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MICROWAVE ANNEALING OF POWDER METALS WITHOUT SINTERING

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Introduction

Powder metallurgy (PM) is a technology for producing solid bodies made of powder materials, for which compressibility is an essential parameter. The compressibility of powder materials is determined by the chemical and phase composition and the particle size and shape. The process for producing powder particles has a significant impact on compressibility since it affects the level of residual mechanical stresses, strain hardening, oxygen and carbon content of the produced powders. Powder annealing is a common technology applied for improving compressibility of produced metallic powders. The goal of annealing is to relax the mechanical stresses generated by the rapid cooling as well as to remove the carbon and oxides formed in the atomisation process on the surface of the metal powder particles. Annealing temperature of iron based powders ranges from 700 to 1200 ºC. The annealing to improve compressibility is carried out in an inert gas reducing atmosphere, usually argon containing from 5 to 25 % of hydrogen. If carbon removing is required, then annealing runs under pure hydrogen. The holding time at the annealing temperature is usually in the range of 1 to 2 hours. Water atomized powder is heat treated in a continuous furnace as a "cake" on a belt. A typical set of annealing parameters is as follows: temperature=1060°C, time=1 h, throughput=2 t/h, H_2-consumption=160 m^3/h (80 m^3/t). The annealing of the atomized powder is the most energy-consuming step in the PM production chain [1]. The energy efficiency of the powder annealing is 14 % compared to the 59 % induction melting efficiency or 28 % for the water atomisation process [2]. The annealing yields a powder in the form of a sinter-cake which is necessary to be transformed into a powder again. Sinter-cake is broken e.g. by mechanical milling in disc mill or attritor [3]. Milling process introduces mechanical stresses to the powder.

There is technology to prevent sinter-cake creating and eliminate the need for mechanical milling after annealing. Patent US3668024 [4] describe the way of controlling the furnace atmosphere that prevents welding of the particles. So that the sinter-cake can be readily broken up after annealing. The powder is continuously passed through an annealing furnace and heated to temperature of 780 to 1150 ºC, while exposed to reducing gas. The dew point of the furnace atmosphere is maintained at a value slightly below equilibrium value throughout the length of the heating zone by adjustment of the rate of flow of the gas to the furnace. The dew point of the supplied and exhausted reducing gas is monitored and controlled throughout the annealing process. The disadvantage of this method is the necessity of precise monitoring and control of the dew point of the process gases, as well as higher consumption of process gases compared to the countercurrent gas flow in the furnace. Another method of preventing caking [5] is to form a mixture of annealed powder with an easily removable inert powder material e.g. sodium chloride. The inert powder separates the metal powder particles during annealing. After annealing, the inert material is removed by washing the powder mixture with a solvent. A disadvantage of such a process is the wet removal of the inert component.

The most efficient, economical and standard method used in the practice is the annealing followed by fine mechanical disintegration of the sinter-cake [3,6-8]. This process is effective to improve compressibility by removing hard oxidic compounds. When using powders in applications requiring magnetically soft materials, the disadvantage of this process is the grinding of the sinter-cake, which causes a re-increase in coercivity due to the insertion of lattice defects and mechanical stresses.

Microwave (MW) heating of materials is used for the synthesis, sintering, curing and heat treatment of ceramic, metal, polymer and composite materials. The main advantages of microwave processing are rapid heating, selectivity of heating and shortening of process times [9,10]. Susceptor assisted microwave annealing was proposed for fabrication of silicon based semiconductors in US20120196453A1 [11]. Acceleration of the heat treatment process has been proposed for some electrochemical devices e.g. Li-ion batteries in US20130266741A1 [12]. Microwave annealing has been used in a method for defect recovery of semiconductors for integrated circuits applications US20150294881A1 [13]. Microwave annealing technology of two different materials, resulting in an interface with the desired properties, was designed to produce CMOS semiconductors US006051283A [14].

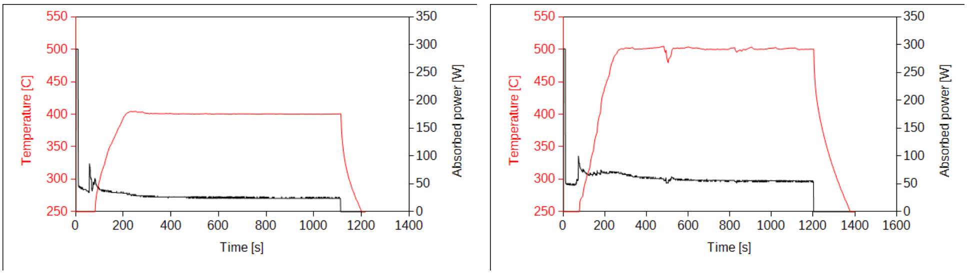
Concern about global warming motivates the analysis of whole powder metallurgy production chain from the viewpoint of environmental impact. The state of the art show that there is significant opportunity for reducing energy using higher energy efficient technology in PM production. The intensification and shortening of process time are the main features of microwave processing that have been successfully applied in several areas of material engineering. The aim of this work was to investigate the possibility of using microwave heating to improve the compressibility of ferromagnetic metal powder systems while reducing the coercivity.

Experimental materials and methods

Ferromagnetic powder alloys were investigated to evaluate the influence of microwave annealing on coercive force and compressibility. Investigated metallic powders were subjected to mechanical treatment by milling or die pressing. Microwave annealing (MWA) was provided in single mode microwave cavity at frequency of 2.45 GHz. Cylindrical microwave cavity with dimensions in diameter of 28 mm and height of 80 mm was equipped with Impedance analyser HiPom and IR pyrometer Optris CT (supplied by UPV-ITACA). Annealed powder was placed in high purity alumina crucible with diameter size of 10 mm and height of 20 mm. Hydraulic press LabTest 5.600 Zl was used to prepare green compact samples, as well as for the compressibility measurements. High energy vibrating ball milling was provided by Lab Wizz 320 equipment. Coercive force (H_c) was measured by coercive force meter ATS-320.

Results and discussion

Iron powder ASC100.29 (supplied by Hogänäs) was uniaxially pressed in closed die at pressure of 800 MPa. Obtained green compact were crushed to powder in a mortar and than MW annealed. MWA process log in Fig. 1 shows smooth regulation regardless of temperature and process atmosphere. Coercive force was measured step by step after each process. Results of coercive force measurement are presented in Tab. 1. It is well known that ASC100.29 is the powder characterized by very good compressibility. Coercive force increases from 210 A/m (as received ASC.29 powder) to value above 320 A/m in green compact. Coercive force slightly decreases after green compact crushing due to partial stress relieving in compressed powder particles. MWA at 500°C for 15 minutes under argon resulted in the highest efficiency (46 %) of the MWA process in terms of reduction of H_c. Shorter time (10 min.) slightly reduces the efficiency (34 %), while lowering the temperature (400°C) has a more pronounced effect (8 %). In case of technically pure iron powder as ASC100.29, ambient air atmosphere is not suitable for MW annealing.



MWA 400°C, argon   MWA 500°C, air

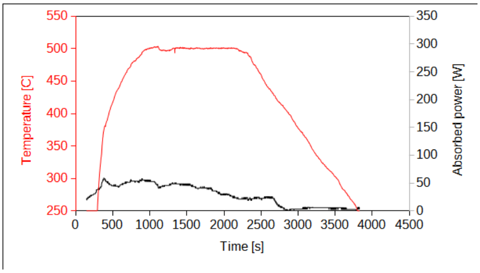
Fig. 1. Iron powder ASC100.29 – microwave annealing process log.

Table 1. Coercive force H_c of iron powder ASC100.29.

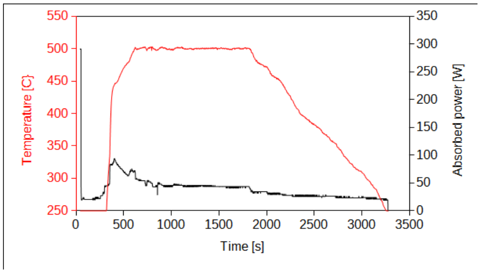
H_c-green [A/m]	H_c-pow [A/m]	H_c-MWA [A/m]	η-H_c [%]	T_{MWA} [°C]	t_{MWA} [min]	Process gas
362	340	185	46	500	15	argon
340	290	267	8	400	15	argon
333	349	230	34	500	10	argon
324	307	600	-95	500	15	air

H_c - Coercive force at 30 kA/m, green - Green compact, pow - Powder obtained by green compact crushing, η-H_c- Efficiency of MWA related to coercive force

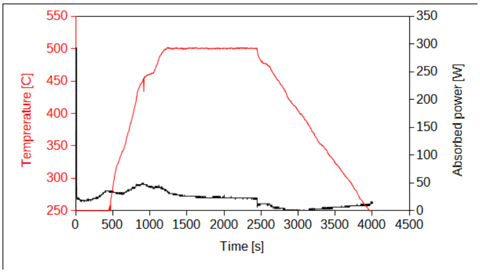
Iron-silicon alloy is a metallic material with limited plastic deformation ability. Higher silicon content leads to lower deformation ability of FeSi alloy, while the coercivity decreases. Atomised Fe6.8Si powder alloy with median particle size of 355 µm and 180 µm was used in this experiment. Fe6.8Si powder with larger particle size distribution was milled for 2 min or 15 min respectively. Coercive force and compressibility of all Fe6.8 powders (as received and milled) were measured and than MWA were applied. In all cases, MW annealing was carried out at 500 °C for 20 min under argon. Time-temperature-absorbtion diagrams in Fig. 2 show smooth regulation of the temperature. Absorbed power curve is slightly different for as received powder and milled powder. The results of compressibility and H_c analysis are summarised in Table 2. The decrease in H_c can be attributed to stress relieving and structure recovering MWA, since the residual oxides could not be reduced in an inert atmosphere of Ar. Coercive force of the rapid solidified atomised Fe6.8Si powder decreased from 68 to 41 A/m after MWA. Increasing the milling process time results in an increase in H_c and a reduction in the particle size of the ground powder. The coercive force of the milled powder increases due to the accumulation of structural defects in the powder particles. The highest efficiency of MWA was achieved in case of milled powder due to positive effect of MWA on recovery processes in this powder alloy. Efficiency of MWA process is higher in powder systems consisting of larger particles. The highest efficiency of MWA related to H_c (64 %) was achieved for short time milled Fe6.8Si powder. In this case, short milling time causes deformation of spherical particles, while particle size reduction was minimal.



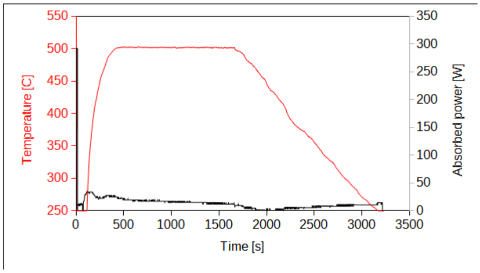
Fe6.8Si 355 µm atomised



Fe6.8Si 180 µm atomised



Fe6.8Si 355 µm milled for 15 min.



Fe6.8Si 355 µm milled for 2 min.

Fig. 2. Fe6.8Si microwave annealing process log.

Table 2. Coercive force H_c of pressed and MW annealed Fe6.8Si powder material.

Powder material	H_c source [A/m]	H_c MWA* [A/m]	η-H_c [%]	β source [%]	β MWA* [%]	η-β [%]
Fe6.8Si 355 µm as received	68 ±3	41 ±2	40	22.85	24.9	9
Fe6.8Si 355 µm milled 15 min	565 ±4	210 ±2	63	43.35	40.6	-6
Fe6.8Si 355 µm milled 2 min	366 ±2	132 ±2	64	21.73	24.1	10
Fe6.8Si 180 as received	76 ±3	68 ±2	11	25.37	24.9	2

H_c - Coercive force at 30 kA/m, β - Relative compressibility, η - Efficiency in relation to H_c and β, *MWA - 500°C, 20 min, argon atmosphere

Compressibility of Fe6.8Si powder is influenced by particle size and shape as well as mechanical properties of the powder particles. Fig. 3 shows relative compressibility of investigated Fe6.8Si powders. Relative compressibility was measured as volume reduction in relation to pressing pressure during continual compression test. Falling curve represents volume reduction in dependence on applied pressing pressure from 0 to 1 GPa. Raising part of the pressing curve reflects relaxation of the green compact in the closed die in dependence on decreased pressing pressure. Compressibility analysis shows increase in compressibility of the Fe6.8Si powder with large particles (as received or milled for 2 minutes). The compressibility of the 15 min powder was increased due to the changed shape and especially the particle size, rather than because of MWA. The highest efficiency of MWA related to compressibility (10 %) was achieved for short time milled Fe6.8Si powder.

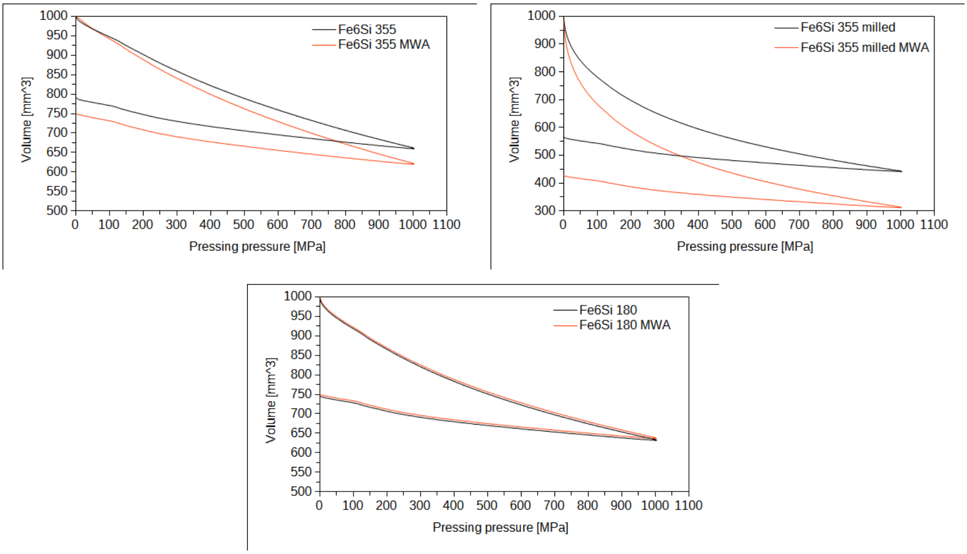
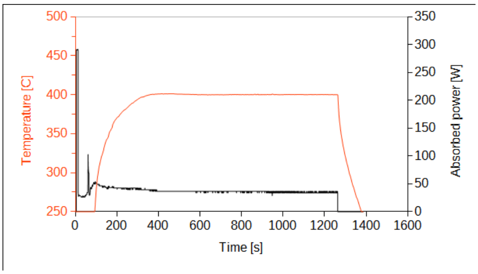


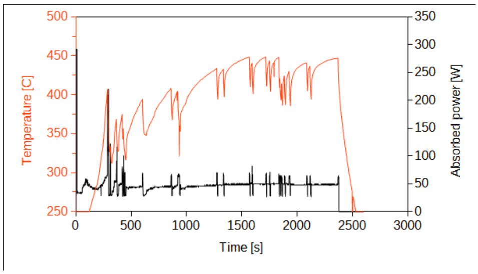
Fig. 3. Compressibility of Fe6.8Si powders.

Amorphous soft magnetic powder alloy $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ (Vitroperm® 800, Vacuumschmelze) was used in another experiment. VITROPERM is an amorphous material in the beginning stages of the manufacturing process. In order to produce the nanocrystalline two-phase structure, the amorphous circular tape cores are tempered at about 550 °C [15]. Vitroperm as received powder was cold die pressed at pressing pressure from 400 MPa to 1000 MPa. It was impossible to obtain consolidated bulk sample. Vitroperm powder pressed at pressure of 800 MPa was MW annealed at temperature of 440ºC for 20 min in air. Coercive force of Vitroperm powder increases from 8±0.5 A/m (as received) to 61±1 A/m (pressed powder). MWA leads to the decrease in H_c to 46±1 A/m. The same powder was MW annealed once more at temperature of 500ºC for 10 min in air to investigate a trend of H_c value. Coercive force after second MWA (58±2 A/m) increases in comparison to first MWA, but the value is still lower in comparison with pressed powder (61±1 A/m). New batch of Vitroperm powder pressed at pressure of 800 MPa with H_c value of 63±1 A/m was MWA at temperature 400 ºC for 20 min under argon. Coercive force of MW annealed Vitroperm achieve 43±1 A/m. MW annealed Vitroperm powders were successfully pressed to the cylinder shape with diameter of 10 mm at pressure of 800 MPa. Relative density of

two step in air MW annealed powder achieved 71.5 % compared to the value of 69.3 % in case of MWA at temperature of 400 ºC under argon. Initial state of crystallization begins at temperature of 480 ºC [16]. Results indicates that ability to be compressed was obtained by partial devitrification of initially amorphous powder sample. The most important is the effect of Cu clustering, which starts prior to crystallization, it is in detail described in [17].
Permalloy, having the composition: 79 % Ni, 16 % Fe, 5 % Mo and 0.5 % Si (also known as Supermalloy), is well known for its high performance as a soft magnetic material, characterized by high permeability and low coercivity. Atomised Permalloy 80 powder (ESPI Metals) was investigated together with laboratory prepared Supermalloy powder. Supermalloy (the same alloy composition as Permalloy 80) was prepared by mechanical alloing (MA) using long term dry ball milling. MA and atomised powder were consolidated at pressing pressure 800 MPa in closed die. Coercive force of the prism shape green compacts with size of 4x5x20 mm was measured. Green compacts were crushed in mortar to obtain the recycled powder. These powders were MW annealed. MWA process of the atomised Permalloy was smooth regulated in comparison with unstable MWA of MA Supermalloy powder, as it is shown in Fig. 4.



MWA - Permalloy 80



MWA - MA Supermalloy

Fig. 4. NiFeMo powder alloys – microwave annealing process log.

Results of coercive force step by step measurements of initial powders, consolidated green sample, crushed green sample and MW annealed powder are presented in Tab. 3. Permalloy powder system can be MW annealed with high efficiency (about 70 %) regardless of powder initial state particle size and shape. Irregular MA Supermalloy powder with median particle size of 70 μm achieves lower coercive force (99) compared to spherical atomised Permalloy powder with median particle size of 45 μm.

Table 3. Coercive force H_c [A/m] of MW annealed Ni79Fe16Mo5Si0.5 powder alloys.

Material	powder1	Green	powder2	MWA	η-H_c [%]
Permalloy atomised	134±2	666±2	456±2	138±2.5	70
Supermalloy milled	347±0.2	436±0.2	340±4.5	99±1.5	71

Powder1 - initial state, Powder2 - crashed green compact, η-H_c - MWA efficiency

High entropy alloy based on equiatomic composition FeSiBAlNiMo (HEA) was prepared by mechanical alloying. The as milled powder alloy was amorphous, as it was presented elsewhere [18]. Coercive force of MA HEA powder was 915 A/m, while MWA at 580°C

for 30 min under argon reduce H_c value to 300 A/m. Efficiency of H_c reduction by MWA process is similar to conventional soft magnetic powder alloys as FeSi and Permalloy.
Oxide dispersion strengthened steel (ODS) was another investigated non-conventional powder alloy. ODS was prepared by mechanical milling as ferritic powder steel with Y2O3 strengthening phase. ODS powder systems are characterized by very limited cold compressibility. Investigated MA ODS was impossible to consolidate using uniaxial cold die pressing in the range of pressing pressure from 250 to 1200 MPa. MWA enabled to achieve a compressibility to relative density of 67.1 % at pressing pressure 500 MPa without spring back and sufficient manipulation strength of the green compact.

In most of the studied powder systems, the regulation of the temperature-time mode of microwave heating was easy to control. The results of experimental microwave annealing of Fe, FeSi, NiFeMo and some amorphous and nanocrystalline powder alloys showed the possibility to achieve improved compressibility and reduced coercive force without the formation of sinter-cake. The effectiveness of reducing coercive force was more significant compared to the efficiency of increasing compressibility. Microwave annealing in inert or air atmospheres may be particularly beneficial in the production of powders for magnetically soft applications.

Conclusions

In this work, the application of microwave heating to metal powder annealing with the focus on ferromagnetic metals and soft magnetic alloys was investigated. Results of all investigated MWA powder systems documents high potential of MW processing for PM technology. Extra benefit can be expected in the field of powder soft magnetic alloys and composites, where low coercivity of powders is required. Microwave annealing can be applied in powder production, where sinter-cake milling is not applicable. Short process time is the known advantage of MW processes. Additional benefit of MW annealing of powders without sintering can be the possibility to use low cost protective furnace atmosphere, even the air in some cases. In 2019 patent No. 288686 [19] has been granted to the method of microwave annealing of soft magnetic powders.

Acknowledgement

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