Preparation and study on performance of submicron nickel powder for multilayer chip positive temperature coefficient resistance*

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Base metal nickel is often used as the inner electrode in multilayer chip positive temperature coefficient resistance (PTCR). The fine grain of ceramic powders and base metal nickel are necessary. This paper uses reducing hydrazine to gain submicron nickel powder whose diameter was 200–300 nm through adjusting the consumption of nucleating agent PVP properly. The submicron nickel powder could disperse well and was fit for co—fired of multilayer chip PTCR. It analyes the submicron nickel powder through x-ray Diffraction (XRD) and calculates the diameter of nickel by PDF cards. Using XRD analyses it obtains several conclusions: If the molar ratio of hydrazine hydrate and nickel sulfate is kept to be a constant, when enlarging the molar ratio of $NaOH/Ni^{2+}$, the diameter of nickel powder would become smaller. When the temperature in the experiment raises to 70–80 °C, nickel powder becomes smaller too. And if the molar ratio of $NaOH/Ni^{2+}$ is 4, when molar ratio of $(C_2H_5O)_2/Ni^{2+}$ increases, the diameter of nickel would reduce. Results from viewing the powders by optical microscope should be the fact that the electrode made by submicron nickel powder has a better formation and compactness. Furthermore, the sheet resistance testing shows that the electrode made by submicron nickel is smaller than that made by micron nickel.

Keywords: submicron, nickel powder, liquid-reduction process, positive temperature coefficient (PTC)

PACC: 7300, 7320D, 7340S

1. Introduction

Nowadays, multilayer chip positive temperature coefficient resistance (PTCR) is usually made by reduction atmosphere co-fired and later oxidation. Its inner electrode is already metalized.[1] Nickel is the most widely used metal not only because it is cheap and convenient to gain but also for the reason that its melting point is higher than positive temperature coefficient (PTC) porcelain forming temperature. But nickel will be easily oxidized in oxidizing atmosphere.[2] Inner nickel electrode should be sintered in reduction atmosphere and nickel is easier to oxidize when temperature rises.[3] So on the one hand it is necessary to improve the antioxidant temperature of nickel and on the other hand we must study on dielectric ceramics sintered in the low temperature.[4] For all the above, inner electrode of multilayer chip PTCR may hold lower sintering shrinkage and should be matched as well as possible with sintering shrinkage of dielectric materials. In order to meet the above requirements, people control parameters of nickel powder with dense quality, morphology,[5] size, purity, crystallinity and so on. Both high bulk density spherical and low dilatable nickel powder are in favour of reducing shrinkage rate in sintering.[6] A lot of methods are used frequently in preparing ultra fine nickel powders: hydroxyl nickel powder heat decomposition, slurry hydrogen reduction, electrochemical, Vacuum distillation condensation, mechanical grinding, spray pyrolysis, liquid-reduction, solid-reduction and so on.[7] And liquid-reduction attracts a lot of attention because the process is simple and parameters such as size and morphology purity are easy to control. Solid-reduction can be divided into several branches, according to different kinds of reducing agents,[8] including polyol process, reducing hydrazine

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water-soluble nickel, salt reduction by pressure hydrogen, reducing hydrazine water-soluble nickel salt reduction by pressure hydrogen reducing hydrazine metal deoxidization.[9] In this paper, we use reducing hydrazine.

2. Experimental

In the experiment, we chose hydrazine reducing nickel sulfate hexahydrate to prepare submicron nickel powders, for the reason that we can obtain spherical ultra fine nickel powder which disperses well and whose diametre is 0.1–0.5 μm through changing nucleating agent and consumption of polyvinyl pyrrolidone (PVP).[10] And we hope to produce submicron nickel powder 200–300 nm by studying on all processes in the experiment. In this paper, we use nickel sulfate hexahydrate as basic material, hydrazine hydrate as reducing agent, triethanolamine as organic protective agent and NaOH for changing PH.[11]

(1) Preparation of precursor solution

Precursor solution A: prepared nickel sulfate solution of a certain concentration, which is mixed with $CuSO_4$ in a certain molar ratio, stirring it with magnetic whisker for 10–30 mins after confining, then we gained blue solution.

Precursor solution B: prepared hydrate solution of a certain concentration, which is mixed with NaOH in a certain molar ratio, stirring it with magnetic whisker for 10–30 mins after confining, then we gained white solution.

(2) Preparation of nanometer nickel powder

Removed the labyrinth sealing device, put the precursor solution A into fume cupboard and heated it at 75 °C, stirring it with magnetic whisker for 5 mins, meanwhile mixing it with precursor solution B, they reacted vigorously, finally we gained submicron nickel powder.

(3) Fetching and treatment of products

Washed the nickel powder first with deionized water and later with alcohol, then heated it for drying. The process is as follows (see Fig. 1).

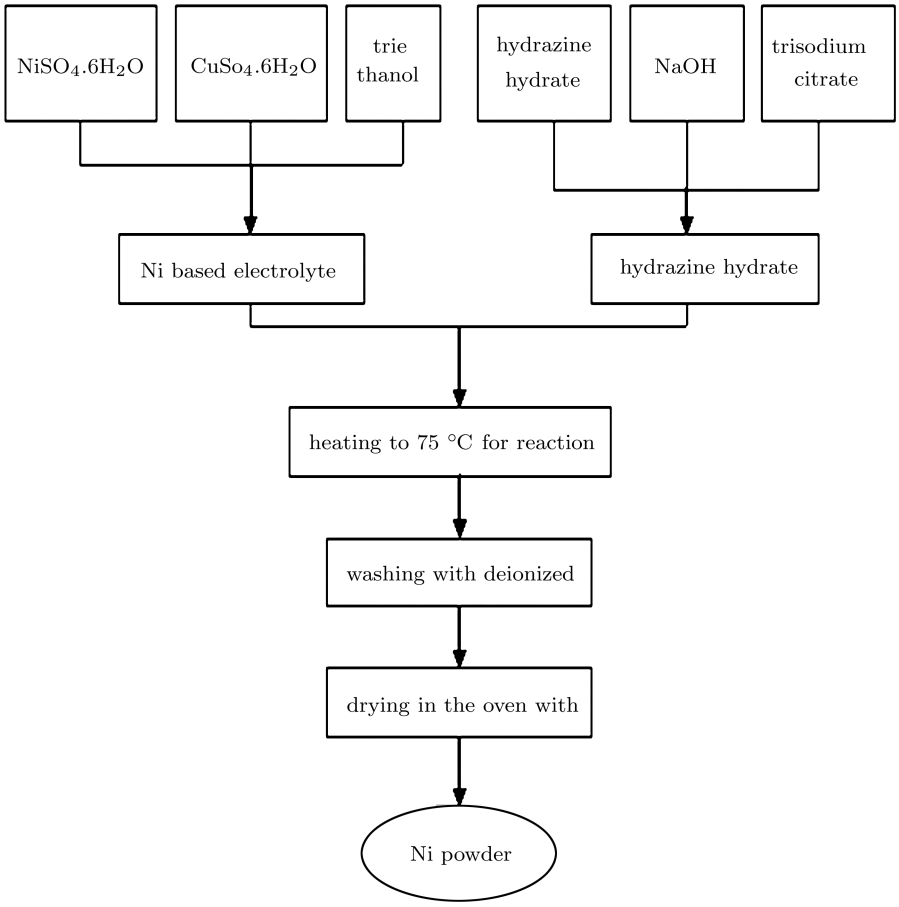


Fig. 1. Preparation of nickel powder to restore the flow chart.

3. Results and discussion

3.1. The effect of NaOH on the size of submicron Ni powder

In order to study different amount of the influence of NaOH on the nano grain size of Ni, on one hand we kept the ratio of hydrazine and nickel sulfate to be a constant, on the other hand used the same concentration of Ni^{2+}, and then changed the ratio of NaOH and Ni^{2+} to 2, 3, 3.5, 4 respectively. Just as Fig. 2, we obtained the submicron Ni XRD picture according to different amount of NaOH. From the standard power diffraction profile (PDF) cards, we calculated the size of Ni powder. It is concluded from Fig. 3 that NaOH had great effect on the size and uniformity of particle. If we do not add

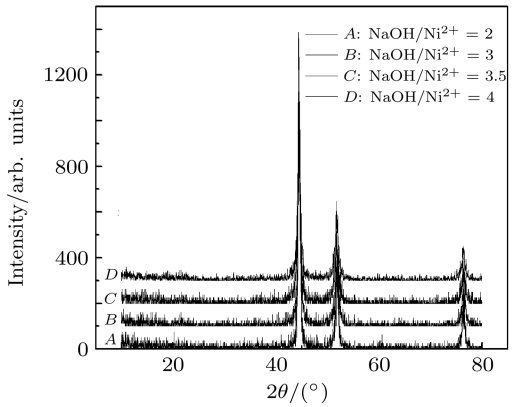


Fig. 2. The amount of NaOH and XRD of the particle size of the powder of Ni.

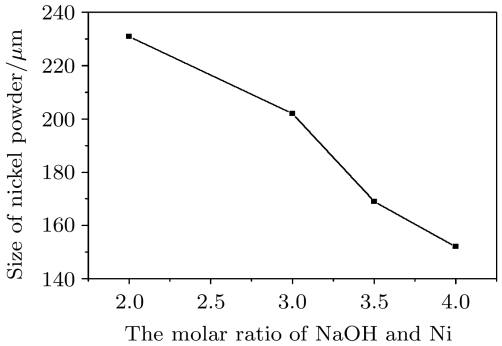


Fig. 3. The relationship between NaOH and the particle size of Ni.

NaOH, we can not obtain Ni powder but only find that the solution becomes pink. With the amount of increasing NaOH, the average size of particle becomes small gradually. The average size of particle was 202 nm when the ratio of NaOH and Ni^{2+} was 2, while the ratio was 4 the size became 152 nm. As the ratio increases the reaction rate becomes too rapid, meanwhile, generates so much gas and bubble that it is difficult to control. Therefore putting appropriate NaOH can reduce the size of particle as well as improving the uniformity, just because multiplied alcohol reduction is prepared, nano metal is a liquid deoxidization and the generating solid particle process includes nucleating, growing, forming, aging. In addition, the size and uniformity have great effect on nucleating and growing. In the preparation of nano Ni powder, putting appropriate NaOH can enhance the reaction rate which has been proved in the experiment and theory. According to studied articles, in basic solution, the reduction potential of hydrazine descends quickly if the concentration of $[OH^-]$ increases while the oxidative potential hydrazine is raised. The result is that it is easy of oxidation and reduction. Furthermore, it shortenes the time whose reactive solution changes from navy blue to black deposition apparently. It is shown that the rate of nucleating and the quantity increases sharply which are beneficial to decrease the size of the particle.

3.2. The effect of reaction temperature on the particle size of Ni powder

In the experiment, we could see that reaction temperature had a great effect on reaction rate and Ni powder size. So we studied the particle size of Ni powder at different temperatures. The XRD pictures which indicated Ni powder changing with reaction temperature were shown as Fig. 4. Calculate Ni powder at the three temperatures, the result is shown as Fig. 5. It could be concluded that after increasing the experimental temperature, the rate accelerated and the particle size of Ni powder reduced. However, if temperature was too high, hydrazine volatilized.[12] So we chose 70–80 °C as reaction temperature in the experiment.

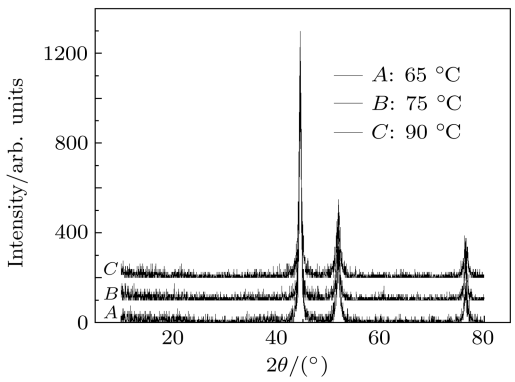


Fig. 4. The XRD of and Ni powder at different reaction temperature.

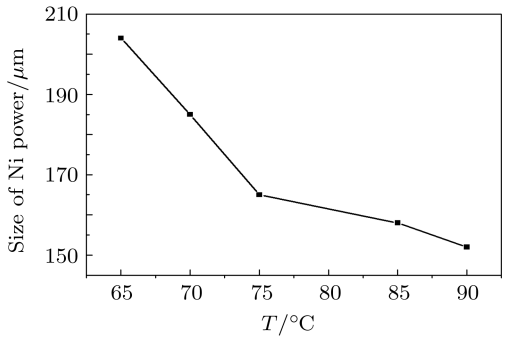


Fig. 5. The relationship between experiment and reaction temperature.

3.3. The effect of organism on the size of submicron nickel powder

The production of nanometer powder needed the polymer or surfactant to be added as the stabilizing agent usually, and we made them to react with the nanometer particles. On one hand, the size and the formation of the nanometer particles could be controlled, on the other hand the stability of the nanometer particles could enhance greatly because of the effect of steric hindrance or electrostatic, which also helped to resist the appearance of polymerized-affection. The $(C_2H_5O)_3N$ could match the metal iron easily, and it was one kind of important nanometer metal polymer stabilizing agent. In order to study the effect of $(C_2H_5O)_3N$ on the size of nickel powder particles, we kept the ratio of NaOH and Ni^{2+}be four, and changed the molar ratio of $(C_2H_5O)_3N$ and Ni^{2+} to 0.2, 0.4, 0.6, 0.8 and 1.0 during the experiment. We obtained different XRD analysis of nanometer nickel particles as Fig. 6 under the different molar ratios of $(C_2H_5O)_3N$ and Ni.

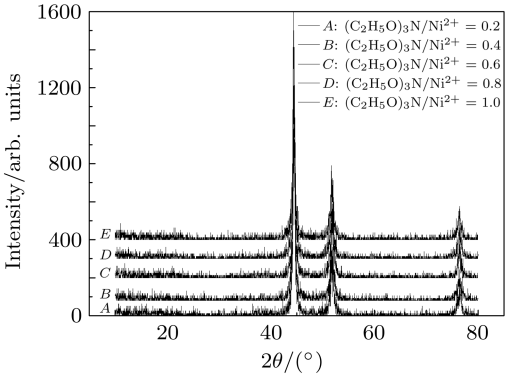


Fig. 6. The XRD analysis of the $(C_2H_5O)_3N$ and the size of nickel powder particles.

We calculated the size of nickel powder particles according to the equation as shown in Fig. 7.

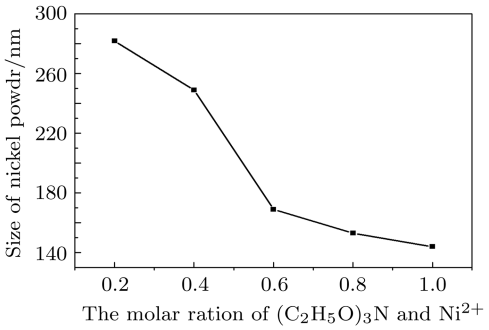


Fig. 7. The relationship between $(C_2H_5O)_3N$ and the size of nickel powder particles.

It was clear that $(C_2H_5O)_3N$ affected the size of nanometer nickel greatly. The size of nickel powder particles became smaller as the amount of the $(C_2H_5O)_3N$ increased.

3.4. The capability of submicron nickel powder electrodes

3.4.1. The comparison about formation of electrodes between submicron nickel powder and micron nickel powder

We made the submicron nickel powders into electrode plasma, published the plasma down to the chip, and fired to electrodes. In the end, we observed the surface formation of these electrodes through metallographic microscope analysis. The comparison about formation of electrodes between submicron nickel powder and micron nickel powder is as follows: for example, Figs. 8 and 9.

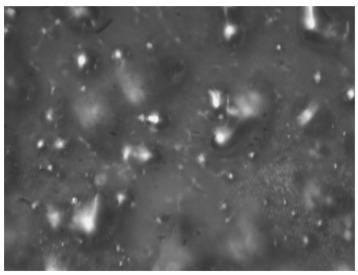


Fig. 8. The formation of submicron nickel powder electrodes.[13]

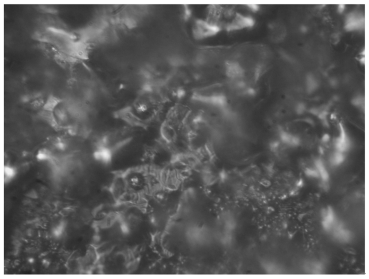


Fig. 9. The formation of micron nickel powder electrodes.

The Figs. 8 and 9 show that the surface formation of the electrodes made by submicron nickel powders was more even, while the density was bigger.

3.4.2. The comparison about capability of electrodes between submicron nickel powder and micro nickel powder

We burned the submicron nickel powder and micro nickel powder into electrodes, and compared their electric properties. Here we mainly compared the difference of sheet resistance. We used four-probe method to measure and compared their forward and reverse sheet resistance. The result was that there was almost no difference. So we used the forward sheet resistance as reference selected object. And we used submicron nickel powder and micro nickel powder to make four PTC chips separately as comparison objects. Concrete contents as shown in Fig. 10.

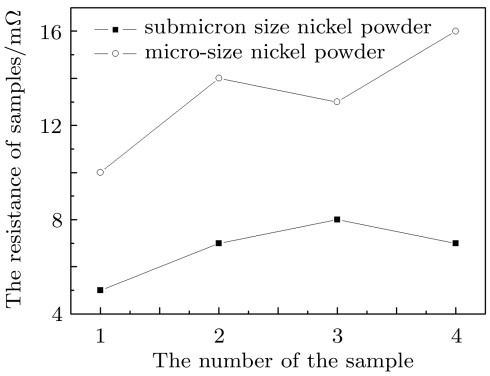


Fig. 10. The sheet resistance comparison of submicron nickel powder and micro nickel powder.

From Fig. 10 we can see, the average sheet resistances are 6.75 and 14.75 mΩ/□, the sheet resistance of electrode made by submicron nickel powder was smaller than micro nickel powder. And it had better effect as the electrode.

4. Conclusions

In the experiment, we used triethanolamine as organic protector, NaOH as adjusting solvent, and hydrated hydrazine to deoxidize nickel sulfate to prepare submicron size nickel powder. The diametre was in the range of 200–300 μm. The results show that it had a good dispersion. We could make conclusions as follows:

(i) Keep the molar ratio of hydrazine hydrate and nickel sulfate be a constant, and change the molar ratio to 2, 3, 3.5, 4, when the molar ratio increases, the diameter of the nickel power becomes smaller. If we add proper NaOH, can decrease the diameter and increase the uniformity.

(ii) Increase the temperature, the reaction rate becomes faster, and the diameter of the nickel power becomes smaller. In the experiment the reaction temperature is between 70 °C and 80 °C.

(iii) When the molar ratio of NaOH /Ni^{2+} is 4, and the molar ratio of $(C_2H_5O)_3N/Ni^{2+}$ is 0.2, 0.4, 0.6, 0.8, 1.0, adding the amount of $(C_2H_5O)_3N$ will make the diametre of nickel powder becoming smaller.

(iv) Using the Metallurgical microscope to observe the electrode formation, we can see that the surface formation of the electrode made by submicron nickel powder is better and the density is bigger. The sheet resistance test shows that the sheet resistance of electrode made by submicron nickel powder is smaller than micro nickel powder. And it has a better effect on the electrode.

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