Investigation of the phase transformation characteristics of Fe-Co elastocaloric refrigeration alloy

Xianfa Li¹, Yongjun Shi¹*, Shuyao Wang¹

¹ Mechanical and Electrical Engineering Institute, China University of Petroleum of Huadong, Qingdao, Shandong Province, 266580, China
*Corresponding author’s e-mail: syjgl@upc.edu.cn

Abstract. Mechanical alloying (AM) and powder metallurgy (PM) have been widely used in many fields especially in the development of new alloy materials due to the advantages of simple process, high material utilization rate and accurate material ratio. In this investigation, experimental procedures were proposed to explore the phase transformation characteristics, elastocaloric refrigeration effect of Fe-Co alloys synthesized by AM and PM. The samples of Fe-Co elastocaloric refrigeration alloy with different phase transformation temperatures and different enthalpy changes have been successfully prepared by changing the initial ratio of Co element. The results show that the phase transformation characteristics have changed with the increase of Co content and showed different changing trends.

1. Introduction
In recent years, with the continuous reduction of non-renewable energy sources, energy issues have increasingly become the focus of attention, in which, the huge energy consumption appears in the field of air conditioning and refrigeration [1, 2]. Therefore, as soon as the new cooling conception was proposed, elastocaloric refrigeration technology has attracted widespread attention from academia and industry due to its highly efficient and environmentally friendly advantages.

Elastocaloric refrigeration technology was proposed at the University of Maryland in 2012 [3] and has been extensively studied. The purpose of heat release and heat absorption of elastocaloric refrigeration can be achieved by changing the symmetry of the crystal structure of the material through the application and removal of an external stress or thermal field to cause the martensite phase transformation and martensite reverse phase transformation of the material. Among many elastocaloric refrigeration materials, shape memory alloys represented by Ni-Ti-based, Cu-based and Fe-based alloys are considered to be the most promising elastocaloric refrigeration materials [4].

Currently, the research on Ni-Ti shape memory alloys and elastocaloric refrigeration alloy have been performed mainly about four aspects including Ni-Ti alloy-based composite materials [5], new manufacturing processes method [6], microstructure [7] and elastocaloric refrigeration mechanism [8], which has been fully studied. In addition, some research about Cu-based electrocaloric refrigeration alloy has also been investigated in recent years [9]. However, little exploration was reported about Fe-based electrocaloric refrigeration alloy [10]. Fe-Co alloy, as a new type of elastocaloric refrigeration material, has the advantages of low price and simple manufacturing process, of which characteristics make it have the potential to replace traditional compression refrigeration material. Its elastocaloric refrigeration effect is derived from the heat-induced reversible non-diffusion of high-temperature austenite and low-temperature martensite phase transformation.
Powder metallurgy technology has the advantages of high material utilization, low power consumption, and less waste [11]. Due to the advantages of powder metallurgy technology, it plays an essential role in solving the problem of new materials and the development of new materials [12]. Therefore, powder metallurgy technology was used to synthesize Fe-Co alloy with different Co content to explore the properties and laws of new elastocaloric refrigeration alloy series. The initial content of the Co element in the Fe-Co sample is set to 5wt%, 10wt%, 15wt%, and 20wt%, respectively. The preparation of experimental samples is divided into three steps. Firstly, the weighed Fe powder and Co powder are mixed and alloyed by a ball mill. Then the mixture of powders was poured into a model and pressed by a press. Thirdly, the samples were sintered and homogenized by a sintering furnace in vacuum environment. In addition, the differential thermal scanner (DSC) was used to analyse the phase transformation characteristics of the alloy and microstructure morphology. Combined with the detection results of SEM, EDS, and XRD, a comprehensive analysis of the alloy's microstructure, phase composition and crystal structure of the composition was also carried out.

2. Experimental procedure

2.1. Phase 1: sample preparation
The influence of Co element on the phase transformation characteristics of Fe-Co alloy were studied by changing the content of Co element in Fe-Co alloy. The initial content of Co element in Fe-Co alloy is 5wt%, 10wt%, 15wt% and 20wt% respectively. In order to fully mix and alloy the Fe and Co powders, high-energy ball mill machine is used for the process. Commercial Fe and Co powders were used and the corresponding mass of Fe and Co powders was weighed with an analytical balance. Then in the case of a ball-to-material ratio (weight ratio) of 10:1, ball milling was performed at a speed of 350r/min for 6 hours.

After the preparation of four groups of Fe and Co mixed powders in different proportion, in order to improve the quality of samples, ~3% of paraffin powder is used as a binder and mixed in the alloyed powder and be poured into the model. The press is used to statically press the powder into a cylinder with a diameter of 15mm and a height of 6mm and the pressure range is controlled between 360~400MPa.

2.2. Phase 2: Sintering process
The four groups of samples were subjected to homogenization heat treatment at 600°C to ensure the Co element will further diffuse to make the element distribution more uniform. At the same time, the grains will re-grow into smaller grains so as to achieve the purpose of improving the thermodynamic. In order to make the material's thermodynamic more excellent, the alloy sample was homogenized at 600°C for 2 hours, and then cooled in the furnace.

After mechanical alloying and static pressure forming, the samples are placed in a vacuum atmosphere sintering furnace. In a vacuum environment, the samples were kept for 30 minutes to ensure the binder completely decomposes which is decomposed at 250°C (binder decomposition temperature). And then heated to 1100°C and kept warm. In 2 hours, the sintering process of the samples was completed.

The samples after the sinter process at 1100°C were transferred to homogenization heat treatment. When Fe-Co alloy samples were in homogenization heat treatment process at temperature of 600°C, the Co element will re-diffuse to make the element distribution of Fe-Co alloy more uniform. At the same time, the grains will re-grow into smaller grains (grain refinement) so as to improve the thermodynamic. Due to this characteristic, homogenization treatment is widely used to refine alloy grains. In order to make the material's thermodynamic more excellent, the alloy specimen was homogenized at 600°C for 2 hours, and then cooled in the furnace.
3. Properties measurement

3.1. Phase transformation characteristics measurement
The samples were cut into the required size using a wire-cut electric discharge machining (WEDM) machine. And then phase transformation characteristics were measured using DSC at a rate of 10°C/min scanning speed within the temperature range of 0°C to 480°C. The results of the phase transformation characteristics were shown in Figure 1 and Table 1.

![Figure 1(a). Phase transformation characteristics result with 5wt% Co content.](image)

![Figure 1(b). Phase transformation characteristics result with 10wt% Co content.](image)

![Figure 1(c). Phase transformation characteristics result with 15wt% Co content.](image)

![Figure 1(d). Phase transformation characteristics result with 20wt% Co content.](image)

Figure 1. Phase transformation characteristics results.

| Number of samples | As (℃) | Af (℃) | Ms (℃) | Mf (℃) | △HA (J/g) | △HM (J/g) |
|-------------------|--------|--------|--------|--------|-----------|-----------|
| NO.1              | 410.13 | 439.90 | 74.18  | 25.03  | -0.77     | 8.29      |
| NO.2              | 409.84 | 439.23 | 57.04  | 28.87  | -0.84     | 3.41      |
| NO.3              | 420.33 | 439.52 | 58.60  | 33.32  | -0.46     | 4.53      |
| NO.4              | 426.55 | 441.25 | 60.96  | 26.39  | -6.18×10^{-2} | 5.03 |

3.2. Microstructure detections
With the help of the X’Pert-Pro ray diffractometer (XRD) shown in Figure 2, the phase analysis of the Fe-Ni elastocaloric refrigeration alloy is carried out. The detection parameters are: the target is a copper target, and the scanning range is 20-100°. The scanning speed is 5/min. Combined with the elemental analysis of the Fe-Ni elastocaloric refrigeration alloy, the phase composition, content and grain size of the corresponding phase of the Fe-Ni elastocaloric refrigeration alloy after sintering at a temperature of 1100 ℃ are explored. The XRD test results are shown in Figure 2.

The samples were characterized for their microstructure with the assistance of scanning electron microscope (SEM), which had an X-ray detector for Energy Dispersive X-ray spectroscopy, and X-ray diffraction (XRD). The samples were cut by a wire electrical discharge machining (WEDM) machine. Samples for microscopy were inlaid in white electric jade powder (WEJP). The WEJP-inlaid samples were polished using silicon carbide abrasive paper, which began from a grit size of 400 and...
subsequently decreasing it to 600, 800, 1200 and 1500. The polishing was performed using 2.5 mm diamond paste followed by 0.5 mm diamond paste.

X-ray diffraction was performed on the X'Pert-Pro which equipped with a CuKα X-ray source and three standard coupled 2-theta plots were acquired with the assistance of X'Pert-Pro. X-ray diffraction scanning was conducted from 20° to 100° (2theta) at a rate of 10°/min. A scanning electron microscope (COXEM EM-30-plus, COXEM-30-plus desktop-scanning-electron-microscope) was applied to capture the microstructural images of the samples. This analysis helped to confirm the results obtained from the X-Ray diffraction. Approximately 40mm² of specimen area was measured. The SEM images obtained were post processed. The microstructure images of the three groups of Fe-Ni elastocaloric refrigeration alloys photographed by SEM are shown in Figure 3, Figure 4, Figure 5, and Figure 6 respectively.
4. Result and discussion

4.1. Phase transformation characteristics

The effect of the starting temperature point and the phase transformation enthalpy value is shown in Figure 7.

From Figure 7, it can be clearly seen that the $As$ is maintained above 400°C and with the increase of Co content, the $As$ first decreases slowly, and then increases rapidly. When the Co content is 20%, the $As$ reaches the highest 426.55°C. Although the $Af$ with Co content shows a trend that first decreases and then rises similar to the $As$, as shown in Figure 8, but with the increase of Co content, austenite $Af$ is extremely small and maintained at about 430°C, that is, the Co content has little effect on $Af$ of the Fe-Co elastocaloric refrigeration alloy.

From Figure 9, it can be clearly seen that the $Ms$ is below 100°C and with the increase of Co content, the $Ms$ first decreases rapidly and then slowly increases. When the content is 10%, the $Ms$ reaches the lowest 57.04°C. Contrary to the change trend of the $Ms$, as shown in Figure 10, the $Mf$ is maintained between 20°C and 35°C, which first increases and then decreases with the increase of Co content. The maximum temperature is 33.32°C when the Co content is 15%.

For the thermal parameter phase transformation enthalpy, which characterizes the key refrigeration performance of Fe-Co alloys, is the enthalpy change value during the martensite transformation and austenite transformation, as shown in Figure 11 and Figure 12, although with the increase of Co content, the austenite phase transformation enthalpy value of phase transformation $\Delta H_A$ shows a trend of first increasing and then decreasing. When the Co content is 10%, the $\Delta H_A$ reaches the maximum value of 0.84J/g, but the overall value is maintained below 1J/g. The Co content has a positive effect on the austenite phase of Fe-Co alloys. The effect of the changed phase transformation enthalpy value is small. Contrary to the change trend of the $\Delta H_A$, the phase transformation enthalpy value of
martensite transformation $\Delta H_M$ first rapidly decreases with the increase of Co content and then slowly rises. When the Co content is 5%, it reaches the maximum value of 8.29J/g. And $\Delta H_M$ is maintained at between 3–9J/g, the Co content has a greater influence on the $\Delta H_M$.

4.2. Microstructure

Using scanning electron microscope and X-ray diffraction, the sintered Fe and Co powders in different proportions were subjected to mechanical alloying and static pressure forming of the samples obtained by the microstructure characterization results are shown in Fig. 7. The comprehensive analysis of sample1 and sample2 by SEM, EDS and XRD results confirmed CoFe$_{15.7}$ (Im-3m 229), Co$_3$Fe$_7$ (Pm-3m 221), and CoFe (Pm -3m 221) phase. With the increase of Co content, the proportion of each phase in Fe-Co alloy is different, thus changing the macroscopic characteristics of the alloy.

When analysed separately, the XRD results are ambiguous because the peaks corresponding to CoFe$_{15.7}$ (Im-3m 229), Co$_3$Fe$_7$ (Pm-3m 221) and CoFe (Pm -3m 221) phase. With the increase of Co content, the proportion of each phase in Fe-Co alloy is different, thus changing the macroscopic characteristics of the alloy.

When analysed separately, the XRD results are ambiguous because the peaks corresponding to CoFe$_{15.7}$ (Im-3m 229), Co$_3$Fe$_7$ (Pm-3m 221) and CoFe (Pm -3m 221) overlap each other. The low-magnification (500) SEM image shown in Figure 8 was obtained with component contrast in the backscatter mode. The contrast seen in the image indicates that there is a different phase. With the help of EDS, the approximate ratio of Fe:Co in each area determined was analysed. The Fe:Co ratios
of area I, area II and area III correspond to CoFe15.7 (Im-3m 229), Co3Fe7 (Pm-3m 221) and CoFe (Pm-3m 221) phases, respectively. Based on the graphic point scanning element analysis of the SEM image in the EDS mode, it is concluded that the phases will overlap each other after the sintering process at 1100°C.

5. Conclusion
(1) The results show that the phase transformation characteristics have changed with the increase of Co content and showed different changing trends.

(2) Through the comprehensive analysis of SEM, EDS and XRD results, CoFe15.7 (Im-3m 229) (bcc), Co3Fe7 (Pm-3m 221), and CoFe (Pm-3m 221) were determined.

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