Tribological properties of Ni$_3$Al matrix self-lubricating composites with a gradient composite structure prepared by laser melt deposition

Yuchun Huang, Tao Ma, Yubo Meng, Haishu Ma and Xiya Liu

1 School of Mechanical Engineering, Henan University of Engineering, No. 1, Xianghe Road, Zhengzhou, 451191, People’s Republic of China
2 State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People’s Republic of China
3 School of Mechatronic Engineering, Xi’an Technological University, 2 Xuefuzhong Road, Xi’an 710021, People’s Republic of China

E-mail: yuchunhuang@haue.edu.cn

Keywords: self-lubricating composites, sliding wear, tribological properties, gradient composite structure, wear mechanism

Abstract
As the contact part of metal-matrix self-lubricating composites during sliding friction, the friction interface layer directly affects the tribological performance of the material. However, the formation of the friction interface layer with outstanding tribological performance is limited by the friction conditions during sliding friction. To address this problem, based on the antifriction and wear resistance mechanisms of the in situ formed friction interface layer of Ni$_3$Al matrix self-lubricating composites (NMSCs) with homogeneous solid lubricant, Ni$_3$Al matrix self-lubricating composites with a gradient composite structure (Ni$_3$Al-GCS) were prepared via laser melt deposition, in which each component layer contained different contents of Sn-Ag-Cu and Ti$_3$SiC$_2$. Dry sliding friction tests of Ni$_3$Al-GCS against GCr15 steel balls were performed under different loading conditions. The results showed that the tribological performances of Ni$_3$Al-GCS in the range of 4–16 N were less affected by the variation of the loading conditions than those of NMSCs. The gradient composite structure of Ni$_3$Al-GCS could reduce the dependence of the tribological behavior on the friction conditions, resulting in excellent antifriction and wear resistance of Ni$_3$Al-GCS in a wide load range. In addition, the gradient composite structure could reduce the sliding contact damage of the friction contact surface of Ni$_3$Al-GCS, and contribute to the formation of friction interface layer rich in the lubrication phase and oxides, thus improving the tribological performance of Ni$_3$Al-GCS during sliding friction. This study provides new approaches for the tribological design of metal-matrix self-lubricating composites in a wide load range.

1. Introduction
Solid self-lubricating is one of the most common methods to improve the antifriction and wear resistance of various mechanical parts. It represents a significant advancement over traditional lubrication methods such as oil lubrication and grease lubrication, which are unable to solve the problems related to friction, wear and lubrication under extreme conditions such as high temperature and heavy load [1–3]. During dry sliding friction, the area formed on the worn surface and subsurface of the solid self-lubricating composites is called a friction interface layer in which the microstructure is different from the substrate [4–7]. The structural characteristics of the friction layer has an important influence on its tribological performance [6]. During sliding friction, the excellent antifriction and wear resistance of the friction interface layer are mainly because the subsurface friction action layer with excellent mechanical property supports the surface lubrication layer with good antifriction property [6–10]. In addition, the substrate layer acts as a support for the upper friction action layer, ensuring the overall strength of the material [6].
Many scholars have conducted numerous experimental researches on the effects of loading conditions and counter pairs on the formation of the friction interface layer and the tribological performance of Ni$_3$Al matrix self-lubricating composites (NMSCs) [6, 11, 12]. Huang et al [11] have studied the tribological performance of NMSCs at different sliding speeds. The results showed that the friction condition has an important influence on the tribological performance of the NMSCs. Under the loading condition of 10 N–0.7 m s$^{-1}$, a higher friction heat and lower shear stress contributed to the formation of a friction interface layer with excellent antifriction and wear resistance. The study of Zhu et al [12] showed that different counterface balls had significant effects on the stability and thickness of the friction interface layer of NMSCs, which in turn affected its tribological performance. Thus, the formation of a friction interface layer with excellent tribological performance during sliding friction is limited by the loading conditions. The tribological behaviors of NMSCs show obvious dependence on the friction conditions during sliding friction.

In recent years, functionally gradient design has been widely used in engineering materials [13, 14]. A study by material scientist Suresh [13] validated that the use of functionally graded materials as coatings could resist the surface deformation and contact damage caused by sliding, rolling, wear and fretting contact. By effectively controlling the gradient variation of the material, an unprecedented opportunity was provided to design a surface layer that inhibited deformation and fracture, which could not be achieved by conventional homogeneous materials. Chen et al [14] have studied the preparation and contact mechanics model of gradient materials, as well as the influence of gradient coating on the contact behavior. The wear resistance of the functionally graded materials under the influence of various factors was analyzed based on the stress field distribution of the contact interface in different contact models. The results showed that a reasonable design of various gradient parameters could effectively improve the antifriction properties of gradient composites [14]. It can be seen that the researches on the design, preparation and performances of gradient composites mainly focused on optimizing the design method and preparation process for better interlayer bonding force and stress distribution, leading to improvements in the mechanical performance and wear resistance. However, in order to reduce the limitation of loading conditions on the formation of a friction interface layer with excellent tribological performance, it is necessary to carry out thorough research on how to construct Ni$_3$Al matrix self-lubricating composites with a gradient composite structure (Ni$_3$Al-GCS) based on the antifriction and wear resistance mechanisms of in situ formed friction interface layer during sliding friction.

As an excellent high temperature structural material, Ni$_3$Al matrix composites have outstanding properties such as high specific strength and good oxidation resistance at high temperatures [15, 16], rendering them applicable in the manufacture of basic mechanical components such as forging dies, turbocharger parts, valves, and piston heads of internal combustion engines [17]. As a typical solid lubricant with low shear strength, high plasticity and ductility, Sn–Ag–Cu can improve the antifriction and wear resistance of solid self-lubricating materials [18–20]. As an ideal reinforcement for metal-matrix self-lubricating composites, Ti$_3$SiC$_2$ has a multilayer structure, which can effectively reduce the friction during sliding process and decrease the contact stress damage of the worn surface material [21, 22]. Moreover, it has a high melting point and high temperature chemical stability, which are ideal properties for laser melt deposition (LMD). Because of its flexibility in design and ease of processing, additive manufacturing has emerged as an ideal method for preparing mechanical parts with complex geometries [23–25]. These properties make additive manufacturing advantageous for use in the preparation of functionally graded materials [26, 27].

Hence, in order to reduce the limitation of loading conditions on the formation of a friction interface layer with excellent tribological performance, and based on the antifriction and wear resistance mechanisms of the in situ formed friction interface layer of NMSCs during sliding friction, Ni$_3$Al-GCS was prepared via LMD so that it can play an excellent antifriction and wear resistance in a wide load range. Furthermore, the design, preparation, tribological properties and self-lubricating mechanism of Ni$_3$Al-GCS were systematically investigated.

2. Experimental details

2.1. Design and preparation of Ni$_3$Al matrix self-lubricating composites with a gradient composite structure

Based on the antifriction and wear resistance mechanisms of the friction interface layer of the NMSCs [6–9], the structure and composition of Ni$_3$Al-GCS were designed such that each component layer contained different contents of Sn–Ag–Cu and Ti$_3$SiC$_2$. The functional characteristics and contents of the lubrication phase and enhanced phase of each component layer of Ni$_3$Al-GCS are shown in table 1. Figure 1 shows the schematic diagrams of the structural characteristics and LMD system for fabricating the Ni$_3$Al-GCS. During sliding friction, it is necessary to systematically design the contents of the lubrication phase and enhanced phase of each component layer of Ni$_3$Al-GCS to achieve good mechanical and tribological performance. As shown in table 1, based on relevant studies [28], the Sn–Ag–Cu contents in the lubrication layer, middle layer and substrate layer of
Ni₃Al-GCS were designed to be 8.0, 6.0 and 4.0 wt%, respectively. The Ti₃SiC₂ contents in the lubrication layer, middle layer and substrate layer of Ni₃Al-GCS were designed to be 12.0, 9.0 and 6.0 wt%, respectively.\[29\].

In addition, the laser power, laser scanning rate and other LMD parameters have important effects on the mechanical property and tribological performance of Ni₃Al matrix self-lubricating composites.\[30\]. Based on relevant studies\[26, 31\], after multiple LMD tests, the optimum technological parameters were as follows: laser power, 2000 W; scanning velocity, 7.2 mm s⁻¹; spot diameter, 6 mm; scanning distance, 3 mm; layer thickness, 0.1 mm.

The chemical compositions of the Ni₃Al-based alloy are listed in table 2. When the element ratio of Sn, Ag and Cu is set to 50:40:10, the Sn-Ag-Cu alloy exhibit an optimal lubrication performance.\[28\]. Based on the optimal addition ratio, powders of Sn, Ag and Cu were selected for preparing the 50Sn40Ag10Cu spherical powder. According to the addition proportion of Ti₃SiC₂ in the Ni₃Al matrix, three kinds of mixed powders of the Ni₃Al matrix and Ti₃SiC₂ were prepared for the preparation of each constituent layer of Ni₃Al-GCS respectively. Subsequently, the starting powders were uniformly mixed in a planetary ball mill. Finally, the Ni₃Al matrix spherical powder containing Ti₃SiC₂ and the 50Sn40Ag10Cu spherical powder were prepared using an LD-QW/500 centrifugal atomization device respectively. Figures 2(a) and (b) show the field emission scanning electron microscopy (FESEM) image and X-ray diffraction (XRD) pattern of the Ni₃Al matrix spherical powder containing Ti₃SiC₂ (particle size: 53–96 μm), respectively. Figures 2(c) and (d) show the FESEM image and XRD pattern of the 50Sn40Ag10Cu spherical powder (particle size: 45–106 μm), respectively.

The thickness of each layer of the gradient self-lubricating composites has an important influence on its mechanical and tribological performance.\[32\]. A multi-factor orthogonal test can be used to optimize three factors: the thicknesses of the lubricating layer, middle layer and substrate layer. If three levels are considered for each factor, the orthogonal table L₉(3⁴) can be selected. Based on a relevant study\[26\], the thickness range of each component layer was preliminarily determined. The combination schemes for the thickness of each layer of Ni₃Al-GCS were designed based on the orthogonal test shown in table 3. The lubricating layer and middle layer had thicknesses of 600–800 μm each, while the substrate layer had a thickness of 6–8 mm. According to the orthogonal test scheme, nine Ni₃Al-GCS samples with different layer thickness combinations were prepared via LMD. Based on the test parameters set in section 2.2, friction and wear tests were performed at 0.2 m s⁻¹–12 N

| Component layer | Functional characteristics | Sn-Ag-Cu contents (wt.%) | Ti₃SiC₂ contents (wt.%) |
|-----------------|---------------------------|--------------------------|-------------------------|
| lubricating layer | rich in lubricating phase and enhanced phase | 8.0 | 12.0 |
| middle layer | supporting the upper lubricating layer | 6.0 | 9.0 |
| substrate layer | ensuring the overall strength of Ni₃Al-GCS | 4.0 | 6.0 |

Table 2. Chemical compositions of Ni₃Al-based alloy (wt.%).

| Composition | Al | Mo | Cr | Zr | B | Ni |
|-------------|----|----|----|----|---|----|
| Content     | 8.0–8.5 | 6.5–7.0 | 5.5–6.0 | 0.1–0.3 | 0.03–0.05 | Balance |
to analyze the tribological performance of each Ni₃Al-GCS sample. The tribological performances of the Ni₃Al-GCS specimens with different layer thicknesses are listed in Table 3. Based on the tribological performance of each sample, the optimal thickness combination of each component layer of Ni₃Al-GCS was determined. When the thicknesses of the lubricating layer, middle layer and substrate layer were 600, 800 µm and 8 mm, respectively, the tribological performance of Ni₃Al-GCS was optimal, with an average friction coefficient and specific wear rate of 0.23 and $5.3 \times 10^{-6} \text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ respectively. The final thickness of the Ni₃Al-GCS is 9.4 mm.

Based on the material design parameters such as lubricant addition proportion, LMD parameters and the thickness of each component layer, Ni₃Al-GCS were prepared using an additive manufacturing system (LDM-8060LMD, Nanjing Zhongke Yuchen Laser Technology Co. Ltd, China). Before LMD, the spherical powders were dried for 20 min at 80 °C using a vacuum drying oven. According to the addition ratio of 50Sn40Ag10Cu and Ti₃SiC₂ in each component layer listed in Table 1, appropriate proportions of the Ni₃Al matrix spherical powder containing Ti₃SiC₂ and the 50Sn40Ag10Cu spherical powder were uniformly mixed. Before preparing the next component layer of the Ni₃Al-GCS, the corresponding mixed spherical powder needs to be replaced.

Table 3. Orthogonal test parameters for the thicknesses of each component layer of Ni₃Al-GCS and corresponding tribological performances at 0.2 m s⁻¹–12 N.

| test number | lubricating layer thickness (µm) | middle layer thickness (µm) | substrate layer thickness (mm) | friction coefficient | specific wear rate ($10^{-6} \text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$) |
|-------------|---------------------------------|-----------------------------|-------------------------------|----------------------|-----------------------------------------------|
| 1           | 600                             | 600                         | 6                             | 0.27                 | 7.8                                           |
| 2           | 600                             | 700                         | 7                             | 0.26                 | 7.6                                           |
| 3           | 600                             | 800                         | 8                             | 0.23                 | 5.3                                           |
| 4           | 700                             | 600                         | 7                             | 0.28                 | 9.4                                           |
| 5           | 700                             | 700                         | 8                             | 0.25                 | 6.8                                           |
| 6           | 700                             | 800                         | 6                             | 0.23                 | 5.9                                           |
| 7           | 800                             | 600                         | 8                             | 0.31                 | 11.7                                          |
| 8           | 800                             | 700                         | 6                             | 0.25                 | 10.7                                          |
| 9           | 800                             | 800                         | 7                             | 0.24                 | 10.3                                          |
Under the optimum LMD parameters, each component layer of the Ni$_3$Al-GCS was prepared in the order of substrate layer, middle layer and lubricating layer, respectively. The Ni$_3$Al-GCS sample has the dimensions of $25 \text{ mm} \times 25 \text{ mm} \times 9.4 \text{ mm}$. Prior to the friction tests, the surfaces of the Ni$_3$Al-GCS samples were polished with emery papers to obtain a low surface roughness. The surface roughness of the as-prepared specimen was measured as $Ra = 0.15 \pm 0.02 \mu m$.

2.2. Friction and wear tests

The friction tests of Ni$_3$Al-GCS and NMSCs were carried out using an MFT-5000 multi-functional tribometer (Rtec, USA) under the same test conditions. As shown in figure 3, a GCr15 steel ball was chosen to be tested against the specimens at room temperature (25 °C) with the following parameters [12]: relative humidity, ~40%–60%; sliding speed, 0.2 m s$^{-1}$; applied loads, 4, 8, 12 and 16 N [8]; friction radius, 5 mm; test time, 90 min. The friction coefficients of the Ni$_3$Al-GCS and NMSCs were automatically measured using a tribometer during sliding friction. The wear volume of the samples was measured to calculate the specific wear rate. The cross-section area of the wear scar was measured using an ST400 profilometer. As shown in figure 4(b), a 2D cross-section profile can be obtained by measuring the 3D profile of the worn surface (see figure 4(a)) along the straight line (AA). The friction and wear tests were repeated thrice to obtain reliable mean values.
2.3. Analysis and microstructural observation

To analyze the wear mechanisms, the worn surface morphologies of the NMSCs and Ni$_3$Al-GCS were observed by electron probe microanalyser (EPMA). The elemental distributions of cross-sections of Ni$_3$Al-GCS were analyzed by energy dispersive spectroscopy (EDS). The hardness of each component layer of Ni$_3$Al-GCS was measured using an HVS-1000 Vickers hardness instrument with a loading force of 1 kg and dwell time of 10 s. The percentage of voids in the Ni$_3$Al-GCS was measured by an image analyzer having an Image-Pro Plus 6 Metallurgical Image Analysis System [33]. The adhesion strengths between the component layers of the Ni$_3$Al-GCS were measured by an automatic scratch tester equipped with a wedge shaped stylus [34]. The metallographic microstructures of each component layer of Ni$_3$Al-GCS were acquired using a VHX-3000 optical microscope. X-ray photoelectron spectroscopy (XPS) was performed to study the elemental states of the worn surface of Ni$_3$Al-GCS. To investigate the wear mechanisms, the morphologies of the wear scar cross-sections of the NMSCs and Ni$_3$Al-GCS were observed using FESEM. The microstructure of the friction interface layer of Ni$_3$Al-GCS was observed using high-resolution transmission electron microscopy (HRTEM).

3. Results and discussion

3.1. Morphology, composition and microstructure analyses of Ni$_3$Al-GCS

The composition, microstructure and mechanical properties of Ni$_3$Al-GCS have an important influence on their tribological properties [15]. As shown in figure 5(a), the Ni$_3$Al-GCS fracture surface can be divided into the lubrication layer, middle layer and substrate layer from the top to bottom. Figure 5(b) shows the local magnification of the interface junction section between the lubricating layer and the middle layer of Ni$_3$Al-GCS. Moreover, the interface of each component layer of Ni$_3$Al-GCS has good interfacial wettability and good bonding. Figure 5(c) shows the backscattered electron image of the fracture surface junction section between the lubricating layer and the middle layer of Ni$_3$Al-GCS. As shown in figure 5(c), the lubricating layer is brighter than the middle layer, indicating a higher Sn-Ag-Cu content in the lubricating layer. Figures 5(d)–(i) shows the
representative elemental distribution images of the cross-section junction section between the lubricating layer and middle layer of Ni$_3$Al-GCS. The element contents of the box labeled regions shown in figure 5(a) are exhibited in the typical EDS maps (see figure 6). The results of elemental distribution and EDS analyses indicate that a gradient distribution of the lubrication phase and enhanced phase in each component layer of the Ni$_3$Al-GCS is realized.

The percentage of voids in the Ni$_3$Al-GCS is found to be 1.5%, indicating that the Ni$_3$Al-GCS has a dense microstructure. The adhesion strength between the substrate layer and middle layer is found to be 263.2 ± 11.0 MPa. The adhesion strength between the middle layer and lubricating layer is found to be 247.3 ± 10.5 MPa. The average hardness values of the lubricating layer, middle layer and substrate layer of Ni$_3$Al-GCS are 628.4, 587.5 and 549.2 HV, respectively. This indicates that the hardness of each constituent layer of the Ni$_3$Al-GCS shows a gradient change. The hardness distribution of the constituent layers of the Ni$_3$Al-GCS correlates closely with their metallographic microstructure, which is verified from the optical microscopy images (see figure 7). The microstructures of each component layer of the Ni$_3$Al-GCS are mainly composed of equiaxed crystals, columnar crystals and cellular crystals. In the substrate layer with the Ti$_3$SiC$_2$ content of 6.0 wt.%, the grain size of the equiaxed crystal is approximately 12–15 μm. In the middle layer with the Ti$_3$SiC$_2$ content of 9.0 wt.%, the grain size of the equiaxed crystal is about 8–10 μm. In the lubricating layer with the
Ti$_3$SiC$_2$ content of 12.0 wt%, the grain size of the equiaxed crystal is about 6–8 μm. As shown in figures 7(b), (d), (f), elongated columnar crystals are gradually refined and the number of granular cellular crystals increases with increasing Ti$_3$SiC$_2$ content of each component layer. Thus it can be seen that the constituent layer of Ni$_3$Al-GCS with a higher Ti$_3$SiC$_2$ content displays a much finer microstructure, indicating that the increase of the Ti$_3$SiC$_2$ content contributes to grain refinement. On the one hand, Ni$_3$Al grains grow along the direction of Ti$_3$SiC$_2$ during LMD. On the other hand, the platy structure of Ti$_3$SiC$_2$ hinders grain growth, thus contributing to the grain refinement of the Ni$_3$Al-GCS [26]. Therefore, a pre-designed Ti$_3$SiC$_2$ gradient content can result in different grain sizes for each component layer of the Ni$_3$Al-GCS.

3.2. Tribological properties of Ni$_3$Al matrix self-lubricating composites with a gradient composite structure

As shown in figure 8, average friction coefficients and specific wear rates of the NMSCs and Ni$_3$Al-GCS against the GCr15 steel balls are obtained after friction and wear tests. At 12 N, the NMSCs and Ni$_3$Al-GCS exhibit optimal tribological performance. The average friction coefficients of the NMSCs and Ni$_3$Al-GCS are 0.24 and 0.23 respectively, and the average specific wear rates are $5.9 \times 10^{-6}$ and $5.3 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$ respectively. This reveals that the tribological performance of Ni$_3$Al-GCS is similar to that of NMSCs at 12 N. In the range of 4–16 N, the average friction coefficients of NMSCs and Ni$_3$Al-GCS are 0.38 and 0.32 respectively, while the average specific wear rates are $8.1 \times 10^{-6}$ and $6.7 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$ respectively. Compared to that of NMSCs, the wear resistance of Ni$_3$Al-GCS at 4–16 N can be improved by approximately 17%. Therefore, the overall tribological performance of Ni$_3$Al-GCS is better than that of NMSCs. In addition, in the range of 4–16 N,
the differences between the maximum and minimum values of the friction coefficients of NMSCs and Ni$_3$Al-GCS are 0.27 and 0.24 respectively. Moreover, the differences between the maximum and minimum values of the specific wear rates of NMSCs and Ni$_3$Al-GCS are $5.3 \times 10^{-6}$ and $2.9 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$ respectively. Therefore, in the 4–16 N range, the tribological performance of Ni$_3$Al-GCS is less affected by the change in loading conditions than that of NMSCs.

The dynamic friction coefficient curves of NMSCs and Ni$_3$Al-GCS at 4, 8, 12 and 16 N are shown in figure 9. The friction coefficients of NMSCs and Ni$_3$Al-GCS at 12 N are lower than those obtained at 4, 8 and 16 N. Additionally, the fluctuation of the friction coefficient with the sliding time at 12 N is more stable than those obtained at 4, 8 and 16 N. Moreover, compared to NMSCs, Ni$_3$Al-GCS takes a shorter time from the initial wear stage to the stable wear stage at 8 and 12 N. Thus, the gradient composite structure can promote Ni$_3$Al-GCS to reach the stable wear stage with excellent tribological performance, reducing the dependence of the tribological behavior on the friction time during sliding friction. In engineering, one of the main purposes of studies on friction and wear is the attainment of a stable wear stage of the friction system as soon as possible and sustenance of the stable wear stage as long as possible [35].

3.3. Analysis of worn surfaces and cross-section morphologies, as well as self-lubricating mechanism of Ni$_3$Al-GCS

Figure 10 shows the representative worn surface morphologies of NMSCs and Ni$_3$Al-GCS under applied loads of 8, 12 and 16 N. As shown in figure 10(a), the worn surface of NMSCs is covered with parallel furrows, indicating that there is no ideal condition for the formation of a stable lubricating layer at 8 N. As shown in figure 10(b), compared to that of NMSCs, the worn surface of Ni$_3$Al-GCS is smoother. In addition, the number of furrows on the worn surface of Ni$_3$Al-GCS is reduced at 8 N, indicating that the major wear mechanism is slight abrasive
As shown in figures 10(c) and (d), the worn surfaces of NMSCs and Ni$_3$Al-GCS are smooth at 12 N, revealing that relatively complete and stable lubricating layers are formed on the worn surfaces. The smooth worn surfaces of NMSCs and Ni$_3$Al-GCS can result in the lower friction coefficients than those obtained at 4, 8 and 16 N. In figure 10(e), some obvious material spalling and cracks are visible on the worn surface of the NMSCs at 16 N, indicating that the main wear mechanism is severe fatigue wear. When the load increases to 16 N, the plastic deformation degree of the worn surface material increases. Under the continuous sliding action of the GCr15 steel ball, the tiny cracks on the worn surface are expanding constantly, increasing the specific wear rate of the material. The fatigue spalling pit on the worn surface of the NMSCs increases the friction coefficient at 16 N. In figure 10(f), some fine cracks can be found on the worn surface of the Ni$_3$Al-GCS at 16 N, indicating that the major wear mechanism is slight fatigue wear. The representative worn surface morphologies of the NMSCs and Ni$_3$Al-GCS show that the tribological performance of Ni$_3$Al-GCS under optimal loading conditions (12 N) is similar to that of NMSCs. Under other loading conditions, the tribological performances of Ni$_3$Al-GCS are relatively good. This indicates that the gradient composite structure of Ni$_3$Al-GCS can reduce the dependence of the tribological behavior on the friction conditions during sliding friction, realizing the excellent antifriction and wear resistance properties of Ni$_3$Al-GCS in a wide load range.

Figure 11 shows the typical EPMA morphologies of the wear scars of GCr15 steel balls against the Ni$_3$Al-GCS under applied loads of 4, 8, 12 and 16 N. As shown in figures 11(a) and (b), some wear debris and furrows are easily distinguished on the worn surfaces of GCr15 steel balls under applied loads of 4 and 8 N. The main wear mechanisms are abrasive wear at 4 and 8 N. As shown in figure 11(c), some flaky transfer film can be seen on the
worn surface of GCr15 steel ball at 12 N. The transfer film produced by the Ni$_3$Al-GCS during dry friction can play a role of antifriction [39]. As shown in figure 11(d), a lot of wear debris can be seen on the worn surface of GCr15 steel ball at 16 N. As the applied load increases to 16 N, due to the increase of the plastic deformation degree of the worn surface material, the specific wear rate of the Ni$_3$Al-GCS increases, resulting in a lot of wear debris adhering to the worn surface of GCr15 steel ball.

In order to further understand the composition and performance of the friction interface layer of Ni$_3$Al-GCS during sliding friction, XPS was performed to study the elemental states of the worn surface at 12 N, and the results are shown in figure 12. The Ni$_2$p spectrum shows a peak at 855.4 eV [40], indicating that Ni is partially oxidized to NiO. The Al$_2$p spectrum shows a peak at 74.3 eV [41], confirming the presence of Al$_2$O$_3$. The Ti$_2$p peak at 458.6 eV [42] and Si$_2$p peak at 102.1 eV [43] match with TiO$_2$ and SiO$_2$ peaks, respectively, indicating the partial oxidation of Ti$_3$SiC$_2$. The Cls peak at 281.6 eV confirms the presence of TiC [44]. Moreover, the Sn$_3$d spectrum shows a peak at 485.6 eV [45], revealing that Sn is partially oxidized to SnO$_2$. The Ag$_3$d spectrum shows a peak at 368.8 eV [20], demonstrating the distribution of Ag on the worn surface of Ni$_3$Al-GCS. The Cu$_2$p peak at 931.2 eV indicates the formation of CuO [45]. Furthermore, the oxidation states of SnO$_2$ and CuO can also be confirmed by O$_1$s spectrum [45]. These oxides such as NiO, TiO$_2$, SnO$_2$, and CuO have remarkable antifriction and wear resistance performance under harsh friction conditions, improving the tribological performance of the friction interface layer of Ni$_3$Al-GCS [20].

To analyze the wear mechanisms of the NMSCs and Ni$_3$Al-GCS, the wear scar cross-sections under applied loads of 8, 12 and 16 N were observed using FESEM. In figures 13(a) and (b), the friction interface layer structure is not visible at the fractured surfaces of NMSCs and Ni$_3$Al-GCS at 8 N. Compared to that of NMSCs, the worn surface of Ni$_3$Al-GCS is flatter at 8 N. As shown in figures 13(c) and (d), the wear scar cross-sections of NMSCs and Ni$_3$Al-GCS can be divided into the friction interface layer and substrate layer at 12 N. During sliding friction, the friction interface layer formed on the worn surface and subsurface due to the physical and chemical reactions of the self-lubricating material, thus improving the tribological performance of the material [6]. The thicknesses of the friction interface layer of NMSCs and Ni$_3$Al-GCS are approximately 1.5 and 3.5 μm respectively. Compared to that of NMSCs, the gradient composite structure of Ni$_3$Al-GCS can contribute to the formation of a thicker friction interface layer. Such a formation of a thick friction interface layer rich in the lubrication phase and oxides would enhance the antifriction and wear resistance of the Ni$_3$Al-GCS, resulting in a low friction coefficient and specific wear rate [20, 46, 47]. In figure 13(e), some significant spallings are observed on the fractured surface of NMSCs at 16 N. Compared to NMSCs, the friction interface layer structure of
Ni₃Al-GCS is more complete, as shown in figure 13 (f). A few microcracks are visible in the subsurface of the fractured surface of Ni₃Al-GCS. During sliding friction, the support of the middle layer to the upper lubricating layer improves the stress distribution between each component layer of the Ni₃Al-GCS [14], reducing the

Figure 12. XPS spectra of typical elements on the worn surface of Ni₃Al-GCS at 12 N: (a) Ni2p, (b) Al2p (c) Ti2p, (d) Si2p, (e) C1s, (f) Sn3d, (g) Ag3d, (h) Cu2p, and (i) O1s.
spalling of the lubricating layer during sliding friction. The gradient composite structure of Ni$_3$Al-GCS can be conducive to resisting the deformation of the friction contact surface and reducing the sliding contact damage, thus reducing the specific wear rate of Ni$_3$Al-GCS during sliding friction [13]. The HRTEM image in figure 14(a) indicates the formation of a nanocrystalline structure in the friction interface layer of Ni$_3$Al-GCS at 12 N. In figure 14(b), many continuous lattice stripes with lattice spacings of approximately 0.241 and 0.264 nm are visible in the local magnification of the red rectangular area in figure 14(a), corresponding to the (111) and (200) crystal planes of Ni$_3$Al. The gradient composite structure of Ni$_3$Al-GCS can contribute to the formation of friction interface layers with nanocrystalline structures, thus improving the wear resistance of Ni$_3$Al-GCS during sliding friction.

Figure 15 shows the schematic diagrams of the self-lubricating mechanism of Ni$_3$Al-GCS. The structure and composition of Ni$_3$Al-GCS before sliding friction are shown in figure 15(a). On the one hand, the lubrication layer is rich in the lubricating phase, which ensures the antifriction performance. On the other hand, the middle layer supports the lubricating layer to ensure good wear resistance [8–10]. During sliding friction, the support of the middle layer to the upper lubricating layer improves the stress distribution between each component layer of Ni$_3$Al-GCS [14], reducing the spalling of the lubricating layer. Moreover, a friction interface layer rich in the lubrication phase and oxides is generated at the friction contact surface of Ni$_3$Al-GCS during sliding friction, as shown in figure 15(b). In summary, the gradient composite structure of Ni$_3$Al-GCS can be conducive to reducing the sliding contact damage of the friction contact surface and to the formation of friction interface layer rich in the lubrication phase and oxides, thus improving the tribological performance of Ni$_3$Al-GCS during sliding friction.
4. Conclusions

In this paper, to reduce the limitation of loading conditions on the formation of a friction interface layer with excellent tribological performance, and based on the antifriction and wear resistance mechanisms of the in situ formed friction interface layer of NMSCs, Ni3Al-GCS were prepared via LMD. The design, preparation, and tribological properties of the Ni3Al-GCS were analyzed, and the following findings were obtained:

(1) Compared to that of NMSCs, the tribological performances of Ni3Al-GCS under applied loads of 4–16 N are less affected by the variations in friction conditions. The gradient composite structure of Ni3Al-GCS can reduce the dependence of the tribological behavior on the friction conditions during sliding friction, leading to excellent antifriction and wear resistance properties of Ni3Al-GCS in a wide load range.

Figure 14. (a) HRTEM image of the friction interface layer of Ni3Al-GCS at 12 N, (b) local magnification of the red rectangular area in figure 14(a).

Figure 15. Schematic diagrams of self-lubricating mechanism of Ni3Al-GCS: (a) before sliding friction; (b) formation of the friction interface layer.
Compared with NMSCs, the gradient composite structure of Ni$_3$Al-GCS can contribute to the formation of thicker friction interface layers (3.5 μm) at 12 N, resulting in the best tribological performance with an average friction coefficient of 0.23 and a specific wear rate of about 5.3 × 10$^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$.

Compared to that of NMSCs, the wear resistance of Ni$_3$Al-GCS in the range of 4–16 N can be improved by approximately 17%. Additionally, the gradient composite structure of Ni$_3$Al-GCS can be conducive to reducing the sliding contact damage of the friction contact surface and to the formation of friction interface layer rich in the lubrication phase and oxides, thus improving the tribological performance of Ni$_3$Al-GCS during sliding friction.

Acknowledgments

This work was sponsored by Natural Science Foundation of Henan (202300410097), Doctor Cultivation Funds of Henan University of Engineering (DKJ2019023), Open Fund of State Key Laboratory of Solid Lubrication (LSL-2108) and Natural Science Basic Research Program of Shaanxi (2021JQ-652). Authors were grateful to X Li and W W Xu in Analysis and Testing Center of HAUE for their kind help with XRD and SEM.

Data availability statement

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

ORCID iDs

Yuchun Huang https://orcid.org/0000-0003-1792-2928

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