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STUDY ON THE MICROSTRUCTURE, ELECTRICAL AND MECHANICAL PROPERTIES OF HOT PRESSING Cr-50 MASS% Ni ALLOYS FABRICATED BY ADDITION OF VARIOUS RATIOS OF NANOSIZED Ni POWDERS

In this work, nanosized Ni (nNi) powders of 50 nm are mixed with Cr and Ni submicron-powders (600 nm) to fabricate Cr-50 mass% Ni alloys by vacuum hot pressing. In order to evaluate the influence of the nanosized Ni powders, different amounts of nanosized Ni powders are added to produce the Cr-(50-x) mass% Ni-x mass% nNi alloys (x = 0, 10, 20 , and 30). The hot pressing was maintained at 1275°C, 48 MPa for 1 h. The microstructure evaluation, mechanical, and electrical properties were performed. The results reveal that mechanical and electrical properties are enhanced when increasing the nNi addition. The Cr-20 mass% Ni-30 mass% nNi presents the highest relative density of 96.53% and the electrical conductivity of 2.18×10^4 Scm^{-1}, moreover, the hardness and transverse rupture strength values increase to 76.1 HRA and 1217 MPa, respectively. Moreover, a more homogeneous microstructure and a decrease in the mean grain size to 3.15 µm are acquired. Significantly, this fabrication procedure (adding 30 mass% nanosized nickel powders) results in the optimal microstructure, electrical and mechanical properties of submicron-structured Cr-(50-x) mass% Ni-x mass% nNi alloys.

Keywords: electrical conductivity; hot pressing; transverse rupture strengt; nanosized nickel powders; Cr-50 mass% Ni alloy

1. Introduction

Nanomaterials have enormous potential to provide structural materials in the future with significant property improvements over today's conventional coarse-grained counterparts. They are expected to be used in various applications based on their excellent and unique optical, electrical, magnetic, biological or mechanical properties [1,2]. Over the past two decades, substantial research efforts have been directed towards the synthesis and sintering of nanosized powders in order to manufacture materials with nanocrystalline grain structure. It would be particularly advantageous to exploit these improved properties to extend the lifetime and robustness of materials [3,4].

The advantages of application of chromium-nickel (Cr-Ni) alloys as structural and tool materials have been already recognized. The excellent properties of Cr-Ni alloys are due to their complex composition. Their good mechanical properties and low cost dramatically increased their popularity in the last decades [5,6]. In addition, various compositions of the Cr-Ni alloys have been widely used in the sputtering of thin films, micro-electro components, panel display boards and optical storage media materials [7,8].

Powder metallurgy (P/M) is a good technique for fabrication of high melting material (such as cobalt and chromium, etc.) with better mechanical properties. Sintering is a useful method for manufacturing parts from powders by heating the material until its particles adhere to each other. However, sintering temperature cannot exceed the melting point of the sintered based materials [9,10]. On the other hand, hot pressing technique as a common technique was performed to fabricate the bulk bodies of the alloys. The hot pressing is another special P/M technology, which can sinter the material with applied stress through a graphite mold to transmit the pressure to the powders. It can obtain the dense material at relatively lower sintering temperature [8-11]. Therefore, it is a novel technique to produce the Cr-Ni alloys.

The aim of this study was to use hot pressing and add various ratios of nanosized Ni (nNi) powder to produce the optimal Cr-50 mass% Ni alloys. The effect of nanosized- and submicron-structured powders on the alloy properties was also a chief concern. In this work, a series of experiments, which

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involved adding various amounts of nanosized nickel powder and utilizing the hot pressing sintering process, were carried out in order to explore the sintering behavior and properties of the Cr-50 mass% Ni alloys. The effects of the microstructural constituents on the mechanical and electrical properties of the alloys were of particular interest. In addition, the feasibility of commercially manufacturing Cr-50 mass% Ni alloys by means of the hot pressing sintering process was evaluated.

2. Experimental Procedure

In our previous work, 99.95% submicron-structured chromium (0.59 ± 0.02 μm) and nickel powders (0.61 ± 0.03 μm) were mixed and then underwent hot pressing sintering to fabricate Cr-50 mass% Ni alloys. The optimal parameters of production of Cr-50 mass% Ni alloys were hot pressing sintering for 1 h at 1275°C, with pressure 48 MPa . In the present study, different amounts of nNi powders (0, 10, 20 and 30 mass%) were added to produce the Cr-(50-x) mass% Ni-x mass% nNi alloys. For the Cr-(50-x) mass% Ni-x mass% nNi alloys, x is the amount of added nNi. The Cr-Ni powder samples with the various amounts of added nNi powders were denoted as 0% nNi, 10% nNi, 20% nNi and 30% nNi, respectively, and the hot pressing was carried out at 1275°C, 48 MPa for 1 h after 1 h ball mixing. A Microtrac X 100 laser was used to analyze the particle size of the nNi powders. The mean particle size of the gas-atomized nNi powders was about 50 ± 2 nm. Particularly, the morphology of the gas-atomized powders showed obvious round shapes, as shown in Fig. 1(a). Generally speaking, gas-atomized powders possess an excellent forming mechanism and sintering characteristics because the particles have a relatively smooth surface [12]. Fig. 1(b) shows the Cr-(50-x) mass% Ni-x mass% nNi alloy with the addition of 30% nNi after 1 h of ball mixing. Significantly, the clear cold welding morphology appeared under the effect of mechanical alloying by ball milling for 1 h, with the nanosized powders binding on the submicron-structured powders and the mixed alloy powders producing many secondary particles.

To evaluate the sintered behavior of the hot pressing sintering (Yu Tai Vacuum Co., Ltd. HPS-1053) Cr-(50-x) mass% Ni-x mass% nNi alloys *via* added various ratio of nanostructured nickel powder, the porosity, hardness, transverse rupture strength (TRS) tests, electrical tests and microstructure observations were performed. Microstructural constituents of the specimens were examined by X-ray diffraction (XRD, Rigaku D/Max-2200), optical microscopy and scanning electron microscopy (SEM, Hitachi-S4700). SEM was also employed to estimate the interface numbers and grain size by calculating the overall interface and grain numbers divided by the unit length in the backscattering electron image (BEI). Porosity tests followed the ASTM B311-08 and C830 standards.

The hardness of the specimens was measured by Rockwell indenter (HRA, Indentec 8150LK) with loading of 588.6 N, which complied with the ASTM B294 and ASTM B163-11 standard methods. The Hung Ta universal material test machine

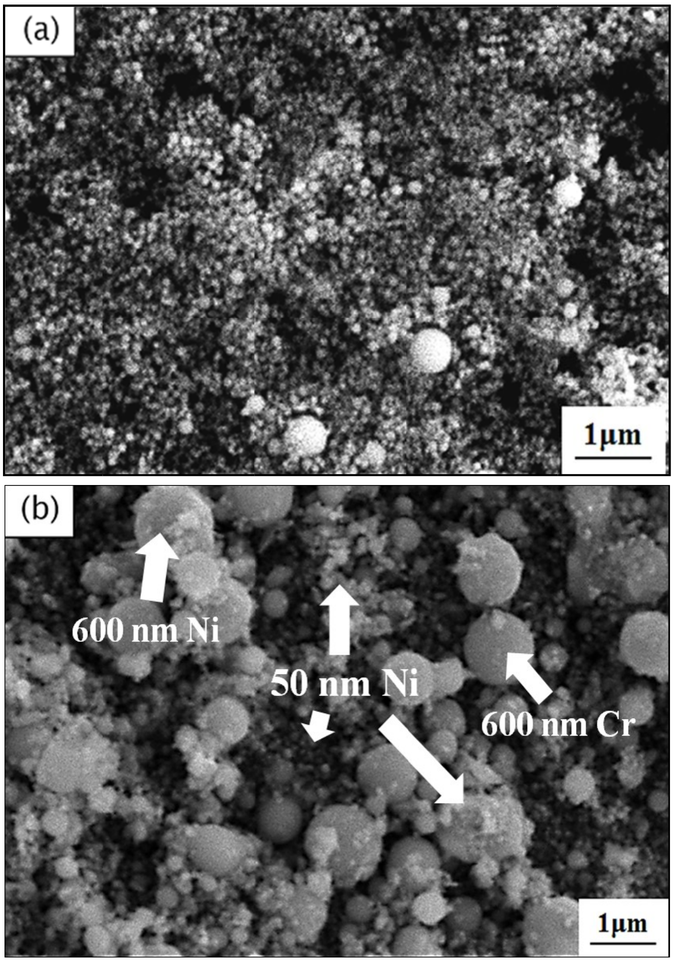

Fig. 1. SEM photographs of the surface morphology (a) nNi powders, and (b) 30% nNi specimen after 1 h ball mixing

(HT-9501A) with a maximum load of 245 kN was used for the TRS tests (ASTM B528-05). Meanwhile, R_{bm} was the TRS, which was determined as the fracture stress in the surface zone. F was the maximum fracture load, L was 30 mm, k was the chamfer correction factor (normally 1.00-1.02), b and h were 5 mm in the equation $R_{bm} = 3FLk/2bh^2$, respectively. The specimen dimensions, used for TRS test, were $5 \times 5 \times 40$ mm^3. Moreover, it needs to slightly grind the surface of the specimen and tests at least three pieces. A four-point probe (LRS4-TG2) was used to measure sheet resistance. In addition, electrical conductivity (σ) was calculated according to the following formula [12,13]:

$$\rho = R/t = 1/\sigma$$

Where the ρ is electrical resistivity, R is the resistance, t is the thickness of the test sheet, and σ is the electrical conductivity (Scm^{-1}), respectively.

3. Results and Discussion

Fig. 2 shows the XRD patterns of the hot-pressed Cr-(50-x) mass% Ni-x mass% nNi alloys fabricated by different additions of nNi powder. The major diffractions appeared in the Cr

(200), (110) and Ni (111), (200), (220) planes; the 2θ values of Cr were 44.39° and 64.58°, and those of Ni were 44.51°, 51.85° and 76.37°; the Cr_3C_2 diffractions (2θ was 39.58° and 42.96°, respectively) also emerged in the hot pressing sintering Cr-50 mass% Ni alloys fabricated by adding different amounts of nNi. It was reasonable to speculate that the chromium produced a chemical reaction with the carbon of the graphite mold, whereby the Cr_3C_2 compounds were generated. Furthermore, the intensity of Ni (111) was slightly enhanced as the added amount of nNi increased. The Cr (200) appeared after the ball milling powders, but disappeared after the various hot pressing sintering treatments. Generally, the XRD diffractions and their intensity depend on the crystal structure [6]. Significantly, all specimens obviously had better crystallinity after hot pressing sintering with the addition of different amounts of nNi powder. Clearly, the adding of different amounts of nNi powders together with the hot pressing sintering process contributed to the overall improvement of the microstructure of the Cr-50 mass% Ni alloys and effectively improved their mechanical properties.

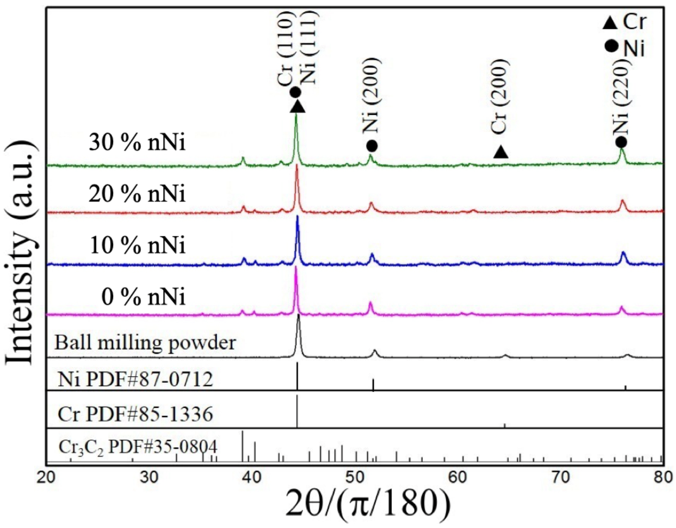

Fig. 2. XRD patterns of hot pressing sintering Cr-50 mass% Ni alloys by different amounts of nNi powders

Fig. 3 shows the relative density and apparent porosity of the hot pressing sintering Cr-50 mass% Ni alloys fabricated by adding different amounts of nNi powder. Relative density of the 0% nNi specimens was 96.29%; increasing the amount of nNi powder added to 10% and 20% enhanced the relative density to 96.31 and 96.41%, respectively. nNi enhanced the sinterability of hot-pressed Cr-50 mass% Ni alloys; therefore, the relative density and apparent porosity were improved with increasing amounts of nNi. The highest relative density (96.53%) appeared in the 30% nNi specimens after 1275°C, 48 MPa, 1 h hot pressing sintering, while the lowest relative density (96.29%) occurred in the 0% nNi specimens. However, increasing the amount of nNi powder (0 → 10 → 20 → 30%) seemed to result in a slight increase in the relative density of the specimens. The apparent porosity also showed a very small declining trend as the added amount of nNi powder increased. The lowest apparent porosity (0.04%) appeared in the 30% nNi specimens after 1275°C, 48 MPa, 1 h hot pressing sintering.

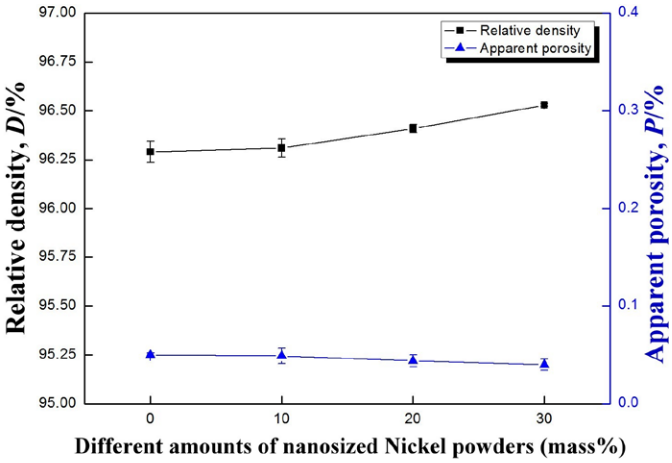

Fig. 3. Comparison of the relative density and apparent porosity of hot-pressed Cr-50 mass% Ni alloys by adding different amounts of nNi powders

A previous study clearly indicated that the internal pores needed a greater diffusion distance to exhaust than the apparent porosity [6,14,15]; thus, it was difficult to remove them solely by the diffusion mechanism. In this study, the melting point of Ni was 1455°C and that of Cr was 1907°C. It is reasonable to suggest that adding larger amounts of the nNi powders with a relatively low melting point and high surface area was helpful to the sintering mechanism of the Cr-(50-x) mass% Ni-x mass% nNi alloys. On the other hand, the nNi powders possessed a relatively higher surface energy. Increasing the added amount of nNi powder effectively resulted in the filling of the smaller closed pores of the incompletely sintered Cr and Ni phases and a decrease in the porosity level. As a result, the full densification of the hot pressing sintering Cr-50 mass% Ni alloys was achieved. Simultaneously, these results were then confirmed by a microstructural investigation (as shown in Fig. 4).

Fig. 4 shows the microstrucutre of the hot pressing sintering Cr-50 mass% Ni alloys fabricated by the addition of different amounts of nNi powder. Notably, there were two different phases uniformly distributed in the hot pressing sintering specimens, as shown in Fig. 4(b), where the bright parts are the nickel-rich grains and the gray parts are the chrome-rich grains. All specimens clearly showed that dramatically closed pores still remained in the grain boundaries of the hot pressing sintering Cr-50 mass% Ni alloys fabricated by the addition of different amounts of nNi powder. However, the grain size decreased slightly from 3.48 to 3.15 μm with the increase of the added amount of nNi powder (0 → 30%), as show in Figs 4(a)-4(d). The microstructure investigations revealed that grain refinement phenomenon did not the inhibit grain growth via the added nNi powders, but it did generate a finer grain ratio in the 30% Ni specimen as a result of the added nNi powders. Effect of the grain refinement was an improvement to the mechanical and electrical properties [4,9].

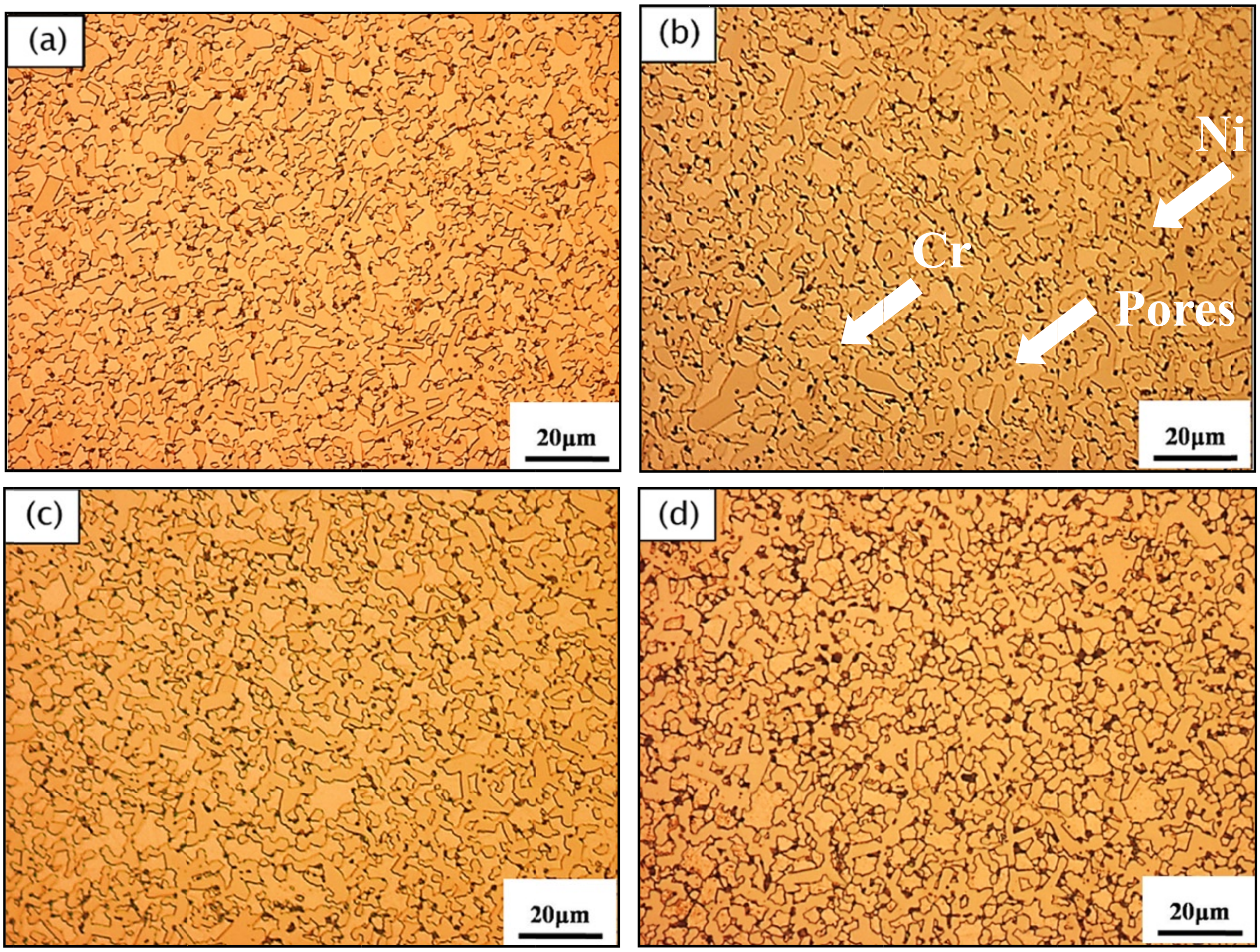

Fig. 4. OM morphologic observations of hot-pressed Cr-50 mass% Ni alloys by adding different amounts of nNi powders (a) 0, (b) 10, (c) 20, and (d) 30 mass%

This agreed with our previous studies and will be confirmed in the following sections.

Fig. 5(a) shows the relation between the interface numbers and grain size of the hot pressing sintering Cr-50 mass% Ni alloys fabricated by different nNi additions. The interface numbers were calculated by the overall interface numbers of the cross chromium/nickel alloys in the unit length of the BEI images. Previous literature has indicated that a structure with more interface numbers has a better microstructure [12,14]. In this work, the interface numbers of the hot-pressed Cr-(50-x) mass% Ni-x mass% nNi alloys obviously increased with increased amounts of nNi powders. However, increasing the added amount of nNi powders ($0 \rightarrow 10 \rightarrow 20 \rightarrow 30\%$) decreased the grain size ($3.48 \rightarrow 3.29 \rightarrow 3.24 \rightarrow 3.15$ μm). Although nanosized powders' sintering has the additional challenge of retaining nanoscaled grain sizes [9, 16], the addition of nNi hinders the rapid grain growth, which improves the sintering performance. Thus the addition of nanocrystalline materials can serve a broad range of ceramic and metallic materials to achieve high densification, compared to micron-sized additions. In this study, the highest value (245) of interface numbers appeared in the 30% nNi specimens, which also possessed the smallest grain size (as shown Fig. 4(d)). As a result, this was beneficial to the microstructural modification, as well as the electrical and mechanical properties.

A previous study [14] indicated that the electrical resistivity increases with increasing the porosity level. The relationship between the relative density and the electrical properties of the sintered Cr-50 mass% Ni alloys was also proven [6]. Increasing the relative density helps improve the electrical properties, which means that the electrical conductivity will be enhanced as the relative density increases. In this research, the electrical conductivity of the hot pressing specimens seemed to be significantly improved after the addition of nNi powders, as shown in Fig. 5(b). The highest relative density and electrical conductivity appeared in the 30% Ni specimens, the values being 96.53% and 2.18×10^4 Scm^{-1}, respectively. It was evident that the higher relative density and lower porosity of the 30% nNi specimens led to the increase in the mean free path of the electrons, which resulted in a better electrical performance. Therefore, increasing the added amounts of nNi powders is assisted to enhance the relative density and improve the electrical properties of the hot pressing Cr-50 mass% Ni alloys. This finding was in agreement with our previous study [6,14].

Fig. 6 shows the hardness and TRS of hot-pressed Cr-50 mass% Ni alloys. Previous investigation revealed there to be a positive relationship between hardness and relative density,

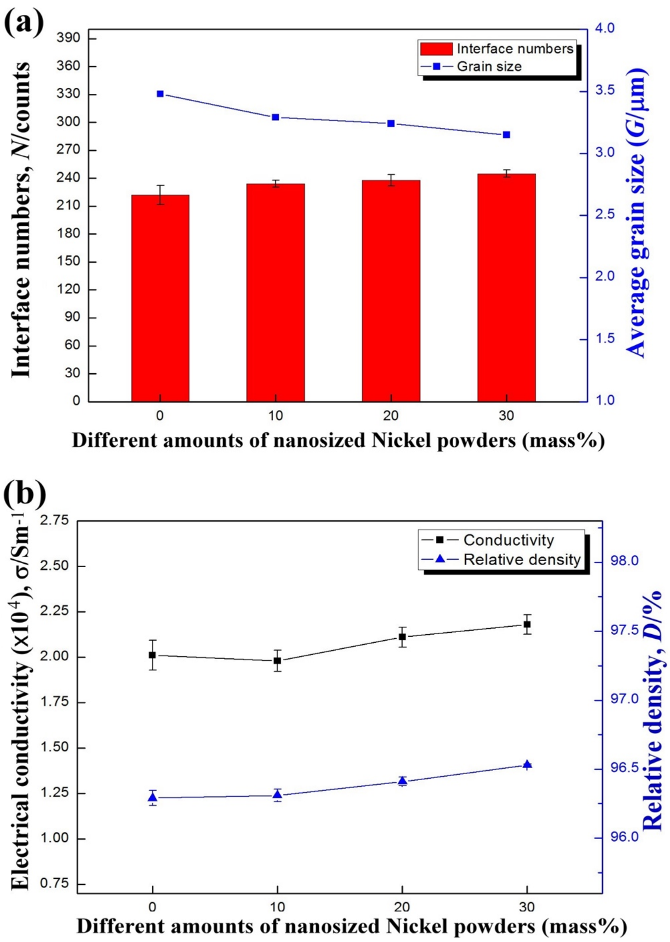

Fig. 5. Comparison of the properties of hot-pressed Cr-50 mass% Ni alloys by adding different amounts of nNi powders (a) interface numbers and grain size, and (b) electrical conductivity and relative density

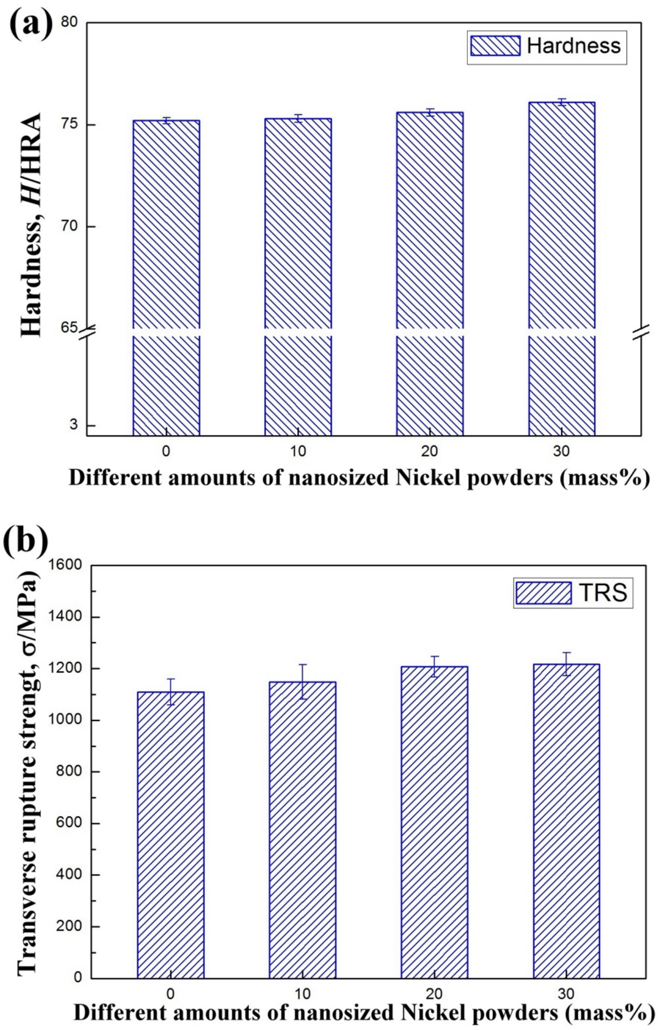

Fig. 6. Comparison of the mechanical properties of hot pressing sintering Cr-50 mass% Ni alloys by adding different amounts of nanosized nickel powders (a) hardness, and (b) TRS tests

with the hardness significantly enhanced as the relative density increased [6]. Moreover, it also showed that decreasing the grain size of the sintered materials effectively enhanced the plastic deformation resistance and hardness. In the present study, increasing the amount of nNi powers added to the hot-pressed alloys slightly enhanced their hardness up to 30%. However, the hardness of the 30% Ni specimens showed an obvious increase, as shown in Fig. 6(a). Due to the improvements in relative density and grain refinement, larger additions of nNi powers obviously enhanced the plastic deformation resistance. As a result, by increasing the addition amounts of nNi powers (0 → 30%) added to the hot pressing specimens, the hardness acquires an enhancement from 75.2 to 76.1 HRA.

In Fig. 6(b), the results of TRS tests were presented. Normally, a higher density provides stronger binding to protect the rupture mechanism of generation [6,14]. Increased amounts of nNi powders caused the grain size and apparent porosity to decrease, respectively. From the point of view of physical metallurgy, the finer grains possessed a greater area fraction of grain boundaries along the line of the mobile dislocations. Therefore, the number of dislocation tangles was more than enough to hold the mobile dislocations and produce a stronger plastic deformation resistance. As a result, the finer grain structure possessed the better TRS. Moreover, above experimental results also suggested that if a structure has more interface numbers (222 → 245), the microstructure is usually better; thus, the TRS value increased with the increasing amounts of nNi powders. The highest TRS value (1217 MPa) appeared in the 30% Ni specimens, the significantly higher bonding strength of which hindered the generation of the rupture mechanism.

Fig. 7 shows the fractographic observations of the hot pressing Cr-(50-x) mass% Ni-x mass% nNi alloys. The fracture surfaces look to be almost the same. All the fractographic images are rather ductile in the Cr-(50-x) mass% Ni-x mass% nNi alloys after the TRS tests, as shown in Figs 7(a)-(d). The increased amounts of nNi powders made the TRS value enhance 10%. Meanwhile, the fracture surface of the specimens showed a more dimpled structure, as shown in Fig. 7(d). The high-magnification fractographic observations of the 30% nNi specimen showed nNi powders attached to the grain boundaries and the trans-granular fracture surface (as indicated by the arrows in Fig. 8).

According to our previous study [6], the nanosized addition of the ductile phase could reduce the grain size and poros-

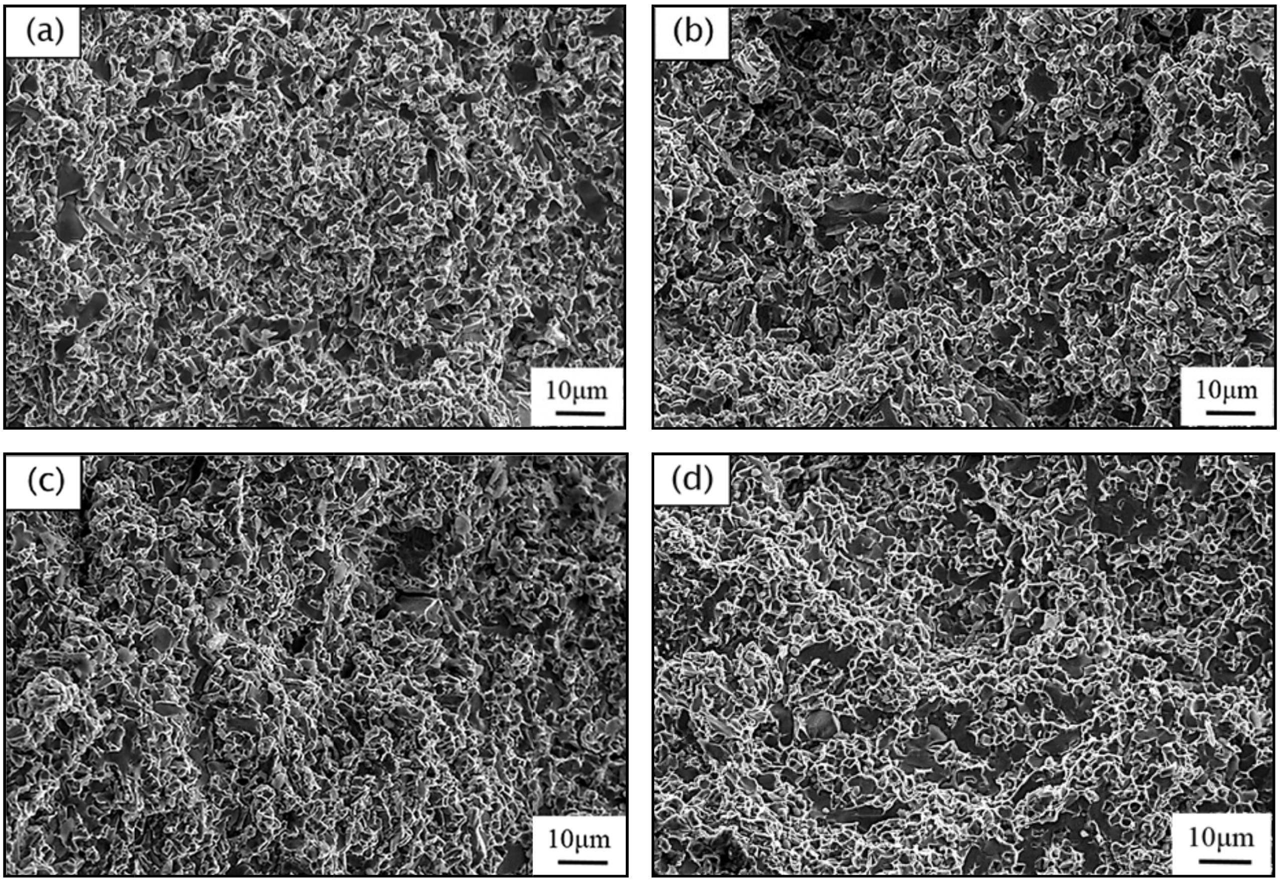

Fig. 7. Fractographic observation of hot-pressed Cr-50 mass% Ni alloys by adding different amounts of nNi powders (a) 0, (b) 10, (c) 20, and (d) 30 mass%

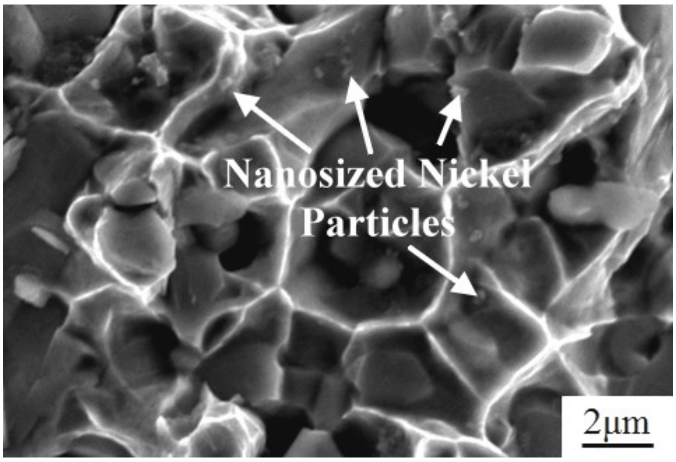

Fig. 8. High-magnification fractographic observation of the 30% nNi specimens after 1275°C and 48 MPa hot pressing sintering for 1 h

ity. The fracture surface trended to the refinement of dimple fracture when increasing amounts of nNi powders. Therefore, it is reasonable to suggest that grain refinement was the main factor in improving the strength of the hot pressing sintering Cr-50 mass% Ni alloys. In addition, the pores easily generated the points of the stress concentration and formed a continuous rupture. Generally, pores located in the grain boundaries cause micro-cracks along the grain of the material to form an intergranular brittle fracture. When micro-cracks are evident in the expansion process, normally the crack propagation energy will be absorbed by the finer particles or precipitates and so hinder the expansion of micro-cracks. When the added amounts of nNi powders were increased, the porosity level decreased and nNi powders attached to the grain boundaries. As a result, the internal structure had a more uniform distribution of nNi particles with a high toughness. This was another factor which resulted in the higher TRS value. According to the above experimental results and discussions, adding 30 mass% nNi powders to the hot pressing sintering process of Cr-50 mass% Ni alloys was the preferred option.

4. Conclusions

In this study, all specimens had a better crystallinity after hot pressing sintering through different additions of nNi powders. Addition of 30% nNi exhibited the best structural, electrical, and mechanical properties, which implied the increased nNi amounts could improve the hot pressing characteristics when the hot pressing parameters were 1275°C, 48 MPa for 1 h. The apparent porosity and electrical conductivity of the 30% Ni specimen were 0.04% and 2.18×10^{4} Scm^{-1}, respectively. Moreover, it possessed the highest TRS value (1217 MPa) and a hardness of 76.1 HRA. Both the hardness and TRS values of the hot pressing sintering Cr-50 mass% Ni alloys were significantly increased due to the various additions of nNi powders. In addition, this study also found that adding a suitable amount of nNi powders (30 mass%) effectively improved the grain size of hot-pressed Cr-50 mass% Ni alloy under high temperatures and resulted in a significant decrease in the grain size (3.48 → 3.15 μm). Consequently, high-density and high-strength hot pressing sintering Cr-(50-x) mass% Ni-x mass% nNi alloys were obtained.

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