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INFLUENCE OF ALUMINA CONTENT ON THE SINTERABILITY OF THE Cu-Al_2O_3 PSEUDO ALLOY (COMPOSITE)

VPLIV VSEBNOSTI GLINICE NA SPOSOBNOST SINTRANJA V SISTEMU Cu-Al_2O_3

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Mechanism and kinetics of the thermally activated processes of the occurring by annealing of cold pressed samples of Cu-Al_2O_3 powder. With electrical resistance measurements in non-isothermal and isothermal conditions and with microstructural analysis, the influence of Al_2O_3 and temperature on the sintering process of $Cu_{(1-x)}$-$Al_2O_{3(x)}$ powders was determined. By measuring the isothermal change of specific electrical resistance at temperatures below the recovering temperature (400–680 K), the kinetics parameters of the process are determined. The sintering was performed in hydrogen at the temperatures of (1073, 1173, 1273) K for (15, 30, 60, 120) min. The results show that with increasing Al_2O_3 content the sintering time increases at all the examined temperatures.

Key words: dispersion strengthening, Cu-Al_2O_3 composite, specific electrical resistance, microstructure

Članek opisuje mehanizem in kinetiko termično aktiviranih procesov med žarjenjem hladno stisnjenih prahov kompozitne zlitine Cu-Al_2O_3. Z meritvami električne upornosti v izotermnih in neizotermnih razmerah in z analizo mikrostrukture je bil raziskan vpliv temperature na proces sintranja kompozitov $Cu_{(1-x)}$-$Al_2O_{3(x)}$. Z meritvami specifičnega električnega upora v izotermnih razmerah pod temperaturo poprave (400–680 K), so bili določeni kinetični parametri procesa. Sintranje se je izvršilo v vodiku pri temperaturah (1073, 1173, 1273) K v časih (15, 30, 60, 120) min. Rezultati meritev kažejo, da čas sintranja raste pri vseh temperaturah z rastjo vsebnosti Al_2O_3.

Ključne besede: disperzijska utrditev, Cu-Al_2O_3, specifična električna upornost, mikrostrukturna analiza

1 INTRODUCTION

Due to its low mechanical strength, a highly conductive copper matrix needs to be dispersion strengthened and new composite materials, with superior characteristics are obtained. The most important application area of these materials, electrical engineering, sets more and more complex demands for the material synthesis. The parameters, which effect the optimization of the characteristics of dispersion strengthened copper, are the dispersoide content and the sintering temperature [1,2,3].

All dispersed systems can be obtained with powder compaction using different methods [4,5]. By cold pressing internal stresses are generated and than relaxed with annealing at increased temperature. In several papers [6,7,8], the mechanism of thermally activated relaxation was determined for the pressed and cold deformed powder mixtures. It has been shown that grain size reduction of the dispersoide leads to an increasing decrease of the rate of relaxation of internal stresses. In this paper the influence of Al_2O_3 content on the kinetics and the mechanism of the thermally activated processes of relaxations of internal stresses in cold pressed samples Cu-Al_2O_3 composite during sintering was investigated.

2 EXPERIMENTAL

The mixture commercial electrolytic copper powder and Al_2O_3 powder in the range of composition 85–95 % Cu and 15–5 % Al_2O_3 was homogenizated in a mixer of the "double-cone" type for 30 min. The mixture was than compacted with a compressive force of 100 MPa from both sides to specimens of size (8 × 32 × 2) mm. The sintering of samples was performed in hydrogen at the temperatures of (1073, 1173, 1273) K for (15, 30, 60, 120) min. The electrical resistance was measured during the sintering using of a two-channel recorder ISKRA TZ-2000 with a sensitivity in the range 10^{-6} V. For microstructural investigation, the sintered samples were, after grinding, electro-polished and electro-etched for 20 s. As electrolyte, the solution of nitric and methyl alcohol of 1 : 2 was used. The microstructural analysis of the sintered samples was performed with an automatic quantitative image analyser.

3 RESULTS AND DISCUSSION

a) Recovering kinetics

The kinetics recovering parameters were determined by measuring the time related electric resistance by

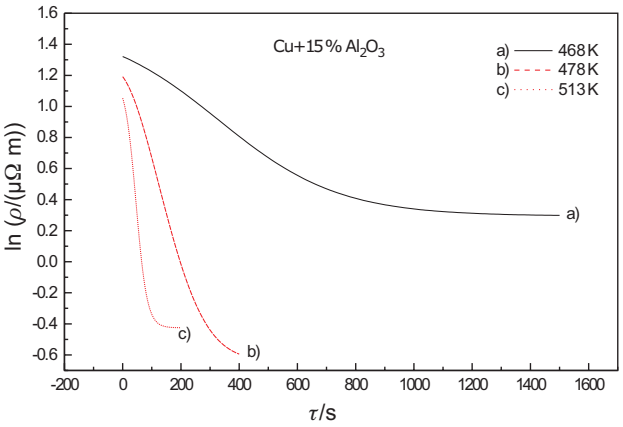

Figure 1: Isothermal dependence specific electrical resistance ln $\rho(\tau)$ on sintering time for the specimens Cu + 15 % Al_2O_3; a) T = 468 K; b) T = 478 K; c) T = 513 K

Slika 1: Izotermna odvisnost ln $\rho(\tau)$ za kompozite Cu + 15 % Al_2O_3; a) T = 468 K; b) T = 478 K, c) T = 513 K

isothermal annealing at (468, 478, 513) K for the sample with 15 % Al_2O_3. The obtained isothermal dependence of specific electrical resistance versus time is shown in **Figure 1** for all temperatures. By differentiation of the curves a, b and c two linear dependences (**Figure 2**) were obtained, which show that the recovering process occurs in two stages. From the slope of $\Delta \ln \rho'/\Delta\tau$ and $\Delta \ln \rho''/\Delta\tau$ the rate k' and k'' was determined for both stages of the recovering process. In both stages a linear dependence the form of ln k on T^{-1} (**Figure 3**) is found and from the slope of the linear dependence the activation energy was determined applying the relation:

$$E_a = R\frac{\Delta \ln k}{\Delta(1/T)}$$

For the samples with 5 % and 10 % of Al_2O_3 the same dependence was obtained as with the 15 % of Al_2O_3 specimen. After differentiation of the curves and the related calculations the results Table 1 were obtained. It is, therefore, confirmed that the relaxation of internal

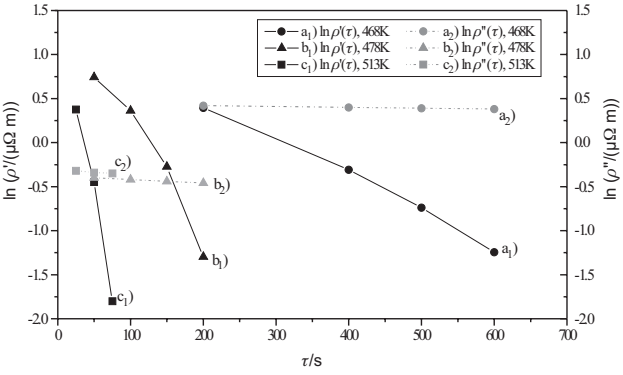

Figure 2: Two new dependences specific electric resistance versus sintering time ln ρ'(τ) and ln ρ''(τ) obtained with differentiation of curves in **Figure 1**. Composites: Cu + 15 % Al_2O_3; a_1, a_2) T = 468 K; b_1, b_2) T = 478 K; c_1, c_2) T=513 K

Slika 2: Odvisnost ln ρ'(τ) in ln ρ''(τ) za kompozite Cu + 15 % Al_2O_3 ; a_1, a_2) T = 468 K; b_1, b_2) T = 478 K; c_1, c_2) T = 513 K

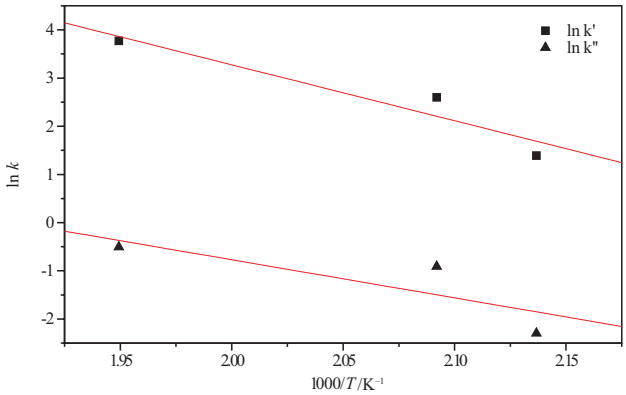

Figure 3: Dependence of rates of change of electric resistance as ln k' = f (1000/T) in ln k'' = f (1000/T) for the curves in **figure 2**. Alloy Cu + 15 % Al_2O_3

Slika 3: Odvisnost ln k' = f (1000/T) in ln k'' = f (1000/T) za izoterme pri kompozitu Cu + 15 % Al_2O_3

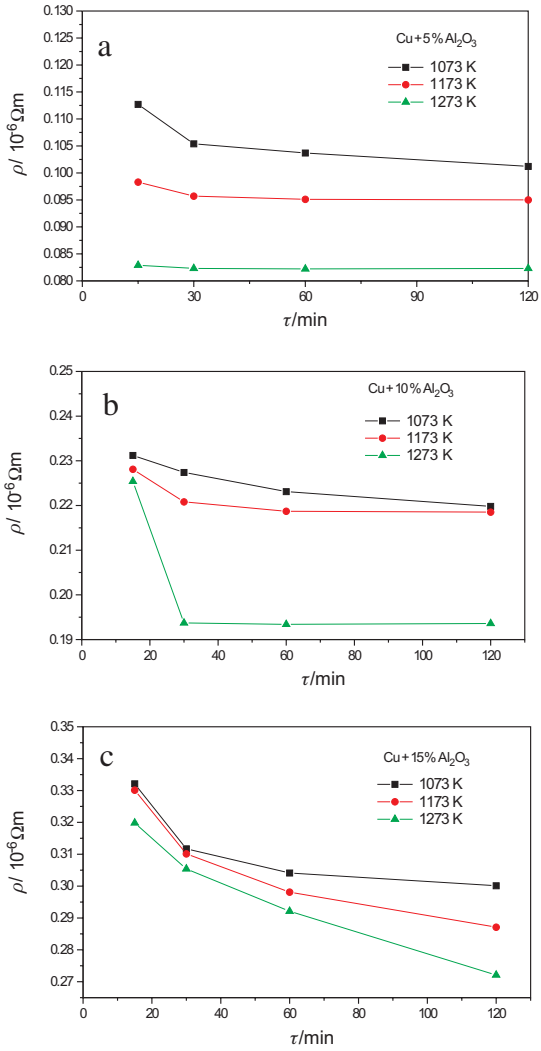

Figure 4: Dependence specific electric resistance versus sintering time for different temperature; a) Cu + 5 % Al_2O_3, b) Cu + 10 % Al_2O_3 and c) Cu + 15 %Al_2O_3

Slika 4: Izotermna odvisnost specifična električna upornost – čas za različne temperature sintranja; a) Cu + 5 % Al_2O_3, b) Cu + 10 % Al_2O_3 in c) Cu + 15 % Al_2O_3

stress in cold pressed specimens in temperature range from 450 K to 650 K occurs in two stages, which are related to the change in the arrangement and concentration of lattice defects in the copper matrix. The first stage consists of the relaxation of internal stresses, introduced into the material by the pressing of powders and of the removal the point defects, while, the second stage of the structural relaxation is related to line defects.

In the first stage the rate of relaxation is considerably faster due to the fact that point defects more efficiently diffract the conductive electrons than the line defects. With the increase of the Al_2O_3 content, the rate of change of electrical resistance is decreased and activation energy related to the relaxation processes is increased.

b) Isothermal sintering

Figure 4 shows the isothermal dependence of the specific electric resistance versus time for different sintering temperatures and the composites: a) Cu + 5 % Al_2O_3, b) Cu + 10 % Al_2O_3 and c) Cu + 15 % Al_2O_3. As

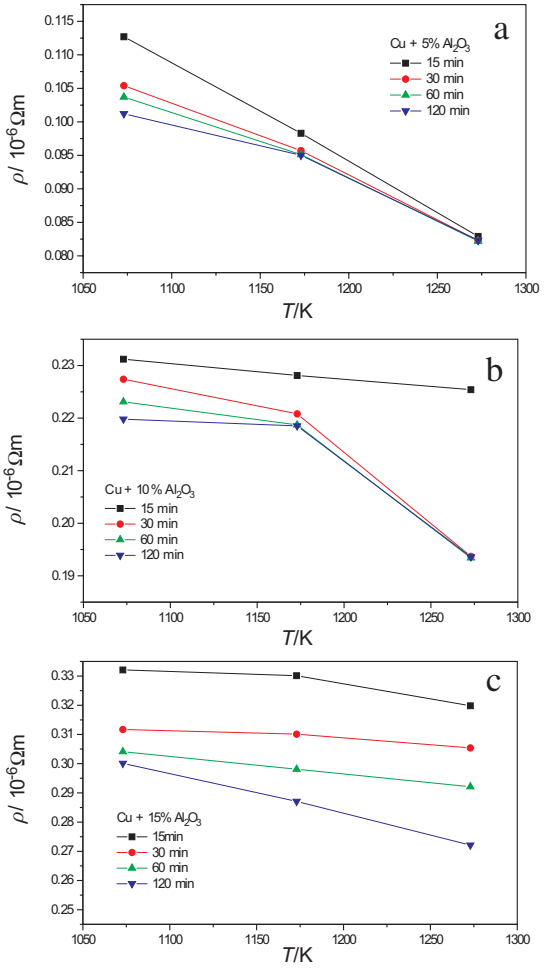

Figure 5: Dependence specific electric resistance versus temperature for determined tempering times; a) Cu + 5 % Al_2O_3, b) Cu + 10 % Al_2O_3 and c) Cu + 15 %Al_2O_3

Slika 5: Odvisnost specifične električne upornosti od temperature za različne čase sintranja; a) Cu + 5 % Al_2O_3, b) Cu + 10 % Al_2O_3 in c) Cu + 15 % Al_2O_3

measure of the structural stability of the system at a determined temperature the time when the electrical resistance achieves a constant value is taken, i. e., $\Delta\rho/\Delta\tau = 0$. For the system with 5 % of dispersoide during sintering at 1073 K the sintering process is not completed after 120 min, at 1173 K the process is finished after 30 min, and at 1273 K after 15 min of annealing. The sintering of the composite with 10 % Al_2O_3 during annealing at 1073 K is not completed after 120 min, at 1173 K, it is finished after 60 min, and at 1273 K after 30 min. For the composite with 15 % of dispersoide, during annealing at the stated temperatures, the sintering was completed even after 120 min.

The results show that with the increasing Al_2O_3 content, the time to the completion of sintering increases. This finding is in agreement with the activation energy for the sintering of composites with (5, 10, 15) % Al_2O_3 (**Table I**). Finally, the sinterability of the Cu-Al_2O_3 composites decreases with the increasing Al_2O_3 content. The diagrams in **Figure 5** show the dependence of the specific electrical resistance of the sintering temperature after different sintering times.

For a given Al_2O_3 content, temperature and for a given time, the specific electrical resistance decrease with increasing sintering temperature. The results also show that with the increasing dispersoide content and for a selected temperature-time regime, the specific electrical resistance increases.

Microstructural analysis (**Table 2**) shows that, with increasing sintering temperature for a given time, the volume share of porosity decreases and that with increasing the Al_2O_3 content, the porosity increases. The porosity, as measure of the structural integrity of the system, has, thus, a significant influence on the specific electrical resistance after sintering and the porosity.

It is also clear that at selected temperatures at which $\Delta\rho/\Delta\tau \neq 0$ after finished sintering, the microstructure has not achieved a stable state. F.i. the the microstructure of the Cu-Al_2O_3 alloy with 15 % of dispersoide, sintered at 1073 K and 1173 K for 120 min indicates to a correlation of the change of specific electrical resistance

Table 1: Kinetic parameters for the recovering process of the pressed composite Cu-Al_2O_3 with (5, 10, 15) % of dispersoide

Tabela 1: Kinetični parametri za proces poprava stiskanih kompozitov Cu-Al_2O_3 za (5, 10, 15) % disperzoida

T/K	k'/ (10^{-3} s^{-1})	k''/ (10^{-3} s^{-1})	E'_a/ (kJ/mol)	E''_a/ (kJ/mol)
Cu + 5% Al_2O_3				
473	17.54	0.2	**24.267**	**34.9026**
513	28.4	0.4		
Cu + 10% Al_2O_3				
473	15.84	0.14	**53.765**	**59.148**
488	23.36	0.27		
498	27.62	0.36		
Cu + 15% Al_2O_3				
468	4.05	0.1	**96.285**	**65.900**
478	13.52	0.40		
513	43.52	0.60		

Table 2: Stereological data on porosity after sintering
Tabela 2: Stereološki podatki o poroznosti sintranih kompozitov

Sintering Parameters	Pore size d/μm			Relative measuring error , %	Volume share of porosity ρ_v/%
	min.	max.	mean		
Cu + 5 % Al_2O_3					
1073 K, 120 min	0.19	9.08	1.14271	3.23202	17.2
1173 K, 120 min	0.17	10.07	1.31927	3.24081	13.9
1273 K, 120 min	0.12	4.8	0.86511	2.48973	10.115
Cu + 15 % Al_2O_3					
1073 K, 120 min	0.2	20.3	2.23306	3.76813	29.9
1173 K, 120 min	0.18	19.97	2.17131	3.65405	28.89
1273 K, 120 min	0.16	14.03	1.93522	3.62367	26.136

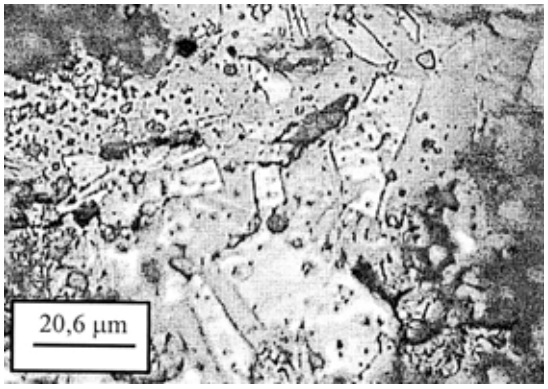

Figure 6: Microstructure of the composite Cu + 15 % Al_2O_3 alloy sintered at 1173 K for 120 min
Slika 6: Mikrostruktura kompozita Cu + 15 % Al_2O_3, sintranega 120 min pri 1173 K

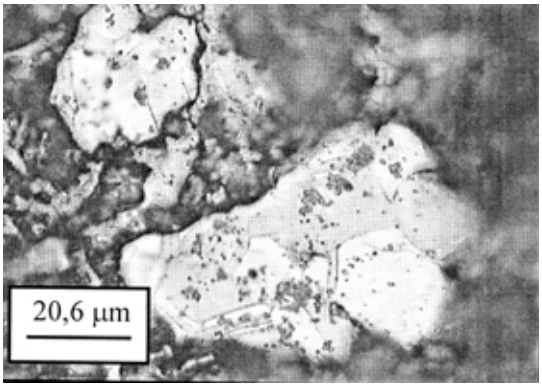

Figure 7: Microstructure of the Cu + 15 % Al_2O_3 composite sintered at 1073 K for 120 min
Slika 7: Mikrostruktura kompozita Cu + 15 % Al_2O_3, sintranega 120 min pri 1073 K

and the grain growth. Namely, for the systems with 15 % Al_2O_3 sintered at 1173 K for 120 min, an unhomogeneus microstructure is achieved, as consequence of anormal grain growth (**Figure 6**), and the specific electrical resistance is lower if compared to the same alloy sintered at 1073 K for 120 min, when a more homogeneus microstructure with grains of a polyglobal shape (**Figure 7**) is obtained. It seems that grain growth decreases the specific electrical resistance because of the decrease of the surface of grain boundaries after sintering.

4 CONCLUSION

On the basis of the results it is concluded that:

- The process of stress relaxation of the cold pressed samples in temperature interval from 450 K to 650 K occurs in two stages. The first stage starts with the relaxation of internal stresses introduced with the pressing of the powder and the removal of point defects. The second stage of relaxation seems to be related to line defects. With increase of the Al_2O_3 content the rate of electrical resistance change decreases while, the activation energy of the corresponding processes increases;
- With the increase of the sintering temperature the time to the microstructural stabilisation is shortened;
- The analysis of the dependence of the specific electrical resistance on sintering time indicates that for the material with a lower Al_2O_3 content a shorter sintering time is needed;
- The analysis of the microstructure of the sintered samples shows that the porosity has a significant influence on the specific electrical resistance, as a measure of the microstructural stability of the system. Also, the analysis of the microstructure indicates a correlation between the specific electrical resistance change and the grain growth. More precisely, grain growth, due to a decrease of the overall surface of the boundaries, is related to the decrease of the specific electrical resistance after sintering.

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