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Properties of rhenium-based master alloys prepared by powder metallurgy techniques

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ABSTRACT

Purpose: The aim of this work was to investigate an effect of phase composition, microstructure and selected properties of the rhenium-based alloys on the conditions of their preparation by mechanical alloying followed by pressure sintering.

Design/methodology/approach: The structure and mechanical and physical properties of the Re-14.0% Ni, Re-13.7% Co and Re-9.1% Fe alloys prepared from pure metal powders by mechanical alloying in a planetary mill for 10 hours followed by sintering conducted for 1 hour at the temperature of 1150°C under the pressure of 600 MPa were investigated.

Findings: The mechanical alloying results in partial dissolving of alloy components into each other, whereas their structure remains unchanged, and in a decrease in average density of powders and average diameter of their particles. As a result of sintering the alloy additives almost fully pass into rhenium-based solid solution. Density and hardness of the sinter compacts and homogeneity of alloying elements distribution were higher at longer times of mechanical alloying.

Research limitations/implications: The obtained results provide complementary information on the possibility of obtaining high-melting alloys by mechanical alloying and on the rate of structural transformations taking place as a result of this process.

Practical implications: The obtained materials can be used as master alloys for the production of contact materials and superalloys, providing higher homogeneity of the chemical composition and microstructure of the final products.

Originality/value: A new method for preparation of rhenium-based alloys by means of mechanical alloying and powder metallurgy techniques has been successfully tested.

Keywords: Metal alloys; Powder metallurgy; Mechanical alloying; Rhenium alloys; X-ray phase analysis; Microanalysis; Mechanical properties; Physical properties

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PROPERTIES

1. Introduction

In modern areas of technology, particularly in the aircraft and space industries, a growing interest in high-melting metals is observed, including rhenium and its compounds. Rhenium is becoming increasingly applied as the component of nickel-based superalloys used e.g. in the production of rotating elements of aircraft engines [1-3]. Initially, it was added to superalloys in the

amount of about 3 mass%, and in their next generations the rhenium content increased to about 6 mass%. An addition of rhenium significantly improves creep resistance of these alloys at high temperatures, which results from microstructure changes taking place in them [3-6].

Another potential area of application of rhenium and its alloys with an addition of iron can be silver-based contact materials, where rhenium should contribute to their longer life due to its electric arc suppression ability [6]. The silver-based electric contacts with an addition of 8.4% Fe and 0.4% Re are already commercially available [7].

The aim of this work was to fabricate rhenium-based materials with an addition of Co, Ni and Fe by means of powder metallurgy technology [8]. The obtained materials can be used as master alloys in the production of Re-Fe contact materials and nickel-based superalloys, Re-Co and Re-Ni type. The use of master alloys instead of pure elements should result in higher microstructure homogeneity of the obtained materials.

2. Experimental

Materials with the chemical composition given in Table 1 were prepared from powders of pure metals of the following purity and average grain size, respectively: Re - 99.9% and 52 μm, Co - 99.5% and 2.5 μm, Ni - 99.5% and 1.8 μm, and Fe - 99.5% and 5 μm.

Table 1.
Chemical composition of the rhenium-based alloys

No	Alloy	Re, mass %	Ni, mass %	Co, mass %	Fe, mass %
1.	Re-Ni	86.0	14.0	-	-
2.	Re-Co	86.3	-	13.7	-
3.	Re-Fe	90.9	-	-	9.1

The mechanical alloying process was conducted in a Retsch PM 400 planetary mill, in the containers with tungsten carbide. The mill operating conditions were the following: 200 rev/min, ball-to-powder mass ratio was 10:1, and diameter of tungsten carbide balls was 8 mm. In order to investigate an effect of alloying time on the properties of the obtained alloys, the changes of their properties and structure were examined after 1, 5 and 10 hours of alloying. The process was conducted in a liquid environment - acetone. The powder materials were consolidated by uniaxial pressing at the pressure of 600 MPa, and the sintering process was conducted for 1 hour at the temperature of 1150°C in a reducing atmosphere.

The JEOL JXA 8230 X-ray micro-analyzer was used to enable microstructure observations by the secondary electron imaging (SEI) and COMPO imaging techniques, and chemical composition analysis in micro-areas, qualitative and quantitative. The determined contents of particular elements have been expressed as averaged values obtained from several points of measurements made with a focused beam, at the scatter of results up to 5%.

The X-ray phase analysis was made using Seifert-FPM XRD 7 diffractometer with the Co K_α specific radiation. Identification of phase composition was made based on the PDF-2 (2007) catalog data from the International Centre for Diffraction Data (ICDD).

Density of the examined materials was measured by the helium method using Micromeritics Accupyc 5500 pycnometer, and the surface area was determined by gas adsorption method (BET) using Micromeritics Gemini 2360 analyser.

Grain size distribution of the examined materials was determined after transforming them into aerosol form. The Fritsch laser particle sizer Analysette 22 Nanotec was used to determine grain size distribution of these materials, and their hardness after sintering was measured by the Brinell method using a steel ball 2.5 mm in diameter and a load of 613 N (62.5 kG)

3. Discussion of results

The X-ray phase analysis (Figs. 1-3) showed that after the process of mechanical alloying the investigated powder materials became two-component mixtures containing great amounts of rhenium, and considerably smaller amounts of Co (with hcp structure), α-Fe or Ni. Taking into account the diffusion process taking place in the powders during milling it was expected that the components of these mixtures will not be pure metals but solid solutions rich in Re, Fe, Co and Ni, with maintained crystalline structure of pure metals and slightly changed lattice constants. This expectation has been confirmed by the X-ray microanalysis (Table 2).

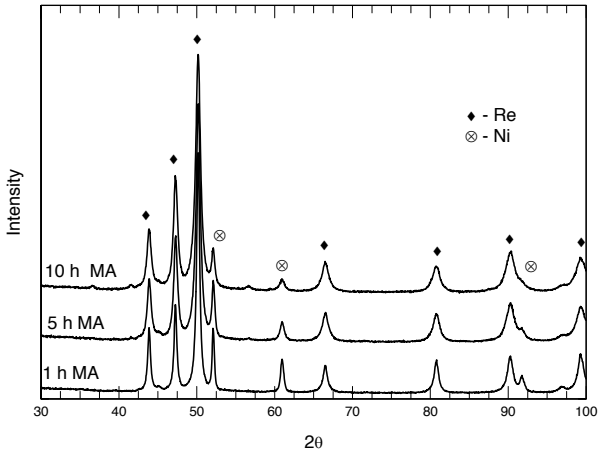


Fig. 1. The X-ray diffraction patterns for the Re-Ni powders after mechanical alloying process conducted for 1, 5 and 10 hours

This analysis also showed that all the materials after the sintering process contained, as the main phase, a solid solution with A3 structure rich with rhenium (Figs. 4-6). In the materials containing iron or nickel small amounts of solid solutions of the A2 or A1 structures, i.e. α-(Fe) or (Ni), were also found, which probably resulted from incomplete diffusion of alloy components during sintering. The contents of these phases in the alloy was regularly decreasing with the time of mechanical alloying applied before sintering.

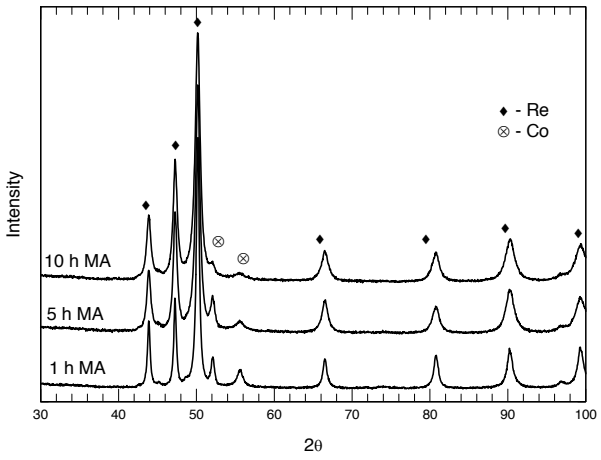


Fig. 2. The X-ray diffraction patterns for the Re-Co powders after mechanical alloying process conducted for 1, 5 and 10 hours

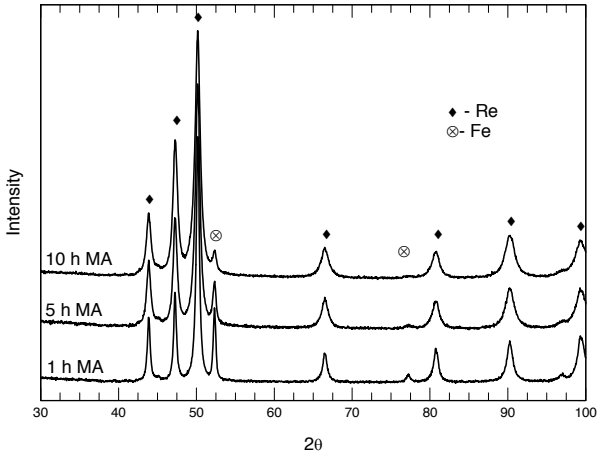


Fig. 3. The X-ray diffraction patterns for the Re-Fe powders after mechanical alloying process conducted for 1, 5 and 10 hours

Diffraction line profiles obtained for the crystalline phases contained in a powder mixture and in the materials obtained from sintering also exhibited characteristic changes dependent on time of mechanical alloying. Broadening of the diffraction lines of powder components with the alloying time was observed, which resulted both from increasing micro-stresses within the particles of a milled powder and from the reduction in an average diameter of their crystallites. Composition inhomogeneity of the solid solutions was of lower importance, which was evidenced by the fact that the centre of gravity of these lines was only slightly changing with the alloying time.

Behaviour of the diffraction lines of the phases of sintered materials was opposite - their width was decreasing with the time of alloying applied before sintering. Besides, shifting of the centres of gravity of their diffraction lines towards greater Bragg angles was also visible, that is towards lower values of interplanar distance d_{hkl} and lower values of lattice constants for these phases. Particularly great were the differences between diffraction patterns obtained for the sinter compacts after milling for 1 hour and 5 hours, whereas they were much smaller between those corresponding to milling times of 5 and 10 hours. This indicates that the reactions leading to structural transformations proceed particularly rapidly at the beginning of the milling process, and longer milling resulted mainly in further homogenisation of the chemical composition.

This phenomenon takes place particularly in the Re-Co alloys (Fig. 5). In these alloys a clear asymmetry of the diffraction lines of the ε-(Re,Co) solid solution, the only component of the sinter compact, is observed already after 1 hour of mechanical alloying. Such behaviour of the Re-Co alloy during sintering has several reasons. One of them is that lattice defects density evidently decreases at the sintering temperature, which results in the increase in material density (Table 3) and in the decrease in the values of lattice constants. It seems, however, that particular importance has the rate of interdiffusion between alloy-forming elements at sintering temperature. After the milling process the alloy still contains two solid solutions with the hcp structure: (Re) and ε-(Co), considerably differing in the values of lattice constants *a* and *c* [9]. Deviations of the values of these constants from the average values for each of both solutions are not great.

Table 2.
Chemical composition determined in micro-areas for the materials under investigation

Material	Area	1 h MA		5 h MA		10 h MA	
		Re [mass %]	X *) [mass %]	Re [mass %]	X [mass %]	Re [mass %]	X [mass %]
Re-Ni	Matrix (bright)	90	10	87	13	86	14
	Grey areas	26	74	30	70	32	68
	Dark areas	1	99	-	-	-	-
Re-Co	Matrix (bright)	91	9	87	13	88	12
	Grey areas	63	37	73	27	85	15
	Dark areas	51	49	-	-	-	-
Re-Fe	Matrix (bright)	93	7	92	8	93	7
	Grey areas	82	18	82	18	83	17
	Dark areas	62	38	-	-	-	-

*) where X denotes Ni, Co or Fe, respectively

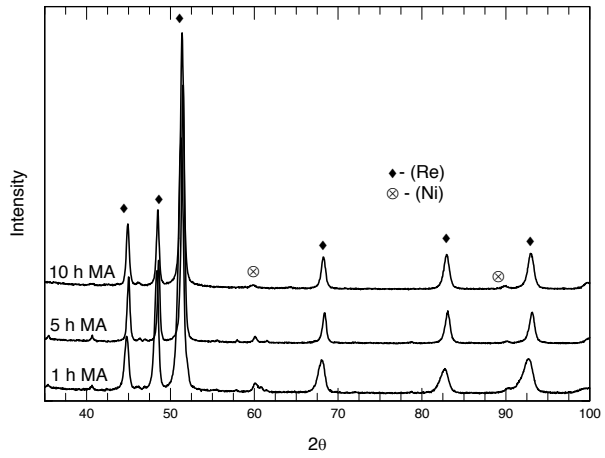


Fig. 4. The X-ray diffraction patterns for the Re-Ni alloys after mechanical alloying process conducted for 1, 5 and 10 hours and after sintering process

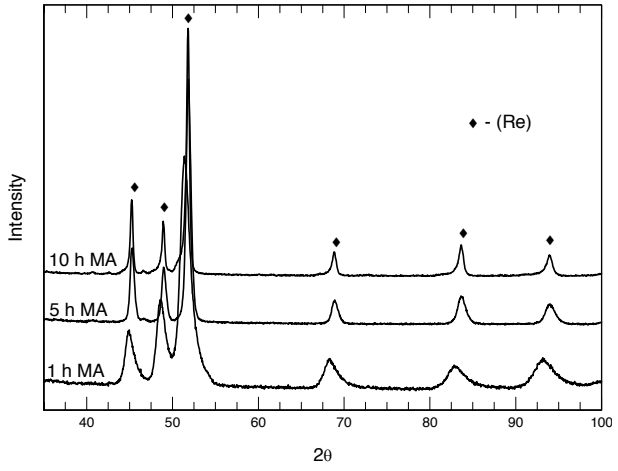


Fig. 5. The X-ray diffraction patterns for Re-Co alloys after mechanical alloying process conducted for 1, 5 and 10 hours and after sintering process

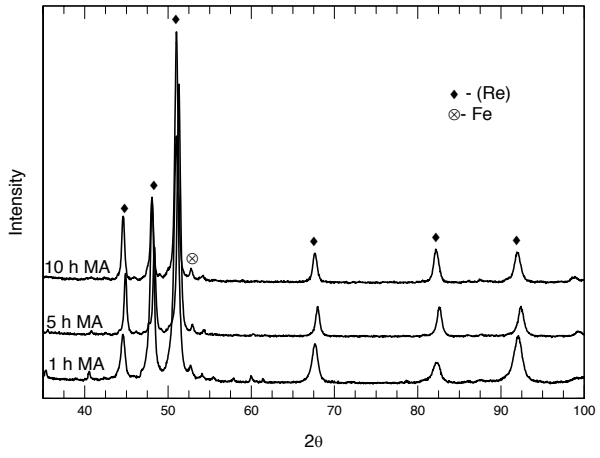


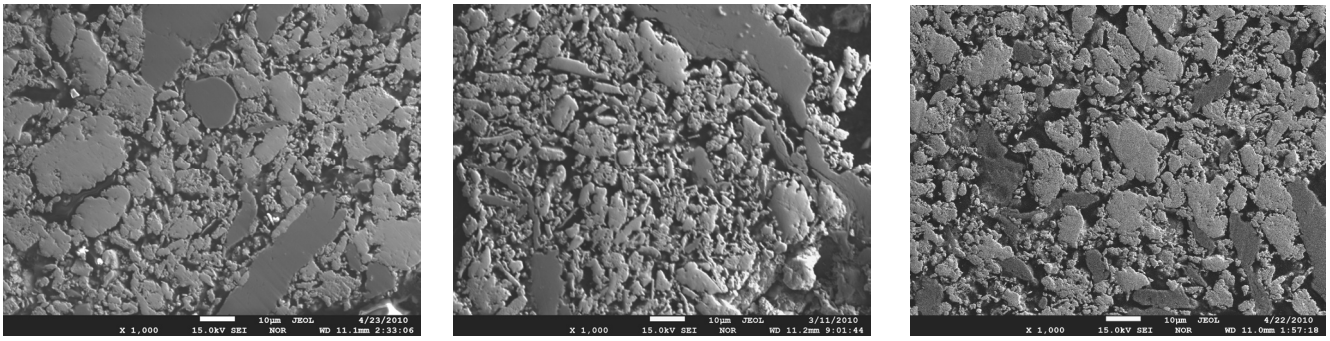
Fig. 6. The X-ray diffraction patterns for Re-Fe alloys after mechanical alloying process conducted for 1, 5 and 10 hours and after sintering process

Sintering of the milled powders for 1 hour at the temperature of 1150°C results in further strong diffusion. As a consequence, in accordance with a binary Co-Re system [10], a single ε-(Re,Co) solid solution is formed, having the values of lattice constants *a* and *c* the more closer to the theoretical values the longer was the time of previously applied mechanical alloying, i.e. the stronger was mutual dissolution of components before sintering. This explains the reasons for low scatter of the values of *a* and *c*, narrowing of the diffraction lines for the ε-(Re,Co) solid solution, and the decrease in their asymmetry. This is the consequence of reaching by the alloy, after mechanical alloying process, of a specific structure dependent on the time of that alloying.

The results from phase analysis were confirmed by those from microstructure analysis. After 1 hour of mechanical alloying, the materials remain a mixture of Re grains and the grains of Fe, Co or Ni, clearly separated from each other (Figs. 7 and 8). In the microscopic images elongated, dark grains can be seen (Fig. 7), with the size reaching several dozen μm and containing Ni, Co or Fe, respectively. The Re grains are brighter and finer. Elongation of the time of mechanical alloying results in clear refinement and further homogenizing of the microstructure so that these materials become a conglomerate of fine grains several μm in size and with mixed chemical composition (Fig. 8).

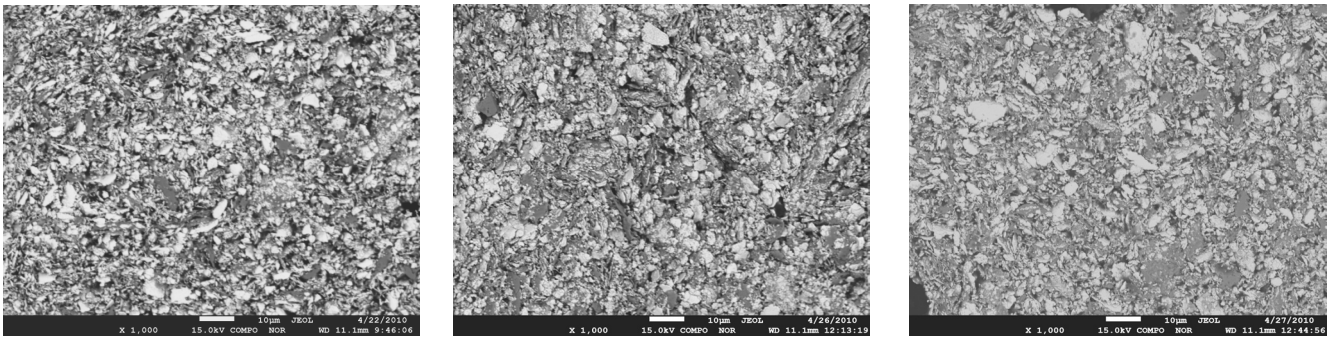
Table 3.
Physical properties of the investigated materials after MA process and after sintering

Material	MA time [h]	Properties of the powders after mechanical alloying			Properties after sintering	
		Density ρ [g/cm^3]	Grain dia. [μm]	Surface area [m^2/g]	Density ρ [g/cm^3]	Hardness [HB]
Re-Ni	1	16.5	8	0.51	11.0	54
	5	15.9	6	0.73	12.2	136
	10	15.2	4	1.43	13.9	218
Re-Co	1	16.3	11	0.74	10.7	66
	5	16.2	8	0.99	10.8	70
	10	14.7	5	1.78	11.1	108
Re-Fe	1	17.1	10	0.55	10.3	45
	5	16.9	6	0.81	10.1	44
	10	16.2	4	1.46	10.7	76



Re-Ni Re-Co Re-Fe

Fig. 7. Microstructure of powder materials after 1 hour of mechanical alloying, SEI image, magn. x1000



Re-Ni Re-Co Re-Fe

Fig. 8. Microstructure of powder materials after 10 hours of mechanical alloying, COMPO image, magn. x1000

It was also found that the alloying time clearly influenced microstructure homogeneity of the alloys after the sintering process, which is evidenced by the images showing distribution of particular elements on the material surface (Figs. 9-11). In these images, the change in a content of an element is reflected by the change in brightness: the black colour corresponds to the smallest content and the white one - to the greatest content of an element.

In all studied cases, the most homogeneous microstructure of the sinter compacts was obtained for the powders subjected to mechanical alloying for 10 hours. In case of the materials alloyed for 1 hour the following characteristic areas can be distinguished: (a) the brightest areas containing a matrix and rich in rhenium, containing also several percent of Ni, Co or Fe; (b) darker, grey areas with the Re content ranging from 20% to 80%, and (c) the darkest areas with the lowest content of Re. With the increase of alloying time, percentage of darker phases, rich in Ni, Co or Fe, clearly decreases, which has been confirmed by the presented results of X-ray phase analysis. Homogenization of the chemical composition proceeded clearly more rapidly in the Re-Co and Re-Fe mixtures than in the Re-Ni mixture (Table 2).

An increase in powder refinement at longer times of mechanical alloying, observed in microscopic examination, was confirmed by the measurements of an average grain diameter Φ (Table 3). The average grain diameter for the materials alloyed for 10 hours dropped to 4-5 μm. The grain size decrease was also confirmed by surface area measurements: an increase up to about 2.5 times was observed at the alloying time increase from 1 hour to 10 hours. It was also found that powder density decreases with the alloying time - the greatest decrease of about 10% was observed for the Re-Co mixture. This decrease may result from increasing number of defects generated within the structure, which is confirmed by appreciable diffraction lines broadening observed in X-ray diffraction patterns for the Re-Co alloy.

The alloying time also clearly influences final properties of the materials. With the increase of alloying time density of the sinter compacts also increases despite its previous drop during alloying. The greatest density increase by about 25% was observed for the Re-Ni alloy.The greatest increase in HB hardness (fourfold) was observed also for this material. An increase in density and hardness is related with the microstructure changes in the alloys and increasing homogeneity of their composition. Lower hardening of the Re-Fe alloy, compared to other tested alloys, results most probably from by 1.5 times lower content of an alloy additive, i.e. 9.1% Fe compared to about 14% Ni or Co in the remaining materials.

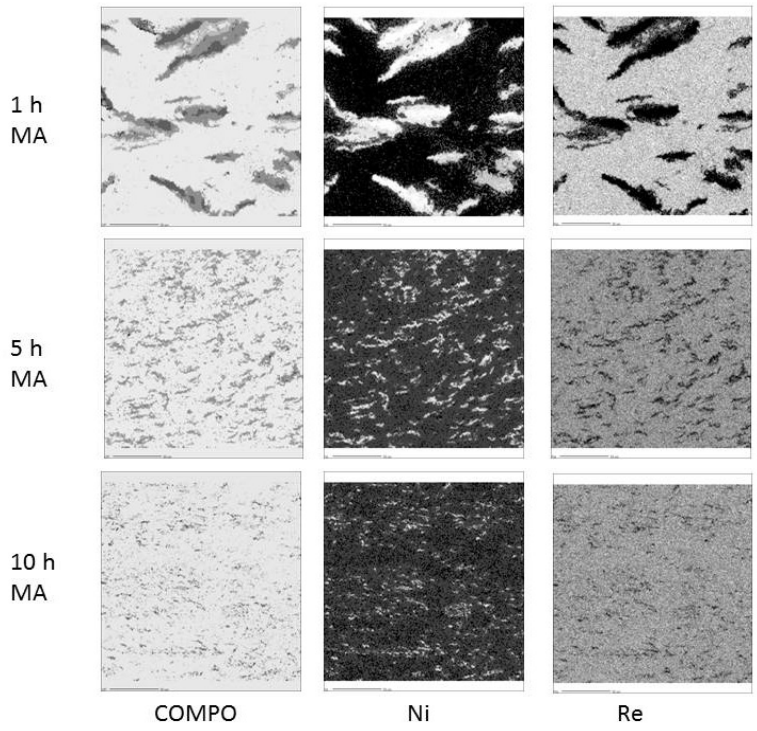


Fig. 9. Distribution of elements in the Re-Ni alloy after the sintering process, magn. x500

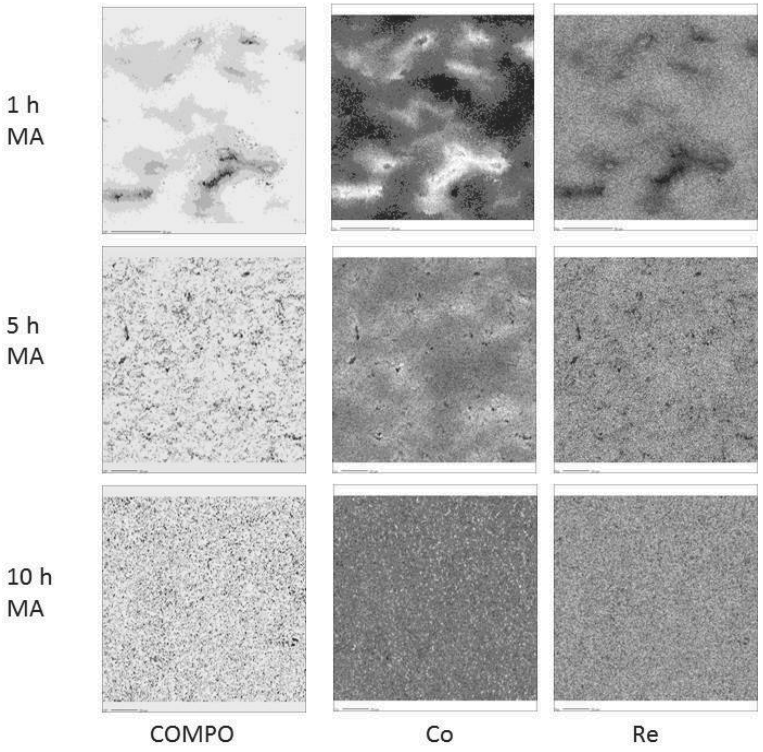


Fig. 10. Distribution of elements in the Re-Co alloy after the sintering process, magn. x500

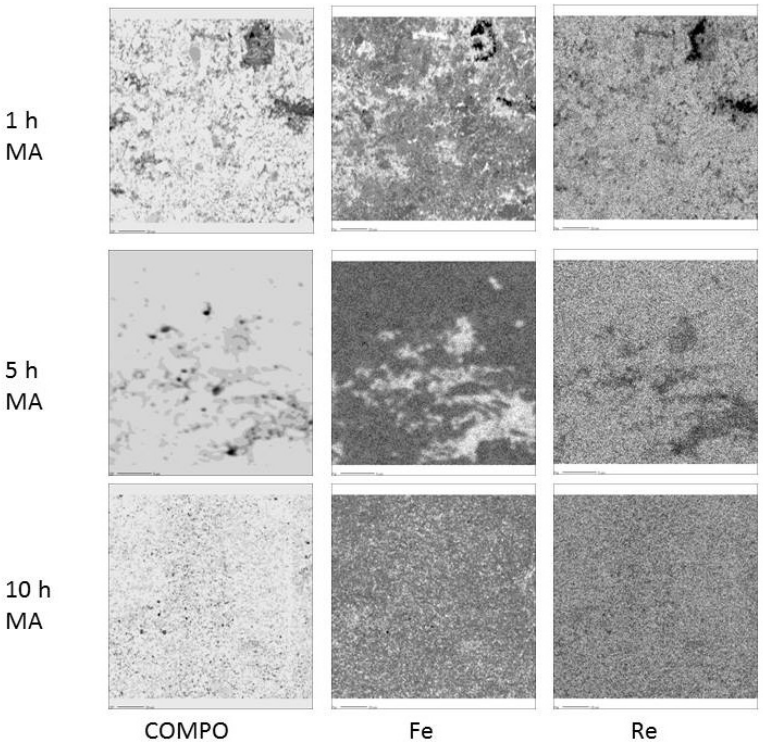


Fig. 11. Distribution of elements in the Re-Fe alloy after the sintering process, magn. x500

4. Conclusions

1. The investigated Re-Ni, Re-Co and Re-Fe powder materials were, after mechanical alloying, a mixture of solid solutions with the preserved structure of pure metals.
2. With the alloying time increase refinement of the materials and composition homogeneity were also increasing, which resulted in the increase in density and hardness of the alloys obtained by sintering of the powders subjected previously to mechanical alloying.
3. The main component of the investigated materials after the sintering process was rhenium-based solid solution, in which alloy additives were almost fully dissolved. The dissolving process was more effective at longer times of milling the powders, and it was the most efficient in case of the Re-Co alloy.

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