VOL. 15, NO. 12, JUNE 2020 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

THE COMPOSITION DEVELOPMENT AND TECHNOLOGICAL ASPECTS OF OBTAINING A NEW ALLOY BASEDON PALLADIUM

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ABSTRACT
The aim of this work is to develop a new solder with a lower melting temperature, relative to standard palladium-based alloys, and improved technological properties using a three-component system additionally doped with boron. As a theoretical basis used approach to the analysis of complex systems developed by Professor Biront V.S. An experimental testing of boron was carried out at a content of 2.2 to 3.1 Wt% as a eutectic-forming substance in solder alloys of palladium. The methodology and technological modes of obtaining a new palladium-based solder alloy with a melting point of 1200 °C are also presented. Tests of the new alloy performed in the conditions of jewellery production gave positive results, on the basis of which its final composition was determined. This methodology was applied in the development of new compositions for noble metal alloys, which are protected by Russian and Eurasian patents.

Keywords: palladium, solder, noble metal alloy, complex system, boron doping, jewelry.

INTRODUCTION
Solders intended for soldering jewelry should correspond to the grade composition and colors of the alloy from which they are made [1-2]. The increase in the world price of palladium and products from its alloys is associated, first of all, with the situation in the jewelry market. A limited set of reliable and technologically advanced palladium-based solders makes it difficult to expand the range to meet the growing demand for these products [3-4]. When developing new solders, it is important to consider their manufacturability during casting and further processing [5-7], and the melting point of the solder should be lower than that metal of product. Usually this is achieved by adding the appropriate alloying elements into the solder [8-10]. In addition, lowering the soldering temperature leads to a decrease in gas saturation of palladium alloys [11-14].

A promising direction is the creation of new grade solder compositions using additional alloying with components that form continuous solid solutions with palladium, as well as elements that form fusible eutectic systems without or with minimal participation of intermetallic compounds. Silicon, boron, germanium and tin are most often used as eutectic-forming components, since these components form eutectic systems near the palladium axis on the state diagram, which can make an additional contribution to lowering the melting temperature of the solder alloy.

Palladium-Based Alloy Analysis
Table-1 shows some properties of standard palladium alloys in accordance with GOST 30649-99. Table-2 shows information on the decrease in the melting temperature of palladium upon the introduction of the second element, which forms a state diagram near the ordinate: first, eutectic transformations (symbol – eut.); and secondly, by achieving a minimum of internal enthalpy in the system of continuous solid solutions (min.), as well as due to the peritectic reaction (per.).

Table-1. Properties of palladium-based alloy [9].

Grade	Estimated density, g/cm3	Melting point (range), °C	Hardness HV, kgf/mm2	
			Solid	Soft
PdAgNi 500-450	11,16	1250÷1280	330	160
PdAgNi 850-130	11,83	1420÷1500	235	125
PdCu 850	11,54	1360÷1415	220	155

An analysis of Table-2 shows that doping palladium with transition metals such as nickel, iron, cobalt, as well as thorium and titanium lowers the melting temperature due to the presence of a minimum of liquidus and solidus lines in the solid solution area on the state diagrams of the corresponding systems. Such a structural state in the temperature range of solidus would be most favorable in solder alloys. However, the chemical composition limits do not allow their use in creating solders for 850 grade palladium alloys.

Bismuth and indium near the ordinate of palladium have only peritectic reactions, and therefore, the use of these components extends the temperature range of crystallization, which does not correspond to the principles of creating solders [15].

VOL. 15, NO. 12, JUNE 2020 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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Most of the other components listed in the Table-2, form eutectic reactions near palladium, which corresponds to the conditions for obtaining solders. However, in all cases considered, a eutectic is formed with the formation of one, and sometimes, two interacting phases of the intermetallic type. This does not allow us to hope for a good manufacturability of solders due to the low level of ductility required to obtain the desired shape of the products by pressure treatment methods. In addition, in palladium systems there are no substances that would form a eutectic system between plastic phase components without intermetallic compounds.

Table-2. The effect of alloying elements on the melting temperature in palladium-based systems [10].

Element	Wt% content	Reaction type	Temperature, °C	Element	Wt% content	Reaction type	Temperature, °C
Al	7,0	eut.	1055	Li	~ 1,0	eut.	1455
B	3,5	eut.	1065	Mg	11,5	eut.	1280
Ba	32,0	eut.	1230	Mn	19	eut.	1350
Be	2,0	eut.	930	Nd	6	eut.	1080
Bi	30,0	per.	935	Ni	40	min.	1237
Ca	7,0	eut.	1090	P	5,5	eut.	780
Ce	20	eut.	1075	Pb	32	eut.	1197
Co	55	min.	1217	Sb	22	eut.	1070
Cr	37	eut.	1315	Si	4	eut.	821
Er	20	eut.	1280	Sm	18	eut.	1078
Fe	30	min.	1310	Sn	25	eut.	1280
Ga	18	eut.	1020	Th	23	min.	1125
Gd	20	eut.	1128	Ti	50	min.	1120
Ge	13,8	eut.	760	V	41	eut.	1340
Ho	20	eut.	1255	Y	13	eut.	1205
In	21÷28	per.	1365	Zn	18	eut.	1350

It follows from the foregoing that a promising direction in the creation of new grade solder compositions is the use of additional alloying with components such as silver, gold, rhodium, platinum, as well as copper, nickel, cobalt, and iron [16-17].

Preliminary experiments on the use of silicon, germanium, tin and boron as eutectic-forming components have shown that near the palladium axis on the state diagram they form eutectic systems that can make an additional contribution to lowering the melting temperature of the solder alloy. The best results are obtained by adding boron.

RESEARCH METHODOLOGY

According to the approach to analysis of complex systems developed by Professor Biront V.S. [8] implies that they can consist of single-phase solid solutions, all of whose components separately form eutectics. Based on this position, the work presents a methodology for experimental testing of boron as a eutectic-forming substance in solder alloys based on palladium.

The palladium-boron diagram (Figure-1) shows that it is advisable to create solder alloys with a content of the latter from 2.2 to 3.7 Wt%. At a lower content, eutectic structures do not form; at a higher content, brittle palladium borides will appear. The eutectic transformation temperature is 1065 °C. We can distinguish alloys that meet these conditions: PdCuB-11.5-3.5, PdCuB-12-3, PdCuB-13-2. Considering the fact that a eutectic is formed when the boron content is 3.1 Wt%, the alloy PdCuB-11-3.5 is chosen for research.

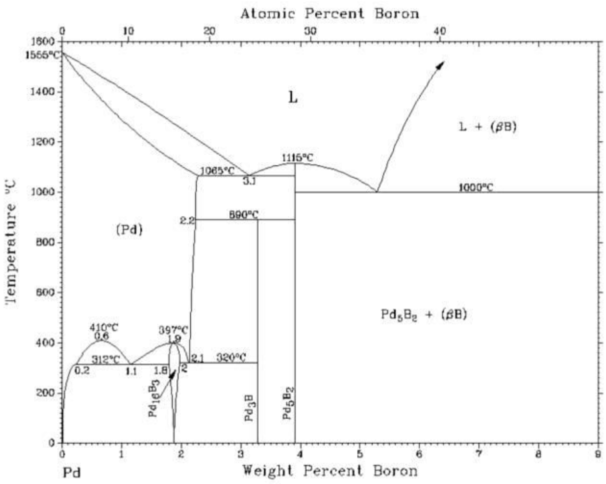

Figure-1. The palladium-boron diagram.

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To prepare the PdCuB-11-3.5 alloy was used a furnace burden consisting of palladium and boron powders, and copper to create the primary heel in a crucible. Samples of powdered palladium and boron were mixed and pressed into tablets weighing 50 g on a hydraulic press with a force of 600 kN. Melting was carried out in an induction furnace with a load of copper on a crucible to form a starting heel, the temperature of which was brought to 1300 °C, after which a palladium-boron briquetted mixture was added portionwise. The temperature of the melt during the entire melting did not exceed 1320 °C. Additional alloying to bring the solder to the grade composition was provided by copper, which forms a simple eutectic with boron (Figure-2).

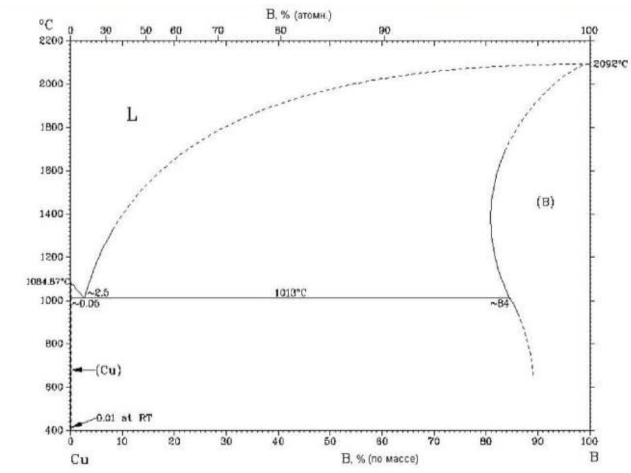
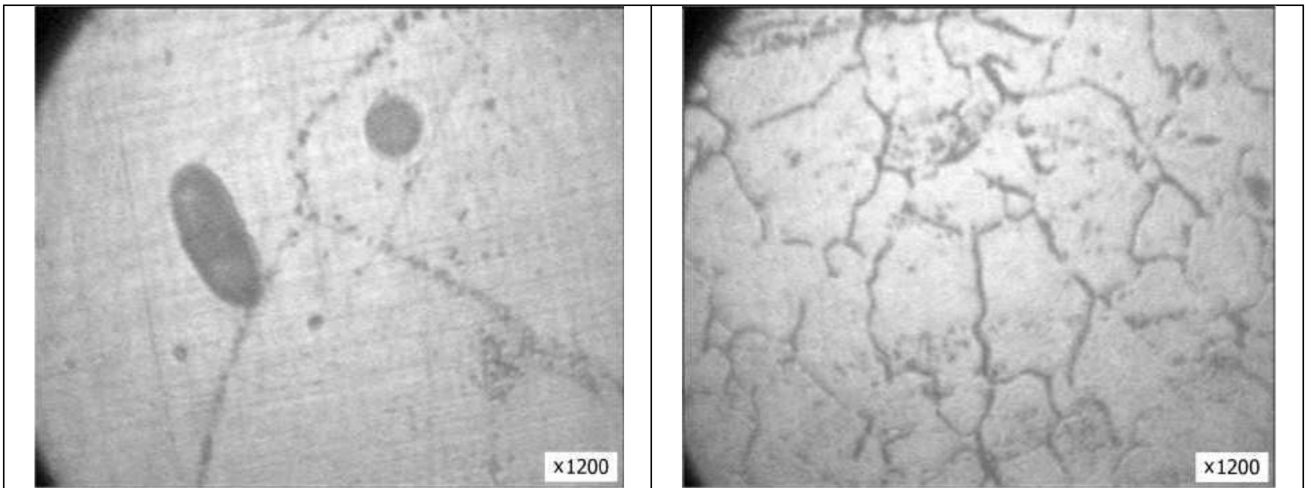


Figure-2. The copper-boron equilibrium diagram.

The obtained melt was poured into a heated metal mold in which an ingot with a diameter of 6 mm was formed. The cast blank part was deformed with intermediate technological anneals between the transitions of drawing in the open flame of a hydrogen burner. The result was a wire with a diameter of 0.3 mm. Testing this wire as a solder showed that its melting temperature was 1200 °C, which corresponds to the requirements for solder materials based on palladium.

RESULTS AND DISCUSSIONS

Figure-3 shows the microstructure of the alloy in a cast and deformed state. It can be seen here that the cast state is characterized by the presence of a solid solution base in the structure along the grain boundaries in which precipitates of the secondary phase are appeared.



a	b

Figure-3. The microstructure of PdCuB-11-3.5 alloy: *a* - cast state, *b* - deformed state.

Taking into account that the melting temperature of the obtained alloy is 1200 °C, the boron content in it can be determined by the two-component palladium-boron system with a value of 3.5 Wt% (Figure-1). The structure of the deformed and annealed alloy contains mainly a solid solution with secondary precipitates along the grain boundaries of fragments corresponding to the composition of the cast alloy.

The hardness of the cast bar was 730 HV, and after water quenching from a temperature of 900 °C - 360

HV. Samples in the form of chips for testing the level of solder properties were made from heat-treated alloy. Tests conducted in the conditions of jewelry production showed that heat treatment of the resulting alloy leads to a decrease in solder properties. This can be explained by the fact that the crystallization of solder alloys in the metallic mold is a nonequilibrium type with a significant reduction of the liquidus temperature and the solidus lines. After heat treatment, the alloys come to an equilibrium state, and their melting point rises.

The test of the PdCuB-11-3.5 alloy rolled strip with a thickness of 1.0 mm gave positive results and recommended for industrial use. In the process of developing technological regimes for soldering jewelry from palladium grade alloys, the final composition of the new alloy was determined, for which RF Patent No. 2447170 “Solder for brazing jewelry from 850 palladium alloy” was obtained.

It should be noted that in this direction, foreign scientists are also conducting research, the results of which were published in [18-21].

CONCLUSIONS

In course of the research, a technology was developed for the manufacture of a new palladium-based solder alloy with a melting point of 1200 °C. Tests of this alloy carried out under conditions of jewelry production gave positive results, on the basis of which the final composition of new alloy was determined. As one of the most effective methods for the manufacture of solder wire from this alloy is the Conform method described in previous publications [22-26].

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