Polskie Towarzystwo Materiałów Kompozytowych
Polish Society of Composite Materials
Kompozyty 11: 3 (2011) 268-273
KOMPOZYTY
COMPOSITES

Janusz J. Bucki[1]*, Elżbieta Fortuna-Zaleśna[1], Maciej Kowalczyk[1], Zbigniew Ludyński[2]

[1] Warsaw University of Technology, Materials Science and Engineering Department, ul. Wołoska 141, 02-507 Warsaw, Poland
[2] Orbit Ltd., ul. Heymana 37, 04-483 Warsaw, Poland
** Corresponding author. E-mail: jbucki@inmat.pw.edu.pl*

Otrzymano (Received) 07.05.2011

MAGNETIC PROPERTIES OF TUNGSTEN COMPOSITES

The magnetic properties of three grades of tungsten composites (heavy alloys): W90.3Ni7Fe1.7Co1, W90Ni4Fe2Mo4 and W93Ni5Cu2 were examined. The dependence between the magnetic field and magnetic induction (hysteresis loop) was measured at room temperature. To determine the Curie temperature, the measurements of magnetic induction versus temperature were carried out (in temperature range 180÷700 K). In order to completely describe the materials, microstructural characterization of the composites was performed in terms of the size and volume fraction of tungsten particles and the chemical composition of the matrix. In the case of the W-Ni-Cu composite no hysteresis loop was registered. The dependency between the magnetic field and magnetization was linear. Moreover the measured (mass)magnetizations was at a constant, extremely low level of 0.0006 emu/g in the examined range of temperatures (180÷700 K). The results obtained for this grade confirmed that the material in the whole temperature range was in a paramagnetic state.

The results obtained for two other grades: W90.3Ni7Fe1.7Co1 and W90Ni4Fe2Mo4 showed that they were slightly magnetic. In the case of these materials, the magnetization measured for the field 27000 A/m was at the relatively low level of 700 Gs. Both materials were difficult to saturate. The character of the hysteresis loops prove that at room temperature, the materials are close to ferro/paramagnetic transition. The Curie temperature is approached from the ferromagnetic side, which is confirmed by the plots of magnetization versus temperature. The Curie temperatures for these grades were estimated as 320 and 460 K, respectively. The results confirmed that the composite with a copper addition is a paramagnetic material whereas the two other grades are partially magnetic.

Keywords: **tungsten composites, tungsten heavy alloys, magnetic properties, microstructure**

WŁAŚCIWOŚCI MAGNETYCZNE KOMPOZYTÓW WOLFRAMOWYCH

W pracy badano właściwości magnetyczne kompozytów wolframowych (stopów ciężkich) o trzech składach: W90.3Ni7Fe1.7Co1, W90Ni4Fe2Mo4 i W93Ni5Cu2. W temperaturze pokojowej badano zależność pomiędzy natężeniem pola magnetycznego a indukcją magnetyczną (pętle histerezy). W celu wyznaczenia temperatury Curie mierzono zmiany indukcji magnetycznej w funkcji temperatury (w zakresie 180÷700K). W celu pełnego opisu materiałów scharakteryzowano strukturę badanych kompozytów. Wyznaczono średnią średnicę cząstek wolframowych, udział objętościowy fazy cząstek wolframowych, a także zmierzono skład chemiczny fazy wiążącej.

Ilościowa analiza mikrostruktury wykazała, że wielkość cząstek wolframowych w badanych materiałach znacznie się różni. Najmniejsze cząstki występowały w kompozycie z dodatkiem molibdenu [*E*(*d*) ~11 µm], największą wielkość cząstek zmierzono w kompozycie z dodatkiem miedzi [*E*(*d*) ~25 µm]. Udział objętościowy fazy cząstek wolframowych zależy od zawartości wolframu oraz rodzaju użytych dodatków stopowych. Jak oczekiwano, najwyższy udział fazy cząstek wolframowych (0,87) uzyskano dla kompozytu o najwyższej zawartości wolframu - W93Ni5Cu2. Najniższa zawartość cząstek wolframowych (0,78) występowała w kompozycie o zawartości wolframu 90,3%. W przypadku kompozytu z najmniejszą zawartością wolframu (90%) udział objętościowy fazy cząstek wolframowych był stosunkowo wysoki - 0,86. Pomiary składu chemicznego cząstek wolframowych i osnowy wykazały, że w materiale tym większość molibdenu, dodanego jako dodatek stopowy, rozpuściła się w cząstkach wolframowych, zmniejszając w ten sposób udział fazy wiążącej.

W kompozycie W-Ni-Cu nie udało się zarejestrować pętli histerezy. Zależność pomiędzy polem magnetycznym a magnetyzacją była liniowa, co jest typowe dla stanu paramagnetycznego. Również zmierzone wartości indukcji magnetycznej były na stałym, niskim poziomie - 0,0006 emu/g, w całym zakresie temperatur. Uzyskane wyniki pozwalają na stwierdzenie, że w zakresie temperatur 180÷700 K badany materiał jest paramagnetyczny.

Wyniki uzyskane dla dwóch pozostałych kompozytów: W90.3Ni7Fe1.7Co1 i W90Ni4Fe2Mo4 potwierdziły, że materiały te są nieznacznie magnetyczne. W przypadku obu kompozytów indukcja magnetyczna zmierzona dla natężenia pola magnetycznego 27000 A/m była na relatywnie niskim poziomie 700 Gs. Oba materiały również trudno się nasycały. Charakter uzyskanych pętli histerezy dowodzi, że materiały te w temperaturze pokojowej znajdują się blisko przemiany ferro/paramagnetyk. Temperatura Curie dla tych kompozytów wynosiła odpowiednio około 320 i 460 K. Krzywe zależności magnetyzacji od temperatury zarejestrowane dla tych kompozytów miały szeroki charakter, co świadczy, że przemiana ferro/paramagnetyk zachodzi w sposób stopniowy (nieostry).

Słowa kluczowe: **kompozyty wolframowe, wolframowe stopy ciężkie, właściwości magnetyczne, mikrostruktura**

INTRODUCTION

Tungsten composites, also known as tungsten heavy alloys (WHA) are metal-metal composites produced by liquid phase sintering of mixed tungsten (90÷97%), nickel, iron, copper, molybdenum and cobalt powders. After proper sintering, the material consists of spherical tungsten particles embedded into a solid solution Ni-Fe-W(Co), Ni-Fe-W(Mo) or Ni-Cu-W matrix. These composites exhibit a unique combination of high density (17÷18.6 g/cm^3), high strength (700÷900 MPa), good corrosion resistance, dumping capability, good thermal and electric conductivity and relatively high ductility, which allow them to withstand moderate amounts of cold working. Their properties make them attractive for many applications e.g.: balance weights, welding electrodes, extruding dies, anti-vibration holders for tools and armour penetrators. The ductility and strength of tungsten composites strongly depend on their microstructure, which in turn is controlled by thermal treatment and trace impurity content [1, 2].

Tungsten composites are increasingly used worldwide as radiation shields. They successfully replace lead, formerly used for this application. The advantage of tungsten composites over lead is the combination of radiographic density, machinability, good corrosion resistance, high radiation absorption, high strength, high melting temperature and, what is always emphasized, lack of toxicity. WHA can provide the same protection as lead with a significantly reduced thickness of the wall of the shields and containers. They are stable at high temperatures, which is important in case of fire, and they are characterized by good mechanical properties. These characteristics result in that this group of materials is used in such applications as: collimators, isotopes containers and different kinds of shields: e.g. syringe shields or nuclear shielding. They are utilized in geologging, pipe-line gamma inspection, industrial radiography, homeland security and border control as well as radiation shielding used in cancer treatment.

For specific applications, the magnetic properties of WHA are important. Non-magnetic materials have to be used whenever the magnetic fields cannot be perturbed in radiation equipment or when shielding is positioned near electrical sensors.

MATERIAL AND EXPERIMENTAL PROCEDURE

The weight percentage compositions of the composites used in this examination were: (I) W90.3Ni7Fe1.7Co1, (II) W90Ni4Fe2Mo4 and (III) W93Ni5Cu2. The materials were examined in an as-sintered condition.

The microstructures of the composites were examined by means of scanning electron microscopy (SEM HITACHI S-3500N equipped with Thermonoran EDS). The investigations included observations of the materials structure and measurements of the chemical composition of the matrixes. The registered pictures (at magnification 500x) were analysed by the image analysis programme Micrometer [3]. The measured parameters included the mean tungsten grain size $E(d)$ and the fraction of tungsten particles V_V. Additionally, Rockwell hardness measurements were conducted.

Magnetic measurements of the studied materials were done in two stages. First, the dependency between the magnetic field and magnetization (hysteresis loop) was measured using a loop tracer [4]. A magnetic field in the range of +27000 A/m to –27000 A/m was produced inside a wired coil, where the sample was inserted. The response of the sample was studied on the basis of a signal received from the pick-up coils, situated close to the investigated materials. The whole unit was controlled by a computer. All data were collected using designated software.

Secondly, magnetic induction versus temperature measurements were carried out. Those measurements were done with a constant field of 8000 A/m and in the temperature range between 180 and 700 K. This investigation was conducted by means of the Physical Property Measurement System by Quantum Design (San Diego) with a VSM Module. The samples were placed inside a superconducting coil. The temperature was controlled on the basis of equilibrium between the cold vapours of helium and energy given by a heater situated close to the measured material.

RESULTS

The SEM images of the investigated composites microstructures are presented in Figure 1. The data obtained from the image analyses, measurements of the chemical composition of the matrixes and hardness measurements are given in Tables 1-3, respectively.

A quantitative description of the microstructures given in Table 1 shows that the grain size in the examined materials differs significantly. The smallest tungsten grains were present in the composite with the molybdenum addition [$E(d)$ ~11 μm], whereas the largest grain size, [$E(d)$ ~25 μm] was revealed in the sample with copper as the alloying element. The volume fraction of tungsten particles depends on the tungsten content and alloying elements. As expected, the highest volume of tungsten particles (0.87) was revealed in the sample with the highest tungsten content - W93Ni5Cu2. The lowest fraction of tungsten (0.78) particles was in sample I, with tungsten content 90.3%. A little surprising was the fact that in sample II with a relatively low tungsten content (90%), the fraction of tungsten particles was high - 0.86. The measurements of the chemical composition of both tungsten particles and the matrix revealed that in sample II most of the molybdenum, added as an alloying element, dissolved in the tungsten particles, thus reducing the matrix volume. The tungsten particles contained molybdenum, whereas its concentration in the matrix was low.

The hardness of all the samples was at a similar level, around 24 HRC.

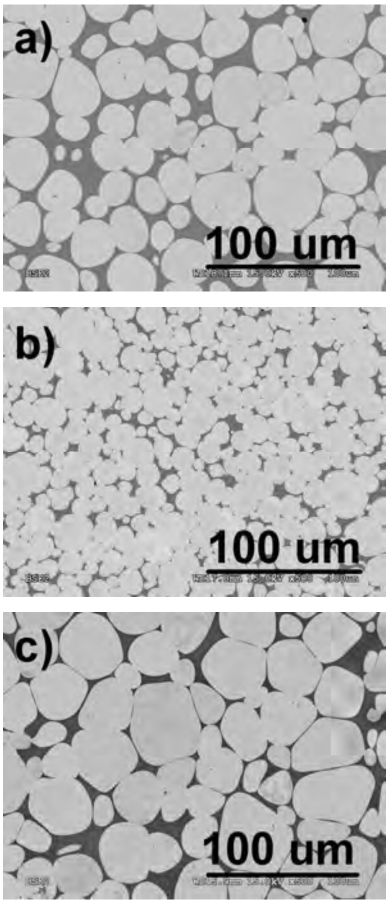


Fig. 1. SEM images of cross sections of: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4, c) W93Ni5Cu2 composites

Rys. 1. Obrazy mikrostruktury kompozytów: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4, c) W93Ni5Cu2

TABLE 1. **Data obtained from image analyses (average tungsten grain size $E(d)$ and volume fraction of tungsten particles V_V)**

TABELA 1. **Dane uzyskane z analizy obrazu (średnia średnica cząstek wolframowych $E(d)$ i udział objętościowy cząstek wolframowych V_V)**

Sample	*E*(*d*) [μm]	*Vv*
I	19.9 ± 0.5	0.78
II	10.9 ± 0.1	0.86
III	25.3 ± 0.9	0.87

TABLE 2. **Results of measurements of chemical composition of matrixes**

TABELA 2. **Wyniki pomiarów składu chemicznego osnowy badanych stopów**

Sample	Chemical composition [wt. %]					
	W	Fe	Ni	Co	Cu	Mo
I	48.1	11.5	36.0	4.4	-	-
II	33.7	19.5	40.1	-	-	6.7
III	42.0	-	47.0	-	11.0	-

TABLE 3. **Results of Rockwell hardness measurements**

TABELA 3. **Wyniki pomiarów twardości metodą Rockwella**

Sample	Hardness [HRC]
I	24 ± 1
II	25 ± 2
III	24 ± 1

The measured hysteresis loops are presented in Figure 2, whereas the diagrams of magnetic induction plotted against temperature are shown in Figure 3.

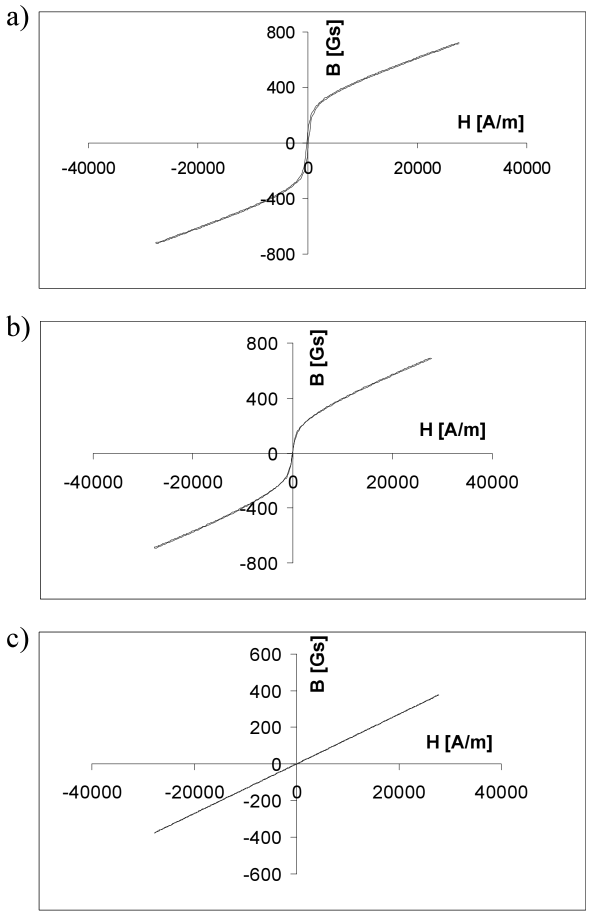


Fig. 2. Magnetic induction *B* [Gs] vs. applied field *H* [A/m] for: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4, c) W93Ni5Cu2

Rys. 2. Zależność indukcji magnetycznej *B* [Gs] od natężenia pola magnetycznego *H* [A/m] dla stopów: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4, c) W93Ni5Cu2

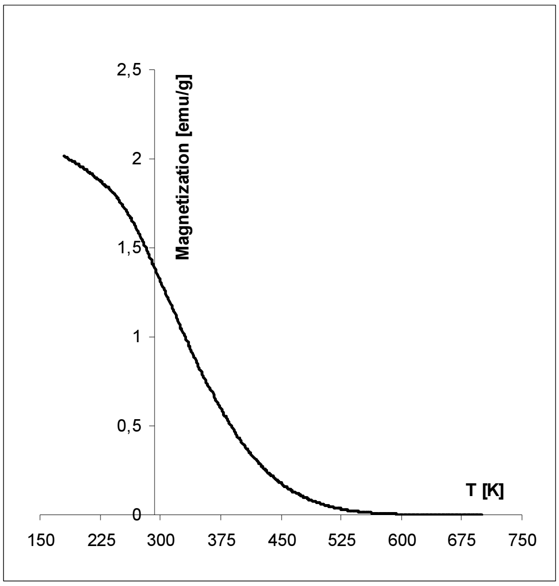
The linear dependence between applied field H and magnetic induction B proves that at room temperature, the composite with the copper addition is paramagnetic.

For composite I and II hysteresis loops were registered. In the range of the applied field, the materials designated as I and II did not saturate/were not saturated (although they were close to the saturation state). The low (small values of *B*) hysteresis loops prove that at room temperature, the materials are close to ferro/paramagnetic transition. At room temperature, the materials exhibit weak ferromagnetic properties typical for the temperature range close to the Curie temperature. The materials are still in a ferromagnetic state, but an increase of temperature induces ferro/paramagnetic transformation.

Magnetization measured at room temperature for the field 27 000 A/m for composites I and II is equal to 720 and 690 Gs, respectively. For comparison, in the same conditions, iron would be saturated with a magnetization of 2.17 T (217 000 Gs).

The shape of the registered loops, as well as the low values of magnetic induction, indicate that the examined materials are very low magnetic. The composites are also difficult to saturate.

a)



b)

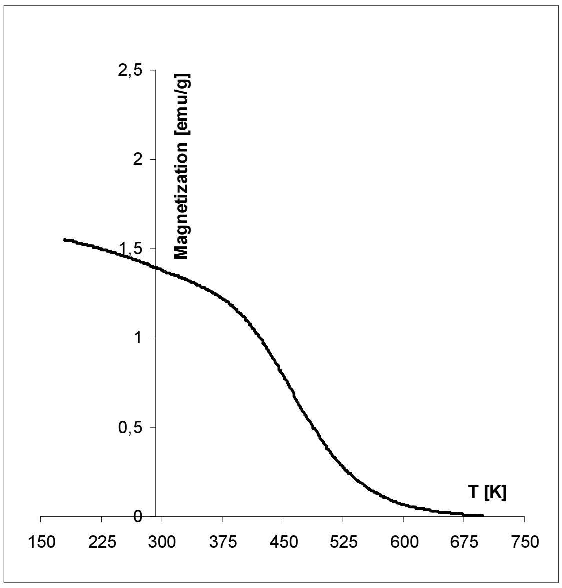


Fig. 3. Plots of (mass)magnetization [emu/g] vs. temperature [K] for: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4

Fig. 3. Wykresy indukcji magnetycznej [emu/g] w funkcji temperatury [K] dla: a) W90.3Ni7Fe1.7Co1, b) W90Ni4Fe2Mo4 w przeliczeniu na 1 gram

The registered values of (mass)magnetization for composite III, with a copper addition were in the range of 0.00061 to 0.00068 emu/g. Such low magnetization values prove that in the measured range of temperatures, the material is in the paramagnetic state.

In the case of the composite with molybdenum, the estimated Curie temperature is 460 K and the material is in the ferromagnetic state at room temperature. In the case of composite I, the estimated Curie temperature is 320 K. This composite at room temperature is already in the transition region. The curves registered for composites I and II are very broad, which indicates that the ferro/paramagnetic transition for these composites is not sharp.

At room temperature, for the applied field 8000 A/m, the measured (mass)magnetization values were equal to 1.4, 1.38 and 0.0006 emu/g, for composites I, II and III, respectively (for this field, materials are not saturated). For comparison, the (mass)magnetizations for Fe, Co and Ni are equal to 218, 161 and 53.4 emu/g, respectively [5].

DISCUSSION

Tungsten composites are fabricated from non magnetic materials like tungsten and copper and ferromagnetic materials like iron, cobalt and nickel.

In literature there is very little information concerning the magnetic properties of tungsten heavy alloys. Usually, their description is limited to the statement that the magnetic properties of particular grades are “nil” in the case of W-Ni-Cu composites or “slightly magnetic” for W-Ni-Fe(Co, Mo) composites. Since it is commonly known that the mechanical properties of W-Ni-Fe grades are superior in comparison to W-Ni-Cu ones, it is important to know if in specific applications these “slightly magnetic” properties could disturb the proper functioning of equipment. This was the reason to examine the magnetic properties of composites produced in Poland and planned to be utilized as radiation shields.

The authors have examined in the past the magnetic properties of W-Ni-Fe-Co alloys [6] in order to check if the measurements of the magnetic properties could be a method for on line testing or estimating the properties of produced heavy alloys which is routinely done in the case of cemented carbides. In that work, saturation, coercivity as well as the Curie temperature of several composites were determined. The results showed that the magnetic properties of the examined composites were low. In the case of some grades, the cold working did not influence the Curie temperature, for the other as-sintered composites, they showed lower magnetic properties. The measured Curie temperatures changes in the range of 55 to 245^{o}C.

Interesting information is presented in Tungsten Products “Tungsten heavy alloys design manual” [7]. The magnetic properties of composites offered by the company are described by magnetic permeability. The grades with a magnetic permeability equal to 1 μ are described as “non magnetic”, the grades with this parameter higher than one are classified as “magnetic”.

What is interesting, the magnetic properties of grades produced by Tungsten Products depends on the Ni/Fe ratio. The 3Ni/Fe grades have magnetic permeability at the level of 1 μ, whereas the 7Fe/Ni grades could have this value above 6 μ, depending on the tungsten content. This is in agreement with the results presented in [6]. The composites with a higher iron content had both higher coercivity and Curie temperature.

CONCLUDING REMARKS

In the present work, the magnetic properties of three grades of tungsten composites, namely: (I) W90.3Ni7Fe1.7Co1, (II) W90Ni4Fe2Mo4 and (III) W93Ni5Cu2 were examined. The materials were examined in an as-sintered condition. Magnetic measurements were done in two stages. In the first step, the dependency between the magnetic field and magnetization (hysteresis loop) was measured. Secondly, magnetization versus temperature measurements were carried out in order to determine the Curie temperature.

In the case of the W-Ni-Cu composite, no hysteresis loop was registered. The dependency between magnetic field and magnetization was linear. Additionally, the measured (mass)magnetizations were at a constant, extremely low level of 0.0006 emu/g in the whole temperature range. The results obtained for this grade confirmed that the material in the examined range of temperatures, 180÷700 K, was in a paramagnetic state.

The results obtained for two other grades: W90.3Ni7Fe1.7Co1 and W90Ni4Fe2Mo4 confirmed that they were slightly magnetic. In the case of these materials, the magnetization measured for the field of 27000 A/m was at the relatively low level of 700 Gs. Both materials were difficult to saturate. The character of the hysteresis loops prove that the materials are close to ferro/paramagnetic transition. The Curie temperature is approached from the ferromagnetic side, which is confirmed by the plots of magnetization versus temperature. The Curie temperatures for these grades were estimated as 320 and 460 K, respectively.

Acknowledgements

This work has been financially supported by the National Centre for Research and Development under contract NR15-0052-10/2010.

REFERENCES

[1] Rabin B.H., Bose A., German R.M., Characteristic of liquid phase sintered tungsten heavy alloys, Int. J. of Powder Met. 1989, 25, 21-27.

[2] Edmonds D. V., Structure/property relationship in sintered heavy alloys, Refractory Metals and Hard Materials 1991, 10, 15-26.

[3] Wejrzanowski T., Computer Assisted Quantitative Description of the Functionally Graded Materials, Master's Thesis, Warsaw University of Technology, Warsaw 2000.

[4] Kulik T, Savage H.T., Hernando A.J., A high performance hysteresis loop tracer, J. Appl. Phys. 1993, 73, 6855-6857.

[5] Cullity B.C., Graham D.C., Introduction to magnetic materials, second edition, John Wiley & Sons 2009.

[6] Bucki J.J., Ludynski Z., Karwata T., Testing of magnetic properties of tungsten heavy alloys, Proc. of European Conf. on Advanced Powder Metallurgy Materials, October 1995, Birmingham, UK, 347-350.

[7] Caldwell S.G., Tungsten Heavy Alloy Design Manual, Tungsten Products Company, http://www.hep.princeton.edu /~mcdonald/e166/Walz/Design%20Manual%20WHA %20.doc

