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The Influence of Stabilizer on the Formation and Tribotechnical Properties of Cu Nanoparticles

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Abstract—The good wear-resistance of state-of-the-art liquid lubricants is due to the formation of complex metal and organometallic films onto the friction surface, reducing the friction and wear. For this purpose, various additives of metal nanopowders are used, especially ones based on copper. The formation and growth of Cu nanoparticles, as well as the tribotechnical characteristics of lubricants, are mainly affected by the choice of stabilizer, because nanoparticles cannot resist the external conditions without protecting their surface. According to quantum chemical studies, the best stabilizer in the series of gelatin, ammonia, sodium borohydride, and sodium citrate is gelatin due to the very large amount of functional groups in its structure. The characterization of physicochemical properties via dynamic light scattering, atomic force microscopy, and electron microscopy, as well as the tribotechnical characteristics of liquid lubricants with stabilized Cu nanoparticles, are consistent with quantum chemical calculations, confirming that Cu nanoparticles stabilized in gelatin possess the better tribotechnical properties than other stabilizers.

Keywords: Cu nanoparticles, stabilizers, atomic force microscopy, electron microscopy, dynamic light scattering, nanotribology, tribology

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INTRODUCTION

One of the simplest and most obvious ways to enhance the tribological properties of lubricants, whether liquid or plastic, is the use of metal cladding additives. Most metals [1–3], oxides [4–6], alloys [7–9], and compositions [10–14] can serve in this role, causing the formation of protective films onto a friction surface and allowing one to increase the tribotechnical characteristics of materials, i.e., to improve the load limits of friction units and reduce wear. It is worth mentioning that copper is the most common component of these additives, being a reliable metal cladding agent.

Metal cladding takes place because the metal composing a lubricant may be released onto the friction surface in a specific range of loads, velocities, and temperatures with formation of a complex highly defective metal film that protects the material from rupture, enabling one to drastically reduce wear. The formation of the film itself is induced by surface modification with nanosized metal particles that may emerge on the surface defects as a result of friction and form new active centers serving as the nucleation sites of the nanostructural metal film. Introduction of nanoparticles into additives enables one to simplify and accelerate the formation of these antifriction films onto the friction surface.

The production of nanoparticles using chemical (bottom–top) or physical (top–bottom) methods encounters difficulties, because nanosized objects are known for their poor resistance to real conditions (in the presence of air oxygen and water) in a lack of stabilization owing to their intense interaction and oxidation and trend to agglomeration, as well as coalescence and coarsening. The stabilizers for these nanoobjects may be atoms, ions, or molecules (ligands), which are able to protect the nanoparticle surface or even prevent it from chemical interaction with the environment. This is very important because of the high chemical activity of nanoparticles, enabling one to avoid their coarsening, which eliminates all the benefits of nanomaterials in comparison with bulk bodies.

In connection with the aforesaid, the present work aims the characterization of the mechanism of stabilization of Cu nanoclusters as the most promising and common metal cladding component of lubricants by ligands, using the quantum chemical computation methods. Furthermore, stabilized nanoparticles are synthesized and lubricants on their basis are subjected to the analysis of their physicochemical and tribotechnical characteristics.

EXPERIMENTAL

Cu nanoparticles were obtained in the presence of stabilizers, such as gelatin, ammonia, sodium borohydride, and sodium citrate.

The Cu nanopowders stabilized in gelatin were prepared through the electrochemical synthesis in an ultrasonic field. Gelatin is based on collagen composed of various peptides, such as glycine, hydroxyproline, and hydroxylysine. The main parameters for size control were the stabilizer content and current density during electrolysis.

The Cu nanoparticles were stabilized with ammonia in accordance with a technique allowing one to oxidize a copper anode in a 1 M NH_4Cl aqueous ammonium chloride solution. Electrolysis was implemented without separating the cathodic and anodic spaces on a fluted titanium vibrocathode at pH 6.5. For equilibrium dissociation of ammonium ions at this pH value, one obtains

$$NH_4^+ \rightarrow NH_3 + H^+;$$

i.e., there is accumulation of ammonia, which is a stabilizer of Cu nanoclusters.

The sizes of Cu clusters were controlled by means of the chemical methods through the variation of reducing agent and stabilizer, as well as their concentrations.

The borohydride method of the Cu nanoparticle synthesis was applied via the following reactions:

$$3CuSO_4 + 2NaBH_4 + 6H_2O \rightarrow 3Cu + 2H_3BO_3 + 2Na_2SO_4 + 7H_2,$$

where $NaBH_4$ sodium borohydride is not only the reducing agent, but also the stabilizer of nanoparticles.

Since Cu cannot be reduced to the primary state using only the citrate ions, the citrate-based method is not classical for the synthesis of Cu nanoparticles because of the formation of complex salts. In this respect, the citrate approach was combined with a borohydride synthesis to obtain Cu nanoparticles, where the reducing agent was $NaBH_4$ sodium borohydride and the stabilizer was $Na_3C_6H_5O_7$ sodium citrate.

The nanoclusters formed were identified from the change in the electrolyte solution color from light yellow to dark brown. The obtained Cu nanopowders were dried until the release of dry substance.

Quantum chemical computations were performed with full optimization of all parameters via the density functional theory (DFT) PBEPBE/Lanl2DZ, using the Gaussian-09 programming package [15]. The stationary points were identified through the calculation of the force constant matrix. All the given structures are the minima in the appropriate potential energy surfaces (PESs).

The physicochemical characteristics of Cu nanopowders (size distribution and particle shape) were studied on a PHYWE atomic force microscope in the semicontact mode a NOVA scanning electron microscope, and a Microtrac NANO-flex laser analyzer using the dynamic light scattering.

The tribotechnical characteristics of lubricants with stabilized Cu nanopowders were measured on a four-ball friction machine (FBM) in accordance with GOST (State Standards) 9490-75 (ASMT D2783) on steel balls (ShKh-15) with Ø1/2", where the evaluation parameters were wear spot diameter D_w at various loads and friction interaction times, critical load P_c, welding load P_w, and load-wear index I_{lw}.

QUANTUM MECHANICAL COMPUTATIONS OF Cu NANOPARTICLE STABILIZATION

As shown earlier in [16], the tightest bonds with a Cu surface are formed by compounds with functional groups containing nitrogen or oxygen atoms with an unshared electron pair. N···Cu complexes are preferable to O···Cu ones. It is thus evident that, the greater the amount of these functional groups in the additive molecule, the stronger its interaction with a Cu cluster surface.

To verify the hypothesis, the interaction between the Cu cluster with Na citrate and Na borohydride molecules, as well as with ammonium chloride and hydroxide and glycine as the main gelatin component, were simulated in the context of the DFT theory under conditions of gas phase and nonpolar media.

In accordance with B3LYP/Lanl2DZ DFT calculation data (Fig. 1), the tightest complexes with Cu clusters were obtained for gelatin peptides (the binding energy with a model tripeptide was found to be 60–80 kcal/mol depending on the environment) and the lemon acid salt (the stabilization energy varied in a range of ~30–40 kcal/mol), which was characterized by a large number of oxygen-containing groups.

The lowest stability was found for structures composed of the Cu cluster with ammonium chloride and hydroxide, which underscores the role of free unshared electron pairs in the resilience of metal clusters. At the same time, the nanostructure is stable due to unshared chloride-anion and water molecule electron pairs, as well as the atypical N–H···Cu hydrogen bridge with a negatively charged Cu cluster center.

Based on these results, better resilience is possessed by complexes formed by extended and ramified peptides with different structures, i.e., gelatin.

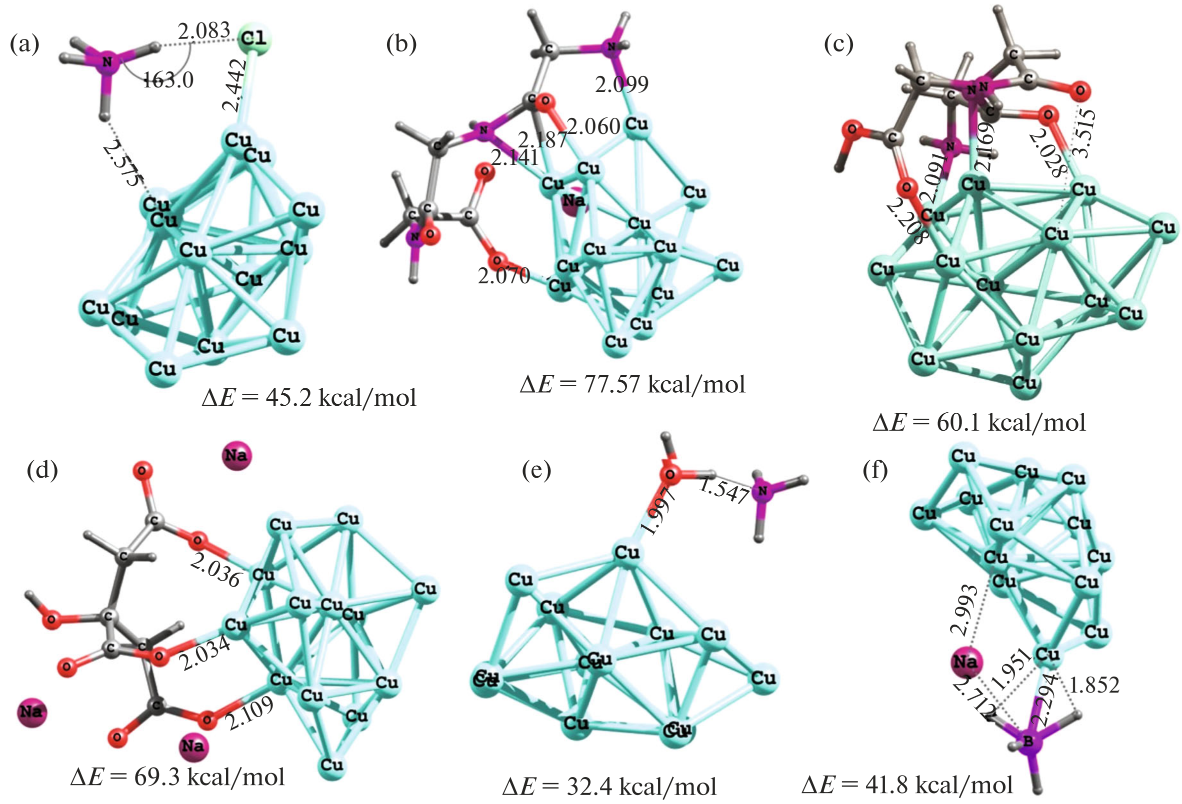

Fig. 1. Structures and energies of Cu_{13} clusters stabilized in (a) ammonium, (b) glycine in an alkaline medium (NaOH), (c) glycine, (d) Na citrate, (e) ammonium hydroxide, and (f) Na borohydride.

It is important to note that attaching one molecule distorts to a large extent the structure of a regular Cu_{13} icosahedron, which can be restored by only embedding several molecules that are uniformly distributed around the cluster.

SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF Cu NANOPARTICLES

To confirm the quantum chemical simulation data, the Cu nanoparticles were synthesized in various stabilizers, such as gelatin, ammonia, Na citrate, and Na borohydride.

Particles were examined via dynamic light scattering (Figs. 2a, 2b), atomic force microscopy (Figs. 2c, 2d), and scanning electron microscopy (Fig. 2e, 2f).

As is seen from the data, stabilized Cu powders exhibit a broad particle size distribution, from several tens to hundreds of nanometers, as they are aggregates of finer particles. This is especially evident in the electron microscopy optical micrographs where spherical particles merge with ~100-nm particles. The samples contain particles of various degrees of dispersion, the dimensions of which are in the nanoscale range, allowing them to be considered nanomaterials.

THE INFLUENCE OF A STABILIZER OF Cu NANOPARTICLES ON THE TRIBOLOGICAL PROPERTIES OF LUBRICANTS

The tribotechnical tests of Cu nanoparticles stabilized with gelatin, ammonia, Na citrate and Na borohydride were carried out on a four-ball friction machine (FBM) (Figs. 3, 4).

It follows from the tribotechnical tests that the best limit and load-bearing capacities, as well as antiwear and antiseize properties, belong to additives based on gelatin-stabilized Cu nanoparticles, which coincides with quantum chemical simulation results. For instance, 10-s tests reveal that the critical load (P_c) of lubricants stabilized in gelatin is 16% higher than that of nanoparticles obtained by the citrate–borohydride method, and the welding load (P_w) is found to be almost doubled. The antiseize characteristics of copper nanoparticles stabilized in gelatin were also better than those in particles stabilized in borohydride, which was evident from the load-wear index (I_{lw}), which increased by 35%.

Furthermore, lubricants with Cu nanoparticles stabilized by gelatin lead to a 30% decrease in wear in comparison with those based on the ammonia-stabilized Cu nanoparticles.

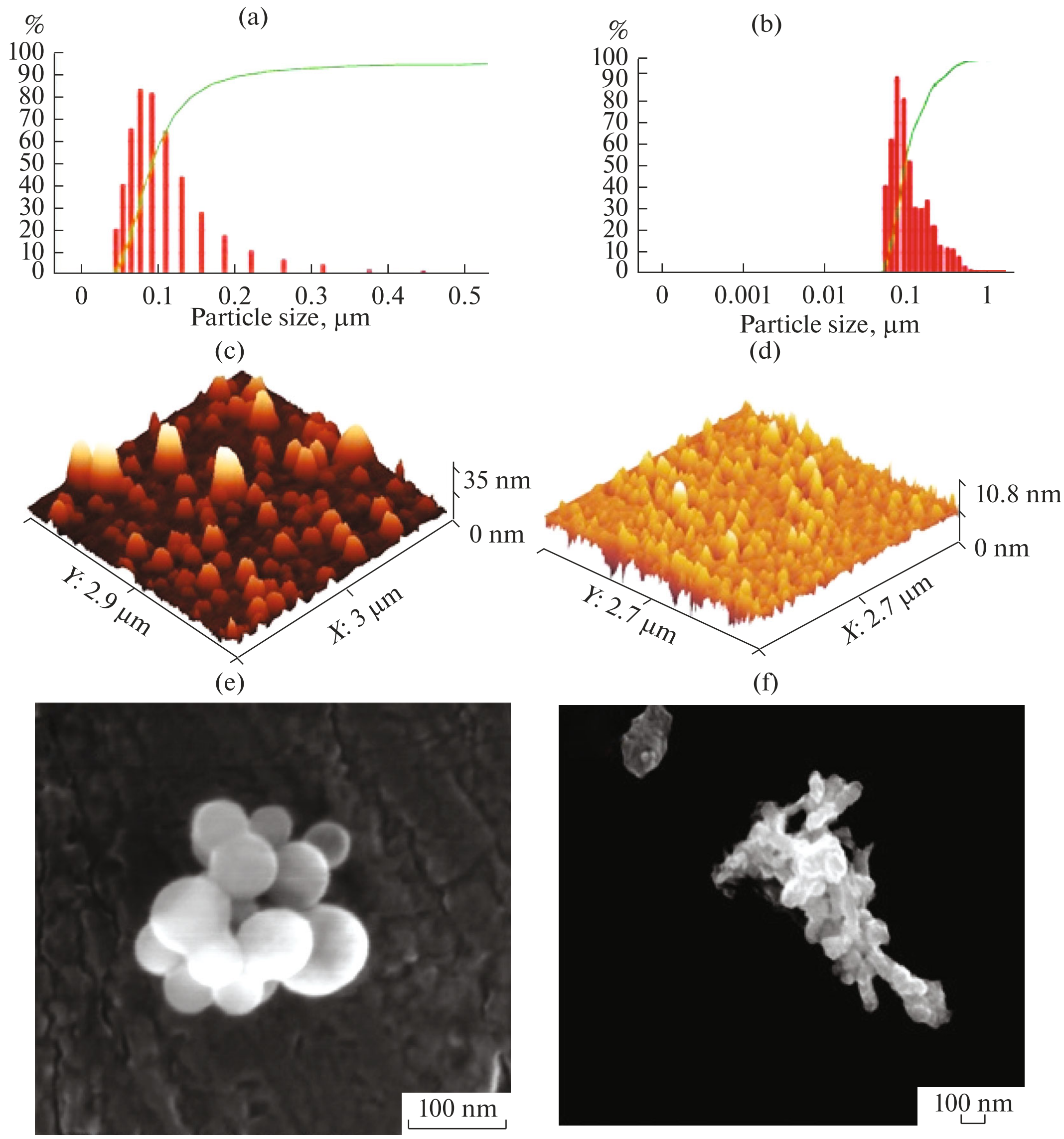

Fig. 2. Physicochemical study of Cu nanoparticles. Size distributions of Cu nanoparticles stabilized with (a) gelatin and (b) Na borohydride obtained via dynamic light scattering. AFM images of Cu nanoclusters stabilized in (c) gelatin and (d) ammonia. Scanning electron microscopy data on shapes and sizes of Cu nanoparticles stabilized in (e) gelatin and (f) ammonia.

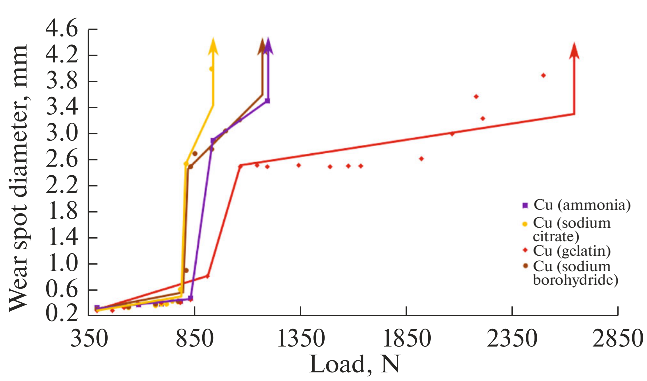

Fig. 3. Load-bearing and limit capacities of lubricants upon the tests of additives based on Cu nanoparticles stabilized by gelatin, ammonia, Na citrate, and Na borohydride using an FBM ($t = 10$ s).

Thus, the Cu nanoparticles obtained in gelatin exhibit better tribotechnical characteristics than do particles stabilized in other agents. This is likely due to the fact the friction interaction of Cu nanoparticles withstood in gelatin makes them steadier to the rupture of the structure, preventing their coarsening and aggregation and allowing them to better fill the micro- and nanoirregularities of the surface friction. This capability and tribochemical transformation of the lubricant [17] lead to the formation of protective metal and organometallic films onto the friction surfaces as a result of the release of the metal and its compounds, improving the tribotechnical properties of lubricants with Cu nanoparticles.

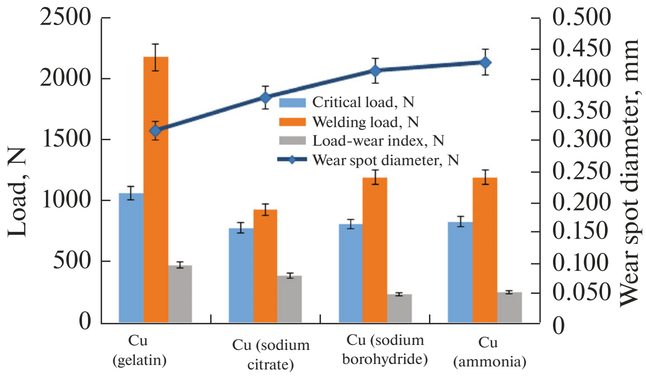

Fig. 4. Antiwear and antiseize properties of lubricants with additives based on Cu nanoparticles stabilized by gelatin, ammonia, Na citrate, and Na borohydride.

CONCLUSIONS

This work was a study of the ability to protect the Cu nanoparticles via various stabilizers. Quantum chemical simulations enabled one to establish that the energy was the highest for clusters with surfaces that has been were stabilized with extended and ramified molecules (i.e., gelatin). This should have an influence on the tribological properties of the lubricants containing stabilized Cu nanoparticles.

The Cu nanoparticles stabilized with gelatin, ammonia, Na borohydride, and Na citrate were obtained as well with determining their size and shape distributions.

The inspection of the tribotechnical characteristics of liquid lubricants based in the metal nanopowders revealed that the best tribological parameters were possessed by lubricants with Cu nanoparticles in gelatin, which was consistent with theory.

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