INFLUENCE OF CHEMICAL COMPOSITION AND VOLUME FRACTION OF PHASES ON THE DEZINCIFICATION RESISTANCE OF BRASSES

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Abstract

Although brasses are resistant to several forms of corrosion, they are susceptible to dezincification – selective dissolution of zinc – which may be responsible for failures in service of casting brass products. The effect of the chemical composition on dezincification resistance of brasses has been investigated. This study includes both commercial alloys and alloys prepared in laboratory in order to evaluate the specific effect of alloying elements such as lead, silicon, aluminium, iron, tin, nickel and arsenic upon the dezincification resistance. The effect of the volume fraction of α phase in the dezincification behaviour has also been studied. Dezincification tests have been carried out according to the ISO 6509 standard. The influence of the various alloying elements in the depth of the dezincificated layer, has been evaluated. The statistic treatment of results enable to the establishment of correlationship between the studied properties and the contents of some elements present in the chemical composition of brasses.

1. INTRODUCTION

The dezincification, form of selective dissolution, is responsible for failures in service of casting brass products, namely plumbing fixtures, fittings, valves and connection systems [1,2,3,4].

This type of dissolution, referred for the first time back in 1866 [5], consists of the selective removal of zinc, leaving a weak porous mass of copper (90% 95% of copper and the remainder in the form of copper oxide), which can result in decreasing of mechanical properties and leakages [1,2,3,6,7,8,9,10,11,12,13]. There are two general types of dezincification: the uniform and the plug type.

High temperatures, chlorine concentrations, CO_2 levels in addition to low pH, water flow rates and conditions of limited aeration are factors that contribute to the acceleration of the dezincification process [3,6,14,15].

As pointed out by several researchers the dezincification resistance of the alloys is dependent on the chemical composition and on the total amount and distribution of phases in the microstructure. This form of dissolution can be minimized by the addition of inhibiting elements, by the use of an alloy with a appropriate effective copper content or by modifications of the microstructure, as a result of heat treatment [6,9,15].

Although tin is successfully used in casting brasses in order to decrease the dezincificationt rate, the best inhibiting effects are obtained by the addition of arsenic, antimony and phosphorous to the alloy [2,3].

All brasses containing more than 15% Zn are prone to dezincification. However the presence of the β phase enhances this process [2,3]. In addition to the amount of β phase the single most important controlling factor is the phase distribution in the microstructure [2,3,9].

2. EXPERIMENTAL PROCEDURE

Some brasses used in this study are commercial alloys, while others have been produced in laboratory, in a medium frequency induction furnace, with additions of aluminium, lead, silicon, iron and tin. These alloys were obtained by casting commercial brasses followed by additions of the alloying elements mentioned above, either alone or combined, and by melting high purity copper and zinc followed by the additions of aluminium, iron or tin. All the alloys were casted into a 25mm diameter rod, by permanent mold casting in iron mould.

Specimens were cut from the obtained brass rods and were analysed by XRF spectrometry to determine the chemical composition.

By applying image analysis techniques to the obtained microstructures, the volume fraction of the different phases has been determined.

Dezincification tests have been carried out according to the ISO 6509 standard [16]. In these tests, specimens with a $100mm^2$ area were immersed in a 250 ml solution of copper chloride (III) at 1% for 24 hours. Solution temperature was kept a 75ºC ± 5ºC.

At the end of each test, the specimen was cutted, polished and observed by optical microscopy. The dezincification depth has been determined by the digital micrometer connected to the optical microscope. For each sample a minimum of 30 measurements of dezincification depth were made. In table 1 is presented the minimum, maximum and mean value of the measurements.

To determine the influence of the volume fraction of the phases upon the dissolution of zinc alloys of different compositions, 13 out a total of 94, were heated at 830ºC, followed by a stabilization period of 30 min, and slowly cooled (at 2ºC/min) to 450ºC. Subsequently, the samples were kept at this temperature for 24 hours followed by rapid quenching in a solution of salted water and ice at ~0ºC. The thermal cycle is presented in figure 1.

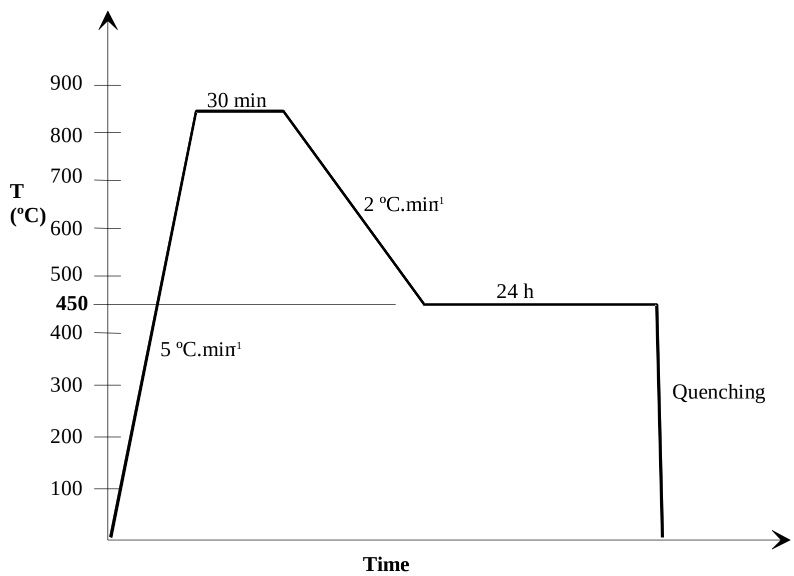


Figure 1 – Thermal cycle used to obtain the equilibrium structure of the alloys.

After the thermal cycle the samples were submitted to the dezincification tests as described above.

3. RESULTS AND DISCUSSION

The chemical composition of the alloys, the volume fraction of α phase and the maximum, minimum and average depth of the dezincified layer are presented in table 1.

The statistical analysis of the relationship between the average of the dezincified layer depth and the chemical composition, expressed in terms of effective copper content* (Cu_E), shows no significative correlation ($r^2 = 0.002$). The same result is obtained even when we consider the individual values for the maximum and for the minimun dezincification depths, instead of the average of the measurements.

The effect of the chemical composition, considering all the elements present on the alloy composition, has been also evaluated by multivariate regression. The following expression, valid for the studied range of compositions, was obtained:

$$\textbf{Dezincification depth } (\mu m) = 364 - 70\ \%Sn - 916\ \%As + 204\ \%Si + 578\ \%Ni - 45\ \%Pb \qquad (1)$$

with a correlation coefficient of 0.31.

According to expression (1) tin, lead and especially arsenic improves the dezincification resistance of brasses. By the other hand, silicon and nickel seems to improve the selective dissolution of zinc. The value of r^2 obtained shows that it is not easy to establish a strong deterministic relationship between the various analysed elements and the dezincification behaviour.

The multivariate regression of all the individual measurements of the dezincification depth, against the volume fraction of the phases, enabled the establishment of the following expression:

$$\textbf{Dezincification depth } (\mu m) = 108 + 0.065\ (\%\alpha)^2 \qquad (2)$$

with a correlation coefficient of 0.41.

* Calculated according to the Guillet expression [17] :
$Cu_E = Cu \times 100 / (Cu + Zn + 2Sn + Pb + 0.9Fe - 1.3Ni + 0.5Mn + 6Al + 10Si$

Table 1 – Dezincification depth, chemical composition and volume fraction of α phase of the alloys.

Alloy	Depth of dezincified layer (µm)				Cu_E	α	Cu	Zn	Pb	Sn	Fe	Ni	Al	Si	P	As
	Average	STDV	Max	Min	%	%	%	%	%	%	%	%	%	%	%	%
1	570	151	873	257	57.74	54.3	59.57	Rem	1.81	0.65	0.69	0.35	0.62	<0.05	<0.05	<0.05
2	178	65	352	109	58.28	53.7	60.10	Rem	1.27	0.10	0.07	0.04	0.59	<0.05	<0.05	<0.05
3	280	136	620	145	57.98	51.3	59.51	Rem	1.31	0.09	0.06	0.06	0.53	<0.05	<0.05	<0.05
4	230	38	361	172	58.16	37.1	59.72	Rem	1.49	0.12	0.07	0.04	0.51	<0.05	<0.05	<0.05
5	225	62	374	117	57.31	47.4	59.01	Rem	1.59	0.10	0.07	0.03	0.54	<0.05	<0.05	<0.05
6	210	111	465	99	58.65	55.4	60.17	Rem	1.28	0.11	0.08	0.04	0.51	<0.05	<0.05	<0.05
7	219	75	412	80	57.93	38.4	59.61	Rem	1.17	0.18	0.07	0.06	0.56	<0.05	<0.05	<0.05
8	198	51	339	124	57.63	37.6	59.36	Rem	1.16	0.15	0.06	0.03	0.58	<0.05	<0.05	<0.05
9	232	51	352	146	58.08	40.9	59.62	Rem	1.52	0.15	0.15	0.12	0.55	<0.05	<0.05	<0.05
10	246	61	418	143	58.09	55.6	59.81	Rem	1.27	0.17	0.11	0.05	0.58	<0.05	<0.05	<0.05
11	244	105	640	138	56.59	31.7	58.74	Rem	1.40	0.13	0.11	0.06	0.72	<0.05	<0.05	<0.05
12	230	73	386	146	57.01	53.7	59.16	Rem	1.35	0.13	0.13	0.06	0.70	<0.05	<0.05	<0.05
13	167	87	440	54	56.73	45.7	58.49	Rem	1.27	0.08	0.06	0.03	0.61	<0.05	<0.05	<0.05
14	554	233	846	160	56.30	53.3	58.70	Rem	1.52	0.47	0.91	0.19	0.67	0.09	<0.05	<0.05
15	736	146	957	311	57.38	68.8	60.20	Rem	2.35	0.67	0.36	0.19	0.89	<0.05	<0.05	<0.05
16	203	95	423	113	56.88	43.6	58.71	Rem	1.19	0.10	0.08	0.04	0.62	<0.05	<0.05	<0.05
17	158	30	222	107	58.06	62.0	60.12	Rem	2.20	0.47	0.26	0.16	0.67	<0.05	<0.05	<0.05
18	175	47	354	92	57.69	57.6	59.55	Rem	1.38	0.13	0.09	0.04	0.63	<0.05	<0.05	<0.05
19	324	73	513	205	58.11	59.5	59.98	Rem	1.23	0.17	0.13	0.15	0.68	<0.05	<0.05	<0.05
20	189	56	365	99	58.61	62.3	60.38	Rem	0.67	0.15	0.09	0.02	0.59	<0.05	<0.05	<0.05
21	277	91	489	147	57.85	57.5	59.84	Rem	1.16	0.12	0.08	0.04	0.65	<0.05	<0.05	<0.05
22	228	72	448	148	57.46	53.5	59.25	Rem	1.23	0.13	0.13	0.06	0.68	<0.05	0.05	0.20
23	302	69	465	150	58.98	57.8	60.33	Rem	1.92	0.84	0.66	0.53	0.44	0.05	<0.05	<0.05
24	176	93	436	95	57.33	42.4	59.51	Rem	1.21	0.16	0.10	0.06	0.75	<0.05	<0.05	<0.05
25	694	59	865	563	56.63	56.9	59.63	Rem	1.93	0.70	0.71	0.42	0.80	0.15	<0.05	<0.05
26	210	54	343	72	60.68	82.1	62.38	Rem	0.82	0.13	0.10	0.01	0.54	<0.05	<0.05	<0.05
27	815	71	956	603	57.76	53.3	61.04	Rem	1.08	0.51	1.01	0.12	1.11	<0.05	<0.05	<0.05
28	174	44	280	108	57.98	48.6	59.95	Rem	1.53	0.11	0.10	0.05	0.68	<0.05	<0.05	<0.05
29	266	32	339	199	58.08	*	61.54	Rem	2.40	1.04	0.34	0.25	1.05	<0.05	<0.05	<0.05
30	266	68	433	129	56.89	*	61.20	Rem	2.33	1.57	0.33	0.25	1.27	<0.05	<0.05	<0.05
31	93	58	302	25	54.98	*	60.45	Rem	2.25	2.73	0.33	0.25	1.50	<0.05	<0.05	<0.05
32	50	31	133	10	52.53	*	59.60	Rem	2.21	4.54	0.32	0.24	1.84	<0.05	<0.05	<0.05
33	739	399	1050	64	55.36	*	61.24	Rem	2.43	0.54	0.33	0.24	2.01	0.06	<0.05	<0.05
34	1065	191	1293	565	50.74	*	60.40	Rem	2.42	0.54	0.32	0.24	3.64	0.08	<0.05	<0.05
35	499	72	595	346	56.48	*	62.00	Rem	2.39	0.54	0.31	0.25	0.83	0.52	<0.05	<0.05
36	725	76	931	628	53.68	*	61.86	Rem	2.37	0.54	0.33	0.25	0.79	1.03	<0.05	<0.05
37	769	44	836	662	47.55	*	61.64	Rem	2.27	0.53	0.40	0.25	0.80	2.34	<0.05	<0.05
38	578	90	745	396	57.72	*	61.47	Rem	3.01	0.54	0.33	0.25	1.20	0.05	<0.05	<0.05
39	697	61	807	579	56.49	*	60.70	Rem	4.11	0.54	0.33	0.24	1.39	0.05	<0.05	<0.05
40	407	176	811	241	55.26	*	60.21	Rem	4.23	1.08	0.33	0.24	1.57	0.06	<0.05	<0.05
41	228	48	348	162	53.47	*	59.53	Rem	4.26	2.16	0.32	0.24	1.77	0.05	<0.05	<0.05
42	206	79	491	131	56.26	34.3	59.38	Rem	0.50	0.03	0.07	<0.02	1.03	<0.05	<0.05	<0.05
43	212	44	290	147	56.16	36.8	59.20	Rem	0.95	<0.02	0.07	<0.02	1.01	<0.05	<0.05	<0.05
44	247	105	433	83	57.09	*	58.36	Rem	1.17	0.55	2.72	0.10	0.40	<0.05	<0.05	<0.05
45	182	97	361	32	55.84	*	56.97	Rem	1.18	0.39	1.93	<0.02	0.32	<0.05	<0.05	<0.05
46	165	36	262	128	58.08	40.2	60.01	Rem	1.24	0.14	0.06	0.07	0.61	<0.05	<0.05	<0.05
47	296	129	528	82	55.13	*	56.17	Rem	1.32	0.37	1.30	0.02	0.34	<0.05	<0.05	<0.05

(cont)

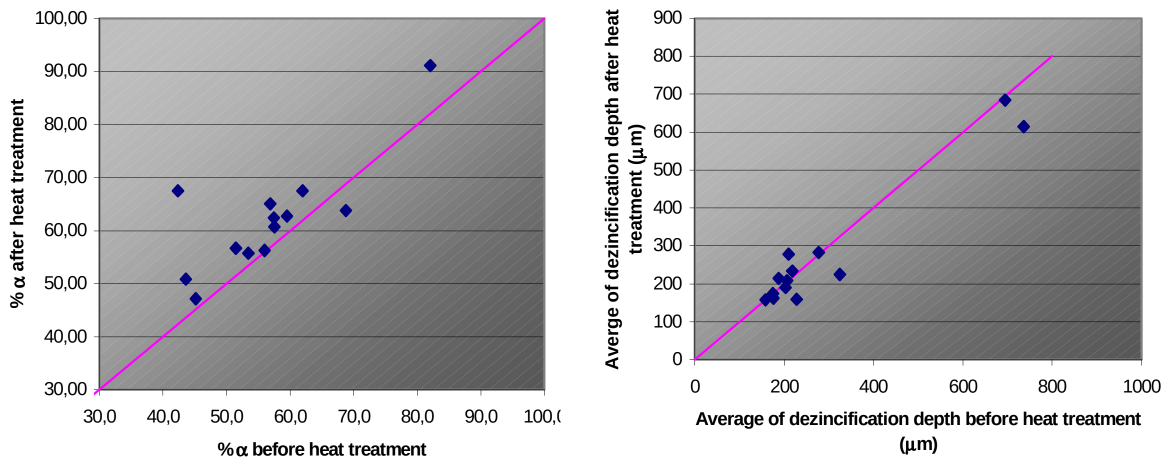
Table 1 – Dezincification depth, chemical composition and volume fraction of α phase of the alloys (cont).

Alloy	Depth of dezincified layer (µm)				Cu_E	α	Cu	Zn	Pb	Sn	Fe	Ni	Al	Si	P	As
	Average	STDV	Max	Min	%	%	%	%	%	%	%	%	%	%	%	%
48	467	71	615	302	60.25	*	61.66	Rem	1.95	0.49	0.32	0.20	0.38	<0.05	<0.05	<0.05
49	438	196	859	197	59.36	*	60.22	Rem	1.85	0.36	0.28	0.17	0.27	<0.05	<0.05	<0.05
50	141	29	208	103	57.98	*	60.17	Rem	1.56	0.19	0.12	0.07	0.71	<0.05	0.05	<0.05
51	298	104	464	154	57.83	*	60.58	Rem	2.10	0.72	0.69	0.56	0.82	0.12	<0.05	<0.05
52	683	68	798	540	58.77	*	60.47	Rem	1.84	0.53	0.69	0.22	0.52	<0.05	<0.05	<0.05
53	282	39	389	216	57.90	*	59.82	Rem	<0.05	0.02	0.09	0.11	0.72	<0.05	<0.05	<0.05
54	167	103	485	72	57.91	*	59.85	Rem	1.26	0.11	0.10	0.09	0.59	<0.05	<0.05	<0.05
55	229	73	394	198	58.18	*	59.66	Rem	1.14	0.09	0.09	0.05	0.52	<0.05	<0.05	<0.05
56	0	0	0	0	62.36	*	65.96	Rem	4.09	2.80	0.62	0.30	0.59	0.07	<0.05	<0.05
57	0	0	0	0	57.00	*	58.88	Rem	1.79	0.67	0.62	0.24	0.59	<0.05	<0.05	<0.05
58	215	38	307	142	58.05	*	60.04	Rem	1.84	0.48	0.63	0.20	0.60	<0.05	<0.05	<0.05
59	0	0	0	0	60.61	*	62.45	Rem	1.35	0.35	0.17	0.12	0.52	<0.05	<0.05	0.09
60	188	96	492	71	56.83	45.2	58.84	Rem	1.22	0.09	0.10	0.03	0.65	<0.05	<0.05	<0.05
61	206	78	409	113	56.93	51.5	59.35	Rem	1.28	0.12	0.08	0.04	0.78	<0.05	<0.05	<0.05
62	218	55	412	137	57.45	56.0	59.32	Rem	1.30	0.17	0.16	0.09	0.66	<0.05	<0.05	<0.05
63	263	55	340	180	58.12	*	60.22	Rem	1.17	0.11	0.18	0.12	0.73	<0.05	<0.05	0.11
64	1497	71	1656	1339	60.28	67.7	59.95	Rem	<0.05	<0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
65	1364	285	1689	731	59.53	75.7	59.55	Rem	<0.05	<0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
66	280	65	388	137	59.20	73.6	59.40	Rem	<0.05	0.35	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
67	248	58	413	161	58.83	*	59.29	Rem	<0.05	0.78	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
68	217	45	321	158	58.65	*	59.32	Rem	<0.05	1.15	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
69	417	141	669	167	67.42	100	67.48	Rem	<0.05	<0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
70	281	68	383	141	66.76	100	67.19	Rem	<0.05	0.55	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
71	263	65	431	153	66.48	100	67.04	Rem	<0.05	0.85	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
72	270	36	323	203	65.80	*	66.71	Rem	<0.05	1.39	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
73	229	64	335	94	65.53	*	66.69	Rem	<0.05	1.78	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
74	1284	304	1654	805	64.99	100	65.05	Rem	<0.05	0.05	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
75	239	37	310	161	64.56	100	64.94	Rem	<0.05	0.60	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
76	159	44	255	77	64.22	*	64.83	Rem	<0.05	0.95	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
77	1429	180	1626	980	61.24	90	61.24	Rem	<0.05	<0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
78	1087	172	1346	546	60.98	80.7	61.16	Rem	<0.05	0.31	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
79	222	65	360	80	60.77	77.4	61.09	Rem	<0.05	0.52	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
80	178	51	259	60	60.58	*	61.04	Rem	<0.05	0.76	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
81	360	104	660	253	55.53	*	55.54	Rem	<0.05	0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
82	98	42	205	37	54.46	*	56.55	Rem	<0.05	3.84	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
83	109	20	171	81	52.44	*	55.37	Rem	<0.05	5.30	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05
84	281	70	404	150	58.13	59.5	58.10	Rem	<0.05	<0.02	0.49	<0.02	<0.05	<0.05	<0.05	<0.05
85	242	85	420	130	58.88	68.5	58.83	Rem	<0.05	<0.02	0.90	<0.02	<0.05	<0.05	<0.05	<0.05
86	189	55	306	107	61.16	81.3	61.24	Rem	<0.05	<0.02	0.46	<0.02	<0.05	<0.05	<0.05	<0.05
87	164	45	254	91	59.86	72.9	61.33	Rem	<0.05	<0.02	<0.02	<0.02	0.49	<0.05	<0.05	<0.05
88	168	129	572	60	57.98	46.8	61.04	Rem	<0.05	<0.02	<0.02	<0.02	1.05	<0.05	<0.05	<0.05
89	499	93	630	335	56.31	*	60.82	Rem	<0.05	<0.02	<0.02	<0.02	1.60	<0.05	<0.05	<0.05
90	461	151	761	217	52.50	*	61.35	Rem	<0.05	<0.02	<0.02	<0.02	3.37	<0.05	<0.05	<0.05
91	149	37	256	67	57.74	53.2	59.63	Rem	<0.05	<0.02	<0.02	<0.02	0.54	<0.05	<0.05	<0.05
92	130	66	291	54	56.00	*	59.38	Rem	<0.05	<0.02	<0.02	<0.02	1.09	<0.05	<0.05	<0.05
93	110	28	201	80	54.83	*	59.43	Rem	<0.05	<0.02	<0.02	<0.02	1.58	<0.05	<0.05	<0.05
94	116	18	156	87	49.36	*	58.72	Rem	<0.05	<0.02	<0.02	<0.02	3.68	<0.05	<0.05	<0.05

The quadratic expression (2) evidences the effect of the volume fraction of α phase upon the depth of the dezincified layer. Because this observation is in disagreement with other findings, it was considered pertinent to make a comprehensive study concerning the influence of the volume fraction of phases on the dezincification resistance of brasses. For this purpose a set of samples were submited to the thermal cycle shown on figure 1.
The results obtained before and after heat treatment are presented on table 2 and illustrated graphically on figure 2.

Table 2 - Effect of heat treatment on volume fraction of α phase and dezincification depth (considering the mean value).

	Before heat treatment		After heat treatment	
Alloy	% α	Average of dezincification depth (μm)	% α	Average of dezincification depth (μm)
15	68.8	736	63.8	614
16	43.6	203	50.9	191
17	62.0	158	67.5	157
18	57.6	175	60.7	174
19	59.5	324	62.8	225
21	57.5	277	62.4	282
22	53.5	228	55.8	159
24	42.4	176	67.5	162
25	56.9	694	65.1	684
26	82.1	210	91.1	278
60	45.2	188	47.2	214
61	51.5	206	56.7	208
62	56.0	218	56.3	234



a) b)

Figure 2 – Effect of heat treatment upon the a) α phase fraction and b) dezincification depth.

Figure 2 shows that heat treatment increases the volume fraction of α phase. However, its effect upon the dezincification depth is negligible (figure 2b)). It should be emphasized that there is considerable spread of the individual measurements of the dezincified layer wich may mask the results shown in figure 2. Hence, we cannot confirm, based only on these experiments, that the % α of the structure affects very significantly the dezincification behaviour of these alloys.

4 – CONCLUSIONS

The main conclusions of this work are the following:

- no significative correlationship between the effective copper content and the dezincification resistance of brasses has been determined;

- considering the influence of the studied elements, it was determined that: tin has a weak effect in the reduction of the dezincification depth, arsenic improves strongly the dezincification resistance, while silicon and nickel appears to increase the dissolution of the alloys by dezincification;

- the volume fraction of the α phase doesn't appear to have a relevant effect in the dezincification resistance of the brasses.

5 - LITERATURE

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