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The influence of phosphorus microalloying on the structure formation of CuZn32Mn3Al2FeNi multicomponent brass

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Abstract: Phosphorus in brass can have both a positive effect, such as improving mechanical properties, increasing corrosion resistance and machinability, and a negative effect, such as adversely affecting weldability and causing cracking. The study of the role of phosphorus in the processes of brass structure formation is of practical relevance, since it helps optimise the properties of the material, reduce the risk of defects, improve treatment processes and control properties and quality. The work covers the study of the role of phosphorus in brass, the need to control its content during production by limiting the share of secondary use. The study revealed the possibility of a positive effect of modifying copper alloys with phosphorus in order to improve performance properties, as well as the prospects of using phosphorus as a safe replacement for lead in brass. The authors assessed the content and distribution of phosphorus impurity at a concentration of 0.005 % in a brass sample of the CuZn32Mn3Al2FeNi grade, studied the nature of its interaction with other components of the alloy and the changes occurring at different temperatures of heat treatment. It has been found that phosphorus actively participates in diffusion processes and forms phosphides in both defective and defect-free blanks. When heated to the hot deformation temperature range, phosphorus redistribution occurs, phosphide locally dissolves, and metastable inclusions form. Due to differences in the concentration of elements in areas adjacent to the phosphide, the brass structure changes leading to the formation of areas different from the matrix β-phase. Manganese phosphide in brass can improve its mechanical properties and cutting ability, but an excess of this compound can lead to problems with strength, crack resistance, and moulding.

Keywords: duplex and multicomponent brasses; phosphorus distribution analysis; silicides; phosphorus; compounds with phosphorus; shape and size of inclusions; effect of heating on microstructure; phosphorus redistribution; manganese phosphide; diffusion processes; metastable inclusions.

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INTRODUCTION

Multicomponent brasses have many promising functional properties, due to which they remain essential materials in the automotive industry and other industries. Despite the long history of research into this engineering material, not all the relationships between structure and properties during technological processing have been fully studied up to date.

There are technological difficulties in the production of semi-finished products and the manufacture of products made of brass caused by its tendency to crack within certain temperature ranges [1]. The state diagrams of multicomponent systems presented in the form of isothermal sections focus on the main components, while not taking into account the redistribution of elements that form reinforcing inclusions – silicides, which are also often complex compounds [2]. Depending on the chemical composition, processing and production conditions, intermetallic compounds in brasses acquire different forms. For example, the presence of manganous phosphides leads to the formation of columnar or lamellar inclusions, and silicon forms intermetallic compounds with manganese that undergo complex shape changes during the nucleation and growth [3]. Depending on the element for alloying brass, one or another shape of inclusions will predominate in the alloy, but intermetallides that differ in geometry from the predominant one will also occur. Moreover, the shape of intermetallic compounds can be modified as a result of mechanical and thermal treatment [4]. Today, metallurgical enterprises use as a source material both pure ores and components, and recycled materials, obtained during their own production. Even if slag is processed, only manual selection of coarse-grained beads of copper, brass, bronze and alloying element is usually carried out, or screening by size is used with subsequent return of the metal part to the metallurgical process. Phosphorus gets into the alloy as a result of secondary use.

Phosphorus and its compounds may be present in brass as an impurity, but its content should usually be small, no more than 0.25–0.3 % by weight. This is associated with the fact that a high phosphorus content can negatively affect the properties of brass. In particular, a high phosphorus content can lead to the following problems:

1) the electrical conductivity of the material decreases: the presence of only 0.04 % of phosphorus reduces the conductivity of pure copper to 80 % (compared to 100 % for copper without phosphorus) [5];

2) brass becomes more brittle and prone to cracking under bending or fracture [1];

3) the presence of phosphorus can lead to undesirable hardening of brass, which can reduce its ability to deform without destruction [6].

Because of these negative effects, high phosphorus content in brass is limited in production.

On the other hand, phosphorus is actively used in the smelting of copper and copper-based alloys. Phosphorus deoxidised copper exhibits higher plastic properties than pure copper, which is explained by the influence of residual phosphorus [5]. Phosphorus is introduced into alloyed brass to reduce the growth rate of the Cu_5Zn_8 compound (γ-phase): the phase is formed more uniformly throughout the volume, which helps improving the mechanical properties of brasses and increasing corrosion resistance [7–9]. In the literature, there are data on the industrial modification of copper alloys with phosphorus [10; 11]; however, the technology used today poses a significant danger to the environment. Theoretically, other methods of modifying brass with phosphorus are also possible, but to perform this operation, the structures of crystal lattice of copper phosphide and silicides must be identical, according to the principles of structural and dimensional correspondence [12].

There are sources that demonstrate the use of phosphorus to replace lead [1]. Adding lead to brass alloys improves the tightness and cutting machinability of the material [13]. However, due to the health hazards associated with lead, stricter regulations on lead content in brass products have been introduced. Frequent use of lead-covered brass in plumbing fixtures could result in toxic lead particles being released into drinking water. An alternative is the more environmentally friendly lead-free brass, which does not contain toxic lead impurities that could leach into drinking water. Moreover, brasses with phosphorus have significantly higher corrosion resistance compared to leaded brass [14].

From the analysis of literary sources, it follows that information on the phosphorus distribution in multicomponent brass is incomplete, and there is no data on the behavior of phosphorus and its compounds, when heated in the hot deformation temperature range. One can assume that the phosphorus redistribution may negatively affect the technological properties of brass.

The aim of this work is to determine the role of phosphorus in the processes of structure formation of multicomponent CuZn32Mn3Al2FeNi brass.

METHODS

The object of study in this work is brass of the CuZn32Mn3Al2FeNi grade (hereinafter referred to as CuZn32Mn3Al2FeNi), in which the matrix is the β-phase, and the reinforcing component is silicide inclusions in the form of a dispersed phase. The role of phosphorus microadditives in structure formation was the subject of the study.

The main methodological approach was a comparative analysis of brass samples in the initial state (a pipe pressed at a temperature of 780 °C with stress-relieving annealing at 500 °C, 1 h), and samples after heating simulating a typical [15] technological process – heating for stamping at 780 °C for 12 min.

Primary studies were conducted by the method of structural analysis of samples in the initial state using an Olympus-GX51 optical microscope (Japan), equipped with a SIAMS 800 microstructure analyser (Russia). The surface was etched to reveal the alloy microstructure. A 1:1 solution of glacial acetic and nitric acid was used as an etchant. The chemical composition was determined using an OBLF QSG 750-II optical emission spectrometer (Germany). A Wilkers microhardness tester mod. 536 from Karl Frank (USA), with a load of HV30, was used to measure hardness using the Vickers method in accordance with GOST R ISO 6507-1. The hardness values were obtained as the arithmetic mean of five repeated measurements of the sample.

Further studies were conducted using a Zeiss scanning electron microscope (Germany) with Bruker software. Additionally, a comparative analysis of changes in the chemical composition of silicides and phosphosilicides upon heating was performed. 350 silicides were analysed after heating to temperatures of 700, 750, 800, and 830 °C.

The paper presents micrographs, obtained using the mapping function, which provide a concept of the chemical composition distribution over the volume of the rod-shaped inclusion in the state after heating. To increase conductivity, gold treatment was performed on a single-target magnetron sputtering device SBC900 (China), using a gold-platinum target in a ratio of 70:30.

X-ray spectral analysis was performed on an EVO18 scanning electron microscope with an EDX detector from Bruker (Germany). The chemical composition of the solid solution and intermetallic compounds of various shapes was determined, the data were processed and summarised in a table.

RESULTS

Table 1 presents the results of chemical analysis of the CuZn32Mn3Al2FeNi alloy. Fig. 1 shows the microstructure of the as-delivered (original) etched samples. The hardness value of the original sample was 184–189 HV. The microstructure consists mainly of grains of β-phase and rounded intermetallic compounds 0.5–4 μm in size (Fig. 2, 3). Rod-shaped inclusions (Fig. 3) up to 30×4 μm in size were detected, single rod-shaped inclusions can reach 70 μm in length. Secondary crystals were identified on the rod-shaped inclusions (Fig. 4). The formation and growth of secondary crystals is caused by a higher level of stress in the inclusion compared to the matrix solution. The hardness of the samples after heating changed insignificantly, within 1–2 HV, which does not exceed the measurement error.

As a result of X-ray spectral analysis, the chemical composition of the phases was determined (Tables 2, 3). Phosphorus was identified in rod-shaped compounds (up to 25 %), and in smaller quantities in individual rounded silicides (up to 3 % of the inclusion weight). Phosphorus was not detected in the solid solution, or at the grain boundaries.

Thus, phosphorus in the multicomponent CuZn32Mn3Al2FeNi alloy is bound completely into compounds. The elemental composition of the rods corresponds to a compound of the $(Mn,Fe)_2P$ type with a Si admixture. In finely dispersed rounded silicides, phosphorus apparently replaces silicon in Me_3Si compounds. The maximum phosphorus concentration is identified in the central part of the inclusion.

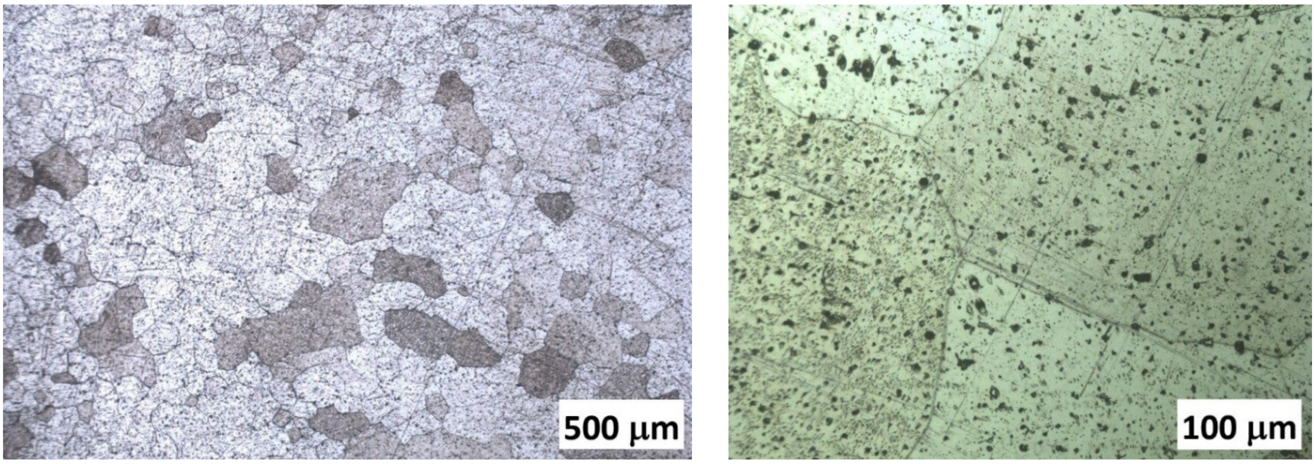
The electron microscopic image with colour indication of chemical elements (Fig. 4) shows a rod-shaped intermetallic compound, which is a manganese-iron phosphosilicide with secondary crystals of manganese silicide. Secondary crystals on the rod consist mainly of iron (Fig. 4 a) and silicon (Fig. 4 b). The intermetallic compound is highlighted in green due to the high content of manganese and phosphorus. The inclusion is a compound of manganese and iron with phosphorus and silicon. The linear scanning method showed that phosphorus interacts mainly with manganese (Fig. 5), their concentration lines completely coincide. The growth of secondary crystals occurs due to iron and silicon.

After heating to hot deformation temperatures, the phosphides are transformed (Fig. 6), due to partial dissolution of the inclusions. In this case, regular-shaped precipitates with an increased phosphorus concentration are identified in the matrix solution (Fig. 7). Probably, such formations take place in areas adjacent to silicides. Linear scanning of these sections showed that after heating to 780 °C, a redistribution of aluminium and phosphorus occurs: the maximum aluminium and phosphorus concentrations coincide, and are shifted relative to the maximum of silicon by 1...2 μm. Thus, phosphorus, along with aluminium, contributes to dispersion strengthening in the CuZn32Mn3Al2FeNi brass. Due to the low phosphorus concentration in the samples, the degree of strengthening was not studied.

Fig. 6 shows a phosphosilicide after heating at 780 °C. Local dissolution of the intermetallic compound is detected. Moreover, a darkened area and structure distortion around the inclusion are revealed. Differences in the concentration of elements lead to areas with different chemical compositions in the areas adjacent to the phosphide (Table 4). Table 4 shows that when heated in the hot deformation range, the main elements are redistributed with the components passing into the solid solution of the matrix.

Table 1. *Chemical composition of the CuZn32Mn3Al2FeNi brass alloy*
Таблица 1. *Химический состав сплава ЛМцАЖН 59-3,5-2,3-0,5-0,3*

Concentration of elements, wt. %										
Cu	**Mn**	**Al**	**Fe**	**Ni**	**Zn**	**Si**	**Pb**	**Cr**	**Sn**	**P**
53.660	3.403	2.438	0.575	0.520	39.220	0.033	0.116	0.004	0.012	0.005



a *b*

Fig. 1. *Microstructure of the CuZn32Mn3Al2FeNi alloy at magnification of:* ***a*** *– 100 times;* ***b*** *– 200 times*
Рис. 1. *Микроструктура сплава ЛМцАЖН 59-3,5-2,3-0,5-0,3 при увеличении:* ***a*** *– в 100 раз;* ***b*** *– в 200 раз*

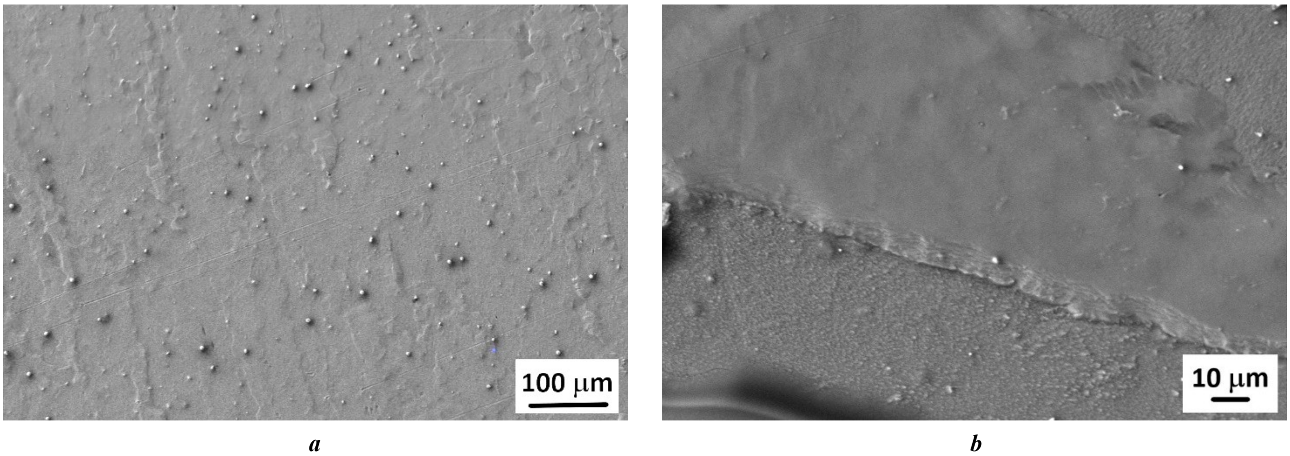


Fig. 2. *Electron micrograph of the structure of the CuZn32Mn3Al2FeNi alloy at magnification of:*
a *– 400 times;* ***b*** *– 1640 times*
Рис. 2. *Электронно-микроскопический снимок структуры сплава ЛМцАЖН 59-3,5-2,3-0,5-0,3*
при увеличении: ***a*** *– в 400 раз;* ***b*** *– в 1640 раз*

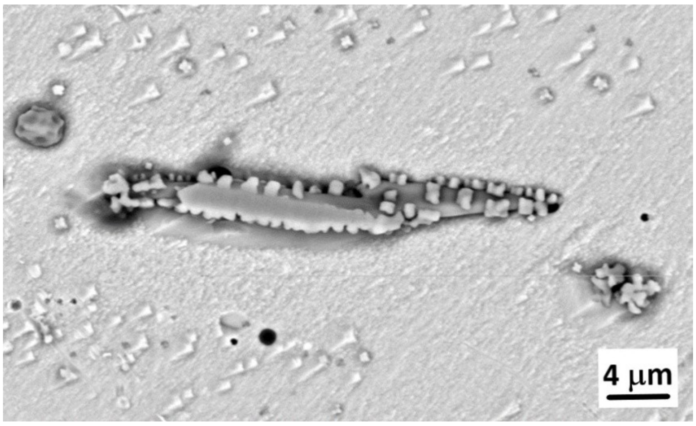


Fig. 3. *Electron micrograph of a rod-shaped inclusion with secondary crystal precipitations*
Рис. 3. *Электронно-микроскопический снимок стержневидного включения*
с выделением вторичных кристаллов

Table 2. *Chemical composition of the solid solution (β-phase)*
Таблица 2. *Химический состав твердого раствора (β-фазы)*

Concentration of elements, wt. %					
Cu	**Mn**	**Al**	**Fe**	**Ni**	**Zn**
57.293	3.521	2.301	0.910	0.524	35.461

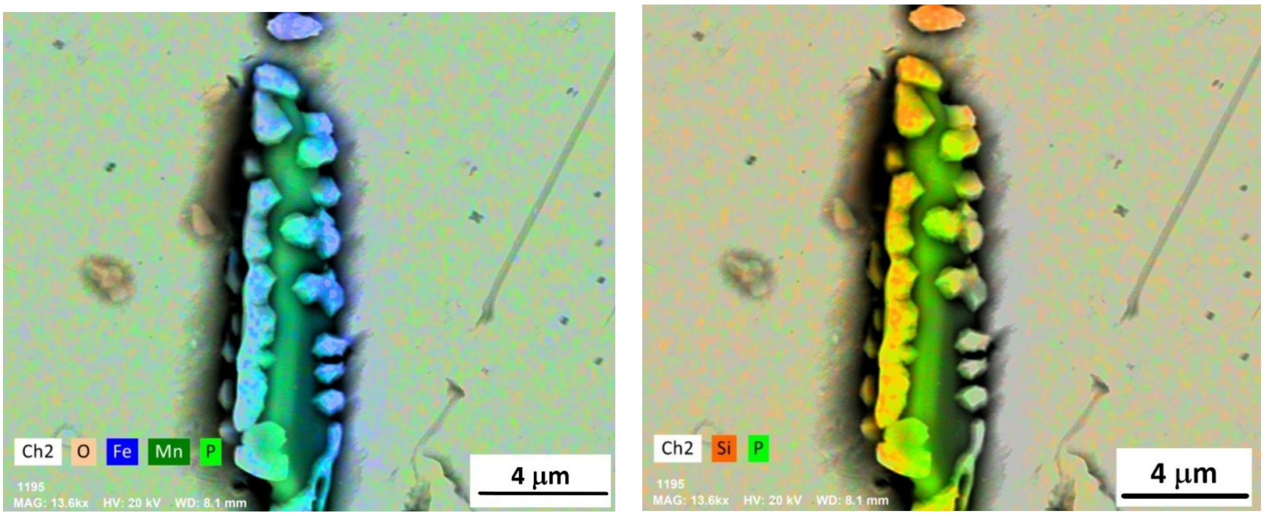
Comparison of the influence of heating temperature on the chemical composition of silicides and phosphosilicides showed that in the hot deformation range of 700…830 °C typical for industrial production, phosphosilicides remain more thermally stable, while silicides have a pronounced Mn/Si ratio maximum at 750 °C and a minimum – at 800 °C (Fig. 8).

DISCUSSION

Currently, the influence of phosphorus on the properties of multicomponent brasses is poorly reflected in domestic and foreign literature. The increased applicability of brasses with phosphorus is associated with the growing attention in the "global West" countries to environmental aspects [1; 14].

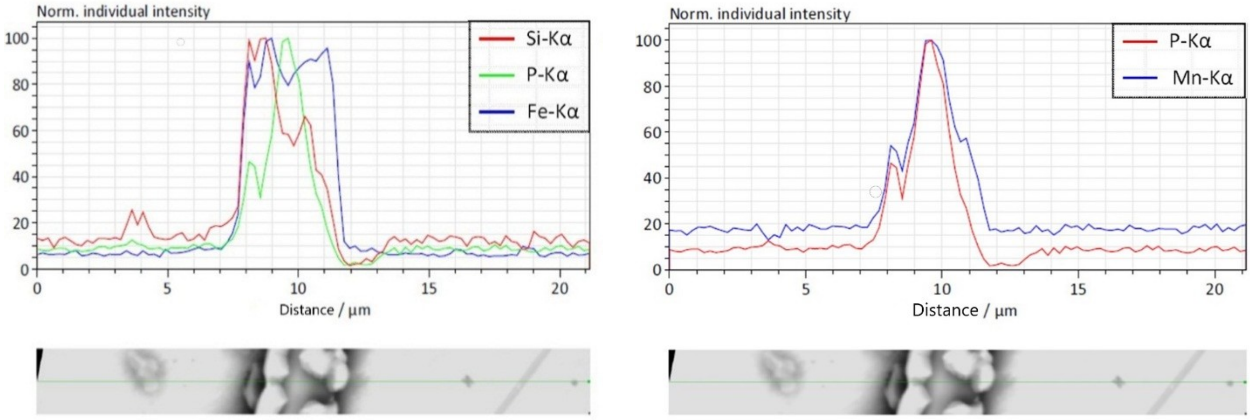
Table 3. *Chemical composition of intermetallic inclusions*
Таблица 3. *Химический состав интерметаллидных включений*

Type	**Concentration of elements, wt. %**						
	Al	**Mn**	**Fe**	**Cr**	**Ni**	**Si**	**P**
Rod-shaped inclusion (Mn,Fe)$_2$P	3.22	32.58	31.57	2.72	1.17	4.47	24.27
Plate (Mn,Fe)$_2$P	1.18	32.09	46.31	2.94	0.41	4.48	12.59
Round silicide	8.43	13.53	57.40	1.58	1.42	17.64	–
Round silicide with phosphorus	5.24	17.46	62.24	1.57	–	10.54	2.94



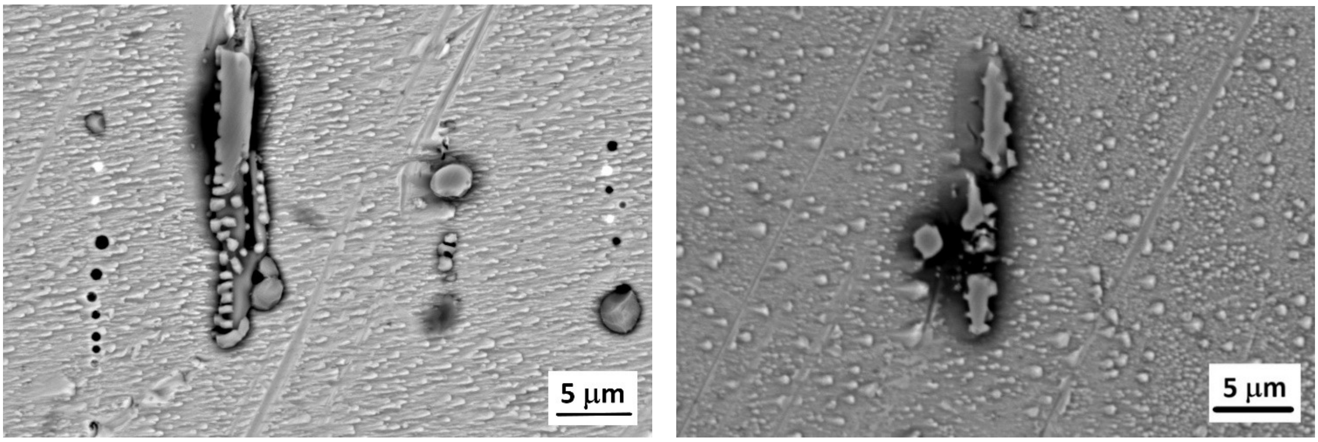
a ***b***

Fig. 4. *Electron micrograph of an inclusion with color highlighting of chemical elements:*
a *– oxygen, iron, manganese and phosphorus;* ***b*** *– silicon and phosphorus*
Рис. 4. *Электронно-микроскопический снимок включения с цветовым выделением химических элементов:*
a *– кислорода, железа, марганца и фосфора;* ***b*** *– кремния и фосфора*



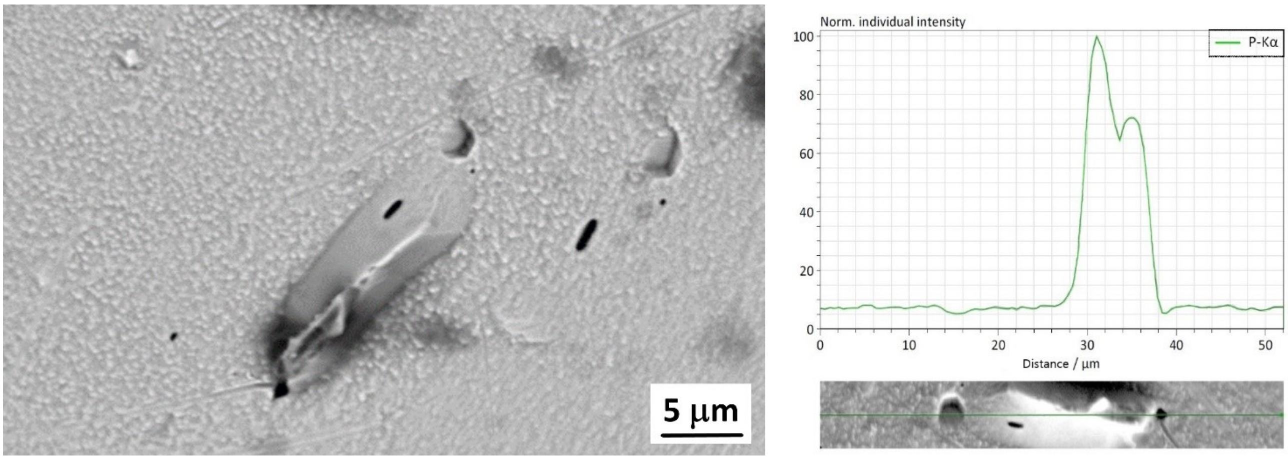
a ***b***

Fig. 5. *Linear scanning of solid solution and silicide for chemical element content:*
a *– silicon, phosphorus and iron;* ***b*** *– phosphorus and manganese*
Рис. 5. *Линейное сканирование твердого раствора и силицида на содержание химических элементов:*
a *– кремния, фосфора и железа;* ***b*** *– фосфора и марганца*



a *b*

Fig. 6. *Electron micrograph of an intermetallic inclusion:*
a *– initial state (after pressing and annealing);* ***b*** *– stamped sample after heating at 780 °C*
Рис. 6. *Электронно-микроскопический снимок интерметаллидного включения:*
а *– исходное состояние (после прессования и отжига);* ***b*** *– отштампованный образец после нагрева при 780 °С*



a *b*

Fig. 7. *Metastable precipitation with increased phosphorus concentration:*
a *– electron micrograph;* ***b*** *– linear scanning*
Рис. 7. *Метастабильное выделение с повышенной концентрацией фосфора:*
а *– электронно-микроскопический снимок;* ***b*** *– линейное сканирование*

Table 4. *Local chemical composition of the solid solution after heating at 780 °C*
Таблица 4. *Локальный химический состав твердого раствора после нагрева при 780 °С*

Location	**Concentration of elements, wt. %**								
	Al	**Si**	**Mn**	**Cu**	**Zn**	**Fe**	**Ni**	**P**	**Cr**
The area adjacent to the phosphide	1.38	1.11	10.54	43.80	27.78	9.70	0.63	4.80	0.73
Solid solution, β-phase	2.47	0.18	3.34	57.72	35.41	0.32	0.47	–	–

The effect of phosphorus on creep and embrittlement of grain boundaries of copper alloys was studied [16–18]. It was shown that phosphorus segregations cannot be the cause of embrittlement and can increase the ductility of polycrystalline copper [17; 18].

Phosphorus in multicomponent brasses actively participates in diffusion processes and forms large rod-shaped phosphosilicides together with manganese, iron and silicon. This work shows that the sizes of such inclusions are many times greater than the sizes of silicides. The formation of iron–manganese phosphosilicides was also noted in [19]. The fact of inclusion growth can be explained by the higher temperature of the formation of manganese phosphides compared to silicides. The authors investigated similar rod-shaped inclusions of the $Me_2(Si,P)$ type before heating for stamping and after heating [19]. It was found that the chemical composition of inclusions of blanks prone to cracking changes upon heating, and inclusions of blanks without cracking are thermally stable. Thus, an increase in the thermal stability of inclusions in the hot deformation range, contributes to an increase in crack resistance.

The ability of iron and phosphorus to form Fe_3P and Fe_2P compounds in two-phase brass is also shown in [10]. It was also considered there, that for copper and iron crystals with a Fe content of more than about 0.3 % by weight, partial decomposition can occur upon quenching from high temperatures, depending on the quenching temperature and cooling rate; lower phosphorus concentrations have not been studied. The authors of [10] note that contamination with iron and phosphorus greatly affects the behaviour of brass semi-finished products during production, since recrystallisation of the metal is difficult, especially in the combined presence of both elements. It is also indicated that α-brass and iron can exist in the form of equilibrium phases. In [20], it was found that such inclusions are γ-Fe. Moreover, depending on the heating temperature and duration, the α-brass matrix contains different amounts of iron. It is shown that suitable heat treatment can increase the amount of these deposits, and that heat treatment, at a temperature of 650 °C is optimal for obtaining the greatest amount of γ-Fe. However, the behaviour of iron in β-brass in the presence of silicon and phosphorus has not been studied. However, based on the results of [10; 19; 21], the presence of silicon and phosphorus inevitably binds iron into silicides and phosphides. Enlargement of inclusions, on the one hand, can promote their chipping during mechanical processing, on the other hand, it can increase wear resistance. The authors note congruent behaviour of manganese and phosphorus concentration lines during scanning of phosphosilicides and phosphorus, and aluminium during scanning of metastable inclusions. To understand how an increase in phosphorus concentration will affect the structure formation of multicomponent brasses, it will be necessary to conduct additional studies, with an increased phosphorus concentration. For this purpose, it is necessary to create a set of experimental brass samples with phosphorus in different concentrations.

The influence of phosphorus on hardness is difficult to estimate due to its low concentration, since other factors that can affect hardness are also active after heating. However, one can assume that an increase in the concentration of phosphorus, not bound in manganese phosphosilicides, will lead to an increase in hardness and an acceleration of the ageing process due to the formation of additional crystallisation centres.

When heated to the temperature of hot deformation of the material, the phosphidosilicide partially dissolves, and the components of the intermetallic compound pass into the matrix, but the change in the chemical composition of phosphosilicides is not as intense as that of silicides. The process is studied in more detail in [21]. It is noted that in the range of hot deformation of multicomponent brasses, phosphosilicides are more thermally stable.

Since the studies were conducted on samples with a low phosphorus concentration, at the microalloying level, it is difficult to trace the effect of the obtained patterns of phosphorus behaviour in brass. It is advisable to study the effect at different concentrations. Additional studies are required, since it is necessary to estimate the solubility of intermetallic compounds with phosphorus in multicomponent brasses.

CONCLUSIONS

It has been found that a significant portion of phosphorus in the multicomponent CuZn32Mn3Al2FeNi brass in low concentration (up to 0.005 % wt.) is bound in manganese phosphosilicides.

When combined with manganese and iron, phosphorus forms rod-shaped inclusions. When scanning, the concentration lines of manganese and phosphorus coincide. Secondary crystals in these compounds consist mainly of iron and silicon.

When heated to the hot deformation temperature, phosphorus is redistributed, the intermetallic compound dissolves, and metastable inclusions are formed, while phosphorus is redistributed together with aluminium.

Phosphosilicides in the range of hot deformation of brasses are more thermally stable than silicides.

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Влияние микролегирования фосфором на структурообразование многокомпонентной латуни ЛМцАЖН

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Аннотация: Фосфор в латуни может оказывать как положительное влияние – улучшать механические свойства, повышать коррозионную стойкость и обрабатываемость, так и отрицательное – негативно сказываться на свариваемости и приводить к растрескиванию. Исследование роли фосфора в процессах структурообразования латуни имеет практическую актуальность, поскольку способствует оптимизации свойств материала, снижению возможности появления дефектов, улучшению процессов обработки и контролю свойств и качества. Работа посвящена исследованию роли фосфора в латуни, необходимости контроля его содержания при производстве путем ограничения доли вторичного использования. Выявлена возможность положительного влияния модификации медных сплавов фосфором с целью улучшения эксплуатационных свойств, а также перспектива использования фосфора в качестве безопасной замены свинца в латуни. Проведена оценка содержания и распределения примеси фосфора в концентрации 0,005 % в латунном образце марки ЛМцАЖН 59-3,5-2,3-0,5-0,3, изучены характер его взаимодействия с другими компонентами сплава и изменения, происходящие при различных температурах термической обработки. Установлено, что фосфор активно участвует в диффузионных процессах и образует фосфиды как в дефектных, так и в бездефектных заготовках. При нагреве в области температур горячей деформации происходит перераспределение фосфора, локальное растворение фосфида и образование метастабильных включений. Из-за различий в концентрации элементов в областях, прилегающих к фосфиду, происходит изменение структуры латуни, что приводит к образованию участков, отличных от матричной β-фазы. Фосфид марганца в латуни может улучшить ее механические свойства и обрабатываемость резанием, но избыток этого соединения может привести к проблемам с прочностью, трещиностойкостью и формованием.

Ключевые слова: двойные и многокомпонентные латуни; анализ распределения фосфора; силициды; фосфор; соединения с фосфором; форма и размеры включений; влияние нагрева на микроструктуру; перераспределение фосфора; марганцевый фосфид; диффузионные процессы; метастабильные включения.

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