

Properties of tungsten heavy alloys, prepared by spark-plasma sintering

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Abstract. In this paper the effect of spark-plasma sintering parameters on the microstructure and mechanical properties of tungsten heavy alloys VNZHK-90 and VNZHK-93 are studied. The basic dependences of the density and strength characteristics from the sintering temperature and velocity are shown. Conclusions about the dependence of the method of preparation of the starting powders on the microstructure of alloys are formulated. It was found that by spark-plasma sintering technique it is possible to achieve the theoretical density of compact heavy alloys during solid-phase sintering. It is shown that the maximum level of alloys mechanical properties is observed when sintering temperature 1300 °C. It is found that the change in the rate of heating does not contribute to change in the density of the samples. At the same time, on the mechanical properties the shrinkage rate has a significant effect.

1. Introduction

Heavy tungsten alloys (HTA) are widely used in various fields and have a number of valuable properties, chief among which is the ability to maintain a high hardness at elevated temperatures. The most widely used alloys VNZH (W-Ni-Fe), VNZHK (W-Ni-Fe-Co), VM (W-Cu), in which the tungsten content ranges from 90 to 98 weight percent. Nickel, iron and copper serve as a binder matrix which holds brittle tungsten grains together, thereby making alloys ductile and easily machined.

The heavy tungsten-based alloys are used as protection from radiation exposure, is widely used in the nuclear industry, in the missile technologies, as components of ammunition. HTA produced by powder metallurgy, in particular, a method of electro-plasma sintering. The properties of the alloy obtained by this method are very different, depending on the choice of the sintering conditions.

The aim of this work was to study the effect of laws modes spark-plasma sintering on the microstructure and mechanical properties of alloys VNZHK-90 and VNZHK-93.

2. Experimental results

2.1. Characteristics of sintered powders

As starting materials for the production of dense compacts using two kinds of powders VNZHK for which data is given in Table 1.

Spark plasma sintering, tungsten powders was conducted at the facility LABOX™ Model 625 (SinterLand, Japan).



Table 1. Data on the source alloy powder VNZHK-90 and VNZHK-93.

Powder	VNZHK -90	VNZHK -93
A method for producing a powder	Mechanical mixing of metal powders W, Ni, Fe, Co	Joint reduction of oxides W, Ni, Fe, Co
The average grain size according to Fisher D_f , μm	4.5	1.6
Bulk density, g/cm^3	3.92	1.7
Composition, wt. %	W	other
	Ni	5.6
	Fe	1.4
	Co	0.73
	O ₂	0.25

The microstructure of the powders obtained by a scanning electron microscope is shown in Figure 1. It is seen that alloy powders VNZHK 90 consist of mechanical mixtures of the individual particles. VNZHK-93 is a sponge-like structure and highlight the department-particles of different composition impossible. Spongy structure explains the low bulk density of the powder.

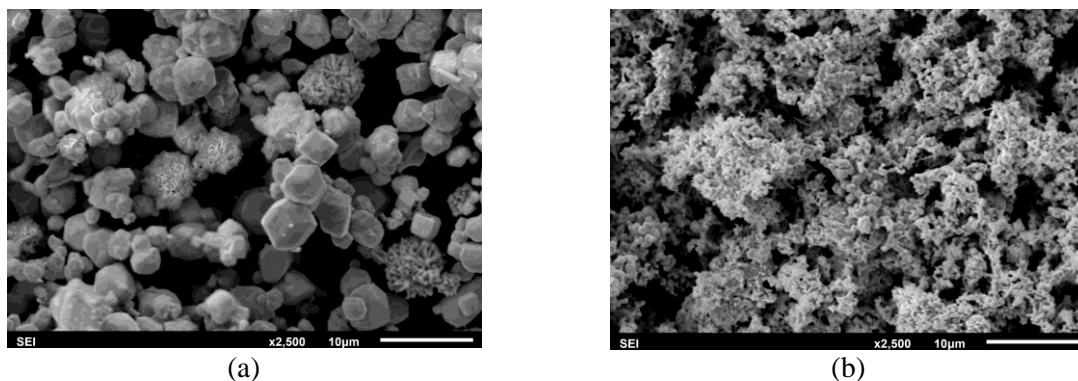


Figure 1. The microstructure of the powders obtained by a scanning electron microscope: (a) – VNZHK-90, (b) – VNZHK-93.

2.2. Spark plasma sintering of alloys VNZHK

2.2.1. Changing the sintering temperature

Was researched the effect of sintering temperature on the microstructure and mechanical properties. The first series of samples were prepared as follows. Sintered samples were heated to various temperatures linearly from 900 to 1400 °C at a heating rate of 100 °C/min and holding at maximum temperature for 20 minutes. The applied external pressure to the powder was constant at 40 MPa. Parameters of the samples are shown in Table 2.

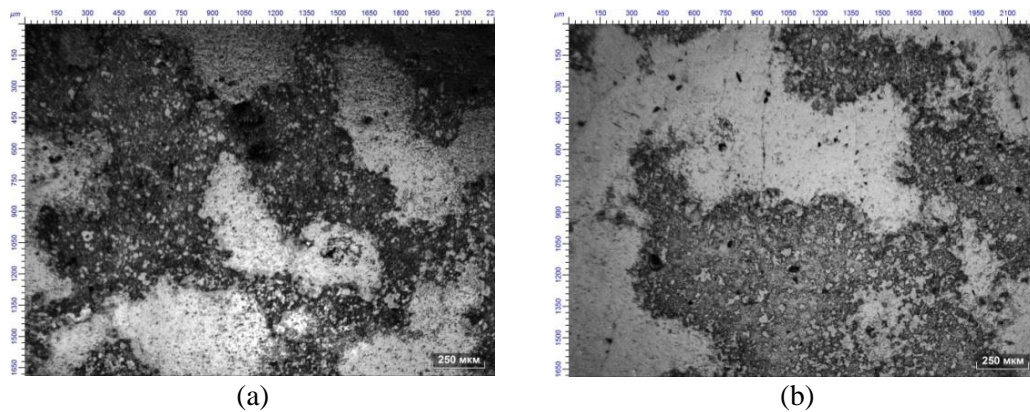
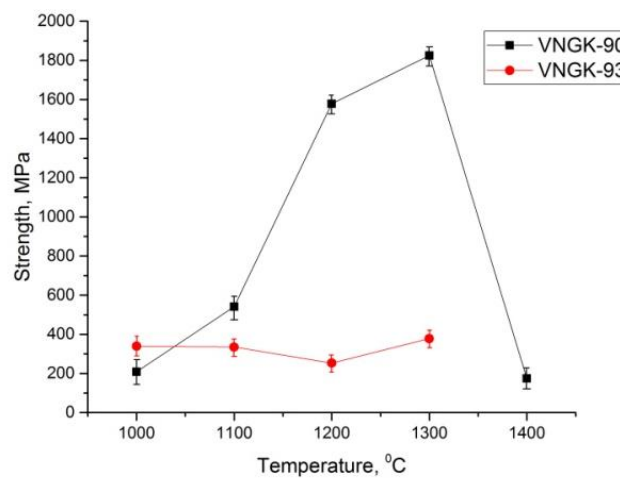
As seen from the table that the alloy VNZH-90 at a temperature of 850 to 900 °C manifested a marked increase in density. In the alloy VNZHK-93 it takes place only at 1100 °C.

Among the samples 1-1 – 6-1 stands out sample 6-1 (VNZHK-90 heated to 1400 °C), with a maximum density - 18.8 g/cm^3 . This value is greater than the theoretical value for the mixture of powders (18.16 g/cm^3). This phenomenon is due to the fact that when the sintering temperature of 1400 °C bundle (Fe, Ni, Co) and softens during pressing occurs squeezing it from the sample.

With an increase in the sintering temperature at the same heating rate significant grain growth occurs and tungsten at 1300 °C the "separation" in pressing zones with large grains of tungsten (light areas in the figure) and a mixture of the binder with tungsten (dark areas). This phenomenon explains the overall increase in the density of alloys with increasing temperature. The microstructures of alloys annealed at 1300 °C at a rate of 100 °C/min are shown in Figure 2.

Table 2. Modes of sintering and the density values for samples obtained by SPS (the first series).

N _o	Alloy	Mode of sintering (Temperature °C - Heating rate, °C/min)	Density (g/cm ³)	Relative density (% TD)
1-1	VNZHK-90	900-100	15.2	84
2-1		1000-100	17.2	95
3-1		1100-100	15.3	84
4-1		1200-100	17.4	96
5-1		1300-100	16.9	93
6-1		1400-75	18.8	100
8-1	VNZHK-93	900-100	13.3	73
9-1		1000-100	13.0	72
10-1		1100-100	17.3	95
11-1		1200-100	17.2	95
12-1		1300-100	17.0	94

**Figure 2.** The microstructure of samples obtained by SPS; $T_{\text{sint}} = 1300\text{ °C}$; heating rate 100 °C/min : *a* – VNZHK-90, *b* – VNZHK-93.**Figure 3.** Dependence of tensile strength of the sintering temperature alloys.

For alloy VNZHK-93 at temperatures above 1100 °C increase in density is observed. This is due to the structure of the starting powders. Unlike alloy VNZHK-90, wherein the structure has been represented by individual particles, and as a result, shrinkage proceeded for a longer time, the powder VNZHK-90 had a spongy structure, so the active stage of the shrinkage proceeds at lower temperatures.

Strength tests were conducted. Their results are shown in Figure 3, a graphic image according to the tensile strength of the sintering temperature.

As might be expected, depending on strength agreement with the data on the density of the samples. For alloy VNZHK-90 an increase in the mechanical properties, which is caused by the overall increase in the density of the samples due to the shrinkage of the active phase. The point on the graph corresponds to a sintering temperature of 1400 °C is released in this series. Alloy, corresponding to it, has dramatically different from other low value of strength. This phenomenon is associated with the extrusion binder during sintering, as stated earlier. Extruding binder resulted in that the sample remained mainly tungsten grains, which are known, are fragile, so the sharp decline of strength at high temperatures naturally.

For the VNZHK-93 alloy residence permit significant changes in mechanical properties are observed. This is also consistent with the data on density, since shrinkage at temperatures in excess of 1100 °C does not occur and the mechanical properties values are in the same range.

2.2.2. Changing the heating rate

When manufacturing a second series of samples was fixed sintering temperature (1300 °C), while the process was performed at different heating rates of 10, 15, and 20 °C/min. The holding time and the applied voltage, remained constant at 20 minutes and 40 MPa, respectively. A second series of parameters of the samples are shown in Table 3.

Table 3. Modes of sintering and densities of the samples obtained by SPS.

№	Alloy	Mode of sintering (Temperature, °C - Heating rate, °C/min)	Density (g/cm ³)	Relative density (% TD)
1-2	VNZHK-90	1300-10	16.9	93
2-2		1300-15	16.8	93
3-2		1300-20	16.6	91
4-2	VNZHK-93	1300-10	17.0	93
5-2		1300-15	16.7	92
6-2		1300-20	16.9	93

As can be seen from Table 3, the maximum value of the density in the alloy VNZHK-90 and alloy VNZHK-93 achieved with a minimum heating rate of 10 °C/min. Dependence of density on the rate of sintering of the alloys is shown in Figure 4.

After analyzing the dependencies, it can be concluded that the density of the alloy sintering rate has no effect.

Figure 5 shows the dependence of microhardness for the alloys VNZHK at different heating rates and $T_{\text{sint}} = 1300$ °C.

As shown in the graphs, the light areas corresponding to the clusters of tungsten grains have significantly higher microhardness values, but with an increase heating rate to 100 °C/min are observed their decrease. This phenomenon can be explained by the fact that at low heating rates are formed tungsten grain size is much greater than at high temperatures.

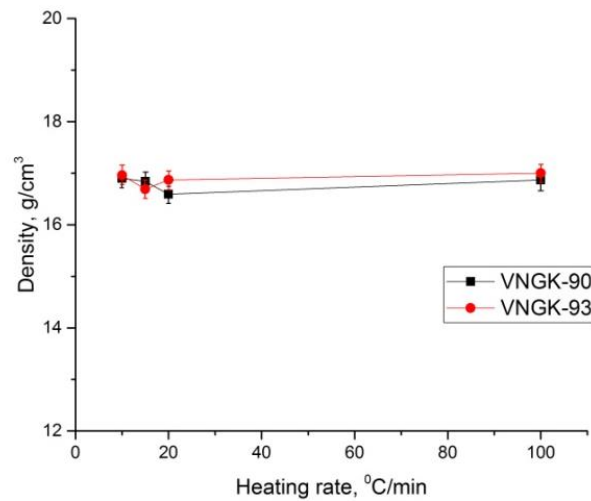


Figure 4. Density dependence on the heating rate of powders.

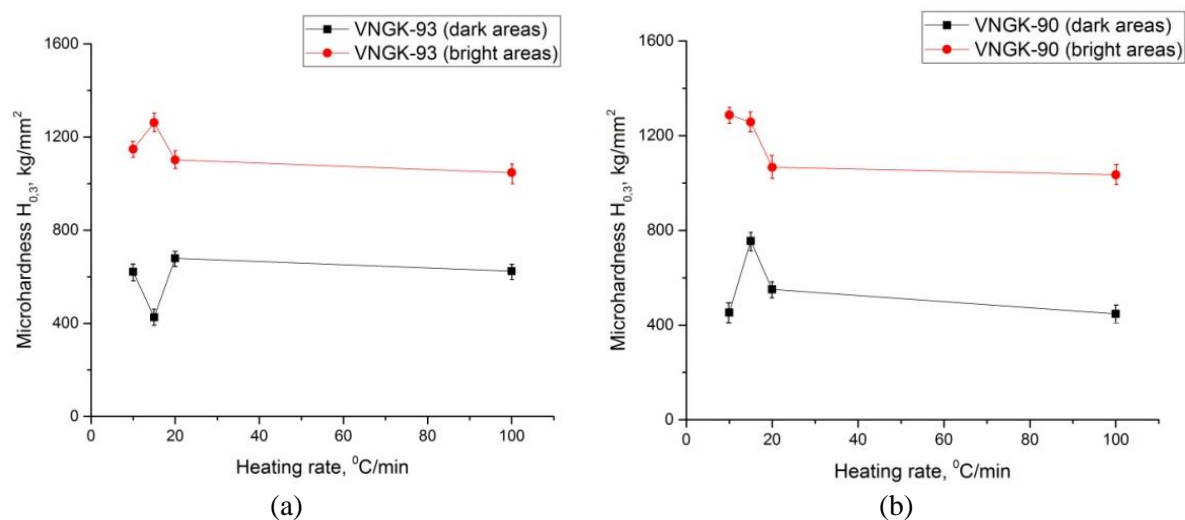


Figure 5. Microhardness dependence of the rate of heating of the powder: *a* – VNZHK-90, *b* – VNZHK-93.

For dark areas that correspond to areas of Ni-Fe-Co ligaments, a tendency to decrease or increase the microhardness of indicators is not observed, because the contribution to the change in value is making only the grain growth of tungsten.

Figure 6 shows the dependence of the strength alloys VNZHK-90 and VNZHK-93 on the heating rate.

It should be noted that these data are correlated depending on the microhardness of alloys. As expected, with a decrease in the heating rate increases the strength characteristics as coarsens grain tungsten. Also, there is a dramatic difference in the values of tensile strength: for the alloy VNZHK-90 (powders obtained by mechanical mixing of the components), the tensile strength values are significantly higher than for the alloy VNZHK-93 (powder obtained by reduction of oxides of the joint). Thus, the mechanical characteristics of the alloys are significantly affected by a method of producing starting powders.

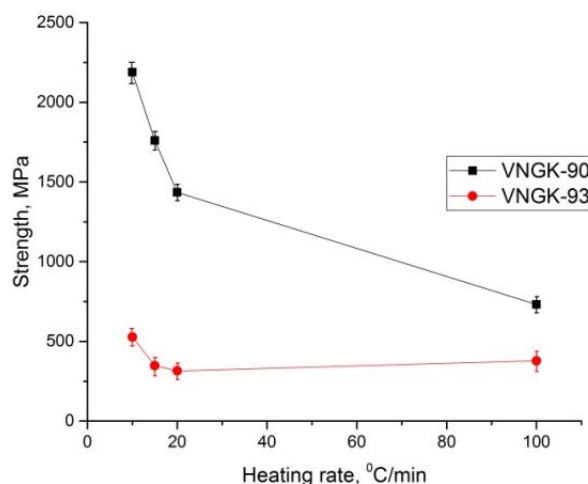


Figure 6. Tensile strength dependence of the rate of heating of the powder.

3. Conclusion

In this paper studied the effect modes spark-plasma sintering on the microstructure and mechanical properties of alloys VNZHK-90 and VNZHK-93. It is found that when spark-plasma sintering achieve the theoretical density of the compacts may heavy alloy by solid phase sintering, as opposed to free sintering at which the maximum density is attained in a melt binder. Was studied the effect of the method of producing powders of sintering kinetics and the final microstructure of the alloy. It is shown that in the case of making a joint reduced mixture of oxides, achieving theoretical density compacts is observed at temperatures up to 200 °C lower than when using a mechanical mixture of powders. It is shown that for the alloys maximum level of mechanical properties when spark-plasma sintering occurs at a sintering temperature of 1300 °C. It is found that the change in the rate of heating does not contribute to change in the density of the samples. At the same time sintering rate has a significant impact on the mechanical properties, due to the more uniform distribution of alloying elements in the more-length-heating. It is shown that the strength of the alloy depends on the morphology of the starting powders. Alloys made from mixtures of powders have high strength values than alloy powders which were obtained by reduction of oxides of the joint.

Acknowledgements

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