THE INFLUENCES OF LOW CONCENTRATION METAL ADDITIVES ON THE STRUCTURE AND PROPERTIES OF SINTERED TUNGSTEN BASED PSEUDOALLOYS

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High density refractory materials, which are in demand in a number of industry branches, are based primarily on sintered tungsten, however, the obtaining of products from them is connected with great energy costs. To decrease the sintering temperature, additives of metals with lower melting temperature are incorporated into refractory tungsten composition, for example, nickel and iron. The quantity of these additives must be minimal for the aim of not decreasing substantially the density of obtained materials.

It has been established that the following phases are available below 1000 °C in W-Ni system: α-phase – solid tungsten solution in nickel with homogeneity field 0-35 % W at temperatures up to 900 °C and 0-41,5 W in the interval from 1000 °C up to melting temperature; β-phase formed as a result of peritectoid reaction; it has a narrow homogeneity field and is the chemical compound of Ni₄W (43,92 W); γ-phase – solid nickel solution in tungsten containing about 4 % Ni [1]. According to equal phase diagram, there are several intermetallic compounds in the system tungsten-iron: WFe₂, W₂Fe₃ (or W₆Fe₇), as well as solid tungsten based solutions ( up to 2,6 at. % at 1677°C), α-iron (up to 14,3 at.% at 1548°C) and γ-iron (up to 1,46 at.% at 1140°C) [2].
Since tungsten possesses a very low plasticity, two techniques have been used in creating mechanocomposites: the first one – preliminary dispersion of tungsten in high energy ball mill during 4 minutes and then mechanical activation of tungsten mixture with 10 % metal-additive during of 2 minutes in the same mill [3]. In this work, the joint mechanical activation mixtures (W 10 % Ni) and (W 10 % Fe) during 4 minutes was used.

Tungsten powders of grade PB1, powders of carbonyl nickel of grade PNK and iron of grade PZHR3 have been applied. Mechanoactivation of initial powders mixtures was conducted in high energy ball planetary mill AGO-2 with water cooling, the argon atmosphere was available ( drum volume 250 cm³, diameter of balls 5 mm, supply 200 g, mounting of sample under processing 10 g, rotation speed of drums around the general axis ~1000 rounds/min).

Scanning electron high resolution microscope MIRA/ TESCAN with an attachment for microroentgenspectral analysis was used to investigate the structure of the obtained samples. Electron probe diameter constituted 5,2 nm, excitement field – 100 nm

Compactibility was determined by ISO 3927-1985 on cylinder samples with a diameter 10 mm, height 12 mm, pressed in steel die mould at pressure 200, 400 и 600 MPa. The compacted samples have been sintered in vacuum at temperature 1350°C.

Compression strength of mechanoactivated compositions was measured on samples with a diameter 10 nm, height 12 mm. The tests were performed on a test machine “Instron” at a loading rate 2mm/min.

The microstructure of sintered compositions was investigated on laps etched with 10 g of K₃Fe(CN)₆, 10 g KOH, 100 ml H₂O, on metallographic microscope MEF-3 of company «Reihert» (Austria ) in different magnifications.

X-ray analysis was performed on diffractometer D8 Advance Bruker (Germany) by powder diffractometry method in configuration 2θ in step by step mode after 0,1°. Phase identification was performed in a diffraction picture recorded in radiation CuKα₁ (1,54051 Å). The specification of structure for phases being obtained was performed by Rietveld method in software “Topas”. Approximation of profiles for peaks, was made with Pseudo-Voigt function. To calculate the background, 7 order polynom Chebyshev was applied. The calculation
for microstructure parameters was performed with the appropriate division of contributions into physical widening of peaks at the expense of crystallites size and microtensions by Warren-Averbach method.

X-ray investigations have shown (fig.1) that tungsten coherent scattering domains constitutes ~ 15 nm in mecanocomposites W – 10 % Ni, nickel coherent scattering domains constitutes ~ 4 nm, as for W - 10 % Fe ~ 34 nm and ~ 6 nm, correspondingly. This speaks about the deep tungsten crystal structure destructions occurring in interacting systems. Tungsten lattice parameter is close to table – a=3,163nm that is no formed solid solutions are noted during this stage.

Fig. 1. Diffractograms for W-Ni and W-Fe samples after 4 min mechanical processing

Since tungsten can chemically interact with nickel and iron, then during the mechanical activation process one can expect the formation of intermetallic compounds. It can be assumed that intermetallic compound with the highest concentration of more fusible metal (in the given case WNи₄ или W₆Fe₇) is primarily formed in these cases on the contact surface. However, quite often these intermetallides are not established X-ray analyses on the contact surface. One can suggest that “cluster” intermetallide phases are formed during the interaction of
tungsten with nickel and iron on contact surface, the locality and mechanical short duration effect hinder their subsequent growth.

Electron microscopic study for tungsten-nickel mechanocomposite powders, obtained in joint one stage activation, has shown that the particles of metals are fine homogeneous (fig.2) Continuous and discrete nickel phases positioning on tungsten particle are found in mechanocomposites by electron microscopy.

![Image](image_url)

Fig 2. Structure and distribution of elements of W-Ni composition, obtained by one stage processing: a – mechanocomposite morphology; b – in Ni characteristic X-ray radiation

Electron microscopy does not reveal any fine continuous iron layers W-Fe system. Iron phase is distributed in tungsten matrix discretely (fig.3) in the form of fine (2-10mkm) and large (20-50mkm) insertions.

It should be noted that W-Ni mixture after one stage processing starts to be compacted only at a pressure 400 MPa. The density of samples compacted at 600 MPa constitutes ~ 10 g/cm³.

W-Fe mechanocomposites yield to compaction already at a pressure 200 MPa, however, compaction pressure increase up to 600 MPa does not increase substantially the density of compactions only
Fig. 3. Distribution of elements in W-Fe mechanocomposition after mechanical processing: characteristic roentgen radiation superimposing of Fe (more dark) and W (gray) onto the structure from 8,3 up to 9,1g/cm³. X-ray investigations of samples sintered from W-Ni mechanocomposites have shown that W-Ni (PDF 65-2673) intermetallide is formed in them, with lattice parameters $a = 5,727(2)$, $c = 3,553$ (fig. 4). The size coherent scattering domains of tungsten constitutes on the average 152nm, of intermetallide -56nm, Tungsten level of microtensions in sintering considerably decreases from 1,05 % up to 0,14 %, it is somewhat higher in intermetallide under formation.

Metallographic investigations of W-Ni samples sintered at 1350°C, have shown that they have fine granular structure and Ni₄W intermetallide particles formed at granular boundaries. (fig. 5). W-Ni
sintered composite samples demonstrate high strength: elasticity limit in compression is 754 MPa due to great consolidation.

Fig. 4. Diffractograms for W-Ni mechanocomposites: a) before sintering; b) after sintering

Fig. 5. Microstructure mechanoactivated tungsten-nickel compositions sintered at 1350 °C

The formation of intermetallic compound Fe₇W₆ (PDF 42-1209) was revealed with lattice parameters \(a = 4.765(6), c = \)
25,938(5) and coherent scattering domains ~ 84 nm (fig. 6), it was revealed
X-ray analyses of the samples sintered from W-Fe mechanocomposite.
Tungsten size coherent scattering domains in these samples ~136 nm, the level
of microstrains in intermetallides is by two times higher than in tungsten.

![Diffractograms for W-Fe mechanocomposite](image)

Fig. 6. Diffractograms for W-Fe mechanocomposite; a) before sintering;
b) after sintering; ▼ – Fe₇W₆

No separate nickel, iron phases are observed X-ray analyses after
sintering of W-Ni and W-Fe samples.

W-Fe samples do not have high strength in comparison with
mechanocomposites with the addition of other metals their elasticity
limit in compression constitutes 155 MPa. Possibly, this is connected
with the formed intermetallides on the contact surface between tungsten
and iron. The presence of these phases: of free tungsten is revealed when
these samples are etched. However, it is very difficult to make a lap
from them since one can note a high porosity (fig. 7)

Irrespective of the density after compaction, these changes in W-
Fe composite are not considerable during sintering, at the same time
they are very essential in W-Ni composite what is proved by the strength of materials (fig.8)

Fig. 7. Microstructure of tungsten-10% iron composite sintered at the temperature 1350 °C in vacuum

Fig. 8. Density for W-Fe and W-Ni samples; 1 – before sintering; 2 – after sintering at 1350 °C in vacuum; a – compaction pressure 200 MPa; b – compaction pressure 400 MPa; c – compaction pressure 600 MPa
Thus, the conducted investigations allow to suggest that clusters are formed from metals interacting between themselves on the contact surface, this is in mechanochemical formation of composites, these clusters are crystallized into particles of intermetallides in subsequent annealing. It should be noted that the strength of material obtained from W-Fe composite is considerably lower than from W-Ni, possibly, the essential difference in coherence of lattices of intermetallides and tungsten is influential (\(\text{Fe}_7\text{W}_6 - \text{W}\) and \(\text{Ni}_4\text{W} - \text{W}\)).

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References