Studying the structural-phase substance of solid and powder brass samples by X-ray diffractometry

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Abstract. The use of powder as an alloying element in the formation of various parts is a modern trend in mechanical engineering. It is common to use the added powder of a completely different type of material, and the requirements for the powder are constantly increasing. At the same time, an important characteristic of any method is the quality of the obtained powder, such as the degree of contamination by foreign impurities and the range of particle sizes. The most acute problem of obtaining powder is to preserve the original (not changed in the process of obtaining) material properties, as well as the need to prevent contamination and oxidation of particles. The aim of the work is to study the structural-phase state of solid and powdered brass samples. To achieve this goal it is necessary to solve the following tasks: to investigate the structural and phase state of a brass sample in the form of a cylinder; investigate the structural and phase state of a brass powder obtained by a high-speed dispersion method.

Results: Using the X-ray microanalysis method, it has been established that the elemental composition of the studied material corresponds to the composition of brass L63; by X-ray analysis, it was found that the samples of the brass cylinder are a mixture of a solid solution of zinc in copper (Cu-Zn) with a zinc content of about 34% of the CuZn phase with a CsCl-type cubic crystal lattice. Brass powder samples have the same phase composition, but with a different ratio of these phases.

1. Introduction
According to literary sources there is about a hundred ways to obtain ultrafine powder (UFP). They are based on phase transformations, chemical interactions, recrystallization, amorphization, high mechanical loads, biological syntheses. Their common disadvantage is that each method is focused on meeting specific powder requirements for chemical composition, size and shape of particles. Most of the existing methods of obtaining UFP are focused on industrial application, but for this it is necessary to evaluate the change in the properties of the material that was exposed. In this work, it is necessary to evaluate the properties of the UDP powder obtained by the high-speed method of dispersion [1]. Properties can be evaluated in different ways, but because of their merits, X-ray structural analysis (XRA) and qualitative phase analysis were chosen [1]–[8].

2. Problem formulation
The aim of the work is to study the structural-phase state of solid and powdered brass samples.

To achieve this goal it is necessary to solve the following tasks:
1. To investigate the structural-phase state of a brass sample in the form of a cylinder;
2. To investigate the structural-phase state of the powder of brass, obtained by high-speed method of dispersion;
3. To compare the obtained results.

3. Theory
For studies by X-ray analysis, brass L63 samples were provided the form of a rod and powder obtained after grinding.

L63 is a two-component alloy of copper and zinc, with a Cu content of 62 ... 65% and Zn 34.22 ... 37.5%, up to 0.5% in it are impurities.

Studies of the structural-phase state were performed by X-ray analysis on a device DRON-3. The diffractograms of the tested coatings were recorded with continuous 2θ scanning with Bragg – Brentano focusing in the copper anode radiation (Co Kα λ = 1.78 Å). The crystalline phases were identified using the JCPDS PDF-2 database of the ICDD structured data bank. The X-ray structural analysis was used to determine the phase composition of the alloys, the lattice parameters, the microstrain of the crystal lattice, the size of the coherent scatter blocks. For decoding radiographs used the data bank JCPDS and PDF.

Radiographic determination of the lattice parameter is based on accurate recording of the positions of the diffraction maxima, which are associated with the size of the unit cell [9] – [11].

Quadratic form for cubic syngonia:

\[
\sin^2 \Theta_{HKL} = \frac{\lambda^2 \cdot (h^2 + k^2 + l^2)}{4 \cdot a^2}
\]

where \( \Theta \) is the angle of reflection;
\( \lambda \) – radiation wavelength;
\( a \) – the lattice parameter;
\( h, k, l \) – reflex indexes.

Working formula:

\[
a = d_{HKL} \sqrt{H^2 + K^2 + L^2}.
\]

The physical broadening of the diffraction line \( \beta(2\theta) \), caused by the presence of both stresses of the 2nd kind (stresses balanced within individual crystallites) and grinding of crystallites, is described by the formula [10]:

\[
\frac{\beta(2\theta) \cos \theta}{\lambda} = \frac{1}{D_{HKL}} + 4e \frac{\sin \theta}{\lambda},
\]

4. Experimental results

In addition to X-ray analysis of samples, the elemental composition of brass L63 was explored by X-ray microscopic analysis using the X-ray electron microscope (SEM) Jeol JSM-5700 with EDX attachment. The research results are presented in figure 1.
Figure 1. The distribution of elements in the characteristic radiation
Al (a), Ni (b), Cu (c), Zn (d).

The established elemental composition is presented in table 1.

| El (keV) | Mass % | Error % | Atom % |
|----------|--------|---------|--------|
| Al K     | 0.45   | 0.34    | 1.07   |
| Ni K     | 0.46   | 0.59    | 0.50   |
| Cu K     | 58.83  | 0.91    | 59.11  |
| Zn K     | 40.26  | 1.18    | 39.32  |
| Total    | 100.00 | 1.00    | 100.00 |

Evaluation of research results (figure 1, table 1) showed that the composition of the studied brass within the experimental error corresponds to the composition of brass L63 in the initial state [12] – [17].

Next, we consider the study of the structural-phase state of the samples in the form of a cylinder and in the form of a powder.

4.1. The study of the structural-phase state of the sample in the form of a cylinder

The X-ray pattern of the cylinder of brass L63 (figure 2) was constructed using the XRA method and it was found that the cylinder of brass L63 (62-65% Cu, 34-37% Zn) is a mixture of two main phases in accordance with the equilibrium state diagram. The main phases are CuZn with a CsCl type cubic lattice with the lattice parameter $a = 2.9556 \ldots 2.9582$ Å (tabular data) and a solid solution of zinc in copper with zinc content from 5 to 11% (at.). The lattice parameter (Cu) with a content of 5% (at.) Zn is 0.3620 nm, and with an increase in the content of Zn from 11.41 to 33.56% (at.) it varies within $0.36327 \ldots 0.36898$ nm, accordingly, that we see in reality. It can be seen that the experimental values of the parameter of the crystal lattices of both phases are close to the values of the parameters of the lattices given in the works of the authors [9].

In addition, a small amount of oxides, including Cu$_2$O, is contained in the L63 brass rod. It should be noted that in the sample there is a texture with the axis “110” along the normal to the end surface for the CuZn phase. Peaks of the (hh0) type are strong, while the intensity of the other peaks is weak, i.e. does not correspond to the theoretical intensity for a bulk sample characteristic of a CuZn compound.

In the case of an FCC structure, a precise determination of the phase lattice parameter (figure 3) is possible from an extrapolation graph of the dependence of the unit cell parameter $a$ on the function $f(\Theta)$, which is as follows:

$$f(\Theta) = \frac{1}{2} \left( \frac{\cos^2 \Theta}{\sin \Theta} + \frac{\cos^2 \Theta}{\Theta} \right). \quad (4)$$
Figure 2. The X-ray pattern of the cylinder brass L63 symmetrical shooting scheme.

This function allows you to take into account the instrumental errors due to the absorption and divergence of the X-ray beam.

Figure 3. Extrapolation dependencies of the unit cell parameter $a$: a – a solid solution of zinc in copper (FCC lattice Fm3m), b – phases CuZn (structure CsCl).

Extrapolation of the value of “a” to $\Theta = f(90^\circ) = 0$ allows to determine the lattice parameter with the minimum error ($\pm 0.0001\,\text{Å}$).

From the extrapolation graphs it can be seen that the lattice parameter of the FCC – phase of $a_{\text{FCC}} = 3.7030.002\,\text{Å}$, which corresponds to the maximum zinc content in the solid solution (about 34 at. %). The lattice parameter of the CuZn phase is $a_{\text{CuZn}} = 2.9490.001\,\text{Å}$, which corresponds to the tabular values of the crystal lattice parameter of this phase (2.95 Å).

4.2. The study of the structural phase state of the powder
In figure 4 the X-ray pattern of powder of L63 brass is presented. Here, as well as for a brass rod, it is characterized by the presence of two main phases: a solid solution of zinc in copper (Cu-Zn) and a phase of CuZn.

![X-ray pattern of the rod L63 brass (powder)](image)

**Figure 4.** The X-ray pattern of the rod L63 brass (powder) according to the scheme of symmetric shooting.

5. Results discussion

Unlike the brass sample (cylinder), the texture is not observed in the powder. This is due to the fact that the particles of the powder are arranged randomly and, therefore, there is no prevailing direction.

The proportion of the phases varies. If in the cylinder a solid solution of zinc in copper prevailed, then in the powder the intensity of the peaks of the CuZn phase was significantly higher. It should be noted that the lines of a solid solution of zinc in copper of FCC-structure delaminate, which indicates the heterogeneity of the solid solution.

Figure 5 shows the fine structure of powdered brass. It can be seen that the reflex consists of several subreflexes. As a minimum, two phases can be distinguished here. The left parts of the FCC phase reflections (zinc solid solution in copper) are designated as (hk)l.

![Fragment of the diffractogram showing the heterogeneity of the solid solution of zinc in copper](image)

**Figure 5.** Fragment of the diffractogram showing the heterogeneity of the solid solution of zinc in copper.

Figure 6 shows extrapolation graphs for precision determination of the lattice parameter of brass powder.
It can be seen that the parameters of the crystal lattices of FCC-phase are $\alpha_{\text{FCC}} = 3.66840.0005$ Å for the right reflexes, for the left reflexes $\alpha_{\text{FCC-L}} = 3.6830.001$ Å. The lattice parameter of the CuZn phase is $\alpha_{\text{CuZn}} = 2.94220.0002$ Å, which corresponds to the tabular values of the lattice parameter of this phase (2.95Å) and is slightly less than the same parameter for the bulk sample of brass L63 (2.9490.001 Å) [18] – [20].

6. Conclusion

Based on the results, the following conclusions were made:

1. By the method of micro X-ray analysis it was established that the elemental composition of the studied material of the powder obtained by the high-speed method of dispersion corresponds to the composition of brass L63.

2. It has been established by X-ray diffraction analysis that the samples of a brass cylinder are a mixture of a solid solution of zinc in copper (Cu-Zn) with a zinc content of about 34% of the CuZn phase with a cubic crystal lattice of the CsCl type. Brass powder samples have the same phase composition, but with a different ratio of these phases.

3. Samples of brass in the form of a cylinder have a pronounced texture type 110, in contrast to the powder sample.

4. Precise measurement of the lattice parameter of both samples gives a value for the CuZn phase close to the theoretical value for bulk samples.

5. In the powder sample of brass, concentration stratification is observed for a solid solution of zinc in copper, which means the presence of several solid solutions with different lattice parameters, and, consequently, with different content of elements.

7. References

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