Moscow State Academy of Fine Chemical Technology named after M. V. Lomonosov

Chemistry and Technology of Rare and Dispersed Elements Department

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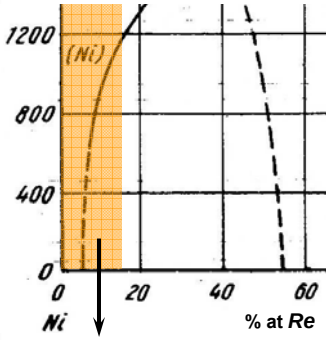
Heterometallic Re, Ni, Co-alkoxides as a precursors for a functional materials synthesis

Moscow, 2011

2. The aim

Our aim is to obtain fine (nanosized) powders of alloys Re-Ni, Re-Co, Re-Ni-Co; simple and complex oxides.



Alloys for aerospace application

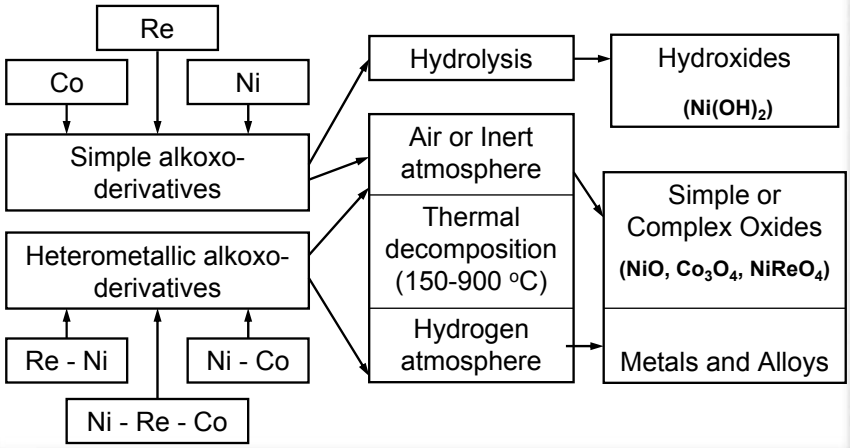
		27 Co T_m=1495 C	28 Ni T_m=1455 C
75 Re T_m=3168 C			

Main questions:

1. Whether Re-Ni-Co alloys can be obtained at low (< 500 °C) temperatures?
2. What particles size thus obtained powders have?

3. Alkoxo-technology

Alkoxo-technology consists of a alkoxo-derivatives synthesis followed by its thermal or hydrolytic decomposition to obtain functional materials.



4. Electrochemical cell

1 – Drying agent (P_2O_5);

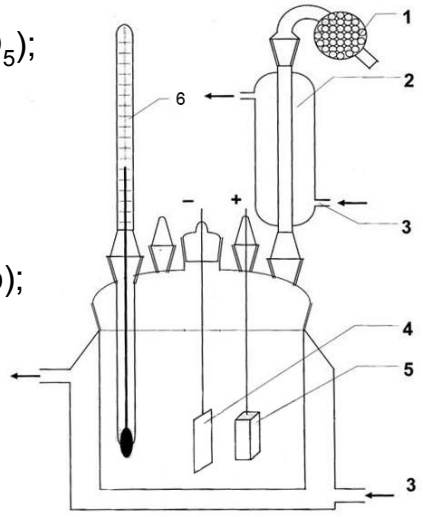
2 – Condenser;

3 – Cooling water;

4 – Cathode (Pt);

5 – Anode (Re, Ni, Co);

6 – Thermometer.

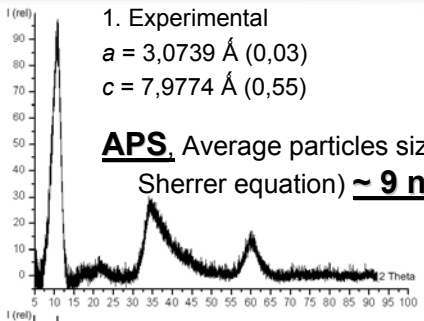


5. Electrochemical syntheses of simple methoxocomplexes

Electrolyte – water-free CH_3OH; background electrolyte (LiCl) – C_{LiCl}=0,025 M; cathode – Pt.

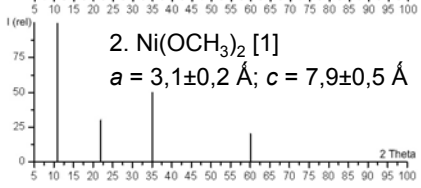
№	Anode	**U**, *V*	**I**, *mA*	**t**, *hrs.*	Product
I	Ni	16	45	21	$Ni(OCH_3)_2$
II	Ni	16	55	7	$Ni(OCH_3)_2$
III	Co	20	65	15	$Co(OCH_3)_2$
IV	Re	31	170	16	$Re_4O_6(OCH_3)_{12}$
V	Ni + Co	9	40	25	$Ni_{2.3}Co_1(OCH_3)_4$

6. XRD and structure of $Ni(OCH_3)_2$



1. Experimental
a = 3,0739 Å (0,03)
c = 7,9774 Å (0,55)

APS, Average particles size (from Sherrer equation) **~ 9 nm**



2. $Ni(OCH_3)_2$ [1]
a = 3,1±0,2 Å; *c* = 7,9±0,5 Å

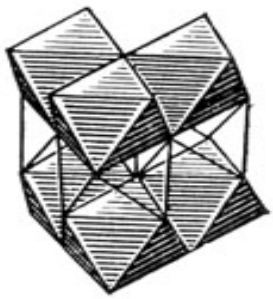
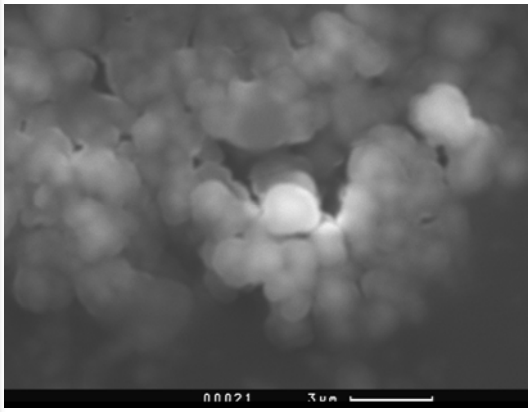
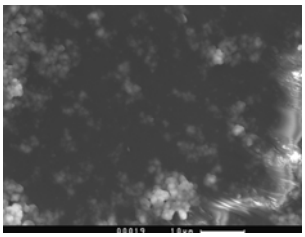


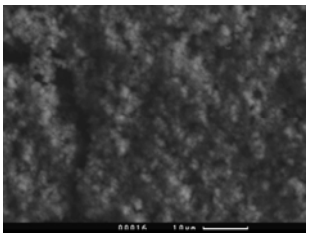
Fig. 1. $Mg(OH)_2$ – type hexagonal structure.

[1] – Rogova T.V., Turova N.Ya., Zhadanov B. V.. About nickel alkoxides // Coordination chemistry, 1985, vol. 11, № 6, pg. 784-788.

7. $Ni(OCH_3)_2$ SEM pictures

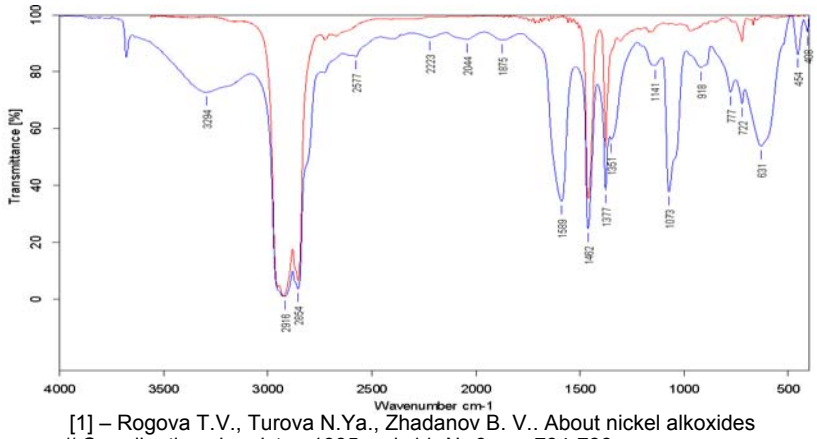






8. $Ni(OCH_3)_2$ IR spectrum

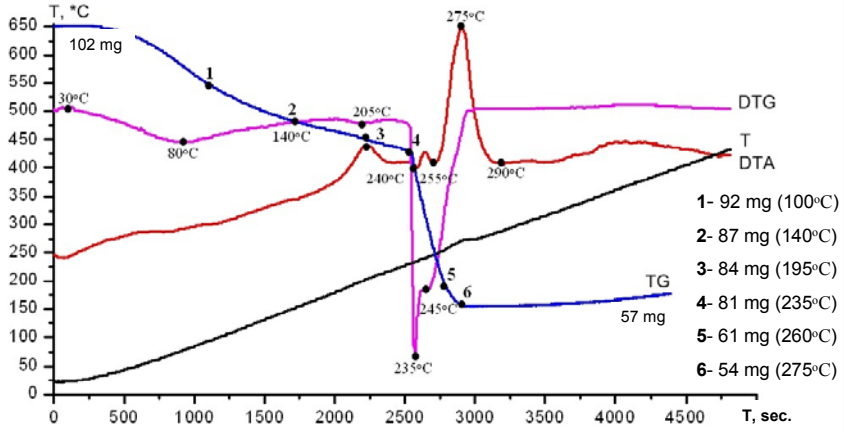
Correlation [1]	v (O-H)	v (C-H)	δ (C-H)	v (C-O)	v (Ni-O)
Wavelenght,cm^{-1}	3294	2916-2577	1589-1351	1141-1073	918-408



[1] – Rogova T.V., Turova N.Ya., Zhadanov B. V.. About nickel alkoxides // Coordination chemistry, 1985, vol. 11, № 6, pg. 784-788.

9. DTG-TGA $Ni(OCH_3)_2$ analysis

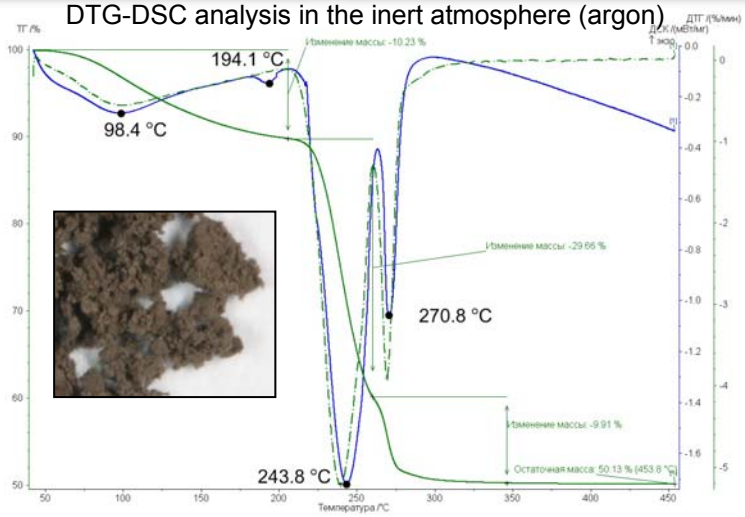
DTG-TGA analysis in air medium



$Ni(OCH_3)_2 \cdot nCH_3OH \rightarrow Ni(OCH_3)_2 \rightarrow NiO$

10. DTG-DSC $Ni(OCH_3)_2$ analysis

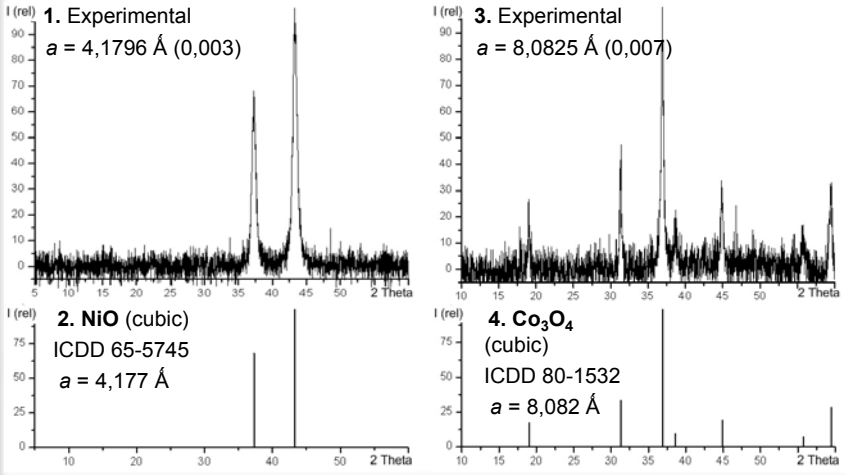
DTG-DSC analysis in the inert atmosphere (argon)



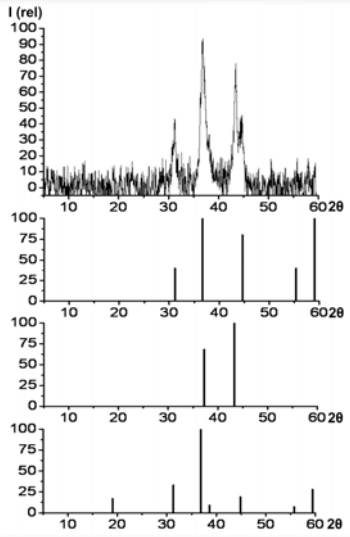
$Ni(OCH_3)_2 \cdot nCH_3OH \rightarrow Ni(OCH_3)_2 \rightarrow NiO$

11. XRD of $Ni(OCH_3)_2$ и $Co(OCH_3)_2$ thermal decomposition products (in air)

$Ni(OCH_3)_2$ | $Co(OCH_3)_2$



12. XRD of $Ni_xCo_y(OCH_3)_4$ thermal decomposition product (in air)



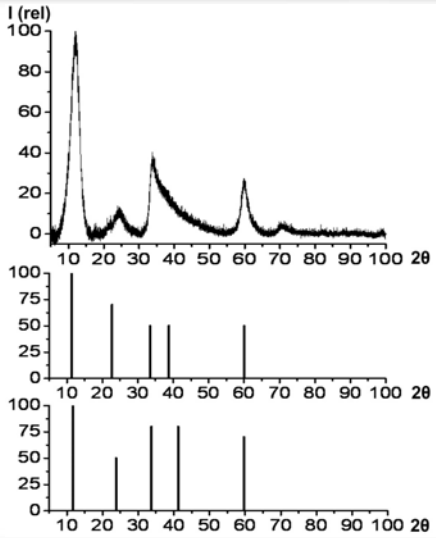
1. Experimental

2. $NiCo_2O_4$ (cubic)
   ICDD 2-1074
   a = 8,128 Å

3. NiO (cubic)
   ICDD 65-5745
   a = 4,177 Å

4. Co_3O_4 (cubic)
   ICDD 80-1532
   a = 8,082 Å

13. XRD of $Ni(OCH_3)_2$ hydrolysis product



1. **Experimental**
   a = 3,0811 Å (0,000)
   c = 23,4128 Å (0,035)

APS, Average particles size (from Sherrer equation) **~14 nm**

2. **$Ni(OH)_2 \cdot 0.75H_2O$**
   ICDD 38-715
   a = 3,080 Å
   c = 23,410 Å

3. **$Ni(OH)_2 \cdot 0.67H_2O$**
   ICDD 22-444
   a = 5,340 Å
   c = 7,500 Å

14. Electrochemical syntheses of heterometallic methoxocomplexes

Electrolyte – water-free CH_3OH; background electrolyte (LiCl) – C_{LiCl}=0,025 M; cathode – Pt.

№	Anode	**U**, *V*	**I**, *mA*	**t**, *hrs.*	Product
VI	Re → Ni	7	30	40	$Re_1Ni_{5.4}(OCH_3)_8$
VII	Re → Ni	65	60	10	$Re_1Ni_{1.3}(OCH_3)_5$
VIII	Ni → Re	26	100	20	$Re_{1.5}Ni_1(OCH_3)_4$
IX	Re → Ni	31	160	61	$Re_{2,7}Ni_1(OCH_3)_4$
X	Re→Co→Ni	20	50	22	$Ni_{7,5}Re_1Co_{0,1}(OCH_3)_{14}$

15. Chemical interaction of Re and Ni simple methoxocomplexes

Rhenium oxomethylate and nickel methylate methanolic solutions, obtained electrochemically (syntheses IV and II respectively) were mixed in methanolic medium with vigorous stirring during one hour.

$$Re_4O_6(OCH_3)_{12} + Ni(OCH_3)_2 + [CH_3OH]_n \rightarrow$$
$$\rightarrow Re_1Ni_{9.8}(OCH_3)_{10} \quad (\mathbf{XI})$$

16. Chemical analysis of heterometallic methoxocomplexes

№	Content, mass. %				**Ni : Re**	Formula
	Ni	M (Re, Co)	C	H		
V	33.51	Re - 14.21 Co - 1.17	12.91	3.55	$Ni_8Re_1Co_{0.1}C_{14}H_{42}$	
VII	31.83	Re - 19.61	8.64	4.67	**5.43 : 1**	$Re_1Ni_{5.4}C_{7.2}H_{46.8}$
VIII	14.71	Re - 37.14	11.08	2.90	**1.25 : 1**	$Re_1Ni_{1.3}C_{4.6}H_{14.5}$
IX	10.76	Re - 51.01	8.57	2.02	**1 : 1.52**	$Re_{1.5}Ni_1C_{3.9}H_{11.0}$
X	6.80	Re - 57.13	5.77	1.49	**1 : 2.7**	$Re_{2.7}Ni_1C_{4.2}H_{12.6}$
XI	45.41	Re - 14.70	9.71	3.00	**9.8 : 1**	$Re_1Ni_{9.8}C_{10}H_{30.6}$

17. IR-spectra comparison

$Re_4O_6(OCH_3)_{12}$	IX	Correlation	XI	$Ni(OCH_3)_2$
543 cm^{-1}	527cm^{-1}	**ν (Re-O) [2]**		
	465 cm^{-1}	**ν (Ni-O) [1]**	456 cm^{-1}	445 cm^{-1}
427 cm^{-1}	422 cm^{-1}	**ν (Re-O) [2]**		
		ν (Ni-O) [1]		415 cm^{-1}

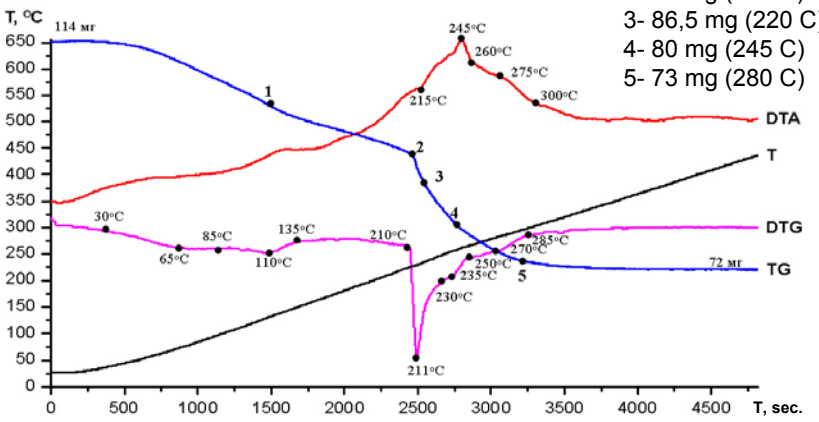
[1] – Rogova T.V., Turova N.Ya., Zhadanov B. V.. About nickel alkoxides // Coordination chemistry, 1985, vol. 11, № 6, pg. 784-788.

[2] – A. I. Ermakov, V. V. Belousov, D. V. Drobot, P. A. Shcheglov / Electronic Structures and Properties of the Rhenium Alkoxo Derivatives // Coordination Chemistry, 2006, Vol. 32, No. 10, pp. 701–706

18. DTG-TGA $Ni_xRe_y(OCH_3)_n$ analysis

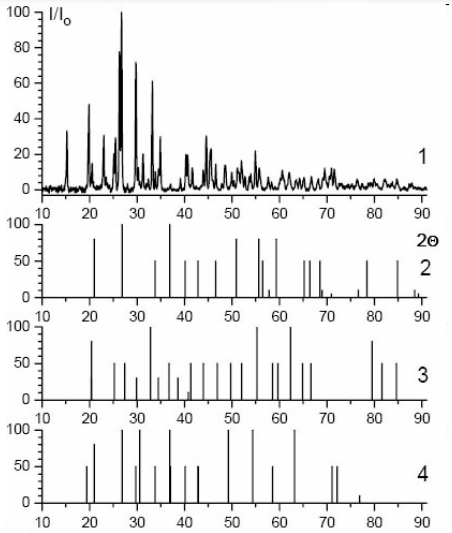
DTG-TGA analysis in air medium

1- 101 mg (120 C)
2- 93 mg (210 C)
3- 86,5 mg (220 C)
4- 80 mg (245 C)
5- 73 mg (280 C)



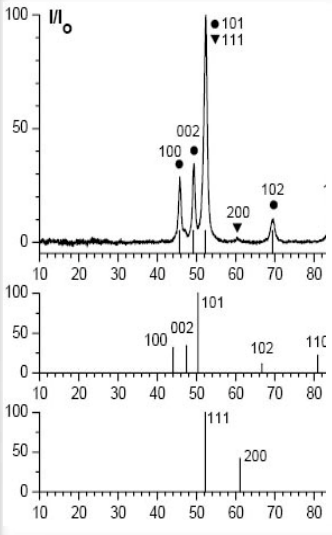
$Ni_xRe_y(OCH_3)_n \cdot nCH_3OH \rightarrow Ni_xRe_y(OCH_3)_n \rightarrow NiReO_4$

19. XRD of $Ni_xRe_y(OCH_3)_n$ thermal decomposition product (in air)



1. Experimental (T_{decomp} = 400°C)
2. $Ni(ReO_4)_2$ ICDD No. 47-0116
3. $Ni(ReO_4)_2 \cdot 4H_2O$ ICDD No. 33-0954
4. $Ni(ReO_4)_2 \cdot 2H_2O$ ICDD No. 32-0697

20. XRD of $Ni_xRe_y(OCH_3)_n$ thermal decomposition product (in hydrogen)

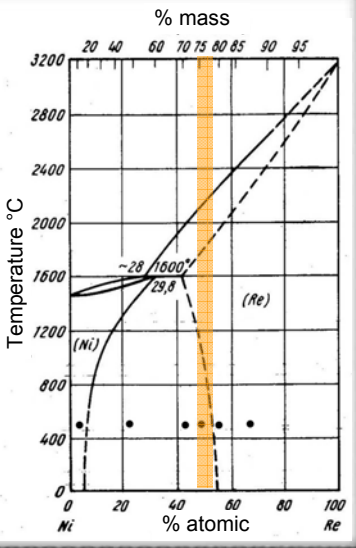


Experimental (T_{decomp} = 500°C)

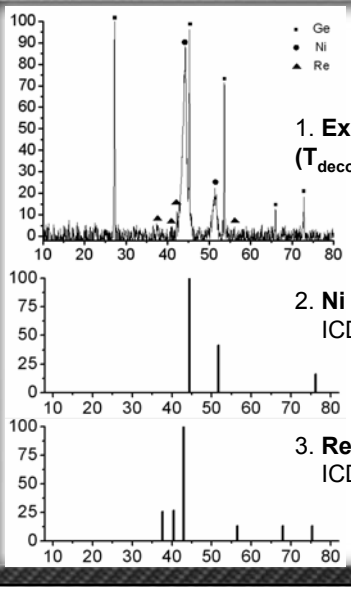
Calculated

Re (hex.) ICDD 88-1735

Ni (cub.) ICDD 65-0380



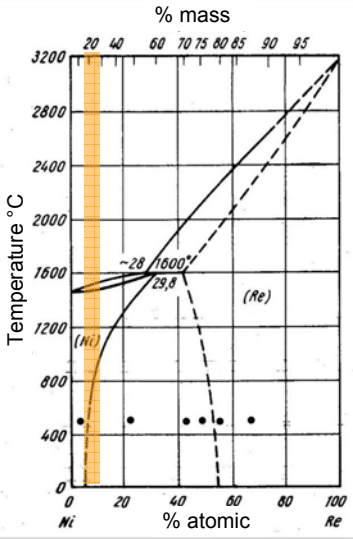
21. XRD of $Ni_xRe_yCo_z(OCH_3)_n$ thermal decomposition product (in hydrogen)



1. **Experimental (T_{decomp} = 400°C)**

2. **Ni (cub.)**
ICDD 65-0380

3. **Re (hex.)**
ICDD 88-1735



22. Re, Ni, Co methoxocomplexes decomposition products

Compound	Hydrolysis product	Thermal decomposition products		
		In air medium	In argon medium	In hydrogen medium
$Re_xNi_y(OCH_3)_z$	-	$NiReO_4$	-	Re – Ni alloy
$Ni_xCo_y(OCH_3)_4$	$Ni(OH)_2$ $Co(OH)_2$	$NiCo_2O_4$ NiO	NiO•CoO	Ni – Co alloy
$Ni(OCH_3)_2$	$Ni(OH)_2$	NiO	NiO	Ni
$Co(OCH_3)_2$	$Co(OH)_2$	Co_3O_4	CoO	Co
$Re_4O_6(OCH_3)_{12}$	-	ReO_3	-	Re
$Ni_8Re_1Co_1(OCH_3)_{14}$	-	$NiReO_4$ NiO	-	Ni-Re-Co alloy

23. Economical efficiency indexes

	Unit	Year 1 January	Year 2 January	Year 3 January	Year 4 January	Year 5 January	Total
Cash Flow	rus.rub.	-9 203 750	677 848	766 782	855 716	944 113	36 044 183
Cumulative Cash Flows	rus.rub.	-9 203 750	-6 033 758	2 255 346	11 611 612	22 028 894	36 044 183
Discount factor		1,000	0,893	0,797	0,712	0,636	
Discounted Cash Flows	rus.rub.	-9 203 750	605 221	611 274	609 082	600 001	22 887 797
Cumulative Discounted Cash Flows	rus.rub.	-9 203 750	-6 378 094	581 089	7 595 153	14 568 336	22 887 797
Investment	rus.rub.	8 935 000	0	0	0	0	8 935 000
Discount factor		1,000	0,893	0,797	0,712	0,636	
Discounted Investments	rus.rub.	8 935 000	0	0	0	0	8 935 000
Payback period, PP	mnth.						24
Net Present Value, NPV							22 887 797
Internal Rate of Return, IRR		-	-	12%	54%	72%	82%
Return on investment, ROI							256%

24. Conclusions

1. Alkoxo-technology has been proved to be an effective route for Ni-Re-Co alloy fine powder synthesis with adjustable metals ratio (RU 2010132289 Pat. Appl.);
2. Varying alkoxide decomposition parameters made possible to obtain simple and complex oxides, hydroxides and alloy fine or nanosized powders;
3. Heterometallic Ni-Re and Ni-Re-Co methoxocomplexes were obtained first time ever, their properties being investigated.

25. Acknowledgements

- Scientific advisor - Prof. Dmitri V. Drobot;
- Yuri V. Syrov and Yuri V. Velikodniy – XRD Analyses;
- Elena E. Nikishina – DTA Analyses;
- Sergey Savilov – DSC Analyses;
- Valeri V. Kravchenko – IR Spectra;

- RFBR for funding (projects 06-03-32444 & 09-03-00328).

26. Acknowledgements

Thanks for listening!

Some questions?