Sintering Effect on the Microstructure And Magnetic Properties of Co-Al_xO_y Composite Compound

Sri Mulyaningsih[1], Setyo Purwanto[2], Mujamilah[2], Wisnu Ari Adi[2], Azwar Manaf[3]

Abstract—**Research on sintering effect on the micro structure and the magnetic properties of composite Co-Al_xO_y materials has been done. The experiment was carried out by high energy milling (HEM) to refine Co and Al sample powder, followed by sintering process. The composition of sample was $Co_{73}Al_{27}$ wt% with weight ratio to the ball was 1:2.7. The milling time was varied within 4.5, 12 and 20 hours, while sintering process was conducted at 384ºC and 484ºC. Several new peaks were found after sintering process and identified as a Co-Al_2O_4 compound. The experiment data shows the saturation magnetization Ms value was decline for the entire sample by the sintering process. The Mr value for the 12h milling was remind stable about 9 emu/gr but, for 4.5 milling was decline from 17.5 to 9.2 and 6.2 emu/gr , while for 20h milling from 13,5 to 9.25 and 8 emu/gr. No visible changes in the microstructure are observed.**

Keywords— **Sintering, Microstructure, Co-Al_xO_y, Milling, magnetic**

I. Introduction

Experiment on the granular alloy magnetoresistance Co- Al-O base material has attracted much attention. This paper is preliminary study on the composite material which is prepared for the system granular alloy magnetoresistance Co-Al-O base materials. In the granular systems, the distribution of the granular size is highly probable that large granules are separated from each other and there are may be a number of smaller granules between them [1]. Co-Al-O should be composed of nonscale Co particles embedded in insulating amorphous oxide to make the super-paramagnetic state. So, the size of the metallic grains must be of nanoscale dimension in order to create the condition of no coupled spin by exchange interaction [2].

Co and Al was design to obtain the nanoscale particle by milled the powder continued to sintering process to get the oxide phase. So, the system become Co particle embedded in the oxide matrix.

II. Experimental

Synthesizing the material was carried out by high energy milling (HEM) to refine the sample powder follow by compaction to form the pellets and ended with sintering process. Composition of the powder was referred to the composition of granular alloy Co-Al_xO_y thin films system which is exhibit the best magnetoresistance value, it was $Co_{73}Al_{27}$ wt% [3]. The milling time was varied within 4.5, 12 and 20 hours [4], while sintering process was conducted at 384ºC and 484ºC. The sintering temperature was obtained from DSC measurement on the sample powder after milling process. The structures of the pellet was analyzed by x-ray diffraction and magnetic behavior was measured by vibrating sample magneto meter (VSM) type OXFORD version 2.1 and SEM for analyzed the microstructure.

III. Result And Discussion

The x-ray diffraction shows several new peaks on the sample after sintering process and identified as a Co-Al_2O_4 composite compound, figure 1, 2 and 3. It was no Al peak found after sintering process so, the system of the material become Co/Co-Al_2O_4/Co. Identification of the peak was done by comparing the x-ray diffraction data to the data base from JCPDS-ICDD.

As shown at figure 1 to 3 below, no Al peak found after sintering process, it means all of Al particle already reacts with Co and O to formed Co-Al_2O_4 compound. The emergence of new phase Co-Al_2O_4, which have different magnetic behavior will influence the behavior of the material. Furthermore, the magnetic behavior of the material will be changed. The discussion about alteration of magnetic behavior will be clear by VSM data in the discussion about magnetic behavior.

Crystallite size is the important factor in the magnetoresistance materials especially in the granular alloy system. The crystallite size can be measured from the x-ray diffraction data by calculating the peak data. The size should be in the nanoscale to form the superparamagnetic state. Quantitative calculation of the granular size was done by calculating the (111) peak as a sample by Scherer equation [5].

$$B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

Which B(2θ) is full width half maximum (FWHM), λ is wave length, L is crystallite size. The crystallite size calculation of the sample after milling and sintering process are shown in the table 1.

As shown in the table 1, crystallite size of the material increased by sintering process and the maximum crystallite size is bellow 20 nm.

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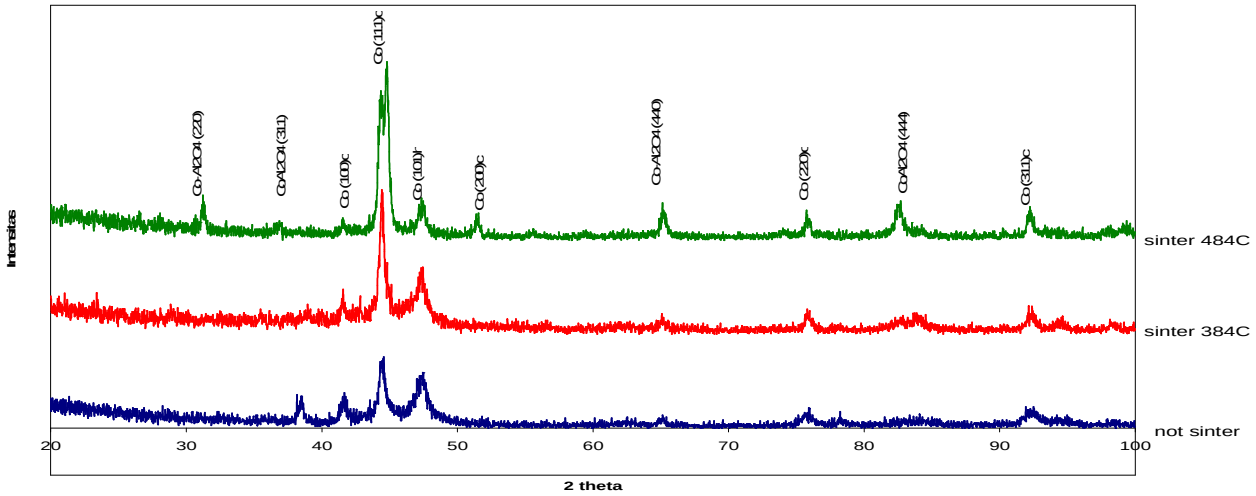


Fig. 1. The X-ray diffraction pattern of material after milling 4,5h and sintering process at 384 and 484ºC

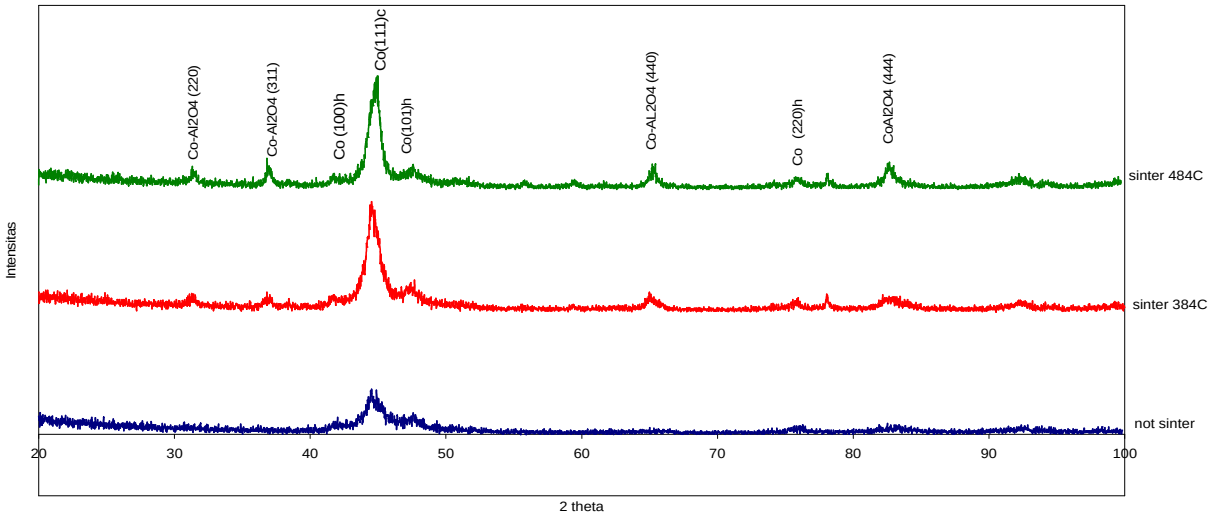


Fig. 2. The X-ray diffraction pattern of material after milling 12h and sintering process at 384 and 484ºC

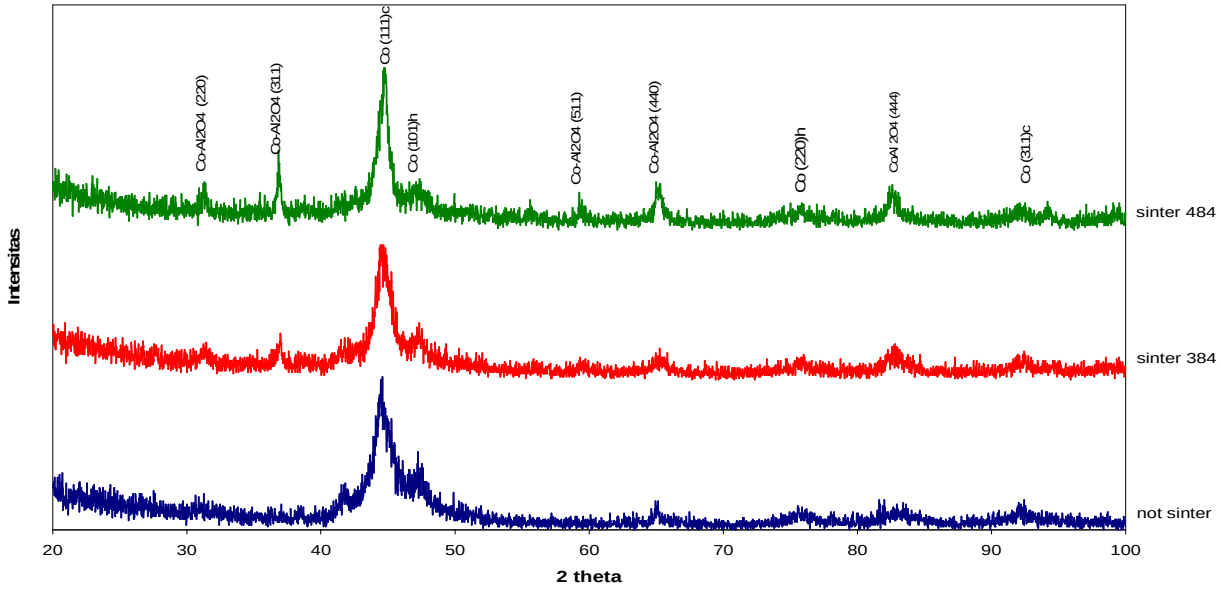


Fig. 3. The X-ray diffraction pattern of material after milling 20h and sintering process at 384 and 484ºC

The more milling time will give smaller the crystallite size. For the sample of 20h milling was appear very small crystallite size, 1,858 nm before sintering and the maximum size after sintering was 4,910 nm. This crystallite size will be play an important role in the superparamagnetic behavior and the magnetoresistence behavior is depending on this evidence.

The magnetic behavior of the material was measured by Vibrating Sample Magnetometer (VSM). Measurement was conduct to the sample after milling and after

sintering process. Figure 5, 6 and 7 below, shows the Hysteresis curve for sample after milling 4.5h, 12h and 20h before and after sintering process.

TABLE 1
THE CRYSTALLITE SIZE SAMPLES AFTER MILLING AND SINTERING PROCESS

Sintering Temperature	Crystallite size		
	4.5 h milled (nm)	12h milled (nm)	20h milled (nm)
Not sinter	10.305	7.154	1.858
384	15.463	7.948	1.940
484	19.878	9.345	4.910

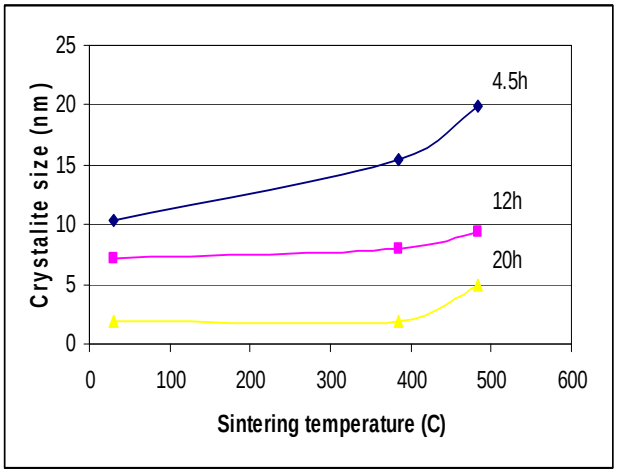


Fig. 4. The crystallite size distribution after milling and sintering process

The magnetic behavior data from the entire sample can be seen at the table 1 and figure 4. The data was obtained by measuring the magnetic saturation (Ms), magnetic remanence (Mr) and coersivity (Hc) from the above hysteresis curve. The distribution of Ms, Mr and Hc are shown in the table 2 and figure 4.

The magnetic saturation (Ms) was decline for entire sample by sintering process, figure 5, 6 and 7. The interaction field depends not only on the separation of the two particles but also on their position relative to the magnetization direction of the particles [6]. As explain above, the system of the material is Co/Co-Al_2O_4/Co, the Co particles separated by Co-Al_2O_4 compound and the magnetization direction of the particles Co supposed had been turned upward by mechanical crash. As the synthesizing of the material was done by milling process, it was hard mechanical crashed done at the powder that probably caused the crystal structure be damage.

The emergence of the new phase which have different magnetic behavior also will influenced the material. As shown in the figure 1, 2 and 3, after sintering process it was appear new phase of Co-Al_2O_4 in the material. According to Robert C. O'Handley [7], the magnetic behavior of Co-Al_2O_4 compound is collinear antiferromagnetic, it means there probably superexchange. Thus, the behavior of Co-Al_2O_4 be influenced the material so the saturation will be decline.

The coersivity (Hc) in the fine particle is exceeding a few hundred oersteds, and it has a striking dependence on their size. It is typically found that the coercivity increases, goes through maximum at about 160Å particle size, and than tends toward zero [6]. As shown in the figure 10, the coercivity of the sample 4.5h milling, go down after sintering process. It can be seen in the table 1, the crystallite size of the material increase by sintering process, and reach 19.878 nm (more than 160 Å) so, the coercivity become decrease. However, the coersivity of the sample 12h and 20h milling, the coersivity tends to increase by sintering process. It can be understood because the crystallite size of both samples still under 160Å even though sintering process was done.

Microstructure of the entire sample shown at figure 5, the magnification was done at 1000 and 2000x by SEM. The information from the picture was only telling about the density of the material which is the higher the sintering process the density of the material will be higher. Actually, we need appropriate information to discuss the influence of micro structure to the magnetic behavior. However, it seems no visible changes on the micro structure data. The higher resolution of the instrument such as high resolution TEM is needed to explore more details about the structure the materials.

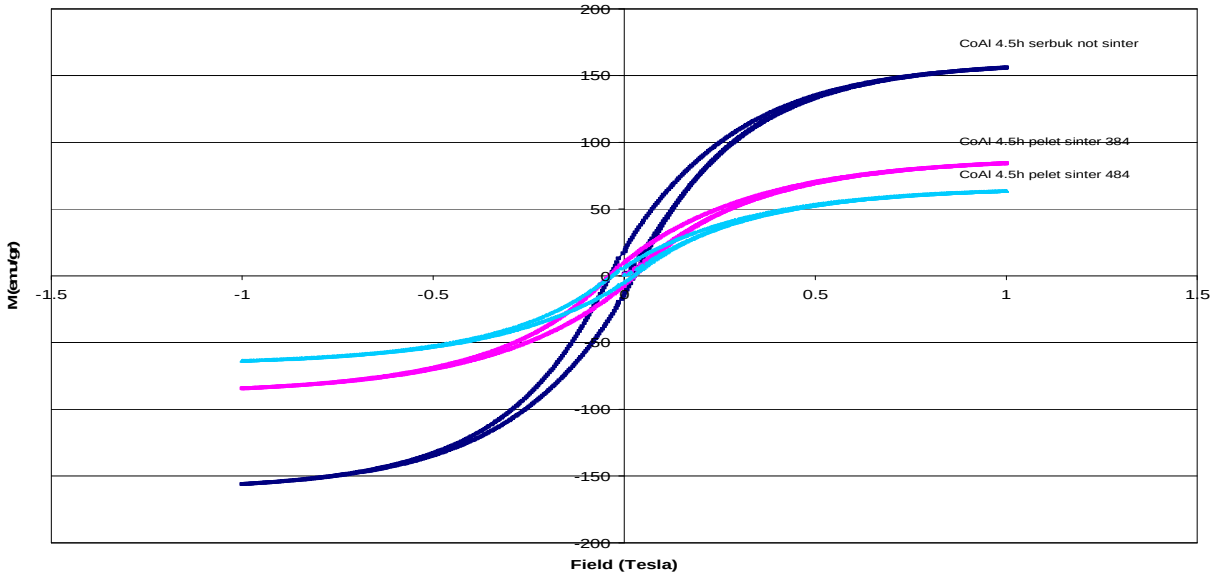
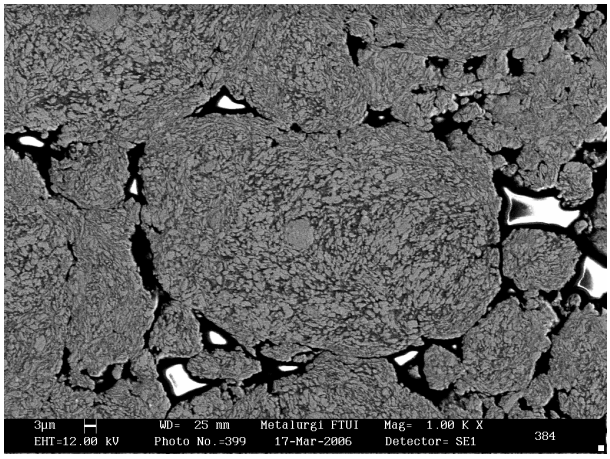
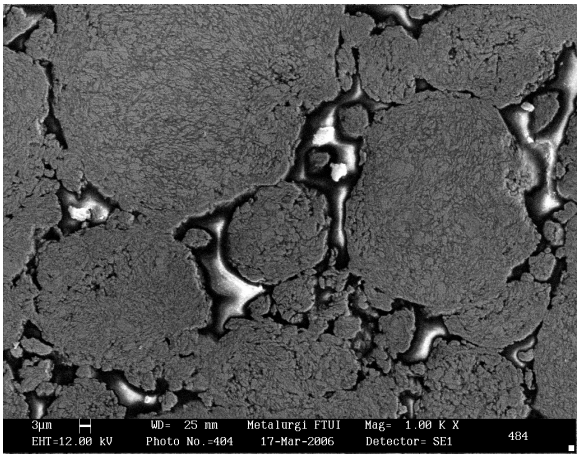


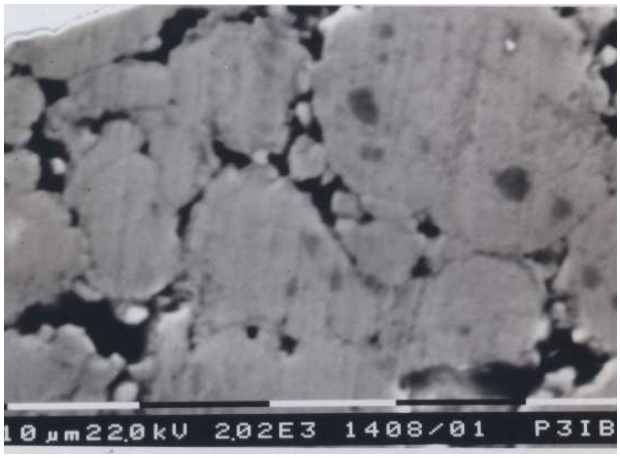
Fig.5. The hysteresis curve of the material after milling 4,5h and sintering process at 384 and 484ºC



(a) 4.5h milled sintered at 384ºC

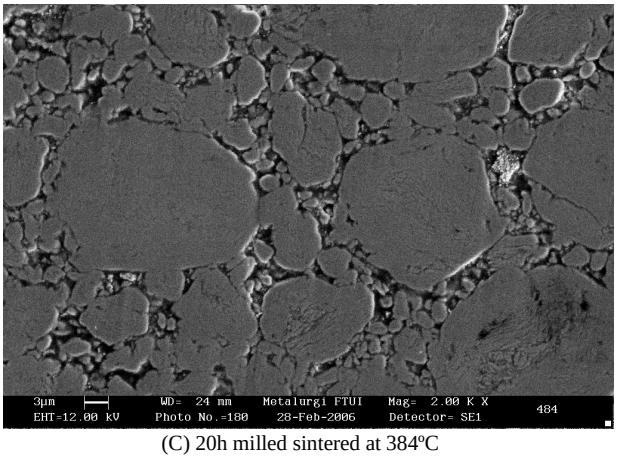


4.5h milled sintered at 484ºC

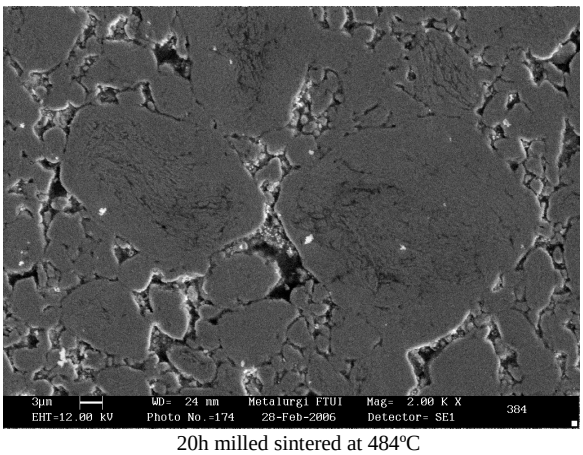


(b) 12h milled sintered at 384ºC

12h milled sintered at 484ºC



(C) 20h milled sintered at 384ºC



20h milled sintered at 484ºC

Fig. 5(a), (b), (c). Microstructure of the sample 4.5h, 12h and 20h milling and sintering at 384ºC dan 484ºC, 2000x magnification

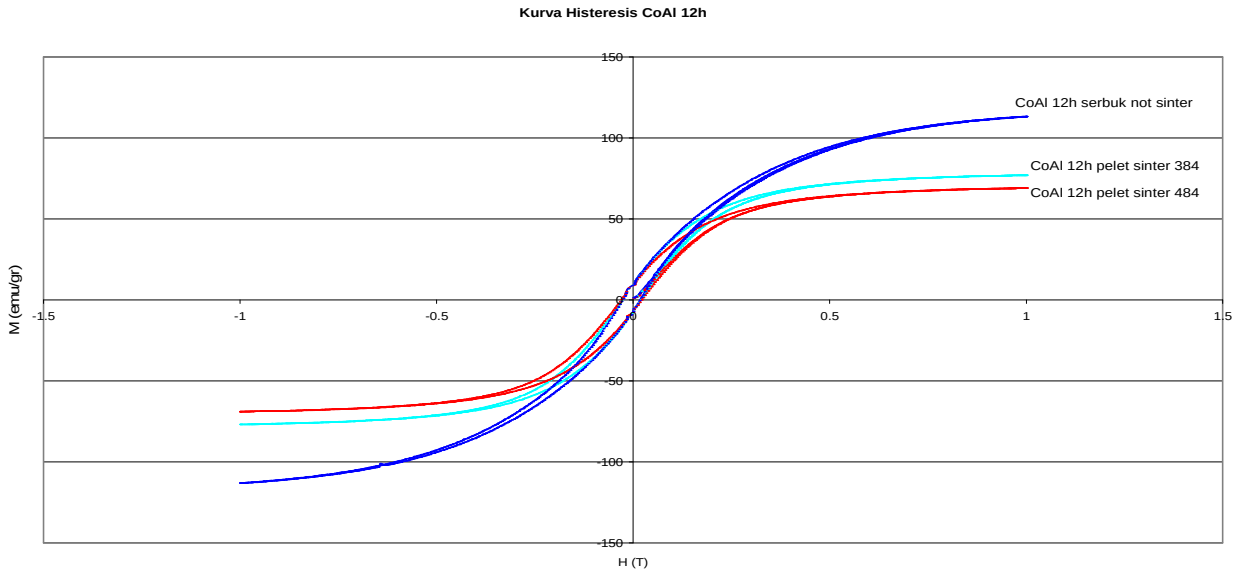


Fig.6. The hysteresis curve of the material after milling 12h and sintering process at 384 and 484ºC

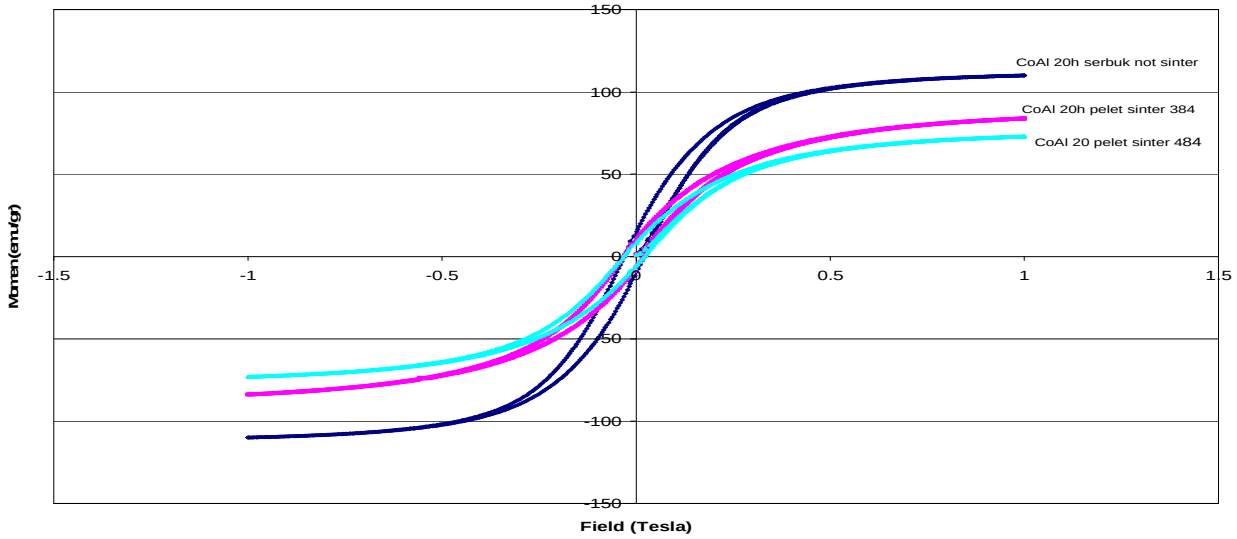


Fig.7. The hysteresis curve of the material after milling 12h and sintering process at 384 and 484ºC

TABLE 2
THE MS, MR AND HC VALUE OF THE MATERIALS

Sample	Ms (emu/gr)	Mr (emu/gr)	Hc (Oersted)
CoAl 4.5h milled,powder not sinter	156	17.5	367
sinter 384	84.4	9.2	376
Sinter 484	63.5	6.2	330
CoAl 12h milled, powder not sinter	113	9.27	275
sinter 383	77	9.27	285
sinter 484	69	9.04	305
CoAl 20h milled, powder not sinter	110	13.5	317
sinter 384	84	9.25	345
sinter 484	73	8	345

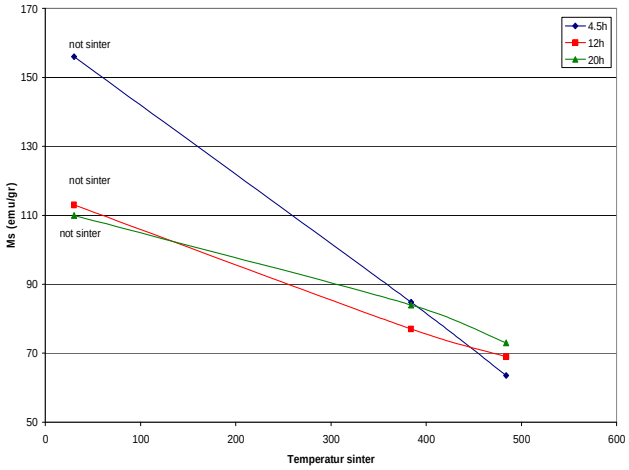


Fig. 8. The distribution value of saturation magnetization Ms of the materials

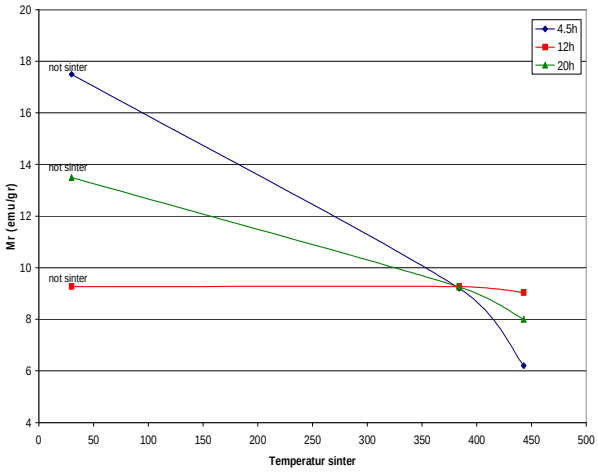


Fig. 9. The distribution value of remanence Mr of the materials

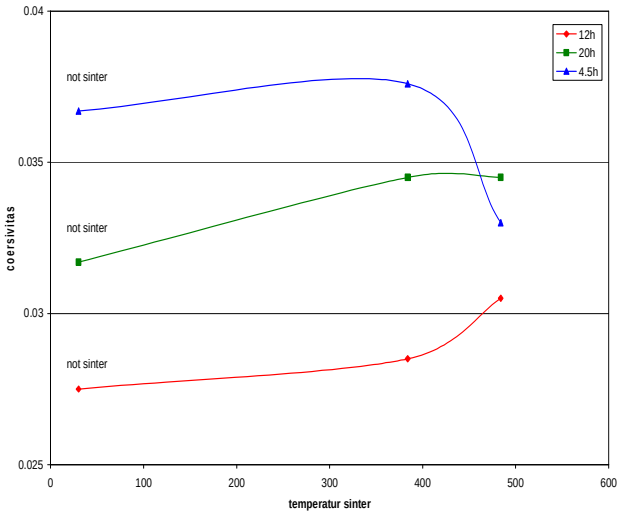


Fig. 10. The distribution value of coercivity Hc of the materials

IV. CONCLUSIONS

1. The milling and sintering process changed Ms value for entire samples, which is all of the Ms value was declined
2. Mr value for the 12h milling was remind stable about 9 emu/gr but, for 4.5h milling was decline from 17.5 to 9.2 and 6.2 emu/gr, while for 20h milling from 13,5 to 9.25 and 8 emu/gr.
3. No visible changes in the microstructure are observed

V. REFERENCES

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