The Non Evaporable Getters with High Throughput Pores and Chalking Resistance Applied to the Hydrogen Maser

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***Abstract*—The effect of Cr addition on the hydrogen sorption characteristics of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0~7.18) series alloys was studied in this paper. With the increase of Cr content, the hydrogen sorption kinetics of the alloy increased from 90 s to 25 s; the hydrogen sorption capacity increased from 2.19 wt% to 2.24 wt%. When x = 7.18, the alloys obtained the best comprehensive hydrogen sorption performance. The spherical powder of optimum $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy was by plasma rotating electrode process (PREP). Then a 400 liter non evaporable getter pump (NEG pump) with $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0, 7.18) spherical powder porous structure was produced. NEG pump's initial hydrogen sorption speed and total hydrogen sorption quantity in 2 hours is 478 L/s·(x=7.18) ,780 Pa·L , respectively.The hydrogen sorption characteristics of Zr-V-Cr NEG pump is better than that of Zr-V-Fe. The contribution of this work solved the contradiction between sorption performance and mechanical properties of NEG pump in the application of hydrogen maser.**

Keywords—$Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$, getters, hydrogen sorption characteristics, the hydrogen maser

I. Introduction

The global satellite navigation system is an important infrastructure for a country. It sends is a valuable information resource that can be shared by sea, land, air, space, military and civilian users Hydrogen maser is the core component of satellite navigation[1-3].They have an advantage of both having good medium and long-term frequency stability performance, such as the Very Long Baseline Interferometry (VLBI) and Square Kilometre Array(SKA)[4-5], etc. For example, both China's BeiDou and European Galileo Satellite System are equipped with hydrogen masers[6,7].The hydrogen maser need a high-vacuum environment during working.The NEG pump is very important for maintaining a high vacuum environment of the hydrogen maser[8].which can sorption the active gases affecting the vacuum degree, such as H_2, CO, O_2, H_2O, and CO_2. Therefore, the development of high-performance new getter alloys and a large hydrogen sorption quantity NEG pumps is crucial for hydrogen maser.

In this paper, a new type of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0~7.18) alloys have been studied and a new type of NEG pumps suitable for hydrogen maser with $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0~7.18) spherical powder porous structure have been developed.

II. Materials and Methods

A. Preparation of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0~7.18) series alloy samples

The alloys with nominal composition of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ *(x=0*, 1.79, 2.69, 3.59, 4.49, 5.39, 7.18*)* were prepared by arc-melting method under a high-purity argon atmosphere (99.9999%). Each composition was re-melted four times to ensure homogeneous compositions of the ingot. Then we crushed the ingots, milling by wet ball milling under a protective atmosphere to prepare alloy powder having 300 mesh in order to tset the performance of the sample.The phases in the ribbons were identified by X-ray diffraction (XRD) using Cu-Ka radiation, model D/max-2200. And the scanning speed was 2/min and the range was 20°-80°.

B. Preparation of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0,7.18) spherical powder samples

The $Zr_{56.97}V_{35.85}Fe_{7.18}$ and $Zr_{56.97}V_{35.85}Cr_{7.18}$ spherical powder were prepared by plasma rotating electrode process (PREP). The Electrode rods which were used for PREP were made by intermediate frequency induction melting furnace. The particle size range of spherical powder was composed of 325 µm.

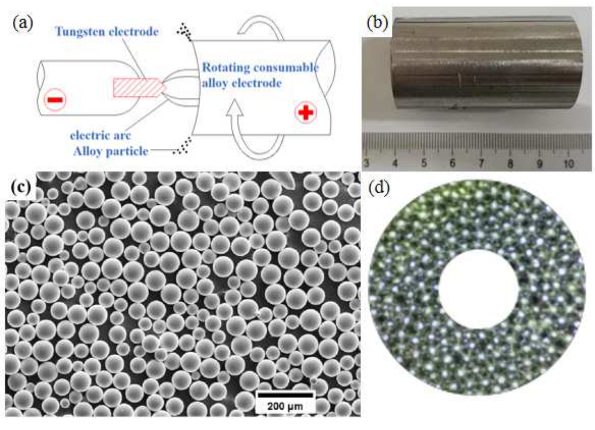

Fig. 1. Principle diagram preparing spherical powder (a), Electrode rods (b) , spherical powder (c) and spherical powder porous plate getter (d) of $Zr_{56.97}V_{35.85}Cr_{7.18}$

C. Preparation of NEG pump with $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0, 7.18) spherical powder

Placing the obtained spherical powder of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0, 7.18) spherical powder into the mold, a disc with an inner diameter of 4 mm and an outer diameter of 10 mm. Then smaples were sintered in loose installation status. The samples were prepared under 3.0×10^{-3} Pa, sintered at 850 °C for 60 min. The Zr-V-Fe and Zr-V-Cr getters with spherical powder were prepared. At the same time, equiping the plate getters into an NEG pump according to Fig. 2.

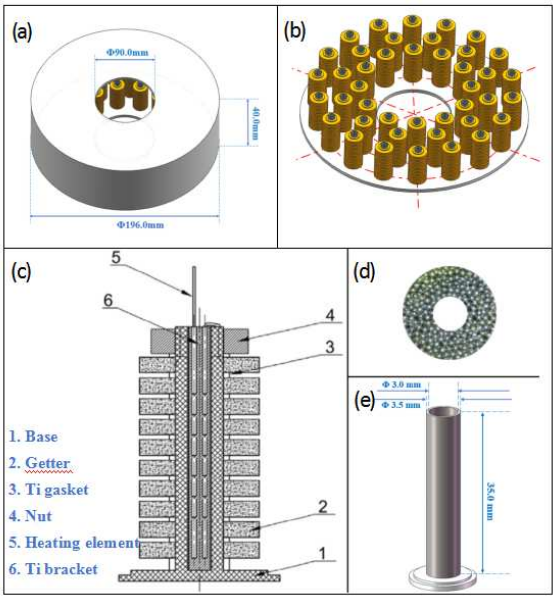

Fig. 2. Structure of non evaporable getter pump (NEG pump) (a) External structural dimensions (b) Internal structure dimensions (c) Structure of the getter unit (d) Structural dimensions of circular getter sheet (e) Structural dimensions of Ti bracket

D. Performance testing of getter and NEG pump

The sorption performance of getter and NEG pump were evaluated by constant volume method and constant pressure method. The National Standard (GB/T 25497-2010) and American Society for Testing and Materials (ASTM f798-97 (2002)) [9] stipulate that H_2 and CO can be used as test gases. In this study, the test gas of constant volume method and constant pressure method was H_2. Both methods were completed in shanghai king material technology Ltd. (Shanghai,China). The constant volume suction performance test system was JE-L1-02.

III. Results and Discussion

A. The effect of Cr addition on the gas sorption performance of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0~7.18) series alloys

The Fig. 3 shows that phase structure of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x = 0-7.18) alloys consist of α-Zr phase and C15-ZrV_2 phase. With the increase of Cr content, the hydrogen sorption kinetics of the alloy increased from 90 s to 25 s; the hydrogen sorption quantity increased from 2.19 wt% to 2.24 wt%; and the plateau pressure at room temperature decreased from 10^{-10} Pa to 10^{-13} Pa. When x = 7.18, the alloys obtained the best comprehensive hydrogen sorption performance. The $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy was not pulverized after hydrogen sorption, and the hardness of the alloy increased from 345.3 to 379.9 HV. Because the $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy has good surface hardness and was not pulverized after hydrogen sorption, it will not cause secondary pollution to the system vacuum in the hydrogen maser in the application.

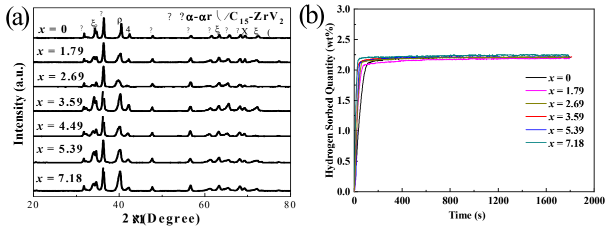

Fig. 3. Phase structure (a) and Hydrogen sorption kinetics curve (b) of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x = 0-7.18) alloys

TABLE I. Hardness of $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy before and after hydrogen sorption

Before and after hydrogen sorption	Sample Performance			
	Hardness (HV)			*Average value (HV)*
Before	347	345	352	343
After	371	383	383	379

B. The research on microstructure of optimum $Zr_{56.97}V_{35.85}Cr_{7.18}$ spherical powder

The optimum $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy with good hydrogen sorption performance and mechanical properties was prepared into spherical powders. The microstructure morphology of spherical powders has been studied. There are two areas observed from the contrast in Fig. 4 image in the $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy. Energy spectrum analysis from TABLEII shows that the white region with a large amount of Zr elements and a very small amount of V and Co elements, which indicates that it is the alpha Zr phase (α-Zr).The grey region with a large amount of V and Cr elements and a very small amount of Zr elements, which indicates that it is the AB_2-C15 phase. The Zr/V/Cr elements distribution was in a periodic pattern. Such arrangement is beneficial for the gas sorption and mechanical properties of the the $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy. Based on the analysis results of XRD, the AB_2-C15 phase in the dark region is C15-Zr$(V_{0.75}Cr_{0.25})_2$ phase.

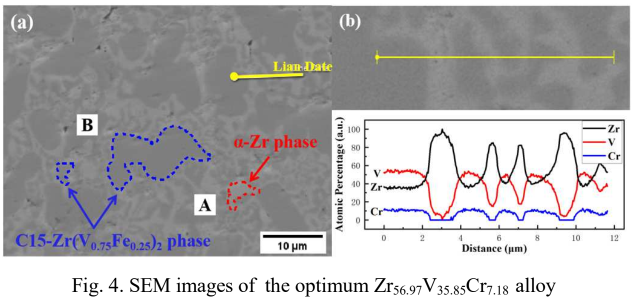

Fig. 4. SEM images of the optimum $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy

Table II. .Energy spectrum analysis of $Zr_{56.97}V_{35.85}Cr_{7.18}$ (wt%)

Region	Element Composition and phases			
	Zr (wt.%)	*V (wt.%)*	*Cr (wt.%)*	*Phases*
A (white)	96.7	3.3	0	α-Zr
B (gray)	35.2	53.8	11.0	C_{15}-Zr$(V_{0.75}cR_{0.25})_2$

This work was supported by the following projects：the National Natural Science Foundation of China (Grants No. 12373078), and Foundation strengthening Program in Technical Field of China (Grants No. 2020-JCJQ-JJ-418).

C. The research for the plate getter and NEG pump with $Zr_{56.97}V_{35.85}Cr_{7.18}$ spherical powder

The plate spherical porous getter with optimum $Zr_{56.97}V_{35.85}Cr_{7.18}$ spherical powder was synthesized by loose powder sintering method (see Fig.2d). 10 pieces porous plate getter were formed a hydrogen sorption unit(see Fig 2c). 42 hydrogen sorption units were assembled into a 400 liter non evaporable getter pump (NEG pump) with $Zr_{56.97}V_{35.85}Cr_{7.18}$ spherical powder porous structure. The hydrogen sorption characteristics of the spherical porous plate getter and NEG pump were studied respectively in Fig. 6 and Fig. 7.

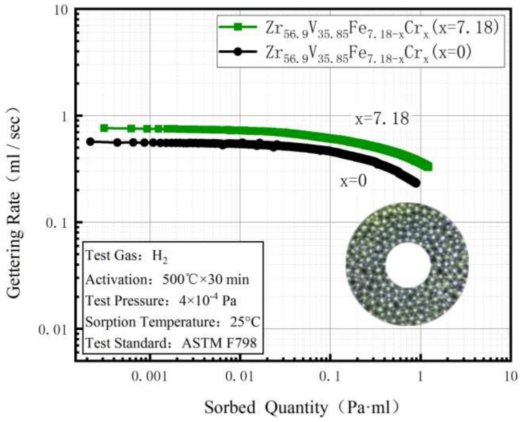

Fig. 5. The hydrogen sorption Characteristics Curves of the spherical porous plate getter.

Table III. Hydrogen sorption characteristics of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0,7.18))

Sample		Sorption Characteristics	
		Initial Rate(L/sec)	***Sorbed Quantity(Pa·L) (Total amount of 2 hours)***
Plate Getter	x=0	0.57	0.89
	x=7.18	0.76	1.23

The Fig. 5 results show that the initial hydrogen sorption rate of the spherical porous plate getter with $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x = 0, 7.18) alloys is 0.57 L/s (x = 0) and 0.76 L/s·(x = 7.18) after 773 K×30 min activation conditions respectively.The total hydrogen sorption in 2 hours is respectively 0.89 Pa·L (x = 0) and 1.23 Pa·L (x = 7.18) under the same activation conditions.It is very obvious that the the hydrogen sorption performance of Zr-V-Cr alloy is better than that of Zr-V-Fe alloy.

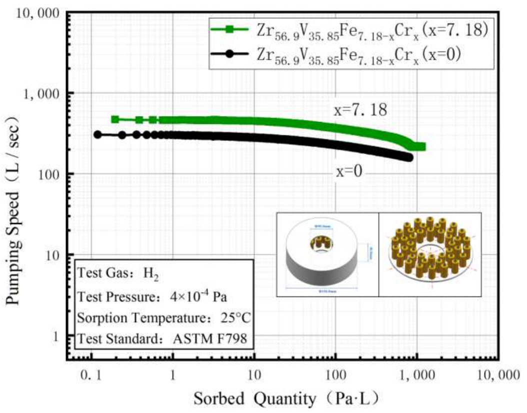

Fig 6. The hydrogen sorption Characteristics Curves of NEG pump

Table IV. Sorption Characteristics($Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x=0,7.18))

Sample		Sorption Characteristics	
		Initial Rate(L/sec)	***Sorbed Quantity(Pa·L) (Total amount of 2 hours)***
NEG pump	x=0	305	568
	x=7.18	478	780

Fig. 6 show that the initial hydrogen sorption rate of NEG pump with $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x = 0,7.18) alloys is 305 L/s·(x = 0) and 478 L/s (x = 7.18), respectively. The total hydrogen sorption in 2 hours is respectively 568 Pa·L (x = 0) and 780 Pa·L (x = 7.18) . These test results show that the hydrogen sorption performance of Zr-V-Cr NEG pump is better than that of Zr-V-Fe NEG pump.

IV. Conclusions

With the increase of Cr content, the hydrogen sorption kinetics of the alloy increased from 90 s to 25 s, the hydrogen sorption quantity increased from 2.19 wt% to 2.24 wt%. The phase structure of $Zr_{56.97}V_{35.85}Fe_{7.18-x}Cr_x$ (x = 0-7.18) alloys consist of α-Zr phase and C15-Zr $(V_{0.75}Cr_{0.25})_2$ phase.

The $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy has good surface hardness and strength after hydrogen sorption. The initial hydrogen sorption speed is 478 L/s·(x=7.18) with NEG pump with $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloys respectively. The total hydrogen sorption quantity in 2 hours is 780 Pa·L The $Zr_{56.97}V_{35.85}Cr_{7.18}$ alloy was not pulverized after hydrogen absorption, and the hardness of the alloy increased from 345.3 to 379.9 HV.The hydrogen sorption Characteristics of Zr-V-Cr NEG pump is better than that of Zr-V-Fe NEG pump.

Acknowledgment

This work was supported by the following projects: the National Natural Science Foundation of China (Grants No. 12373078), and Foundation strengthening Program in Technical Field of China (Grants No. 2020-JCJQ-JJ-418).

Uthors gratefully acknowledge the support from the Instrumental Analysis & Research Center, Shanghai University.ShangHai King Material Technology Ltdthe National Natural Science Foundation of China and Foundation strengthening Program in Technical Field of China

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