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RELATIONSHIP BETWEEN MIXING CONDITIONS AND PROPERTIES OF SINTERED 20AlN/80Cu COMPOSITE MATERIALS

WARUNKI MIESZANIA A WŁAŚCIWOŚCI SPIEKANYCH MATERIAŁÓW KOMPOZYTOWYCH 20AlN/80Cu

In the technology of heat-sink composite materials powder preparation process becomes very important. It should assure the uniform distribution of reinforcement in the matrix and to avoid of any changes of chemical composition of starting materials. In the present study the mechanical alloying process was carried out with the composition of AlN20-Cu (in % vol.). To obtain the powder mixtures different mixing conditions (e.g. rotation speed, ball to powder mass ratio, mixing time) were used. There were analyzed the grain size, microstructure and chemical state of prepared mixtures after mixing process. Then the hot-pressing of composite materials were conducted. The close correlation between mixing conditions and properties of AlN-Cu composites was observed.

Keywords: Mechanical Alloying, Sintering, Ceramic-Metals Composites, Heat-sink materials

W przypadku wytwarzania materiałów kompozytowych przeznaczonych na odbiorniki ciepła w układach elektronicznych szczególnego znaczenia nabiera proces przygotowania mieszanin proszków. Powinien on zapewniać równomierne rozmieszczenie wzmocnienia w osnowie kompozytu oraz wyeliminować niekorzystne zmiany fazowe materiałów wyjściowych. W prezentowanej pracy przeprowadzono proces mechanicznej syntezy proszków o składzie 20AlN-80Cu (% obj.). Analizowano wpływ warunków procesu mieszania (tj. prędkości obrotowej młynka, stosunku masy kulek do masy proszku (BPR), czasu mieszania) na uziarnienie, mikrostrukturę oraz skład fazowy otrzymywanych mieszanin. Następnie proszki poddano procesowi spiekania pod ciśnieniem. Stwierdzono wyraźne zależności pomiędzy warunkami procesu mieszania a właściwościami otrzymywanych materiałów kompozytowych.

1. Introduction

Microelectronic circuits require contact with a high thermal conductivity, controlled low coefficients of thermal expansion of heat-sink materials to remove heat generated during their work [1]. The fulfilment of these requirements by the conventional materials is practically impossible. At the present, many studies are being carried out worldwide devoted to the design and fabrication of advanced materials, characterized by a very good thermal conductivity, such as Cu-Mo, Cu-Be, C_F-Cu, SiC-Cu, SiC-Al, AlN-Al [2-3] and, in the last few years, AlN-Cu composite materials [4-6]. Especially the last example looks to be very attractive as a heat dissipation material. Aluminium nitride has advantageous mechanical and electrical properties and the low thermal expansion coefficient (4.0×10^{-6} 1/K) close to that of silicon (2.7×10^{-6} 1/K), which permits avoiding high residual thermal stresses being induced [7]. This property is

very important, since the failure of electronic devices is the most often due to high residual stresses induced as a result of the mismatch between the thermal expansion coefficients of the substrate and the semiconductor component. The thermal conductivity of polycrystalline aluminium nitride is slightly below 200 W/mK. Copper with its thermal conductivity of about 400 W/mK is always used wherever high thermal and electric conductivities are required, but its application range is limited because of the unsatisfactory mechanical properties, especially at elevated temperatures. Moreover, the high thermal expansion coefficient of copper (16.5×10^{-6} 1/K) may result in considerable residual stresses being induced and in thermal dilatation occurring when the copper components are subjected to substantial temperature variations. The heat or electric current transport in copper depends primarily on its purity. This is why the preparation procedure of the composite powder mixture is of particular importance. It should assure the uniform

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distribution of reinforcement in the matrix and to avoid of any changes of chemical composition of starting materials. One of the very popular methods of preparing ceramic-metal composite powders is mechanical alloying proposed by Benjamin [8] in the 1960s. This process depends on many factors, often related with one another, such as the type of the mill, the milling speed and time, the type of the atmosphere, the milling temperature, the material of the mill lining and of the balls, the ratio of the ball-to-powder weights, etc. [9]. All mentioned parameters have a great effect on properties of obtained composite materials.

The main aim of present study was to determine the technological parameters of the mechanical alloying process of AlN and Cu powders and to correlate them with the microstructure and properties of obtained composites materials. Independently the particular characterization of changes in morphology of powder mixtures were made.

2. Experimental

The materials intended for mechanical alloying process were a copper powder (purity 99.5%) and an aluminum nitride powder (purity 99%) manufactured by the NewMET Koch Co. The average grain size of the Cu powder was d_{Cu} = 19.2 µm with the relatively wide scatter from 1 to even 100 µm, and that of the ceramic AlN powder was d_{AlN} = 2.8 µm with the scatter from 1 to about 20 µm. Both the Cu powder grains and the AlN powder grains formed large agglomerates.

The milling operation was conducted in air atmosphere using a Pulverisette 6 Fritsch planetary ball mill with a 250 ml vial. The chamber lining and the milling balls (∅10 mm) were made of tungsten carbide added with cobalt. The powder mixture to be processed had the composition: 80 vol% Cu + 20 vol% AlN.

In order to find how the milling speed, the duration of the mixing operation, and the ball-to-powder weight ratio (BPR) affect the microstructure and the properties of the final material, the processes were conducted at various parameters (Table 1).

TABLE 1

Technological parameters of AlN-Cu mechanical alloying process

Series no.	Rotational speed (rpm)	Ball to powder ratio BPR	Time (h)
Series 1	ω_1=100	1:1	1-16
Series 2		5:1	1-8
Series 3	ω_2=200	1:1	1-16
Series 4		5:1	1-8

After the chosen stages of mixing process the microstructure, grain size distribution and phase composition were examined. The grain size distribution of the powder mixtures was determined using a television image analysis system (Clemex). The grain size distribution was examined as a function of the Feret diameter (d) and, hence, the average Feret diameter (d_{AVG}) was determined. The microstructure of the AlN-Cu powder mixtures obtained was examined using Leo 1530 scanning electron microscope. In order to estimate the degree of uniformity of the mixtures, we analyzed (within selected regions) the distribution of the elements on the surface using the EDX method. The Microlab 350 analyzer was used for examining the surface morphology of the powder mixtures and for a local analysis of their chemical composition by the AES method. XPS, with its high-resolution spherical analyzer of kinetic energy, was utilized for determining the chemical composition of the individual components of the composites. Due to the possible oxidation of copper powder during mixing process, there was carried out the annealing process of selected powder mixtures in hydrogen atmosphere (T=700°C, t=30 min).

Before sintering, the powders (annealed and not-annealed) were pressed in a steel die under a pressure of 0.2 MPa to cylinder form samples ∅30×10 mm in size. Then, the samples were densified in an isostatic press (120 MPa), placed in a graphite die and sintered in a hot-press (of the Thermal Technology Astro type) in an argon atmosphere at a temperature of 1050°C. All the samples were sintered under a pressure of 30 MPa for 60 min.

3. Results and discussion

There was stated the significant dependence between the mixing conditions and the grain size of obtained powder mixtures. The analysis shows that, during the mixing process, the AlN-Cu grain size varies considerably depending on the mixing time. As the mixing time increases, the average grain size decreases even to below 10 µm. But rotational speed of the mill and ball-to-powder ratio

play more important role. The figure 1 shows the dependence of average grain size from the mixing conditions.
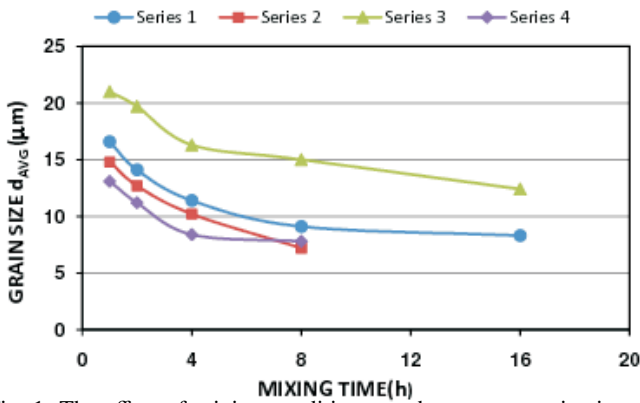

Fig. 1. The effect of mixing conditions on the average grain size of 20AlN-80Cu powder mixtures

As it can be seen higher BPR ratio allows for the quick-er breaking up the grains. It is the result of the higher energy of mixing with the higher value of BPR. It is not so clear for the relationship between the rotational speed and grain size of powders. Especially when we compare Series 1 and Series 3. Higher rotational speed (for Series 3) caused increase of average grain size in relation to Series 1. With the initial grain size below 20 μm, the grain size initially (after 1 h) slightly increased and, then, after further 8 h of mixing, it decreased continuously to about 15 μm. The detailed analyses of grain size showed the bimodal distribution of particles after 1 h mixing (Figure 2). In addition to the decidedly largest powder fraction with the grain size below 5 μm, another maximum appears within the grain size range between 30 and 35 μm. As the mixing time increases, the number of grains with grain sizes of 10-20 μm increases at the expense of the smallest grains. This may suggest the formation of AlN-Cu composite grains.
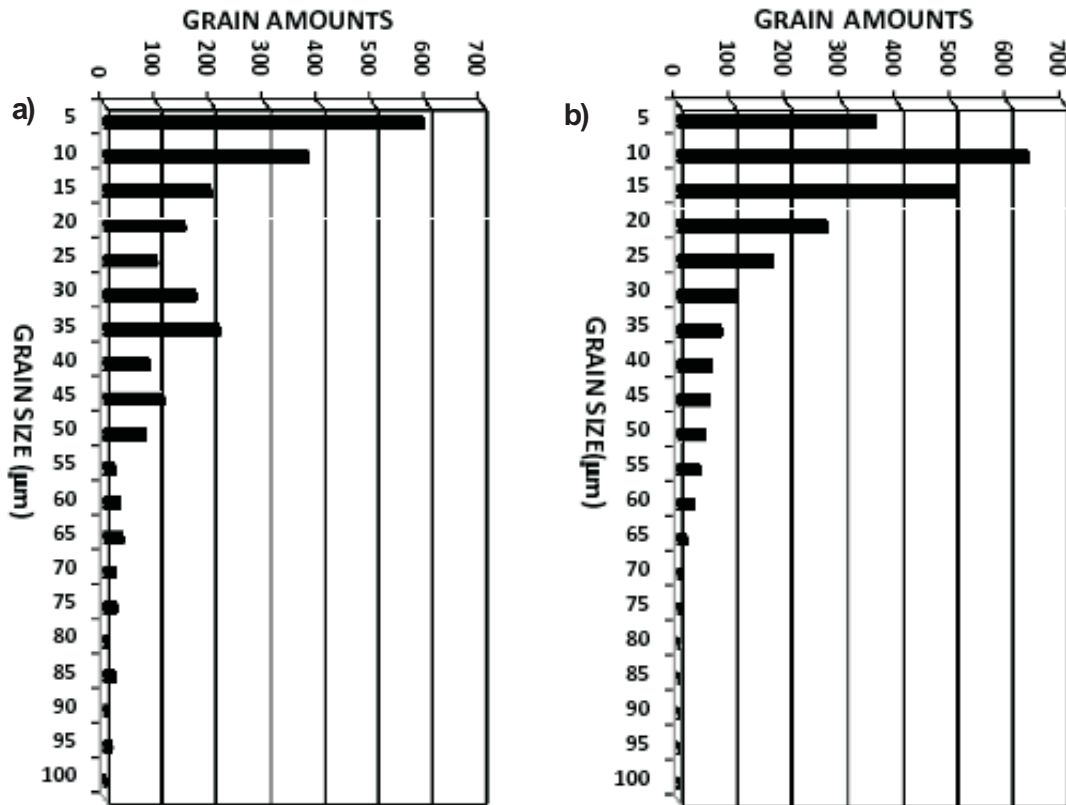

Fig. 2. Grain size distribution of AlN20-Cu powder mixture (Series 3) for different mixing times: a) 1 h, b) 4 h

The character of the grain size variation observed in this series is consistent with the theory of the mechanical synthesis. During the initial phase of the mixing process, the slight increase of the grain size occurs as a result of the individual grains being welded with one another. During the next stages, the grain size decreases characteristically because of the grains being broken which results in the entire powder volume becoming more uniform. Undoubtedly, this effect is due to the increased rotary speed of the mill employed in Series 4. The higher the BPR, the greater the energy involved in the process and the higher its dynamics, since the mass being processed is greater. In effect, the changes of the powder morphology proceed more rapidly. Also

for Series 1 and Series 2 this effect was not observed. In these cases the energy of mixing is insufficient to create the composite particles, and the decrease of grain size is caused only by milling of copper powder. To confirm to results obtained from this analysis, the powders were subjected to microstructural examinations.

The microstructural examinations have shown that, at a low mixing energy (Series 1), practically, the process of mechanical alloying does not occur. As early as in the initial stage of the mixing process, the powder structure only contains single composite grains, but their number does not increase with increasing mixing time. When the mixing energy is increased by increasing the share of the balls mass with respect to that of the powder (Series 3), the number of composite grains substantially increases. The time necessary for the powder mixture to become uniform strongly depends on the BPR coefficient: the higher this coefficient, the shorter the time to achieve this uniformity. The rotational speed of the mill also affects the rate and character of the changes in the powder structure. Initially, the grain shapes are close to spherical. As a result of the grains being broken as the milling process is continued, sharp edges appear and the grains acquire fake-like shapes.

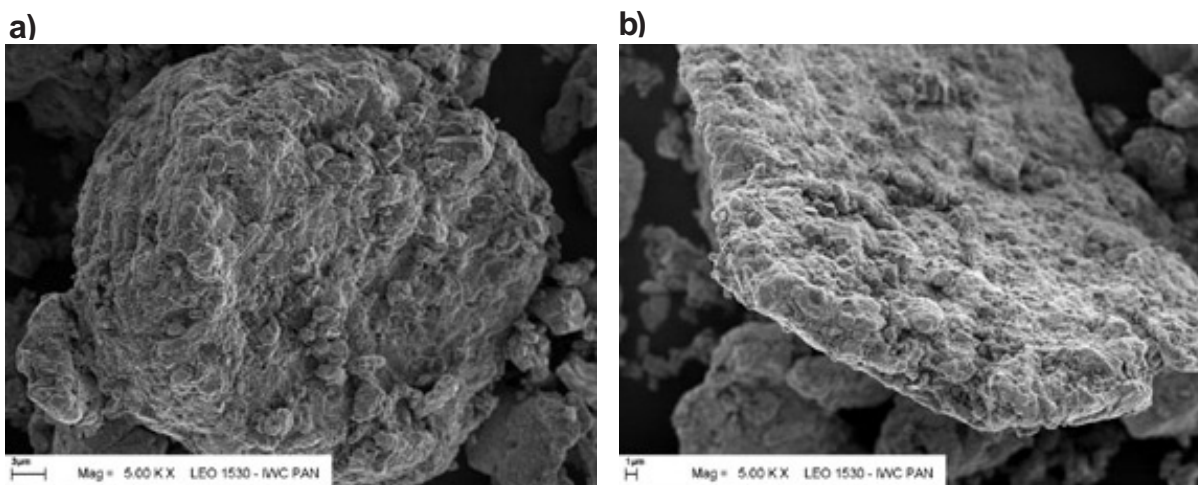Figure 3 shows exemplary photographs of the AlN20-Cu powders synthesized by mechanical alloying.

Fig. 3. SEM images of 20AlN-80Cu powder mixtures after mechanical alloying process: a) Series 3 (mill speed $\omega2$=100 rpm, BPR 5:1, time 1 h), b) Series 4 (mill speed ω_2=200 rpm, BPR 5:1, time 1 h)

When conducted in an oxidizing atmosphere, the mechanical alloying of metallic powders may change the phase compositions of the starting materials. At a high energy of the mixing process, the temperature inside the mill may increase considerably and the metallic phase may be oxidized. There was observed the change of colour of powder mixtures after the mixing with higher rotational speed (Series 2 and Series 4). None changes in phase compositions was stated using XRD analyses. To find definitely whether oxides form on their surface, the AlN-Cu powder mixtures were subjected to a surface analysis of the chemical composition using an Auger-Microlab 350 high-resolution scanning electron analyzer.

In the samples of Series 1 and 3 (rotational speed ω_1=100 rpm) the examinations revealed no changes of the chemical composition in the surface layer of the powders (the spectrum obtained coincided with the standard spectrum of copper), whereas marked changes were observed in the samples processes at the higher rotational speed of the mill. A typical survey XPS (X-ray Photo- electron Spectroscopy) spectrum obtained for Series 2 is shown in Fig.4.

The XPS results, which give average information about the surface chemical composition of the samples, obtained for Series 2 and 4 (ω_2=200 rpm) have shown that the chemical composition of the surface of the composites is similar. The identified signals came from Cu2p, Al2s, N1s, C1s and O1s which were partially contaminants of the sample surface (oxide and hydroxide compounds of carbon). It is also possible that carbon and oxygen were left on the surface after the mixing process itself. We reported this in our earlier study [3] in which we found that, after 16 h of mixing, oxygen and carbon impurities (2 wt% and 3 wt%, respectively) might remain on the surface. In view of the fact that a strong oxygen signal was recorded on the sample surface (Fig.4), the Cu2p3 peak of the copper spectra, obtained for each sample Series, was deconvoluted, which permitted determining the chemical state of this element. It appeared that in Series 2 and 4, Cu is in the second oxidation degree (Cu^{2+}) forming compounds of the CuO type (933.0

eV, 933.2 eV) and Cu(OH)$_2$ type (934.9 eV, 935.0 eV). Fig.3b shows the XPS copper Cu2p3 peaks obtained for Series 2 and 4 in which we can see well-marked shifts of the Cu peaks towards bonds of lower energy. These shifts suggest that the Cu surface has been oxidized. Such behaviour of copper powder can be predicted, so the annealing process of powder mixtures in hydrogen atmosphere was conducted. In the effect of this operation the chemical state of copper has radically changed. The Cu2p3 peak of copper moved to the metallic state of this element (Fig.5).
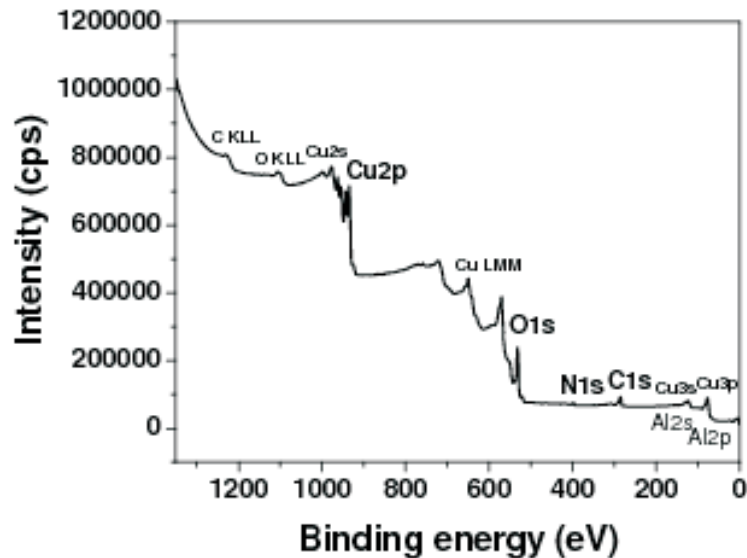

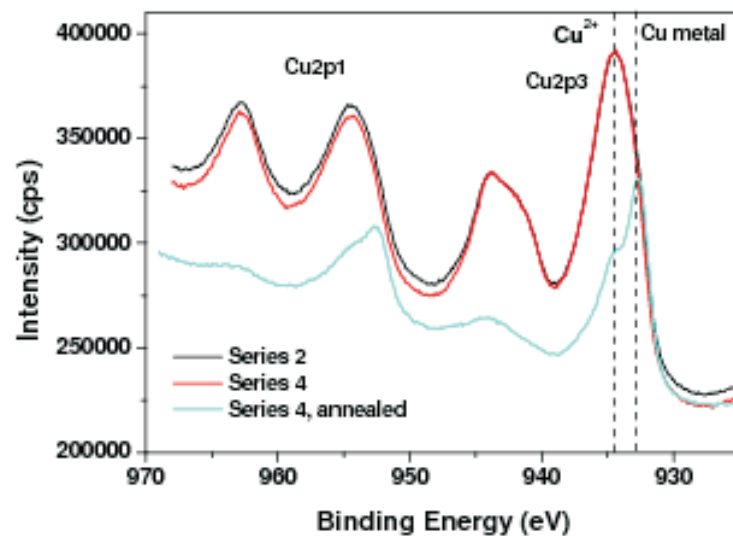Fig. 4. Typical XPS survey spectrum for AlN-Cu powders (Serie 4)

Fig. 5. XPS Cu2p spectra in narrow scan of binding energy for chosen AlN-Cu powder mixtures

Next step of work was to check how the mixing conditions and chemical state of powder mixtures effect on the properties of AlN-Cu composites. The sintering process was conducted for all 4 series of powder mixtures without annealing process, and for Series 2 and 4 after annealing. The density measurements of 20AlN-80Cu composites were made according to the hydrostatic method. For the assumed volume content, theoretical density of composites was defined, adopting the density of aluminium nitride ρ_{AlN} = 3.20 g/cm^3 and copper density ρ_{Cu} = 8.96 g/cm^3. The above density for the composition 20% AlN – 80% Cu was – ρ_T = 7.8 g/cm^3. Table 2 shows the results of measured densities of obtained AlN-Cu composites.

TABLE 2

Densities of sintered 20AlN-80Cu composite materials

Series no.	After mixing process		After annealing process	
	Measured density (g/cm³)	Relative density (%)	Measured density (g/cm³)	Relative density (%)
Series 1	5,89	75,5	–	–
Series 2	4,84	62,5	6,64	85,1
Series 3	6,05	77,6	–	–
Series 4	4,96	64,1	7,42	95,0

The obtained results shows the great relationship between conditions of mixing process and densities of AlN-Cu composites. There was stated that thin layer of copper oxide created on the surface of copper during the mixing process make impossible obtaining of materials with high relative density. It can be improved by annealing of powder mixture in reduction atmosphere. After this operation the relative density increase up to 20% in comparison to powders not-annealed, achieving maximum value above 95% (for Series 4) of theoretical density. The lower densities for powders from Series 1 and Series 3 result from irregular distribution of ceramic particles in copper matrix. As it can be seen on the microstructure photographs (Figure 6) the great amount of pores are located between the ceramic grains. Aluminium nitride particles form the agglomerates with non-consolidated structure. It is caused by fact that aluminium nitride is sintered at temperature above 1600°C, and the sintering temperature of AlN-Cu composite did not exceed the melting point of copper (1083°C). That is why so important becomes the obtaining of powder mixtures characterising by uniform distribution of ceramic particles in copper matrix.
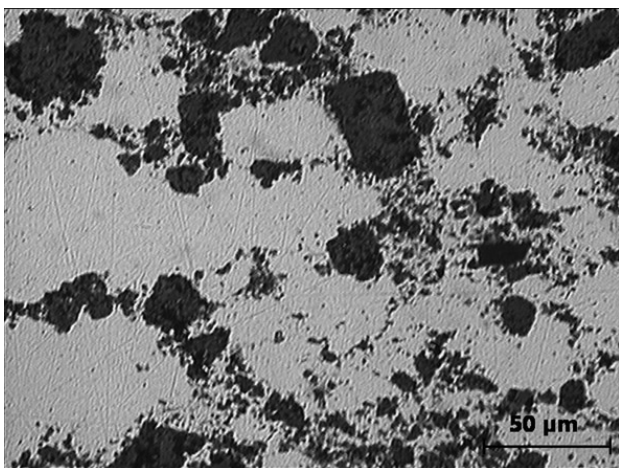

Fig. 6. Microstructure of 20AlN-80Cu composite materials sintered from the annealed powder mixture for Series 4

4. Summary

AlN-Cu metal matrix composite have been investigated in the present study. The fabrication process included preparation of powder mixtures in high-energy planetary ball mill and sintering of 20AlN-80Cu composition. The effect of mixing conditions on the properties of composite was described. The major conclusions were summarized below.

1. The grain size, morphology and chemical state of powder mixtures depends on mixing time, rotational speed of mill and ball to powder ratio.

2. In the case of fabrication of materials intended for heat dissipation elements, where the chemical purity is very important, the powder preparation process should be provided in the specific controlled conditions. For easily oxidized copper powders protective atmosphere or annealing process after mixing is needed.

3. To obtain well-densified AlN-Cu composites it is necessary to get uniform distribution of ceramic particles in copper matrix. Forming of the agglomerates of aluminium nitride powder causes increase of intergranular porosity. High rotational speed and high value of BPR should be used.

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