ISSN 2070-2051, Protection of Metals and Physical Chemistry of Surfaces, 2017, Vol. 53, No. 2, pp. 287–293. © Pleiades Publishing, Ltd., 2017. Original Russian Text © V.S. Rudnev, I.V. Lukiyanchuk, M.M. Serov, B.L. Krit, G.D. Lukiyanchuk, D.P. Farafonov, 2017, published in Fizikokhimiya Poverkhnosti i Zashchita Materialov, 2017, Vol. 53, No. 2, pp. 185–191.

> NEW SUBSTANCES, MATERIALS AND COATINGS

Catalytic Properties of Metallic Fibers Fabricated by Tempering of Melt on a Rotating Heat-Receiver

V. S. Rudnev^{*a*, *b*, *, I. V. Lukiyanchuk^{*a*}, M. M. Serov^{*c*}, B. L. Krit^{*c*}, G. D. Lukiyanchuk^{*d*}, and D. P. Farafonov^{*e*}}

^a Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia

^b Far Eastern Federal University, Vladivostok, 690950 Russia

^c Moscow Aviation Institute (National Research University),

GSP-3, 125993 Russia

^d PJSC Dal'pribor, Vladivostok, 690105 Russia

^e Federal State Unitary Enterprise All-Russian Scientific Research Institute of Aviation Materials State Research Center of the Russian Federation, Moscow, 105005 Russia

*e-mail: rudnevvs@ich.dvo.ru

Received February 24, 2016

Abstract—Metallic fibers fabricated by the method of directly suspended melt-droplet extraction are promising for application in catalysis as carriers of catalytically active compounds and as catalytic systems themselves due to their physicochemical properties, structure, surface defects, and low hydrodynamic resistance of porous permeable materials formed from them. The catalytic activity of fibers based on copper, nickel, iron, aluminum, and titanium, also containing noble, transition, refractory, and rare-earth metals, in the reaction of CO oxidation has been estimated. Among the studied samples, fibers based on copper, copper– nickel alloy, and Nichrome with addition of noble metals have been found promising to perform further studies for their application as catalysts of oxidation–reduction reactions.

DOI: 10.1134/S2070205117020204

INTRODUCTION

The search for and development of new types of catalytic materials are of great scientific and practical interest. Recently, significant attention has been paid to catalysts based on inorganic fabrics, gauzes, and nonwoven fabric materials of different shapes and chemical compositions, for example, based on carbon, hydrocarbon, ceramic, and metallic fibers [1-3]. Application of such carriers and catalysts on their basis having a developed surface (and low hydrodynamic resistance to gas or liquid flow) allows conducting processes at short contact time values and, through attainment of complete transformation of reagents, creates extensive possibilities for selecting variants of their packing [3, 4]. Materials based on metallic fabrics and fibers can be characterized with refractoriness, resistance to thermal shocks, mechanical strength, high thermal conductivity and electroconductivity, and specific magnetic characteristics. At present, porous materials based on metallic fibers are applied as noise and radio-wave absorbers as filters and packing media [5, 6].

One advanced, technologically reliable ways of fabrication of inorganic fibers and porous materials from them is the method of directly suspended melt-droplet extraction (DSMDE). This method enables one to form elongated fibers of an equivalent diameter of 30- $80 \,\mu\text{m}$, and individual particles of a length of $3-10 \,\text{mm}$, as well as porous nonwoven sheet materials. One of the advantages of the DSMDE method consists in application of crucibleless melting, which allows fabrication of fibers made of refractory and chemically active metals, including nickel, copper, titanium, zirconium, and heat-resistant, corrosion-resistant, and hardly deformable steels and alloys [4, 5, 7-9]. Pulling the fiber from the melt by means of the DSMDE method occurs at cooling rates of up to 10^6 K/s, which results in formation of a metastable structure and the appearance of solidification structures on the fiber surface (Fig. 1). In the end, fibers can be characterized with an increased concentration of defects on the surface and chemical activity, while some concentration of dopants or impurity elements on the fiber surface may not be excluded.



Fig. 1. Surface of the fiber (a) fabricated by the DSMDE method [7]; fractograph (b) of the surface of fracture of the fiber made of the alloy in the Ni–Al–Co–Re–Ti system [5].

Noble metals and some oxides of transition and rare-earth metals are known to be catalytically active in reactions of oxidation—reduction of organic and inorganic compounds [10]. Due to specific features of fabrication and structure, DSMDE fibers made of alloys based on transition metals or those containing noble, transition, or rare-earth metals may be of interest for catalysis both as catalytically active systems and as carriers of catalytically active compounds. In addition, heat- and corrosion-resistant alloys with rareearth and refractory metals can be used at elevated temperatures and in corrosion-active media during various chemical reactions.

The objective of the present work was to reveal the catalytic activity of a number of DSMDE fibers of different compositions in the model reaction of oxidation of CO into CO₂. Fibers based on the following systems were selected for the study: Al-Mg-Cu, Fe-Cr-Al, Fe-Cr-Al-Pt, Ni-Cr-Al-REM, Ni-Cr-Al-Pt-Ir-Hf, Ni-Cr-Al-Hf, Ni-Cr-Al-Pt-Ir-Hf, Ni-Cr, and Ni-Cu-Fe. Titanium and copper fibers were also used. At the current stage of study, samples were examined as received and did not undergo additional modification.

MATERIALS AND METHODS

The fibers composition was determined using an X-MET 7500 X-ray fluorescence portable analyzer (Oxford Instruments, United Kingdom).

The cross section of fibers fabricated by the DSMDE method has a shape similar to lamellar (Fig. 1b), whereas the fiber thickness constitutes a characteristic determining the solidification conditions. Fiber thickness *d* was measured using a micrometer: the average value was calculated from 5–15 measurements. Specific geometric surface $S_{\text{spec geom}}$ was calculated according to the formula $S_{\text{spec geom}} = 4/\rho d$, where ρ is the alloy density, assuming that the area of fiber butt ends is infinitely smaller than that of their side area. If the alloy density was unknown, it was calculated using the handbook data on metal density and the obtained data on the elemental composition of fibers.

X-ray images of some metallic fibers were obtained using a Bruker D8 ADVANCE diffractometer (Germany) in CuK α -radiation.

The catalytic activity of fiber samples in the reaction of oxidation of CO into CO₂ was determined from the dependence of the CO conversion on temperature. Samples of metallic fibers for catalytic tests were selected in such a way as to make their geometric surface area equal to about 50 cm^2 . The prepared samples (Fig. 2, upper row) were placed into the reaction zone of a tubular quartz reactor between quartz sand layers. The catalytic-test conditions were a BI-CATflow 4.2(A) flow-type catalytic system (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Russia), gas-mixture composition 5% CO + air, and rate of gas flow through the reactor (volume 3 cm^3) 50 mL/min. At each temperature, a sample was preliminarily held for 20 min to ensure homogeneous bulk temperature distribution, after which CO and CO₂ concentrations were measured at the reactor inlet and outlet using a PEM-2 gas analyzer (Institute of Catalysis, Russia).

RESULTS AND DISCUSSION

DSMDE fibers were fabricated at the Chair of Technologies of Automated Design of Metallurgical Production of the Moscow Aviation Institute by a group headed by Dr. of Technical Sciences M.M. Serov.

The metallic-fiber diameter, the alloy density, and the calculated specific geometric surface area are shown in the table.

The results of catalytic tests of fiber samples in the reaction of oxidation of CO into CO_2 are shown in Figs. 3 and 4. As is seen from the data of Fig. 3c, the samples of fibers of the Al-Mg-Cu system are virtually inactive in the reaction of CO oxidation up to 500°C. The activity in Fe-Cr-Al systems is slightly higher (Fig. 3a). Note that, at identical calculated geometric surfaces (50 cm²/g), the activity of needle-shaped Fe-Cr-Al samples is higher than that of sim-

Iron-alloy-based fibers Al-Mg-Cu Ti Cu Fe-Cr-Al Fe-Cr-Al-Pt Initial samples After catalysis Nickel-alloy-based fibers Ni-Cr-Ti-W-Mo-Nb Ni-Cr-Al-P3M Ni-Cr-Al-Pt-Hf Initial samples After catalysis

Ni-Cr-Al-Mo-Hf

Ni-Cr-Al-Pt-Ir-Hf Ni-Cu-Fe-Mn-Si

Fig. 2. Photographs of metallic-fiber samples prepared for catalytic tests and after tests.

ilar fibers, which may be the result of several factors. The real surface area of needle-shaped samples must be larger than that of fibers, which yields large values of CO conversion at the same temperature. Second, according to data of X-ray fluorescence analysis, needles and fibers differ in composition with respect to impurities. It is worth mentioning that introduction of 0.5 wt % of platinum into the system (Fe–Cr–Al–Pt



Fig. 3. Temperature dependencies of the CO conversion in the first cycle of catalytic tests for fiber samples made of: (a) iron alloys; (b) nickel alloys; (c) valve metals (Ti, Al alloy), copper and copper–nickel alloy Ni–Cu–Fe–Mn–Si (Monel). \uparrow – increase and \downarrow – decrease of temperature.

system, Fig. 3a) does not increase the fiber activity in this reaction. One can suggest that its concentration on the surface is insignificant.

Under the experimental conditions, fibers in nickel-based systems manifest activity at temperatures

above 400°C: the temperature at which the CO conversion is 10% $T_{10} \ge 400$ °C (Fig. 3b). Additional introduction of platinum and/or iridium into the composition of nickel fibers results in the increase of their activity (Fig. 3b). Most probably, unlike in Fe–Cr–Al systems, noble metals are present on the fiber surface in nickel-based systems (8–10 wt % Pt in the alloy).

Under the experimental conditions, the most active are samples of copper fibers with the T_{10} value equal to 200°C. For the Cu–Ni system alloy with the nickel content of 63 wt % $T_{10} = 280$ °C. In both cases, 100% of CO conversion into CO₂ is attained for the specified sample.

Figure 4 shows the diagrams of the CO conversion at 500°C (X_{500}) for all the samples and half-conversion temperature T_{50} —the temperature at which 50% of the initial CO is converted into CO₂. Note that, for some samples, the value of conversion X (%) at a certain temperature could be different upon heating and cooling of the tested samples or upon further heating cooling cycles (Figs. 3, 4). These facts are reflected in the presence of the hysteresis loop for the value of X, % in Fig. 3a and discrepancies in X_{500} , % or T_{50} , % in Fig. 4. The "clockwise" hysteresis loop indicates deactivation of the samples, while the "counterclockwise" one indicates their activation.

Changes in the activity of fibers must be the result of interaction of the sample surface with the contact reaction mixture ($CO + CO_2 + air$) and elevated temperature. These factors may yield the formation of oxides and other compounds on the sample surface.

In the case of neglecting the presence of noble and rare-earth metals in some samples, the obtained series of activity of the fibers under study in CO oxidation depending on their composition corresponds, in general, to that of transition-metal oxides. For instance, at measurements of the CO oxidation rate in mixtures with a stoichiometric component ratio at 227°C, the following series was established: $Co_3O_4 > CuO >$ $MnO_2(Mn_2O_3) > NiO > Fe_2O_3 > TiO_2$ [11, 12]. According to the data of Figs. 3 and 4a, the series of activity in CO oxidation (in descending order) for the studied fiber samples can be written as follows: Cu > $Ni-Cu-Mn-Si > Ni-Cr-Al-Pt-Ir-Hf \approx Ni-Cr Al-Pt-Hf > Ni-Cr-Ti-W-Mo-Nb \approx Ni-Cr-Al-$ REM > Fe-Cr-Al-needles > Ni-Cr-Al-Mo-Hf > $Fe-Cr-Al-fibers \ge Fe-Cr-Al-Pt > Al-Mg-Cu > Ti.$

The samples' catalytic activity in CO oxidation must be related, among other factors, to formation of corresponding oxides on the surface (noble metals could be present on the surface aside from oxides). However, the attempt to control the formation of oxides after catalytic tests by the X-ray-diffraction method failed because of the complexity of creating a flat surface with flattening of fiber samples and, evidently, negligible thickness of the formed oxide films. For instance, X-ray diffraction patterns of the initial



Fig. 4. CO conversion at 500°C (X_{500}) in the (1) first and (2) second cycles of catalytic tests for fiber samples made of different alloys (a); CO half-conversion temperature (T_{50}) in the (1) first and (2) second cycles of catalytic tests (b) at heating (direct change 1, 2) and cooling (reverse change 1', 2').

aluminum and titanium fibers before and after catalytic tests contain only reflections characteristic of aluminum and titanium.

The formation of oxides on the surface is indicated by changes in the color of fiber samples in the course of catalytic tests (Fig. 2): for example, the surface of aluminum fibers becomes slightly yellowish, that of titanium fibers became blue-violet, samples in the Fe–Cr–Al system (Fechral) in the forms of fibers and needles become brown, golden-pink copper fibers and the copper–nickel alloy sample become black, and other nickel-based alloys acquire a golden color.

According to [13], heating at 400-450°C in air results in formation of an amorphous oxide film of a thickness of ~5 nm on the surface of aluminum and its alloys. At temperatures equal to and higher than 450°C, the film thickness increases up to 20 nm, which is believed to be caused by the transition from the aluminum oxide amorphous structure to its crystal structure. Blue-violet oxide films on the titanium surface are formed upon oxidation by atmospheric oxygen and have a thickness of ~51 nm [14]. According to [15], the blue color of the titanium sample must be related to the presence of TiO and Ti₂O₃ oxides on its surface. The black color of copper fibers upon catalysis corresponds to formation of the copper-oxide (CuO) film. According to the data of [16], a noticeable interaction of copper with O₂ starts at 200°C: first, Cu₂O forms at temperatures up to 377°C, while two-layer dross with an internal layer consisting of Cu₂O and an external one consisting of CuO forms at $T > 377^{\circ}$ C. In our case, a noticeable CO oxidation on copper fibers also starts at $T > 200^{\circ}$ C (Figs. 3c, 4b), which may indicate the activity of the surface layer of copper oxides. The brown color of Fechrals upon catalysis may correspond to the presence of Fe₃O₄ (black) and Fe₂O₃ (α -Fe₂O₃, dark red, and γ -Fe₂O₃, brown) oxides on the surface. According to the data of [17], FeO does not form at temperatures below 570°C. The goldish color of nickel fibers upon catalytic tests must be related to formation of a thin oxide film containing NiO on their surface. For instance, the golden oxide layer on the nickel coating is obtained by thermal treatment at 400°C and a holding period of 1.5 h [18].

CONCLUSIONS

The catalytic activity of a number of DSMDE fibers based on copper, nickel, iron, aluminum, and titanium, including those containing noble, transition, refractory, or rare-earth metals, in the reaction of CO oxidation into CO_2 has been investigated. Such fibers are promising for testing as catalysts of other oxidation—reduction reactions. Fibers made of nickel-based alloys without noble metals and those based on iron, aluminum, and titanium are characterized by low activity. They are promising in application as carriers of catalytically active compounds.

Special interest in catalysis is concerned with the possibility of using the DSMDE method to produce porous materials, fibers, and needles made of various inorganic compounds, including by mixing fibers of different chemical compositions in catalyst preparation.

System	Description	<i>d</i> , mm	ρ, g/cm ³	$S_{\rm spec \ geom}, \ {\rm cm^2/g}$
Al–Mg–Cu (corresponds to aluminum alloy 1105)	Fibers $l = 10-20$ cm	0.10 ± 0.01	2.80	138
Titanium of technical pure grade (corresponds to VT1-0)	Fibers $l = 10 - 30$ cm	0.07 ± 0.01	4.505	125
Copper of technical pure grade (corresponds to M3, M2, or M2r)	Soft fibers $l = \sim 0.5$ cm	0.068 ± 0.006	8.94	66
Iron-based alloys (Fechrals)		<u> </u>		
Fe–Cr–Al fibers (correspond to steel Kh23Yu5)	Fibers $l = 5-20$ cm	0.052 ± 0.005	7.25	106
Fe–Cr–Al – needles (correspond to steel Kh23Yu5)	Needles $l \approx 0.5$ cm)	0.057 ± 0.007	7.25	97
Fe-Cr-Al-Pt	Fibers $l = 5 - 15$ cm	0.050 ± 0.004	7.35	108
Nickel-based alloys (Nichromes)		I		
Ni-Cr-Al-REM, Ni-base	Brittle fibers $l = 10 \text{ cm}$	0.045 ± 0.005	7.34	120
Ni–Cr–Al–Pt–Ir–Hf, Ni–base	Fibers $l = 3 - 10 \text{ cm}$	0.047 ± 0.004	8.86	96
Ni–Cr–Al–Mo–Hf, Ni–base	Fibers $l = 2 - 10 \text{ cm}$	0.044 ± 0.002	8.08	113
Ni–Cr–Al–Pt–Hf, Ni–base	Fibers $l = 3 - 10$ cm	0.051 ± 0.007	8.307	94
Ni–Cr–Ti–W–Mo–Nb (corresponds to alloy EP-648)	Brittle fibers $l = 1-5$ cm	0.042 ± 0.004	8.26	116
Copper-nickel alloy		·		
Ni–Cu–Fe–Mn–Si (corresponds to Monel NMZhMts28-2.5-1.5)	Fibers $l = 5-20$ cm	0.041 ± 0.005	8.82	112

Characteristics of metallic fibers: composition, average diameter d, alloy density ρ , calculated specific geometric surface $S_{\text{spec geom}}$

If one does not take into consideration the presence of noble and rare-earth metals in some samples, then the activity of the fibers under study in CO oxidation correlates with the activities of the alloy main metal oxides known from the literature data. Therefore, the preliminary oxidation of the fiber surface by different methods, including thermal, electrochemical, and plasma–electrolytic ones, promotes the formation of metal–oxide catalysts and carriers. As was shown earlier [4], canvas materials formed by the DSMDE method can undergo plasma–electrolytic treatment.

It is evident that, aside from oxidation, to increase the catalytic activity of catalysts based on DSMDE fibers, other physicochemical methods can be applied, e.g., extraction—pyrolysis, sol—gel synthesis, impregnation, and electrodeposition.

Application of metallic porous fiber materials differing in nature fabricated by the DSMDE method opens various possibilities for production and design of catalytically active materials.

REFERENCES

- 1. Barelko, V.V., Khrushch, A.P., Cherashev, A.F., et al., *Kinet. Catal.*, 2000, vol. 41, no. 5, pp. 655–661.
- Balandina, T.A., Larina, T.Y., Kuznetsova, N.I., and Bal'zhinimaev, B.S, *Kinet. Catal.*, 2008, vol. 49, no. 4, pp. 499–505.
- 3. Chub, O.V., Ermakova, A., Suknev, A.P., et al., *Katal. Prom-sti*, 2008, no. 1, pp. 5–8.
- Zheltukhin, R.V., Krit, B.L., and Serov, M.M., Pribory, 2012, no. 8 (146), pp. 18–22.
- Farafonov, D.P., Degovets, M.L., and Serov M.M., *Tr. Vseross. Inst. Aviats. Mater.*, 2014, no. 7, art. 02. http://viam-works.ru/plugins/content/journal/uploads/ articles/pdf/681.pdf. doi dx.doi.org/ doi 10.18577/2307-6046-2014-0-7-2-210.18577/2307-6046-2014-0-7-2-2

- 6. *Poristye pronitsaemye materialy. Spravochnik* (Porous Permeable Materials: Handbook), Belov, S.V., Ed., Moscow: Metallurgia, 1987.
- Borisov, B.V. and Serov, M.M., Russ. J. Non-Ferrous Met., 2013, vol. 54, no. 5, pp. 407–411.
- 8. Antsyferov, V. and Serov, M., *Manufacturing of a Rapid Solidification Materials and Fibers*, Saarbrücken: LAP Lambert Academic Publ., 2014.
- 9. Volfkovich, Yu.M., Filippov, A.N., and Bagotsky, V.S., Structural Properties of Porous Materials and Powders Used in Different Fields of Science and Technology, London: Springer, 2014.
- Kataliticheskie svoistva veshchestv. Spravochnik (Catalytic Properties of Substances. Handbook), Gorokhovatskii, Ya.B., Ed., Kiev: Naukova Dumka, 1977, vol. 4.
- 11. Boreskov, G.K. and Marshneva, V.I., *Dokl. Akad. Nauk SSSR*, 1973, vol. 213, no. 1, pp. 112–115.
- 12. Boreskov, G.K., *Kataliz. Voprosy teorii i praktiki. Izbrannye trudy* (Catalysis. The Problems on Theory and Practice. Selected Works), Novosibirsk: Nauka, 1987.

- 13. Schmitz, Ch., Handbook of Aluminum Recycling: Fundamentals, Mechanical Preparation, Metallurgical Processing, Plant Design, Essen: Vulkan, 2006.
- 14. Bai, A.S., Lainer, D.I., Slesareva, E.N., and Tsypin, M.I., *Okislenie titana i ego splavov* (Oxidation of Titanium and its Alloys), Moscow: Metallurgiya, 1970.
- 15. Ganzulenko, O.Yu., *Vopr. Materialoved.*, 2014, no. 1, pp. 79–86.
- Khimicheskaya entsiklopediya (Chemical Encyclopedia), Knunyants, I.L., Ed., Moscow: Bol'shaya Rossiiskaya Entsiklopediya, 1992, vol. 3.
- Yukhnevich, R., Bogdanovich, V., Valashkovsky, E., and Vidukhovsky, A., *Technika Przeciwkorozyina*, Warszawa: Wydawnictwa Szkolne i Pedagogiczne, 1973.
- Odnoralov, N.V., *Gal'vanotekhnika v dekorativnom iskusstve* (Galvanic Engineering in Decorative Arts), Moscow: Iskusstvo, 1974.

Translated by D. Marinin