TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 59, Issue I, March, 2016

STUDY ON THE CHROME INFLUENCE ON THE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF THE TUNGSTEN BASED ALLOYS

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Abstract: *In this paper we have presented the studies and the researches done by the authors on the chrome addition effect on the mechanical properties and microstructure of the heavy alloys from the W-Ni-Fe system. The experimental results have shown that the chrome addition up to 3 wt. % in the W-Ni-Fe system, have influenced the density, elongation and the yield limit of the sintered samples. These results could be explained by the segregation observed on the interphase boundaries between the W based matrix and the chromium compounds with the Ni, Fe and O elements. Also, an interphase corrosion is produced from where is explained the lowering of the mechanical properties analyzed.*

Key words: *Tungsten heavy alloy (THA); W-Ni-Fe composites; liquid phase sintering (LPS); sintering atmosphere.*

1. INTRODUCTION

The increasing requirements of different technical branches, especially the top ones, for materials both with a wide range of properties and of the highest quality, have directed and determined intense research work, mainly focused on two directions: one which tries to attain the theoretical capability of the already-obtained materials, and the second trying to design and manufacture new materials.

Despite all the efforts that have already been made, no existing material has reached the limit of its theoretical capability. The main reasons for this were the imperfections of the manufacturing technologies, which, despite their spectacular development during the 20th century, have not succeeded in completely eliminating imperfections from the structure of materials, imperfections which influence the materials' physical-mechanical properties. The current level of such properties places the materials at a longer or shorter distance from the limit of their theoretical capabilities. Consequently, research can still find ways to reach the capability record of each material. These ways involve obtaining more information on the formation of material structure, the mechanisms that act during structure formation, and the influence factors. Thorough knowledge of the manner of structure development during the manufacturing processes allows one to control and direct them towards the desired purpose, and leads, finally, to an increase in the material performance. These ideas also apply to the materials known as hard alloys, composite, biphasic materials, of refractory nature, due to their high tungsten content.

Heavy tungsten alloys (hereinafter referred to as HTA) constitute that category of materials whose main component is tungsten, which is alloyed with one or more transition metals, such as Ni, Cu, Fe, Co, etc. These materials have characteristic embedded, biphasic microstructures, whose main phase is made of spheroid tungsten grains, vcc crystallized, embedded in a more ductile matrix, made of a solid metal or alloy metal solution, saturated in tungsten, and fcc-system crystallized.

HTA have a unique combination of properties, consisting of: high density, higher mechanical strength, high ductility, good corrosion resistance, high radiation absorption capacity, good processability, and remarkable tenacity. HTA have also started to be used in the military field, as kinetic energy penetrators. They have been used in the manufacturing of γ and X-ray protective screens, aircraft counterweights, inertia weights for different aircrafts, etc.

The levels of these properties can be changed within very large limits, according to the required HTA applications, through composition and microstructure, which is in turn determined by the parameters of the manufacturing technology. In terms of composition, there are different opinions about the limits of tungsten content variation, between which the above-mentioned materials can be considered as HTA. These limits vary between 30 and 90% w/w according to Gurwell [1, 2, 3, 4, 6], and W 90 and 98 wt% in Metals Handbook [5]. The limits of tungsten content of HTA should be set according to the system of the elements in which they are embedded, so that the microstructure corresponds to a composite material with embedded structure, and density exceeds a certain limit, for example, 12.103 kg/m^3.

Despite the progress, the opportunities for HTA performance improvement have not been exhausted. There have remained a series of unsolved mechanisms, as well as a series of technological parameters that can be optimized. Moreover, heat treatment and plastic deformation processing can be applied after sintering, which have a beneficial effect on HTA properties [7, 8, 9, 10]. All these, together with the scientific interest in HTA, HTA application perspectives, and, last but not least, the domestic availability of the necessary raw materials, as well as the demand for HTA semi-products in different technical areas have appealed to the authors of this paper.

2. EXPERIMENTAL PART

The fact that there are an impressive number of different HTA manufacturing conditions, which have determined sets of properties with very different values, practically makes establishing some quantitative correlations between the manufacturing parameters and the values of the HTA properties extremely difficult. Therefore, since the raw material available to the authors of this paper was tungsten powder manufactured domestically by SC SINTEROM SA in Cluj-Napoca, with a history and characteristics different from the tungsten powders used within different works involving HTA, the authors had to conduct a series of experiments in order to establish the influence of different factors on the properties of HTA obtained using the mentioned tungsten powder [11,12, 14].

The purpose of the experiments performed for Cr alloying was to introduce chromium into the premixture intended for the matrix. First, the powders intended for the matrix alloy were homogenized, and then the alloy was mechanically prealloyed, before being finally mixed with the tungsten powder. For this purpose, in order to study the effects of Cr alloying, chromium variation ranged between 0 and 3wt%, and tungsten variation ranged between 90 and 95%. The Ni / Fe ratio and the technological parameters were maintained constant. The data on the density, tensile strength and elongation were compared to similar properties of HTA with the same W content, but without Cr. The powders used for mixture preparation had the following characteristics:

- The tungsten powder manufactured by S.C. SINTEROM S.A. Cluj-Napoca, with:
  - Average particle diameter, d50 3.6 μm
  - Specific surface, SB 782 cm^2/g
  - Apparent density, ρa 3.99 g/cm^3
  - Oxidization degree 0.16 %
- Nickel carbonyl powder, INCO 123 sort, with:
  - Nickel content min 99.7%
  - Oxygen content 0.10%
  - Carbon content 0.05-0.10%
  - Iron content max 0.01%
  - Average particle size 4-7 μm
  - Apparent density 1.8-2.5 g/cm^3
  - Specific surface min340 cm^2/g
- Höganäs iron powder, NC 100.24 sort, with:
  - Iron content min 99-38%
  - Carbon content max 0.02%
  - Oxygen content max 0.03%
  - SiO2 content max 0.25%
  - Granularity < 63 μm

- Apparent density 2.26g/cm^3

- Chromium powder, with:
  - Chromium content 99,8%

Four powder mixtures were prepared for each percent of tungsten content, with the names, composition, and theoretical density specified in table 1. The mixtures were prepared as follows:

Table 1

Sample type	Composition, [wt%].				Theorethical density, [g/cm^3]
	W	Ni	Fe	Cr	
90-0	90	7.0	3.0	0	17.12
90-1	90	6.3	2.7	1	17.05
90-2	90	5.6	2.4	2	16.98
90-3	90	4.9	2.1	3	16.92
91-0	91	6.3	2.7	0	17.31
91-1	91	5.6	2.4	1	17.24
91-2	91	4.9	2.1	2	17.17
91-3	91	4.2	1.8	3	17.1 1
92-0	92	5.6	2.4	0	17.50
92-1	92	4.9	2.1	1	17.43
92-2	92	4.2	1.8	2	17.37
92-3	92	3.5	1.5	3	17.30
93-0	93	4.9	2.1	0	17.75
93-1	93	4.2	1.8	1	17.70
93-2	93	3.5	1.5	2	17.68
93-3	93	2.8	1.2	3	17.61
94-0	94	4.2	1.8	0	17.91
94-1	94	3.5	1.5	1	17.84
94-2	94	2.8	1.2	2	17.74
94-3	94	2.1	0.9	3	17.70
95-0	95	3.5	1.5	0	18.12
95-1	95	2.8	1.2	1	18.05
95-2	95	2.1	0.9	2	17.97
95-3	95	1.4	0.6	3	17.90

Composition of Cr alloyed W-Ni-Fe HTA.

First the powders for the matrix alloy were premixed in a Turbula blender for 30 minutes; then they were mixed for a short time (30 seconds) in the planetary grinder. Finally, the premixtures were homogenized with the tungsten powder for 30 minutes in the Turbula blender. Out of each mixture, five cylindrical specimens, section of 1 cm^2, were pressed under a pressure of 200 MPa, in order to determine density. The same pressure was also used to manufacture three specimens for the tensile test. Sintering was performed at a temperature of 1500 °C for 1h, in hydrogen atmosphere. The heating speed to the liquid phase sintering temperature was 5 ^{0}C/min. The specimens were cooled with the furnace down to 1000 °C, then directly in the cold area of the furnace.

The sintered state density was determined, and then tensile tests were performed on the universal ZD-10 machine, in order to determine breaking strength and elongation. The variation curves of the density, tensile strength, and breaking elongation were drawn according to the chromium content for every composition in table 1. They are given in figures 1 to 3. Before discussing the results of chromium matrix alloying, shown by the curves in figures 1, 2, and 3, we should make some notes, as follows: the HTA mechanical properties (tensile strength and breaking elongation) largely depend on HTA contiguity. High contiguity determines low mechanical strength and ductility. The dihedral angle represents the equilibrium between the energy of tungsten grain boundaries and the interface energy between (solid) tungsten and the (liquid) matrix during sintering.

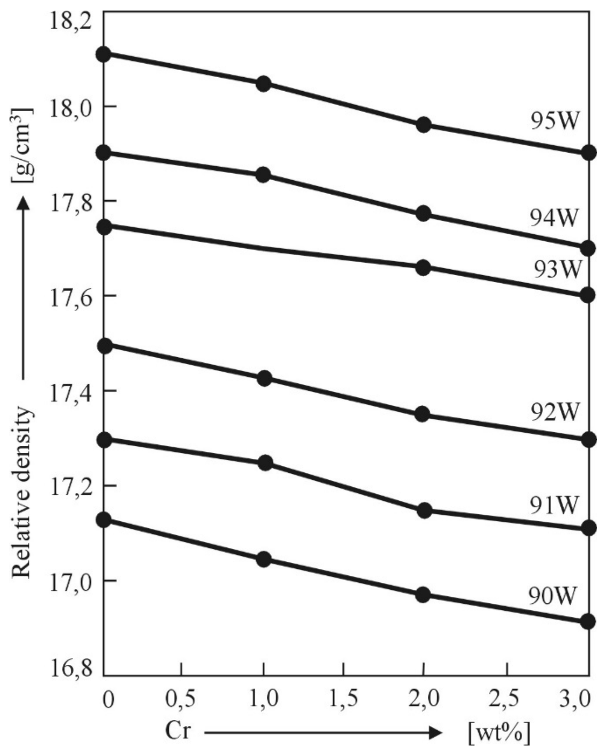

Fig.1. Variation in the density of HTA of the W-(Ni-Fe-Cr) system according to Cr content.

A small dihedral angle means either higher tungsten grain boundary energy, or lower (W) solid – (matrix) liquid interface energy. Consequently, the dihedral angle has a powerful influence on contiguity. In order to reduce contiguity, a small dihedral angle is therefore necessary.

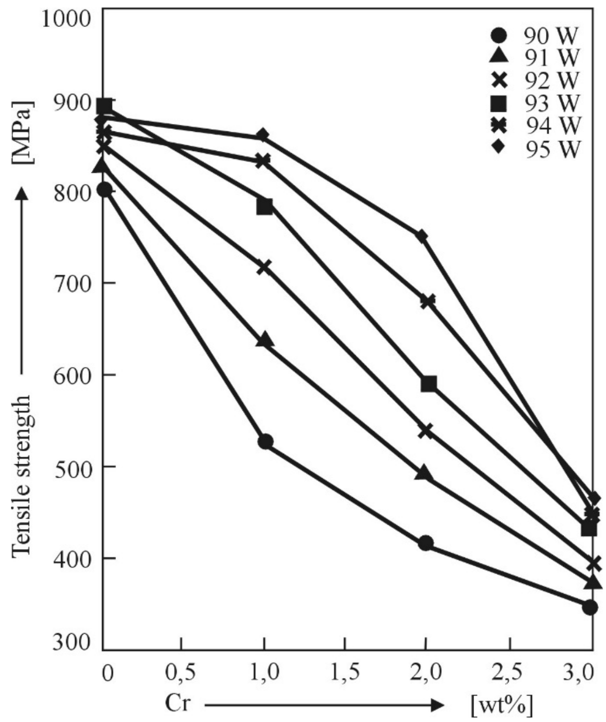

Fig.2. Variation in the tensile strength of HTA of the W-(Ni-Fe-Cr) system according to Cr content.

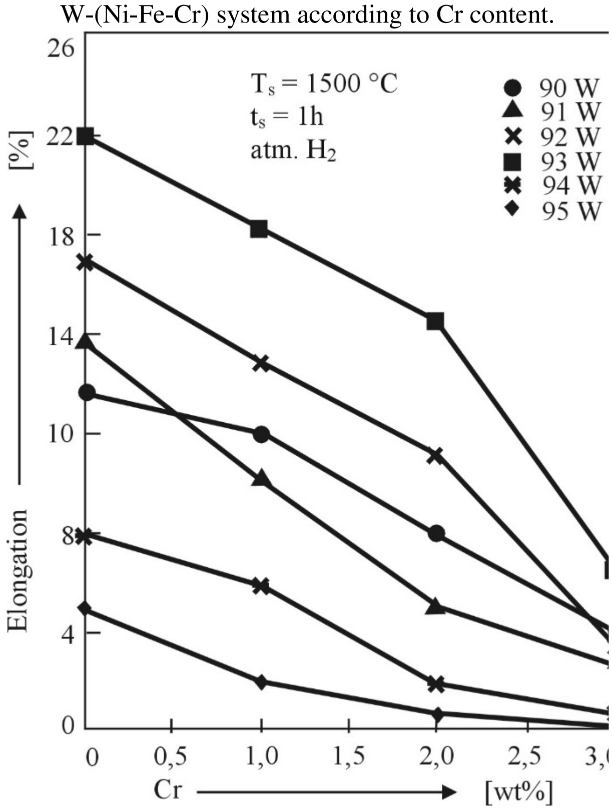

Fig.3. Variation in the breaking elongation of HTA of the W-(Ni-Fe-Cr) system according to Cr content..

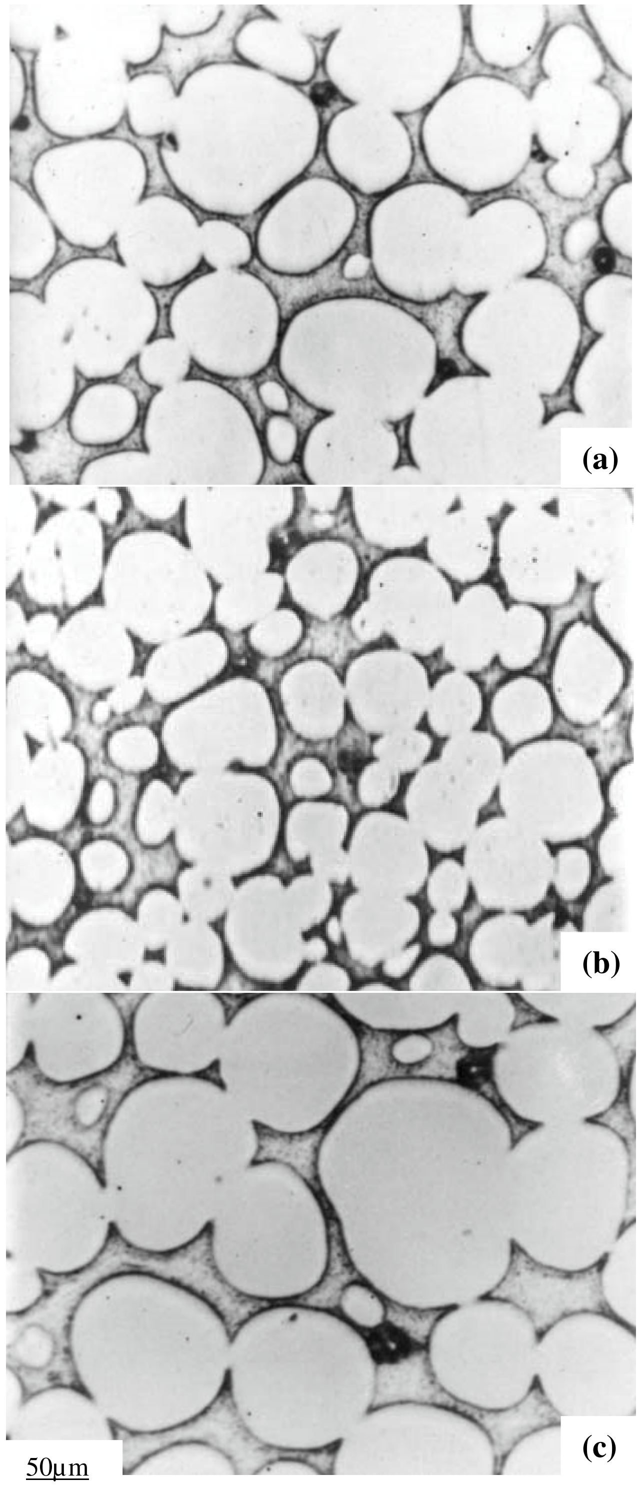

Fig.4. Microstructure of 93W(Fe-Ni-Cr) HTA with Cr 0; 1 and 3 wt%, respectively, sintered at 1500 °C, 1 h, protective H_2 atmosphere.

On the other hand, a smaller dihedral angle also means high mechanical strength of the W – matrix connection. Due to higher contiguity and larger dihedral angles, the alloys that have Cr in their matrices will obviously have lower mechanical properties than the alloys with similar W content, but without Cr in their matrices. In case Cr is added in the form of pre-alloyed Ni-Fe-Cr powder, the liquid phase will have higher Cr content in the initial sintering stage.

During sintering W diffuses towards the liquid, and Cr in the liquid towards the W grains. The Cr content in the liquid will be in this case very low, and thus its effect will considerably decrease. When we analyze figures 1, 2, and 3, we notice that density decreases almost linearly with the increase in Cr quantity for all HTA with W 90-95 wt%. In the case of tensile strength, the strongest effects can be seen in HTA with W 90 wt%, the maximum value corresponding to Cr 2 wt%, followed by HTA with W 91 wt%, the maximum value corresponding to Cr 3% addition. In the case of breaking elongation, the alloy with W 95 wt% comes first again, followed by the alloy with W 94 wt%, with similar Cr addition.

3. RESULT AND DISCUSSIONS

Figure 1 shows the relative density curves. We notice that the relative density of the sintered specimens decreased from 18.05 g/cm3 to 16.92 g/cm3. This decrease leads to lower mechanical properties of the studied Cr alloyed W-Ni-Fe alloys. When Cr content increases from 1 to 3%, tensile strength will decrease from 900 MPa to 400 MPa, as in figure 2. Specimen elongation quickly decreased from 22 to 1% in the case of the analyzed alloys, as in figure 3.

Figures 4a, b, and c show the optical micrographs of 93W(Fe-Ni-Cr) alloys with Cr 0, 1, and 3 wt%, respectively. When we compare figure 4a and figures 4b and c, we notice a reduction in the W grain size. Cr addition obviously hinders W grain growth. Cr forms clusters in the alloys, which determines low density and mechanical properties. When Cr content increases, the clusters will be larger, and will form interfaces with W, Ni, Fe, and O. The clusters are distributed along alloy interface, and induce high internal tensions and potential local fractures, which significantly reduces the alloys' mechanical properties.

4. CONCLUSIONS

- The quantity of alloying elements of tungsten, which are found in the binding alloy, and the binder/tungsten quantity ratio have a powerful influence on HTA density and mechanical properties. The variation in the theoretical density according to tungsten content, and binder content, respectively, continuously increases, respectively decreases.
- While in the case of HTA of the W-Ni-Fe system, all the curves of the mentioned measures show maximum values in case of W 93 wt%, and approximately equal values at the ends of the variation curves [13], in the case of HTA of the W-(Ni-Fe-Cr) system, the influence of composition is dramatically diminished.
- When Cr content increases from 0 to 3 wt%, the tensile strength and the relative elongation of the 93W–(Ni–Fe-Cr) alloy decrease from 870MPa to 430 MPa, and from 22 to 8%, respectively.
- The element Cr forms interfaces with the elements W, Ni, Fe, and O, and segregations along the alloy interface, which causes interface corrosion, and determines low mechanical properties of the mentioned alloys.

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Studiul influentei cromului asupra proprietatilor mecanice si microstructurii aliajelor grele din sistemul W-Ni-Fe

Rezumat: Au fost efectuate studii si cercetari privind efectul adaugarii cromului asupra proprietăţilor mecanice şi microstructurii aliajelor grele din sistemul W-Ni-Fe. Rzulatatele experimentale au indicat faptul că prin adaugarea de crom în proporţie de 0-3%gr in aliajul W-Ni-Fe, valorile densitatii relative, alungirii si a limitei de curgere sunt diferite in raport cu acelasi aliaj fara crom. Prin adaugare de crom, limita de curgere, densitatea relativă şi alungirea au scazut datorita faptului ca elementul crom formează inter-faze cu elementele W, Ni, Fe şi O şi segregă la interfaţa aliajelor, ceea ce duce la coroziune la interfaţă, de unde rezultă şi proprietăţile mecanice mai scăzute ale acestor aliaje.

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