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Microstructural parameters of dispersion strengthened Cu–Al_2O_3 materials

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Abstract The aim of the article was to evaluate the microstructural parameters of Cu–Al_2O_3 dispersion strengthened materials with different volume fraction of Al_2O_3 phase. For analyses of dispersoids Al_2O_3, the extraction carbon replica was used. The distribution of Al_2O_3 particles in the matrix was estimated by three methods (quadrant count method, polygonal method, and by interparticle distances), these methods showed that particle distribution in material with 1 vol.% of Al_2O_3 is very close to the Poisson point process (PPP), which is a model of randomly distributed points. Particle distributions in materials with 8 and 10 vol.% of Al_2O_3 achieve features of regularity proved mainly by the spherical contact distance.

Introduction

Materials with both good strength and good electric or thermal conductivity can by produced by powder metallurgy. A variety of binary and ternary systems prepared by powder metallurgy are known, based on Cu. The applied powder metallurgy technologies are different. In [1], a list of materials prepared by mechanical alloying is given. Good results were obtained by dispersion strengthening of the Cu matrix using Al_2O_3, TiC, ThO_2, SiO_2, TaC, ZrO_2, Y_2O_3, TiB_2, etc. However, the majority of works deal with single or multicomponent matrix dispersion strengthened using Al_2O_3. Different preparation technologies were described as mechanic mixing, oxidation and reduction, reactive milling, mechanical alloying etc. W. Schatt and K. P. Wieters, in their monography [2], evaluated the possibilities of hardening and the high temperature stability of dispersion strengthened Cu. Different technologies and different second phase particles were used. The review of a large number of references showed that the preferred method of introduction of dispersed particles into the Cu matrix is the high energy milling of metallic and second phase particle powder mixtures followed by hot compacting. The microstructure of compacts produced by this technology is microcrystalline, due to the reduction of grain growth during the heat treatment caused by the dispersed particles. Problems were reported with creep properties of very fine grain compacts, but advances for dispersion strengthened Cu were described in [3].

Composite Cu–Al_2O_3 is used as electrodes for spot-welding, for electric power switchers, electric motors and heat exchangers, and for cold parts of gas turbines or generators [4]. The wide scale of binary and ternary systems on the Cu basis, prepared by different technologies of powder metallurgy exists nowadays, the survey of mechanically alloyed systems is listed in [1]. The aim of the work is the quantitative analysis of the second phase particles distribution in the Cu–Al_2O_3 system prepared by mechanical alloying method.

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Experimental material

The samples, Cu–Al_2O_3 system with nominal volume fractions of 1, 8, and 10 vol.% of Al_2O_3 (marked A, B, C), were prepared by reaction milling and mechanical alloying at Technical University in Vienna. The basic operation was the homogenization milling of CuAl alloy in attritor in an oxidizing atmosphere. The oxygen from CuO, which was formed during the homogenization milling, was transformed into the Al_2O_3 phase at further heat treatment. Redundant CuO was removed from the mixture by annealing in $H_2 + H_2O$ atmosphere. The mixture was compacted by cold pressing, sintering, and hot extruding. The material is described in more detail in work [5].

Results and discussion

The phases identification, microstructural parameters, and the Al_2O_3 phase volume fraction determination

The microstructure of Cu–Al_2O_3 material was fine grained. The Al_2O_3 secondary phase particles were homogeneously distributed in the copper matrix. Metallographicaly observed larger particles were arranged in bands due to the hot extrusion (about 30%). The extraction carbon replica image of the material with smaller particles of secondary phase of size in the range from 50 nm to 70 nm is shown in Fig. 1. Particles were distributed individually or in clusters with diameter approx. 380 nm in the microstructure. Particles distributed individually were in minority. Diffractogram taken from the extraction carbon replica proved the presence of Al_2O_3 phase, Fig. 2.

The real volume fraction of Al_2O_3 secondary phase particles was determined using the metallographical cross section. The average values and their variances are listed in Table 1. For material, B the value of the nominal volume fraction is in the confidential interval of planar fractions mean values estimation, while for materials A and C, the values of nominal volume fraction were below the corresponding intervals. Differences in nominal and real volume fractions value differ slightly only and it is possible to refer them to the Al_2O_3 formation process by transformation mechanism "in situ." It was shown that the real volume fraction was overvalued. It can be assumed that the reason is mainly in the presence of FeO inclusions, which get into the material from the milling environment during the mechanical alloying, and Cr and Ni, oxygen detected on EDX occurs in material mainly like Al_2O_3 phase, FeO phase appears in material in insignificant amount, Fig. 3.

Analyses of Al_2O_3 particles distribution by different statistical methods

The three Cu–Al_2O_3 experimental materials were metallographicaly prepared and observed by scanning electron microscopy at the magnification, which allowed a good identification of the coarser particles with maximal possible number of particles in the observed area. Five localities

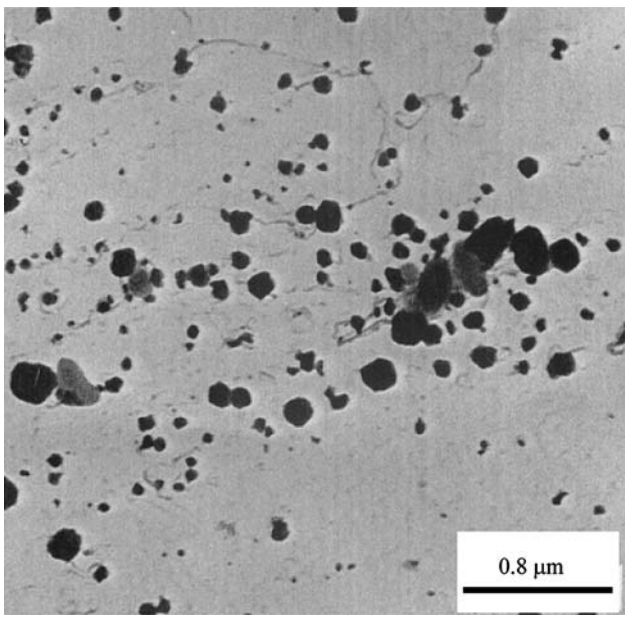

Fig. 1 Extraction carbon replica image of Cu–Al_2O_3 material

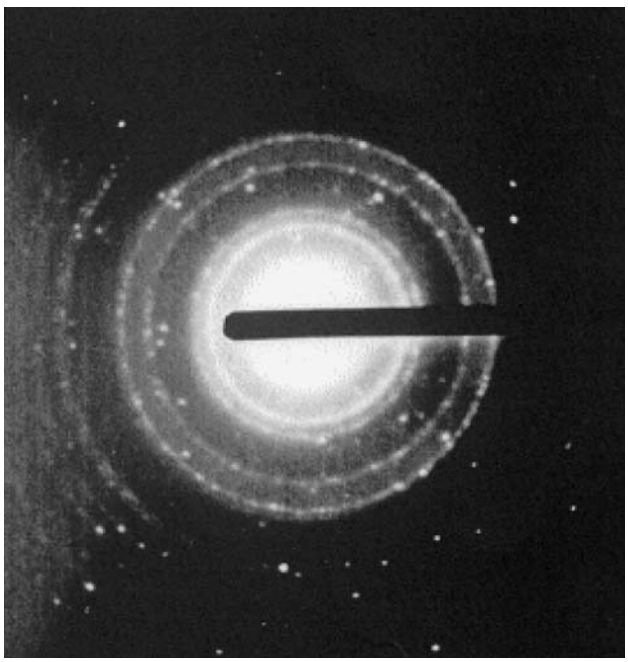

Fig. 2 Diffractogram taken from extraction carbon replica of Cu–Al_2O_3 material

Table 1 Global parameters of Al_2O_3 secondary phase particles

Sample	Number of particles	$f_{(N)}$ vol. (%)	$f_{(R)}$ (%)		Intensity (μm^{-2})	
			$\bar{x}$	s	$\bar{x}$	s
A	120	3	3.93	0.478	0.285	0.036
B	366	8	7.82	0.697	0.562	0.031
C	265	10	12.40	0.491	0.535	0.047

$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ is average and $s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n \cdot (n-1)}}$ is standard deviation

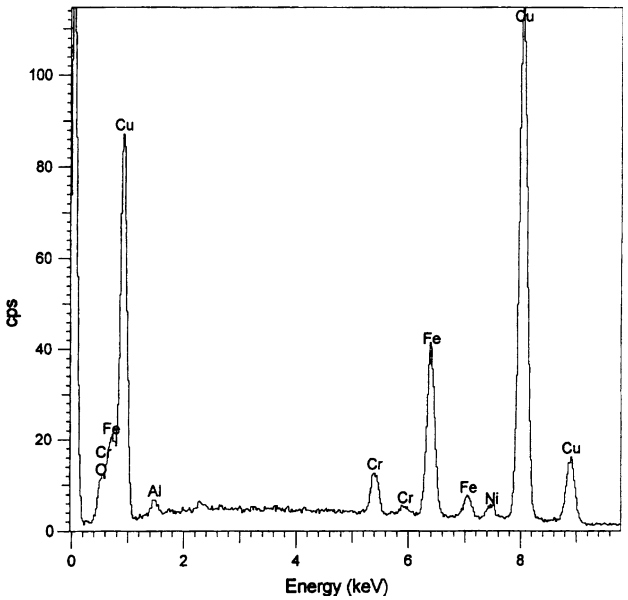

Fig. 3 EDX spectra from Cu–Al_2O_3 material

were selected for every material cross section, the SEM images were stored in digital form and then processed by image analysis.

Since the Al_2O_3 particle sizes were very small compared to their mutual distances, it is possible to assume them as the point objects and instead of individual particles to use their centroids for analysis of their distribution. Particle centroids distribution was analyzed by the following methods:

Quadrant counts method

The index of dispersion ID and index of clusters size ICS [6] are plotted in dependence on the number of subareas for individual microstructures, Fig. 4.

From the measured data of ID and ICS, it is possible to state that particles in the material A exhibit a tendency to the random (incidental) microstructural distribution. For materials B and C, the features of certain arrangements exist, which are especially significant for material C. Average ID values for material A are in the region defined by quantile curves, and with 95% probability, it can be stated that particles in this material are distributed randomly.

Polygonal method

This method is based on evaluation of corresponding Voronoi tessellation instead of original pattern. Namely, to any point of the pattern (centroids), a polygonal cell is attached. It is formed by all points in the plane (cross-section image in this case) lying closer to this centroid than to any other point of pattern. So the Voronoi tessellation was generated using the centroids of Al_2O_3 dispersion particles in A, B, C samples [7, 8]. The example of image treatment from the original microstructure up to the Voronoi tessellation from the centroids is on the Fig. 5. Basic statistical characteristics of geometrical parameters of Voronoi cells are used for comparision with known point arrangements [5].

The cell areas of Voronoi tessellation based on particle centroids were analyzed for evaluation, see Table 2.

Since the variance and the coefficient of variance of corresponding Voronoi cell areas for evaluated materials are bellow the Poisson point process (PPP) values, it can be stated that particles in analyzed microstructures are located with strong tendency to the regular arrangement. It is also clear, that differences in particle arrangement evaluated among microstructures are not too strong. Skewness and kurtosis not closed to the corresponding PPP values suggest the fact, that particles in analyzed microstructures are not randomly arranged.

Interparticle distances

The term "interparticle distance" (e.g., for characterization of the materials or processes, which take place in them) is more or less intuitive idea, and does not have a generally valid, universal definition, therefore, it cannot be assigned the generally valid range of values. At first, we must select one of the exactly defined types of "distances" considering the process studied, and to interpret or compare their properties within the selected framework. The quantification of the heterogeneous particle systems is frequently made by the mean distance determined as the cube root of the average volume per particle. Since it is determined by the number of particles in the volume unit only, it does not depend on the spatial distribution of particles. An interparticle distance sensitive to particle distribution—"*mean interparticle distance*" is based on the chord lengths of the generated systems of isotropic uniform stochastic straight

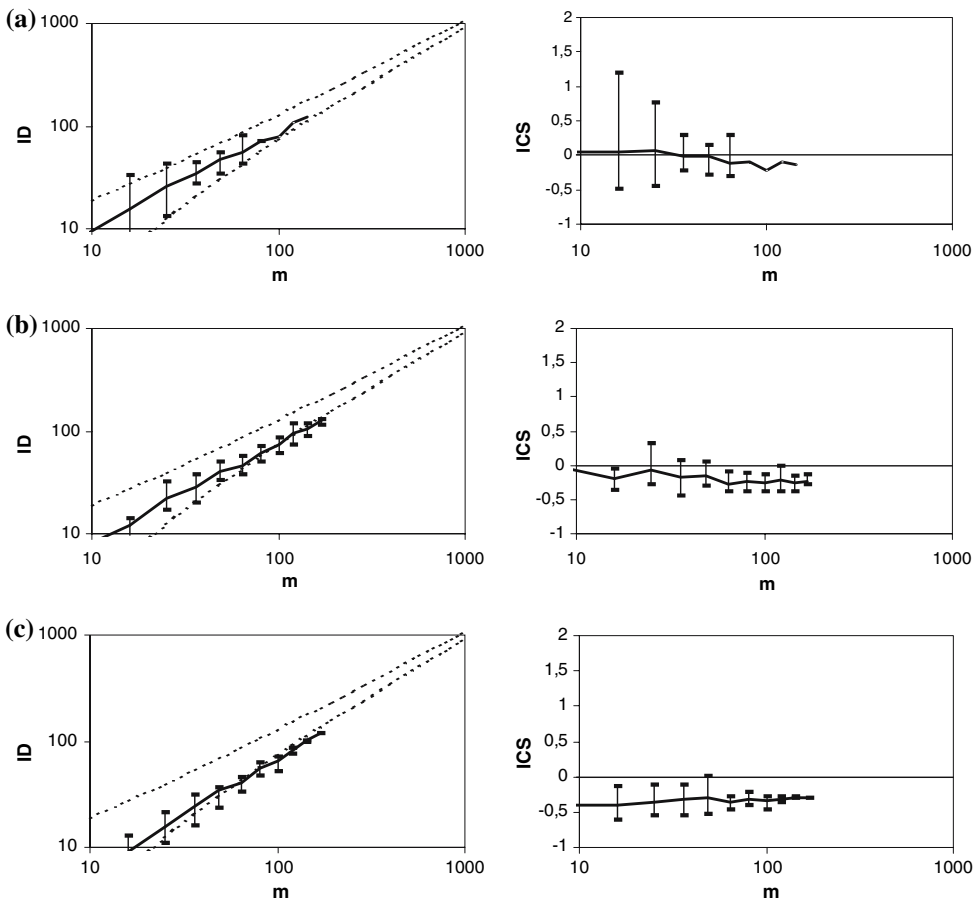

Fig. 4 ID and ICS of Cu–Al_2O_3 material: (**a**) 1% Al_2O_3, (**b**) 8% Al_2O_3, (**c**) 10% Al_2O_3

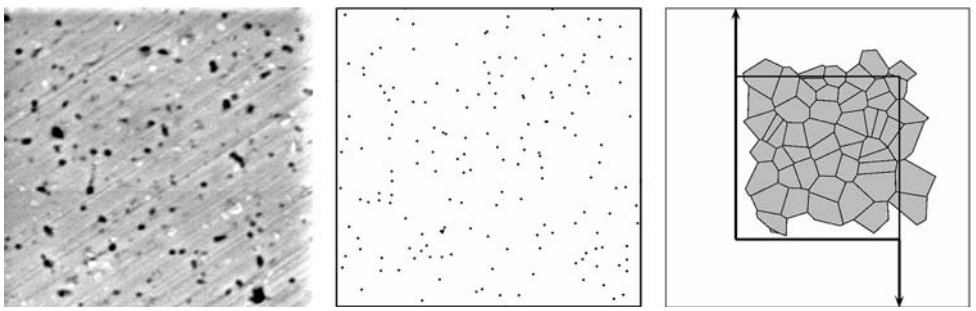

Fig. 5 Steps of microstructure image treatment from SEM image (left) through the particle centroids obtained by image analysis (middle) to Voronoi tessellation (right) for A material

Table 2 Parameters of Voronoi tessellation cells of corresponding Al_2O_3 particles

Sample	Number of particles	$Var_{(a)}$	$CV_{(a)}$	$Skewness_{(a)}$	$Kurtosis_{(a)}$
A	120	0.200	0.424	2.285	1.467
B	366	0.187	0.450	2.503	2.131
C	265	0.150	0.395	2.108	1.402
PPP	–	0.281	0.529	1.033	4.600

lines intersecting the object studied. It is often referred to as the "mean free path" between the particles. Another known definition —"*mean visibility*"—is the mean value of the distance from the randomly selected point of the matrix to the nearest particle in the randomly selected direction. This distance can be described as the "mean visibility in a forest" (for the plane case). The analysis of interparticle distances was made by two definitions: the minimum distance λ_ρ and the distance of the spherical contact λ_θ [9].

(a) *Mean minimum distance* λ_ρ

This is the mean value of the distance between the nearest particles. It describes well the distance within the particle clusters, however, it does not have any information about the distances between clusters, therefore its physical and metallurgical interpretation is problematic.

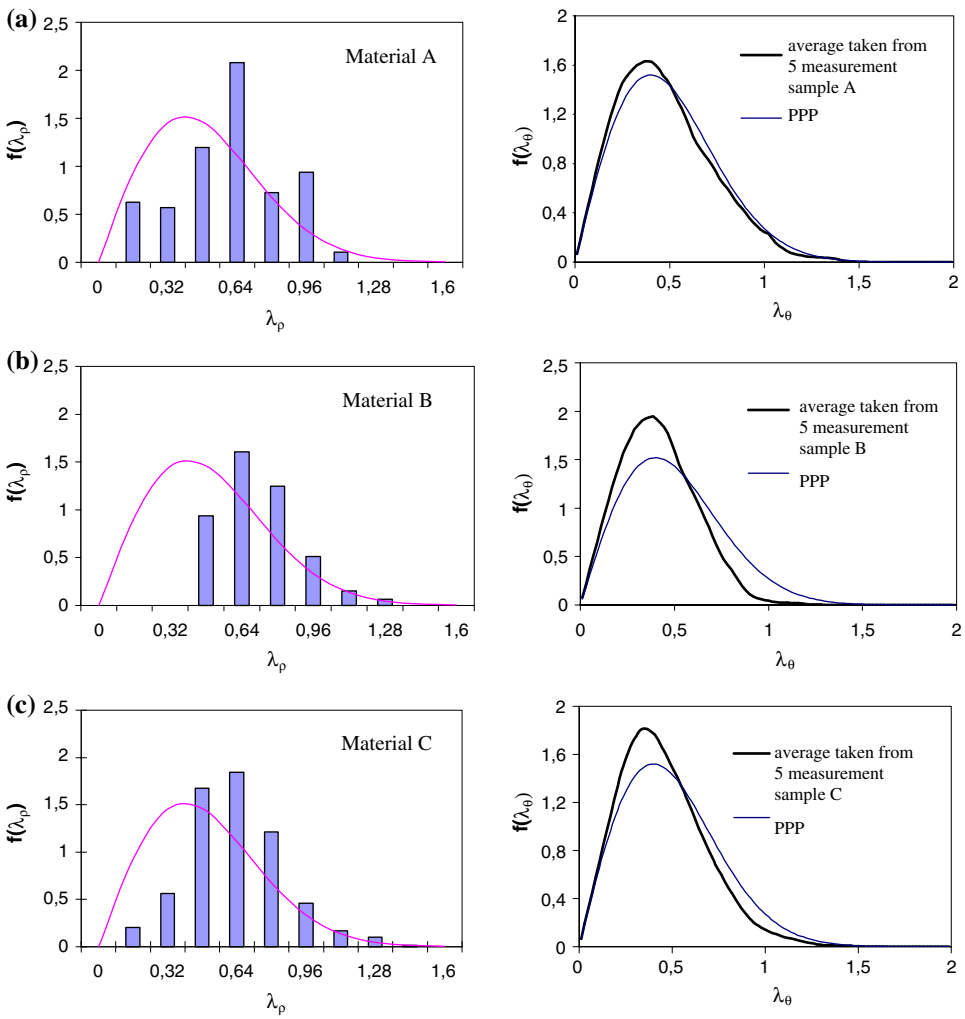

Fig. 6 Probability density function of (**a**) minimum distance λ_ρ, (**b**) of spherical contact λ_θ for A, B, C samples compared with corresponding function for PPP

(b) *Mean path of spherical contact* λ_θ

It is defined as the mean value of the distance from the randomly selected point of the matrix to the nearest particle. It determines the distribution of sizes of the maximum spheres inscribed into the matrix in its internal points, therefore, it depends on the spatial distribution of particles [10]. It has suitable limit properties, and can be easily measured manually. From the physical and metallurgical point of view, it can be interpreted, e.g., as the characteristic of the minimum diameters of dislocation loops of the emitted F-R sources. Therefore, it can be optimal definition for distance of particles in the dispersion strengthened systems.

The probability density function λ_ρ was estimated by histogram constructed from the set of all distances (i.e., distances of all five images were included into the one set). The estimation of probability density function λ_θ was obtained by numerical derivation of corresponding distribution function, obtained by the calculation directly from the centroid coordinates separately for each image. Average of five distribution function values (one for each sample of evaluated image) was used as final value of distribution function. Probability density functions for individual samples were again compared with the corresponding PPP functions, Fig. 6.

The f(λ_ρ) function is shifted to the higher values as for the PPP functions for all investigated samples. Knowing the functions for computer simulated point sets [5, 11, 12], it can be stated that particles in the investigated samples have the tendency to the regular arrangement. This assumption is proved by the f(λ_θ) too, where the function extremes of investigated samples are shifted to the lower values, which also indicates the existence of certain regularity in Al_2O_3 particles arrangement in composite materials.

Conclusions

From the results of the work, the following conclusions can be formulated:

1. In the Cu–Al_2O_3 system, using the carbon extraction replica method analysis, Al_2O_3 particles were identified as the majority secondary phase with mean diameter of 60 nm, which was distributed individually or in $\sim$380 nm size clusters.
2. The real volume fraction of coarser Al_2O_3 phase determined from the metallographical cross sections was slightly different to the nominal volume fraction. The overvaluation was done due to the presence of inclusions, especially the FeO phase from the milling environment.
3. The Al_2O_3 particle distribution in the matrix determined by quadrant count method, polygonal method, and using the interparticle distances showed that particles in material A (1 vol.%) are close to the random distribution. Particles in materials B and C (8 and 10 vol.%) exhibit the features of regular distribution, which was proved especially by the analysis of spherical contact distance λ.

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