Submitted: 24.10.2023.
Accepted: 01.11.2023.
https://doi.org/10.2298/SOS231024055N

Structural Features of Near Equiatomic FeCo-2V Semi-hard Magnetic Alloy Prepared by MIM Technology

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Abstract

The structural properties of a magnetically semi-hard near equiatomic FeCo-2wt%V (FeCoV) alloy produced by Powder Injection Moulding (PIM) (option by fine metal powder - Metal Injection Moulding (MIM) technology) were investigated in this paper. Starting granulate was prepared by mixing FeCoV powder with a low-viscosity binder. After injection, the green samples were first treated with a solvent and then thermally with the same aim of removing the binder. MIM technology was completed by high-temperature sintering for 3.5 hours at temperatures from 1370 ^{O}C to 1460 ^{O}C in a hydrogen atmosphere, which provides the necessary magnetic and mechanical characteristics.

The influence of sintering temperature was investigated concerning the aspects of the processes of structural transformation by the methods of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The appearance of an intense diffraction peak of the α'-FeCo phase (crystal structure type B2) was registered for all investigated samples. Structural parameters particle size D_{max}, Feret X, and Feret Y exhibit constant increase with increase of sintering temperature.

Keywords: FeCoV alloy, MIM technology, structural properties, particle size D_{max}, Feret X, Feret Y.

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1. Introduction

Magnetic alloys based on iron and cobalt are known for their exceptional combination of high values of magnetic induction of saturation and Curie temperature. Fig. 1. shows the correlation between high values of magnetic induction of saturation and high values of Curie temperature of commercial alloy VACOFLUX®50 based on iron and cobalt composition 49Fe49Co2V (VACUUMSCHMELZE GmbH & Co. KG - Germany [1, 2]). Most magnetically soft and magnetically semi-hard materials have Curie temperatures between 350 ^{O}C and 550 ^{O}C, while only VACOFLUX 50 alloy has a ferromagnetic-paramagnetic transition temperature of about 950 ^{O}C, which makes it extremely important because it is unique with this property.

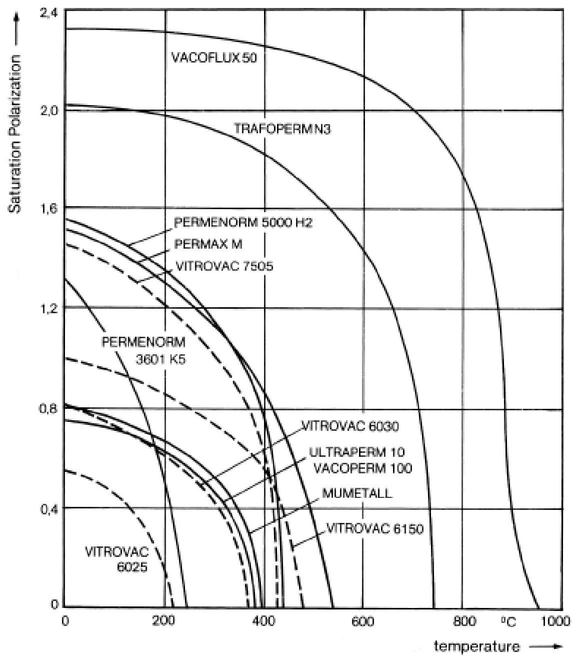


Fig. 1. Correlation of magnetic saturation polarization J_S and Curie temperature of iron and cobalt-based alloy VACOFLUX 50 49Fe49Co2V compared to other magnetically soft and magnetically semi-hard materials [2].

At operating temperatures of about 700 ^{O}C, it retains high values of magnetic induction of saturation above 2 T, and at temperatures of about 800 ^{O}C values of magnetic induction of saturation are above 1.6 T. Amorphous magnetic soft alloys with relatively high values of magnetic permeability based on cobalt (VITROVAC 6150 $B_S \approx 1$ T; $T_C \approx 480$ ^{O}C) [3], or based on iron (VITROVAC 7505 $B_S \approx 1.4$ T; $T_C \approx 420$ ^{O}C) [4, 5], are not competitive for applications at extremely high operating temperatures.

Based on the technology of injection of powder composites with molten binder, efficient production of ceramic or metal parts with complex geometries has been achieved [6-12]. PIM technology is widely used for the production of components of magnetically soft and magnetically hard materials. There are ceramic CIM (Ceramic Injection Molding) magnets (eg ferrite) or metal MIM (Metal Injection Molding) magnets (eg alloys based on Fe, Co, or based on a combination of FeCo, as is the case with FeCoV alloy). The obtained alloy samples have functional properties that directly depend on the applied technological parameters. MIM manufactured parts with complex geometries and high saturation magnetization and high Curie temperature, making them useful for high-temperature and power-dense applications (e. g. aviation devices).

Alloys of FeCoV systems usually contain 45-55 wt.% Fe, 45-55 wt.% Co and 1.5-2.5 wt.% V. Increasing the vanadium content (4 - 7 wt.%) leads to excellent mechanical properties but significantly reduces the magnetic induction of B_S saturation. It is also possible to introduce titanium in a small percentage (0.4 - 1.4 wt.% Ti) instead of vanadium to achieve even better mechanical properties [13]. The 49Fe49Co2V alloy is studied for its combination of good magnetic properties and improved mechanical and thermal properties compared to other alloys in the FeCoV system. Binary alloys of Fe − Co systems containing 33-55 wt.% Co are very brittle due to the formation of an ordered superlattice at temperatures below 730 ^{O}C. Addition of about 2 wt.% V prevents transformation into an ordered structure and enables a relatively high value of electrical resistivity (significantly higher values compared to other alloying elements, W, Ti, Mo, Mn, Ta, Cu, Ni,…).

Using MIM technology, it is possible to obtain magnetically soft alloys of the FeCo system without the addition of vanadium at significantly lower sintering temperatures (of about 980 ^{O}C [14]) compared to standard sintering temperatures, which are usually in the range between 1300 ^{O}C and 1400 ^{O}C. However, alloys of the vanadium-free FeCo system cannot be used for many applications where high HV hardness values are necessary (V is an alloying element that provides very good mechanical and suitable electrical properties). Alloys of FeCoV system with equal participation of Fe and Co, and with 2 - 5 wt.% V also has a high electrical resistivity (due to the addition of vanadium), which significantly reduces losses due to eddy currents. It should be noted that iron-cobalt based amorphous alloys prepared by in-rotating water melt-spinning technique exhibit high electrical resistivity accompanied by specific applications in sensorics [15].

In this study, we have characterized iron-cobalt based near equiatomic Fe49Co49V2 alloy samples produced by MIM technology followed by the sintering process. Sintering was performed during 3.5 hours: from 1370 ^{O}C to 1460 ^{O}C, and structural features were investigated as a function of sintering temperature.

2. Experimental procedure

Toroidal samples of 49Fe49Co2V alloy were produced by MIM technology so the initial granulate was prepared by mixing FeCoV powder with a low-viscosity binder [16]. After injection (injection molding machine Battenfeld HM 600/130), the green samples were first treated with a solvent and then thermally with the same aim of removing the binder. Finally, MIM technology is completed by high-temperature sintering that provides the necessary magnetic and mechanical characteristics [17-19]). Sintering was performed for 3.5 hours at temperatures from 1370 ^{O}C to 1460 ^{O}C in a hydrogen atmosphere. Crystallinity was investigated by XRD pattern (Philips PW 1050 diffractometer using Cu-K_{α} radiation λ = 0.154 nm and Bragg–Brentano focusing geometry with step/collection time scan mode of 0.05 ^{O}/s). Microstructural characterization was performed with a scanning electron microscope (SEM JEOL JSM-6390 LV).

3. Results and Discussion

The X-ray diffraction patterns of 49Fe49Co2V alloy samples sintered from 1370 ^{O}C to 1460 ^{O}C are presented in Fig. 2. All patterns exhibit the main diffraction peak of α'-FeCo phase (crystal structure type B2), which increases with an increase of sintering temperature.

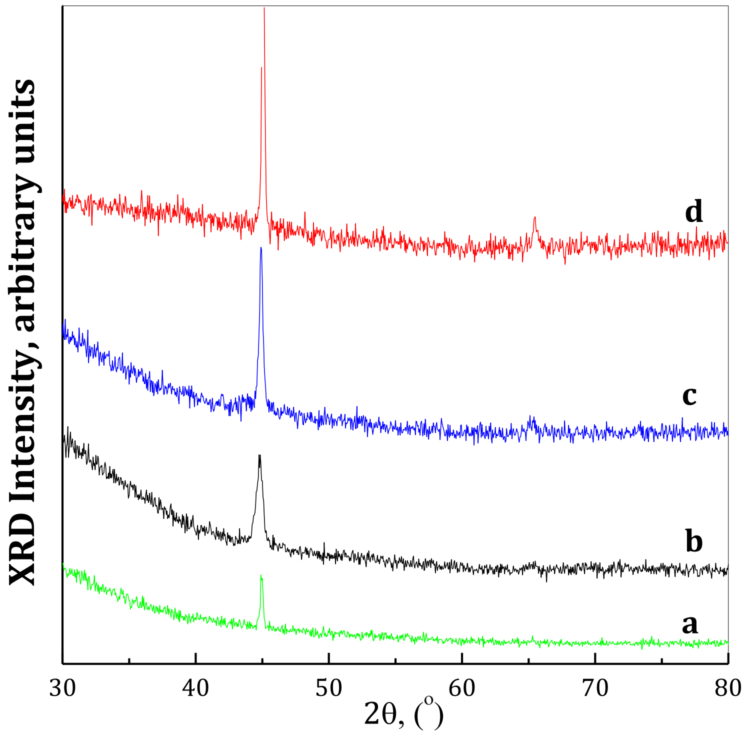


Fig. 2. The XRD patterns of 49Fe49Co2V alloy samples sintered at temperature a) 1370 ^{O}C, b) 1400 ^{O}C, c) 1430 ^{O}C, and d) 1460 ^{O}C in a hydrogen atmosphere.

The microstructures of the 49Fe49Co2V alloy samples were investigated from the surfaces of the tested samples using scanning electron microscopy - SEM. Fig. 3. shows examples of microstructure sequences used to obtain quantitative parameters of stereological analysis of samples sintered at a) 1370 ^{O}C, b) 1400^{O}C, and c) 1430 ^{O}C (the analysis included 3 sequences with about 120 samplings). From the presented microstructures, it can be first noticed that during sintering, powder particles were melted, which is directly proportional to the sintering temperature, i.e. at higher temperatures, neck growth and loss of particle individuality are more intense. The space between particles significantly changes shape due to pore closure, which leads to an increase in sample density (so-called intermediate sintering phase that takes place at 1370 ^{O}C, 1400 ^{O}C, and

1430 ^{O}C which is shown in Fig. 3. a, b, c respectively). In the final stage of sintering, at the highest temperature of 1460 ^{O}C, the particles completely lose their individuality due to melting (Fig. 3.d), and the crystallization process is the most intensive.

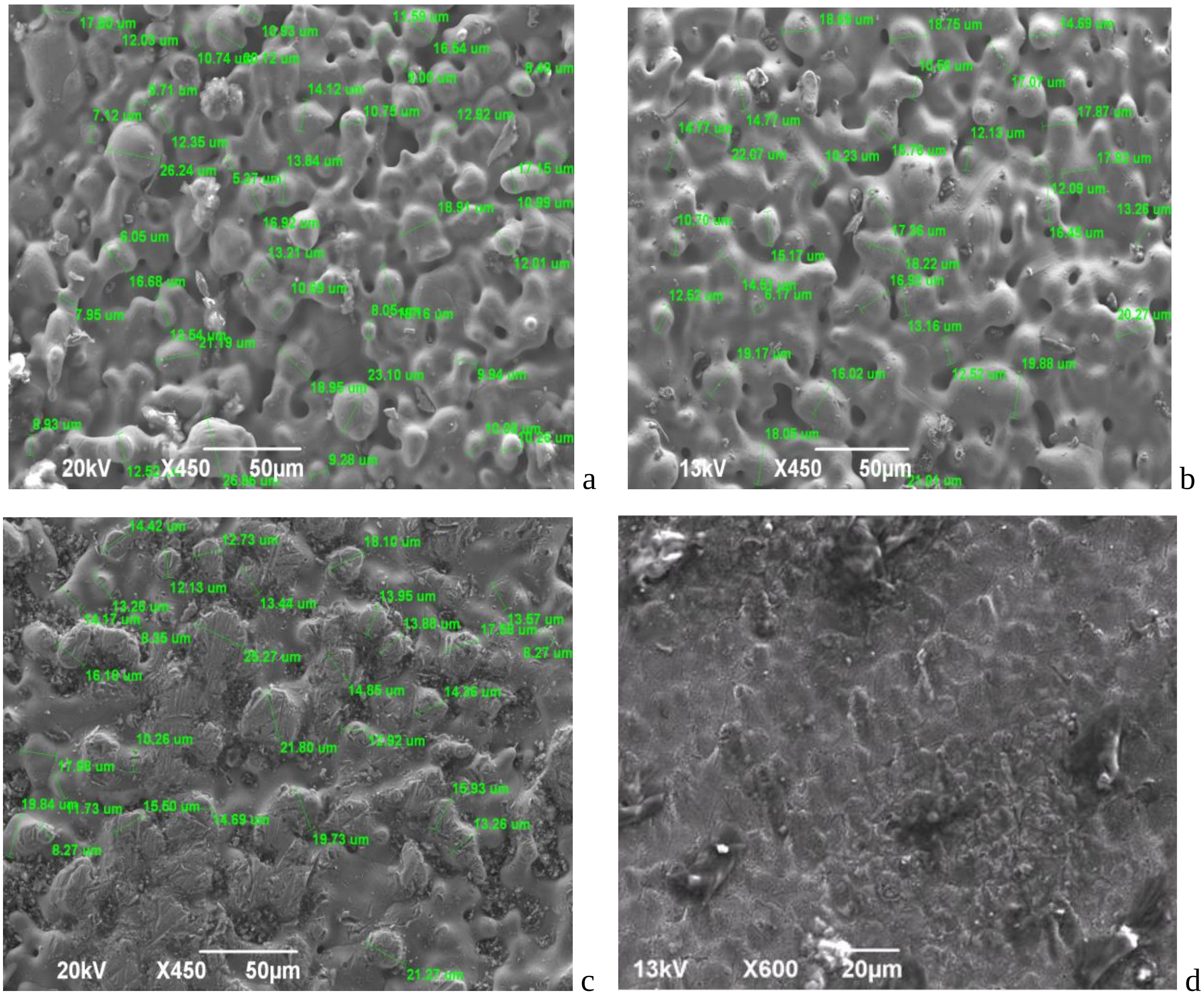
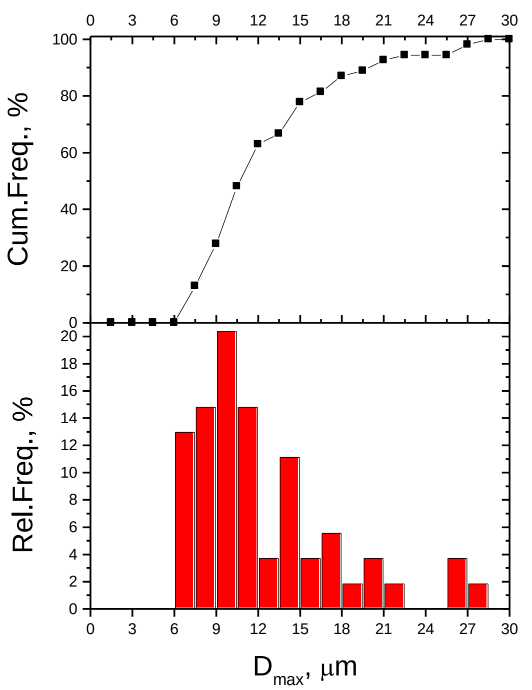


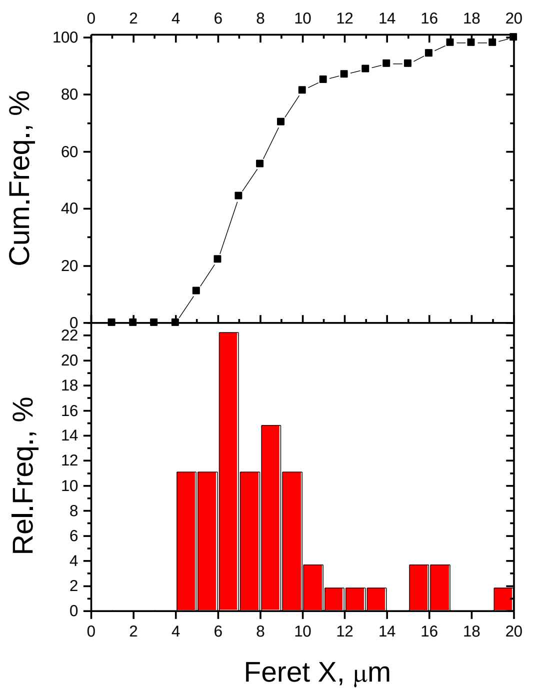
Fig. 3. Microstructures of 49Fe49Co2V alloy samples produced by MIM technology sintered at a) 1370 ^{O}C, b) 1400 ^{O}C, c) 1430 ^{O}C, and d) 1460 ^{O}C.

Histograms of relative frequency and cumulative curve of distribution of D_{max}, Feret X, and Feret Y particle size parameter values obtained by stereological analysis of 49Fe49Co2V alloy sample sintered at 1370 ^{O}C are shown in Fig. 4, while Table I shows minimum, maximum, and mean values of monitored particle parameters of the same test sample. Most particles have a size of about 6 μm to 17 μm (mean value is about 12.4 μm), and for Feret X and Feret Y, the mean values are about 8.3 μm and 9.1 μm, respectively.

Tab. I Minimum, maximum, and average values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of 49Fe49Co2V alloy sample sintered at 1370 ^{O}C.

FeCoV-1370 ^{O}C	D_{max}, μm	Feret X, μm	Feret Y, μm
MIN	6.33	4.33	3.75
MAX	27.11	19.07	18.52
MEAN	12.42	8.32	9.12





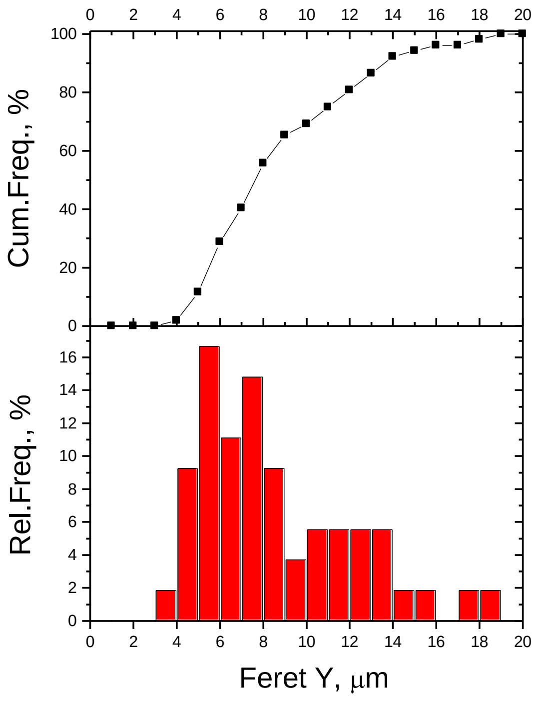
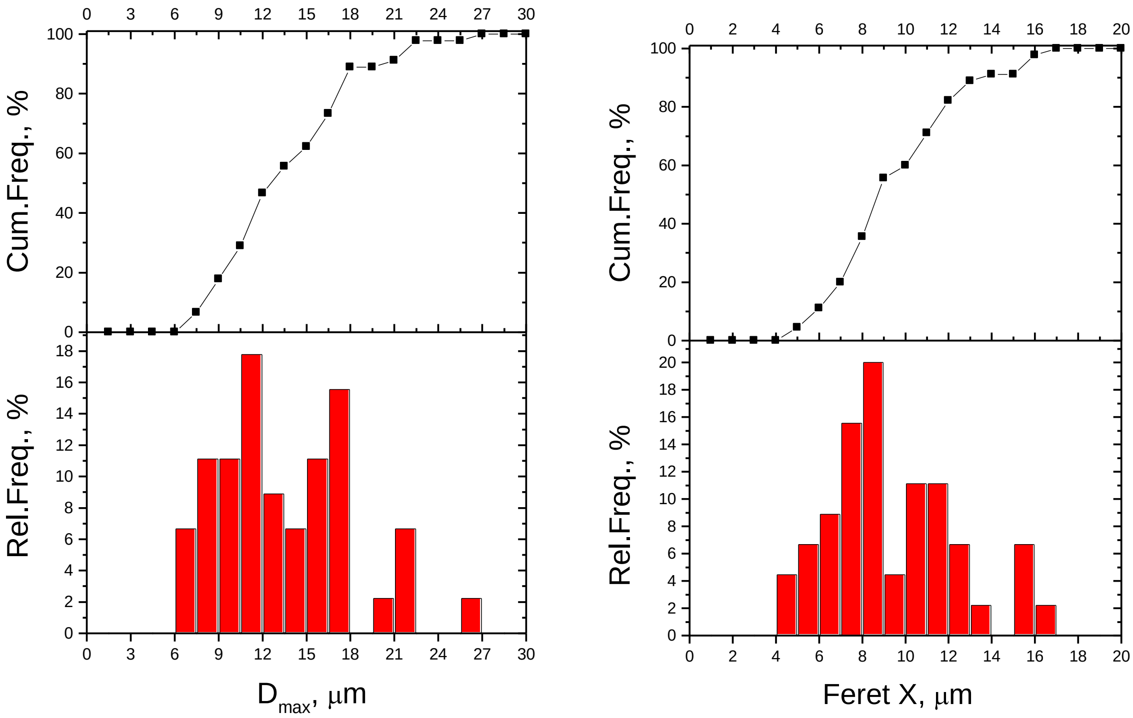


Fig. 4. Histograms and cumulative curves of distribution of values of D_{max}, Feret X, and Feret Y particle size parameters of 49Fe49Co2V alloy sample produced by MIM technology, sintered at 1370 ^{O}C.

Histograms of relative frequency and cumulative curve of distribution of D_{max}, Feret X, and Feret Y particle size parameter values obtained by stereological analysis of 49Fe49Co2V alloy sample sintered at 1400 ^{O}C are shown in Fig. 5, while Table II shows minimum, maximum, and mean values of monitored particle parameters of the same test sample. Most particles have a size of about 7 μm to 18 μm (mean value is about 13.5 μm), and for Feret X and Feret Y, the mean values are about 9.4 μm and 9.5 μm, respectively.

Tab. II Minimum, maximum, and average values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of 49Fe49Co2V alloy sample sintered at 1400 ^{O}C.

FeCoV- 1400 ^{O}C	D_{max}, μm	Feret X, μm	Feret Y, μm
MIN	6.53	4.62	4.62
MAX	26.87	16.17	18.66
MEAN	13.44	9.43	9.46



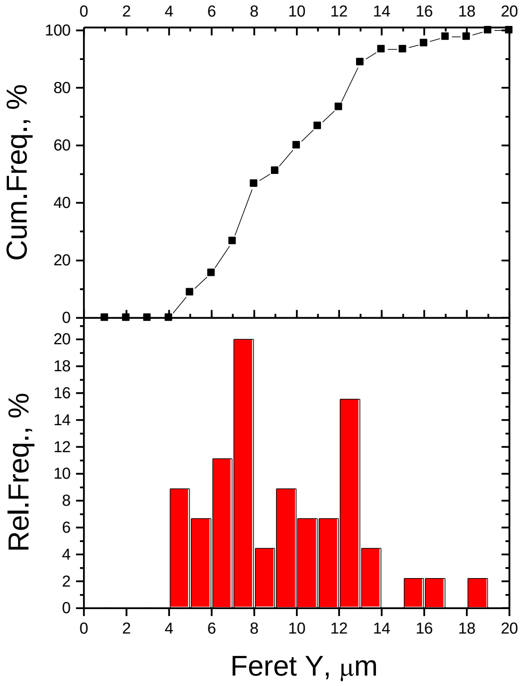


Fig. 5. Histograms and cumulative curves of distribution of values of D_{max}, Feret X, and Feret Y particle size parameters of 49Fe49Co2V alloy sample produced by MIM technology, sintered at 1400 ^{O}C.

About the results of the stereological analysis obtained with the sample sintered at 1370 ^{O}C, a slight increase in all three monitored parameters was observed after the increase of the sintering temperature by 30 ^{O}C. The choice of sintering temperatures was made with a gradual increase of only 30 ^{O}C in order to optimize the microstructures and therefore all other functional properties of the MIM technology synthesized samples of 49Fe49Co2V alloy.

The histograms of the relative frequency and the cumulative curve of the distribution of the values of the particle size parameters D_{max}, Feret X, and Feret Y obtained by stereological analysis of a sample of 49Fe49Co2V alloy sintered at 1430 ^{O}C are shown in Fig. 6. Table III shows the minimum, maximum and mean values of the monitored particle parameters of the same sample. Most particles have a size of 10 μm to 20 μm (mean value is about 15 μm), and for Feret X and Feret Y, mean values are about 10 μm and 11 μm, respectively.

Tab. III Minimum, maximum, and average values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of 49Fe49Co2V alloy sample sintered at 1430 ^{O}C.

FeCoV- 1430 ^{O}C	D_{max}, μm	Feret X, μm	Feret Y, μm
MIN	8.03	4.91	6.06
MAX	24.11	17.62	16.46
MEAN	14.95	10.23	10.84

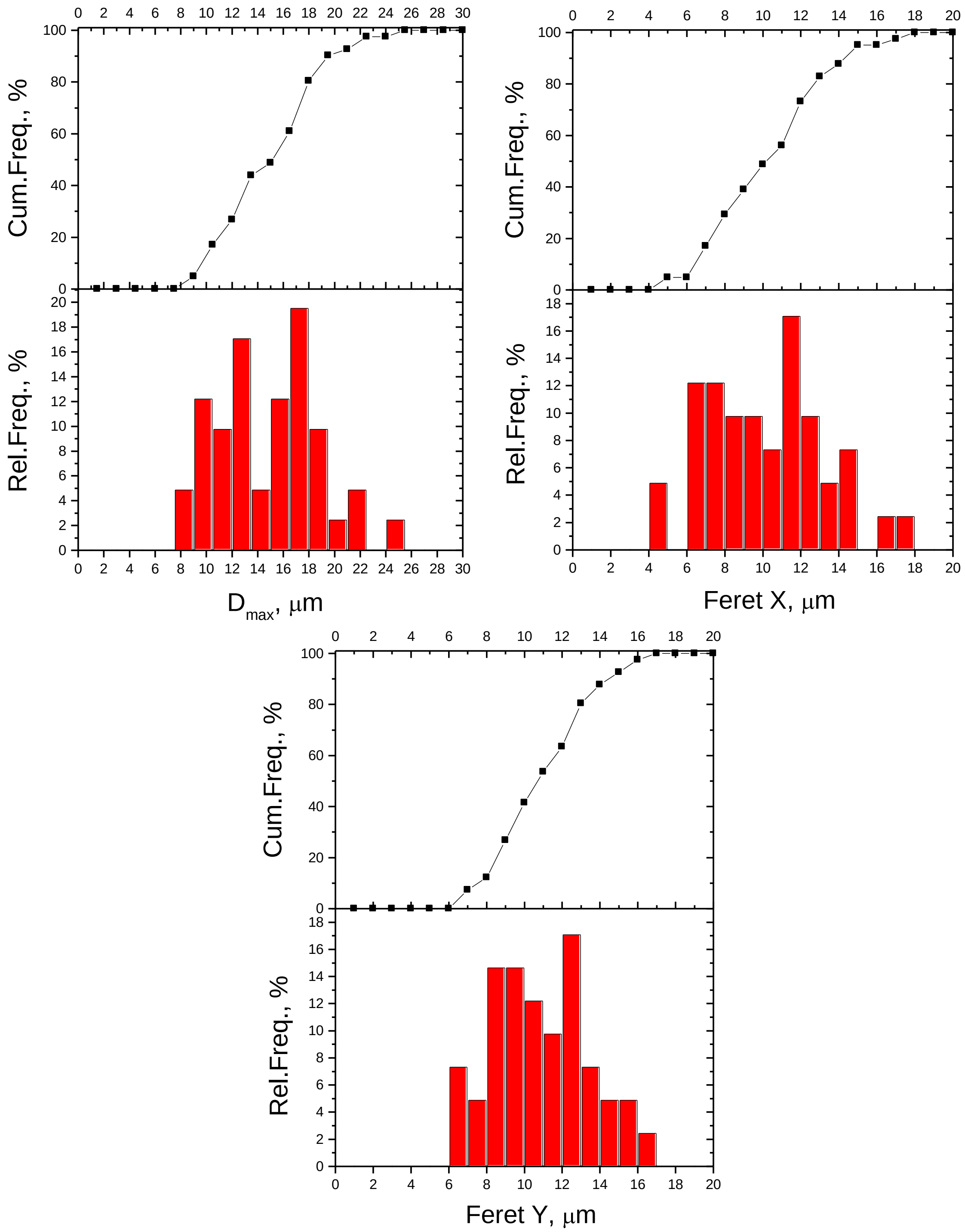


Fig. 6. Histograms and cumulative curves of distribution of values of D_{max}, Feret X, and Feret Y particle size parameters of 49Fe49Co2V alloy sample produced by MIM technology sintered at 1430 ^{O}C.

Concerning the results of the stereological analysis obtained with samples sintered at 1370 ^{O}C and 1400 ^{O}C, a further increase in all three monitored parameters was noticeable after a further increase in the sintering temperature. Table IV shows the comparative values of the monitored parameters (particle size D_{max}, Feret X, and Feret Y) of all tested samples.

Tab. IV Comparative values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of all test alloy samples 49Fe49Co2V.

	D_{max}, μm	D_{max}, μm MEAN	Feret X, μm MEAN	Feret Y, μm MEAN
1370 ^{O}C	6-17	12.42	8.32	9.12
1400 ^{O}C	7-18	13.44	9.43	9.46
1430 ^{O}C	10-20	14.95	10.23	10.84

A comparison of the cumulative frequencies of the D_{max} particle size parameter, 49Fe49Co2V alloy samples sintered at 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C is shown in Fig. 7.

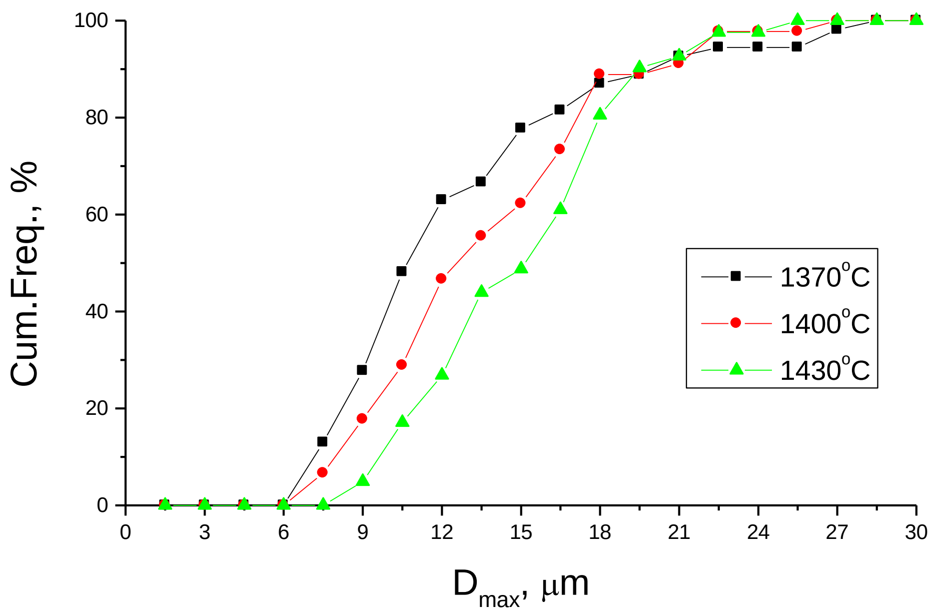


Fig. 7. Cumulative frequencies of particle size parameter D_{max} of 49Fe49Co2V alloy samples sintered at 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C.

A comparison of the cumulative frequencies of the Feret X parameter of the 49Fe49Co2V alloy samples sintered at 1370 ^{O}C, 1400^{O}C, and 1430 ^{O}C is shown in Fig. 8, and the cumulative frequencies of the Feret Y parameter are shown in Fig. 9.

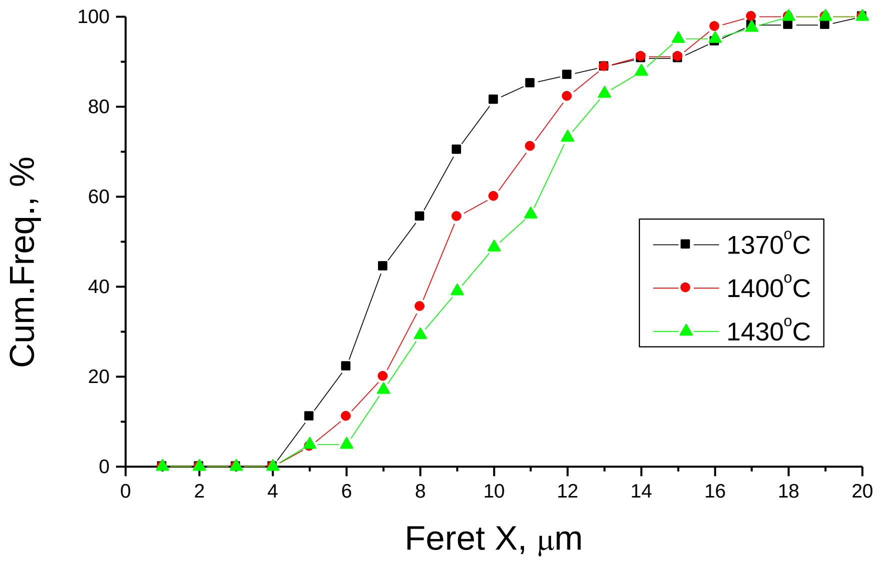


Fig. 8. Cumulative frequencies of particle size parameters of Feret X samples of 49Fe49Co2V alloy sintered 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C.

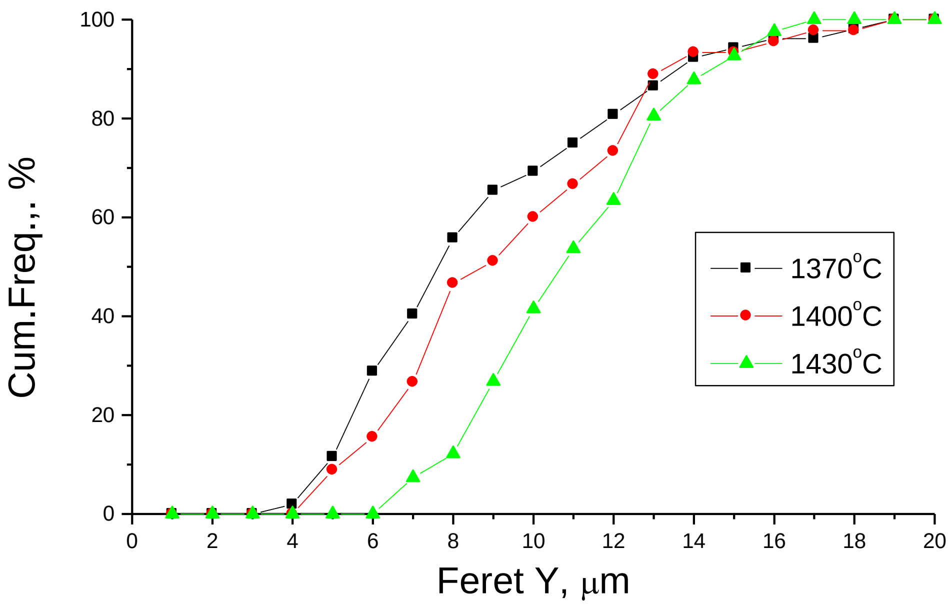


Fig. 9. Cumulative frequencies of particle size parameters of Feret Y samples of 49Fe49Co2V alloy sintered at 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C.

From the comparative curves of cumulative frequencies of values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of all tested samples, a constant and gradual increase of all three parameters with an increase in sintering temperature of 30 ^{O}C is noticeable. In this way, the microstructure of the samples sintered at 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C was gradually optimized, while the microstructure of the sample sintered at 1460 ^{O}C shows that the melting point of the particles was reached at this highest temperature. Experiments devoted to the hole-making method in 49Fe49Co2V rod samples prepared by a vacuum arc-melting furnace and heat treated at 900 ^{O}C show the microstructure that contains a dual phase of BCC and B2 with the matrix grain size of about 40-50 μm [20]. Therefore, MIM technology offers the successful preparation of intermetallic FeCoV components that can be used competitively in strategic applications, for example, the aerospace motor rotor.

4. Conclusion

On the microstructures of 49Fe49Co2V alloy samples examined using a scanning electron microscope - SEM, it can be noticed that during sintering, powder particles are melted directly in proportion to the sintering temperature. At higher temperatures, neck growth and loss of particle individuality are more intense, and the space between particles significantly changes shape due to pore closure. This leads to an increase in sample density (so-called intermediate sintering phase that takes place at 1370 ^{O}C, 1400 ^{O}C, and 1430 ^{O}C). The values of monitored parameters (particle size D_{max}, Feret X, and Feret Y) of tested samples exhibit a constant and gradual increase with increasing sintering temperature. In the final stage of sintering, at the highest temperature of 1460 ^{O}C, the particles completely lose their individuality due to melting.

Acknowledgments

This work is partially funded by the Ministry of Science, Technological Development and Innovations of the Republic of Serbia (project no. 451-03-47/2023-14/200132, Faculty of Technical Sciences in Čačak, University of Kragujevac).

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Сажетак: У раду су приказана истраживања структурних својстава магнетно-полутврде легуре FeCo-2wt%V (FeCoV) произведене технологијом бризгања композита праха са растопљеним везивом (опција бризгања финих металних прахова - (MIM) технологија). Почетни гранулат је припремљен мешањем FeCoV праха са везивом ниске вискозности. Након бризгања, зелени узорци су прво третирани растварачем, а затим термички са истим циљем уклањања везива. MIM технологија је завршена високотемпературним синтеровањем у трајању од 3,5 сати на температурама од 1370 ^{O}C до 1460 ^{O}C у атмосфери водоника, чиме су обезбеђене потребне магнетне и механичке карактеристике. Утицај температуре синтеровања на процес структурне трансформације испитиван је методама рендгенске дифракције (XRD) и скенирајуће електронске микроскопије (SEM). За све испитиване узорке регистрована је појава интензивног дифракционог пика α'-FeCo кристалне фазе (структура типа B2). Структурни параметри величине честица D_{max}, Feret X и Feret Y показују константно повећање са повећањем температуре синтеровања до 1430 ^{O}C, док на вишим температурама долази до потпуног топљења синтерованих честица.

Кључне речи: FeCoV легура, MIM технологија, структурна својства, величина честице D_{max}, Feret X, Feret Y.