Investigation of the corrosion resistance of graphene-nickel composite micro-parts

Wenhua Suo ∗, Yi Wang, Yaotang Ji, Zhuangzhuang Liu, Jing Liu, Shanfei Wang, Hongli Suo and Min Liu

Laboratory of Superconducting Materials, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, People’s Republic of China

* Author to whom any correspondence should be addressed.
E-mail: suowenhuabj@163.com and wangyibg@bjut.edu.cn

Abstract
Nickel-based microparts possess a short lifetime owing to their rapid dissolution in corrosive environments. To mitigate this phenomenon, composite microparts of graphene/Ni were prepared using UV-LIGA technology; their corrosion behavior was examined in acid, alkali, and salt solutions as well as after subjecting them to heat-treatment processes. The microstructures were investigated with scanning electron microscopy (SEM), x-ray diffraction (XRD), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). Corrosion resistances were characterized through various electrochemical tests and compared with those of pure Ni microparts. The results demonstrate that the surface oxidation layer (i.e., the protective layer) of the microparts was readily destroyed in NaCl and H2SO4 solutions without the formation of a passivation film; however, a passivation film was formed in the NaOH solution. The corrosion rates of graphene/Ni in NaCl, NaOH, and H2SO4 corrosion solutions were reduced by 73%, 22%, and 84%, respectively, relative to those of pure Ni microparts. This can be primarily attributed to the homogeneous dispersion of graphene in the Ni matrix, which refined the grain size, and the impermeability and chemical stability of graphene, which lengthened the diffusion path of the corrosive medium. In addition, heat treatment of the graphene/Ni microparts at 200 °C increased the corrosion resistance by a factor of nearly one with little change in microhardness, which can be attributed to the removal of internal stress and the increased proportion of CSL grain boundaries. Corrosion occurred at the interface between nickel and graphene, lengthening the corrosion path.

1. Introduction
Nickel-based composite microparts are characterized by their hardness, resistance to various corrosion environments, and wear resistance. They are widely used in the aerospace, ocean, precision machinery, automotive, biomedical, and petrochemical fields [1–6]. In recent years, numerous reports have detailed the doping, microstructure, and mechanical properties of nickel and nickel-based composites [7–10]. Refined grains such as nanoparticles of SiO2 [11, 12], SiC [13], CeO2 [14], Cr2O3 [15, 16], Al2O3 [17], BN [18], ZrO2 [19], and carbon nanotubes [20] have been doped into the nickel matrix to improve the properties of the composite. Owing to its impermeability, light weight, atomic thinness, wear resistance, inertia, and mechanical strength, graphene has also been widely used in the preparation of lightweight composite materials [21] with superior performance. Materials made by MEMS [22] are difficult to meet the performance requirements in some special environments, such as acid, alkali and high temperature. Relative to other adulterants, the honeycombed two-dimensional network structure of graphene [23–26] provides it with excellent potential barriers and shielding properties [27–31] which can inhibit the passage of corrosive media and significantly lengthen the diffusion path of the corrosive solution, thus enhancing the corrosion performance of microparts.
In recent years, numerous groups have developed graphene/metal matrix composites to improve their corrosion properties. Yasin et al. [32] used electrochemical co-deposition to deposit nickel and graphene composite coatings on the surface of stainless steel. The corrosion resistance of the composite coating increased and then decreased with the increase of the concentration of graphene in the dielectric, and the corrosion resistance of the composite coating was enhanced at a graphene concentration of 0.2 mg ml\(^{-1}\). Y. raghupathy et al. [33] studied the effect of graphene oxide (GO) on the microstructure and corrosion behavior of Cu-GO composite coatings. They found that steel coated with Copper-GO had greater corrosion resistance compared to bare steel and pure copper-coated steel. The improved corrosion resistance of Cu-GO coatings was related to the high texture and high permeability of GO to Cu ions and \(\text{O}_2\) dissolved in the chloride medium. Kumar et al. [34] studied the corrosion resistance of Ni and Ni-graphene. The addition of graphene refined the grain size to 20 nm. The corrosion rate in 3.5% NaCl decreased from 3.236 \(\text{mil} \text{y}^{-1}\) to 1.370 \(\text{mil} \text{y}^{-1}\). Unfortunately, challenges originating from the ease of agglomeration of graphene nanosheets have not been resolved. Graphene poses challenges including poor dispersion and uneven lamellare distribution, a problem which is magnified when deposition must take place over a long period of time for the fabrication of microdevices and precision components. Feng et al. [35, 36] studied the effects of sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and their mixed surfactants on the dispersion of graphene. It was found that when the SDS:CTAB ratio was 9:1, graphene exhibited the highest dispersion. But the graphene-nickel composites have not been systematically studied in corrosive environments, and the corrosive properties in high temperature environments have not been elaborated.

In this study, pure Ni and graphene/Ni microparts were prepared using the electrodeposition method; ensuing changes in the microstructure and grain size of the samples were examined. The corrosion behavior of the two types of samples in three different solutions (NaCl, NaOH, and \(\text{H}_2\text{SO}_4\)) was studied by potentiometric polarization and impedance spectroscopy. Given that properties of pure nickel microparts were improved by introducing graphene, the effect of heat treatment (at various temperatures) on these properties was subsequently studied; the basic mechanism by which heat treatment enhances the properties of graphene/Ni microparts is described.

2. Experimental procedures

The preparation process of the microparts consists primarily of the following steps: constructing the mask plate; SU-8 lithography; electroforming.

2.1. The SU-8 lithography

To prepare high-precision graphene/Ni composite microparts, a high-precision SU-8 glue mold [37, 38] was first ensured; functional patterns of the required microparts were made on the gold-plated silicon wafer. The photolithography process involves cleaning the silicon substrate, glue application and homogenization, pre-baking, exposure, post-baking, development, and blow-drying. A macroscopic photograph and microscopic morphology of the photoresist film are illustrated in figures 1(a)–(b).

2.2. Electrodeposition and heat treatment

GPLs [36, 39] were from Nanjing XFNANO Materials Tech Co. Ltd. The average size of platelets is 0.5–2 \(\mu\text{m}\) and with thickness of 0.8–1.2 nm. Electroforming was carried out in a Watt’s bath (\(\text{Ni} (\text{NH}_2\text{SO}_4)\_2 \cdot 4\text{H}_2\text{O} 350 \text{g l}^{-1}\), \(\text{NiCl}_2 10 \text{g l}^{-1}\), \(\text{H}_2\text{BO}_3 40 \text{g l}^{-1}\), \(\text{C}_6\text{H}_5\text{O}_2 \cdot \text{H}_2\text{O} 2.5 \text{g l}^{-1}\), \(\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na} 0.1 \text{g l}^{-1}\), saccharin 1 g l\(^{-1}\)) on the glue mold. All the chemical reagents used in the experiments were analytically pure. The electroforming equipment was a DF-101S/Z thermostatic magnetic stirrer (speed range: 0 ~2600 R min\(^{-1}\), heating power: 800 W, voltage:220 V/50 Hz), equipped with a THD-T1 ultrasonic generator (power: 600 W, working voltage: 220 V). Prior to electroforming the graphene/Ni matrix composite microparts, graphene (0.1 g l\(^{-1}\)) was dispersed in a 0.26 g l\(^{-1}\) SD-\(\text{H}^+\) and 0.037 g l\(^{-1}\) hexadecyl trimethyl ammonium bromide solution; the pH was fixed between 9 and 10 and 1 ml of hydrazine hydrate (80%) [40] was added for reduction. The graphene dispersion was combined with the Watt’s bath at a 1:8 ratio to form a 250 ml mixture. The experimental process is shown in figure 2. The cathode was the prepared 1 cm \(\times\) 1 cm \(\times\) 600 \(\mu\text{m}\) glue mold placed parallel to the pure nickel plate used as the anode. The cathode to anode area ratio was 1:3, electrode spacing was 3 cm, deposition temperature was 50 °C, current density was 7 A dm\(^{-2}\), and the electroforming time was 56 h. A combination of ultrasound and stirring was employed to mitigate the tendency of non-uniform graphene dispersion due to prolonged electroforming (with stirring speed range of 100–300 R min\(^{-1}\), heating power of 800 W, and ultrasonic power of 600 W). Prior to each experiment, the nickel plate and glue mold were cleaned with acetone, ethanol, and deionized water for 15 min using ultrasound before finally being blown dry and immersed in the electroforming solution.
The electroformed parts were ground and polished to yield 600 μm electroformed microparts, as illustrated in figures 3(a)–(c). Finally, the graphene/Ni composite microparts were optimally heat-treated for 2 h in a tube furnace at temperatures of 200 °C, 300 °C, 500 °C and 700 °C to eliminate micropart defects. Ar + 4 vol% H₂ was continuously fed into the furnace during both heating and annealing to prevent sample oxidation.

2.3. Corrosion tests
Electrochemical techniques were employed to study the corrosion-protection performance of the microparts. Electrochemical tests were carried out using a CHI60E potentiostatic instrument (Shanghai Chenhua Instruments). The working electrode was the micropart being tested, the counter electrode was Pt, and the reference electrodes were Ag/AgCl (in conjunction with the neutral solution) and Hg/HgO (in conjunction with the acid or alkaline solution). The corrosive media were separate solutions of 3.5 wt% NaCl (neutral), 5 wt% NaOH (alkaline) and 5 wt% H₂SO₄ (acidic). The corrosion medium for the heat-treated graphene/Ni composite microparts was 3.5 wt% NaCl. Each test was performed at least three times at room temperature (approximately 25 °C) to ensure repeatability. Prior to initiating the experiments, the samples were immersed in the corrosion solution for 1 h. The open-circuit potential was measured between –1 V and 0.5 V for 400 s. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the open-circuit potential in
the frequency range of 0.01 Hz to 100 kHz. The EIS diagram was fitted to an equivalent circuit (EEC) and analyzed with Zview2 softwares at a scanning rate of 0.1/s; the intersection of the Tafel curves was extrapolated from the anode and cathode polarization curves at a scanning speed of 2 mV s\(^{-1}\) to calculate the corrosion potential and corrosion current density.

2.4. Materials characterization
The surface and cross-sectional morphologies of the microparts were observed using FESEM (QUANTA FEG650) and TEM (HRTEM Tecnai G20, FEI, Netherlands) to characterize the location and grain size of graphene; TEM samples were prepared by ion thinning. Transmission Kikuchi Diffraction and Electron Backscattered Diffraction (EBSD) were conducted on a high-resolution SEM (QUANTA FEG650) complemented by an EBSD detector (NordlysMax2) with a step size of 5 nm, a voltage of 30 kV and working distance of 10–13 mm running with KHL-channel5 software. Characterization and analysis of crystal structures on the sample surface was conducted before and after heat treatment by EBSD. Analysis of the phase composition, grain size and weave coefficients of the miniature parts was conducted using XRD (Bruker-D8 Advanced x-ray Diffraction) and energy dispersive x-ray energy spectroscopy (EDAX). An HXD-2000 digital microhardness tester was used to estimate the hardness of the microparts with a load of 0.98 N, while a G200 nanoindentation scanner was used to analyze the elastic modulus of the composite microparts.

3. Results and discussion
3.1. Comparison of the microstructures of Ni and graphene/Ni microparts
The surface morphologies of the pure Ni and graphene/Ni composite microparts are illustrated in figures 4(a)–(b). The surface of pure Ni is smooth, while the grain size is relatively small. However, there are obvious black areas on the surface of the graphene/Ni composite microparts which are distributed uniformly on the graphene sheets (arrow in figure 4(b)). The microstructure on the surface of the graphene/Ni composite microparts indicates that graphene is adsorbed on the surface of the material during the deposition process, increasing the nucleation sites of Ni\(^{2+}\). This hinders the growth of crystals and results in the Ni grains being refined and neatly arranged. The EDS analysis figure 4(c) of pure Ni indicates that the electrodeposited material consists mainly of Ni, with trace amounts of doped C element impurities. However, EDS results (figure 4(d)) corresponding to the electrodeposition process of graphene/Ni composite microparts demonstrate the existence of both Ni and C; the increased C confirms the incorporation of graphene in the electrodeposition process.

X-ray diffraction experiments were performed to characterize the surfaces of pure Ni and graphene/Ni (Gr/Ni) composite microparts prepared by electrodeposition. The XRD patterns are shown in figure 5(a), the Ni and
graphene/Ni microparts exhibited no significant differences with respect to their XRD peak positions. The XRD peaks at 44°, 53°, and 76° correspond to the (111), (200), and (220) crystal planes of FCC Ni; the addition of graphene did not alter this crystal structure. We could not, however, locate the diffraction peak of graphene, the amount of which may have been below the detection limit. The peak shape of the (220) peak in the spectrum becomes sharp with the addition of graphene, indicating better crystallinity and high orientation intensity. The peak position shifts slightly to a higher value of 2θ and the diffraction peak appears broadened with the addition of graphene, which may be due to the reduction in grain size as the addition of graphene promotes the nucleation of nickel atom grains and inhibits the grain growth. Pure Ni and Gr/Ni composite microparts both produced a strong preferred orientation in the (111) plane. However, the degree of selectivity in (111) and (200) faces of graphene/Ni composites decreased, while the degree of selectivity in (220) face increased, indicating that graphene has a strong promoting effect on crystal growth in (220) face and an inhibiting effect on crystal growth in (111) and (200) faces. This is caused by the change of cathode surface energy due to the adsorption of graphene on the cathode during electroforming.

Based on the Berube and L’Esperance methods, the texture coefficient (T) was calculated from the XRD peak intensity using equation (1).

\[
T = \frac{I_{hkl1}/I_{0(hkl)}}{\sum I_{hkl}/I_{0(hkl)}} \times 100\%
\]

where \(I_{hkl1}\) is the peak intensity of the microparts, and \(\sum I_{hkl}\) represents the sum of all diffraction peak intensities. Indicator 0 is the peak strength of the standard Ni sample for JCPDS file card number 87–0712. Figure 5(b) presents a histogram of the texture coefficients of the Ni and graphene/Ni microparts, which confirm that the pure Ni microparts exhibit a preferred orientation in the (200) direction with a maximum Tc value of 46%, while the preferred orientation of the graphene/Ni composite microparts is (220) with a maximum Tc value of 35.7%. These results suggest that the incorporation of graphene during electroforming process changes the selective orientation pattern of Ni. An increase in the (220) orientation increases the surface free energy, which results in a higher electron transition energy associated with the electrochemical corrosion process inhibiting corrosion.

Figures 6(a), (e) present the transmission electron microscopy (TEM) images of the nickel and graphene/Ni microparts following ion thinning, respectively. Figures 6(b), (f) present the selected area electron diffraction (SAED) patterns of the nickel and graphene/Ni microparts following ion thinning, respectively. From the enlarged image (c') in figure 6(e), it can be seen that graphene is primarily distributed to the junctions and inside the nickel grains. In addition, some folds can be observed in the pattern (as indicated by the arrows). These folds primarily represent characteristic structures inherent to the graphene lamellae and whose effect is to reduce the surface energy to make the material structurally stable. The SAED patterns presented in figures 6(b) and (f) also illustrate that the grain size of graphene/Ni is smaller that of pure nickel.

Figures 6(c), (g) present the IPF diagrams of pure Ni and graphene/Ni micro parts. Again, compared with the IPF diagram of pure Ni in figure 6(c), the grain size of the graphene/Ni microparts in figure 6(g) was significantly reduced indicated by the disappearance of large grains and the formation of numerous smaller one. The grain size plots of pure Ni and graphene/Ni presented in figures 6(d), (h) illustrate that the grains size of pure Ni are widely distributed with a significant increase in the proportion of grains larger than 5 μm. In contrast, the graphene/Ni microparts possessed a more uniform grain size distribution with an increased proportion of grains smaller than 5 μm. The average grain size of pure Ni was calculated to be 11.08 μm, while
that of graphene/Ni was 0.94 μm. This discrepancy can be attributed to the following phenomena: the addition of graphene provides more abundant nucleation sites for the nickel grains, which increases the chance of recrystallization, and hence, the refinement of grain size; the addition of graphene also restricts the formation of grain boundaries, while also hindering their slip to strengthen the fine grains. The addition of graphene was also effective in filling the cavity cracks in the cast layer. These observations are consistent with the XRD results.

Figures 7(a)–(d) illustrate the changes in grain orientation following heat treatment at 200, 300, 500 and 700 °C. Different color depths for each grain correspond to different orientations, while similar color depths correspond to similar orientations. The inhomogeneous equiaxed grains in the plots gradually transform into evenly distributed equiaxed grains as the growth process progresses. Figures 7(e)–(h) presents the grain boundary distributions corresponding to heat treatments at 200, 300, 500 and 700 °C. The grain boundaries in different shades of gray represent small angular grain boundaries from 2° to 5°, large angular grain boundaries from 5° to 15° is black, and ∑3 double grain boundaries in red. The proportion of special grain boundaries ∑3 tended to increase and then decrease as the heat-treatment temperature increased, reaching a peak at 200 °C.

Figures 7(i)–(l) presents the statistical analysis of the grain sizes corresponding to 200, 300, 500 and 700 °C. The average grain size is 1.48 μm at 200 °C, 4.23 μm at 300 °C, 16.68 μm at 500 °C and 27.82 μm at 700 °C, indicating that the grain size increases with increasing heat-treatment temperature, while the twin boundary ratio decreases from 0.334 (200 °C) to 0.029 (700 °C) (figure 7(m)). The grains underwent a recrystallization and growth process to generate twinning. The main reasons for these trends are as follows: more dislocation and layer dislocation energy is generated within the composite micropart owing to the presence of graphene, contributing further energy to the recrystallization process of grains such that they become equiaxed; graphene hinders the grain boundary migration process of the pure nickel recrystallized grains (the more uniformly the graphene is dispersed, the more obvious the hindering effect); the high thermal conductivity of graphene accelerates the cooling efficiency of the composite, leading to greater refinement of the recrystallized grains. The twinning boundary energy evolved during heat treatment was much lower than the random large-angle twinning boundary energy, thereby reducing the energy of the entire grain boundary. Samples with different grain-size distributions and extent of twinning were prepared by heat treatment; their corrosion behavior were further investigated.

3.2. Electrochemical corrosion behavior of microparts

This section is divided into five parts which examine the electrochemical corrosion of pure Ni and graphene/Ni composite microparts in corrosion solutions of 3.5 wt% NaCl, 5 wt% NaOH, and 5 wt% H₂SO₄ and mechanical properties of pure Ni and graphene/Ni composite microparts.

3.2.1. Open-circuit voltage (OCP)

Figure 8 presents the open-circuit potential (OCP) and immersion time for the Ni and graphene/Ni composite microparts after stabilization in separate solutions of 3.5 wt% NaCl, 5 wt% NaOH and 5 wt% H₂SO₄ for 400 s. In both the 3.5 wt% NaCl and 5 wt% H₂SO₄ solution, the potential decreases slowly with time before and after
graphene addition—likely due to the erosion of Cl- or SO₄²⁻ which results in the passivation film corroding and dissolving before it is sufficiently formed, corresponding to a slow and unstable decrease in the OCP. The OCP of the graphene/Ni microparts in 3.5 wt% NaCl and 5 wt% H₂SO₄ solutions increased from −0.112 V to −0.104 V and from −0.195 V to −0.155 V of pure Ni, respectively (with a positive shift in potential). The OCP of graphene/Ni microparts was consistently higher than that of pure Ni throughout the test [41]. Improved corrosion resistance can be attributed to grain refinement and the impermeability effect associated with graphene in the nickel matrix. As the test time progressed, the OCP values of the microparts decreased to a more negative potential, which can be attributed to the continuous diffusion of the corrosion solution into the interior of the microparts and resulting in corrosion on the metal surface. However, in the 5 wt% NaOH solution, the potential of the microparts before and after graphene addition slowly increased with time as a result of the continuous formation of the passivated film Ni(OH)₂. The OCP of the Ni sample and graphene/Ni microparts was −0.154 V and −0.035 V, respectively. This positive shift in potential as a result of graphene addition indicates that the grain refinement, Ni(OH)₂ passivation film, and graphene impermeability contributed collectively to the corrosion resistance of the Ni microparts.

3.2.2. Potentiodynamic measurement
The electrochemical corrosion behavior of Ni and graphene/Ni was investigated using Tafel polarization studies in the 3.5 wt% NaCl, 5 wt% H₂SO₄ and 5 wt% NaOH media. Tafel tests were performed by polarizing the
working electrode at ±200 mV from their respective OCP values. Each measurement was performed three times to verify the reproducibility of the results. The Tafel polarization curves of the Ni and graphene/Ni composite microparts are presented in figures 9(a)–(c) and the relevant corrosion parameters are listed in table 1, where $E_{\text{corr}}$ denotes the self-corrosion potential and $I_{\text{corr}}$ denotes the self-corrosion current. The corrosion rate, $R_{\text{corr}}$, can be calculated from the $I_{\text{corr}}$ value of equation (2).

$$R_{\text{corr}} = \frac{kM}{N\rho}I_{\text{corr}}$$

where $K$ is a constant (3270 mol a$^{-1}$), $M$, $N$, and $\rho$ are the atomic weight of the metal, number of electrons lost per metal atom during anodic dissolution, and metal density, respectively.

As can be seen from figure 9(a), the corrosion potentials ($E_{\text{corr}}$) of the pure Ni and graphene/Ni microparts are $-0.625$ V and $-0.496$ V, while the corrosion current densities ($I_{\text{corr}}$) are $6.867 \times 10^{-5}$ A cm$^{-2}$ and $1.866 \times 10^{-5}$ A cm$^{-2}$ in 3.5 wt% NaCl solution.
1.840 \times 10^{-5} \text{ A cm}^{-2}, \text{ respectively. It was observed that the addition of graphene both increased the Ecorr and reduced the Icorr (relative to that of pure Ni) on the surface of the graphene/Ni microparts. The corrosion rates of pure Ni and graphene/Ni were 0.74000 \text{ mil} \cdot \text{yr}^{-1} and 0.1985 \text{ mil} \cdot \text{yr}^{-1}, \text{ respectively—having been reduced by 73% through the addition of graphene. The reduced susceptibility of the microparts to Cl}^- \text{ attack indicate the protective nature of graphene addition due to its high impermeability. It is postulated that the increase in surface energy associated with the (220) texture results in enhanced passive film formation on graphene/Ni microparts. The extent of Ni passivity and tendency for electrochemical corrosion are generally found to be dependent on its crystallographic orientation, which determines the surface free energy per unit area of the material. The high impermeability of graphene impedes the diffusion of Ni^{2+} ions through the micropart cross-section. In the Cl\textsuperscript{−} solution, the reaction formula is as follows:

$$Ni + Cl^- \rightarrow Ni(Cl)_{aq} \rightarrow Ni(Cl) + e^-$$ (3) 

$$Ni(Cl) + OH^- \rightarrow Ni(Cl)(OH) + e^-$$ (4) 

$$Ni(Cl) + Cl^- \rightarrow NiCl_2 + e^-$$ (5)

Cl\textsuperscript{−}, H\textsubscript{2}O and OH\textsuperscript{−} are adsorbed on the metal surface, which hinders the formation of passivation film and causes the dissolution of passivation film and the emergence of active metal region. The adsorbed chloride ions and nickel ions form NiCl\textsubscript{2} and dissolve rapidly.

Figure 9(b) shows illustrates, due to the absence of passivation in the 5 wt% H\textsubscript{2}SO\textsubscript{4} solution, the Ecorr of the microparts shifted negatively from −0.227 V to −0.239 V following graphene addition, while the self-corrosion current density decreased from 2.588 \times 10^{-4} \text{ A cm}^{-2} to 2.021 \times 10^{-4} \text{ A cm}^{-2}. The corrosion current density of graphene/Ni is slightly lower than that of the pure Ni microparts over the entire potential range; however, the corrosion current density does not vary significantly in the range of −0.5 V to 0 V. Here, the impact of graphene addition on corrosion performance was not evident; the corrosion rate decreased from 2.7912 \text{ mil} \cdot \text{yr}^{-1} to 2.1797 \text{ mil} \cdot \text{yr}^{-1}. In the absence of a passivating film, we observe that the addition of graphene refines the grain size, inhibits the formation of microcracks—effectively hindering the corrosion of H\textsubscript{2}SO\textsubscript{4} on the microparts. In the SO\textsubscript{4}\textsuperscript{2−} solution, the reaction formula is as follows:

$$Ni + SO_4^{2−} \rightarrow NiSO_{4(ad)} + 2e^-$$ (6) 

$$NiSO_{4(ad)} \rightarrow Ni^{2+} + SO_4^{2−}$$ (7)

The adsorption of sulfate anion(SO\textsubscript{4}\textsuperscript{2−}) [42] prevents the formation of passivation film on the surface of micro parts, thus accelerating the dissolution of materials.

As illustrated in figure 9(c), the Ecorr of the microparts shifted slightly in the negative direction from −0.960 V to −0.678 V in the 5 wt% NaOH solution following the addition of graphene. The self-etching current density decreased from 1.846 \times 10^{-4} \text{ A cm}^{-2} to 2.878 \times 10^{-4} \text{ A cm}^{-2}, which is nearly 20% lower than that of pure Ni. This can be attributed to the formation of a compact Ni(OH)\textsubscript{2} passivation film. The formation of a passivation film reduces the corrosion behavior of OH\textsuperscript{−} on the microparts, have reduced the corrosion rate from 1.9892 \text{ mil} \cdot \text{yr}^{-1} to 0.3101 \text{ mil} \cdot \text{yr}^{-1}. These comprehensive results demonstrate that, also in the 5 wt% NaOH, the addition of graphene refines the grain size and increases the number of nucleation sites of the passivation film (leading to an increase in its proportion)—improving the overall corrosion resistance of graphene/Ni microparts. The main corrosion reaction formula is as follows:

$$Ni + H_2O \rightarrow Ni(H_2O)_{ad} \rightarrow Ni(OH)_{ad} + H^+ + e^-$$ (8) 

$$Ni(OH)_{ad} + H_2O \rightarrow Ni(OH)(H_2O)_{ad} \rightarrow Ni(OH)_2 + H^+ + e^-$$ (9)

$$Ni(OH)_2 \rightarrow NiO + H_2O$$ (10)

$$Ni(OH)_2 \rightarrow NiOOH + H^+ + e^-$$ (11)

Insoluble Ni(OH)\textsubscript{2} covers the surface of the corroded microparts and produces a passivation zone (approximately −400 mV to 400 mV) where the corrosion current density is almost independent of potential. When the potential increases to about 420 mV, the anodic corrosion current density increases sharply, indicating that the Ni(OH)\textsubscript{2} passivation film is broken down and pitting occurs on the surface of microparts.

3.2.3. EIS measurements

EIS was employed to measure the dielectric properties of the Ni and graphene/Ni nanocomposite microparts in a solution of 3.5 wt% NaCl, 5 wt% NaOH and 5 wt% H\textsubscript{2}SO\textsubscript{4}. Relevant data are presented in table 2. Figure 10 presents the Nyquist diagram of the test results, where the dots represent measured experimental data. The larger the capacitive electric resistance, the greater the electrochemical transfer resistance (thus, corresponding to a higher corrosion resistance). Figures 10(a)–(c) illustrates how the arc diameters of graphene/Ni composite
microparts are larger than those of pure Ni microparts, indicating that the addition of graphene contributes to improved grain refinement and enhanced corrosion resistance relative to that of pure nickel.

Zview2 software was used to fit the electrochemical impedance spectrum, yielding the equivalent circuit diagram as shown in figure 11. The relevant parameters obtained after fitting are shown in Table 2. $R_s$ represents the resistance of the solution; the solution impedance varied negligibly before and after the addition of graphene, indicating the homogeneity of the test solution. $R_{ct}$ is the charge transfer resistance, which also exhibited only significant differences between the two samples. The higher the value, the more difficult it is for the charge to pass through the interface between the metal matrix and solution, and the more difficult the corrosion process. The charge transfer resistance of Ni in NaCl, NaOH and H$_2$SO$_4$ solution is 5737 $\Omega$, 7135 $\Omega$, 272.1 $\Omega$, respectively, while the charge transfer resistance of graphene/Ni is 43900 $\Omega$, 25649 $\Omega$, 644.9 $\Omega$. The charge transfer process is hindered in the microparts with graphene owing to its grain-size refinement non-permeability. CPE-T represents the capacitance between the formed corrosion product and the micropart. The presence of CPE is related to surface uniformity. As can be seen from the figure, as the $R_{ct}$ value of the Ni graphite composite microparts increases, the diameter of curve within the semicircle becomes larger. It shows that the corrosion resistance of the composite microparts is better than that of the bare nickel.

### 3.2.4. Bode diagram

Figure 12 illustrates the Bode diagrams of pure Ni and graphene/Ni microparts in a solution of 3.5 wt% NaCl, 5 wt% NaOH and 5 wt% H$_2$SO$_4$. Modulus and phase values of impedance are often used to evaluate the stability of passivation films. The larger the value of $|Z|$, the closer the phase angle is to 90°, and the more stable the passivation film [43]. The Bode plot can be divided into three sections based on the excitation frequency. In 3.5 wt% NaCl (shown in figure 12(a)), the curve of $|Z|$ is relatively flat in the higher frequency range, corresponding to the resistance of electrolyte solution. In the medium frequency range, due to the dominant effect of the microparts’ surface capacitance, the slope of the $|Z|$ value curve is close to 1, while the phase angle reaches a maximum (approximately 45°). At low frequencies, the $|Z|$ curve tends to flatten out because the resistance of
the tiny parts dominates the impedance. In addition, the Bode plot provides more qualitative details by analyzing the variation of the impedance modulus at 0.01 Hz. Following the addition of graphene, $|Z_{0.01\text{ Hz}}|$ gradually increased from $3.94 \times 10^3 \ \Omega \cdot \text{cm}^2$ to $2.34 \times 10^5 \ \Omega \cdot \text{cm}^2$, reflecting an improved corrosion resistance. In 5 wt% H$_2$SO$_4$ (shown in figure 12(b)), the curve of $|Z|$ is relatively flat in the higher frequency range; in the intermediate frequency range, the curve of the $|Z|$ value increases slightly though is still relatively flat while the phase angle reaches a maximum of about 70°. At low frequencies, the slope of the $|Z|$ curve is close to zero because the resistance of the microparts dominates the impedance. In addition, following the addition of graphene, $|Z|$ increased from $1.99 \times 10^5 \ \Omega \cdot \text{cm}^2$ to $5.37 \times 10^5 \ \Omega \cdot \text{cm}^2$ at 0.01 Hz also reflected an improved of corrosion resistance. These results demonstrate that there is no new interface in the electrochemical process and the corrosive medium does not penetrate the interior of the microparts. Therefore, the addition of graphene effectively protection the nickel-based microparts. In the 5 wt% NaOH (shown in figure 12(c)), the curve of $|Z|$ is relatively flat in the higher frequency range. In the intermediate frequency range, the slope of the $|Z|$ curve is close to 1, while the phase angle reaches a maximum at approximately 80°. At low frequencies, the $|Z|$ curve tends to flatten out because the resistance of the tiny parts dominates the impedance. $|Z|$ gradually increased from $5.39 \times 10^5 \ \Omega \cdot \text{cm}^2$ to $3.00 \times 10^5 \ \Omega \cdot \text{cm}^2$ following the addition of graphene, further reflecting an improvement in corrosion resistance. Collectively, these findings demonstrate that the addition of small amounts of graphene (0.1 wt%) to nickel-based microparts improves their corrosion resistance, whether in acidic, alkaline, or neutral solutions.

The corrosion processes of Ni and graphene/Ni are presented in figure 13. The addition of graphene prolongs the corrosion path of the corrosive medium and refines the grain, mainly due to the impermeability and chemical stability of graphene.

### 3.2.5. Mechanical properties of microparts

Figure 14 presents the Vickers hardness of pure Ni and graphene/Ni composite microparts. The Vickers hardness value of electrodeposited Ni microparts is about 310 HV. The addition of graphene reduces the grain size of Ni-based microparts and increases the Vickers hardness value to 550 HV, a nearly 80% gain. These findings demonstrate that the addition of graphene can significantly improve the hardness of nickel-based microparts, mainly because graphene in the fine Ni matrix inhibits dislocation movement and plastic flow. At the same time, the inherent high mechanical strength of graphene contributes to a higher microhardness of the composite.

Figures 15(a) and (b) respectively present the load-displacement curves of pure Ni and graphene/Ni microparts, respectively, obtained from the nanoindentation experiment. Figures 15(c) and (d) are the elastic modulus of Ni and graphene/Ni microparts, respectively. Relative to pure nickel microparts, the grain size was reduced from 11.08 μm to 0.94 μm by introducing graphene. As a result, a comparison of the two sets of curves in figures 15(a) and (b) shows that there is a significant change in the load difference required to press at the same.
depth of 2000 nm and at the same loading rate of $1 \times 10^{-1}\text{s}^{-1}$. As can be seen from the figure, both Ni and graphene/Ni microparts exhibit obvious creep behavior (i.e., plastic deformation) during the load keeping stage. The elastic modulus of graphene/Ni is about 238 GPa, higher than the 228 GPa of pure Ni—demonstrating that the addition of graphene can significantly improve the plastic deformation of microparts.

### 3.3. Corrosion properties and vickers hardness of graphene/Ni following heat treatment

Figure 16 presents the open-circuit voltage, Tafel, EIS, and Bode diagram for the graphene/Ni composite microparts in 3.5 wt% NaCl solution in the as-cast state and following heat treatment at 200, 300, 500, and 700 °C. The OCP and Tafel diagrams of the five types of microparts are shown in figures 16(a)–(b). The OCP values reflected the thermodynamic conditions of the corrosion process. It can be seen that the open-circuit voltage of

---

**Figure 14.** Vickers microhardness measurements of Ni and graphene/Ni composite microparts.

**Figure 15.** (a)–(b) are the load-displacement curves of Ni and graphene/Ni composite microparts at a loading rate of $1 \times 10^{-1}\text{s}^{-1}$, and (c)–(d) are the elastic modulus graphs of Ni and graphene/Ni composite microparts at a loading rate of $1 \times 10^{-1}\text{s}^{-1}$, respectively.
the microparts annealed at 200 °C is higher than that of the as-cast microparts. In addition, the corrosion current density of $1.341 \times 10^{-5}$ A dm$^{-2}$ at 200 °C is approximately one third that of the corrosion current density of $1.840 \times 10^{-5}$ A dm$^{-2}$ for the as-cast graphene/Ni microparts; the corrosion rate is increased by a factor of approximately nearly one (demonstrating improved corrosion resistance) as derived from the Tafel diagram. The Nyquist and Bode diagrams of the microparts before and after heat treatment are presented in figures 16(c)–(d). A common feature in the Nyquist diagram of all the specimens (figure 16(c)) can be observed, that is, the existence of a capacitive semicircle within the measured frequency range. The semicircle size corresponding to the annealed samples was larger than that of the as-cast samples, while the semicircle size of the annealed samples at 200 °C was larger than that of the annealed samples at 300 °C, 500 °C and 700 °C, and significantly larger than that of the as-cast samples. Figure 16(d) shows a comparison of the Bode plots of graphene/Ni before and after the heat treatment. The impedance $|Z|$ value, the greater the phase angle is close to 90°, the greater the stability of the passive film. It can be seen that the impedance and phase angle of the sample annealed at 200 °C is the largest, while the impedance corresponding to the as-cast state is the smaller, and the impedance of the sample annealed at 700 °C is the smallest. In conclusion, heat treatment at 200 °C can improve the corrosion resistance of graphene/Ni microparts, mainly due to the removal of hydrogen atoms in the microparts, improvement of residual internal stress, reduction of cracks, recrystallization of grains, increase in annealing twins, and increase in interfacial energy. When the annealing temperature was higher than 300 °C, the corrosion resistance decreased because the grain size increased, the grain boundary area decreased, and more chloride ions were adsorbed onto the surface of the microparts—thus inhibiting the formation of the passivation film. Therefore, both twin density and grain size significantly influence the corrosion resistance of the material. We further note that, all other things equal, twin density has a greater influence on the corrosion resistance of the material than grain refinement.

Figure 17 shows the Vickers hardness of the graphene/Ni composite microparts before and after the heat treatment. The Vickers hardness of the electrodeposited graphene/Ni microparts was approximately 550 HV, decreasing gradually with the increase in heat-treatment temperature; the hardness decreased by a factor of 1 when it reached 300 °C. The Vickers hardness decreases slightly at 200 °C, which is mainly due to the removal of internal stress at 200 °C and does not affect the grain size. However, the decrease in hardness following high-temperature treatment can primarily be attributed to the decrease in grain boundary area due to grain
nucleation and growth. The proportion of $\sum 3$ special grain boundaries first increased and then decreased, while the inhibition of dislocation movement decreased—decreasing the microhardness decreased significantly.

4. Conclusions

- In this study, pure Ni and graphene/Ni composite microparts were successfully prepared using UV-LIGA technology. The addition of graphene increased the grain orientation from (200) to (220), increased the potential barrier, and reduced the grain size by 38% - as confirmed by TEM.

- Compared with pure Ni, the corrosion rates of the graphene/Ni microparts decreased by 73%, 22% and 84% in 3.5 wt% NaCl, 5 wt% $H_2SO_4$ and 5 wt% NaOH solution, respectively. Passivation in 5 wt% NaOH solution film resulted in a decrease in the nearby carrier density and an increase in chemical stability, while no passivated film was formed in the solutions of 3.5 wt% NaCl and 5 wt% $H_2SO_4$. The corrosion resistance of graphene/Ni in $H_2SO_4$ was less than that in the neutral and alkaline solutions, which may be related to the strong corrosivity of $SO_4^{2-}$ resulting in the lack of an opportunity to form a passivation film.

- Heat treatment and the removal of hydrogen atoms from the material improved the residual internal stress of the microparts, reduced or eliminated cracks, while improving grain recrystallization and grain growth. At 200 °C, the increase in grain size is not obvious, and the microhardness is varied slightly relative to that of as-cast graphene/Ni; but the corrosion rate is increased by a factor of approximately nearly one, which can mainly be attributed to the increase in the $\sum 3$ grain boundary based on the nanocrystalline grain size. A further increase in the heat-treatment temperature results in the formation of microcrystals. With an increase in the grain size, microcracks also increased and the $\sum 3$ grain boundary decreased, resulting in the deterioration of the corrosion resistance of the materials.

Acknowledgments

The authors acknowledge the financial support from the Natural Science Foundation of Beijing (No. 2212025); This work was supported by the Science and Technology Program of Beijing Municipal Education Commission (No. KM202010005007).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
ORCID iDs

Wenhua Suo https://orcid.org/0000-0002-3216-9615
Zhuangzhuang Liu https://orcid.org/0000-0003-1978-213X

References

[1] Lorenz H et al 1998 Fabrication of photoplastic high–aspect ratio microparts and micromolds using SU-8 UV resist Microsyst. Technol. 4 143–6
[2] Yi L et al 2005 Swelling of SU-8 structure in Ni mold fabrication by UV-LIGA technique Microsyst. Technol. 11 1272–5
[3] Murray R P et al 2020 A defect-resistant Co–Ni superalloy for 3D printing Nat. Commun. 11 4975
[4] Martin M L et al 2020 Dominant factors for fracture at the micro-scale in electrodeposited nickel alloys Sensors and Actuators, A, Physical 314 33487884
[5] Shinohara N A and Shimomura K I 2009 Corrosion resistance of nickel and nickel-base alloys in caustic alkalies Corros. Eng. 18 527–31
[6] Bakht B and Akbari A 2013 Nanocrystalline Ni–Co alloy coatings: electrodosposition using horizontal electrodes and corrosion resistance, Journal of Coatings Technology & Research 10 285–95
[7] Dong S Y et al 2004 Properties and strengthening mechanism of brush plated nanoparticle reinforced composite coatings Transactions of Nonferrous Metals Society of China 14 182–5
[8] Fayyaz O et al 2021 Enhancement of mechanical and corrosion resistance properties of electrodeposited Ni–P–TiC composite coatings Sci. Rep. 11 5327
[9] Sen R et al 2011 Effect of stirring rate on the microstructure and microhardness of Ni–CeO2 nanocomposite coating and investigation of the corrosion property Surface & Coatings Technology 205 3847–55
[10] Wang D S et al 2019 Cabbage-like WS2/Ni bilayer thin film for improved tribological property Surf. Coat. Technol. 358 50–6
[11] Ratajksi T et al 2018 Microstructural characterization of SiO2/Ni nanocomposites electrodeposited from a sulphate bath modified by PEI Mater. Charact. 142 476–91
[12] Ratajksi T et al 2020 Effect of PDDA surfactant on the microstructure and properties of electrodeposited SiO2/Ni nanocomposites Mater. Charact. 163 110229
[13] Cui W et al 2018 Simulation and characterization of Ni–doped SiC nanocoatings prepared by jet electrodeposition Ceram. Int. 44 5500–5
[14] Jin H et al 2018 Synthesis and properties of electrodeposited Ni–CeO2 nano-composite coatings Rare Met. 37 148–53
[15] Srivastava M et al 2010 Improvement in the properties of nickel by Nano-Cr2O3 incorporation Surface & Coatings Technology 205 66–75
[16] Rasooli A et al 2018 Cr2O3 nanoparticles: a promising candidate to improve the mechanical properties and corrosion resistance of Ni-Co alloy coatings Ceram. Int. 44 6466–73
[17] Szczygiel B and Kolodziej M 2005 Composite Ni/Al2O3 coatings and their corrosion resistance Electrochem. Acta 50 4188–95
[18] Sangeetha S and Kalaignan G P 2015 Tribological and electrochemical corrosion behavior of Ni-W/BN (hexagonal) nano-composite coatings Ceram. Int. 41 10415–24
[19] Araghvani R et al 2012 Investigations on corrosion proceeding path and EIS of Ni–ZrO2 composite coating Surf. Eng. 28 508–12
[20] Kim S K and Tae-Sung O H 2011 Electrodeposition behavior and characteristics of Ni-carbon nanotube composite coatings Transactions of Nonferrous Metals Society of China 21 s68–72
[21] Yoshina A et al 2016 Novel aluminum-graphene and aluminum-graphite metallic composite materials: Synthesis and properties J. Alloys Compd. 663 439–59
[22] Raduscher F J et al 2017 A miniature electron ionization source fabricated using microelectromechanical systems (MEMS) with integrated carbon nanotube (CNT) field emission cathodes and low-temperature co-fired ceramics (LTCC) Int. J. Mass spectrom. 422 162–9
[23] Ding R et al 2018 A brief review of corrosion protective films and coatings based on graphene and graphene oxide J. Alloys Compd. 764 1039–55
[24] Li Q et al 2019 Thermodynamics and kinetics of an oxygen adatom on pristine and functionalized graphene: insight gained into their anticorrosion properties Physical Chemistry Chemical Physics: PCCP 21 12121–9
[25] Hsieh Y P et al 2014 Complete corrosion inhibition through graphene defect passivation ACS Nano 8 143–8
[26] Muresan L M 2021 Metal–graphene nanocomposites with improved mechanical and anti-corrosion properties Corrosion Protection of Metals and Alloys Using Graphene and Biopolymer Based Nanocomposites, (Boca Raton, FL: CRC Press) 133–48
[27] Chang W et al 2020 Characterizing corrosion properties of graphene barrier layers deposited on polycrystalline metals Surf. Coat. Technol. 398 126077
[28] Wang B et al 2021 Deposition mechanism and corrosion resistance of Ni-graphene composite coatings prepared by pulse electrodeposition Int. J. Electrochem. Sci. 16 6
[29] Gergely A 2017 A review on corrosion protection with single-layer, multilayer, and composites of graphene Corros. Rev. 38 155–225
[30] Camilli L, Yu F, Cassidy A, Hornekær L and Bøggild P 2019 Challenges for continuous graphene as a corrosion barrier Corros. Rev. 36 62
[31] Tsuchikin V N and Vasilenko E A 2011 Electrodeposition and properties of composite coatings based on nickel[(II) Rias. J. Appl. Chem. 84 2005–7
[32] Yasin G et al 2018 Synthesis of graphene–like Ni/graphene nanocomposites as an efficient anti-corrosive coating: effect of graphene content on its morphology and mechanical properties J. Alloys Compd. 755 79–88
[33] Raghupathy Y et al 2017 Copper–graphene oxide composite coatings for corrosion protection of mild steel in 3.5% NaCl Thin Solid Films 636 107–15
[34] Kumar C, Venkatesha T V and Shabarad R 2013 Preparation and corrosion behavior of Ni and Ni–graphene composite coating Mater. Res. Bull. 48 1477–83
[35] Moussavi R, Bohroolumo M E and Dellowar F 2019 The effect of surfactant on the microstructure and corrosion resistance of electrodeposited Ni-Mo alloy coatings Anti-Corrosion Methods and Materials (ahead of print) 66 631–7
[36] Bai F et al 2020 Performance of graphene dispersion by using mixed surfactants. Materials Research Express 7 095509
[37] Lou J et al 2003 A nano-indentation study on the plasticity length scale effects in LIGA Ni MEMS structures J. Mater. Sci. 38 4137–43
[38] Du L et al 2011 Mechanism analysis of ultrasonic treatment on SU-8 swelling in UV-LIGA technology. IET Micro and Nano Letters 6 900–3
[39] Li M et al 2017 Graphene platelet (GPL)/nickel (Ni) laminate coatings for improved surface properties Adv. Eng. Mater. 19 1600795
[40] Kamil M P et al 2020 Direct electro-co-deposition of Ni-reduced graphene oxide composite coating for anti-corrosion application Mater. Lett. 273 127911
[41] Tseluikin V N 2017 Electrodeposition and properties of composite coatings modified by fullerene C60 Protection of Metals and Physical Chemistry of Surfaces 53 433–6
[42] Bonin L, Vitry V and Delaunois F 2018 Corrosion behaviour of electroless high boron-mid phosphorous nickel duplex coatings in the as-plated and heat-treated states in NaCl, H2SO4, NaOH and Na2SO4 media Mater. Chem. Phys. 208 77–84
[43] Jyotheender K S, Gupta A and Srivastava C 2020 Grain boundary engineering in Ni-carbon nanotube composite coatings and its effect on the corrosion behaviour of the coatings Materialia 9 100617