

Investigation on the preparation and mechanical properties of porous Cu₃₅Ni₁₅Cr alloy for a molten carbonate fuel cell

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The preparation process of porous Cu₃₅Ni₁₅Cr alloy was studied in this paper. The effect of ball milling time and sintering temperature on the porosity of Cu₃₅Ni₁₅Cr alloy was identified. It was found that 18 h ball milling and 950 °C sintering are the most promising parameters for the preparation of porous Cu₃₅Ni₁₅Cr alloy. The products have a ~62 % porosity. The alloy consists of an α phase and β phase. The influence of deformation temperature and loading rate on the mechanical properties of Cu₃₅Ni₁₅Cr alloys was investigated. The results show that with decreasing deformation temperature, the yield strength and elastic modulus of the porous alloy increase. With the increase of loading rate, the yield strength of these alloys shows an increasing trend, but the elastic modulus is on a steady level.

Keywords: molten carbonate fuel cell; Cu₃₅Ni₁₅Cr alloy; porosity; preparation; compression test

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1. Introduction

The molten carbonate fuel cell (MCFC) is one of the most promising energy conversion devices which transforms the chemical energy into electric power. Zero pollution, high efficiency of power generation, and recycle use of exhaust heat are the main advantages that make MCFC attractive for a variety of applications [1]. Anode is an important component of the MCFC. Due to the excellent permeability and existence of pores, the porous metals are widely used in the electrode pole of the fuel cells. The pores provide channels for the movement of free electrons and fuel gas [2]. The anode of MCFC is now mostly made from porous nickel based alloys. Yet the scarcity of nickel resources has hindered the wide use of those MCFCs. Copper, a kind of cheaper anode material which can replace nickel, has been explored and found to be a more suitable material. Copper alloys, with their combination of high thermal conductivity and acceptable mechanical strength and toughness over a wide range of temperatures, are likely the best candidates for complex structural applications

subjected to conditions of extreme heat flux under load. It has been reported that the addition of nickel into a copper anode could improve the electrochemical properties. It also has been found that adding Cr can improve the high temperature performance of the alloys dramatically, including the corrosion resistance and creep resistance [3]. Because of good conductivity and sintering properties, the porous CuNiCr alloy is considered to be an ideal material for the anode of MCFCs.

Since the electrodes need to be cooled with gas, thermal shocks may happen at the electrolyte/anode interface. In addition, the porous alloys employed for structural components in MCFC applications are often subjected to compression loads and high temperature simultaneously. The interaction of compression load and high temperature may lead to intense stress concentration in the components of porous alloy. Such a concentration of stress around the pore often results in catastrophic failure of the components [4]. Due to these concerns, investigations aiming at increasing the heat-resistance of metallic alloys are immediately needed. However, the current studies on MCFC anode materials are mainly aimed at the porous Ni alloy [5–12]. Thus, it is noted that despite the fact

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that porous Cu alloys are attractive materials for MCFCs, few papers focus on the mechanical properties of porous Cu alloy in high temperatures and only limited data are available in the literature. The factors affecting the high temperature properties of porous CuNiCr alloy have not been previously reported. Based on this situation, in order to provide a theoretical basis for the application of porous CuNiCr copper alloy in MCFC as anode materials, a novel porous alloy Cu₃₅Ni₁₅Cr (35 wt.% of Ni and 15 wt.% of Cr) has been prepared on the basis of concepts and results of earlier works [13–17]. Attention was focused mainly on elucidating the influence of ball milling time and sintering temperature on the porosity in this alloy. The effect of deformation temperatures and loading rates on the compressive mechanical properties in this alloy was also identified.

2. Materials and methods

The microstructures of powders and alloys were determined using a field emission scanning electron microscope (FE-SEM), equipped with an energy dispersive X-ray spectrometer (EDX) to measure the element concentration. The concentration data were obtained using a 20 kV and 15 mA beam. The porosity values of alloys were measured using the Archimedes principle (ASTM, C373-72). The mechanical properties of cylindrical samples (Φ 8 mm \times 12 mm) were assessed by compression tests at high temperatures in a RDL05 electronic creep-fatigue testing machine. In order to ensure uniform heating of samples, after achieving the experiment temperature, the samples were soaked for 30 min, then the data began to be collected. For each condition 3 samples were deformed. Before the experiments, the samples were carefully polished.

3. Preparation of porous CuNiCr alloys

Porous Cu₃₅Ni₁₅Cr alloys were fabricated by powder sintering using the pre-alloyed powders. Both the carbonyl Ni powders of average diameter

3 to 4 μ m and Cr powders with average particle size of 5 to 8 μ m, which were near spherical, and air atomized Cu powder, having a mean particle size of 25 to 35 μ m, were used as raw materials. The schematic preparation process is shown in Fig. 1.

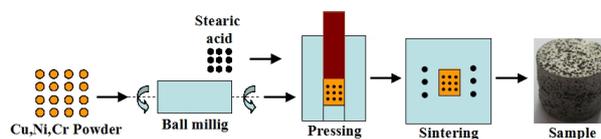
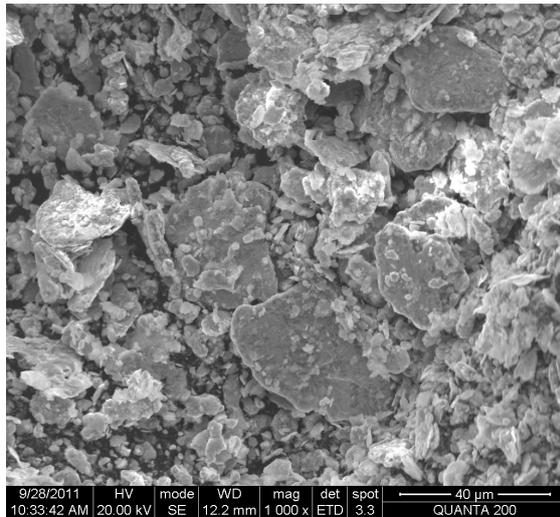


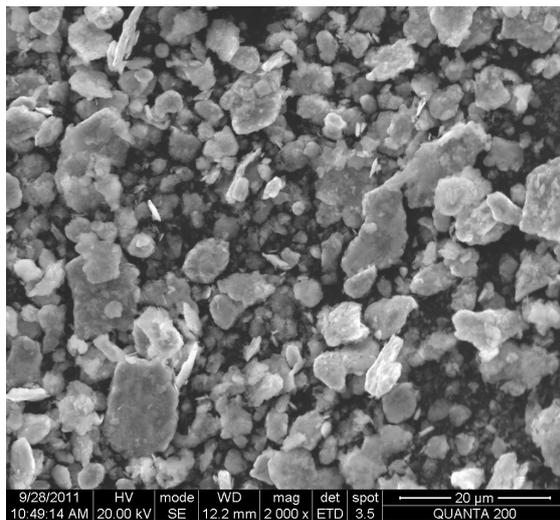
Fig. 1. The schematic preparation process of porous alloy.

Carbonyl Ni powders, Cr powders and air atomized Cu powder were mixed first in a dry air condition by high energy ball milling at four different mixing times: 6 h, 12 h, 18 h and 24 h. After the mixing, SEM observations were performed. Microstructure images of the mixed powders are given in Fig. 2. The powders obtained after 6 h mixing (Fig. 2a) have a flake shape. After 12 h mixing, the size of the particles has been constantly refined and the particle began rounding. However, the size distribution is nonuniform. After 18 h milling, the shape of mixed powders (Fig. 2b) appears to be uniform. With the further increase of milling time, the morphology of the powders has not changed too much, implying that 18 h is long enough for this ball milling procedure.

Mixed powders were then blended with 3 % stearic acid as a pore forming agent and then loose packed into a graphite mould with a diameter of 12 mm and height of 15 mm. The green samples were subsequently heated at controlled temperatures to remove the stearic acid and finally sintered in a tube furnace in hydrogen environment to avoid oxidation. The thermo-gravity measurement conditions were as follows: a heating rate of 5 °C/min in H₂ gas environment with gas flow of 50 mL/min. In this experiment, the temperature was set at 300 °C, which ensured the highest decomposing rate of stearic acid. In order to evaluate the effect of sintering temperature on the porous alloy, the sintering temperatures were set to different levels, 850 °C, 950 °C, 1050 °C. The whole heating schedule was plotted in Fig. 3.



(a)



(b)

Fig. 2. SEM images of mixed powder after different ball milling times: (a) 6 h, (b) 18 h.

4. Results and discussion

4.1. Effect of ball milling time

During sintering of mixed powders, the homogenization of the powders can largely decide about the extent of the sintering shrinkage, thus, has an important effect on the pore size and porosity of porous metal materials. Fig. 4 shows the effect of ball milling time on the porosity of porous alloy at different temperatures. As can be seen from the graph, for all testing temperatures, the ball milling

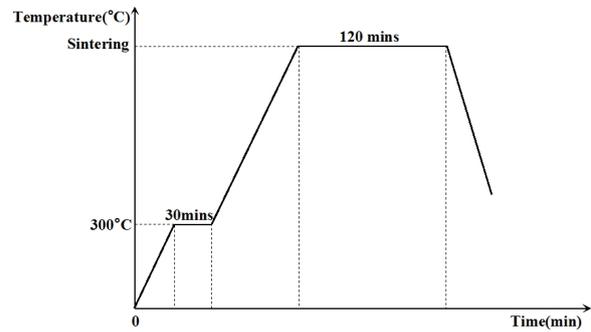


Fig. 3. The heating schedule for the preparation of CuNiCr porous alloy.

time had a great impact on the porosity. With the increase of milling time, the porosity of alloys increased. When the ball milling time was 18 h, the porosity of sintered powder product reached the peak. With further increase of the time to 24 h, results entered the decline stage. The reason is that if the ball milling time is not long enough, the particle size is relatively large, and Ni powder and Cr powder are nonuniformly dispersed in the flaky Cu matrix. With an increase of milling time, the particle size of the powder decreases, and powder sedimentation rate decreases sharply. This may result in a decrease in the bulk density and an increase in porosity. With increasing the milling time to 18 h, the porosity reached about 60 %. When the milling time was extended to 24 h, the alloy powders became very fine, the specific surface area increased, the sintering activity of the powders improved. This could result in an increase in the sintering shrinkage speed and a decrease in porosity. In addition, three trend lines at the temperatures of 850 °C, 950 °C and 1050 °C are almost parallel to each other, but the difference of the porosity value for each temperature is apparent. It implies that the sintering temperature has a significant influence on the porosity in this alloy.

4.2. Effect of sintering temperature

Sintering temperature is one of the most important factors that affects the mechanical properties of porous alloy. Research on the influence of sintering temperature on porosity in porous alloys is urgently needed. The porosity as a function of

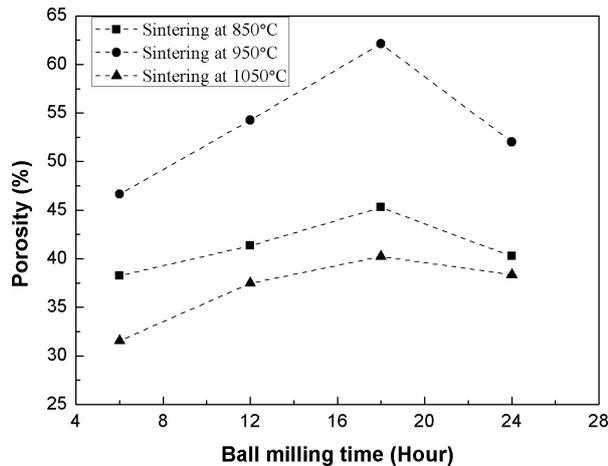


Fig. 4. The effect of ball milling time on the porosity of porous alloy at different temperatures.

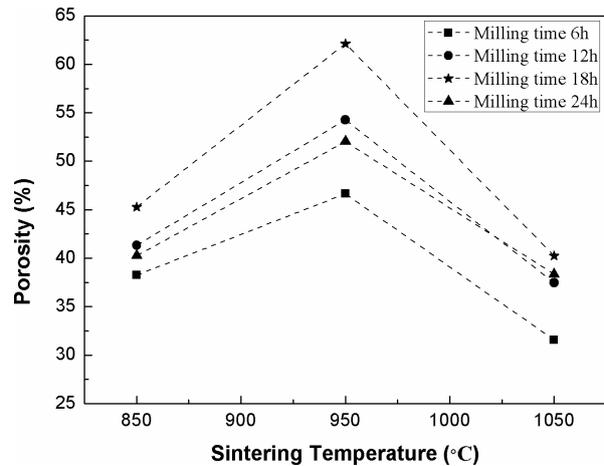


Fig. 5. The effect of sintering temperature on the porosity of porous alloy at different ball milling times.

sintering temperature is depicted in Fig. 5. Four series of porosity measurements with different ball milling times were performed. As can be seen from the graph, the sintering temperature has a profound influence on the porosity value. With an increase of sintering temperature, from 850 °C to 950 °C, the porosity of the four alloys increases. With a further increase of the sintering temperature, from 950 °C to 1050 °C, the porosities decrease sharply. The reason is that upon heating at 850 °C, a sintering neck was gradually formed and certain amount of pores appeared. When sintering temperature raised to 950 °C, due to the improvements of grain boundary diffusion and particle surface diffusion, plenty of voids were formed, which resulted in a higher porosity than that at 850 °C sintering. Further increase in the temperature to 1050 °C, caused that the diffusion ability of metal atoms was further enhanced, sintering neck grew very fast, the diameter of pores decreased or the pores even vanished, and this resulted in a decline in porosity value.

Generally, the porous alloys employed for structural components in MCFC applications are required to have a 60 to 70 % porosity. Through the above experiments, it was found that 18 h ball milling and 950 °C sintering are the most appropriate parameters for the preparation of porous CuNiCr alloy. The products have a ~62 % porosity, and fulfill the industry requirements. In the

following discussion, all of the microstructure characterizations and mechanical property tests are presented just for this particular alloy.

4.3. Microstructure characterization

The microstructure of porous Cu35Ni15Cr alloy is shown in Fig. 6. It can be seen that the alloy consists of two phases. The white phase depleted with Cr is α phase, the dark grey area contains a large amount of Cr is β phase, as pointed out in Fig. 6b. Using the EDS measurement, the average composition of these two phases was determined, as listed in Table 1. From the images of Cu35Ni15Cr alloy, it can be found that the α phase appears as an alloy matrix, and β phase with a granular shape is distributed uniformly in the α phase. Fig. 6b shows the microstructure at a higher magnification: a gap due to the collection of β phase in a small area is observed, which shows that the distribution of the β phase is loose (marked by red circle). The black areas in the images are the pores, although their shape is not regular, they have a near uniform distribution.

4.4. Effect of compression temperature

In order to evaluate the mechanical properties of the porous alloy, high temperature compression experiments with a loading rate of 10^{-1} s^{-1} were

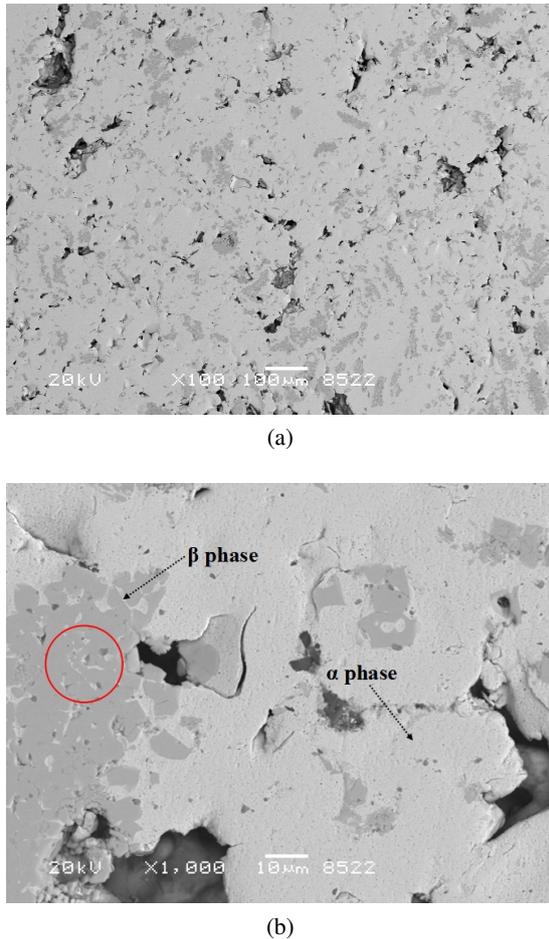


Fig. 6. SEM images of porous alloy.

carried out. The tests were performed at 550 °C, 600 °C, 650 °C. Typical engineering stress-strain curves are shown in Fig. 7a. From the current image, it can be found that all stress-strain curves can be divided into three stages: elastic region, stress plateau region and densification region. In the first stage, the yield strength of the alloys exhibits a high sensitivity. The yield strengths of the porous alloys at different temperatures are shown in Fig. 7b; with the increase in temperature, the strength value decreases from ~ 120 MPa to

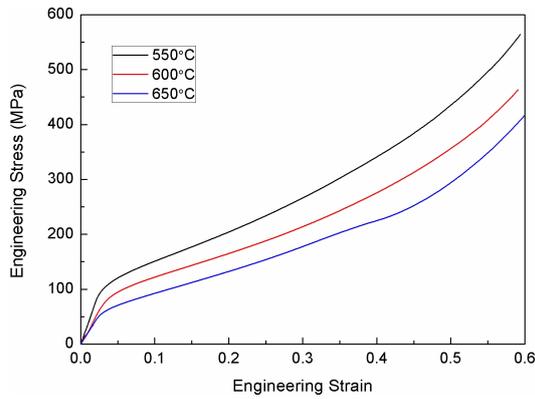
Table 1. The average composition of two phases.

	Cu-wt.%	Ni-wt.%	Cr-wt.%
α phase	60.7	37.74	1.56
β phase	4.26	5.48	90.26

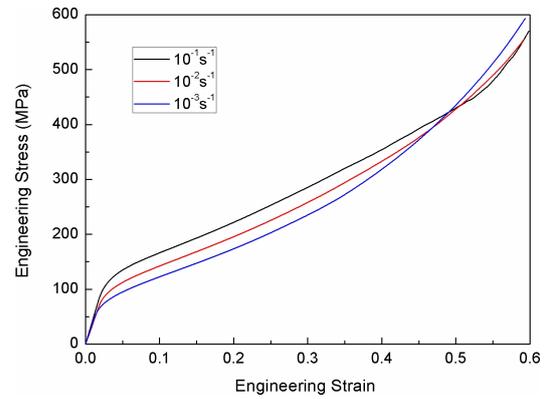
~ 60 MPa. This is mainly caused by the following reasons: (1) with temperature increase, the kinetic energy of metal atoms and the number of slip systems increase, which improves the dislocation mobility to a certain extent; (2) in high temperature environment, it is easy for alloys to undergo dynamic recovery and recrystallization, which eliminates strain hardening process and softens the materials; (3) elevated temperature significantly reduces the intergranular shear resistance, so that the grain boundary slip becomes more easy, thereby alleviating the stress concentration between the grains. The deformation behavior of porous Cu35Ni15Cr alloy at high temperature is governed by the mentioned factors. Another property which changes rapidly with temperature is the elastic modulus. The elastic modulus as a function of testing temperature is also depicted in Fig. 7b; with the increasing of temperature, the elastic modulus decreases from ~ 4.2 GPa to ~ 2.1 GPa. The reason is that higher temperatures causes a strengthening of atom vibrations, makes an increase in atom energy, finally weakening the binding force between the atoms. Under the same stress level, an alloy tested at higher temperature produces larger strain, and shows an obvious drop in elastic modulus.

4.5. Effect of strain rate

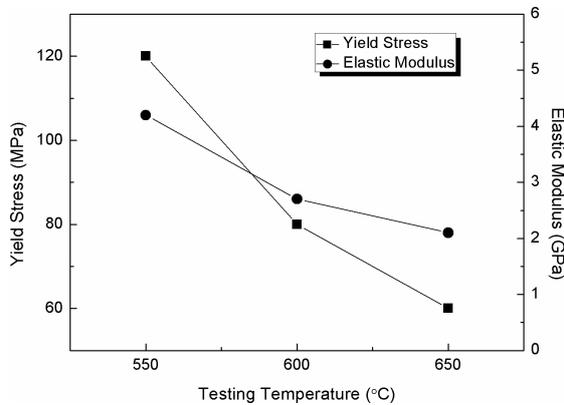
In order to assess the effect of strain rate on the mechanical properties of Cu35Ni15Cr alloy at high temperature, compression test was carried out under different loading rates ($10^{-1}/s$, $10^{-2}/s$, $10^{-3}/s$) at 550 °C. Typical engineering stress-strain curves are shown in Fig. 8a. From the current image, it can be found that all of the stress-strain curves have a similar shape and can be divided into three stages, as described in the previous text. The yield strengths of these alloys are shown in Fig. 8b. It can be seen from the figure that with the increase of the loading rate, the strength value increased from ~ 85 MPa to ~ 420 MPa. When the strain rate is high, the external macroscopic deformation is fast, but the internal microstructure deformation is delayed. Defects, such as dislocations, cannot move, which produces the accumulation and aggregation and improves the deformation resistance.



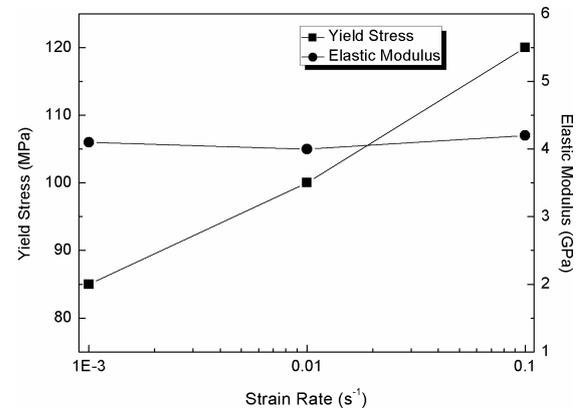
(a)



(a)



(b)



(b)

Fig. 7. (a) typical stress-strain curves at different temperatures, (b) the effect of testing temperature on the yield stress and elastic modulus.

Fig. 8. (a) typical stress-strain curves at different strain rates, (b) the effect of strain rate on the yield stress and elastic modulus.

On the other hand, during the short deformation process, the internal state of this alloy cannot fully complete the dynamic recovery and recrystallization, which also results in the improvement of yield stress. The elastic modulus as a function of strain rate is also depicted in Fig. 8b. But, unlike the influence of testing temperature, with the increasing of strain rate, the elastic modulus fluctuates more or less around a constant level. It means that the external deformation velocity has little impact on the internal atomic bonding force.

5. Conclusions

Compared with Ni based alloys, porous copper alloys have been found to be suitable materials for the use in MCFCs because of their combination of

high thermal conductivity and acceptable mechanical strength. In order to provide a theoretical basis and an experimental support for the application of porous copper alloy in MCFC field, this study concerned the conditions of preparation and mechanical properties of porous alloys (Cu35Ni15Cr). A summary of the key conclusions is as follows:

1. 18 h ball milling and 950 °C sintering are the most appropriate parameters for the preparation of porous Cu35Ni15Cr alloy. The products have a ~62 % porosity.
2. The porous Cu35Ni15Cr alloy is made up of α phase and β phase.
3. The yield strength and elastic modulus of the porous alloy increase continuously with decreasing deformation temperature.

With the increase of loading rate, the yield strength of these alloys shows an increasing trend, but the elastic modulus does not change too much.

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