

Ni/GO nanocomposites and its plasticity

You Li*, Guofeng Wang, Qi Liu, and Mo Yang

National Key Laboratory of Precision Hot Processing of Metals, Harbin Institute of Technology, Harbin, P.R. China

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Abstract – Ni/GO nanocomposites were prepared with an AC pulse electro-deposition method. The morphologies of the deposits, crystal structure and mechanical properties of the nanomaterials were examined using scanning electron microscope (SEM), X-ray diffraction and a tensile testing machine respectively. Studies show that the addition of graphene oxide (GO) results in nano-particles of electrodeposited Ni aggregating to form micro-convexes for which (2 0 0) plane is the preferential growth orientation, accelerating the growth of nucleus, improving the crystallization and inhibiting the growth of grain. The room-temperature tensile elongation was up to 9.89% when GO = 0.1 g/L; the breaking strength reached 625 MPa when GO = 0.03 g/L; the tensile elongation in 450 °C was 232%, which presents a good superplasticity when GO = 0.08 g/L.

Key words: Ni/GO composites, Superplasticity, Nanomaterials, Electrodeposition

1. Introduction

Plastic forming [1–3] in the conventional scale and micro-nano scale are quite different. In the micro/nano-scale forming, materials have strong scale effects. When applying nano materials to a forming process, there will still be a plenty of interior material-grains, even if the size of the parts is achieved at the micro-nano scale. The scale effect, however, will be much less significant, comparing to the use of micro-scale-grain materials.

There are many ways for creating metal sheets by forming. AC pulse electrodeposition is a relatively convenient, fast, and easy way. Compared with the vapor deposition, electrodeposition has merits such as only needing simple equipment, easy operation and low cost. Compared with DC deposition, the current density of AC pulsed electrodeposition is higher and the nucleation rate is faster, which promotes grain refinement and is conducive to the formation of nano-materials [4].

Graphene is a type of the material that consists of carbon atoms [5, 6]. Those sp² hybridized orbital carbon atoms form a two dimensions one-atom-thick layer material in a hexagon lattice fashion, resembling honeycombs. The bonds between carbon atoms in a graphene material are flexible, which leads to a bending deflection when sustaining an external force, rather than atom re-arrangement, thus stabilizing the whole structure and possessing a better mechanical property. Graphene oxide [7] is unreduced graphene with many functional

groups on surface, making it easier to react with other substances. This is in favor of a composite material production.

2. Experiment

2.1. Preparation of Ni/GO nanocomposites

Ni/GO nanocomposites were made by AC pulse electrodeposition with a stainless steel plate in plating solution that contained 0.75 M nickel sulfamate, 0.1 M nickel chloride, 0.5 M boric acid, 0.1 g/L sodium lauryl sulfate, 1 g/L saccharin, and graphene oxide (GO). Before electrodeposition, the stainless steel plate was polished by #800, #1500, #2000 grit sandpapers, after that ultrasonic cleaned in acetone and ethanol for 5 min, then rinsed with distilled water, finally dipped into 5% dilute hydrochloric acid solution to be acid-washing and activated for 5 min. Nanocomposites were made under the condition of magnetic stirring in 50 °C, 3 A dm⁻² current density, 2 h electrodeposition time and a Ni plate of 99.6% purity as anode.

2.2. Characterization

The phases in the final products were established using a D/MAX-RB X-ray diffractometer (Rigaku Incorporation, Japan) with Cu K α radiation ($\lambda = 1.54178$). The scanning rate was 4° min⁻¹. The morphology was characterized by a Sirion 200 scanning electron microscope (FEI Incorporation,

*e-mail: liyou_magic@sina.com

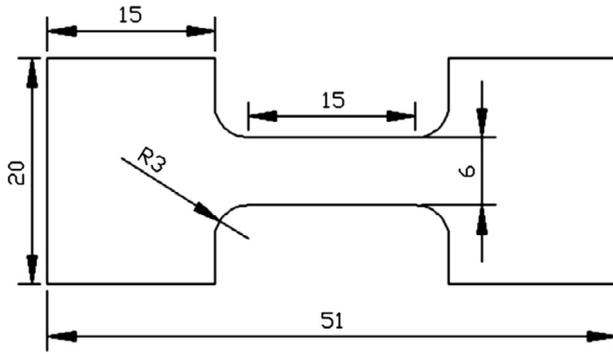


Figure 1. Dimensions of a tensile sample.

Holland). Tensile testing was performed on an Instron-5500 universal testing machine with strain rate $6.67 \times 10^{-4} \text{ s}^{-1}$. Tensile specimens were cut by line cutting into the size as shown in Figure 1. Temperature controlling error of the high temperature environmental chamber that supported to the universal testing machine was $+1 \text{ }^\circ\text{C}$. Thermal equilibrium time of tensile specimens was 20 min before each high temperature tensile test in which the temperature was $450 \text{ }^\circ\text{C}$ and the strain rate was $2 \times 10^{-3} \text{ s}^{-1}$.

3. Characterization analysis

3.1. SEM characterization

The SEM results of Ni and Ni/GO nanocomposite are shown in Figure 2. In the SEM figure of pure Ni, the particle size reaches nano scale and particles are well-distributed. The surface is smooth and compactness is good. During the electrodeposition process, GO covered the surface of Ni, which made the surface of nanocomposites unsmooth and nanoparticles forming to micro-convexes with cracks between them. The coating got thicker in electrodeposition progress. On the surface of coating, growing points that good for grain nucleating gradually trended to be uneven, causing larger diversity between deposition rates at different parts of cathode. Those parts with higher deposition rate were shaped into micro-convexes. Surface state of cathode turned uneven. Undulating topography were formed and electric fluxline were distributed non-uniform on the surface of nanocomposites. Point discharge showed at the tip of the micro-convexes, which made nickel ion get electron preferentially, then restored to Ni atom.

3.2. Structural characterization

Figure 3 shows the XRD patterns of pure Ni and Ni/Go nanocomposites, comparing that with JCPDS standard cards shows that the plane which the XRD patterns mark is the plane of Ni. Peaks where angle $2\theta = 44^\circ, 52^\circ, 93^\circ$, respectively correspond to the position of Ni (1 1 1), (2 0 0), (3 1 1) plane, in which the (2 0 0) plane's texture degree is stronger, indicating that (2 0 0) plane is preferred orientation. The material is face-centered cubic structure.

From the XRD patterns of pure Ni and Ni/Go Nanocomposites, taking the (2 0 0) plane which has the strongest

diffraction peak as example, since GO is added during the electrodeposition, the diffraction peak's half-width is narrowed, which shows that the addition of GO promotes the formation of nickel atoms nuclei, thus suppresses the growth of grain. The result can also be seen in the scanning image in Figure 2. During the electrodeposition process, the formation of nuclei and the growth of grain were two competing processes. When a large amount of nuclei were formed in the deposition surface, the growth of grain was greatly inhibited. And due to the adding of GO, the growth of deposited Ni atoms was decreased and the formation rate of nucleation was enhanced; while after the GO was added, the diffraction peak of nanocomposites turned sharper and the degrees of crystallinity were increased significantly.

3.3. The changes for the amount of graphene

For nano-Ni, the elongation is $5 \times 10^{-5} \text{ s}^{-1}$ at low strain rate $5 \times 10^{-5} \text{ s}^{-1}$ and decreases to 2.3% at high strain rate $5 \times 10^{-2} \text{ s}^{-1}$. While ZrO₂/Ni nanocomposites get the highest elongation 5.1% when stain rate is $5 \times 10^{-5} \text{ s}^{-1}$ and reache the lowest elongation 1.2%, when stain rate is $5 \times 10^{-2} \text{ s}^{-1}$ at room temperature. Experiment results so far show that the vast majority of nanocrystalline materials have poor plasticity in room temperature [8]. The elongations of nano-Ni that tested in different strain rates by Torre and others are not more than 3% [9].

Figure 4 is engineering stress-strain curve with different proportions of GO, measured by an Ni/GO nanocomposites tensile test where the stain rate was $6.67 \times 10^{-4} \text{ s}^{-1}$ and the temperature was room temperature.

As Figure 4 shows, in the condition that the strain rate is $6.67 \times 10^{-4} \text{ s}^{-1}$, the elongation of Ni/GO nanocomposites is about 7 ~ 8%, about 2 ~ 4 times of average elongation of nano-nickel when the addition of graphene was 0.03 ~ 0.08 g/L; the elongation is highest, achieving 9.89% when the addition of graphene is 0.1 g/L, which indicate that the addition of GO could improved the elongation of nanocomposites in room temperature. GO induces point discharge during electrodeposition process, which leads to the micro-convexes cracks. When the addition of GO was low, the specimens fractured before plastic deformation because of the cracks during tensile test, so the plasticity was reduced; when the addition of GO was high, the fine mechanical property of GO offset negative factors caused by point discharge, which improved the elongation and plastic formability of nanocomposites.

The breaking strength of Ni/GO nanocomposites made by pulse electrodeposition can achieve 625 MPa that is 1.79 times of normal coarse-grained nickel's (the breaking strength of normal coarse-grained nickel is about 350 MPa). In this experiment, the main reason for breaking strength was not well improved is that the addition of GO increases the probability of point discharge in electrodeposition, making the micro-convexes cracks increased in nanocomposites and the cracks covered with a small amount of GO, which although significantly improved the plasticity but did not improve the breaking strength of nanocomposites.

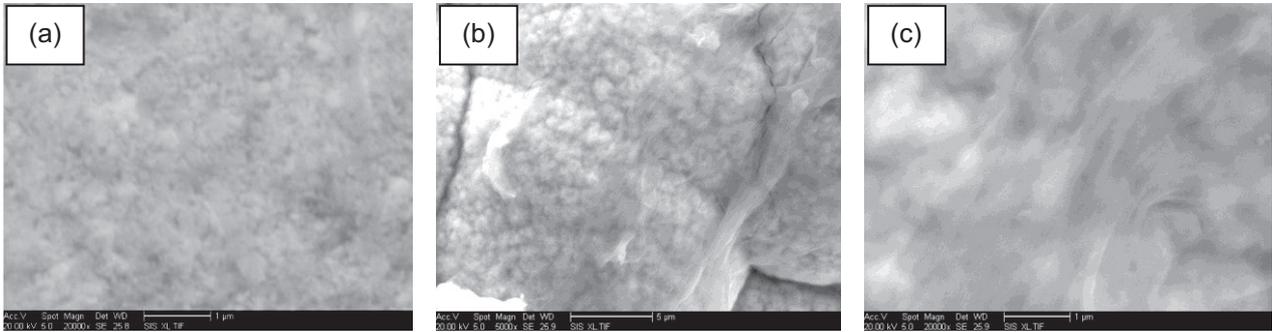


Figure 2. SEM images of Ni and Ni/GO nanocomposite. (a) Ni, (b) Ni/GO (5000×), (c) Ni/GO (20,000×).

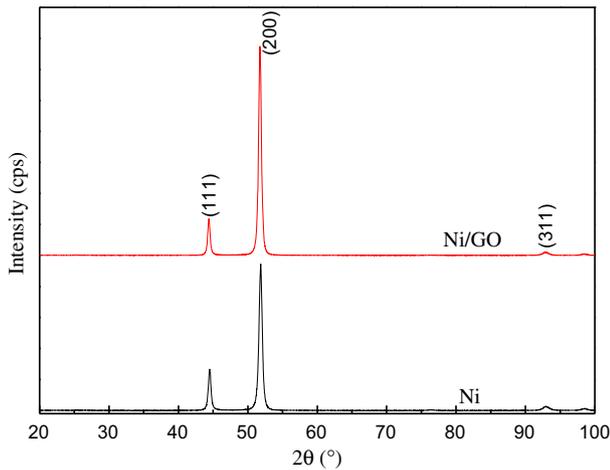


Figure 3. XRD patterns of Ni and Ni/GO nanocomposite.

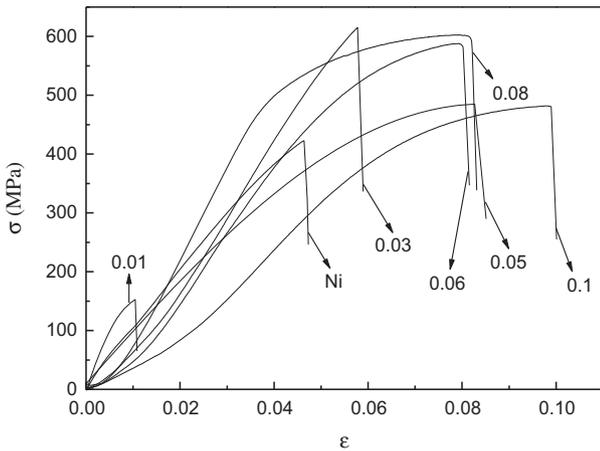


Figure 4. Engineering stress-strain curves of the material measured at a room temperature.

Figure 5 presents a scanning electron microscope (SEM) image of the tensile fracture with the addition of GO comes to 0.08 g/L at room temperature. The figure shows that the fracture surface has uniformly distributed dimples. Explanation on the fracture mechanism of the material is plastic fracture, and the GO was found in the sample, indicating that GO is involved in the tensile fracturing process of the composite.

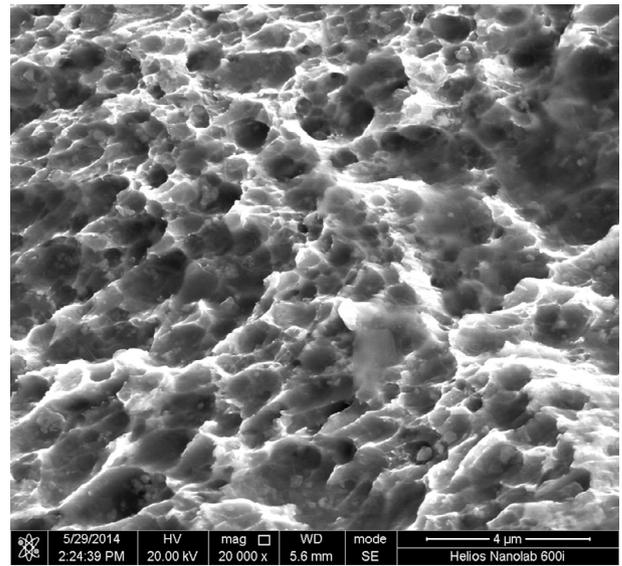


Figure 5. SEM images of the tensile fracture.

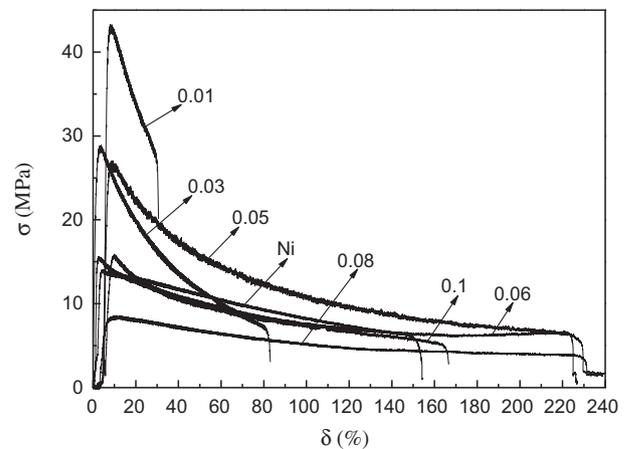


Figure 6. Stress-elongation curves at high temperature.

Figure 6 is the high temperature stress-elongation curve with different amounts of GO. As the Figure 7 shows, when $GO \geq 0.04$ g/L, the elongation of electrodeposited nanocomposites is higher than pure nickel; when $GO > 0.05$ g/L,

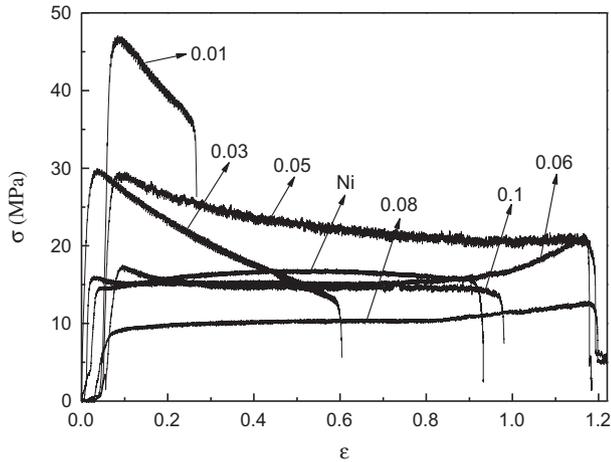


Figure 7. True stress-strain curves at high temperature.



Figure 8. The samples subjected to the tensile tests.

the elongation of most nanocomposites could reach more than 200% and be very stable; while $GO < 0.04$ g/L, the elongation of electrodeposited nanocomposites becomes lower than pure nickel. The main reason is that GO led to the point discharge in the electro deposition process and formed big projection grains. In the process of high-temperature tensile test, micro cracks between grains led to fracture. When the addition of graphene comes to 0.08 g/L, the elongation could reach to 232% in 450 °C. This temperature is 270 °C lower than the ordinary temperature for superplastic which is 0.5 T_m (T_m is the melting point of pure nickel), ultimately low temperature superplasticity achieved. When the addition of graphene comes to 0.1 g/L, the elongation decreases, the main reason for which is that amount of GO is excessive, and micro cracks between grains led to fracturing. The tensile stress existing in the micro

crack mainly depends on the binding force of the metal and GO.

Figure 7 is the true stress-strain curve of high temperature plastic deformation of the material with different amounts of GO and Figure 8 shows some samples after stretching in high temperature. These figures show that there was no constriction of the nanocomposites after the test. The size and stability of grains are two of the factors on material's superplasticity. The different superplastic performances of Ni/GO nanocomposites are closely correlated with the addition of GO changing the inner organization.

4. Conclusions

Ni/GO nanocomposites were prepared successfully with an AC pulse electrodeposition method. Following conclusions may be drawn from the test and analysis conducted:

- 1) The addition of GO caused point discharge, making nano-particles of electrodeposited Ni aggregate to form micro-convexes, between which there were cracks. Compared to pure Ni, smoothness and density of the electrodeposited Ni were decreased;
- 2) The addition of GO did not influence the deposit formation of Ni and did not change the plane of the preferred orientation, but improved the formation of nuclei, inhibited the growth of grain and increased the crystallinity;
- 3) Adding GO could significantly extend the elongation of Ni/GO nanocomposites in room temperatures, e.g., achieved 9.89% when $GO = 0.1$ g/L. The breaking strength was, however, not increased significantly, e.g., it was 625 MPa when $GO = 0.03$ g/L;
- 4) When $GO > 0.05$ g/L, the elongation could all reach above 200%, achieving low-temperature superplasticity, e.g., when $GO = 0.08$ g/L, elongation could reach 232%.

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References

1. S.X. McFadden, R.S. Mishra, R.Z. Valiev, A.P. Zhilyaev, A.K. Mukherjee, Low-temperature superplasticity in nanostructured nickel and metal alloys, *Nature* 398 (1999) 684–686.
2. Y. Saotome, H. Iwazaki, Superplastic backward microextrusion of microparts for micro-electro-mechanical systems, *J. Mater. Process. Technol.* 119 (2001) 307–311.
3. S.L. Semiatin, P.N. Fagin, J.F. Betten, A.P. Zane, A.K. Ghosh, G.A. Sargent, Plastic flow and microstructure evolution during low-temperature superplasticity of ultrafine Ti-6Al-4 V sheet material, *Metall. Mater. Trans. A* 41 (2010) 499–512.
4. C. Liu, K. Wang, S. Luo, Y. Tang, L. Chen, Direct electrodeposition of graphene enabling the one-step synthesis of graphene-metal nanocomposite films, *Small* 9 (2010) 1203–1206.

5. J. Bai, X. Zhong, S. Jiang, Y. Huang, X. Duan, Graphene nanomesh, *Nature Nanotechnol.* 5 (2010) 190–194.
6. R. Lv, M. Terrones, Towards new graphene materials: doped graphene sheets and nanoribbons, *Mater. Lett.* 78 (2012) 209–218.
7. O. Akhavan, E. Ghaderi, Toxicity of graphene and graphene oxide nanowalls against bacteria, *ACS Nano.* 4 (2010) 5731–5736.
8. C.C. Koth, D.G. Morris, K. Lu, A. Inoue, Ductility of nanostructured materials, *Mater. Res. Soc. Bull.* 24 (1999) 54–58.
9. T.F. Dalla, S.H. Van, M. Victoria, Nanocrystalline electrodeposited Ni: microstructure and tensile properties, *Acta Mater.* 50 (2002) 3957–3970.

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