

Recent Progress on the 0D Nanomaterials in Metals for Lubrication

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Abstract: Over the past two decades, metal-matrix composites reinforced with nano-materials have been extensively used in various prominent fields, such as aerospace, shipbuilding, and food machinery, etc., owing to their demonstrated good chemical, mechanical, and tribological properties. Nevertheless, understanding fundamental effects of nanomaterials in the friction and wear performances of metals has not been systematically reviewed by subdividing them from 0D dimensionality. Herein, this review summarizes the recent advances on tribological applications of 0D nanomaterials in the metals involving ferrous metals, nonferrous metals, and special metals, with the underlying friction-reducing and wear resistance mechanisms. In addition, practical application prospects, as well as future challenges and important recommendations of nanomaterials are briefly summarized, that are needed to boost the development of nano-tribology and expand the diversity of practical applications.

Keywords: 0D, Nanomaterials, Metal matrix, Friction, Wear, Mechanisms.

1. Introduction

Metals and alloys are essential in mechanical systems due to their good electrical [1-3] and thermal conductivity [4-6] and ductility [7-9]. However, almost all mechanical systems with moving parts are inescapably susceptible to friction. This is the main factor of energy losses, mechanical failures and the inefficiencies. According to statistics, the friction and related phenomena account for nearly 20% of total annual energy consumption worldwide [10, 11].

Metal and alloy materials have been widely used in the field of tribology, such as bearing manufacture and surface engineering. However, unique softness and high chemical reactions of the metals and alloys lead to them being subjected to severe friction and wear [12-15]. Metal matrix nanocomposites (MMNCs) have therefore taken the unique step of using nano-lubricants to enhance metal and alloy substrates, leading to an effective bonding of micron-sized reinforcing phase to the substrate for achieving the desired friction and wear reductions. Over the past decades, nanomaterials have been confirmed to own different friction mechanisms at different nanoscales. 0D nanomaterials can form tribofilms on the friction surface during wear to protect the substrate material [11, 16, 17].

Herein, this paper focuses on the effects of nanomaterials on the tribological properties of metal matrix materials and the progress of their research. Chapters 2 to 4 discuss 0D nanomaterials to enhance the anti-wear and wear resistance of metal matrix materials. Chapter 5 concludes the first four chapters and provides an outlook on the future development of nanolubricants with a view to providing useful guidance for the design of friction nanocomposites.

2. Ferrous Metal

Wang et al. [18] prepared $\text{Fe}_{40}\text{Mn}_{40}\text{Cr}_{10}\text{Co}_{10}/10 \text{ vol\%TiC}$ by mixing ball milling and spark plasma sintering, investigated their mechanical properties and wear resistance. The sintered bulk material indicated the homogeneous

distribution of $\text{Fe}_{40}\text{Mn}_{40}\text{Cr}_{10}\text{Co}_{10}$ and grain refinement in the composites after being sintered at 1373 K for 15 min. The compressive strength and the hardness of the $\text{Fe}_{40}\text{Mn}_{40}\text{Cr}_{10}\text{Co}_{10}$ adding to 10 vol% TiC were significantly enhanced, if compared to those of the pure $\text{Fe}_{40}\text{Mn}_{40}\text{Cr}_{10}\text{Co}_{10}$. Meanwhile, the wear resistance analysis indicated that the friction coefficient, wear depth and width of the composite decreased.

Feldspar et al. [19] experimentally explored the changes of structure, mechanical and tribological properties of powder metallurgy iron base composites through adding to reinforce with ultrafine particulates. The experiment results showed that powder metallurgy iron with additives promoted the reduction of friction coefficients by 2–3 times, enhanced the critical seizure pressure 2–5 times and the decrease of wear by almost 2–4 times compared to the base powder metallurgy material. It could be concluded from these results that the addition of 0.2–0.3 wt.% of ultrafine-grained diamonds, 0.5 wt.% of chromium borides, and 0.2–0.5 wt.% of alumina or oxides mixture resulted in a significant improvement of tribological properties.

Bushueva et al. [20] obtained amorphous boron-powder layers (ABPLs) on austenitic chrome-nickel steel surface via atmospheric electron beam cladding. The role of structure transition of ABPLs on wearing quality of austenitic chrome-nickel steel surface was investigated. The anti-wear of the clad layers was tested against loose abrasive particles (dry sand rubber/wheel abrasion test). It was suggested that modified layer nearly consists of iron borides by the X-ray analysis (Fig. 1b), and the wear resistance of the coatings was 2–3 times better than that of base material (12X18H9T steel). It was found that three zones form on the steel surface layers during cladding of the amorphous boron powder through optical microscopy (Fig. 1a). It was observed that a lamellar eutectic between borides, and the eutectic structure was composed of high strength boride plates and ductile γ -Fe increased and positively influences the adhesion of the clad layers.

Singla et al. [21] successfully fabricated iron-based

hardfacing alloys with rare earth additions by the shielded metal arc welding process with pre-placement technique. In addition to examine the effect of dry sliding wear parameters, developed a regression equation and validated with test cases. Structural analysis for the morphology of worn surfaces and corresponding wear debris indicated that rare earth additive alloys possessed a significant improvement in macrohardness and wear resistance. Friction and wear testing found that the addition of rare earth kept 4 wt.% exhibited excellent wear resistance behavior. It was seen that the microstructure of hardfaced alloys represented the existence of interrupted M_7C_3 carbide network in Fig. 1c(i-iv). It was noteworthy that an obvious grain refinement in the microstructure when rare earth addition was up to 4 wt.%. With further increase of rare earth addition from 4 to 6 wt.%, the refinement effect became feeble and the microstructure began to coarsen again. The diamond nanoparticles were implanted into alloy steel by the

laser impact peening (LSP) method to reduce wear [22]. The wear testing showed that the friction coefficient and wear loss of the alloyed steel were reduced to 0.31 and 4 mg, respectively (Table 1).

Deng et al. [23] experimentally studied the friction coefficient and wear rate of 45# hardened steel on Al_2O_3/TiC ceramic composites the additions of CaF_2 solid lubricants using scanning electron microscopy. Fig. 8 illustrated the schematic diagram of the formation process of self tribofilm on the wear track. The mechanisms were determined to be an in-situ formed self tribofilm between the ring-block sliding couple. This dense self tribofilm acted as solid lubricant film between the sliding couple, and thus significantly reduced the friction coefficient and the wear rate. The friction coefficient and the wear rate were found to reduce with an increasing content of CaF_2 up to 10 vol%, and with further increased in CaF_2 content, the wear rate increased rapidly.

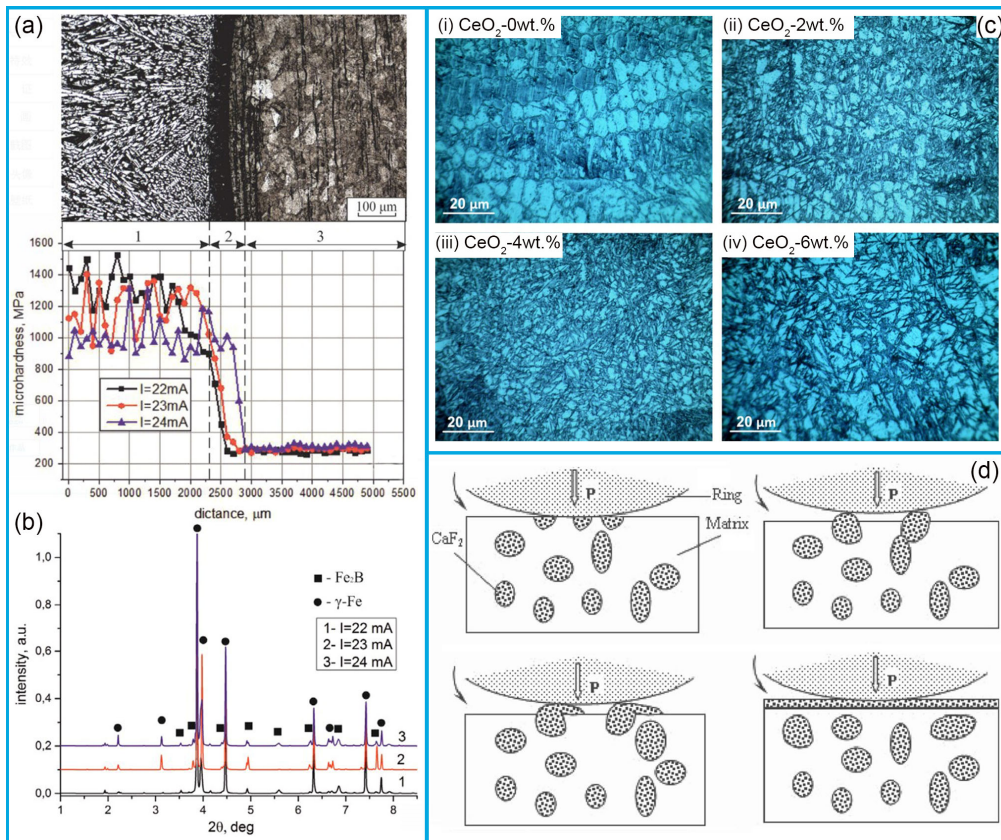


Figure 1(a). Structure and microhardness of the coatings: 1–boride zone; 2–transition zone; 4–steel 12X18H9T, (b) X-ray diffraction patterns of coatings obtained using different beam currents [20]; (c) Optical micrographs with different rare earth additions, (i) CeO₂–0 wt.%, (ii) CeO₂–2 wt.%, (iii) CeO₂–4 wt.% and (iv) CeO₂–6 wt.% [21]; (d) Schematic diagram of the formation process of self tribofilm between the sliding couple [23].

Meng et al. [24] manufactured the test matrix from 28Cr stainless steel using shot-peened for various periods prior before electro/electroless coated. The effect of the test matrix with electroless nickel phosphorous coatings on friction behaviors was investigated. The results indicated that shot-peening showed a remarkable increase to the friction behaviors of the electroless coatings, but had a bad effect on the commercial coating system.

Chu et al. [25] evaluated anti-wear behaviors of SKD11 steels with lubricating oil containing various volume concentrations of diamond nano-particles. The formula for calculating the tribological properties of the composite with different concentrations of nano-diamond lubricating oil additives was as follows:

$$f = \frac{T}{F_N r_u} \quad (1)$$

Herein, F_N : normal load applied to the system (N); T : the frictional torque measured in the process (Nm); and r_u : the distance (m). The average wear amount of oil under the concentration of four kinds of nano-diamond additives was shown in the Fig. 2d. With the increasing concentration of diamond, the wear rate of the composite decreased significantly. The friction coefficients obtained were shown in Table 1. It was observed that, among various concentration of diamond nano-particles, 3 vol% nano-diamond additive concentration was the most favorable for reducing wear loss.

The friction and wear behaviour of nanodiamond glycol dispersions in stainless steel-stainless steel friction contact was reported using a pin-disk tribometer [26]. The ND glycol dispersions endowed the stainless steel with low friction and wear. The coefficient of friction decreased from 0.16 to 0.11 as the ND concentration increased from 0 to 1.1 wt.%.

3. Nonferrous Metals

Ye et al. [27] reported the microstructure and composition of the self-lubricating Ti(C, N)-based cermets, which were fabricated through solid carburization. Subsequently, the wear behavior of cermets containing graphite phase was evaluated using a block-on-ring tribometer. The carbon content in binder phase was found to gradually increase with the extension carburizing time. When the carbon content exceeded the solubility in the binder, excessive carbon precipitated and formed graphite phase. It could be concluded from the wear results that the volume loss of cermets containing graphite phase was half of that without graphite due to the formation of smooth film on the worn surface of cermets.

Lu et al. [28] produced the Ni-based alloy/CeF₃/graphite high temperature self-lubricating composites containing different graphite addition amounts (0, 1, 3 and 5 wt.%) through powder metallurgy method. The effects of graphite addition amount on the friction and wear performances of the composites both at room temperature and 600 °C in air in

sliding against high speed steel (W18Cr4V) were investigated using a pin-on-disk high temperature tribometer. It was found that the wear rates of both pin and disk were remarkable reduced due to the graphite additives at room temperature. However, the wear rate of the disk was higher compared with that pure materials at 600 °C. Moreover, the wear behavior of high speed steel at 600 °C was controlled by the hardness of composites.

Zhao et al. [29] fabricated the FeS self-lubricating film on 1.1 mm Ni55 coating by ion sulfurizing under an atmospheric H₂/Ar/H₂S (150:50:20) flow at a temperature of 280 °C, and experimentally explored the anti-friction behaviors of composites. The friction-reduction model of the FeS film was observed, as shown in Fig. 2a. At the initial worn stages, the friction pairs were segregated completely by the FeS lubricating film (Fig. 2a ii and iii). The ideal adhesion with Ni55 coating is helpful for FeS film to keep the anti-friction performance for longer periods of time (Fig. 2aiv). Under a high load and frictional heat, some plastic deformation zones with distortion and defects could be produced (Fig. 2aiv). It was concluded that FeS film showed better self-lubricating performance under artificial seawater by decreasing the friction coefficients of the Ni55 coatings lubrication, compared with dry friction and deionized water lubrication conditions. Furthermore, auxiliary lubrication and cool effect of seawater, contributed to the self-lubricating performance of FeS film in seawater.

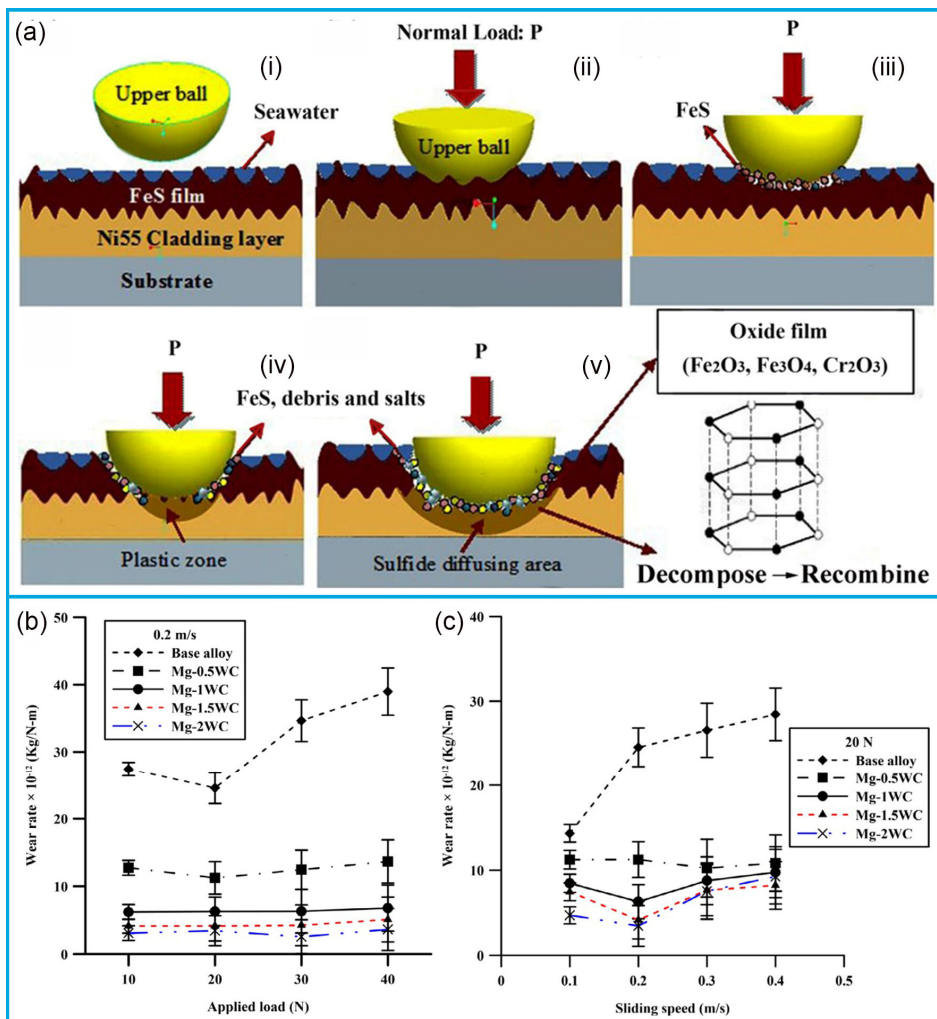


Figure 2(a). Friction-reduction model of FeS film under artificial seawater [29]; Variation of wear rate with (b) load and (c) sliding speed for base alloy and composites [30].

Banerjee et al. [30] produced Mg-WC nanocomposites through ultrasonic vibration assisted stir casting method. The friction and wear behaviors of fabricated composites were experimentally studied using pin-on-disk type tribotester at room temperature under dry sliding condition. Wear tests were performed under four different loads and four different sliding speeds, Fig. 2b showed the variation of wear rate of Mg nanocomposites and base alloy with load at sliding speed of 0.2 m/s. It was observed that wear rate of base alloy was notably higher than Mg-WC nanocomposites at all operating loads. For nanocomposites, wear rate remained almost same with change in applied load from 10 N to 40 N. Composites containing higher mass fraction of WC showed better wear resistance at all operating loads. Micro-hardness of nanocomposites increased with weight percentage of WC and in turn increases the wear resistance. Fig. 2c showed the variation of wear rate with sliding speed at 20 N load. It was observed that wear rate of base alloy increased rapidly when sliding speed changed from 0.1 m/s to 0.2 m/s. The Mg-WC nanocomposites showed better tribological behavior in composites. It was concluded that hardness value of composites increased with increasing in the amount of WC nano-particles, and wear resistance of composites increased with an increasing the number of WC contents.

Singh et al. [31] fabricated a cold forged copper-based composite with the nano-WC particle reinforcer through stir cast technique. The tribological performances of composites were systematically investigated under dry sliding condition by pin-on-disc machine. The results indicated that friction coefficient with sliding distance showed fluctuating behavior, then the wear resistance of both forged and without forged nano composite increased compared to commercial copper.

Ouyang et al. [32] reported the synergistic lubricating effect of CaF₂ and Au lubricants as additives on tribological performances of spark-plasma-sintered ZrO₂ (Y₂O₃) matrix

composites from room temperature to 800 °C in sliding against an alumina ball. The self-lubricating ZrO₂(Y₂O₃)-30CaF₂-30Au composite showed a friction coefficient of 0.36–0.50 and a wear rate of 1.67×10^{-6} – 3.55×10^{-6} mm³/Nm in the full temperature range. It was concluded that plastic deformation and flow of additives played a crucial role in the formation of a self-lubricating film on the tribo-contact surface. At low temperatures, the Au lubricant is extruded from the subsurface layer to the sliding surface, and formed a discontinuous Au lubricating film. At 400 °C or more, the composite showed the presence of a smooth CaF₂ lubricating film containing metallic Au lubricants.

Sharma et al. [33] produced rare earth particulate aluminium alloy composites using a high temperature stir-casting machine followed by the mechanical and tribological behaviors. Mechanical testing suggested that addition 2.5 wt.% of cerium oxide in the Al-6061 base alloy promoted the increase of micro hardness by 17.02%. Similarly, the value of Rockwell hardness of the Al-6061 base alloy increased by 33.80% by addition 2.5 wt.% of cerium oxide and increased only by 16.31% when no cerium oxide was incorporated. The results of wear tests showed an improvement of wear rate about 87.28% when compared to Al-6061 alloy the addition of 2.5 wt.-%-CeO₂.

Reddy et Al. [34] fabricated Al6061/carbon black nanopowder composites through liquid metallurgical technique. The effect of the reinforcement was evaluated on the important physical properties such as wear property studies. Hence, Al6061/ carbon black composites were measured by dry sliding wear tests using a pin on disc wear testing machine. The wear results exhibited reduction in wear volume compared to the unreinforced alloy specimens and the friction coefficient was lower at higher loads. The wear loss of nanopowder composites as well as the matrix alloy increased with the increase in applied load.

Table 1. Friction and wear behaviors of 0D-nanomaterials in metal matrix composites.

Matrix	Reinforcement	Tested conditions	Tribological results	
			COF	Wear
20Cr2Ni4A alloy steel [22]	diamond nanoparticles	440 carbon steel (30 N, 5 mm/s, 60 min, RT)	0.31	Wear loss: 4mg
SKD11 steels [25]	3 vol% nano-diamond particles	wear test machine (blocks-on-ring, 3.54, 4.33, and 5.11MPa, 4.87, 6.084 and 7.30m/s)	0.071	Wear loss: 0.0206 g
stainless steels [26]	3.7 wt.% nano-diamonds	AISI440B stainless steel (pin-on-disc, 0.05 m/s, 100 N)	0.11	Wear rate: $\sim 0.63 \times 10^{-6}$ mm ³ /Nm

4. Special Alloys

Tyagi et al. [35] investigated the possible synergetic action of a combination of low and high-temperature solid lubricant. The nickel-base composites containing nano-powders of silver and hexagonal boron nitride were obtained using a powder metallurgy method. Meanwhile, the wear and tribological behaviors of composites were explored in the range from room temperature to 600 °C through dry sliding wear tests against a ring made of AISI52100 steel using a flat-on-flat configuration under a constant load of 20 N and fixed sliding speed of 1m/s. It was concluded that the friction coefficients increased with increasing temperature. Nevertheless, the lower friction coefficients of silver and hexagonal boron nitride containing composites compared to those of base alloy having no lubricant were observed over

wide ranges temperatures which has been attributed to the presence of solid lubricants and their synergy.

Xin et al. [36] fabricated a self-lubricating composite coating NiCrAlY/Cr₃C₂(NiCr)/Cu/MoO₃ on GH4169 alloy substrate through laser cladding with hard phase Cr₃C₂(NiCr) as the reinforcing agent and Cu-MoO₃ as the primary fillers. The friction properties of the composite coating were further studied from 25 °C to 800 °C in air with a ball-on-disk tribometer against Si₃N₄ ball counterfaces and a dual-mode three-dimensional surface profiler. The Synergistic lubricating effect among lubricants CuMoO₄, CuO, MoO₃, NiO, and Cr₂O₃ were responsible for reducing friction and wear of the composite coating at different temperatures. Particularly, CuMoO₄ exhibited excellent friction-reducing and anti-wear abilities when temperature more than 600 °C, it was the main reason for lower friction coefficient and smaller

wear rate.

Shi et al. [37] reported synergistic effects of multiple additives in self-lubricating composites for using in high temperature friction and wear applications. The sliding friction and wear rates of NiAl based self-lubricating composites with different solid lubricant additions (PbO, Ti₃SiC₂-MoS₂, Ti₃SiC₂-WS₂) were successfully explored from room temperature to 800 °C with a pin-on-disc configuration. Fig. 5a-c was a schematic illustration which showed the wear mechanisms of NiAl-Ti₃SiC₂-MoS₂ during the sliding progress at different temperatures. At room temperature, as shown in Fig. 5a, for the thermal stress, the low temperature solid lubricant (MoS₂) were squeezed out and spread on the worn surface during the sliding process. A complete tribo-film containing low temperature solid lubricant was formed on the worn surface (see Fig. 5b), and the worn surface was covered by a tribo-film containing abundant Mo-Ti-Si-Oxides (see Fig. 5c). The results showed that NiAl based alloy when compared with NiAl-PbO, NiAl-Ti₃SiC₂-MoS₂ and NiAl-Ti₃SiC₂-WS₂ had the high friction coefficient and wear rate over a wide range of temperatures. NiAl-Ti₃SiC₂-MoS₂ showed the excellent tribological properties from room temperature to 800 °C, which was attributed to the formation of the self-lubricating layer on the worn surface during the sliding process. Meanwhile, the good oxidation protection film of TiO₂ and SiO₂ mixture could also have antifriction effect on friction surfaces. The friction coefficients of NiAl-

Ti₃SiC₂-MoS₂ were about 0.12–0.29, and the wear rates were about 4.1–6.0 × 10⁻⁵ mm³/Nm.

Jayabharathy et al. [38] successfully prepared AZ91 magnesium alloy based Titanium dioxide (TiO₂) and graphene reinforced hybrid metal matrix composite materials via stir casting technique. The wear volume loss of composite materials was assessed under dry sliding test through pin on disc tribometer. It was found that wear volume loss was lower for hybrid composite material than the unreinforced magnesium alloy which was predominant as load increased. The results indicated that coefficient of friction value even for higher load was lower than AZ91 alloy, and the coefficient of friction value of the reinforced materials were lower than matrix material for all the test load conditions. Normally, it was concluded that the hardness of the material increased, the wear resistance property was greatly improved and wear rate was less.

Battaz et al. [39] have studied the friction behavior of a NiCrBSi coating lubricated by CuO nanoparticle suspension (nano-lubricant or nanofluid) in a polyalphaolefin (PAO6). Friction reduction properties were obtained using a block-on-ring tribometer, where blocks were coated with a NiCrBSi alloy using the laser cladding technique. The study led to the following conclusions: all nano-lubricants tested exhibited reductions in friction compared to the base oil; the antifriction behavior of the nanoparticles on the wear surfaces could be attributed to third body and tribo-sinterization mechanisms proved by EDS and XPS results, respectively.

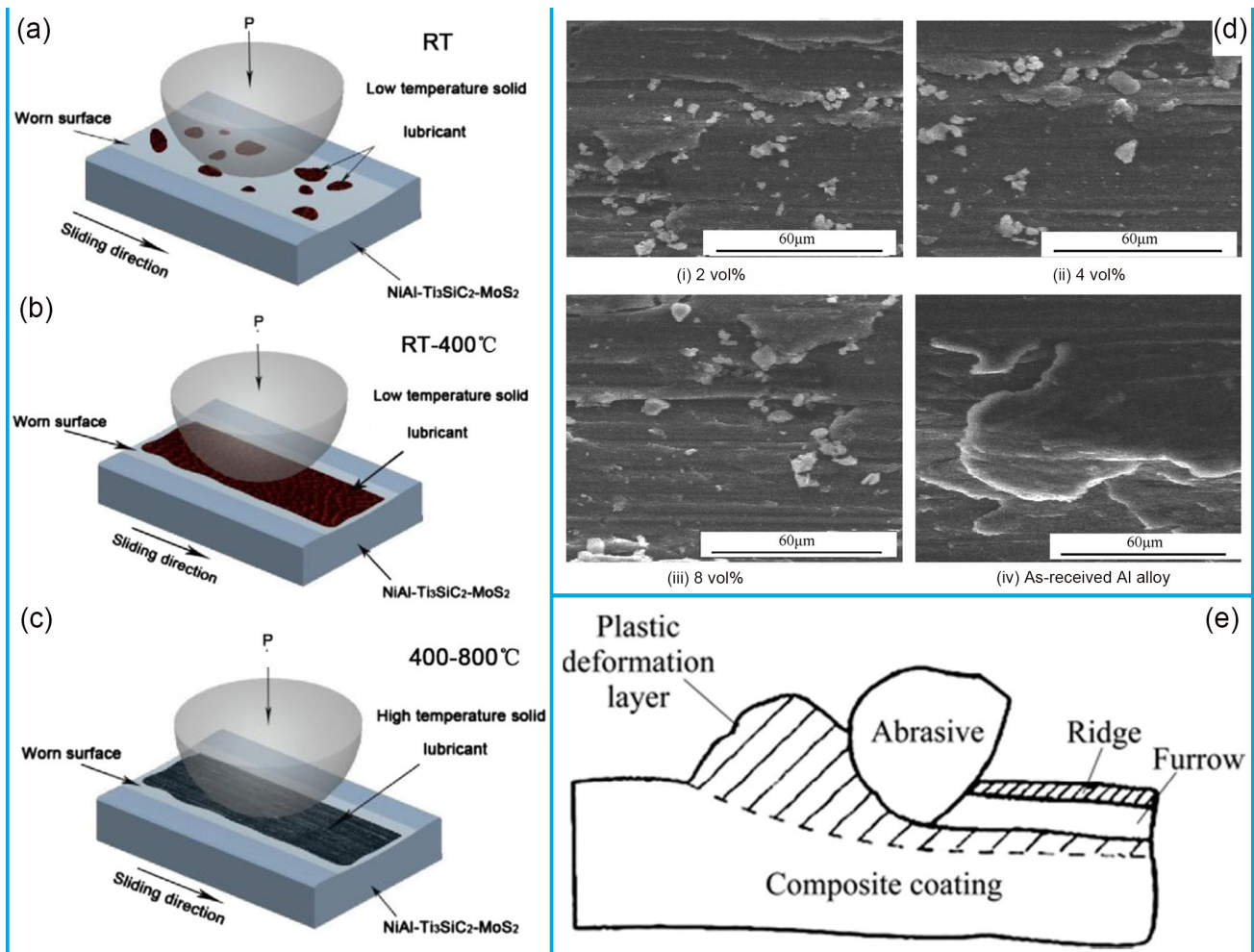


Figure 3(a-c). A schematic illustration that showed the wear mechanisms of NiAl-Ti₃SiC₂-MoS₂ during the sliding progress at different temperatures [37]; (d) Wear morphology of Al-TiB₂ surface nano composites (i) 2 vol%, (ii) 4 vol% and (iii) 8 vol% and (iv) As-received Al alloy [40]; (e) Schematic diagram of multi-plastic deformation wear and abrasive wear [41].

Kishan et al. [40] prepared the nanocomposite surface layer by reinforcing TiB₂ particles on 6061-T6 Al alloy by friction stir process. The wear morphology of Al-TiB₂ surface nanocomposites and base metal Al alloy were seen in Fig. 6c. It could be observed that the wear tracks were larger in the base metal Al alloy as compared to the Al-TiB₂ surface nanocomposites due to the occurrence of hard TiB₂ particles.

He et al. [41] fabricated the Ni-based alloy composite coatings containing nanostructured Al₂O₃-40%TiO₂ multiphase ceramic particles on the surface of 7005 aluminum alloy via plasma spray technology. And the microstructure and tribological properties of the composite coatings were evaluated. The schematic wear mechanisms were depicted in Fig. 7c. Under the ploughing and extruding of GCr15 counterpart, the composite coating experiences yield flow and plastic deformation, leading to delamination and ridge. The wear mechanisms were mainly multi-plastic deformation wear, fatigue wear and adhesive wear.

Khodabakhshi et al. [42] experimentally studied the surface properties of AA5052 Al-Mg alloy through grain refinement. The distribution of ultrafine hard nanoparticles (2 to 6% volume fractions of 50 nm titanium dioxide) was processed through reactive friction stir processing. And the tribological behavior of the alloy with grain refinement and distributed hard nanoparticles were further explored during sliding wear. The friction coefficient and wear rates as well as macro- and micro-features of the worn surfaces indicated that the wear mechanism (at 3-7 kgf and 0.5 m/s) was abrasive, and concluded that the wear rate decreased with increasing volume fraction of the hard inclusions with a significant reduction in the friction coefficient. In addition, the anti-wear property could be improved >125% (compared with the annealed alloy) at 6 vol% TiO₂.

Esther et al. [43] developed AA2124/4wt.-%-B₄C nanocomposite coatings on Ti-6Al-4V through friction surfacing to improve the anti-wear property, and fabricated the composite via conventional stir casting method. It was observed that homogenous distribution of nano B₄C particles and extremely fine grains in the composite coating. The composite coating improved the wear resistance of the titanium alloy substrate due to the reduction in effective contact area, lower coefficient of friction and excellent interfacial bonding.

5. Conclusions and Outlooks

Friction and wear are always unavoidable challenges for mechanical systems. Achieving low friction and wear between moving surfaces are of great physical and technological interests, since they are directly responsible for the working efficiency, service life, and application precision of mechanical systems. In recent years, fields of tribological research concentrate on the ferrous metal, non-ferrous metal and special alloys effects of surface microstructure and nanoadditives.

The excellent friction reduction and anti-wear behaviors of nanoadditives have been increasingly recognized, making them very attractive for tribological applications both in nano-/micro-scale and macro-scale systems. 0D-nanoadditives, those are various nanoparticles, have proven to be effective as a solid lubricant for coatings, solid materials, lubricants and surface microstructure due to their size effect. The incorporation of 0D-additives provides an effective approach to ferrous metal, nano-ferrous metal and special alloys that is

crucial to attractive friction-reducing and anti-wear behaviors of the composites.

Although the novel designs in ferrous metal, nano-ferrous metal and special alloys for controlling the friction and wear indicate broad application prospects, many challenges still remain open to researchers. The effect of nanoadditives on tribological behavior can be complicated because defects and contamination are often inevitably present in them and degrade their desired tribological properties and reproducibility. Consequently, the assessment of complexity for the wear behavior of nanocomposites should be conducted for eliminating the potential hazards associated with their tribological applications.

This article has completely introduced several successful tribological applications of nanoadditives in ferrous metal, nano-ferrous metal and special alloys. These findings aid in understanding the metal-related tribological behaviors of composites and thus widen their application in various industries. It is expected that the present works could offer the possibility for the next generation nano-applications with the superior tribological properties, as well as stimulate the further development of nanotechnology.

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