

Electrolytic extractions obtained from Cu-Zr and Cu-Ce alloys and their X-ray phase analysis

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Materials

ABSTRACT

Purpose: The aim of the investigations is the formation of electrolytic extractions from Cu-Zr and Cu-Ce model alloys containing microadditions of Zr and Ce amounting to about 0.1% by weight and their identification by X-ray diffraction analysis.

Design/methodology/approach: Electrolytic extractions were obtained by the anodic dissolution of the alloys. In the X-ray analysis the comparative method was applied.

Findings: The activity of anodic dissolution of the investigated alloys was determined basing on the mass of the electrolytic extraction and the time of dissolution of the alloy in solutions of the electrolytes with different chemical compositions and a different complexive effect to copper and different pH.

Research limitations/implications: The qualitative X-ray phase analysis permits to identify the main intermetallic phases of the investigated alloys in a limited range, mainly due to experimental reasons.

Practical implications: The results of these investigations indicate a distinct relation between the mass and the kind of the dissolved phase and the value of the electrochemical potential of the active dissolution of the alloys.

Originality/value: The revealing of this relation is of practical importance in regard to the accuracy of the results of the phase and crystal analysis carried out by X-ray diffraction examination.

Keywords: Metallic alloys; Copper alloys; Microadditives Zr and Ce; Anodic dissolution; X-ray phase analysis

1. Introduction

Copper alloys, particularly bronzes, are widely applied due to some favourable practical properties, such as: good strength and plasticity, wear resistance and extreme corrosion resistance in atmospheric conditions, even in seaside conditions. The processing of these alloys is, however, limited by their brittleness at elevated temperature of plastic deformation. In order to reduce this effect to its minimum bronzes are modified by introducing microadditives [1÷4]. This leads to the appearance of additional intermetallic phases in the matrix of the solid solution- α resulting from the phase-equilibrium system, which is specific for copper

and microadditives. The optimal application of modifiers in the casting and processing of bronzes requires, therefore, a good knowledge of the stable phase-equilibrium system and full phase identification of the formed metallic and non-metallic inclusion in investigated model alloys of the type Cu-Zr and Cu-Ce. The published phase-equilibrium binary systems of these alloys differ within the range of the stoichiometry of the occurring phases, the determination of the dissolubility of the alloy components, with respect to temperature of the formation and composition of the fluids and solid phases [5÷8]. Due to the rather small content of these phases in the investigated materials their identification by X-ray analysis of massive samples is complicated. This is most often carried out making use of electrolytic extractions [9]. These

are obtained by the anodic dissolution of massive samples at a controlled electrochemical potential. In effect, the dissolved metal is transformed during the electrolysis into ions dissolved in the electrolyte [10÷12]. In the case of bronzes the copper undergoes anodic dissolution, whereas the other phases form an undissolved anodic deposit, which is the final product for X-ray phase analysis.

Essential is the composition of the solution applied in the process of dissolving the samples of copper and its pH, because copper can be dissolved anodically as simple ions Cu^+ and Cu^{2+} or complex ions with cyanide ligands $[\text{Cu}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$ or ammonia $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Sulphate solutions are usually acidified to $\text{pH} \approx 3$ and even $\text{pH} \approx 1$. Ammonia solutions display an alkaline reaction with $\text{pH} \approx 10$, and cyanide solution is more alkaline, up to $\text{pH} \approx 13$ [13,14].

The aim of the investigations was to select and optimize the chemical composition of electrolyte solutions and to determine their activity in the anodic dissolution of the investigated alloys, and also to determine the influence of the conditions of electrochemical separation on the effect of phase identification of the model alloys Cu-Zr and Cu-Ce by X-ray diffraction analysis.

2. Experimental procedure

The material for the test has been got in laboratory conditions at ENSMSE¹ and IMN² Gliwice, basing on pure components: Cu 99,99% (OFHC, quality c.10100 according to ASTM), with an impurity content: (Bi, Pb, O₂, Se, Te) – 10ppm; S-18ppm; P-3ppm; (Hg, Zn) – 1ppm and Ce 99,9% (CERAC Inc. Milwaukee), Cert. C-1055 with (Fe, La, Pr, Nd) < 0,05%; (Al, Ca, Fe, Mg, Si, Y) < 0,01% and Zr 99,8% (Zirconium sponge Koch–Light Lab. Ltd. Colnbrook) – only to lab. applications. The melts obtained at IMN Gliwice were used in the production of Zr alloys oxygen-free copper, smelted in a vacuum of the kind Cu 99,99% (MOOB) with a chemical composition according to PN-87/H-82120. The melts were obtained in a graphite crucible in a vacuum induction furnace or in a protective atmosphere Ar+H₂. After melting they were heat-treated in the homogeneous annealing range of 720-750°C for 5 hours, and then cool-forged. The chemical composition of these alloys is to be seen in Table 1.

Electrochemical investigations included the determination of the active potential of dissolution of the tested alloys in adequately selected chemical reagents (Table 2) and the anodic dissolution at the determined values of the potential within the range of active dissolution and the passive area (Table 3). It was, however, necessary to determine the curves of anodic polarization $I=f(E)$ determining the dependence of the rate of dissolution on the assumed potential and the ranges of active dissolution and anodic passivation of the metal [15]. Basing on this relation the potential E_d was determined, at which the ratio of the dissolution rate of the matrix to inclusions reached its maximum.

The curves of polarization of the investigated alloys were determined making use of the potentiodynamic method of linear voltamperometry applying a glass electrolyzer equipped with a diaphragm of glass sinter separating the anodic space from the

cathodic one (Fig.1) and the potentiostat PGP 201. The potentiodynamic curves of the anodic polarization of the alloy CuZr(2) determined various solutions by means of the programme Voltmaster 1 have been presented in the diagram (Fig.2).

Table 1.

Chemical composition of the used specimens

Ordinal number	Designation of alloy	Origin	Chemical composition in mass %						
			Zr	Ce	Bi	Pb	Sb	S	Cu
1	CuZr (1)	ENSMSE	0,13	-	0,001	0,004	0,0002	0,001	res.
2	CuZr (2)	IMN	0,11	-	0,0001	0,0003	0,0002	0,0008	res.
3	CuCe (4)	ENSMSE	-	0,13	0,001	0,004	0,0002	0,002	res.

Table 2.

The composition of electrolytes-solutions applied for the anodic dissolution of the investigated alloys

Ordinal number	Electrolyte	Chemical composition
1	Oettl's solution	15g CuSO ₄ 5g H ₂ SO ₄ 5g C ₂ H ₅ OH 100ml H ₂ O
2	Ammonium acetate solution: - ammonium acetate (4M) - ammonia (2,5M)	30,8g CH ₃ COONH ₄ 4,25g NH ₃ 100ml H ₂ O
3	Cyanide solution: - sodium cyanide	19,6g NaCN 100ml H ₂ O
4	Ammonium acetate solution: - ammonium acetate (5M)	38,5g CH ₃ COONH ₄ 100ml H ₂ O

X-ray examinations of electrolytic extractions were carried out by means of an X-ray diffractometer type Siemens D5000 applying radiation of the anode $\lambda\text{CuK}\alpha/\text{Ni}$ (40kV, 30mA). The electrolytic extractions, deposited on the absorbent paper were analysed in the range 2θ from 3÷100, applying the step-scanning method, at steps 0,02°2 θ . The obtained diffraction patterns were subjected to X-ray phase analyses, making use of the programme Diffract AT Serch/Match.

Table 3.

Electrochemical active potentials of dissolution

No.	Alloy	Number of electrolyte	Potential of dissolution [mV] in regard to NEK
1	CuZr (2)	1	200
2	CuZr (2)	2	-250
3	CuZr (2)	3	-650
4	CuZr (2)	4	50
5	CuZr (1)	2	-250
6	CuZr (1)	3	-650
7	CuCe (4)	2	-250
8	CuCe (4)	3	-650

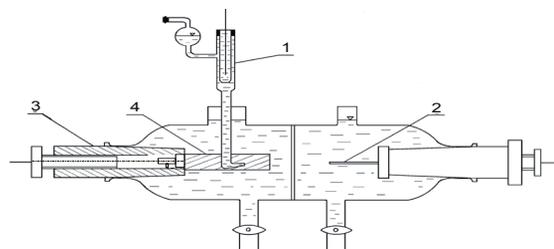


Fig. 1 Diagram of an electrolyzer for the anodic solution of copper alloys: 1- Haber-Lugin capillary with a reference electrode, 2 – auxiliary electrode, 3 – holder of the tested electrode, 4 – sample

¹ENSMSE - Ecolé Nationale Supérieure des Mines de Saint-Etienne (France)

²IMN – Institute of Nonferrous Metals, Gliwice (Poland)

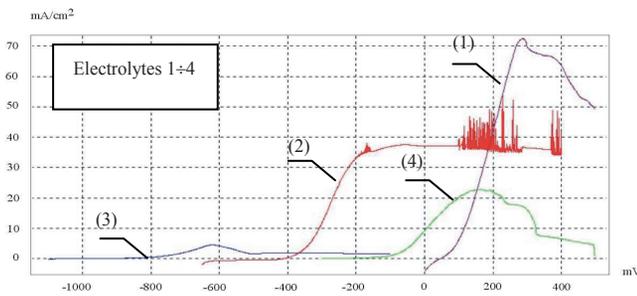


Fig.2 Potentiodynamic curves of anodic polarization for the alloy CuZr (2) created by the method of linear voltamperometry for various electrolytic solutions

3. Results and discussion

Electrolytic solutions applied in the anodic dissolution of copper alloys were selected with respect to the values of the stationary electrochemical potential of copper and also the value of pH. In Oettl's solution copper displays the most positive electrochemical potential at pH approaching 1. The most negative potential displays copper in sodium cyanide solution with pH about 13 ($E_{I=0} \approx -0,7V$). This is undoubtedly due to the complexive effect of the applied electrolytes versus the copper ions and the concentration of free copper ions in the solution connected with the durability of the generated complex. The activity of electrolyte solutions in the process of dissolution of the investigated alloys was assessed basing on the decrease of the mass of the dissolved sample and the precipitated anodic deposit and the time of dissolution, as well as the dissolution index (Table 4.)

It has been found that taking into account the mass of the obtained electrolytic extraction versus the mass of the dissolved sample of CuZr (2) and the time of dissolution, the most effective solutions are No.1 and No.3; with regard to the rate of dissolution, however, resulting from the current intensity in the case of the selected potential of the anodic process the solution No.2 is most effective. Anodic dissolution of CuZr (1) runs also fastest in solution No.2. But as far as the mass of the electrolytic extraction is concerned solution No.3 proved to be the most effective. In the case of the alloy CuCe(4) the most active is also solution No.3.

The results of X-ray phase analysis of electrolytic extraction have been gathered in Tables 5 and 6. It has been found that electrolytic extractions obtained on absorbing paper display distinct diffraction lines of not fully amorphous filter material (within the range about 15 and 23°2θ) which did not coincide with the diffraction lines of electrolytic extractions.

The phase analysis of electrolytic extractions of the model alloy CuZr(2) permits to identify the main phases: Cu₅Zr and Cu Zr and probably Cu₉S₅, Zr₃S₂, CuCl as well as pure copper. A phase analysis of the electrolytic extraction of CuZr(1) confirmed the existence of the following phases: Cu₅Zr and CuZr (Table 6). Most effective in revealing this phase proved to be the solution No.2 and least effective – solution No.3. The standard phase analysis of the electrolytic extraction of the

model alloy CuCe(4) displayed mainly the presence of the phase: Cu₅Ce and Cu₆Ce (Table 5) and α-Ce₂(SO₄), CeO₂ as well as pure copper. The presence of rather strong diffraction lines characteristic for metallic copper may prove the uncomplete dissolution of the alloy matrix. Moreover, the diffraction patterns obtained for these model alloys (Cu-Zr) differ both in the presence of diffraction lines and their intensity, the width of the diffraction lines and the level of the background. This may prove the instability of conditions of the process of electrolytic dissolution of the investigated alloys.

Table 4.

The influence of the conditions of the anodic dissolution of alloys on the efficiency of the process

No.	Alloy	Number of electrolyte	Reduction of	Increase of	Time of dissolution [min.]	Indicator of dissolution [min ⁻¹]
			mass of the specimens [g]	the filter mass [g]		
1	CuZr (2)	1	7,66	0,08	1060	9,85·10 ⁻⁶
2	CuZr (2)	2	7,99	0,02	1030	2,43·10 ⁻⁶
3	CuZr (2)	3	0,94	0,01	1220	8,72·10 ⁻⁶
4	CuZr (2)	4	3,97	0,01	1260	2,00·10 ⁻⁶
5	CuZr (1)	2	5,80	0,02	840	4,11·10 ⁻⁶
6	CuZr (1)	3	0,66	0,01	1160	1,31·10 ⁻⁵
7	CuCe (4)	2	7,57	0,02	1470	1,80·10 ⁻⁶
8	CuCe (4)	3	1,49	0,03	2830	7,11·10 ⁻⁵

Table 5. Results of the X-ray phase analysis of electrolytic extractions of model alloy CuCe (4)

Line No.	Alloy CuCe (4)				Identified phase					
	Electrolyte				Cu ₅ Ce (17-22)			Cu ₆ Ce (5-660)		
	No.2		No.3		d(hkl)	I/I ₀	hkl	d(hkl)	I/I ₀	hkl
1	3.152	21					3.165	40	202	
2	3.019	18	3.016	100	3.010	60	101	3.024	10	211
3	2.809	26	2.794	88			2.813	90	013	
4			2.601	98			2.656	80	113	
5	2.539	46			2.561	60	110	2.545	100	004
6	2.379	24					2.381	60	302	
7	2.349	11					2.355	60	121	
8	2.308	100	2.303	80			2.313	100	213	
9	2.273	30	2.275	77	2.219	50	200	2.271	80	022
10	2.187	18			2.173	100	111	2.183	40	122
11	2.152	28	2.133	68			2.149	80	204	
12	2.105	22					2.107	60	221	
13	1.977	44					1.981	90	401	
14	1.966	48	1.955	63	1.953	20	201	1.967	90	102
15			1.892	65			1.881	20	015	
16	1.752	15					1.753	40	124	

Summing up, it may be said that the number of revealed diffraction lines and the relative intensities depend essentially on the kind of the electrolyte solution applied for the dissolution at the investigated model alloys. This suggests a distinct dependence of the mass and kind of the dissolved phase on the value of the electrochemical potential and the active or passive state of the surface of the dissolved alloy versus NEK. This dependence requires, however, further experimental proofs.

Table 6.
The result of X-ray phase analysis of electrolytic extractions of the model alloy CuZr(2)

Diff. line No.	Electrolyte							Identified phase						Other phases		
	No.1		No.4		No.2			No.3								
	d(hkl)	I/I ₀	d(hkl)	I/I ₀	Cu ₅ Zr (40-1322)		CuZr (49-1484)									
		5,87	I/I ₀	d(hkl)	I/I ₀	d(hkl)	I/I ₀	d(hkl)	I/I ₀	hkl	d(hkl)	I/I ₀	hkl	d(hkl)	I/I ₀	Phase
1		5,336	26													Absorbent paper
2		3,888	24													Absorbent paper
3			100													Absorbent paper
4		2,419	24											3,12	100	CuCl
5		2,127	24	2,406	11	2,409	9									
6	2,089	53									2,113	38	201			
7		2,069												2,088	100	Cu
8		1,998	43	2,065	10			2,0714	100	311	2,066	100	111			
9	1,917	41		1,985	10	1,994	7	1,9832	34	222	1,985	14	20 $\bar{2}$			
10														1,808	46	Cu
11	1,634	18		1,731	10			1,717	18	400						
12	1,354	2	1,324								1,655	16		1,633	30	CuCl
13	1,279	9		2				1,3221	22	511	1,311	13	202	1,354	6	CuCl
14	1,243	4	1,215											1,278	20	Cu
15																

4. Conclusions

1. Electrochemical dissolution of copper alloys modified with Zr and Ce is an effective method of separating an adequate mass of electrolytic extractions for X-ray crystal analysis of intermetallic phases in the, investigated alloys.
2. The activity of electrolyte solutions applied for the anodic dissolution of the investigated alloys Cu-Zr and Cu-Ce depends on the presence of the components generating complexes in the solution and its pH; a lower pH is connected with a higher potential of the active dissolution of the alloy.
3. Anodic dissolution of the investigated alloys runs most quickly in a solution of sodium cyanide, but then the amount of electrolytic extractions is at its minimum, due to the strong complexive effect of cyanide ions and the aggressivity versus the anodic material.
4. The most favourable solution used to dissolve the obtained model alloys Cu-Zr and Cu-Ce and to isolate the structural components is ammonium acetate solution with ammonia.
5. The qualitative standard X-ray phase analysis permits to identify the main phases of the investigated alloys in a limited range, chiefly due to experimental and interpretational reasons connected with the application of the comparative method.

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