Electroplating of Co-W and Co-Mo Alloys from Na_2WO_4 Ionic Melts

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The cathodic reduction processes of cobalt (II), tungsten (VI) and molybdenum (VI) in Na_2WO_4 melts are discussed. Electrochemical behavior of cobalt in a tungstate melt, as well as the effect of electrolysis conditions on the composition and structure of Co-W and Co-Mo alloys deposits from tungstate-molybdate melts is also studied. With a decrease in the concentration of cobalt ions and an increase in the concentration of molybdenum (tungsten) ions in the melt, the phase composition of cathodic deposits is shown to change from individual cobalt to individual molybdenum (tungsten) via a series of cobalt-molybdenum (tungsten) compounds of various compositions.

Keywords: Co-W and Co-Mo alloys, ionic melts, tungstate-molybdate melts, electroplating

Electrolysis of aqueous solutions and melts is often used for obtaining the Ni-W and Ni-Mo alloys. However, most if not all of literature data show that some undesirable side processes occur in aqueous solutions. They result in the diminution of current efficiency and, in some cases, are responsible of incomplete cathodic reduction of molybdates or tungstates. Most melts considerably also suffer from this disadvantage. The literature has many studies on electrodeposition of metalic Mo, W, Co and Co-Mo alloys from ionic media.[1-9] Electrochemical behavior of nickel as well as electroplating of nickel-molybdenum (tungsten) alloys from oxide tungstate-molybdate nickel-containing melts was studied in our previous work [10]. In the earlier works [11-13], common regularities of codeposition of iron family metals with titanium from halide melts were found. In relation with this, of a practical and theoretical interest are the common regularities of codeposition of nickel and cobalt with tungsten or molybdenum.

Molybdenum (tungsten) and cobalt metals have different crystal lattices, namely, scc and fcc, respectively. Standard electrode potentials of these metals differ by 0.07 V in a halide melt, as NaCl-KCl at 1073 K and by 0.08-0.28 V (depending on the basicity of the melt) in a halide–oxide melt, as NaCl-KCl-Na_2MoO_4 (Na_2WO_4)-$CoCl_2$ at 1023 K [14]. In both melts, the potentials of molybdenum (tungsten) deposition are more positive than that of cobalt deposition. Under these conditions continuous electrodeposition of molybdenum (tungsten), cobalt, and molybdenum (tungsten)-cobalt alloys with various composition depending on the bath composition and the electrolysis conditions may be obtained. Coherent deposits may be plated only on graphite, copper, nickel, or noble-metal substrates in a protective atmosphere over the bath.

Oxide tungstate-molybdate Na_2WO_4-MO_3 (M=Mo or W) melts have been used earlier [15,16] in electroplating molybdenum (tungsten) coatings. In such melts, as was found in [10], the deposition potentials of molybdenum (tungsten) are more negative than that of nickel. The same relation may obviously be expected in the case of cobalt.

In this work, we studied the electrochemical behavior of cobalt ions in a Na_2WO_4 melt and the possible electroplating of Co-W and Co-Mo alloys from such molten bath. These alloys are of practical importance in the production of cobalt-containing structural materials by means of the high-temperature electrochemical synthesis of molybdenum and tungsten carbides. Cobalt additives substantially increase the ductility of molybdenum and tungsten as pure metals.

Experimental part

The used melts were: Na_2WO_4-CoO-MoO_3 and Na_2WO_4-WO_3-MoO_3 prepared from pure substance (Sigma-Aldrich, 99%). Working temperature was in the range 1123-1173 K.

As the main technique of investigation, we used cyclic voltammetry with the scan rates of $5{\cdot}10^{-3}$ to 10 V/s corresponding to either quasi-steady-state or transient polarization conditions.

Experiments were carried out in air atmosphere in a quartz reactor. The design of electrochemical cell, preparation of reagents, methods of monitoring and estimating the kinetic parameters of the electrode process were described in [10]. The reference electrode was a platinum-oxygen electrode, namely, a Pt wire immersed in a 80 mol% Na_2WO_4-20 mol% WO_3 melt and blown round with air in a cell provided with an alundum diaphragm.

The deposits obtained were studied by X-ray diffraction analysis, X-ray energy dispersive microanalysis and metallographic method with the use of DRON-4.0, Cameca, and Neophot-21.equipments. The microhardness was measured with a PMT-3 equipment.

Results and discussions

An analysis of equilibrium potentials was made in aqueous solutions for the most popular system containing citric complexes of Co(II) and molybdate anions.[17,18] The well-known material balance equations made possible to calculate the distribution of the ionic species components and to use this information for the estimation of equilibrium potentials of the corresponding cathodic processes. The conclusion was that the reduction of cobalt (II) is possible, but the complete tungsten or molybdate reduction is possible only at sufficiently negative potentials where the reduction of H^+ ions should prevail. Thus the thermodynamic regularities are indicative of the certain

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complications regarding the electrolysis of aqueous solutions. In this connection, the main attention was focused in this work on the melts.

Electrochemical behavior of Cobalt (II) ion in a tungstate melt

A reduction wave was observed at -0.8 to -0.9V in voltammetric curves (fig. 1) recorded from a Na_2WO_4 melt containing cobalt (II) oxide. An increase in the Co(II) concentration led to the increase in the wave height and to its shift of potential in the positive direction.

The reduction process of Co(II) proceeded in a single stage. An increase in the polarization rate to 5.0 V/s made it impossible to determine the mechanism of the process. Potentiostatic electrolysis at potentials of the wave observed resulted in cobalt metallic coating. The dependence of peak current density (i_p) on the concentration of cobalt oxide at various polarization rates (v), (fig. 2) was linear.

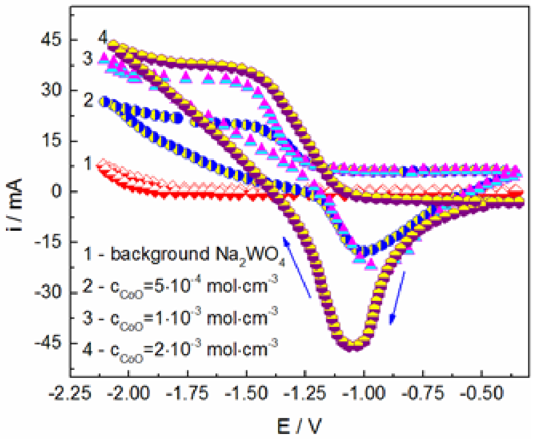


Fig. 1. Voltammetric curves on Pt electrode from various melts:(1) individual Na_2WO_4 bath and (2-4) the bath containing different CoO concentrations; T=1173K and scans rate of 10 mV/s.

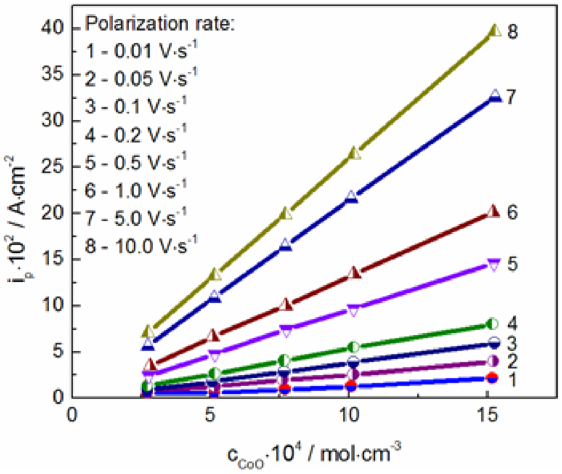


Fig. 2. The dependence of peak current density on the CoO concentration in Na_2WO_4 melt at various scans; Pt cathode, T=1173K.

Also we found that the $i_p/v^{1/2}$ ratio was nearly constant in a polarization rate range of 0.05 to 2.0 V/s (fig. 3).

The mass transfer constant i/nFC corresponding to the steady-state voltammetric dependences and characterizes the supply of reagent Co(II) to the electrode surface, was equal to (2.1-2.7) 10^{-4} cm/s that confirms the diffusion control of the process of Co(II) reduction. Hence, under these polarization conditions, the formation rate of Co metal grains did not limit the process in question.

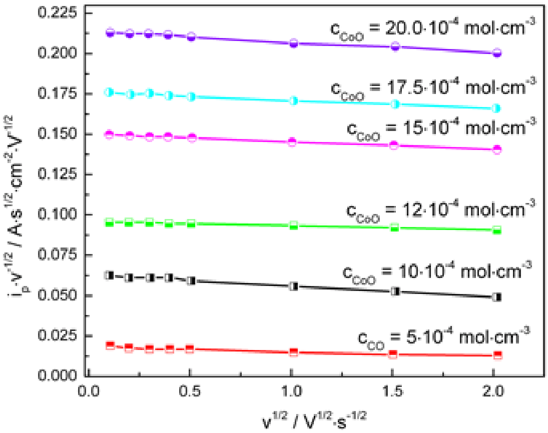


Fig. 3. The $i_p/v^{1/2}$-$v^{1/2}$ dependence for the electrochemical reduction of cobalt (II) ion containing Na_2WO_4 melts for different concentration of CoO at T=1173K, Pt cathode.

Linear dependence of the cathodic peak current with the cobalt (II) oxide concentration, the constancy of $i_p/v^{1/2}$ ratio in a wide range of the polarization rates, and the i_p/nFC value indicate that the diffusion of Co(II) ions to the electrode surface is the limiting stage of the electrode process.

The electrodeposition mechanism may be explained based on a supposition about the existence of acid-base equilibria in tungsten melts, in which tungstate and bitungstate ions are involved [10]. Upon the addition of cobalt (II) oxide, the activity of oxygen ions increased, due to the equilibrium (1):

$$CoO \leftrightharpoons Co^{2+} + O^{2-} \qquad (1)$$

Therefore the electrode process under these conditions may be written as a two-electron transfer:

$$Co^{2+} + 2e^{-} \leftrightharpoons Co \qquad (2)$$

According to the experimental dependence of the equilibrium potential of the cobalt electrode on the cobalt (II) oxide concentration in a sodium tungstate melt, the number of electrons per an electrochemically active Co(II) ion equals 1.9-2.2. Similar values were obtained by recording the steady-state voltammetric curves which were analyzed in a semilogarithmic E-log $i/(i_d-i)$ coordinates;i-the current density and i_d- the limiting current density. The slopes of these linear dependences at various CoO concentrations were 103 to 122 mV, while n was 1.7 to 2.1. A theoretical slope of the reversible two-electron reaction is 112 mV.

The agreement of the experimentally estimated slope with the theoretical value indicates the reversibility of the charge transfer stage for Co electrodeposition from Na_2WO_4 melt. This was also confirmed by other following experimental observations. The deposition potential and the half-wave potential are independent of the polarization rate up to 0.2V/s, and the dependence of the equilibrium potential on CoO concentration was well described by the Nernst equation.

The number of electrons involved in the electrode process was also determined from the difference between the peak and half-peak potentials of the cyclic voltammetry curves: $E_{p/2}-E_p=2.2$ RT/nF. At various CoO concentrations and scan rates of 0.05 - 0.2 V/s,the number of transferred electrons fell in a range of 1.7 to 2.0.

At a scan rate higher than 0.5 V/s, the reversible electrode process became quasi-reversible. This was manifested also in the deviation from the i_p-$v^{1/2}$ linear dependence and in the dependence of the peak and half-peak potentials on the scan rate. Thus, analysis of the experimental data obtained allowed us to conclude that reversible processes involving cobalt (II) reduction and Co metal deposition may proceed in a sodium tungstate melt.

Electrochemical co-reduction of Co(II) and W(VI) ions [as well as co-reduction of Co(II) and MO(VI) ions] with from a Na_2WO_4 bath and electroplating of Co-W (or Co-Mo) alloys

Upon addition of tungsten (VI) oxide to Na_2WO_4 melt, $W_2O_7^{2-}$ ions are formed in the bath [16] and these bitungstate ions are cathodically reduced:

$$W_2O_7^{2-} + 6e^- \leftrightarrows W + WO_4^{2-} + 3O^{2-}, \qquad (3)$$

that was thoroughly studied in [15]. The difference between the deposition potentials of cobalt and tungsten is 0.070 to 0.105 V at 1173K, and, by contrast to halide and halide–oxide melts,the reduction potential for cobalt is more noble than for tungsten in an oxide melt. As the blank bath for electroplating Co-W alloys of diverse compositions, we took a Na_2WO_4-1.5 mol% WO_3 melt. From this bath, upon its purification by preliminary electrolysis, tungsten coatings were electroplated with the use of a tungsten soluble anode in a temperature range of 1123 to 1173K at cathodic current densities of 0.04-0.14 A/cm^2 in order to determine the structure of tungsten metal deposits. It was found that using a current density of 0.04-0.10 A/cm^2, W coatings have a columnar structure with a layer thickness of 150-200 µm and a microhardness of 340-420 kgf/mm^2. The maximum thickness of the coatings was 500 µm. When co-depositing two metals, the tungsten anode was replaced with a more noble cobalt anode, and the electrolysis was carried out at a cathodic current density of 0.05-0.12A/cm^2 in the afore mentioned temperature range (1123-1173K). The WO_3 concentration was maintained in a range of 0.1-1.5 mol%, while the CoO concentration was varied from 0.01 to 1.0 mol%, so that the molar tungsten-to-cobalt ion ratio was changed from 150 to 0.1. The results of experiments for coatings deposited on Ni substrate are summarized in table 1.

As table 1 shows, an increase in the CoO concentration or the temperature, as well as a decrease in the cathodic current density, lead to an increase in the cobalt content in the deposit. From the melts containing 0.08-1.0 mol% CoO at temperature of 1123 to 1173K, continuous dense layers of CoW and Co_3W intermetallic compounds are deposited sequentially. The formation possibility of the latter is confirmed by binary phase Co-W diagram [19]. Both compounds have fine-crystalline or lamellar structure (fig. 4a), and their microhardness is 840 and 500 kgf/m^2 respectively (fig. 4b). From the Na_2WO_4-CoO melts containing WO_3, at a current density of up to 0.05 A/cm^2, continuous cobalt metal layers with a block or columnar-block structure, thickness of lower than 50 µm and microhardness of 150-180 kgf/m^2 are deposited. Upon further thickening of cobalt coatings or with an increase in the current density above 0.05 A/cm^2, they transform into dendrites. The analysis of cobalt and tungsten concentration distribution among the coating and nickel substrate indicate the mutual diffusion of the coating and substrate elements, which provides a good coherence between them.

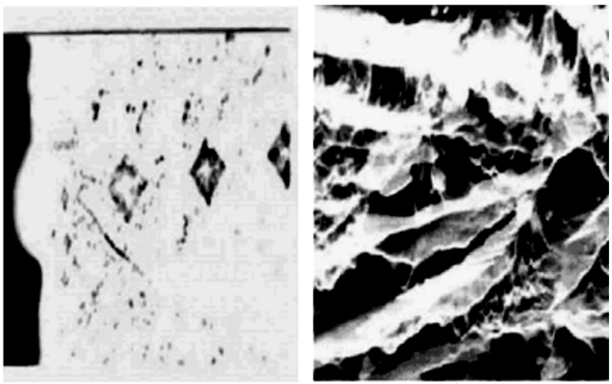

a) b)

Fig. 4.(a) SEM surface image of the Co_3W coating (x 800) and (b) a micro photo of the cross section of a nickel specimen electroplated with Co_3W (x400) at 0.7 mol% CoO content and 0.2 mol% WO_3 content, T=1173K, i_c=0.07 A/cm^2, and t=1.5 h

Adding molybdenum (VI) oxide to the cobalt oxide containing Na_2WO_4 melt results in the appearance of the bimolybdate ion reduction wave:

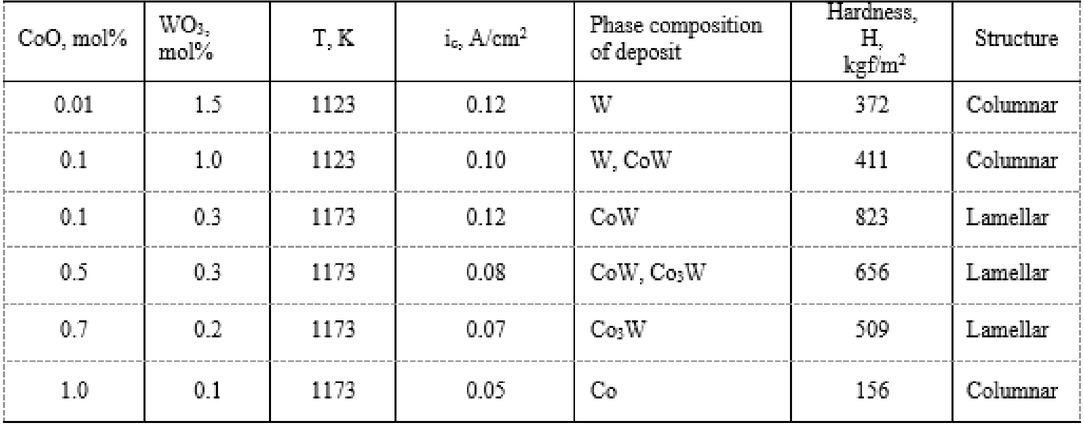
$$Mo_2O_7^{2-} + 6e^- \leftrightarrows Mo + MoO_4^{2-} + 3O^{2-} \qquad (4)$$

that was studied in detail in [19]. The difference between the deposition potentials of cobalt and molybdenum is 0.060 to 0.090 V at 1173K, the cobalt’s one being more positive. The technique of plating the alloys is similar to that described above from the original bath of the following composition: Na_2WO_4-5.0 mol% MoO_3. The results of experiments using a steel substrate are listed in table 2.

The regularities of Co-Mo alloys electroplating are similar to those observed in the case of Co-W alloys. The MoO_3 content in this bath was maintained in a range of 1.0 to 5.0 mol%, while the CoO concentration was varied from 0.01 to 2.0 mol%, so that the molar molybdenum-to-cobalt ion ratio fell in a range from 500 to 0.05. From the baths containing 0.1-0.8 mol% CoO at temperature of 1123 to

Table 1

EFFECT OF ELECTROLYSIS CONDITIONS ON THE COMPOSITION AND STRUCTURE OF Co-W ALLOYS DEPOSITED ON NICKEL SUBSTRATE FROM Na_2WO_4-CoO-WO_3 MELTS



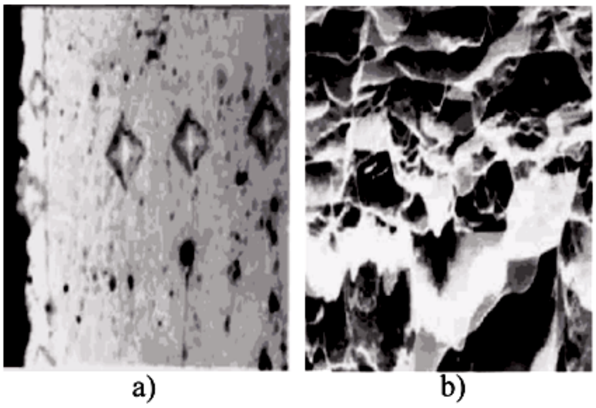
CoO, mol%	WO_3, mol%	T, K	i_c, A/cm^2	Phase composition of deposit	Hardness, H, kgf/m^2	Structure
0.01	1.5	1123	0.12	W	372	Columnar
0.1	1.0	1123	0.10	W, CoW	411	Columnar
0.1	0.3	1173	0.12	CoW	823	Lamellar
0.5	0.3	1173	0.08	CoW, Co_3W	656	Lamellar
0.7	0.2	1173	0.07	Co_3W	509	Lamellar
1.0	0.1	1173	0.05	Co	156	Columnar

Table 2

EFFECT OF ELECTROLYSIS CONDITIONS ON THE COMPOSITION AND STRUCTURE OF Co-W ALLOYS DEPOSITED ON STEEL SUBSTRATE FROM Na_2WO_4-CoO-WO_3 MELTS

CoO mol%	MoO_3 mol%	T K	i_c A/cm^2	Phase composition of deposit	Hardness, H kgf/m^2	Structure
0.01	5.0	1173	0.07	Mo	185	Columnar
0.01	2.5	1123	0.10	Mo	179	Columnar
0.1	0.5	1123	0.07	Mo, CoMo	293	Columnar
0.1	0.2	1173	0.08	CoMo	650	Lamellar
0.5	0.2	1173	0.08	CoMo, Co_3Mo	524	Lamellar
0.8	0.2	1173	0.07	Co_3Mo	387	Lamellar
1.5	0.1	1173	0.05	Co	150	Columnar
2.0	–	1123	0.04	Co	164	Columnar

1173K, continuous CoMo and Co_3Mo layers were deposited sequentially on the cathode. The possibility of the formation of these intermetallic compounds is confirmed by the Mo-Co phase diagram [20]. Both alloys have fine-crystalline or lamellar structure (fig. 5a),with microhardness decrease from 650 to 390 kgf/mm^2 when the molybdenum-to-cobalt ratio is decreased (fig. 5b). From the baths free of MoO_3 at a current density lower than 0.05 A/cm^2, continuous cobalt metal layers with block or columnar-block structure were deposited. The analyses of the cobalt and molybdenum concentration distribution in the coating and steel substrate indicate that there is a mutual diffusion of the coating and substrate elements, which also provides a good coherence between them.



a) b)

Fig. 5.(a) SEM surface image of the cobalt metal coating (x800) and (b) a micro cross-section photo of a steel specimen covered with cobalt (x400) at 1.0 mol% CoO content, T=1173K, i_c=0.05 A/cm^2, and t=1.0 h

Conclusions

The results demonstrate that molybdenum (tungsten)-cobalt alloys may be plated on cathode as continuous layers from oxide melt baths. Changing the content of the corresponding components in the melt, the temperature, and the current density may control the composition and structure of the deposit. The general regularities of the electroplating are similar to these typical of the molybdenum (tungsten)-nickel alloys.

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References

1. SENDEROFF, S., MELLORS, G.W., J.Electrochem.Soc., **114**, 1967, 556-560.
2. KIPOROS, G. SADOWAY, D., J.Appl.Electrochem., **18**, 1988, 823-830.
3. WATANABE, T., NAOE, T., MITSUO, A., KATSUMATA, S., Journal of The Surface Finishing Society of Japan, **40**, 1989, 458-462
4. NAKAJIMA, H., NOHIRA, T. HAGIWARA, R, Electrochem.Solid-State Lett., **8**, 2005, C91-C94
5. COSTOVICI, S., MANEA, A., VISAN, T., ANICAI, L., Electrochim.Acta, **207**, 2016, 97-111.
6. MALYSHEV, V.V., Protection of Metals, **43**, 2007, 548-553.
7. MALYSHEV, V.V., GAB, A., GAUNE-ESCARD, M., Materials and Manufacturing Processes, **23**, 2008, 748-751.
8. LIU, Y.H., ZHANG, Y.C., JIANG, F., FU, B.J., SUN, N.B., Journal of Nuclear Materials, **442**, 2013, S585-S591.
9. ZHANG, S., WEN, Y., ZHANG, H., Powder Technology, **253**, 2014, 464-466.
10. MALYSHEV, V.V., USKOVA, N.N., Zashch. Met., **39**, no. 1, 2003, p. 10.
11. SHAPOVAL, V.I., KOROBKA, Yu.V., ZARUBITSKAYA L.I., Ukr. Khim. Zh., **59**, 1993, p. 378.
12. ZARUBITSKAYA, L.I., KOROBKA, Yu.V., SHAPOVAL, V.I., Ukr. Khim. Zh., **61**, 1995, p. 42.
13. ZARUBITSKAYA, L.I., KOROBKA, Yu.V., SHAPOVAL, V.I., Zh. Prikl. Khimii, no. 3, 1998, p. 12.
14. NOVOSELOVA, I.A., MALYSHEV V.V., SHAPOVAL, V.I., Zh. Prikl. Khimii, 1997, **70**, no. 8, p. 282.
15. MALYSHEV, V.V., GAB, A., POPESCU, A.M., CONSTANTIN, V., Rev. Chim. (Bucharest), **62**, no.11, 2011, p. 1128.
16. MALYSHEV, V.V., SOLOVIEV, V.V., CHERNENKO, L.A., ROZHKO, V.N., Materials Science & Engineering Technology, **45**, no. 11, 2015, p. 67.
17. SURVILA, A., ZUKAUSKAITE, A., Elektrokhimiya, **31**, no.11, 1995, p. 1254.
18. GOMEZ, E., PELLICER, E., VALLES, E., J. Electroanal. Chem., **556**, 2003, p. 137.
19. MALYSHEV, V.V., NOVOSELOVA, I.A., SHAPOVAL, V.I., Zh. Prikl. Khimii, **69**, no. 8, 1996, p. 1233.
20. WHEELER, N.S., J. Res. Natl. Inst. Stand. Technol., **100**, 1995, p. 641.

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