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Manufacturing Cu-Pb alloys and studying efficiency in resisting oxidation

Wytwarzanie stopów Cu-Pb i badanie ich odporności na utlenianie

Binary alloys of copper and lead were produced by casting these elements in specially designed moulds with dimensions appropriate to the tests to be carried out on them. The effectiveness of these alloys in resisting oxidation was then studied in an atmosphere of a mixture of sodium chloride vapour and sodium sulphate at specific concentrations and heating the mixture to 180°C. Recently, corrosion has become a major problem in the overall performance of many engineering devices due to automotive exhaust gases produced by the internal combustion engine, which leads to corrosion of materials that make up some components of engineering industries. Copper also has good corrosion performance due to the formation of a copper oxide layer, which has made it the most important material in industrial applications. Through this research, we have achieved the desired goal as the alloys produced have shown their efficiency in resisting saline and acidic conditions and at high levels. The best sample is Cu₉₅Pb₅ and Cu₉₀Pb₁₀ with little difference between them in terms of efficiency. The aim of this work is to produce alloys and study their efficiency in resisting oxidation at high temperatures.

Keywords: copper, lead, binary alloys, oxidation

1. Introduction

A new metal is formed from a homogeneous composition of two, three or more metallic elements, or even from a mixture of non-metallic and metallic elements. This is known as an alloy. It is made up of elements that are combined by heating to a certain temperature and then solidifying. Alloys offer new properties and benefits as they are generally harder than their original components, display decreased ductility and may even demonstrate reduced conductivity. Their individual metal crystals are very malleable, soft and show high electrical conductivity. Pure metals are therefore only used for certain applications. Alloys are generally more resistant to corrosion and less affected by changing atmospheric conditions. Their hardness varies depending on the heat treatment used

Binarne stopy miedzi i ołowiu zostały wytworzone metodą odlewania w specjalnie zaprojektowanych formach o wymiarach dostosowanych do badań. Odporność stopów na utlenianie została zbadana w atmosferze mieszaniny oparów chlorku sodu i siarczanu sodu w określonych stężeniach i po podgrzaniu mieszaniny do 180°C. Korozja jest poważnym problemem, zaburza funkcjonowanie wielu urządzeń inżynierskich. Jej źródłem są m.in. spaliny wytwarzane przez silniki spalinowe. Miedź ma dobre właściwości antykorozyjne ze względu na warstwę tlenku miedzi, tworzącą się na jej powierzchni w wyniku utleniania. Z tego względu jest głównym materiałem stosowanym w przemyśle. Badane stopy miedzi i ołowiu wykazały wysoką odporność na działanie soli i kwasów w dużych stężeniach. Najlepsze wyniki uzyskano dla stopów Cu₉₅Pb₅ i Cu₉₀Pb₁₀ (różnica między nimi była niewielka). Celem pracy było zbadanie odporności wytworzonych stopów na utlenianie w wysokich temperaturach.

Słowa kluczowe: miedź, ołów, stopy binarne, utlenianie

while their conductivity depends on alloy grade [1]. Copper is the most commonly used element. It is second only to gold, silver and platinum. It also has the same FCC aluminium frame and it melts at 1085°C [2–4]. Lead has been used for radiation shielding since ancient times due to its favourable physical and chemical properties. Thanks to technical advanced, spectroscopic analysis has shown that due to its high density makes it a heavy metal. Thanks to this property, it was found to be the best radiation-absorbing material, making it suitable for shielding and is still widely used today [5–6].

Oxidation in a broad sense is the increase in the positive valence of a metal element during a chemical reaction. When a metal combines with an atom or molecule and loses electrons, this reaction is called oxidation [7]. Corrosion occurs naturally when metals come into contact with oxygen and react to form metal oxides. Acidity

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or low pH, electrical conductivity, oxygen concentration and water temperature all affect the rate of corrosion. Minerals dissolve when the water is very low in dissolved salts or in the presence of certain water-borne ions, in addition to corrosion. Corrosion is a universal challenge, economically motivated in both developed and developing countries, with unintended consequences such as reduced productivity due to deterioration of industrial equipment and infrastructure, accidents and significant economic losses. Every year, industries such as the chemical, energy, transport, food processing and construction sectors suffer of billions of dollars in devastating corrosion-related losses [8–9]. The three main types of alloys are binary, ternary and multi-component. Binary alloys are actually composed of two constituent elements. Ternary alloys have three constituent elements. Multicomponent alloys are among the most common commercial alloys and consist of more than three constituent elements [10].

2. Theoretical background

2.1. General background of alloys

The fundamental properties of structural alloys are still being investigated empirically. In fact, it is difficult to derive a suitable formula that can predict which metal elements in particular proportions can be mixed and treated at a heating temperature to produce a given property or group of properties. However, there are rules that can describe the valuable behaviour of a particular set of alloys. These rules are statements about the reasonable sizes of constituent atoms in alloy structures and the types of phases that can be predicted from the valence of the constituent atoms. The rules are rigorously explored by empirical methods and can be described almost in terms of physical fundamentals [10–11].

The properties of a range of alloys can be easily studied using alloy phase diagrams. The phase diagram is defined as a graphical representation of the number and types of phases that can be predicted in an alloy. When phases have reached thermodynamic equilibrium, phase diagrams show pressure, temperature and composition functions. Solid, vapour or liquid phases with various disordered and ordered crystal structures are possible. The phase diagram cannot indicate how quickly equilibrium will be reached. It is critical to ensure that alloys are into stable equilibrium states and to determine which phases are present when the phase diagram is assigned empirically [10].

2.2. Mechanism of oxidation and oxide crust growth

When a metal or alloy surface is exposed to oxygen, a single oxide layer (monolayer) forms which rapidly undergoes a process known as chemical adsorption. As a result, oxide nuclei form at the top and grow to cover the surface of the metal or alloy with a thin oxide layer. The growth processes of this primitive layer involve either a movement of metal ions into a form (substrate) or a movement of oxygen ions from the gas side, as metal ions move from the interface (oxide-metal) to the interface (gas-oxide), while oxygen ions move from the gas-oxide interface to the metal-oxide interface. It should be noted that the movement of these different ions is governed by diffusion laws [12].

Wagner investigated the mechanism by which an oxide layer grows by using typical cases with varying growth rates and the way in which oxygen ions and metal ions interact. As shown in Fig. 1, his research yielded the following results [13]:

1. If the oxide layer formed is porous, oxygen molecules can pass through it and interact with the metal or alloy at the interface (metal-oxide; Fig. 1a).
2. In the case of a non-porous oxide layer, an oxidation reaction occurs in the interface (air-oxide), where metal ions diffuse from the interface between the metal and an oxide towards the outer

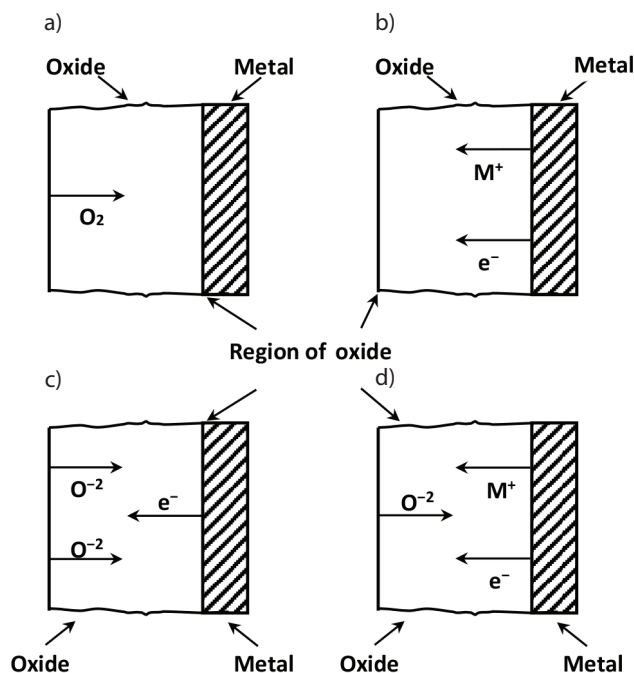


Fig. 1. Oxidation mechanism: a) porous oxide layer, b) non-porous oxide layer – reaction in the interface air-oxide, c) non-porous – reaction in the interface metal-oxide, d) combination of the reactions b) and c)

Rys. 1. Mechanizm utleniania: a) porowata warstwa tlenkowa, b) nieporowata warstwa tlenkowa – reakcja na granicy powietrze-tlenek, c) nieporowata warstwa tlenkowa – reakcja na granicy metal-tlenek, d) połączenie reakcji b) i c)

surface (air-oxide), while electrons also migrate in the same direction to complete the reaction (Fig. 1b).

3. An oxidation reaction may occur at the interface if on oxide layer is non-porous (metal-oxide). When oxygen ions diffuse into the interior through the oxide layer to interact with the metal at the separating surface (metal-oxide), electrons become free and move towards the separating surface (air-oxide; Fig. 1c).
4. The last possible case is a combination of the second and third, where the oxygen ions diffuse inwards, although the metal ions and electrons move outwards, and the reaction occurs wherever the ions meet through the oxide layer (Fig. 1d).

3. Experiment technique

3.1. Manufacturing alloys

The alloy manufacturing process took place in two stages:

1. Oven preparation and casting of moulds – a gas oven was manufactured for this purpose, and the stainless steel moulds were designed and manufactured locally.
2. Melting and casting of alloys – The elements to be cast were weighed and then placed in an oven with a graphite cover. When the mixture was ready, the molten metal was poured into the moulds [14].

3.2. Sample preparation and analysis

In this work, alloys of Cu-Pb were prepared by the alloying method in different proportions (Table 1). Copper ($Z = 29$ and purity 99.9%) was placed in an alumina crucible and then melted in an oven (melting point: 1085°C) for 15 min. Afterwards lead ($Z = 82$ and 99.7% purity) was added (melting point: 327°C), where they were melted together for 5 min. The molten material was poured into an iron mould with a round shape of 1 cm diameter and 6.5 cm deep. Density was obtained by using the Archimedes rule [15].

Table 1. The physical properties of the prepared alloys
Tabela 1. Właściwości fizyczne przygotowanych stopów

Sample	Composition	Diameter [cm]	Volume [cm ³]	Density [g/cm ⁻³]	Thickness [cm]
A ₁	Cu ₉₅ Pb ₅	1.2	2.566	8.512	2.27
A ₂	Cu ₉₀ Pb ₁₀	1.2	2.780	8.288	2.46
A ₃	Cu ₈₅ Pb ₁₅	1.2	2.249	9.000	1.99
A ₄	Cu ₈₀ Pb ₂₀	1.2	2.351	8.726	2.08

a)



b)

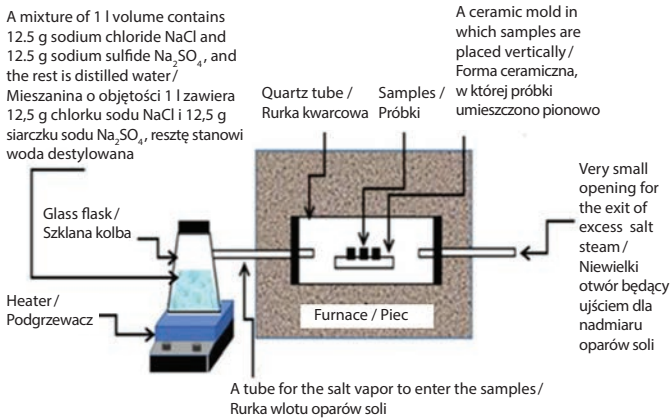


Fig. 2. The system used in the oxidation process: a) general view, b) scheme

Rys. 2. System zastosowany w procesie utleniania: a) widok ogólny, b) schemat

3.3. Design of the oxidation test system

The corrosion test was carried out in a specially designed oven using the cyclic oxidation method or thermal cycles at 180°C and normal atmospheric pressure, each cycle lasting 4 h, and in an environment of sodium sulphate and sodium chloride vapour, using an oxidation system that contains a beaker with a mixture of sodium sulphate and sodium chloride with 1 l of water, heated to boiling point. The vapour of the mixture is transferred into the furnace at a temperature of 180°C to test the behaviour of samples (alloys) of all types:

- Tests were conducted for the 4 manufactured binary alloys over a period of 120 h, at a rate of 4 h for each thermal cycle.
- The samples were weighed before conducting the test.
- The dimensions of each model were calculated to determine its surface area before conducting the test in order to estimate the weight change per unit area.
- The forms were placed in a mould and in the oven after reaching the set temperature (180°C). After 4 h, the samples were removed from the oven, allowed to cool for 1 h, and weighed. This

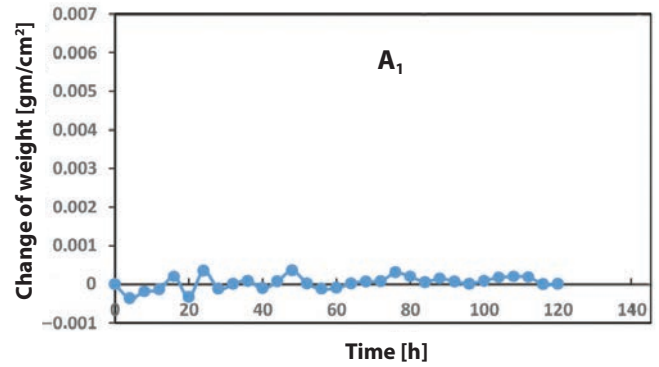


Fig. 3. Oxidation kinetic of binary alloy Cu₉₅Pb₅

Rys. 3. Kinetyka utleniania stopu binarnego Cu₉₅Pb₅

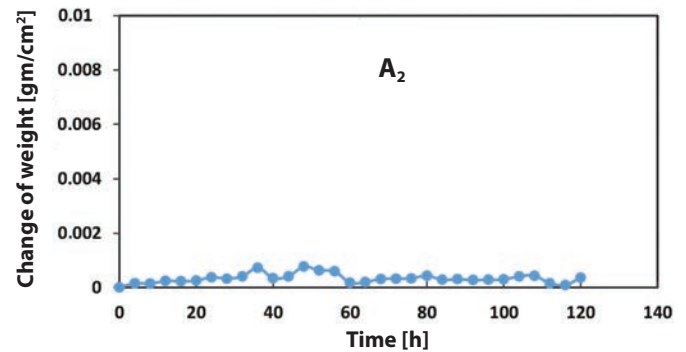


Fig. 4. Oxidation kinetics of binary alloy Cu₉₀Pb₁₀

Rys. 4. Kinetyka utleniania stopu binarnego Cu₉₀Pb₁₀

process was repeated until 120 h are reached, and the shape represents the oxidation system that was produced.

4. Results and discussion

Sample A₁ shows high stability throughout the cyclic oxidation period, and the reason is due to the formation of copper phases and copper-lead phases with high resistance to oxidation in salty and acidic conditions. Moreover, the oxide layer is thin, sticky, and demonstrates high adhesion, thus protecting the alloy from the external environment, and we found high weight stability during the oxidation cycle period as shown in Fig. 3.

We discovered a high stability throughout the period by studying the oxidation kinetics of sample A₂ as shown in Fig. 4, which indicated the formation of a layer protecting the sample against corrosion and the external salt environment. Also, different concentrations of copper-lead phases were formed inside the alloy, and this was confirmed by an examination. These stable and formed phases protect the alloy from corrosion and cracks that occur in the ingots as a result of exposure to harsh conditions. There was no evidence of any colour change or in the dimensions of the sample that would indicate failure, and it remained in its production location (Photo 1).

Through the oxidation kinetics of the sample A₃, as shown in Fig. 5, there is a high stability throughout the period, which indicates the formation of a layer protecting the sample against corrosion and ensuring resistance to the external acidic environment. This means the formation of different phases of copper and copper-lead inside the alloy. This is confirmed by an SEM-EDS examination and XRD (Fig. 6, 7). This stable crust should provide protection or the alloy from corrosion and for the cracks that occur in the alloys as a result of exposure to harsh conditions. By observing



Photo 1. Image of sample: a) before corrosion test, b) after corrosion test
 Fot. 1. Obraz próbki: a) przed badaniem korozyjnym, b) po badaniu korozyjnym

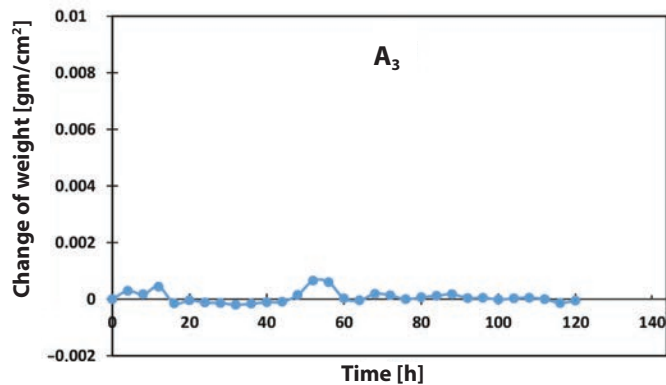


Fig. 5. Oxidation kinetics of binary alloy $\text{Cu}_{85}\text{Pb}_{15}$
 Rys. 5. Kinytyka utleniania stopu binarnego $\text{Cu}_{85}\text{Pb}_{15}$

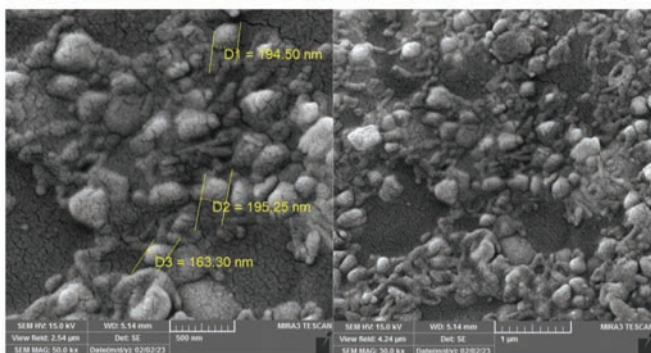


Fig. 6. The image of A_3 alloy by SEM
 Rys. 6. Obraz stopu A_3 wykonany metodą SEM

the samples after the end of the test, there was no evidence of any change in colour or in the dimensions of the sample.

We noticed a high stability throughout the period by studying the oxidation kinetics of sample A_4 (Fig. 8) indicating the formation of a layer protecting the sample against corrosion and the external salt environment. Also, different concentrations of lead-

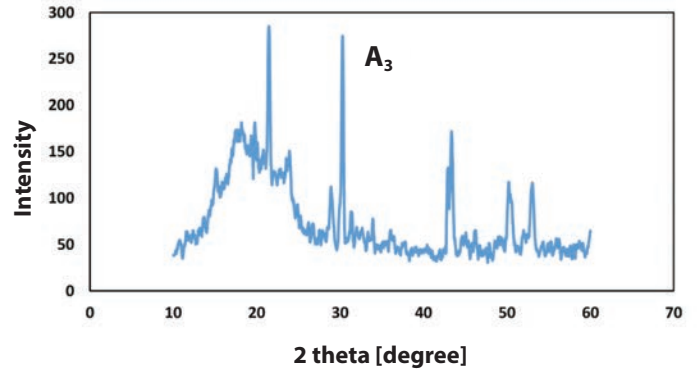


Fig. 7. XRD for the sample A_3
 Rys. 7. XRD dla próbki A_3

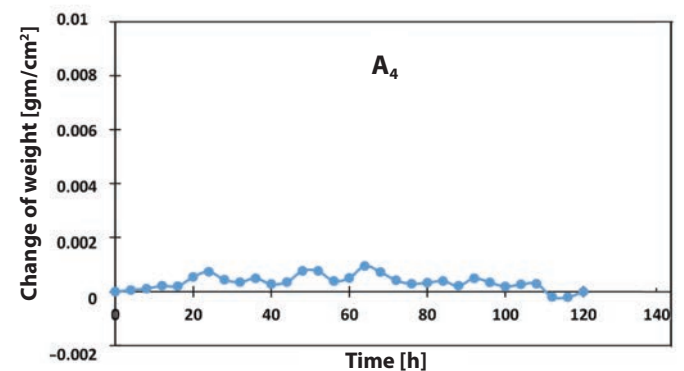


Fig. 8. Oxidation kinetics of binary alloy $\text{Cu}_{80}\text{Pb}_{20}$
 Rys. 8. Kinytyka utleniania stopu binarnego $\text{Cu}_{80}\text{Pb}_{20}$

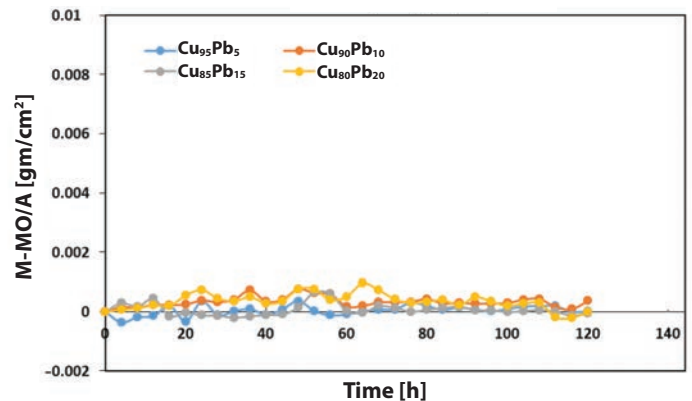


Fig. 9. Oxidation kinetic of binary alloys
 Rys. 9. Kinytyka utleniania stopów binarnych

-copper phases were formed inside the alloy, which was confirmed by an examination. These stable and developed phases protect the alloy from corrosion and cracks that occur in the ingots as a result of exposure to harsh conditions. We found a slight change in the rate of weight $[\text{gm}/\text{cm}^2]$ change with time $[\text{h}]$, but this change did not affect the alloys' efficiency. As a result, the collected alloys showed no change in colour or dimensions.

Finally, the differences in the oxidation kinetics between all the manufactured alloys can be seen through Fig. 9, and here we find very few differences between them.

5. Conclusion

We found that all samples produced showed good oxidation efficiency, but to varying degrees. The $\text{Cu}_{95}\text{Pb}_5$ and $\text{Cu}_{90}\text{Pb}_{10}$ alloys performed best because the weight change in their surface area was less than that of the $\text{Cu}_{85}\text{Pb}_{15}$ and $\text{Cu}_{80}\text{Pb}_{20}$ alloys, indicating that the higher the percentage of lead, the less efficient the alloy is in resisting oxidation, but the greater its efficiency in attenuating nuclear radiation.

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