

Features of obtaining surface-modified metals with minimal carbon footprint*

L. A. Yachmenova, Candidate of Engineering Sciences, Assistant of the Department of General and Technical Physics¹

A. G. Syrkov, Doctor of Engineering Sciences, Professor of the Department of General and Technical Physics¹,
e-mail: Syrkov_AG@pers.spmi.ru

V. R. Kabirov, Post-Graduate of the Department of General and Physical Chemistry¹, e-mail: vkabirov1@gmail.com

¹Empress Catherine II Saint Petersburg Mining University, Saint Petersburg, Russia.

The work is devoted to the development of scientific and technological principles, detailing the physico-chemical mechanism of obtaining dispersed metals (Ni, Cu) from oxide raw materials with a minimum carbon footprint, using non-traditional reducing agents. The ideology of solid-state hydride synthesis (SHS) of metals is the basis for solving these tasks. The special trait of SHS is the realization of reduction the metal in an open flow system (flow reactor) by element-hydride ($E = \text{Si, C}$) reagents in the temperature range of thermostability of the latter in the gas phase. The use of ethylhydridesiloxane (EHS) vapor as a silicon-hydride reagent allows not only to reduce the metal from solid oxide, but also to form a protective film on the metal with thermo- and chemically stable Si – C bonds in the film structure. The aim of the work was to develop approaches based on SHS of metals, allowing to drastically eliminate the carbon footprint in the process of metal reduction, as well as to study the features of the mechanism of metal reduction and modification using quantum chemical modeling.

This work shows that the sequential reduction of metal oxides by the silicon hydride reagent EHS (stage I) and methane (stage II) under SHS conditions achieves almost complete reduction (degree of reduction $\alpha = 99.5\%$) to metal in stage I if no more than 2.5% vol. H_2 is added to the EHS vapor. The CO_2 emission in this case is 0.03–0.05 tons of CO_2 per ton of metal. This parameter is more than ten times lower than in known metallurgical processes in industry. With the help of Gaussian-09, Gaussview and HyperChem software packages it has been established by calculation that the adsorption energy values on metal (Cu, Fe) of EHS reagent and modifiers in the form of quaternary ammonium compounds (QAC) are in the range of 58–127 kJ/mol. This corresponds to the chemical interaction in the metal-adsorbate system and agrees with XP-spectroscopy data obtained earlier. The developed ways of carbon footprint decrease as well as the procedures of selection and prediction of properties of dispersed metal additives to technical lubricant (industrial oil I-20) are implemented with economic effect.

Key words: metallic copper, nickel, adsorption, dispersed metals, modified surfaces, quantum-chemical modeling, carbon footprint.

DOI: 10.17580/nfm.2023.02.06

Introduction

The greenhouse effect is a global ecologic threat in XXI century, caused by emission of millions tons of carbon dioxide, which is a post-product of many types of manufacturing, which are the basis of the modern economy [1–3]. Emissions of metallurgic enterprises are making up at least 8% of global CO_2 emission [1, 4–5]. Although, processes of extraction metals from ore, widely used in industrial scales, cause CO_2 detachment. These are processes of metal reduction by solid carbon reagents or direct reduction of solid-phased raw materials by hydrocarbon gases and, foremost, natural gas (methane), including converted natural gas [6–7]. One of the possible ways of decreasing carbon footprint consists in usage of untraditional reducing agents [3–4, 6]. Besides, metallurgic industrial technologies are highly conservative and were debugged in decades. Because of that, respectively realistic way of solving this problem can be delicate «fusion» of raw material processing into known process by new reducing agents or orientation onto low-tonnage production of metallic powder with improved properties, for example, they can be used as an additive for lubricants, protective coating

and other required on practice compositions [6, 8, 9]. Dispersed metals with high-hydrophobic and corrosion resistant surface [10–12] are of particular interest for the application in microelectronics and composites industry. Among innovative approaches in metallurgy and industry overall [13–15] should be noticed intense attention to nanostructured metallic materials development [16–18]. Perspective here are methods of plasma nanotechnologies [19–20], introducing carbon nanostructures into metallic matrix [21–23], layering different sized molecules-modifiers on metal [24–26], solid-state hydride synthesis of dispersed metals (Ni, Fe, Cu, Zn) with hydrophobic surface [6, 27–28]. Authoritative experts consider, that the last method based on solid metal compounds reduction by fugitive heat-resistant hydrogen compounds ($E = \text{N, C, Si}$) in open flowing system, as well as layering substances, which worth donor-acceptor actions, on metal, possess high potential in obtaining metallic products with minimal carbon footprint [29–30]. However, specific technical solutions in this trend and reasoning of decreasing carbon footprint mechanism practically have not been discussed in special scientific literature. Concerned methods of metal synthesis represents complex processes, research of which not always can be achieved through instrumental analysis

*The article is published as a platform for discussion.

and requires deepen investigation on micro- and nano-levels, including quantum-chemical modeling. By controlling metal surface properties, which was obtained from factory environment, through both chemical modifying [16, 25] and physical manipulation [30–32], encounters with a typical problem of presence of oxide layer on a metal [26–28]. Existence of oxide film on metal often complicates passing of targeted chemical reactions in process of metal modifying, and by application protective coating may reduce adhesion in system of metal-covering or system stability overall [6, 30, 33].

By developing metals with method of solid-state hydride synthesis (SHS) there is no such problems, because synthesis takes place in reducing environment of silicon hydride reagents, methane, and other hydrides; reduction, metal modification and protective film forming happen

in the same process on the same equipment [6, 27, 30]. Organohydridesiloxanes (methyl- and ethylhydridesiloxane) are low-toxic reducing agents for SHS of metals [6, 28] and perspective modifiers for layering on industrial metal powders [24–26]. The actual way of studying the mechanism of carbon footprint decreasing and strengthening of chemical resistance of metal in mentioned processes is researching the details of donor-acceptor interaction metal-silicon hydride reagent (modifier) through modern experimental and theoretical methods.

The purpose of the present work is to develop approaches based on SHS of metals, which allows to significantly reduce amount of carbon footprint in process of reduction of metal, and also detail physical-chemical mechanism of reduction and modifying of metal by using quantum-chemical modeling and software packages Gaussian-09, Gaussview and HyperChem.

Materials and methods

As initial solid-phased raw material for obtaining metals were used chlorides of Ni(II), Cu(II), Fe(II) or oxides of previously mentioned metals and olenegorsky superconcentrate (in comparative experiments), which is similar in composition to Fe_2O_4 [6]. Dichlorides of nickel and copper were qualified as “chemically pure”. Oxides of Ni(II) and Fe(II) as “pure”, Cu(II) oxide as “pure for analysis”. Reducing of mentioned solid substances to metals realized through heating in flowing installation, scheme of which imaged on **Fig. 1**, within surrounding of different hydride reagents (methane, purified nature gas, vapor of methyl-dichlorsilane, ethylhydridesiloxane and others). In several experiments, into gas phase were added molecular hydrogen (extra pure) from balloon in safe concentrations (less 3%). Before lapping into system of hydride reducer, initial solid reagents were dried through heating to a constant mass. Structure of solid phase in process of reducing was defined by methods of X-ray diffraction analysis (DRF-2.0 instrument) and X-ray photoelectron spectroscopy (Escalab 220iXL instrument). Chemical elements in solid products of SHS were identified through X-ray fluorescence analysis (Bruker S4 Explorer), EDX spectroscopy (analytical attachment to electron microscope Nanolab). Before lapping into reactor, hydrogen, methane (nature gas) were additionally cleared from oxygen micro-traces and moisture through methods, described in previous works [27–28]. As reducers also were used vapors of distilled silicon-organic liquids: methyl-dichlorosilane (MDCS), methylhydridesiloxane (MHS) and ethylhydridesiloxane (EHS). Were used reactors in glass performance (from quartz glass) and enlarged reactor from stainless steel with thermal insulation (**Fig. 2**). Specific amount of avowed CO_2 was defined by gas chromatographic method on Chrom-42 with instrumental error $\pm 0.025 \text{ g}(\text{CO}_2)/\text{g}(\text{Me})$. Degree of nickel reducing to metal in SHS were controlled in situ by changing magnetic flux, by installing glass reactor with sample inside inductance coil of micro-webermeter F5050 [27–28, 34]. As initial bases for layering

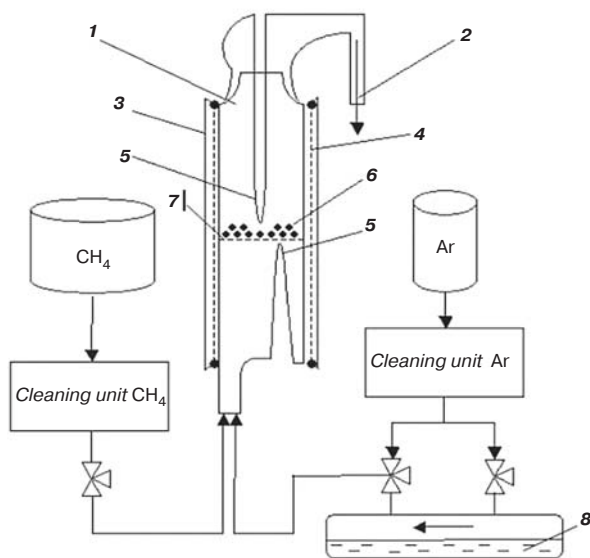


Fig. 1. Fundamental scheme of flowing type installation for solid synthesis [27–28]:

1 – reactor; 2 – exit gas; 3 – thermal insulation layer; 4 – nichrome wire winding for heating; 5 – thermocouple pocket; 6 – initial sample (MeO ; MeCl_2 or metal powder); 7 – sample net; 8 – liquid reagent (MDCS, EHS (HSL-94) or MHS (HSL-94M))



Fig. 2. Stainless steel installation for obtaining large portions (around 1 kg) of dispersed surface-modified metals (Ni, Cu, Fe)

quaternary ammonium compounds (QAC) and EHS were used industrial powders of copper PM1 and nickel PNK (UT3). As surface modifiers — samples based on QAC Triamon (TU 6-14-1059-83) and Alkamon (GOST 10106-75) laid from gas phase, and also silicon organic liquid HSL-94 based on EHS. Hydrophobic properties of obtained metallic products were evaluated through gravimetric desiccator method. Adsorption of water on the metal were controlled independently by measuring intensity of indicative pike 01s with binding energy of 532.3 ± 0.1 eV [27–28].

Quantum-chemical calculations were carried out through software Gaussian-09, Gaussview and HyperChem. First two gaussian's packages were used for calculation of charge on initial metal and adsorbate, and also for adsorption energy of modifiers on metal evaluation; HyperChem for electrophilic-nucleophilic properties of modifiers [35–37] characterization.

Considering recommendations of previous works [35, 38], for modeling of metal-adsorbate interaction were chosen metal's ($Me = Cu, Fe$) crystallographic edge (111) and surface fragment in terms of cluster of 18 atoms as most stable ones [36]. Modeling by using HyperChem software was carried out according to half-empiric method MNDO [39]. The computational error in calculating the adsorption energy of the modifier on metal according to the used methods [35, 38] did not exceed 8 kJ/mol.

Experiments were done on the equipment of departments of metallurgy, general and technical physics, automation of technological processes and production, as well as at the branch of the Problems of Mineral Resources Processing Center at the department of general and physical chemistry, and at the Nanotechnology Center of St. Petersburg Mining University.

Research results

Decreasing the carbon footprint under the combined influence of reducing agent during solid-state hydride synthesis of metals

The prospects of processing solid-phase raw materials in condition of SHS with methylchlorosilane vapors and then with methane to obtain dispersed metal products (Ni, Fe, Cu) with high hydrophobic properties and heat resistance were shown in works [6, 27–28]. It was suggested to use vapors of organosilicon liquid based on EHS in order to keep the protective organosilicon film on the metal and get rid of hydrogen chloride emission [6, 8]. The treatment of metal oxides (340 °C), however, failed to achieved deep reduction to metals. Therefore, the second step, higher temperature (500–600 °C) treatment in methane was necessary not only to break the Si-H-bonds of chemisorbed EHS, but also to completely reduce the oxide [28]. At this final stage, the release of CO_2 is inevitable at the distraction of $Me - O$ -bonds in the presence of CH_4 , which was verified by experiments [6]. The release of CO_2 is impossible when metal oxide is reduced at the first stage by silicon-hydride reagent (either MDCS or EHS),

due to the high bond strength and thermo stability of the Si – C-bond in the structure of the reducing agent molecule. Therefore, the idea of this part of the work was to complete the deep reduction of metal oxide in EHS in the first stage.

The measured degree of reduction to metal (α) during NiO treatment with HSL-94 vapors based on EHS with a small amount of added molecular hydrogen ($C_{H_2} < C_{EHS}$) allows to completely reduce the oxide ($\alpha = 99.5\%$) in 550 minutes, which is shown on diagram Fig. 3. Under the same conditions, treatment with MDCS vapors gives $\alpha = 88\%$. For comparison, without the addition of hydrogen to EHS $\alpha = 65\%$.

When Ni, Cu, Fe and $NiCl_2$ oxides are reduced using H_2 -additives during processing in an EHS medium at the first stage, solid products are eventually obtained that have a full set of analytical maxima characteristic of the corresponding metal phases, which is shown in diffractograms (Fig. 4).

For example, during the sequential reduction of $NiCl_2$ or NiO by EHS vapors with the addition of H_2 , and then in a methane medium, three analytical diffraction maxima of metallic nickel are observed in the diffractograms of the corresponding solid products: 1.25; 1.75; 2.02 (obtained from $NiCl_2$) on curve (a) or 1.24; 1.75; 2.02 (reduction from NiO) on the curve (b). Single conditionally silicide peaks corresponding to the interplane distance $d = 2.23$ (Fig. 4, a) or $d = 2.63$ (Fig. 4, b) do not allow to identify any of the known crystalline phases of nickel silicide. The SHS mechanism, which is carried out in the region of thermal stability (340 °C) of the SiH bond of the silicon hydride reagent EHS, prevents the competing process of bulk metal silicification with the formation of interatomic Ni – Si bonds [6, 28, 30]. The peaks named above with $d = 2.23$ or $d = 2.63$ in their intensity are 5–10 times inferior to the intensity of the maxima from the metallic phase of nickel (Fig. 4, a, b). Despite the fact that the processing of the initial solid-phase raw materials takes place when heated in silicon hydride and hydrocarbon gas media with an increase in temperature from 340

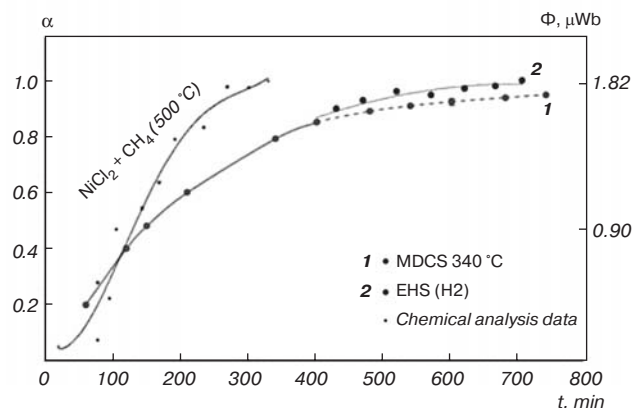


Fig. 3. Dependence diagram of the degree of reduction to metal: 1 – treatment of NiO with MDCS vapors at 340 °C (Ni mass is 5 g, 4 m²/g surface); 2 – treatment of NiO with HSL-94 and added H₂ (2 vol.%)

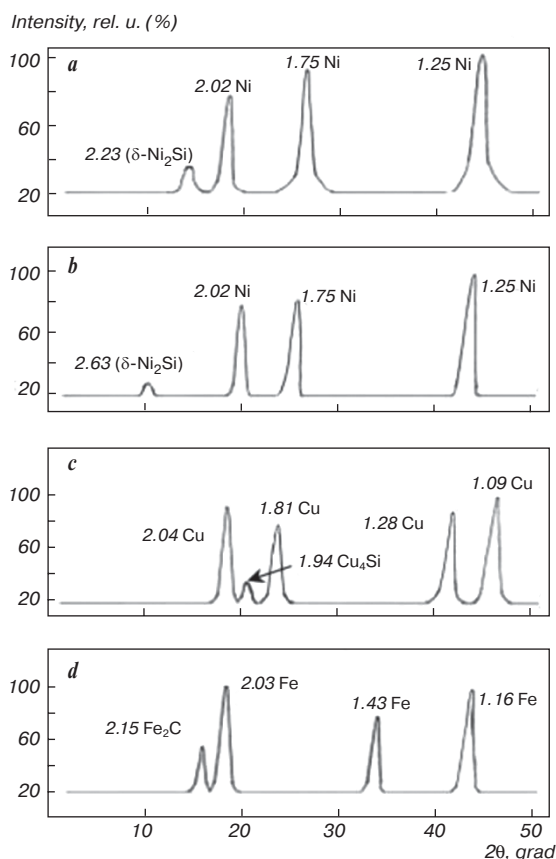
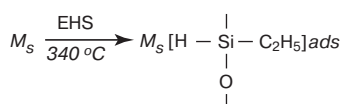


Fig. 4. The XRD diffraction patterns of solid SHS products obtained by sequential reduction of solid metal compounds in EHS vapor with H_2 -additive (2.5 vol.%) under 340 °C and CH_4 (600 °C); from *a* – $NiCl_2$; *b* – NiO ; *c* – CuO ; *d* – $Fe(II)$ oxide

to 600 °C, the processes of silicification and carbidization are not typical for all three metals (Ni, Cu, Fe). It is coming from the data of **Fig. 4** and is explained like such. Under SHS temperature conditions, when the destruction of Si – H and C – H bonds of the reducing agent is prevented at the appropriate stages of synthesis, low-valent forms (states) of silicon or carbon are not formed, which are favorable for the formation of silicides and metal carbides [6, 28].

At the first stage of reduction in vapors of organosilicon liquid HSL-94, the active substance of which is EHS, in addition to reduction to metal, EHS chemisorption occurs on surface metal atoms (M_s) [6] according to the scheme:



The above scheme justifies the expediency of subsequent higher-temperature treatment in methane. The presence on the metal surface of a very chemically active hydride hydrogen in Si – H bond of the EHS molecule reduces the corrosion resistance of the metal reduced in the EHS medium with the addition of H_2 . Treatment in methane (600 °C) completely destroys Si – H

bonds in the sample, which is confirmed by the IR-spectra of solid products [28] and, apparently, compacts the structure of the surface layer, including due to additional “crosslinking” of EHS molecules when Si – H and C – H break bonds [40].

Information of chemical structure of SHS metallic products, gotten by suggested method in **Table 1**, demonstrates that content of metal, silicon and carbon was close to equivalent concentrations of elements in metallic samples, produced by scheme $MeO + MDCS + CH_4$ [6, 27–28]. Minimum silicon content is found in Fe-product, which was gotten from OSC, that has many times less specific surface (3 m^2/g) than Ni- and Cu-metallic products. Chemical analysis data also show that formation of metal silicides and carbides (in case of iron) does not occur, confirming the results of X-ray diffraction analysis in **Fig. 4**.

Therefore, EHS vapor treatment with additive of molecular hydrogen allows faster reduction of metal oxides then when treated with MDCS vapor. Small hydrogen molecules get into the deepest parts of oxide more easily than EHS. A monomolecular film of EHS on a metal (in the scheme above) is not a block to hydrogen molecules. Low concentration of H_2 , not more than 2.5 vol.%, is safe in the context of the possibility of ignition upon contact with air in case of a reactor depressurization. In response to low concentration of H_2 , hydrogen is mainly used to reduce the metal oxide to a metal, which minimizes potential gas corrosion in the metal lattice (“hydrogen embrittlement”) [41–43].

Matching with industrial processes for producing metals, where carbon- and methane-containing reducing agents are used, shows that in the studied processes of reduction to metal, the amount of released is at least 10 times lower and amounts to 0.03–0.05 tons of per ton metal. It should be noted, that the latest order of magnitude numbers for emissions are at the level error of the gas chromatographic method by which emission was measured. Suggested approach to the reduction of oxide raw materials to metal, besides considerable reduction carbon footprint, also provides energy saving. Maximum recommended temperature for the process in the second stage – 600–650 °C. In industrial processes, it requires a minimum of 700–800 °C for direct ironmaking and more than 1000 °C for realization of a metallurgic processes from **Table 2**. Besides that, when directly producing iron

Table 1
Chemical composition of SHS metallic products

Sample	Me, wt.%		Si, wt.%		C, wt.%
	Chem. an.*	RFA	Chem. an.	RFA	Chem. an.
$NiCl_2 + EHS(H_2) + CH_4$	96.1 ± 0.2	–	2.2 ± 0.1	–	1.5 ± 0.1
$NiO + EHS(H_2) + CH_4$	95.9 ± 0.2	95.7	2.3 ± 0.2	2.0	1.6 ± 0.1
$CuO + EHS(H_2) + CH_4$	95.4 ± 0.1	94.9	2.4 ± 0.6	–	1.5 ± 0.2
OSC + $EHS(H_2) + CH_4$	94.4 ± 0.4	–	0.8 ± 0.4	–	1.5 ± 0.1

*Chem. an. — Chemical analysis; RFA — X-ray fluorescence analysis; EHS — ethylehydridesiloxane; OSC — Olenegorsk superconcentrate.

Table 2

Comparison of CO₂ emission (carbon footprint) for known and offered metallurgical processes

Process	CO ₂ emission in t CO ₂ /t (of metal)
Steel obtaining in domain process through oxide raw material reducing with solid carbon [1–3]	1.9
Direct obtaining of iron through reducing of rolled slag with converted nature gas (CO+H ₂ at 700–800 °C) [1, 4]	0.5
Copper obtaining with pyrometallurgical methods [41]	5.7
Consistent reducing of CuO by EHS vapor with H ₂ addition (2.5 vol.%) and methane	0.03
Consistent NiO reducing with analogic program	0.04
Consistent reducing of Olenegorsk superconcentrate (similar structure to Fe ₃ O ₄) by EHS vapor with H ₂ addition (1.0–2.5 vol.%) and methane (nature gas)	0.05

is made by reduction in converted natural gas, the carbon content in the metal product can reach 30 mass. % [44]. Suggested approach, which uses methane (natural gas), reduces carbon content by up to 1,5 mass. % (Table 2).

Metal-reducer (modifier) system modeling

Table 3 shows the values of the energy of the lowest unoccupied molecular orbital (LUMO) calculated using the HyperChem program for substances that were studied as reducing modifiers in works [6, 27–28]. Substances that have negative LUMO energy values (methylammonium, the QAC-based Alcomon preparation) are characterized by electrophilic properties [39]. They have little promise as reducing agents and no examples of their use in this capacity have been found in the literature. Starting with the preparation Triamon based on the preparation tris-(β-oscetyl) methyl ammonium methyl sulfate (TOMAM), the energy of HBMO becomes positive (+0.38 eV), indicating a better ability than Alcomon to donate electrons. Among the substances than illustrated in Table 2 there are traditional reducing agents (CO, CH₄, H₂), the nucleophilic properties of which increase in the series: CO < CH₄ < H₂.

Basically, the above series does not contradict the data on the chemical activity of the listed reducing agents in processing iron oxides below 477 °C, which were obtained from the results of gas chromatographic analysis of the reaction products [3, 5, 45]. An increase in nucleophilic properties in the above series means an increase in the ability of a substance to donate electrons. Based on the foregoing, it can be assumed that the LUMO energy (nucleophilic properties) can be the primary evaluation criterion for using the substances listed in Table 2 as effective reducing agents or modifiers that can interact with other substances (including metals) according to the donor-acceptor mechanism. Of particular interest is ethylhydridesiloxane EHS, the active substance of organosilicon liquid HSL-94 (GKZh-94 according to GOST 10834–76). The vapor of this liquid is already used as a reducing agent for Ni, Fe, Cu compounds and as a modifier for industrial Ni, Fe, Cu, and Al powders [6, 28]. In traditional practice, HSL-94 is an industrial water repellent for various materials and tools, applied from solutions [40].

Table 3

Range of electrophile-nucleophile properties increasing of reducing agents (modifiers) (arrows show how electrophile and nucleophile nature of molecules changes)

Substance	LUMO energy*, eV
Methylammonium	-3.45
Alcomon	-1.95
TOMAM (Triamon)	0.38
MDCS	0.65
CO	1.56
Methylhydridesiloxane	2.29
Ethylhydridesiloxane	2.37
SiH ₄	2.79
Methane	4.33
H ₂	4.78

*LUMO — lowest unoccupied Molecular Orbital;
MDCS methylidichlorsilane.

From Table 2 it follows that EHS can be a good reducing agent, not inferior to methylhydridesiloxane with a smaller hydrocarbon radical (-CH₃) at the silicon atom. The use of EHS in combination with stronger reducing agents: CH₄ and H₂ is also justified, as discussed in section 1 of this article above. When selecting “partners” for EHS, of course, other factors must be taken into account: reduction chemistry, toxicity, fire hazard of the substance, adsorbability on Me oxide, diffusion rate, etc. [6, 41, 45]. Therefore, SiH₄ is not suitable in this capacity, because it is explosive and fire hazardous, and upon oxidation it forms hardly volatile oxides and oxyhydrides of silicon [6, 46]. Comparing the LUMO of methylhydridesiloxane and EHS (Table 3, Fig. 5), calculated using the HyperChem program, can be noted slightly more pronounced electrophilic properties of the first reducing agent (MHS). Since the chemisorption of organohydridesiloxane on a metal during SHS is associated, according to XPS data, with a shift of electron density from the metal to unoccupied 2p silicon orbitals according to the M → Si scheme [6, 27–28], then MHS apparently has some advantage as electron acceptor to form stronger metal-silicon interactions.

In quantum-chemical calculations of the adsorption of molecules on metals, two positions of the adsorbate

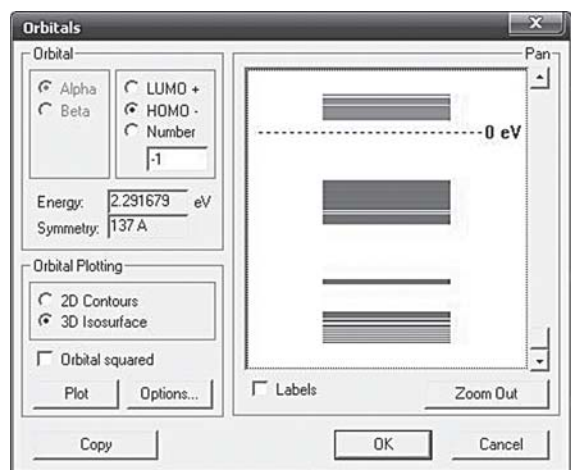


Fig. 5. Screenshot of a computer screen when calculating LUMO energy for MHS using the HyperChem program

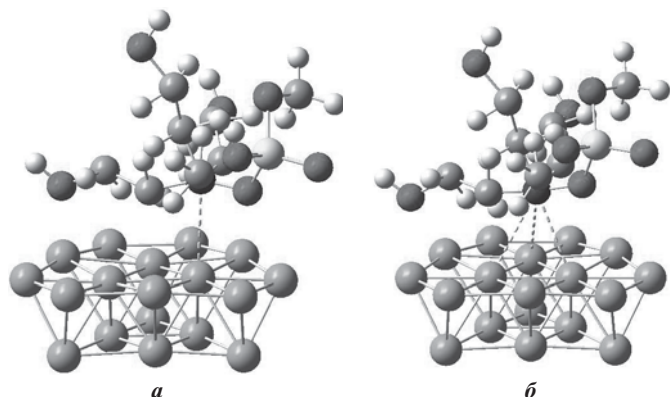


Fig. 6. Adsorption of a tris-(oxyethyl) methylammoniummethylsulfate (TOMAM) molecule on a Cu (111) cluster:
a — in the on top position; *b* — in the hollow position (blue ball is a nitrogen atom)

molecule are usually of interest [35, 38]: on top — the central atom of the adsorbate (nitrogen or silicon) above the metal atom (Fig. 6, *a*); hollow — this atom of the adsorbate molecule is located opposite an empty space where there are no metal atoms (Fig. 6, *b*).

For these two positions, the adsorption energies E_{ads} and the changes in charge of adsorbate central atom (N or Si) resulting from the adsorption ΔQ of different molecules were calculated (Table 4).

Analysis of the data in Table 4 shows that the adsorption energy modulus varies from 58 to 127 kJ/mol, this indicates the chemical interaction of Triamon (*T*) and Alkamon (*A*) molecules based on quaternary ammonium

Table 5

Sorption characteristics of samples ($P_{H_2O}/P_0 = 0.98$, $t = 20$ °C; 168 h), integral friction index D when added to lubricant I-20 (0.5 wt.%); service life in lubrication, h

Sample	Cu/A	Cu/T	Cu/T/A	SHS products	
				Cu/EHS (H_2) + CH_4	Fe/EHS (H_2) + CH_4
H_2O vapor sorption, mmol/m ²	1.6	1.4	1.2	0.04	0.03
Integral index D in lubricant	1300	1100	270	120	100
Service life in the mixer transmission, h	3700	4050	4500	5600	6300

Table 4
 Adsorption energy and charge change during adsorption on metal

Sample	Adsorption site	E_{ads} , kJ/mol	ΔQ , rel. units
Cu/T	On top	-127	0.653
	Hollow	-134	0.678
Cu/A	On top	-83	0.583
	Hollow	-97	0.552
Cu/EHS	On top	-64	0.423
	Hollow	-73	0.510
Fe/T	On top	-118	0.645
	Hollow	-122	0.653
Fe/A	On top	-75	0.553
	Hollow	-91	0.561
Fe/EHS	On top	-58	0.390
	Hollow	-65	0.455

compounds (QAC) with the metal. The same can be said about the interaction of EHS with copper and iron. In the “hollow” position, the adsorption energy and ΔQ are higher in all cases, which can be associated with an increase in the number of contacts of the adsorbate molecule (Fig 6, *b*) with the metal surface [35, 37]. The calculation data presented concern the adsorption of molecules on atomically pure metal surfaces. In reality, QAC molecules are adsorbed either on an oxidized metal surface (PM 1 copper) or on one stabilized by salts of organic acids (PMS-1 copper). Therefore, the relationship between the adsorption energies of QAC and, for example, EHS, which is chemisorbed on a freshly formed metal surface during SHS, may differ from that given in Table 4. This is clearly illustrated by the properties of metals modified by different methods. Water-repellent and antifriction properties were selected, which depend on the strength of chemical interaction (adhesion) in the metal-modifier system [23–25] (Table 5).

Generally, for Cu/A, Cu/T and Cu/T/A samples, the nature of the change in properties is confirmed by data for Eads (Table 4) and XPS from work [28]. Adsorbed Triamon in the Cu/T sample interacts more strongly with copper and has higher properties than Alkamon adsorbed on copper (Cu/A). Due to hydrocarbon radicals (average C_{17-}), nitrogen in sample Cu/A interacts weaker with the metal. This affects the stability of the Cu/A system and a decrease in water-resistant properties (maximum H_2O adsorption), as well as an increase in the integral friction index when Cu/A is introduced into a lubricant based

on industrial oil I-20. The sequential application of T and A to the metal in the Cu/ T/A sample gives a synergistic effect: minimal water sorption, the lowest D value measured by the acoustic emission method on an ARP-11 device [25–26, 28]. In addition, of the samples with layered QAC (Table 5) for Cu/ T/A , the longest service life is observed (4500 hours) before replacing the lubricant in the transmission of the anchor mixer in the polymerization shop of LLC “Stavrolen” (PJSC “Lukoil”). Even higher performance is demonstrated by dispersed metal products obtained by the SHS method using combined treatment with hydride reducing agents (EHS with the addition of H_2 and treatment in a CH_4 environment). The proposed embodiment of SHS and methods for predicting the water-repellent and antifriction properties of dispersed metal lubricant additives have been implemented at GMC company with an expected economic effect of 8 million russian roubles/year. For comparison: the service life of I-20 base oil is 3700 h, of industrial lubricant IGP-18 with special additives — 5200 h, which is 8–20% lower than that of I-20 with additives of SHS products from Table 5.

Thus, quantum-chemical calculations, which were done in this second part of the work, allowed to place in a row different reducing agents, including nitrogen-containing based on QAC, by efficiency of their action and compare it with known literature data. At the same time, the expediency of using hydride reducers-modifiers to decrease the carbon footprint in the first part of the work is additionally justified. Calculation of the adsorption energy of reducing agent molecules on metals makes it possible to quantify the intensity of chemical interaction in the system “metal – reducing agent chemisorbed during SHS”. This interaction largely determines the practically important properties of metal products, including their water stability and anti-friction effect of the surface.

Conclusions

1. In this paper it is shown that in obtaining dispersed metal products ($S = 3–60 \text{ m}^2/\text{g}$) that have a protective film of organosilicon origin on the surface, by sequential reduction of oxide raw materials with EHS (stage I) and then with methane (stage II) under conditions of solid-state hydride synthesis, metal ($Me = Ni, Cu, Fe$) can be reduced almost completely (degree of reduction $\alpha = 99.5\%$) already at the 1st stage, if no more than 2.5 vol.% H_2 is added to EHS vapor. At the same time, CO_2 emission is negligible (0.03–0.05 t of CO_2 per 1t of (Me)), which is more than 10 times lower than in known metallurgical processes, where solid carbon reducing agents or hydrocarbons, including natural gas (methane), are used as reducing agents.

2. For the first time, the adsorption energies of EHS and quaternary ammonium compounds (QAC) on surface clusters of copper and iron were calculated by quantum chemical modeling using Gaussian-09 and Gaussview software products along with the hybrid functional B3LYP. It was found that the values of the adsorption energy lie in the range of 58–127 kJ/mol, which corresponds to the

chemical interaction of EHS and QAC molecules with metal. These calculations are consistent with the previously obtained data by XP-spectroscopy [6, 25, 28]. The results of the work were used to predict the properties and selection of metal additives for technical lubricants (industrial oil I-20) during the practical implementation of dispersed antifriction additives for transmissions at a mineral resource complex enterprise.

References

1. Mitrova T., Gayda I., Kapitonov S., Melnikov Y., Perdereau A., Sheveleva N., Siginevich D., Grushevenko E. Decarbonization of Oil & Gas: International Experience and Russian Priorities. Moscow: SKOLKOVO, 2021. 158 p.
2. Lazich Yu. V., Popova I. N. Trends And Issues Of The Development Of The Metallurgical Industry Of Russia. *Beneficium*. 2020. Iss. 2. pp. 16–24.
3. Dr. Vincent Chevrier Presents in “Ironmaking with Alternative Reductants” Webinar by AIST. Midrex. June 22, 2020. URL: <https://www.midrex.com/story/dr-vincent-chevrier-presents-in-ironmaking-with-alternative-reductants-webinar-by-aist/> (Access Date: 04.12.2023).
4. Schenck J., Lungen H. B. Potentials of Direct and Smelting Reduction Processes for an Efficient Application in Europe. *Chernye Metally*. 2017. No. 2. pp. 25–31.
5. Duarte P., Becerra J. Production of High-Carbon Directly Reduced Iron at Tenova Hyl. *Chernye Metally*. 2016. No. 6. pp. 24–30.
6. Syrkov A. G., Prokopchuk N. R. Dispersed Iron Obtaining by the Method of Solid-State Hydride Synthesis and Problem of hydrophobicity of metal. *CIS Iron and Steel Review*. 2021. Vol. 21. pp. 16–22.
7. Quiroz Cabascango V.E., Bazhin V. Yu. Nickel Oxide Reduction in CO/CO_2 Gas Mixture in Reverberatory Furnaces. *Journal of Physics: Conference Series*. 2020. Vol. 1515. 022028.
8. Ageev E. V., Ageeva E. V., Khardikov S. V. Structure and Properties of Sintered Corrosion-Resistant Steel Manufactured from Electroerosive Powders. *CIS Iron and Steel Review*. 2021. Vol. 22. pp. 88–91.
9. Ageev E. V., Ageeva E. V. Composition, Structure and Properties of Hard Allow Products from Electroerosive Powders obtained from TSK10 Hard Alloy Waste in Kerosene. *Non-ferrous Metals*. 2022. No. 2. pp. 48–52.
10. Zhao Y., Xu J.-B., Zhan J., Chen Y.-Q., Hu J.-M. Electrodeposited Silica Films Combedded with Template and Corrosion Inhibitor for Active Corrosion Protection. *Applied Surface Science*. 2020. Vol. 58. 145242.
11. Tranasekaran P., Su S.-H., Liu Y.-H., Lu K.-L. Hydrophobic Metal-Organic Frameworks and Derived Composites for Microelectronic Applications. *Chemistry – A European Journal*. 2021. Vol. 27, Iss. 67. pp. 16543–16563.
12. Yang Z., Liu X., Tian Y. Novel Metal-Organic Super-Hydrophobic Surface Fabricated by Nanosecond Laser Irradiation in Solution. *Colloids and Surface A: Physicochemical and Engineering Aspects*. 2020. Vol. 587. 124343.
13. Baake E., Shpenst V. A. Resent Scientific Research on Electrothermal Metallurgical Processes. *Journal of Mining Institute*. 2019. Vol. 240. pp. 660–668.

14. Litvinenko V. S., Tsvetkov P. S., Dvoynikov M. V., Buslaev G. V. Barriers to Implementation of Hydrogen Initiatives in the Context of Global Energy Sustainable Development. *Journal of Mining Institute*. 2020. Vol. 244. pp. 428–438.
15. Lutskiy D. S., Ignatovich A. S. Understanding the Hydrometallurgical Recovery of Copper and Rhenium When Processing Off-Grade Copper Concentrates. *Journal of Mining Institute*. 2021. Vol. 251. pp. 723–729.
16. Malaki M., Xu W., Kasar A., Menezes P., Dieringa H., Varma R., Gupta M. Advanced Metal Matrix Nanocomposites. *Metals*. 2019. Vol. 9, Iss. 3. 330.
17. Brichkin V. N., Vorobiev A. G., Bazhin V. Yu. Mining Institute's Metallurgists: a Tradition Serving the Country, Science and Production Industry. *Tsvetnye Metally*. 2020. No. 10. pp. 4–13.
18. Farberova E. A., Katysheva A. Y., Tingaeva E. A., Smirnov S. A., Starostin A. G. Research of Possibility of Using Chemical Method of Fine Metal Particles Reduction for Bactericidal Sorbents Production. *ChemChemTech*. 2020. Vol. 63, Iss. 3. pp. 46–53.
19. Popova A. N., Klimenkov B. D., Grabovskiy A. Yu. Scientific School of Plasma Nanotechnologies and Plasma Power Engineering in Mining University. *Izvestiya VUZ. Applied Nonlinear Dynamics*. 2021. Vol. 29, Iss. 2. pp. 317–336.
20. Pristinskii Yu. O., Peretyagin N. Yu., Kuznetsova E. V., Peretyagin P. Yu. Mechanical Properties of Hard WC–Co Spark Plasma Sintering. *Russian Engineering Research*. 2019. Vol. 39. Iss. 12. pp. 1029–1033.
21. Letenko D. G., Ivanov A. S., Fitsak V. V. Preparation of Fullerenes and Their Derivatives and Their Introduction into Copper Alloys. *Tsvetnye Metally*. 2023. No. 8. pp. 46–50.
22. Nosov V. V., Vozhyakovskiy A. P., Korolev I. A., Kulbada D. A. Influence of 2D Graphene Nanostructures on the Strength Characteristics of a Composite Material. *Tsvetnye Metally*. 2023. No. 8. pp. 14–18.
23. Denisova O. V., Karapetyan K. G. Carbon Materials Surface Modified with Transition Metals Ions. *Tsvetnye Metally*. 2023. No. 8. pp. 56–61.
24. Silivanov M. O., Vinogradova A. A., Research of the Parameters of the Boundary Friction of Tribosystems in the Introduction of Surface-Modified Al-Samples. *Journal of Physics: Conference Series*. 2019. Vol. 1384. 012067.
25. New Materials. Preparation, Properties and Applications in the Aspect of Nanotechnology. Eds. by K. L. Levine, A. G. Syrkov. New York: Nova Science Publishers, Inc., 2020. 249 p.
26. Applied Aspects of Nano-Physics and Nano-Engineering. Eds. by K. L. Levine, A. G. Syrkov. New York: Nova Science Publishers, Inc., 2019. 308 p.
27. Kushchenko A. N. Features of the Formation of Sorption Properties and Hydrophobicity of Metals Containing Ammonium and Organosilicon Compounds in the Surface Layer: Abstract of Diss. ... Candidate of Technical Sciences. St. Petersburg, 2020. 22 p.
28. Nazarova E.A. Influence of Adsorption of Ammonium and Silicon–Organic Compounds on the Tribochemical Properties of Metals (Al, Cu, Ni): Abstract of Diss. ... Candidate of Chemical Sciences. St. Petersburg, 2016. 20 p.
29. Morachevskiy A. G. Review on book: M. A. Meretukov, M. A. Tsepin, S. A. Vorobiev, A. G. Syrkov. Clusters, Structures and Materials of Nanosize: Innovative and Technical Perspectives. *Russian Journal of Applied Chemistry*. 2006. Vol. 79, Iss. 5. p. 865.
30. Yartsev I. K., Bakhareva V. E., Vlasov V. A. Material Science. Modern Nonmetallic Constructive Materials. St. Petersburg: TsNII KM “Prometey”, 2006. 110 p.
31. Tomaev V. V., Polischuk V. A., Vartanyan T. A., Mjakin S. V., Leonov N. B., Semenova A. A. Studies of Zinc and Zinc Oxide Nanofilms of Different Thickness Prepared by Magnetron Sputtering and Thermal Oxidation. *Optics and Spectroscopy*. 2021. Vol. 129. pp. 1033–1037.
32. Petkova A. P., Granzulenko O. Yu. Features of Colour Ultradense Multidimensional Nanobarcodes Created on the Surface of Items Made of Non-Ferrous Metals and Their Alloys. *Tsvetnye Metally*. 2023. No. 8. pp. 19–25.
33. Stepanov S. N., Larionova T. A., Stepanov S. S. Study of Aluminum Influence on the Adhesion of Stainless Steel in Flame Spraying. *Journal of Mining Institute*. 2020. Vol. 245. pp. 591–598.
34. Pankina G.V., Chernavskii P. A., Kazak V. O., Lunin V. V. Cobalt and iron oxides dispersed onto activated carbons: The size effect. *Russian Journal of Physical Chemistry A*. 2015. Vol. 89. pp. 1065–1069.
35. Nechaev I. V., Vvedenskii A. V. Quantum Chemical Modeling of the Interaction in MeN(H₂O)_M (Me = Cu, Ag, Au; N = 1-3; M = 1, 2) System. *Condensed Matter and Interphase Boundaries* 2019. Vol. 21, Iss. 1. pp. 105–115.
36. Rogozhnikov N. A. Quantum-Chemical Study of the Adsorption of Pb²⁺ Ions on Au(111). *Russian Journal of Electrochemistry*. 2018. Vol. 54. pp. 902–911.
37. Rogozhnikov N. A. Quantum-Chemical Simulation of the Adsorption of OH⁻ Ions on Au(111). *Russian Journal of Electrochemistry*. 2021. Vol. 57. pp. 22–29.
38. Hay P. J., Wadt W. R. *Ab initio* Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *The Journal of Chemical Physics*. 1985. Vol. 82. pp. 299–310.
39. Clark T. Computer Chemistry. Moscow: Mir, 1990. 383 p.
40. Andrianov K. A., Khananashvili L. N. Technology of Elementorganic Monomers and Polymers. Moscow: Khimia, 1973. 400 p.
41. Zhukov V. P., Scopov G. V., Kholod S. I., Barbin N. M. Copper Pyrometallurgy (Theory, Practice, Statistics, Economics). Ekaterinburg: Sluzba operativnoy poligrafii Administrativno-khozaystvennogo upravleniya Uralskogo otdeleniya RAN, 2016. 640 p.
42. Mineev G. G., Mineeva T. S., Zhuchkov L. A., Zelinskaya E. V. Theory of Metallurgical Processes. Irkutsk: Izdatelstvo IrGTU, 2010. 522 p.
43. Malakhov A. I., Zhukov A. P. Bases Metal Science and Theory of Corrosion. Moscow: Vyshaya Shkola, 1978. 192 p.
44. Hadzhikov A. S., Harlamin P. S., Hazhinova N. S. Kinetics and Mechanism of Interaction of Iron Oxides with Methane. *Proc. of IX All-Union Conference on Kinetics and Mechanism of Chemical Reactions in Solids, Chernogolovka*, 1986. Vol. 2. pp. 159–160.
45. Krikliviy D. I., Klimovich N. A. Research of Activity of Gas Reducers and Methods of Their Selection in High-Temperature Processes. *Zhurnal Prikladnoy Khimii*. 1991. Vol. 64, Iss. 11. pp. 2242–2249.
46. Tropin D. A., Fedorov A. V. Calculation of Flammability Limits of Silane–Oxygen and Silane–Air Mixtures. *Combustion, Explosion, and Shock Waves*. 2016. Vol. 52. pp. 40–44. NFM