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Fabrication of nano-structured materials by high-pressure sintering

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ABSTRACT

Purpose: The aim of this work was to fabricate nanocrystalline powders and high-density bulk materials using a sintering method with limited grain growth so as to maintain nanocrystalline structure of the materials also after sintering.

Design/methodology/approach: The size of crystallites and physical properties of the obtained nano-crystalline powders and sinters made from these powders were examined. The studied materials were pure copper and the following powders: Cu+1%WC, Cu+3%WC, Cu+3%AlNi and AlNi. The technology for preparation of nano-structured powders was used, which included milling the powders in ball mills and their sintering in a pressing furnace.

Findings: It was found that the objective of this work can be achieved provided that high-pressure sintering is used, in which the stages of compacting and sintering proceed simultaneously over a short period of time.

Research limitations/implications: It is recommended to perform further studies aimed at checking the possibility of using the proposed method of nanomaterials fabrication in the case of the materials with other chemical composition.

Practical implications: This work broadens possibilities of metal powder sintering technology by fabrication of bulk nanocrystalline materials.

Originality/value: The results from his work shall be useful in determining conditions for fabrication of nanocrystalline or sub-microcrystalline materials by the sintering method.

Keywords: Powder metallurgy; Metal sintering; Nanomaterials; Crystallite size

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The nanocrystalline materials exhibit many unique properties, which are different from those of the materials having typical grain size. It is possible to fabricate nanocrystalline alloys with the phase composition, which can hardly be obtained in case of conventional materials. The nanocrystalline structure enables considerable improvement in the material properties: plastic (including the possibility of achieving super-plasticity), magnetic, corrosion resistance, etc. [1-6].

The nanomaterials are most frequently produced as powders, thin films or isolated nano-sized particles. To the methods of their fabrication belong mechanical synthesis, high-energy disintegration and vacuum spraying [7-12]. The possibility of fabrication of bulk materials with required shape and nanocrystalline structure using, for instance, hot pressing of powders with the nanometric size of crystallites is of great practical importance.

In the classical powder metallurgy the consolidation process proceeds usually in two stages: pressing is followed by sintering of the formed compacts [5]. However, the sintering process leads to grain growth, which is a disadvantageous phenomenon particularly in case of consolidation of nanocrystalline powders. For that reason special techniques have to be used, in which processes of pressing and sintering occur simultaneously [13].

Sintering of a powder with simultaneous use of an external pressure speeds up the process of compacting and reduces its temperature. As a result, the sinters obtained are of high-density,

which is close to that of bulk materials, and the grain growth process is considerably restricted. The aim of this work was to investigate the possibility of using this method to fabricate nanocrystalline materials.

2. Materials and methodology

The materials selected for sintering were nanocrystalline powder components from pure powder of electrolytic copper, copper powder with an addition of 1% WC, 3% WC or 3% AlNi, and pure, hard and brittle intermetallic phase AlNi. These were prepared in a planetary ball mill Retsch PM 400 type by wet milling in acetone. The ball-to-powder mass ratio (BPMR) was 4:1. A container and balls made from tungsten carbide were used for milling mixtures of copper powder and tungsten carbide, whereas other powders were milled in a steel container with steel balls.

The tests with preparing AlNi powder were conducted in three stages. In the first stage profiles of the AlNi phase obtained by synthesis of a mixture of elementary powders were subjected to crushing by means of a press. The crushed pieces of the AlNi phase were then dry-milled in a ball mill until granulation below 0.315 mm was reached and next wet-milled in acetone. In this case, the BMPR parameter was 30:1.

The pressure sintering was conducted using the Fritsch DSP 25 AT hot press with programmable sintering temperature, time of sintering and cooling, pressure during sintering and heating rate. High-density graphite die (1.83 g/cm^3) was used, which was heated directly by a flowing current. Temperature on a die surface was measured using optical pyrometer. The tests with pressure sintering of the powders were performed using compression pressures from 15 to 40 MPa, temperatures within a range from 600 to 800 °C (copper powders) or 1100 °C (AlNi) and the heating rates from 25 to 450 °C/min. Tests with sintering these powders were also conducted in a chamber furnace under reducing atmosphere, at the temperatures of 570 °C and 1100 °C.

The structure and selected properties of the powders obtained by milling and of the sintered samples were analysed. The X-ray structural analysis methods were used to determine phase composition of the samples by means of the XRD-7 diffractometer with Co Kα radiation. Crystallite size was determined from the Scherrer equation [14]. In the calculations an effect of the microstresses, caused by severe cold deformation occurring during milling, on the diffraction line broadening was taken into account [15]. Besides, density of the pressure-sintered samples and their Rockwell hardness (HRB or HRA) have been measured.

3. Results and discussion

The results from crystallite size measurements made for the powders examined have been presented in Table 1. The results from examination of the physical and mechanical properties of selected sinters (after high-pressure sintering process) are given in Table 2. The measured crystallite sizes and density of sinters made from nano-structured powders after the process of pressure sintering, cold pressing and sintering in a chamber furnace under reducing atmosphere are presented in Table 3.

Table 1.
The size of powder crystallites after milling in a planetary mill

Material	Diameter of the crystallites [nm]	Comments
Cu	>> 200	Starting powder
Cu	31	After milling
Cu+1% WC	62	After milling
Cu+3% WC	59	After milling
Cu+3% AlNi	59	After milling
AlNi	52	After milling

Table 2.
The properties of the powders after pressure sintering

Material	Pressure [MPa]	Density [g/cm^3]	Porosity [%]	Hardness HRB
Cu	20	8.56	4.5	51.8
Cu	30	8.70	2.9	56.9
Cu+1% WC	20	8.37	6.6	53.5
Cu+3% WC	30	8.75	3.2	58.6
Cu+3% AlNi	30	8.53	2.9	57.7
AlNi	30	5.72	2.9	72.0*

* – HRA

Table 3.
The crystallite size and density of the obtained compacts

State of a material	Examined properties	Material: Cu	Material: Cu+1% WC
After classical sintering at 570 °C	Crystalline size [nm]	85	97
	Density [g/cm^3]	7.67	7.83
After sintering in a pressing furnace at 600°C	Crystalline size [nm]	54	74
	Density [g/cm^3]	8.70	8.37
After sintering in a pressing furnace at 800°C	Crystalline size [nm]	95	94
	Density [g/cm^3]	8.76	8.39

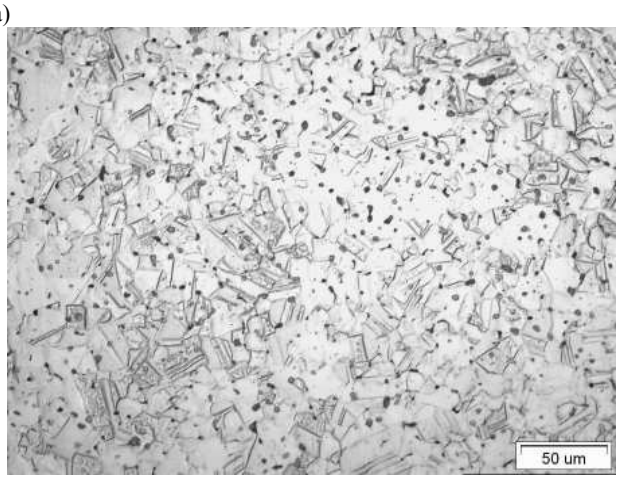
		Material: AlNi
After classical sintering at 1000 °C	Crystalline size [nm]	68
	Density of a compact [g/cm^3]	3.32
	Density of a sinter [g/cm^3]	3.87
After sintering in a pressing furnace at 1100°C	Crystalline size [nm]	59
	Density of a compact [g/cm^3]	3.32
	Density of a sinter [g/cm^3]	5.72

These results show that the size of crystallites obtained during powder milling was about 60 nm and even twice smaller in case of pure copper. The sinters obtained from high-pressure sintering process and also from classical sintering conducted at low temperature maintained a nanocrystalline structure. During pressure sintering relatively small growth of crystallite size was observed and the material had high density. In the samples subjected to low-temperature classical sintering the growth in crystallite size was greater, and the obtained material was of substantially lower density. The presence of the alien hard phase inclusions in copper (WC or AlNi) did not result in substantial decrease in grain growth rate, as it was expected. Instead, these inclusions reduced the rate of grain refinement during milling and

resulted in increased porosity of the sinters, especially those obtained at lower temperatures of sintering.

The structure of pure copper after classical sintering and after pressure sintering, which is shown in Fig. 1, proves also that classical high-temperature sintering causes much more intensive grain growth than pressure sintering. Analysis of diffraction line profiles and the attempts to calculate diameter of copper grains showed that the crystallite sizes were non-measurable by the Scherrer method in case of classical sintering, which means that the crystallites are several times greater than 200 nm.

a)



b)

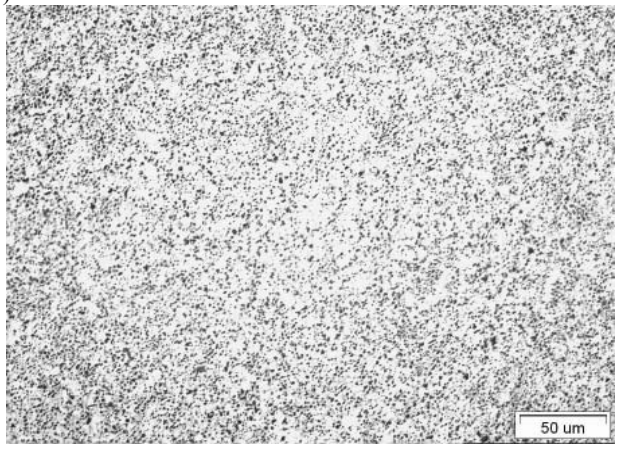


Fig. 1. Microstructure of a sample from pure copper: (a) sintered by classical method, pressing pressure – 500 MPa, sintering at 900 °C for 1 hour (large bright grains and dark pores are visible); (b) pressure-sintered, pressing pressure – 30 MPa, sintering at 800 °C for 2 min. (persisting strong grain refinement is visible)

Results from density measurements performed for the samples from pure copper in dependence on a pressing pressure during pressure sintering are presented in Fig. 2. It was found that an increase in pressing pressure clearly increases density of the sinters at lower temperatures of sintering. When higher sintering pressures are applied, the maximum density of the sinters can be achieved at lower temperature. An increase in pressing pressure results also in the increase in material hardness.

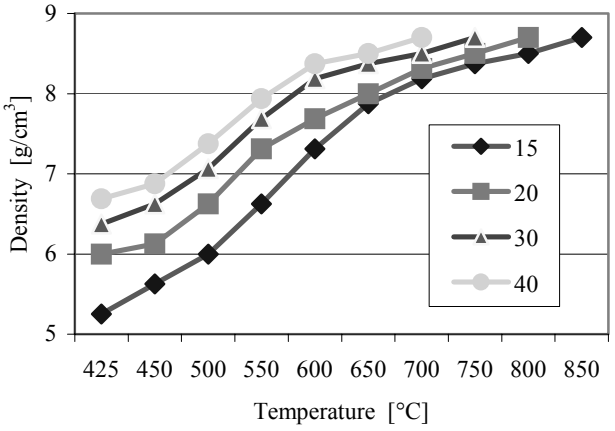


Fig. 2. An effect of pressing temperature and pressure on a density of the sintered compacts from pure copper during high-pressure sintering. Pressing pressures: 15, 20, 30 and 40 MPa

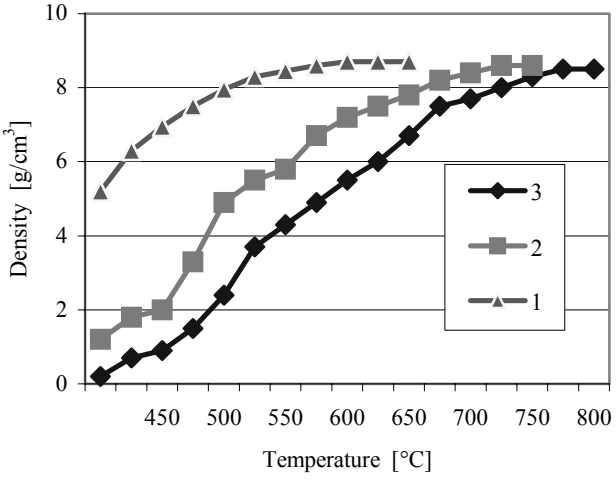


Fig. 3. An effect of temperature and heating rate on a density of the sintered compacts from pure copper during high-pressure sintering. Pressing pressure 20 MPa, heating rates: 1 - 25 °C/min., 2 – 100 °C/min., 3 – 200 °C/min

An effect of the heating rate on density changes of pure copper during pressure sintering is shown in Fig. 3. Three heating options were applied: very slow, slow and rapid temperature increase, with ensured correct heating of the punch and die.

The tests on pressure sintering of the AlNi phase were also carried out at very high heating rate of about 450^0C/min. within a temperature range from 20 to 1100^0C. During the heating cycle strong overheating of a punch in comparison with a die was

observed. This heating method can be used only in the case of high-melting materials so as not to exceed melting point of the material sintered. The curves shown in Fig.3 illustrate an effect of temperature increase on the phenomenon of material compression during pressure sintering. At slower heating, the process of rapid compression of the material takes place at lower temperature, and the sintered material reaches a maximum density at lower temperature. The initial state of the material inserted into a die is also of great importance during pressure sintering process. As the starting material a metal powder or a compact obtained by cold pressing under the pressure of 200 MPa, which were put into a die, were used.

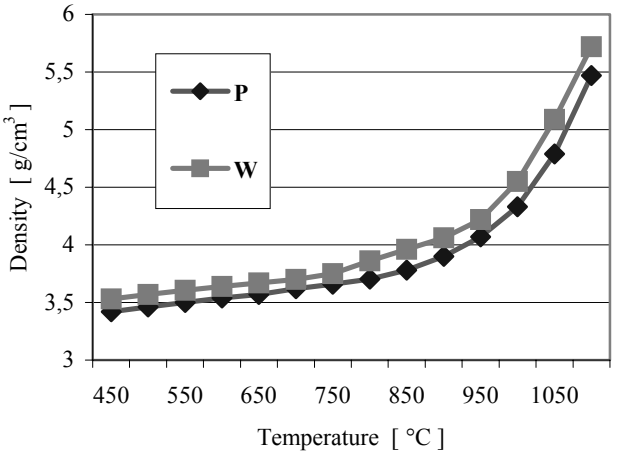


Fig. 4. An effect of a temperature of high-pressure sintering on a density of the AlNi compacts. Pressing pressure – 30 MPa. Starting material: P – powder, W - compact

Fig. 4 shows an effect of a state of starting material on the density changes during pressure sintering process and on final density of the sintered compact obtained from the AlNi powder. A beneficial effect of using ready-made compacts has been observed. However, after compressing of the copper powder the same material densities were obtained in a final stage of the process independently on its initial form Probably the same densities might also be achieved in case of the AlNi phase, but at considerably higher temperature of sintering.

4. Conclusions

1. Successful tests with fabrication of the copper-based and AlNi - based powders of a nanocrystalline structure have been carried out by milling of the starting powders in a planetary mill.
2. The obtained powders were characterised by the crystallite size within a range of 30 – 60 nm. As a result of pressure sintering conducted under the conditions described above, the crystallites size increased to 54 – 95 nm, depending on the type of powder and sintering parameters.
3. The results from this work indicate that the presented method of pressure sintering of metal powders based on simultaneously applied compressing and sintering at the maintained suitable values of pressure, heating rate, final temperature and sintering time makes it possible to prepare bulk materials of a nano-crystalline structure.

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