size of weighs (weighted amounts) of the samples prepared for chemical analyses, amounting – except for chromium determination – from 2g to even 5g [3, 9–11, 13] irrespectively of the choice of the employed methods and analytical techniques [7]. Such big weighs are reflected neither in sensitivity nor in precision of the used methods e.g. absorptive spectrometry, photometry or potentiometry. The discussed sizes of the sample weighs may

Table 2. Comparison of the results of determining the content of Cr, Ni and Si in copper alloys using chemical and AAS methods (variants of the AAS technique according to the analytical scheme – Fig.2)

Element	Chemical methods	AAS (variant 1)	AAS (variant 2)	AAS (variant 3)
Cr, mas. %	0.76 0.71	0.75 0.70	0.74 0.70	
Ni, mas. %	2.39 2.32	2.37 2.30	2.38 2.31	
Si, mas. %	0.60 0.56			0.59 0,55

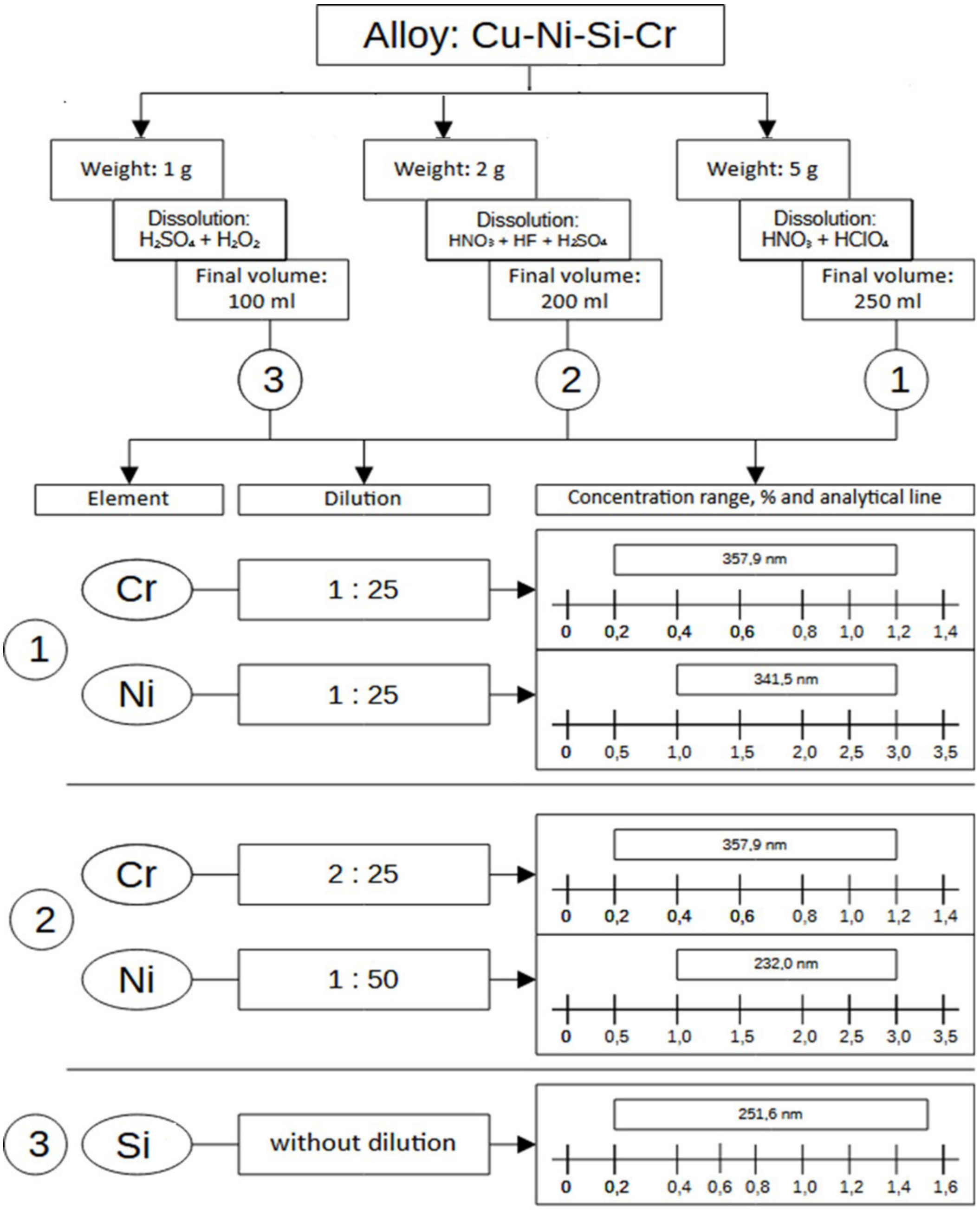

Fig. 2. The comprehensive analytical diagram for determination of Cr-Ni-Si in the Cu-Sr-Ni-Si alloys by AAS technique

only to a small extent eliminate the occurring segregation of chromium (undissolved pieces) in the analysed samples and eliminate or at least reduce considerably the errors in chromium determination in the discussed alloys. The preparation of the samples and models for chemical analyses by AAS technique was performed according to 3 variants, being described below in accordance with Fig. 2. Variant I: determination of silicone content in the discussed alloys was carried out by AAS technique, with the application of procedure given by D. Thormahlen and E. Frank [15] with the use of (3N) sulphuric acid (VI) with the additive of 30% hydrogen peroxide solution (Fig. 2). Variant 2: the weighed amount of the sample amounting to 5.000 g was placed in a beaker and digested in 50 ml of nitric acid (V). After termination of turbulent reaction, 50 ml of chloric acid (VII) was added and the solution was evaporated to thick white fumes (ca 20 min.) After cooling down, 150 ml of wate was added with the aim to dissolve salts. The, the solution was transferred quantitatively to measuring flask of 250 ml capacity. To determine the level of chromium and nickel, the initial solution was appropriately diluted (Fig. 2). Variant 3: The weighed amount of the sample, being equal to 2.000 g was placed in a Teflon beaker and 15 ml of nitric acid (V) and 5 drops of hydrofluoric acid were added. Then, 20 ml of sulphuric acid (V) were introduced and the solution was evaporated to fumes, leading the mentioned process until the complete dissolving of chromium oxides, and the content of the beaker was transferred quantitatively to 200 ml measuring flask. To determine chromium and nickel content, the initial solution was appropriately diluted (Fig. 2). The obtained results, a part of which is found in Table 2, with the consideration of variants for digestion of the samples given in Fig. 2. may be considered as satisfying. The relative standard deviations of the obtained results of chemical analysis of the discussed alloys by Aas technique were equal to: Cr – 1.4%, Ni – 1.0% and Si – 1.6%, respectively.

Summing up

Alloys Cu-Ni-Sr-Cr are fully valuable replacers of beryllium bronzes in the machine, mining, chemical and electrical industries. They may be employed *inter alia*, in manufacture of tools for resistance welding of element made from carbon, alloy, stainless and acid-resistant steels. They do not contain toxic beryllium, and in connection with this fact, the problems with the disposal of scraps and waste as well as with the rigoristic rules of work health and safety do not appear [2, 3, 7, 8]. From the technological viewpoint, the process of chromium dissolving in copper is difficult and time consuming and final content of chromium in copper alloys is dependent on the space of melting (material of crucible, atmosphere of smelting, protective coating and refiners), temperature of bath and time of smelting, size of the introduced chromium pieces and oxygen content in in the bath [1–5]. The mentioned factors have a deciding importance in the studies of chemical composition as well as of the structure of the copper and chromium alloys, constituting simultaneously the significant source of the errors, especially in respect of chromium content in final products. Therefore, observing the technological conditions of smelting the discussed alloys is undoubtedly basic and most important factor, ensuring obtaining the final product with the set properties. It should be also mentioned that the results of chemical analyses cannot be the only one check of the quality of the obtained alloys. Too short time of smelting (below the optimum, being set for a given temperature and time of smelting and the sizes of chromium pieces) may cause that the structure of the alloy may contain the aggregations of not completely dissolved chromium in the matrix. The results of the tests of the chemical composition are dependent, in this case, on the site of the sampling the material for analyses. Even in the case when the analysis reveals the required chromium content, the segregation of the mentioned component precludes obtaining the optimal structure and physical-mechanical properties after heat treatment (supersaturation and ageing). The precision of the suggested method was established on the grounds of the results of the analysis of a series of the samples, the chemical composition of which was determined by other methods and also, when the synthetic samples were used. The obtained results the part of which was given in Tab. 2, revealed a satisfying precision (accuracy). The relative standard deviations of the obtained results of chemical analyses of the discussed alloys by AAS technique amounted to: Cr – 1.4%, Ni – 1.0% and Si – 1.6%, respectively.

The developed method is characterized by a simplicity of performance, it is convenient and quick.

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