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**FORMATION OF COPPER HYDRIDE DURING SPONTANEOUS DISSOLUTION
OF Cu-Zn AND Cu-Cd ALLOYS WITH HYDROGEN DEPOLARIZATION**

**POWSTAWANIE WODORKU MIEDZI PODCZAS SAMORZUTNEGO ROZTWARZANIA
STOPÓW Cu-Zn ORAZ Cu-Cd W WARUNKACH DEPOLARYZACJI WODOROWEJ**

Comparison of the processes of spontaneous dissolution of brasses and CuCd alloy under hydrogen depolarization was made. Observations of specimens surface using a scanning microscope during the reaction were carried out. An identification of phases of solid products of the dissolution by means of X-rays diffraction analysis was performed. Among the solid products of the dissolution a separate phase of copper hydride was found. The lattice parameters of copper hydride obtained after the dissolution process of brasses and CuCd alloy are identical.

Dokonano porównania procesów samorzutnego roztwarzania mosiądzów i stopu CuCd w warunkach depolaryzacji wodorowej. Przeprowadzono obserwacje powierzchni próbek po reakcji przy użyciu mikroskopu scanningowego. Identyfikację fazową stałych produktów reakcji roztwarzania wykonano z zastosowaniem dyfrakcyjnej analizy rentgenowskiej. Wśród stałych produktów reakcji stwierdzono obecność wodoru miedzi. Parametry sieci wodoru miedzi są identyczne po procesie roztwarzania mosiądzów oraz stopu CuCd.

1. Introduction

During a spontaneous dissolution of Cu-Zn and Cu-Cd alloys under hydrogen depolarization the hydrogen ions undergo reduction in an amount equivalent to that of the dissolved zinc or cadmium. In connection with this process the possible formation of either copper hydride or solid solutions of hydrogen, both in the alteration region and in the growing layer of copper was taken into consideration.

The formation of interstitial solid solutions of hydrogen in copper has been described by several workers [1–7]. Such solutions are formed: (i) during cathodic reduction of hydrogen

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on copper, (ii) during the flow of hydrogen through copper membranes, or (iii) during the isothermal annealing of copper at temperatures of 200–900°C and under a hydrogen pressure of several atmospheres. The formation of solid solutions of hydrogen in copper does not change the crystal lattice of the metal [7].

It is generally believed that the hydride phase is formed by a chemical reaction. This reaction was studied and described by Warf and Feitknecht [8]. Copper hydride crystallizes in the hexagonal system with the following parameters: $a = 2.89$, $c = 4.63$ Å [8, 9] and it is not a stable substance; it undergoes fast decomposition especially in the presence of oxygen. Lieser and Witte [10] studied the dissolution of hydrogen in copper at temperatures between 450 and 680°C under hydrogen pressure of 1 atm. On the basis of X-ray diffraction analysis they suggested that a hexagonal lattice having parameters nearly identical with those obtained by Warf and Feitknecht [8] is formed.

The results of the studies on the spontaneous dissolution of brasses were published earlier [11–19]. In this work the spontaneous dissolution of α -, β' -, γ -, and ε -brasses [11–19] in deaerated 2.0 M solution of H_2SO_4 will be compared with unpublished data on the dissolution of Cu-Cd alloy under the same conditions.

2. Experimental

The preparation of α -, β' -, γ -, and ε -brasses, their homogenization, preparation of samples for spontaneous dissolution in 2.0 M deaerated solution of sulfuric acid, the way of preparing the solutions, corrosion tests etc., were described in detail in the previous papers [11–19]. Compositions of investigated brasses were following: α -brass (Cu30Zn); β' -brass (Cu47.3Zn); γ -brass (Cu64.3Zn) and ε -brass (Cu82.3Zn).

Cu-Cd alloy was made from oxygen-free, copper and cadmium of 99.95% purity. The metals were placed in a quartz tube that was sealed at the top under vacuum. The tube was slowly heated up to temperature 300°C and then temperature was changed in steps of 50°C and annealed for one hour in each of these temperatures. This procedure was continued until the temperature of 1100°C was reached. At this temperature the sample was kept for 2 h with occasional shaking. The solidified alloy was subjected to homogenization at 400°C for 24 h. The alloy contained 75.0 wt.% of cadmium. Specimens were cut vertically to the ingot axis using a spark cutter: into discs of the diameter amounted to about 1.65 cm and of height about 0.2 cm. Basing upon X-ray diffraction it was found that the alloy is a single phase.

The specimens were dissolved in closed glass tube, filled with 20 ml of 2.0 M solution of H_2SO_4 containing no dissolved oxygen. Preparation of the acid was given in the previous paper [11].

The specimens were dissolving at $70 \pm 0.1^\circ C$ during about 22 days. Every few hours the capsules were opened, the samples were weighed and solutions were analysed for cadmium content and possible traces of copper.

Phase identification was performed using an X-ray diffractometer DRON-3.0. Filtered radiation Cu was used. Observations of specimens surface during the reaction using a scanning electron microscope were carried out.

3. Result and discussion

Studies on the spontaneous dissolution of brasses and Cu-Zn alloy under hydrogen depolarization were carried out in the solution of sulfuric acid carefully deaerated and purified. In this system, the α -brass does not undergo corrosion¹. The β' -brass dissolves very slowly; i.e. the average dissolution rate of the Cu-47.3 atom-% Zn brass during 50 days at 85°C is ca. $1.9 \cdot 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$. The γ -brass dissolves less slowly; e.g. the average dissolution rate of the Cu-64.4 atom-% Zn brass during 26 days at 85°C is $1.5 \cdot 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ [12]. The ε -brass (82.3 atom-%) dissolves very quickly. The dissolution rates in the range of temperature from 65 to 85°C are very similar. The dissolution process was completed after about 6 days [20].

The Cu-Cd alloy (75 wtg.% of cadmium) dissolves very quickly, similarly to ε -brass. The dissolution process was completed after about 4 days.

a) observation of the specimens surface during reaction

The β' -, γ - and ε -brass surface changed with the progress of the reaction. The microphotographs of the surface of these brasses were given in earlier papers [11, 16, 17].

Prior to the dissolution of specimens of Cu-Cd alloy were of the silver colour. With elapsing time pink spots appeared on the sample and after about two days whole surface became uniformly pink. This process is illustrated by photographs of the surface of the examined samples (Fig. 1).

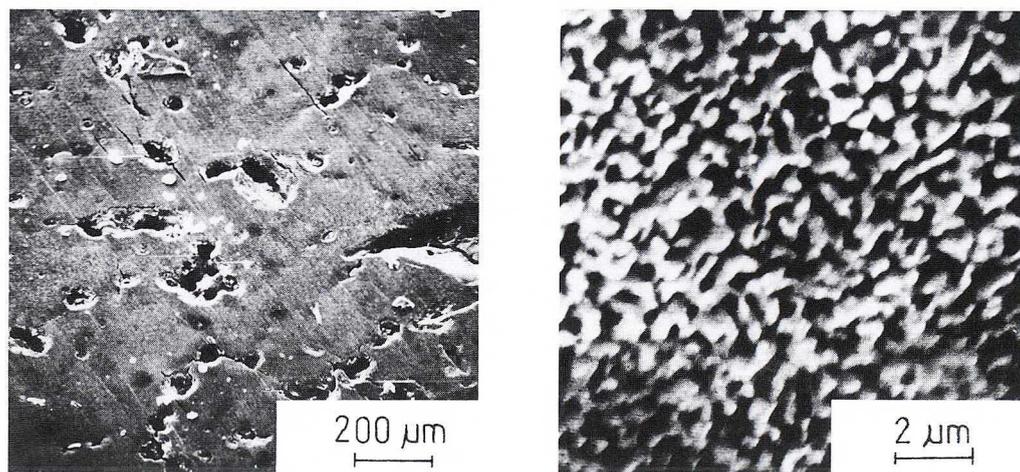


Fig. 1. View of the surface of a specimen of δ phase Cu_3Cd_3 which was dissolving during 22 days at 70°C:
a, b – various magnification

¹ The experiment were carried out at temperature 85°C for 78 days.

It can be seen in Fig. 1a that a lot of holes on the surface were present. The appearance of the surface (Fig. 1b) is very similar to that observed for γ -brass after dissolution at temperature 65°C for 30 days [16]. In both cases surface layers were found to be pure copper.

The cross-section of δ -Cu₅Cd₈ sample² after 22 days dissolution at 70°C is shown in Fig. 2. From Fig. 2a it can be seen that few crevices were present, but the morphology of the cross-section (Fig. 2b) is similar to the morphology of the surface of sample (Fig. 1b).

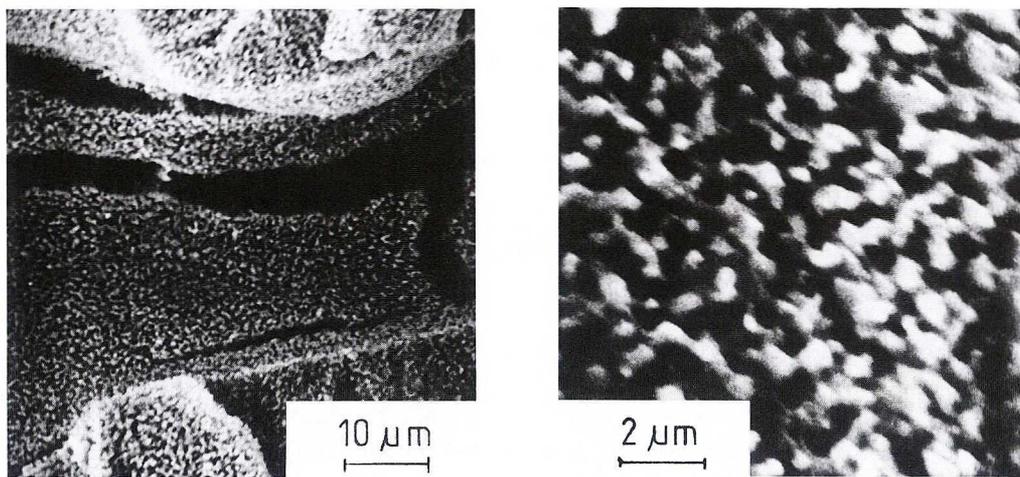


Fig. 2. Photomicrograph of the cross-section of the sample of δ phase Cu₅Cd₈ which was dissolving during 22 days at 70°C: a, b – various magnification

b) X-ray diffraction studies

The experiments were performed to examine the phase composition of both pretreated and treated samples of brasses and Cu-Cd alloy.

The X-ray pattern obtained for the specimen of β' -brass prior to dissolution shows only the peaks due to β' -brass, namely those at 110, 200 and 211 [12]. β' -brass of the B2 structure has a lattice parameter of 2.95 Å [21,22]. In the case of the dissolution of β' -brass, X-ray diffraction did not show the presence of any phases other than that of β' -brass, β_1 -bainite, and metallic copper [12]. These results did not suggest the hydride formation. Thus, the X-ray photoelectron spectroscopy (ESCA, XPS) was applied to study chemical and electronic state of surface atoms [14]. The serious disadvantage of this technique, especially as related to this work, is impossibility to detect a hydrogen presence. However, there is fully justified expectation that electronic states of copper atoms are considerably affected by the hydrogen when it forms hydride bonds or even solid solution, with a resulting chemical shift of Cu2 p_{3/2} peaks in XPS spectra as well as the shift of Auger

² Phase identification of Cu-Cd alloy will be given in later part of this text.

$\text{CuL}_3\text{M}_{4.5}\text{M}_{4.5}$ band. It is indirect way to study hydrogen-copper interactions. The following samples were studied: the specimen of β' -brass prior to dissolution, the sample of β' -brass dissolved in 2.0 M H_2SO_4 for 4.5 h at 85°C (low fraction reacted), the sample of β' -brass dissolved for 34 days at 85°C (high fraction reacted), electrolytic copper and the sample of copper hydride synthesized by the method of Warf and Feitknecht [8].

In the case of Cu(0) and Cu(I) the $\text{Cu}2\text{p}_{3/2}$ band is composed of single peak at about 933.0 eV. For Cu(II) the $\text{Cu}2\text{p}_{3/2}$ band consists of the principal peak at about 934.2 eV and a satellite band at the mean distance of about 7.5 eV. In examined samples those satellites were not observed and thus Cu(II) was absent.

The $\text{Cu}2\text{p}_{3/2}$ binding energies of Cu(0) and Cu(I) do not differ and these two states can be distinguished by an analysis of the $\text{CuL}_3\text{M}_{4.5}\text{M}_{4.5}$ band. This band is represented by a d^8 final state which results in 1S (914.5 eV), 1G (918.5 eV), 3P (916 eV), 1D (920 eV) and 3F (921 eV) final state terms. The 1G term is the most prominent line and its energy either 918.5 or 916 eV for Cu(0) or Cu(I) respectively, is used for a chemical state determination.

The $\text{Cu}2\text{p}_{3/2}$ band of β' -brass prior to dissolution contains only one peak coming from metallic copper (932.8 eV). This band for copper hydride and the brass samples etched in sulfuric acid contains also a minor peak on the low-binding-energy side. Its position at about 931 eV is much lower than that of metallic copper. Moreover, this peak intensity increases with the time of exposition towards hydrogen-generating conditions. These observations lead to the conclusion, that copper atoms in the surface phase are affected by hydrogen atoms.

Examination of Auger $\text{CuL}_3\text{M}_{4.5}\text{M}_{4.5}$ bands give an additional argument. In the case of β' -brass beside the principal peak 918.5 eV also a small one at 916 eV is present; it can be assigned to 1G term resulting from Cu(I) presence. This peak grows distinctly in the spectra of acid treated samples simultaneously with the growth of the $\text{Cu}2\text{p}_{3/2}$ 931 eV peak intensity. These observations leads to the conclusion, that after the β' -brass exposition to hydrogen-generating conditions, a significant number of copper atoms is demetallized. Comparing the structure of respective Auger and XPS bands it can be stated, that an electronic state of surface differ from that one in Cu_2O .

Beside chemical shifts of photoelectron and Auger peaks, copper-containing compounds can be characterized with the use of Auger parameter. This is a great advantage of this parameter, that it is not dependent on a surface charging. The discussion of the Auger parameter for this system is given elsewhere [14].

The presence of the $\text{Cu}2\text{p}_{3/2}$ at 931 eV with negative chemical shift -2 eV with regard to metallic copper, and the Auger parameter of about 1847 eV are the "fingerprints" of a hydrogen-copper chemical species. The value of Auger parameter corresponds very well to the value of the synthetic copper hydride.

In the case of samples of γ -brass, phase identification was performed by using an X-ray diffractometer Tur M62 with a goniometer HZG4. Fe-filtered radiation from a Co anode was used. The X-ray pattern obtained for the specimen of γ -brass prior the dissolution shows only peaks coming from γ -brass, crystallizing in a cubic lattice, type $D 8_2$. The lattice parameter amounts to 8.875 Å [16]. In the solid products of dissolution reaction of γ -brass the following phases are present: pure copper, copper hydride and the matrix γ -brass (this

last phase appears the only for the samples characterized by a relatively low fraction reacted) [16].

The X-ray pattern obtained for the specimen of ϵ -brass prior to dissolution shows only the peaks due to ϵ -brass, the tested material is a single phase. ϵ -brass crystallizes in the hexagonal system. The lattice parameters are: $a = 0.275$ nm; $c = 0.428$ nm, $c/a = 1.556$. This brass contained 82.3 at % of zinc [17]. After dissolution at 65°C for 6 h of the sample of ϵ -brass the patterns were taken at various time intervals. The number and intensity of peaks vary with elapsing time after ending the dissolution process. In the diffraction pattern made immediately after completion of the dissolution process, there are two peaks, not so intensive, coming from copper hydride: 0002 CuH and 0004 CuH. After next 90 min from the end of the dissolution, there are as many as six visible peaks coming from copper hydride. Two of them $11\bar{2}0$ and $20\bar{2}0$ are intensive and are doublets of radiation Co $K\alpha_1$ and Co $K\alpha_2$. Copper hydride is unstable. With elapsing time the relative intensities of the peaks coming from copper hydride are smaller. Finally after 60 d, there are no more peaks coming from this phase [17].

The lattice parameters of CuH resulting from the interplanar distances are slightly different from those given by Warf and Feitknecht [8]. In the system under investigation the copper hydride lattice parameters amount to: $a = 0.283$ nm, $c = 0.468$ nm, $c/a = 1.654$. From these lattice parameters the interplanar distances were calculated. The conformity of the distances calculated and those determined experimentally, is rather poor [17]. The same procedure was applied to copper hydride obtained during a simultaneously dissolution of Cu-Cd alloy (see Tab.).

TABLE

d_{hkl} values and relative peak intensities of copper hydride

h k l	d_{JCPDS}^a	I_{JCPDS}	d_{exp}^b	I_{exp}	d_{calc}^c	d_{calc}^d
10 $\bar{1}0$	0.253	30	0.246	100	0.245	0.250
0002	0.231	30	0.234	100	0.234	0.231
10 $\bar{1}1$	0.222	100	0.217	30	0.217	0.220
10 $\bar{1}2$	0.171	8	0.168	70	0.169	0.170
11 $\bar{2}0$	0.146	10	0.141	85	0.141	0.144
10 $\bar{1}3$	0.131	8	0.132	6	0.132	0.131
20 $\bar{2}0$			0.123	35	0.123	0.125
11 $\bar{2}2$	0.123	14	0.121	2	0.121	0.122
20 $\bar{2}1$	0.122				0.119	0.121
0004					0.117	0.116

^a d_{JCPDS} ; I_{JCPDS} – the d_{hkl} values and relative peak intensities are given according to JCPDS-8-256; the lattice parameters are: $a = 0.292$ nm; $c = 0.462$ nm.

^b d_{exp} ; I_{exp} – taken from Fig. 6b; the relative peak intensities refer to the CuH phase only.

^c d_{calc} – calculated for lattice parameters: $a = 0.283$ nm; $c = 0.468$ nm; using the iteration method.

^d d_{calc} – calculated from data of Warf and Feitknecht [8]; $a = 0.289$ nm; $c = 0.463$ nm.

Prior to the Cu-Cd alloy dissolution X-ray tests were made. The specimen was prepared using the standard procedure – like that for testing spontaneous dissolution; it was, therefore, ground on emery papers. Additionally, a powder specimen was examined, which was obtained by triturating in a crucible. In Figs 3 and 4 there are the diffraction patterns of the examined specimens.

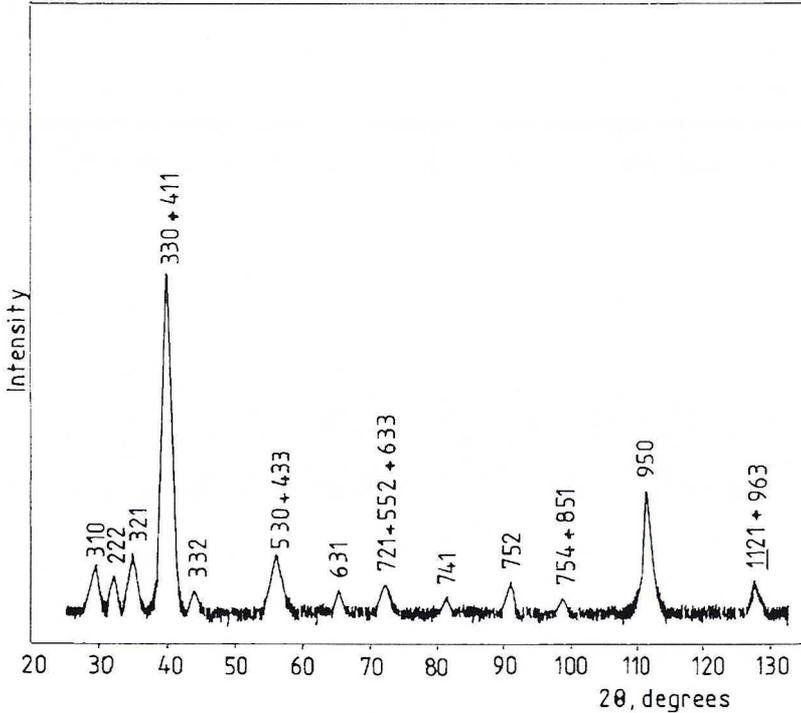


Fig. 3. Diffraction pattern of a specimen of δ phase Cu_5Cd_8 before the dissolution process

Using JCPDS standards the phase identification was carried out. Initial material was a single-phase. It was δ -phase Cu_5Cd_8 with Cu_5Zn_8 -type structure. It was space-centered cubic crystal lattice with the atoms number of boths components of 52 [21].

A comparison of the diffraction patterns of the specimen after grinding on emery papers (Fig. 3) with one taken from a powdered sample (Fig. 4) indicates the existence of texture in the material tested. Moreover, relative intensities of the peaks in Fig. 3 are not so intensive as peaks obtained for powder specimen (Fig. 4).

An extrapolation function (Fig. 5) was applied to the experimental data shown in Fig. 4 for the determination of lattice parameter [23]. The value of this parameter is 0.9615 nm for tested alloy with 75 wt. % Cd. Theoretical calculated diffraction patterns (JCPDS) is related to the alloy containing 73.9 wt.% Cd and its lattice parameter is 0.9589 nm. According to Pearson data [21] for the same alloy composition the lattice parameter is 0.9615 nm. The

literature data on the change of lattice parameter with the change of δ phase Cu_5Cd_8 composition are unknown. Consequently, it is difficult to discuss the obtained value.

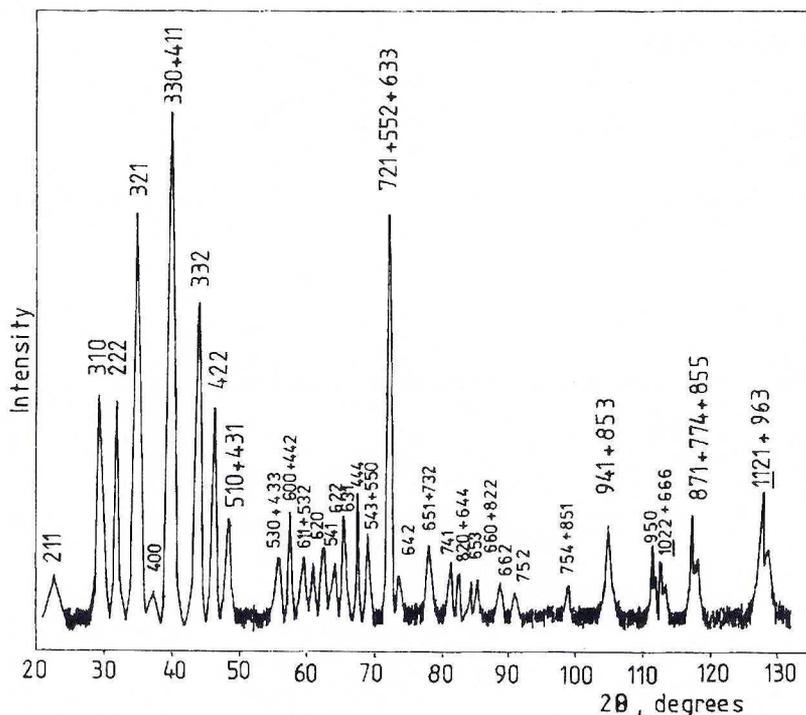


Fig. 4. Diffraction pattern of a powder specimen of δ phase Cu_5Cd_8 before the dissolution process

A phase identification of solid products of the reaction for specimen dissolved at 70°C for 4 days, i.e. for the specimen with high fraction reacted³ (0.94 ± 0.01), is described as an example. In Fig. 6a–c diffraction patterns for such specimen are shown. The patterns were taken at various time intervals after ending the dissolution process. In the diffraction pattern shown in Fig. 6a and taken immediately after ending the dissolution process, there are peaks coming from phases: pure copper, copper hydride and δ phase Cu_5Cd_8 . The presence of the peaks coming from matrix is surprised, because of high fraction reacted. It seems that the specimen is very porous and effective penetration of X-rays is deeper than for solid specimen.

In the diffraction pattern shown in Fig. 6b, which was made 2.5 h after ending the dissolution process, the relative intensities of peaks coming from copper hydride are higher

³ Fraction reacted $\alpha = \frac{m_o - m}{m_o}$; where m_o and m are the mass of cadmium in the Cu–Cd alloy samples before corrosion took place and at time t after dissolution started, respectively.

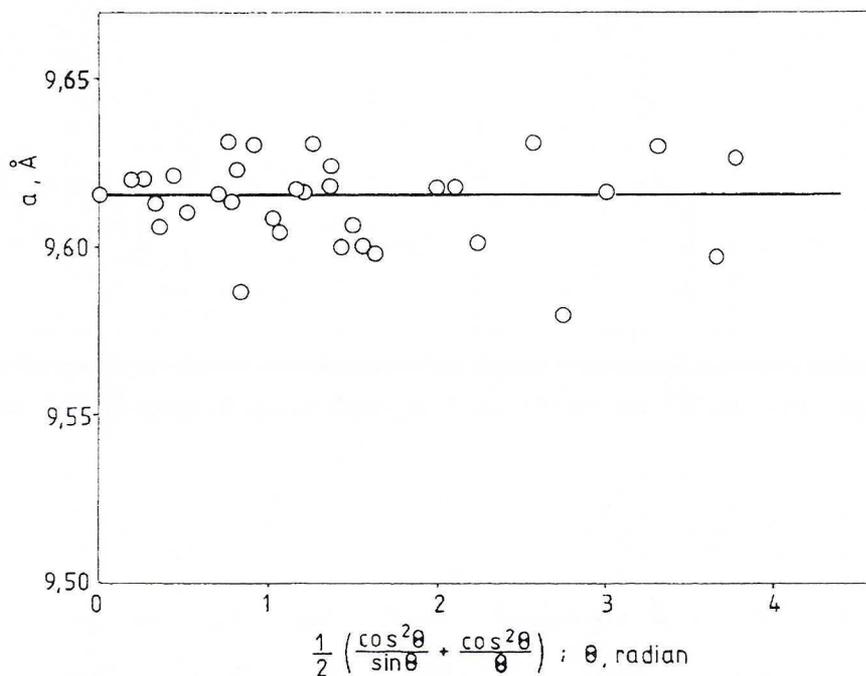
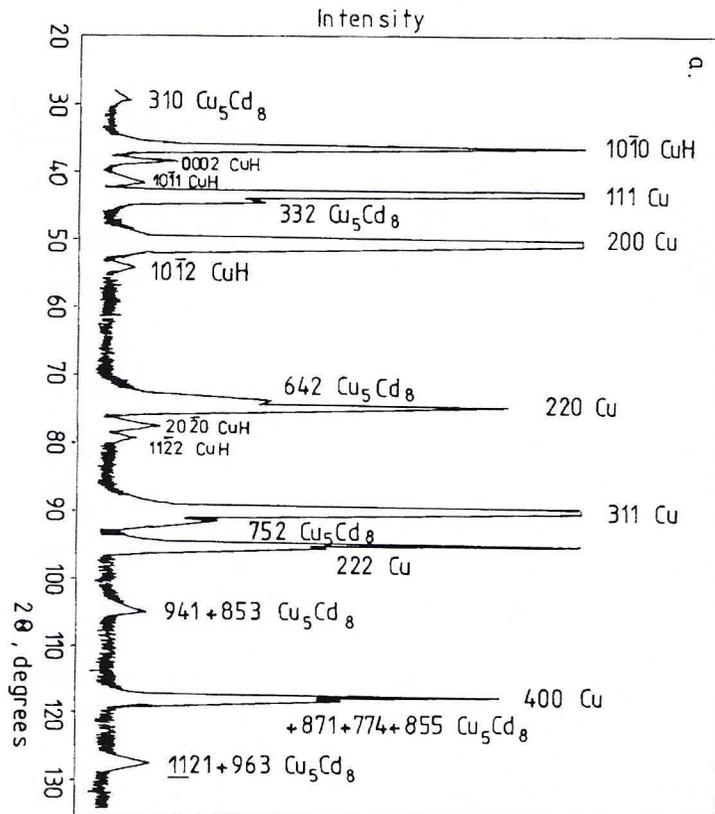
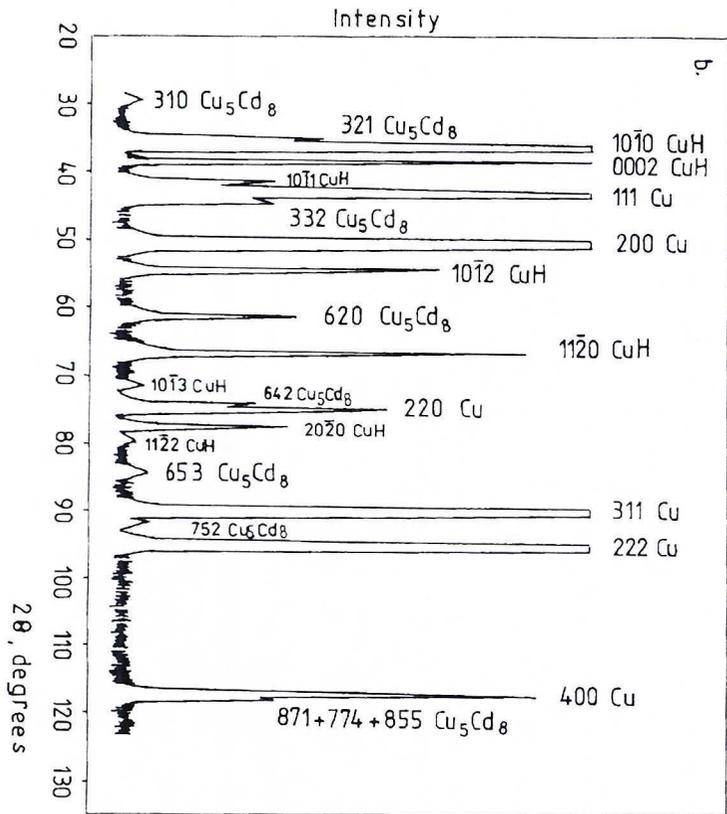


Fig. 5. Determination of lattice parameter of δ phase Cu_5Cd_8

than those obtained immediately after ending the dissolution process (Fig. 6a). Moreover, the number of peaks coming from copper hydride increased. The increase of the relative intensities and increase of the number of peaks coming from copper hydride with elapsing time after ending dissolution process is quite similar to the formation of CuH during spontaneous dissolution of a brass. It seems to show that the reaction between hydrogen and copper occurs secondarily, after the reduction of hydrogen ion. The specimen, in spite of the completion of the dissolution process, is far from being stable. A transformation in the copper lattice towards copper hydride formation is still going. This process can continue because hydrogen is still present in the specimen. It seems to support the fact that during the dissolution process the solid solution of hydrogen in copper is formed, and further transformation of the lattice towards the formation of copper hydride structure requires some time to elaps.

As we know, copper hydride is unstable. It is reflected in further change of the diffraction pattern (Fig. 6c). The number and the relative intensities of peaks coming from copper hydride decreased. It can be seen, that peaks coming from the products of oxidation of the copper are present.

The interplanar distances were calculated from previously determined [17] lattice parameters of copper hydride. These values can be compared with those determined experimentally after the process of the dissolution of δ phase of Cu_5Cd_8 alloy (see Tab. 1). The agreement of the calculated and experimental values is good, and it seems that the lattice parameters of copper hydride obtained during the



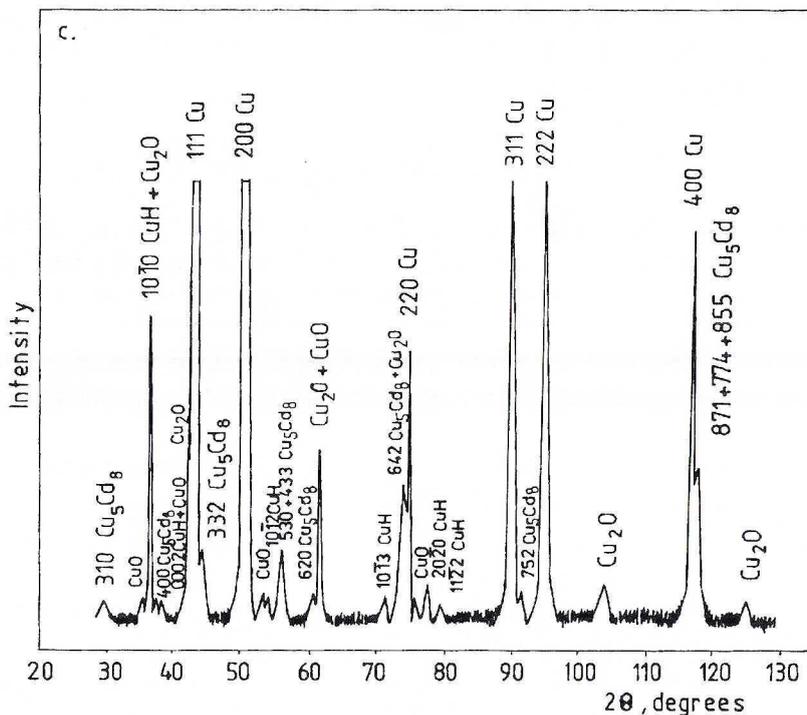


Fig. 6. Diffraction pattern of a specimen of δ phase Cu_5Cd_8 which was dissolving during 4 days at 70°C : a – immediately after completion of the dissolution process, b – 2.5 h and c – 69 h after the completion of the dissolution process

brass as well as δ phase of Cu_5Cd_8 alloy dissolution are exactly the same. The comparison of the relative intensities of the peaks coming from copper hydride with the JCPDS standard shows that CuH is textured. It is obvious, because the initial material used to prepare specimen was also textured (see Fig. 3).

Diffraction patterns of the specimens dissolved at 70°C for time longer than 4 days were made. During this dissolution process fraction reacted is almost unity. It means that the dissolution process is completed but the sample is still in the electrolyte, under hydrogen pressure (product of reaction). Secondary reaction between hydrogen and copper is still running with the formation of copper hydride. As a proof of this fact are peaks coming from copper hydride in diffraction patterns obtained for the specimens dissolving for 7, 12 and 22 days. Some characteristic features of the process can be noticed: the relative intensities of peaks coming from copper hydride with elapsing time after removing the sample from the solution are getting smaller and smaller. The increase of relative intensities and the increase of number of peaks coming from copper hydride was not observed for this same sample in different time intervals after removing it from the electrolyte. It can be seen, that after completion of the dissolution process (consumption of one of the reagents – cadmium), the

formation and decomposition of copper hydride is still taking place. With elapsing time from completed dissolution process the relative intensities and number of peaks coming from copper hydride is decreasing.

4. Conclusions

1. The process of spontaneous dissolution of β' -, γ -, ε -brass and δ phase Cu_5Cd_8 under hydrogen depolarization is selective; only zinc or cadmium enters the solution.
2. For each of these alloys, one of the solid products of the reaction of the dissolution is copper hydride.
3. Solid solution of hydrogen in copper is the first stage of copper hydride formation.
4. After the dissolution process of brasses and δ phase Cu_5Cd_8 lattice parameters of copper hydride are the same.
5. In case of δ phase Cu_5Cd_8 , after time of reaction longer than 4 days, fraction reacted is almost equal to 1.

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