

## Effect of Rare Earth Elements on The Sorption Characteristics of Nanostructured Zr-base Sinter Porous Getter Prepared by Mechanical Alloying

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### Abstract

The effect of rare earth (RE) elements, including Ce and La, on the sorption properties of Zr-Co getters was investigated in this work. The phase evolution, microstructural characteristics of getter powders were studied by means of X-ray diffraction method, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The nanostructured Zr<sub>3</sub>Co intermetallic compound has been produced by mechanical alloying of the elemental powder. In all mechanical alloying experiments, the ball to powder weight ratio was 15:1. The phase evolution and microstructural change of powders during mechanical alloying and activation process were investigated by means of X-ray diffraction and scanning electron microscopy. The results showed that after an optimum mechanical alloying time (16 h), the amorphous phase was produced. The result showed that after an optimum activation process the synthesized nanostructured powders show enhanced pumping properties and gas sorption response. The studies revealed that Zr-Co-RE can be activated at lower temperature than Zr-Co getters and show better sorption properties.

**Keywords:** Zirconium-Cobalt Getters; Activation; Rare Earth elements; Sorption; Mechanical alloying.

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## Introduction

In general, getters are classified in two main categories: evaporated and non-evaporated getters [1-2]. Non-evaporable getters (NEGs) have been widely used since they can be exposed to air prior to usage and can absorb gas repeatedly through activation process [3-4]. The field of possible application spans, for example, from lighting (fluorescent lamps, sodium lamps) to gas purification, vacuum thermal insulation, achievement of ultrahigh vacuum (getter pumps), etc[3-10].

NEGs are widely used to absorb the residual active gases ( $H_2$ , CO,  $CO_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ , etc.) in ultra-high vacuum systems and sealed devices [7-14]. With the advantage of suitable size, chemical sorption property and heat activation compatible with industrial bonding technologies, NEG getters are currently playing an effective role in electronic device packaging for maintaining the internal vacuum level or inert pressure. Highly porous alloys or powder mixtures of Zr, Ti, Al, V, Fe and other metals are considered as the base materials for NEG getters [4-6]. Ti, Ti-Zr-V, Zr-V-Fe or  $ZrV_2$  getters are typical NEG, which have been studied in the literature [13-18]. Recently, Zr-based materials attracted considerable interest of researchers as the getter materials. Zr-Co-RE (RE indicating rare earth elements) getter materials exhibit a wide range of gas sorption capability, low activation temperature 200–500 °C which are more suitable for general use with better safety and no environmental risks, compared with most of Zr-based getter materials [19-22].

It has been theoretically shown that RE elements can significantly affect the activation process of the getters [19-20]. The role of the rare earth elements on the sorption characteristics of the Zr-Co getter films has been studied in the literature [19-

20]. It is interesting to note that the similar studies on sorption characteristics of Zr-Co sintered porous getters have remained untouched. Moreover, a deeper understanding of the activation process and its role on the sorption characteristics of Zr-Co sintered porous getters are needed. Therefore, in order to understand the mechanism of getting process, it is necessary to examine the influence of activation conditions and RE elements on the sorption properties of the Zr-Co getters. The present work aims at investigating the effects of Ce, La and activation conditions on sorption characteristics of Zr-Co sintered porous getters.

## Experimental procedure

Commercial Zr (99.9%) and Co (99.9%) powders were prepared from Sigma Aldrich, USA. The average particle sizes of Zr and Co were 150 $\mu$ m and 200 $\mu$ m, respectively. Cerium (98%) and lanthanum (98%) bulk species were prepared from Russian, and used without additional processing. Mechanical alloying (MA) was performed in a planetary ball mill (Retsch PM 400) under a high-purity argon atmosphere (99.999%) for various times. Hardened steel vial and balls (10 mm diameter) at the ball to powder weight ratio of 15:1 were used. A mixture of powders with the composition of 77wt.%Zr-23wt.%Co and 75wt.%Zr-22wt.%Co-1.5wt.%Ce-1.5wt.%La were milled in argon atmosphere at the room temperature. Weighting, filling, and handling of the powders were performed in a glove box under the 2 bar pressure argon atmosphere. The obtained powder was pressed for 10 s by a dual hydraulic press under controlled atmosphere to form a tablet with 10 mm diameter and 1.3 mm thickness with a density of 4 gr/cm<sup>3</sup>. In this work, the getters were mounted in the

vacuum test system, pumped and degassed by mechanical and diffusion pumps to reach  $10^{-5}$  Torr by vacuum gauges. The getter was then activated at a chosen temperature in a resistance furnace and subsequently cooled down quickly to room temperature. Schematic drawing of a setup is used in this work shown in Fig. 1.

The morphological changes of powders upon mechanical alloying were studied by a TESCAN field emission scanning electron microscope (FE-SEM). X-ray diffraction (XRD) was performed using Co-K $\alpha$  radiation with a Philips X'Pert Pro diffractometer operated at 15 kV and 40 mA.

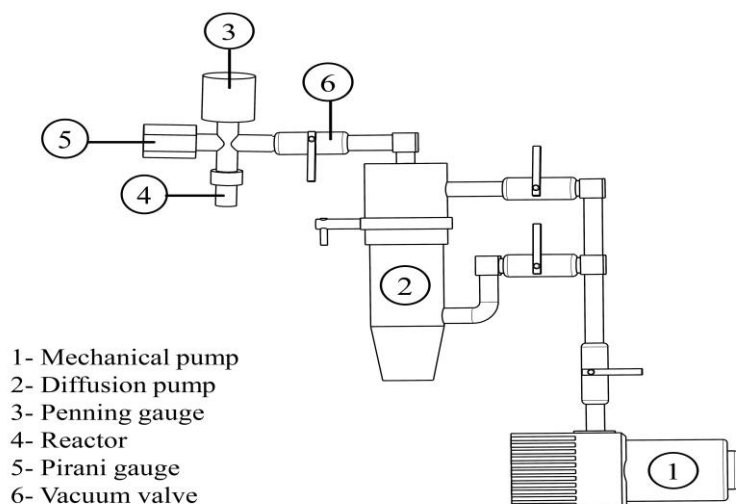


Fig1. Schematic drawing of vacuum setup system.

Activation was performed at temperature range from 280 to 330 °C for different times. Table 1 shows the activation conditions of getters. The study

of the activation conditions and the capacity of getter to maintain vacuum are the essential issues of the present work.

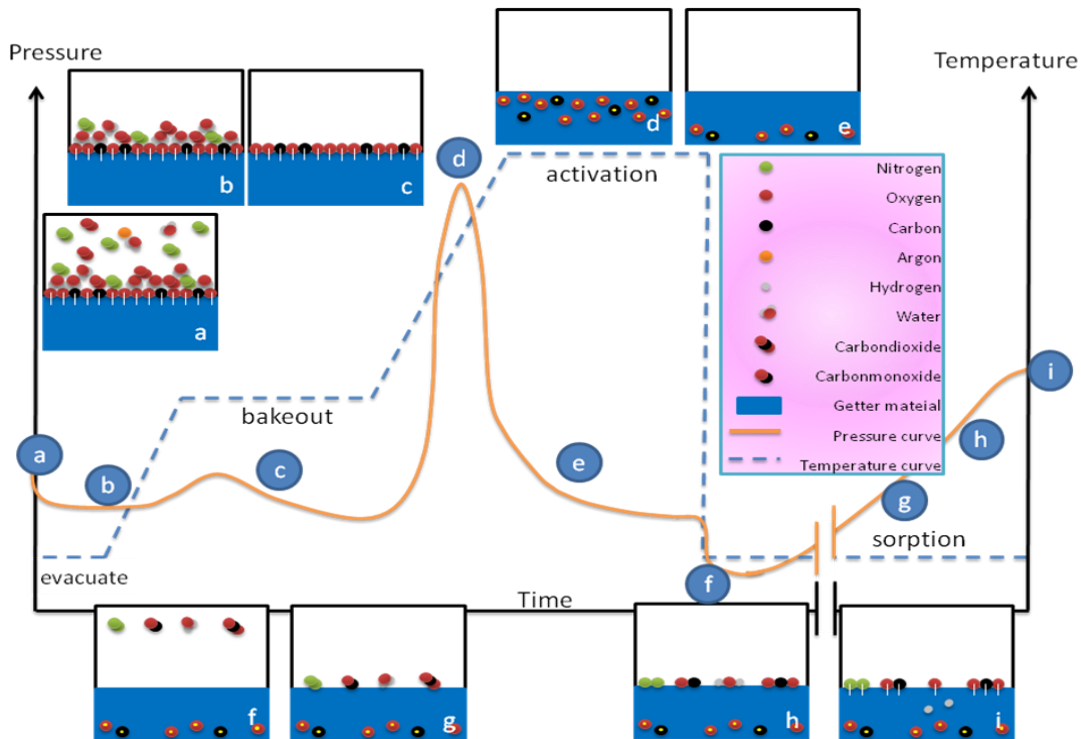
Table1. Activation condition of getters.

Code	Activation Temp. (°C)	Activation Time (min)	Composition
28020	280	20	Zr <sub>77</sub> -Co <sub>23</sub>
28040	280	40	Zr <sub>77</sub> -Co <sub>23</sub>
28060	280	60	Zr <sub>77</sub> -Co <sub>23</sub>
30020	300	20	Zr <sub>77</sub> -Co <sub>23</sub>
30040	300	40	Zr <sub>77</sub> -Co <sub>23</sub>
30060	300	60	Zr <sub>77</sub> -Co <sub>23</sub>
33020	330	20	Zr <sub>77</sub> -Co <sub>23</sub>
33040	330	40	Zr <sub>77</sub> -Co <sub>23</sub>
33060	330	60	Zr <sub>77</sub> -Co <sub>23</sub>
28020R	280	20	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
28040R	280	40	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
28060R	280	60	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
30020R	300	20	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
30040R	300	40	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
30060R	300	60	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
33020R	330	20	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
33040R	330	40	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>
33060R	330	60	Zr <sub>75</sub> -Co <sub>22</sub> -Ce <sub>1.5</sub> -La <sub>1.5</sub>

**Results and discussion**

Activation at high temperature under high vacuum is necessary for getters to obtain clean surfaces. Fig. 2 schematically shows the activation mechanism and activation curve (pressure-temperature-time curve). According to this figure, activation and sorption process can be divided into four stages: (1) Evacuation process in which gas molecules present in the chamber are evacuated (marked by a-b in Fig. 2). (2) Bake-out process in which second layer of gas molecules are disjointed from the surface (marked by b-c in Fig. 2). (3) Activation process in which the surface-adsorbed gas and bulk-dissolved hydrogen are released, and the superficial oxide layer covering air-exposed getter surfaces disappears (marked by c-d and e in Fig. 2). (4) Sorption process in which gas molecules adsorbed into the surface. This process continues until the surface of the getter is saturated (marked by f-i in Fig. 2).

The reactor's pressure during bake-out and activation process decreases continuously. However, in the presence of a getter, the reactor's pressure is increased at first and eventually decreased in the bake-out stage. Then by starting activation stage, the pressure increased suddenly, which is consequence of desorption of gases [15]. During activation, the NEG surface is progressively reduced. This is achieved by heating to a temperature high enough to decompose the oxides and to diffuse oxygen from the surface into the bulk of the getter. So, physical phenomenon that can be correlated to the reduction of the surface oxide can be used to monitor the activation process. In a sintered porous getters, the specific surface area is high and for Zr-based getter, the addition of Co causes the expansion of lattice parameters and so, increasing in bulk diffusion [19-22]. Rare earth elements can deplete oxygen from interstitial sites near Zr to enhance getter activity [19,20].



**Fig2. Schematic of activation curve (pressure-temperature-time curve) and evaluation of getter surface.**

(Fig 3) shows the activation curves of two different getters (with and without RE elements) which were activated at 280 °C for 20 min. It is of interest to see that activation temperature is decreased by adding Ce and La. This phenomenon can be well explained by the aid of thermodynamic data [19].

(Table 2) shows the free energy of formation of Ce, La, Zr and Co oxides indicating that the most stable compounds,

still more than ZrO<sub>2</sub>, are Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>. By heating the getter, dissociation of zirconium oxide is occurred and RE oxides is formed according to relation 1 and 2, which is favourite in getter activation. This fact explains decreasing of activation temperature of Zr-Co-RE getters compared to the Zr-Co getters.

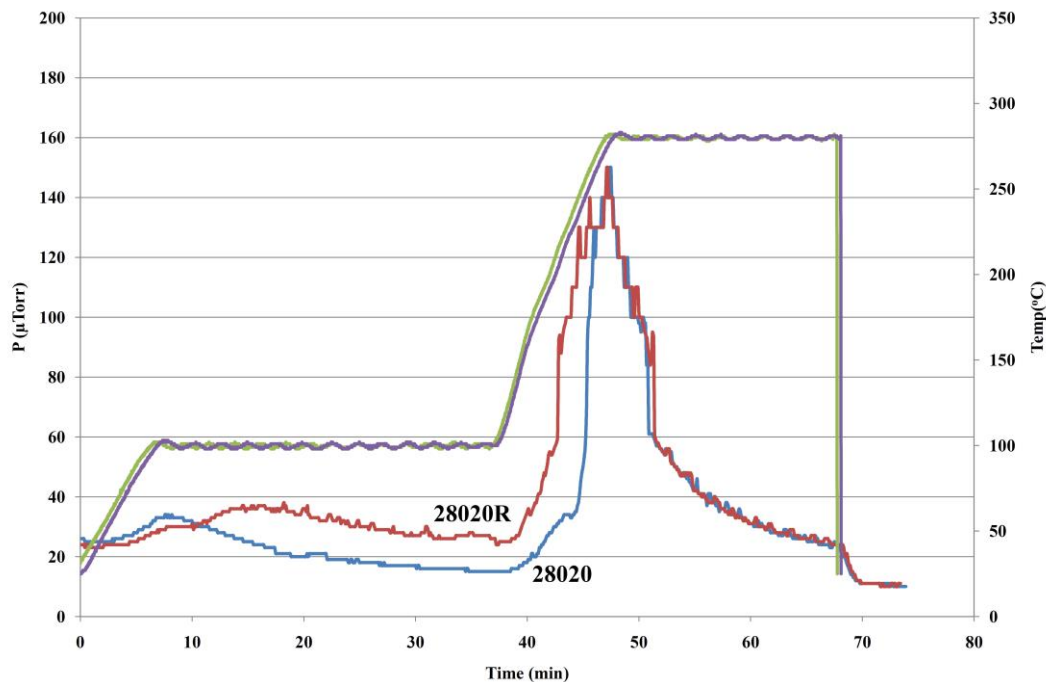
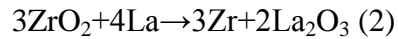
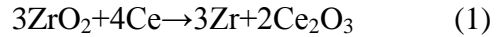


Fig3. The activation curve of two different getters which is activated in 20 min at 280 °C.

Table 2. Free energy of formation of Ce, La, Zr and Co oxides [19].

Compound	$\Delta G^\circ$ (KJ/mol)
ZrO <sub>2</sub>	-1042.8
Co <sub>3</sub> O <sub>4</sub>	-774.0
Ce <sub>2</sub> O <sub>3</sub>	-1706.2
La <sub>2</sub> O <sub>3</sub>	-1705.8

(Fig 4) shows the gas sorption properties of Zr-based getters prepared with different compositions and activation conditions. The results revealed that the gas sorption property of the getter that was

activated at 330 °C for 60 min is better than that of the getters activated at lower temperature and shorter time. The relatively higher porosity and specific surface area increase the diffusing channel

of gas molecules, which accelerates the surface gas diffusion and improves the gas sorption capacity of the getters at room temperature [18-20]. It can be observed that the gas sorption properties of the getters increase with adding of Ce and La elements. This behavior can be described by the lower Gibbs free energy of  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  in contrast to the  $\text{Zr}_2\text{O}_3$  [19]. Fig. 5 shows the morphology of Zr-Co powder milled and activated at different temperatures and times. A porous netlike metallurgical structure is formed among the particles. This porous structure provides an enough mechanical strength and increase surface area of the getters and maintains a suitable gas sorption capacity as well.

Increasing activation temperature up to 330 °C and prolonging activation time up to 60 min resulted in formation of nanostructure  $\text{Zr}_3\text{Co}$  phase as it is evident in Fig. 6. By formation of nanostructure of  $\text{Zr}_3\text{Co}$  phase the specific surface area and sorption properties are increased. It is worth mentioning that the nanoscale structure of the synthesized  $\text{Zr}_3\text{Co}$  product with grain size in the range of 10-15 nm and with numerous grain boundaries is favorable to be used as a getter. Moreover, in the nanoscale  $\text{Zr}_3\text{Co}$  intermetallic powders the real surface area increases drastically, therefore, it seems that our synthesized nanostructured  $\text{Zr}_3\text{Co}$  powders will present a high capacity for gas sorption in contrast to the crystalline  $\text{Zr}_3\text{Co}$  powders.

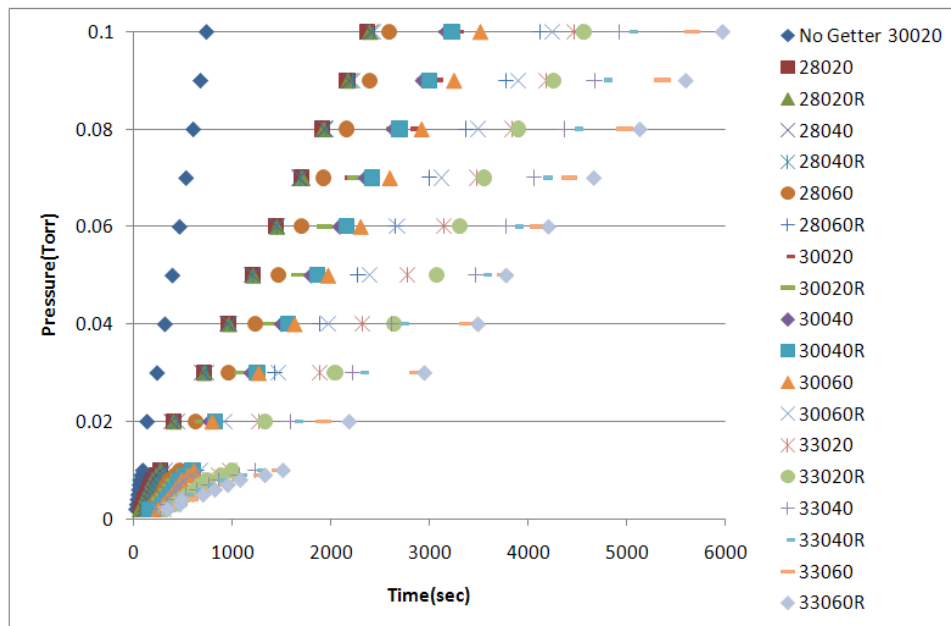


Fig4. Gas sorption property of Zr-based getters prepared in different compositions and activation conditions.

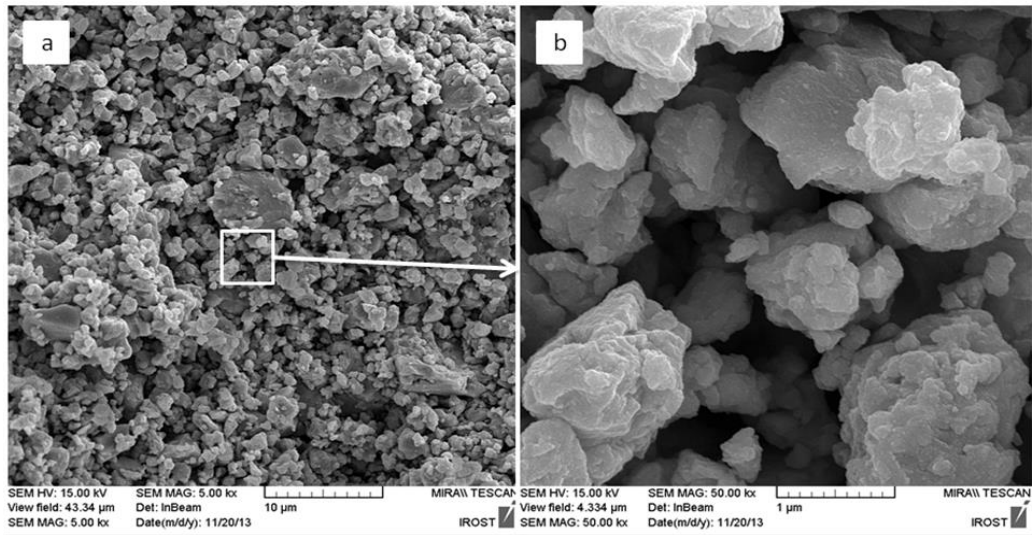


Fig5. SEM micrographs of the Zr-Co-RE getter prepared after 16hr ball mill without activation

(Fig 7) shows the XRD pattern of Zr-Co getters at different activation conditions compared to that of for 16 hr ball milled powder without activation process. As can be seen, after activation, the orthorhombic

Zr<sub>3</sub>Co phase which is favorable for absorbing hydrogen was appeared. Co enlarges the lattice parameter of Zr and in turn accelerates the rate of the diffusion process [19-20].

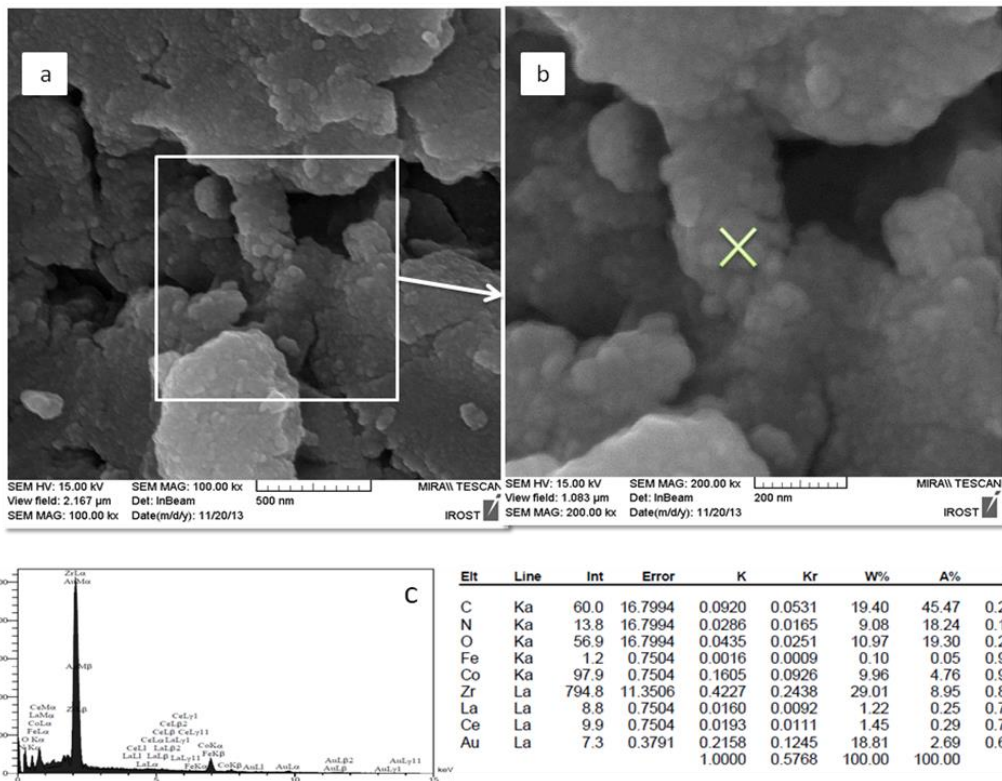


Fig6. SEM micrographs and EDS analysis of the Zr-Co-RE activated at 330 °C for 60 min.

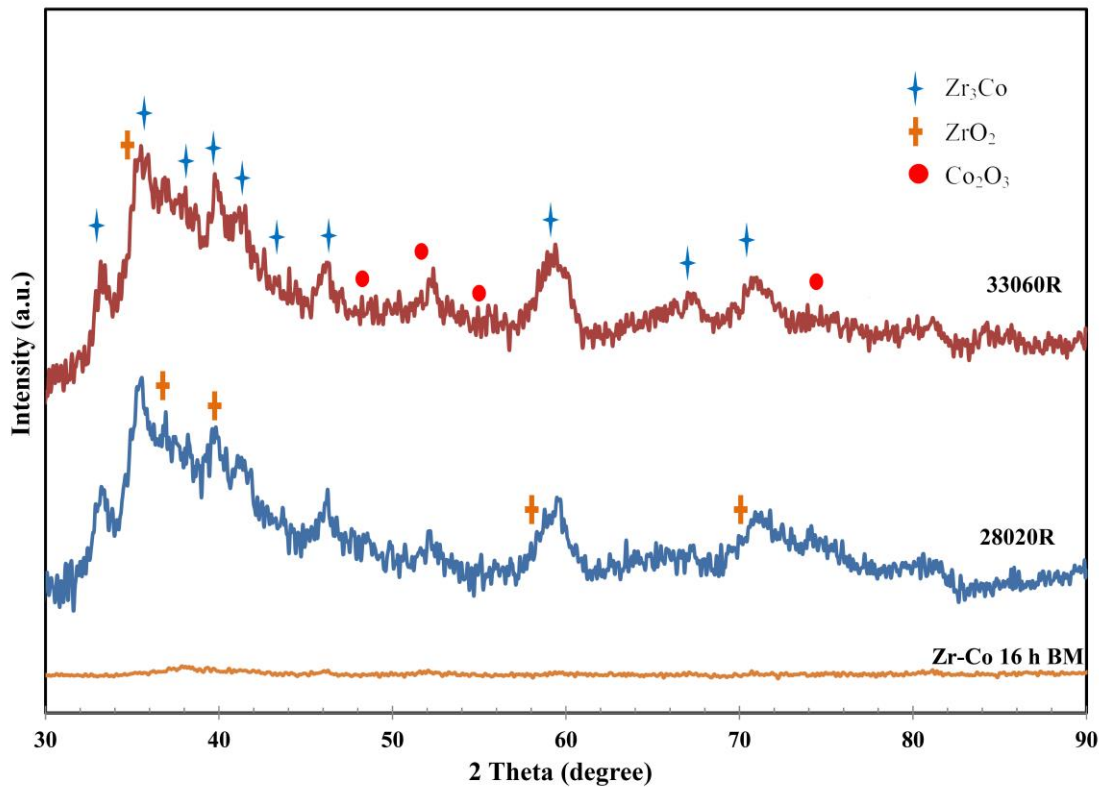


Fig7. XRD profiles of Zr-based getter at different activation condition.

It is interesting to note that nanostructure  $Zr_3Co$  can increase the specific surface area and grain boundaries which can provide fast diffusing paths. This can significantly enhance the sorption capacity of the sintered porous getters.

### Conclusions

In this study, the effects of Ce, La and activation conditions on sorption characteristics Zr-Co sintered porous getters were investigated. The following conclusions can be drawn from this study:

(1) Formation of  $Zr_3Co$  phase which is key important phase in sorption process of Zr-Co getters was observed after ball milling process and activation treatment.

(2) Formation of nanostructure  $Zr_3Co$  phase increased the specific surface area and grain boundaries which can significantly enhance the activation and sorption properties by activating the high diffusivity mechanisms of diffusion.

(3) Zr-Co-RE sinter porous getters exhibit better sorption properties and lower activation temperature in contrast to the Zr-Co one.

(4) It was shown that longer activation time and higher activation temperature improve the sorption capacity due to the microstructure modification.

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