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RHENIUM, NICKEL, COBALT ALKOXIDES PROPERTIES AND DECOMPOSITION PRODUCTS

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New technology to obtain Re, Ni, Co hydroxides, simple and complex oxides, fine and nanosized powders of metals and alloys has been developed. Mono- and heterometallic nickel, rhenium and cobalt alkoxides with adjustable metal content were used as precursors to produce final powders.

Key words: *Aerospace Ni-Re superallo, fine powder, soft chemistry, alkoxide precursor.*

Introduction

Nickel-based superalloys containing rhenium (6 – 10%) are known to exhibit excellent mechanical strength and creep resistance at high temperatures, good surface stability, corrosion and oxidation resistance [1]. They are generally applied in fields such as: aerospace, industrial gas turbine, electronics, e.g. for turbine blades in hot sections of jet engines [1 – 4]. Some state–of–the–art methods are used to produce these alloys; with all of them including melting of the metals involved. Taking into account huge difference in the melting points of base metal (nickel, 1726 K) and doping metal (rhenium, 3360 K), obtaining of chemically homogeneous alloy becomes an extremely difficult task. The same problem arises in case of complex ceramics. Moreover, these processes are energy-consuming because of the necessity to maintain very high temperatures for a long time. It is of common knowledge that chemical uniformity of precursor compound leads to a homogeneous distribution of doping elements in alloys and general chemical composition stability. In the last decades in the context of continuous increase in energy prices, more and more attention is being paid to energy-efficient technologies.

Soft chemistry techniques have already been applied to refractory materials and alloys synthesis [5 – 10].

In the present work we have applied alkoxide route for the preparation of nickel-based alloys using trimetallic nickel–rhenium–cobalt methoxocomplexes as a precursors.

Material and Methods

The conditions of the syntheses are listed in the table 1. Individual metal methoxocomplexes were obtained electrochemically (table 1, Syntheses **I**–**IV**). To obtain bi- and trimetallic methoxocomplexes both consequent anodic dissolution (table 1, Syntheses **V**–**X**) of metals and chemical reaction between individual methoxocomplexes were applied (table 1, Synthesis **XI**). It is well known that some metal alkoxides are water-sensitive and could decompose in the air; therefore, all operations and storage of such compounds are performed in dry inert atmosphere. The latter involves mixing of nickel methoxide and rhenium oxomethoxide in the methanolic media with stirring at room temperature for at least 1 hour. Once the desired amount of metal was dissolved or the chemical reaction completed, the resulting liquid is transferred into a glass flask and subjected to solvent vacuum evaporation to yield final powder.

Table 1. Syntheses conditions

#	U, V	I, mA	τ, hrs	Anode	#	U, V	I, mA	τ, hrs	Anode
I	16	45	21	Ni	**VI**	7	30	40	Re – Ni
II	16	55	7	Ni	**VII**	65	60	10	Re – Ni
III	20	65	15	Co	**VIII**	26	100	20	Ni – Re
IV	31	170	16	Re	**IX**	31	160	61	Re – Ni
V	9	40	25	Ni + Co	**X**	20	55	20	Re – Co – Ni
XI	Chemical interaction of 100 ml 0.049 M solution **I** and 9.25 ml 0,054 M solution **IV**								

The former was performed in a glass electrochemical cell with water cooling and a condenser [7 – 9]. To prevent the decomposition of the compounds formed the tube with drying agent (P_2O_5) was used. We have used water-free methanol (Merck KGaA, purity > 99.5%, water < 0.1%) as an electrolyte; a 2 cm^2 platinum plate as a cathode; nickel, cobalt and rhenium plates as an anode. Methanol was dehydrated before it was involved in synthesis by means of boiling with magnesium shavings followed by distillation. Water-free methanol is known to be an insulating media, for that reason we had to use a background electrolyte – lithium chloride. Lithium chloride (Neftegazhimkomplekt, purity > 99.0%, water < 0.4%) was annealed (180 – 200 °C) in vacuum (p ~ 1,3 Pa) for 40 – 60 min to dehydrate it. The concentration was chosen to be 0.025 M to provide optimal conductivity and low chlorine concentration. The process was controlled by measuring current, voltage, temperature and anode mass loss. The consequences of dissolution are shown in the column «anode» of table 1 («+» stands for simultaneous dissolution).

The complexes obtained were analyzed by means of chemical analysis, X–Ray powder diffraction, IR spectoscopy, SEM and thermal analyses (DTG, TGA, DSC) in air and inert atmosphere. Nickel was determined using titration with EDTA against murexide [11], cobalt – photometric micro-determination with nitroso-R salt [12], rhenium – gravimetrically as nitron perrhenate $C_{20}H_{16}N_4{\cdot}HReO_4$ [13], carbon and hydrogen – organic microanalysis with CHN–O–RAPID (Heraeus GmbH, Germany). X–ray diffraction patterns were obtained on XRD 6000 powder diffractometer (Shimadzu, Japan) with Cu Kα-radiation; SEM analysis was performed on JSM-7401F (Jeol, Japan) system; IR spectra in the range 4000–400 cm^{-1} were taken on EQUINOX 55 spectro-meter (BRUKER, Germany) between IR-transparent KRS-5 plates in liquefied petrolatum to prevent decomposition; thermal analysis in the air was performed on Q–1500 D derivatograph (MOM, Hungary) with heating up to 430°C with 5°C/min rate DSC 204 F1 Phoenix (NETZSCH, Germany). Thermal decomposition of the complexes was accomplished in the air, argon atmosphere and hydrogen atmosphere. The quartz tube with the powders was placed in the pipe furnace. The tube inlet and outlet were equipped with H_2SO_4 vessels to dehydrate argon and hydrogen. Gas flow should be no less than 0.2 LPM. Heating rate was established to be 5°C/min, cooling rate 10-15°C/min. All decomposition products were identified using XRD analysis. Particles size distribution was determined on the Delsa™ Nano analyzer (BECKMAN COULTER, USA).

Results and Discussion

At the first stage of the investigation individual nickel, rhenium and cobalt methocomplexes $Ni(OCH_3)_2$ (**I, II**) $Co(OCH_3)_2$ (**III**) and $Re_4O_6(OCH_3)_{12}$ (**IV**) were obtained using anodic dissolution of rhenium, nickel and cobalt in absolute methanol respectively. The said methoxo-derivatives were characterized by XRD, SEM, IR and thermal analysis.

The XRD pattern of **I** is presented on the Fig. 1 with corresponding literature data for $Ni(OCH_3)_2$ [14]. Four wide peaks at the pattern indicate that the said compound has a distorted hexagonal layered $Mg(OH)_2$ structure with P-3m1 space group (cell parameters: a = 3.074 Å; c = 7.977 Å). FWHM of first peak (2 θ = 10.89 °) was measured to be 3.092 ° and according to the Debye-Shrerrer equation the corresponding grain size is as low as 90 Å. Complexes **III**, **V** was found to have the same structure. The SEM picture of **I** is presented at Fig. 2. It is easy to see that average particles size is around 1 μm. The difference in calculated and visible sizes of particles can be explained by a strong tendency for nanoparticles to agglomerate. The IR spectrum of **I** contains methoxo–derivatives ν (C–O) intrinsic peak at 1073 cm^{-1} and few peaks in the metal-oxygen region: ν (Ni–O(R)–Ni) at 631 cm^{-1} and ν (Ni–O(R)) at 454 and 408 cm^{-1}, with the former intensity being twice as great. There is also a weak peak at 3294 cm^{-1} correlated to ν (O–H) of absorbed methanol. According to the IR spectrum, $Ni(OCH_3)_2$ has a continuous structure with Ni–O(R)–Ni bridges. The IR spectra of **III** are almost alike: ν (C–O) at 1066 cm^{-1}; ν (Co–O(R)–Co) at 606 cm^{-1}; ν (Co–OR) at 450 cm^{-1}.

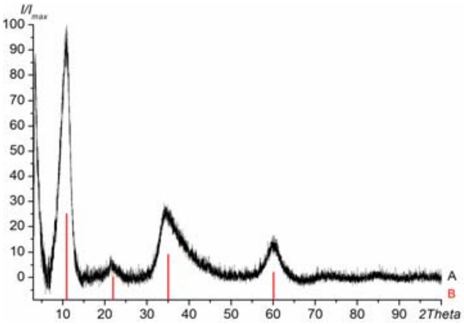

Fig. 1. XRD pattern of I (top) and data for $Ni(OCH_3)_2$ [15] (bottom).

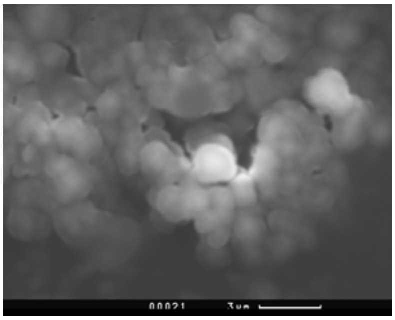

Fig. 2. SEM picture of I.

The thermal decomposition mechanism in the air and inert atmosphere was studied by means of DTA/DTG and DSC/DTG techniques respectively. The DTA/DTG curves of **I** are shown at Fig. 3. At the initial stage of heating in the air (below 100 °C) absorbed methanol evaporation is taking place followed by partial evaporation of ligand (up to 195 °C); the thermal decomposition of **I** in the air begins at around 235 °C. According to the DTA peak, the final product (NiO) starts to crystallize at 255 °C. The thermal decomposition of **III** in the air begins at 185 °C with the formation of CoO followed by oxidation to spinel Co_3O_4 at 235 °C. The thermal behavior of **I** in the inert atmosphere deviates slightly. The thermal decomposition begins at 210 °C and ends at 270 °C with the crystallization of NiO; on the contrary, the DSC curve of **III** contains exo-effect at 307 °C and the final product is CoO (instead of Co_3O_4 in the air). The XRD pattern, the crystal structure, the IR spectrum and the thermal analysis of **IV** were reported by our colleagues [8, 15].

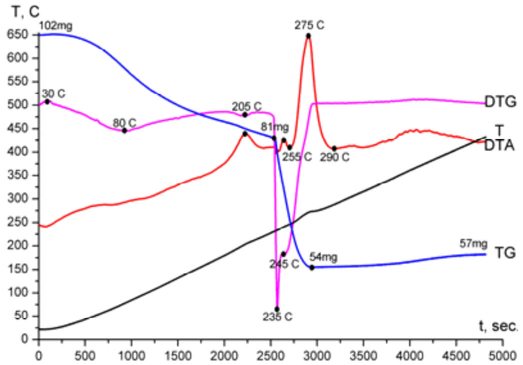

Fig. 3. DTA/DTG curves of I.

The hydrolytic decomposition of **I** – **III** leads to the formation of nickel and cobalt hydroxides with the same structure and a slightly larger grain size determined from Debye-Sherrer equation (140 Å in case of **I**).

At the second stage of our investigation bi- and trimetallic nickel-rhenium methoxodervatives were obtained and analyzed. The XRD analysis has shown that compounds **X**, **XI** with low rhenium have the same structure as **I**. Bimetallic compounds **VI** – **IX** with high rhenium are X–Ray amorphous. The results of the chemical analyses and the IR spectra peaks positions are shown in Table 2. It leads us to a supposition that compounds **VI** –**XI** do not have direct nickel–rhenium bond, but these metals are linked by means of oxygen or oxygen-ligand bridges. Having compared the obtained IR spectra for **VI** –**XI** with the ones for **I** – **IV**, we determined a shift in the peak positions. This can be used as the evidence of molecularly mixed nickel rhenium precursor compounds formation.

Table 2. Chemical compositions and IR-spectra peaks of heterometallic complexes

#	Ni, wt %	Re, wt %	Formula	Positions of IR peaks, cm^{-1}		
				ν (C–O)	ν (Ni–OR)	ν (Re–OR)
VI	31.83	19.61	$Ni_{5.4}Re_1(OCH_3)_8$	1041	640w, 457	909, 550, 418
VII	14.71	37.14	$Ni_{1.3}Re_1(OCH_3)_5$	1039	639, 458	908, 527, 424
VIII	10.76	51.01	$Ni_1Re_{1.5}(OCH_3)_4$	1050	652, 465	907, 523, 431
IX	6.80	57.13	$Ni_1Re_{2.7}(OCH_3)_4$	1058	654, 465	934, 530, 425
X	33.51	14.21	$Ni_8Re_1Co_{0.1}(OCH_3)_{14}$	1045	640w, 456	916, 553, 420
XI	45.41	14.70	$Ni_{9.8}Re_1(OCH_3)_{10}$	1049	640w, 455	913, 548, 422

The thermal decomposition mechanism of **VI** –**XI** in the air is determined from DTA/DTG curves. The DTA/DTG curves of **X** are shown at Fig. 4. Gradual evaporation of the absorbed methanol and some part of the ligand gives way to the final decomposition at 210 °C. Even low rhenium content in the bimetallic complex X leads to multistage product crystallization (the main DTA peak at 245 °C is followed by another three). Additional studies are required to determine all the intermediates.

All the collected data involving the composition, the structure and the thermal properties of the precursor compounds allowed us to develop a technology to carry out the synthesis of various powders. Depending on the thermal decomposition conditions we can obtain fine or even nanosized powders of nickel, rhenium and cobalt oxides, hydroxides or alloys with any desirable metals content. This content can be set at the precursor synthesis stage and remains almost constant after thermal treatment. All the decomposition products we have obtained are summarized in Table 3.

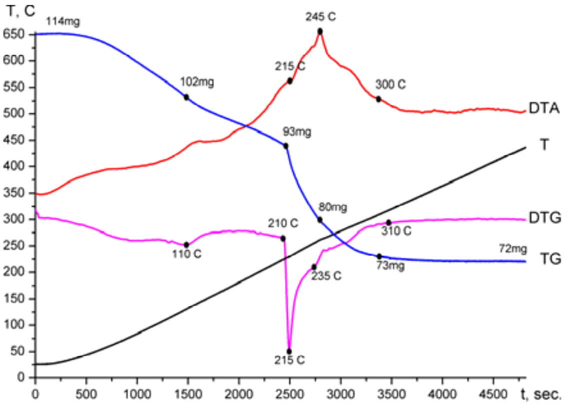

Fig. 4. DTA/DTG curves of X.

Table 3. Precursor decomposition products obtained and analyzed (*TBD - to be defined)

Precursor compound	Hydrolysis products	Thermal decomposition products		
		In air	In inert gas	In hydrogen
$Ni(OCH_3)_2$	$Ni(OH)_2$	NiO	NiO	Ni
$Co(OCH_3)_2$	$Co(OH)_2$	Co_3O_4	CoO	Co
$Re_4O_6(OCH_3)_{12}$	TBD*	ReO_3, Re_3O_{10}	ReO_2	Re
$Ni_XCo_Y(OCH_3)_N$	$xNi(OH)_2$ $yCo(OH)_2$	$NiCo_2O_4$, xNiO, yCo_3O_4	xNiO·yCoO	xNi – yCo solid solution
$Ni_XRe_Y(OCH_3)_N$	TBD*	$NiReO_4$, xNiO, $yReO_3$	TBD*	xNi – yRe solid solution
$Ni_XRe_YCo_Z(OCH_3)_N$	TBD*	$NiReO_4$, xNiO, $yReO_3$, vCo_3O_4	TBD*	x Ni–yRe–zCo solid solution

*N - depends on X, Y, Z; TBD - to be defined.

Finally, let us discuss the case of nickel-rhenium-cobalt alloy powder synthesis with content of metals close to that in aerospace superalloys. The precursor compound **X** with adjusted content of metals was thermally threated at 350 °C for 2 hours in the hydrogen atmosphere to produce the final powder (its size distribution and the XRD pattern are shown at Fig. 5 and 6) respectively. The Ni-based solid solution (sp.gr. Fm3m; a = 3,570 Å) obtained has slightly shifted the XRD peaks indicating the presence of rhenium and cobalt. The rhenium content can be estimated as 14 wt.% according to the cell parameter and the data cited in literature [16].

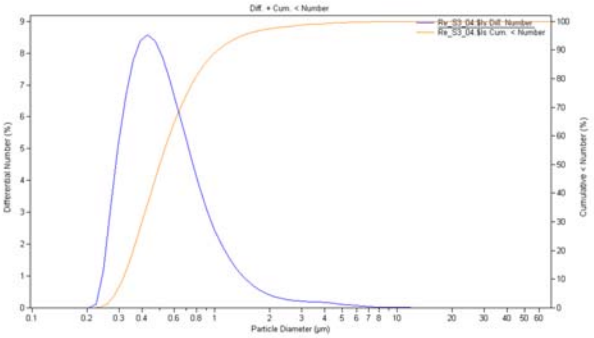

Fig. 5. Particles size distribution of X decomposition product in hydrogen.

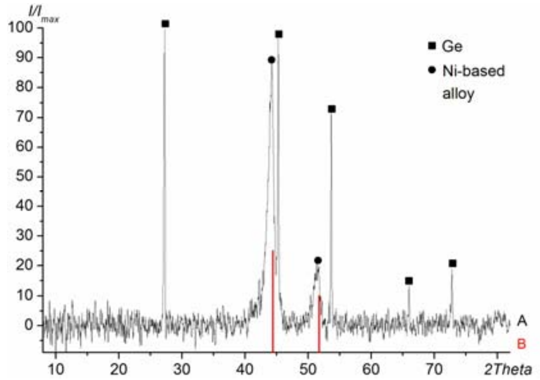

Fig. 6. XRD pattern of X decomposition product in hydrogen (top) and data for Ni ICDD card # 65-0380 (bottom).

The average size of particles is D_{50} = 501 nm and we believe that it can be decreased further by means of changing decomposition conditions. Therefore methoxo-derivatives can be effectively applied as precursors to obtain metals, alloys, ceramic powders.

Conclusions

Variations in alkoxide decomposition parameters made it possible to obtain simple and complex oxides, hydroxides and alloy powders. Electrochemical technique to obtain Ni–Re–Co individual and heterometallic methoxocomplexes was developed. The heterometallic Ni–Re and Ni–Re–Co methoxocomplexes were obtained for the first time ever; their properties are being investigated. The alkoxo-technology has been proved to be an effective method for the Ni–Re–Co alloy fine powder synthesis with adjustable content of metals (Pat. RU2445384). Thermal decomposition product particles size was found to be D_{50} = 501 nm and it can be decreased further.

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