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RESEARCH ARTICLE

PREPARATION AND PORE STRUCTURE OF NI-CR-MO-CU FIRST ORDER GRADIENT POROUS MATERIALS

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ABSTRACT

The support of Ni-Cr-Mo-Cu porous material was prepared by the activation reaction sintering method using Ni, Cr, Mo and Cu element powders as raw materials, and then by brushing the element powders with different particle sizes on the surface of the support, after vacuum sintering, Ni-Cr-Mo-Cu gradient pore size porous material was obtained. Phase composition, morphology, element distribution and pore structure parameters were tested by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Electronic Differential System (EDS), pore size tester and other test methods were used to characterize. The results show that the Ni-Cr-Mo-Cu gradient porous material membrane layer is relatively complete and the elements are evenly distributed. The maximum pore size of the matrix is 13.3 μm , and permeability is 96.3 $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{KPa}^{-1}$. When the D_{50} of the brushed powder is 20 μm , the maximum pore size of the first order gradient pore size porous material is 10.4 μm , the permeability is 83.7 $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{KPa}^{-1}$. Compared with the matrix material, the permeability of the first order gradient porous material decreased by 13.1%, and the filtration accuracy was improved on the basis of retaining high permeability.

KEYWORDS

Ni-Cr-Mo-Cu, porous material, pore structure, permeability, filtration accuracy

1. INTRODUCTION

Porous materials have both metallic structure and excellent pore function of porous materials. Compared with ceramic porous material, it has the characteristics of higher specific strength, and is extensive used in chemical industry, metallurgy, medicine, aerospace and other fields (Zhou et al., 2023; Okulov et al., 2023; Wu et al., 2020; Dutta and Roy, 2023; Chen et al., 2023). At present, the filtration of porous metal materials in harsh environments has received much attention, but there are still some problems such as low filtration accuracy and small permeability. Studies have shown that gradient porous materials can effectively improve filtration accuracy on the basis of maintaining a good permeability (Ji et al., 2020). Therefore, the research and application of gradient porous materials are now the focus of research.

A group researcher used 48-75 μm Al and Ti powder as raw material to prepare TiAl first order gradient porous material by activation reaction sintering method (He et al., 2010). Through the experiment, it can be concluded that when the membrane layer is increased to 20 μm , the maximum pore size decreases from 34.07 μm to 8.08 μm , and the permeability decreases by 18.6%, which can effectively improve the filtration precision. A group researchers prepared porous Ni-Cr-Fe support by reactive powder synthesis method, then mixed low-particle size Ni, Cr and Fe uniformly on the support surface, and prepared gradient porous Ni-Cr-Fe alloy by vacuum sintering (Wu et al., 2019). The influence of film thickness on film permeability was studied. Through the experiment, it can be concluded that when the thickness of the first order gradient membrane is 80 μm , and the second order gradient membrane thickness is 30 μm , the maximum pore size is 6 μm , the permeability is 936 $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{KPa}^{-1}$,

and the permeation flux is better, and the filtration accuracy is higher. A group researcher prepared FeAl intermetallic compound porous materials with quasi-continuous gradient and discrete gradient by using pore-forming agents, and tested the pore structure properties of the two materials (Lazinska et al., 2015). The experiment resulted in the following conclusions that the permeability of the quasi-continuous gradient porous materials was nearly two times higher than that of the porous materials with discrete gradient. However, the above materials do not have good corrosion resistance, unable to cope with strong acid or strong alkali environment, in order to make materials, especially a variety of expensive materials can achieve its filtration performance in a variety of environments, and easy to use after recycling, the preparation of corrosion resistant filtration materials has become a hot spot.

The main types of Ni-Cr alloys are Inconel series, Corronel series, Cr30Ni70 and so on. Cr20Ni80 is the first Ni-Cr alloy to be used, which has a high temperature oxidation corrosion resistance, corrosion resistance in oxidizing acids is much higher than Monel alloy, and it is very stable in organic media (Sun et al., 2022). Inconel alloy is a kind of complex multicomponent alloy, which not only has the ability to resist oxidation corrosion at high temperature, but also has high mechanical properties. Ni and Cu can form continuous solid solutions, and the typical Ni-Cu alloy is Monel alloy (Dai et al., 2013). It combines the corrosion resistance of Ni and Cu. This series of alloys has high corrosion resistance in halogen elements, neutral aqueous solutions, strong alkali solutions and moderate temperature hydrochloric acid, sulfuric acid, phosphoric acid. It is particularly resistant to corrosion in hydrofluoric acid, and its corrosion resistance is second only to platinum and silver. Ni-Mo alloys have excellent corrosion resistance to strong reducing media, especially

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hydrochloric acid (Mousari et al., 2016). Ni60Mo20Fe20 is the earliest Ni-Mo alloy developed, and then there is the alloy Ni65Mo28Fe5V, which is resistant to boiling HCl, H₂SO₄ and HF corrosion.

Typical Ni-Cr-Mo alloys are Hastelloy series alloys and Chromet series alloys without W (Liu et al., 2022). This kind of alloy has a high resistance to chloride and acid corrosion. HastelloyC is resistant to various concentrations of hydrochloric acid and hydrofluoric acid at room temperature, moreover the corrosion resistance of hydrochloric acid at 70°C is also better than that of HastelloyA and Chromet3. The corrosion resistance of this alloy at 65°C is better than that of HastelloyC in the mixed medium of hydrochloric acid and nitric acid. In addition, there are a variety of corrosion resistant alloys stainless steel, as well as titanium alloy, aluminum alloy and so on. Among them, the most used is a variety of stainless steel, such as ferritic stainless steel, martensitic stainless steel, austenitic stainless steel, duplex stainless steel, precipitation hardening stainless steel and so on. These types of alloys have poor corrosion versatility, and only have good corrosion resistance in certain medium environments. Low-carbon alloy steel with good corrosion resistance, as it is now relatively mature, primarily includes: low-carbon alloy steel with atmospheric corrosion resistance, salt water corrosion resistance, sulfuric acid dew point corrosion resistance, and with sulfur corrosion resistance.

In summary, Ni-Cr alloy has good corrosion resistance in oxidizing media, while Ni-Cu and Ni-Mo alloys have excellent corrosion resistance in reducing media. In the metal nickel, the Ni-Cr-Mo alloy with Cr and Mo still has a single-phase austenitic structure, and shows excellent comprehensive corrosion resistance, not only in the oxidizing medium, but also in the reducing medium has excellent corrosion resistance. Especially in the oxidizing acid containing F, Cl plasma, in the oxidizing acid or oxidizing agent with a solution of reducing acid, in the oxidizing acid and reducing acid mixed acid, in the wet chlorine and chlorine-containing aqueous solution, it has excellent corrosion resistance that other corrosion resistant alloys are difficult to compare.

Ni-Cr-Mo-Cu quaternary alloy is designed on the basis of summing up empirical rules. It has excellent corrosion resistance and can adapt to strong acid and alkali environment, and is expected to be used for filtration and separation in harsh environment in metallurgical process. A group researchers prepared Ni-Cr-Mo-Cu porous alloys with Cr content difference by activation reaction, and soaked them with dense Ni and dense Cu in 30wt% H₃PO₄ solution (Yang et al., 2021). The results show that the mass loss rates of Ni-Cr-Mo-Cu porous materials with 10% and 30% Cr content are 0.0651wt% and 0.32wt%, but the mass loss rates of dense Ni and dense Cu are 1.64wt% and 3.58%. This indicates that compared with Cu and Ni, porous Ni-Cr-Mo-Cu has better corrosion resistance in acidic medium solution. A group researchers also pointed out that Ni-Cr-Mo-Cu dense alloy can produce a thick passivation film in high concentration of acid, showing good corrosion resistance (Pan and Yang, 2011). However, there are few researches on the filtering function of Ni-Cr-Mo-Cu porous materials in harsh environment.

In this paper, Ni, Cr, Mo, Cu powder is used as raw material to prepare porous material support by activation reaction sintering (previous studies have shown that the pore structure is optimal when Cr content reaches 30% (Xide et al., 2021). Then the first order gradient Ni-Cr-Mo-Cu porous material was prepared by vacuum sintering with the same proportion of elemental powder with different particle sizes. The preparation method of gradient membrane was systematically studied, the influence of first order gradient on filtration accuracy and permeability was compared and analyzed. The ultrasonic seismic performance of first order gradient porous materials was characterized, which provided experimental basis for the application of graded Ni-Cr-Mo-Cu porous materials.

2. EXPERIMENT

The powder mass ratio of each element w(Ni): w(Cr): w(Mo): w(Cu) = 55:5:10:5 is evenly mixed by the roller ball mill with high purity and particle size of 38~74 μm, and green compact with dimension of Φ25 mm × H4 mm was pressed at 60 Mpa and then sintered in vacuum sintering furnace to obtain the support material of porous Ni-Cr-Mo-Cu.

Ni, Cr, Mo and Cu powders with the same composition ratio and particle size of 18-23 μm were uniformly brushed on the surface of porous support bodies, sintered at 1100 °C and held for 2 h to obtain a first order gradient porous material, labeled as 1# sample. The phase, morphology, element distribution and pore structure properties of Ni-Cr-Mo-Cu porous materials with first order gradient were characterized by XRD SEM, EDS and pore size tester (FBP-III). The seismic performance of the sample was analyzed by ultrasonic instrument. After the sample was cleaned and fully

dried, the ultrasonic shock test was carried out for 30 h. After 30 h, using SEM, determine the surface morphology of the treated sample.

3. RESULTS AND DISCUSSION

3.1 Phase Analysis

Figure 1 shows the XRD patterns of different samples after vacuum sintering. As seen in the diagram, the phase composition of the support body after vacuum sintering is Ni, NiCu and Cr_{1.12}Ni_{2.88}, and the phase composition of 1# is the same as that of the matrix, and the diffraction peaks of the two samples do not shift significantly, which means that the film layer of the gradient pore size sample is consistent with the surface composition of the matrix.

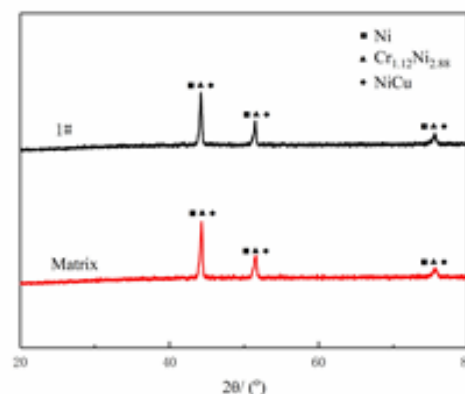


Figure 1: XRD patterns of different samples after vacuum sintering

3.2 Matrix Preparation

The surface morphology of Ni-Cr-Mo-Cu support body is shown in Figure 2. As illustrated in Figure 2 (a), Pores of the matrix is smooth and distributed tightly with obvious pore structure and well-connected sintering neck without cracks. The surface of the sample is flat because the sample is formed by pressing before sintering. The average gradient measured by the instrument is 13.3 μm, and the permeability is 96.3 m³·m⁻²·h⁻¹·KPa⁻¹. As demonstrated in Figure 2 (b), the pores are abundant and evenly distributed, and there is no phenomenon of local fracture stratification, which lays the foundation for good filtration permeability. The abundant through hole structure is one of the necessary conditions for maintaining high permeability.

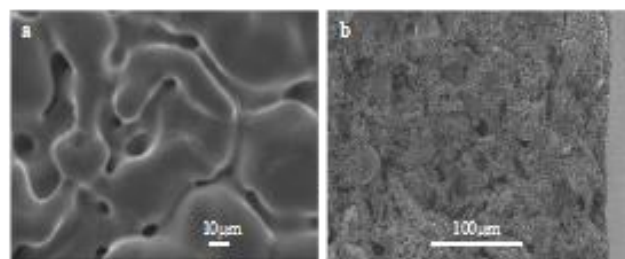


Figure 2: SEM images of Ni-Cr-Mo-Cu porous material matrix (a) Surface ; (b) Cross-section

3.3 Preparation of The Film Layer

3.3.1 First Order Gradient Pore Size Ni-Cr-Mo-Cu Porous Material

To examine the influence of first order gradients on material filtering performance, the first order gradient porous membrane was prepared by brushing Ni, Cr, Mo, Cu powder with a median diameter of D50 with 20 μm, respectively. Through testing, the pore structure parameters of first order gradient porous material and matrix are listed in Table 1.

Table 1: Main pore structure parameters of the first order gradient Ni-Cr-Mo-Cu porous material and matrix

Sample	Permeability m ³ ·m ⁻² ·h ⁻¹ ·KPa ⁻¹	Maximum pore size /μm
Matrix	96.3	13.3
1#	83.7	10.4

Table 1 suggests that, when compared to the support body, the permeability and maximum pore size of the 1# sample changed only slightly. The permeability decreased from $96.3 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{KPa}^{-1}$ to $83.7 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{KPa}^{-1}$, a decrease of 13.1%, and the maximum pore size decreased to $10.4 \mu\text{m}$. Figure 3 shows the SEM surface and side morphology of 1# sample. It can be seen from Figure 3 that the pores are abundant and evenly distributed, the pore structure is complete, and the pore size is slightly small. And the film thickness of sample 1# is about $20 \mu\text{m}$, and the surface coated film layer can be clearly seen, and the pore diameter of the film layer is smaller than that of the support body. The combination of the film layer and the support body is well, and the thickness of the film layer is uniform.

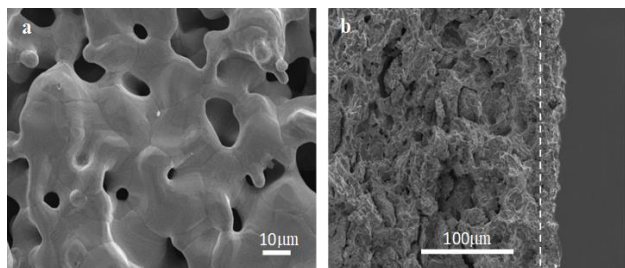


Figure 3: SEM images of sample 1# (a)Surface; (b) Cross-section

Figure 4 is the line scan energy spectrum of 1# sample. It can be seen from the figure that Ni, Cr, Mo and Cu elements are well diffused on the surface of the sample film layer, and the four elements are alternately diffused and evenly distributed. Figure 5 shows the side morphology and energy spectrum analysis diagram of the first order gradient porous material, and Figure 5 (a), (b), and (c) represent the energy spectrum analysis results at positions 1, 2, and 3 of the morphology respectively. The C element in the

figure is caused by a small amount of carbon deposited in the vacuum furnace. There is little difference in element content, indicating that the coating of first order gradient film does not affect the composition of the material.

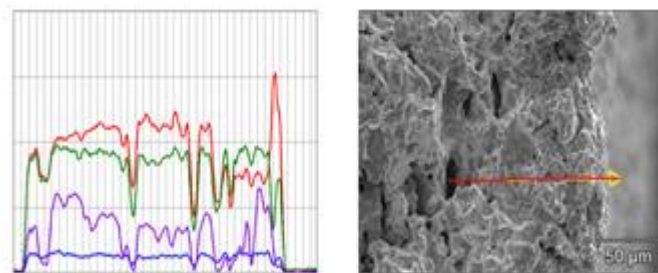


Figure 4: 1# sample linear scanning spectrum diagram

3.3.2 Seismic Performance

Seismic performance analysis is significant for testing mechanical properties of porous materials. After ultrasonic cleaning, the 1# sample was subjected to ultrasonic shock test for 30 h, and then characterized by scanning electron microscopy. The results showed that following the test, the boundary between the sample film layer and the substrate was obvious, and no phenomena such as film collapse, or fracture occurred. The maximum pore diameter of sample 1# was $10.2 \mu\text{m}$ and the permeability was $83.1 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{KPa}^{-1}$. Pore structure parameters of sample 1# did not change significantly before and after the experiment, indicating that the filtration performance of sample 1# was relatively stable. The experimental results show that the Ni-Cr-Mo-Cu porous material membrane with first order gradient pore size is closely bonded to the matrix, and the bonding strength is good.

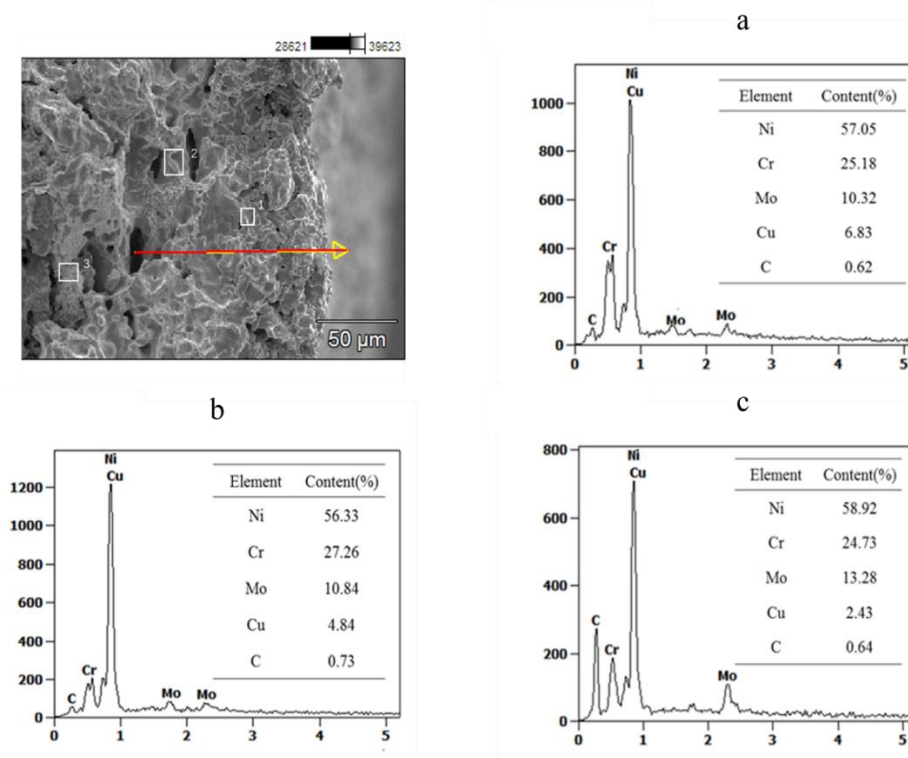


Figure 5: 1#The cross-section morphology and energy spectrum analysis diagram of the sample

4. CONCLUSION

The first order gradient Ni-Cr-Mo-Cu porous material with the same ratio and different particle sizes was obtained after vacuum sintering. The phase, morphology, element distribution and pore structure parameters of the Ni-Cr-Mo-Cu porous material were investigated, and the following findings could be drawn:

Ni-Cr-Mo-Cu porous material support was prepared by activation reaction sintering method. The support structure is complete, the permeability is good, and the average pore diameter is $13.3 \mu\text{m}$, the permeability is $96.3 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{KPa}^{-1}$.

The gradient pore size porous material was prepared by brush coating. When the median diameter D50 of the powder coated is $20 \mu\text{m}$, the membrane structure of the first order gradient porous material obtained is complete, the maximum pore diameter is $10.4 \mu\text{m}$, the permeability is $83.7 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{KPa}^{-1}$, and the permeability is reduced by 13.1%.

The gradient pore size porous material was prepared by brush coating. When the median diameter D50 of the powder is $20 \mu\text{m}$, the porous material with first order gradient pore size is obtained. The ultrasonic shock test of the sample with first order gradient pore size is carried out for 30 h. The results indicate that the adhesion between the film layers and that of the sample with a first order gradient is good.

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