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(54) A POWDER MATERIAL WITH MAGNETIC PROPERTIES AND THE METHOD OF PREPARATION OF THE POWDER MATERIAL WITH MAGNETIC PROPERTIES TO BE USED FOR MANUFACTURING COMPOSITE PRODUCTS

(57) A material in the form of a powder with magnetic properties, according to the invention, is characterised in that it is a nano-structural cermet powder in a Ti-Mo-C-Ni system and it comprises 6-70 mass% nickel in proportion to the sum of the mass of constituent elements containing molybdenum and titanium carbides, with the Mo/Ti ratio between 0.1 and 0.4 g/g.

The method of preparation of the material in the form of a powder with magnetic properties to produce composite products by mixing and soaking powders, characterised in that nano-structural powders of molybdenum oxide and titanium oxide with the MoO_3/TiO_2 mass content of 0.1÷0.4 and a carbon material in the amount of above 45 mass% are mixed, and then a nickel powder in the amount of 3÷40 mass%, relative to the mixture mass of titanium and molybdenum oxides and carbon. Then all constituent elements are ground under inert atmosphere, in ambient temperature to homogenise. The resulting product of grinding is isothermally soaked in the temperature range of 1050 - 1500°C, under inert atmosphere, for 2 - 5 h to produce a nano-structural cermet powder in the Ti-Mo-C-Ni system.

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Description

[0001] The subject of the invention is a powder material with magnetic properties and the preparation method of the powder material with magnetic properties to be used for manufacturing composite products, such as polymer, ceramic and cermet composites which can be used as alternative catalysts, instead of noble metals, in a variety of reactions, including CO_2 reduction, hydrogenation reactions, desulphurisation, denitriding (removal of sulphur and/or nitrogen compounds from industrial wastes and liquid fuels, i.e. petrol and/or crude oil), isomerisation of hydrocarbons, steam reforming, hydrodeoxygenation (HDO), recycling of industrial wastes in the paper industry, production of hydrogen, magnetic resonance imaging in biomedicine, and for adsorption processes.

[0002] WO2005053881 provides information about a magnetic iron-based powder which contains niobium (formerly columbium), silicon, calcium, manganese, magnesium, carbon, boron, aluminium, titanium, molybdenum, chromium, copper, gold, nickel, vanadium, phosphorus, or their combinations. The material can be used in dampeners, containing a chamber and a piston that reciprocates in the chamber. The patent description PL115937 discussed a nickel-based magnetically soft alloy which contains 75.5-76.5 wt% Ni, 0.3-0.6 wt% Mn, max 0.015 wt% C, max 0.008 wt% S, 2.5-3.5 wt% Mo, 4.8-5.8 wt% Cu, 2.5-3.5 wt% Nb, 1.7-2.3 wt% Ti, max 0.01 wt% Zr, 0.1-0.3 wt% Si, max 0.008 wt% P, max 0.01 wt% O_2, with the rest being made up of Fe. Induction smelting of the alloy is conducted in vacuum furnaces. Zackrisson, A. Larsson and H.-O. Andren in Microstructure of the Ni binder phase in a TiC-Mo2C-Ni cermet; Micro,32 (2001) 707-712, discussed a cermet composite whose Ni binder phase contains TiC (titanium carbide) and Mo_2C. The cermet composite can be treated as an attractive material used in heavy-duty cutting tools. The composite is produced using Ti, Mo and Ni powders at the proportions of 49, 15, 14, respectively (22 wt%), sintered in vacuum at 1520°C for 90 min. YoungKwan Kim, Jae-HyeokShim, Young WhanCho, Hyo-Seung Yang and Jong-Ku Park in Mechanochemical synthesis of nanocomposite powder for ultrafine (Ti, Mo)C-Ni cermet without core-rim structure, International Journal of Refractory Metals & Hard Materials 22 (2004) 193-196, discussed a cermet composite whose Ni binder phase contains ultra fine (Ti,Mo)C titanium carbide. The cermet composite can be treated as an attractive material used in heavy-duty cutting tools. While it contains 80 mass % TiC and 20 mass % nickel, the cermet composite is produced using Ti, Mo, graphite and Ni powders in the process of mechanochemical grinding in a high speed grinder, sintered in vacuum at 1420°C for 2 h. Jon-Erik Mogonye in Solid Lubrication Mechanisms in Laser Deposited Nickel-Titanium-Carbon Metal Matrix Composites. Master of Science, University of North Texas, December 2012, discussed Ni-Ti-C composites obtained with Laser Engineered Net Shaping (LENS), one of rapid prototyping technologies. The resulting Ni-TiC-Graphite is characterised with a low friction coefficient (0.1) and with higher hardness and wear resistance than those of pure nickel obtained in the same conditions. Jasmine Imani Keene in Characterization of a Ti(Mo)C-Ni Cermet for Use in Impact Resistant Sandwich Panels, a thesis presented to the faculty of the School of Engineering and Applied Science University of Virginia, December 2013, discussed a formation method of Ti(Mo)C-Ni composite panels with a cellular structure, characterised with high compression strength of 2.7 GPa, elasticity module of 380 GPa, flexural strength of 520 GPa and fracture toughness of 15 $MPa \cdot m/^{1/2}$. The composite is made up of carbide ceramics (83 vol%), a Ni binder phase (15 vol%) and pores (1.6 vol%). M. M. Kulak and B. B. Khina in Selfpropagation high-temperature synthesis in the Ti-C-Ni-Mo system on application of powerful ultrasound, Journal of Engineering Physics and Thermophysics,87(2) (2014) 333-343, discussed a method of lowering the synthesis temperature of a cermet composite in the process of Self-Propagating High Temperature Synthesis in a Ti-C-Ni-Mo system, owing to ultrasounds, an additional source of energy.

[0003] Y. F. Yang, S. B. Jinb and Q. C. Jiang in Effect of reactant C/Ti ratio on the stoichiometry, morphology of TiCx and mechanical properties of TiCx-Ni composite; Cryst Eng Community, 2013, 15, 852-855; DOI: 10.1039/c2ce26767e reported a method of formation of a composite containing TiC in the Ni binder phase. According to the method, 30 mass% of 50 μm nickel powder, 25 μm titanium and 20 nm multi-walled nanotubes are mixed. At the first stage, the powders were pressed to achieve 75% of theoretical density. At the second, they were heated in vacuum at the rate of 40 deg/min until they achieved the temperature of self-ignition, kept at the temperature for 30 sec and then cooled down to room temperature. Composites with a stoichiometric mole ratio of C/Ti had the most favourable mechanical properties, including hardness (12.6 GPa), flexural strength (270 MPa) and fracture toughness (9.8 $MPam^{1/2}$). T. Viatte, T. Cutard, G. Feusier and W. Benoit in High Temperature Mechanical Properties of Ti(C, N)-Mo2C-Ni Cermets Studied by Internal Friction Measurements, Journal de Physique IV, Colloque C8, supplement au Journal de Physique 111, Volume 6,1996; Stellram S.A., Rte de lIE-traz, 1260 Nyon, Switzerland, discussed a method of obtaining a Ti(C,N)-Mo2C-Ni composite with good mechanical and chemical toughness when applied in high speed cutting tools. The composite was sintered at 1723K for 120 min, including 60 min using the HIP method, at 30 bar, under argon atmosphere. The nickel content was 10 mass%, i.e. approximately 6.4 vol%. At high temperature background, molybdenum had a favourable effect on the hardness of the binder phase and positive influence on the relaxation and long distance displacements. MA Qian and L.C. Lim in On the disappearance of Mo2C during low-temperature sintering of Ti(C,N)-Mo2C-Ni cermets, Journal of materials science, 34 (1999) 3677 - 3684, discussed a mechanism of Mo_2C disappearance in nickel during the sintering of Ti(C,N)-based or TiC-based cermets at 1200 °C in vacuum. J.C. LaSalvia, D.K. Kim, R.A.Lipsett and M.A. Meyers in Combustion Synthesis in the Ti-C-Ni-Mo System: Part I, Micromechanisms, Metallurgical and materials transactions A, 26A (1995) 3001-3009, discussed a synthesis mechanism of TiC composites whose Ni binder phase is characterised with varied morphology, depending on SHS process conditions. Mart Viljus, Jüri Pirso, Kristjan Juhani and Sergei Letunovitś in Structure Formation in Ti-C-Ni-Mo Composites during Reactive Sintering, Materials science (MEDZIAGOTYRA), 18(1) (2012) 62-65, discussed a method of forming Ti, Ni, M and C composites with a method of reactive sintering of nano-structural Ti, Ni, M and C powders, with varied phase composition and morphology depending on technological parameters. The composites have a better microstructure and are cheaper, compared to their conventionally obtained counterparts. Hiroyuki Hosokawa, Kiyotaka Katou, Koji Shimojima, Ryoichi Furushima and Akihiro Matsumoto in Effect of Ni Contents on Microstructures and MechanicalProperties for (Ti0.8Mo0.2)C-Ni Cermets, Materials Transactions, 55(9) (2014)1451 - 1454, discussed composites with varied nickel content (10-40 mass%) formed using the mechanical alloying method in which at the I phase Ti, Mo and C powders were mixed and at the second phase Ti, Mo, C and Ni powders were mixed for 72 and 96 h, respectively. The hardness of the composite was found to decrease with a decreasing nickel content and its fracture toughness was increasing as the grinding was progressing.

[0004] The mechanical properties of (Ti,Mo)C- composites (a Ni-based solid solution) are partly known. However, there exists no body of literature on methods of formation of Ti-Mo-C-Ni systems with attractive magnetic features.

[0005] A material in the form of a powder with magnetic properties, according to the invention, is characterised in that it is a nano-structural cermet powder in a Ti-Mo-C-Ni system and it comprises 6-70 mass% nickel in proportion to the sum of the mass of constituent elements containing molybdenum and titanium carbides, with the Mo/Ti ratio between 0.1 and 0.4 g/g.

[0006] The purpose of the present invention is a method of preparation of a material in the form of a powder with magnetic properties to produce composite products. The present invention is characterised in that through mixing and soaking of powders a mixture of nano-structural powders of molybdenum oxide and titanium oxide is formed, with the MoO_3/TiO_2 mass proportion in the range of $0.1 \div 0.4$ and carbon material in excess of 45 mass%. In the following stage, $3 \div 40$ mass% nickel powder relative to the mass of the mixture is added and then the whole mixture is being ground under inert atmosphere, at ambient temperature to homogenise. Then, the resulting product of grinding is isothermally soaked in the temperature range of 1050 - 1500°C, under inert atmosphere (e.g. that of argon), for 2 - 5 h to form a nano-structural cermet powder in a Ti-Mo-C-Ni system.

Activated carbon and/or black carbon and/or nano-structural carbon is used as the carbon material.

The reduction of nickel oxides occurs at the temperature of approximately 700°C, the carbothermal reduction of molybdenum oxide occurs at 900°C and above 1050°C the carbothermal reduction of titanium oxides to titanium carbide takes place. While TiC is being formed, a cermet powder is formed. The powder contains, among others, (Ti,Mo)C phases, Ni alloy and elemental carbon (C), which is easy to remove.

[0007] The advantage of the invention is that powder obtained in this way displays specific magnetic properties, i.e. paramagnetism, ferromagnetism, antiferromagnetism and superparamagnetism while at the same time it is accompanied by attractive mechanical properties, such as high hardness. The solution can be obtained at the phase boundary, i.e. an intermediate layer is formed on the surface of ceramic and metal particles which binds the base with the reinforcement which provides conditions enabling the consolidation of the elements of the composite which is characterised with attractive mechanical and magnetic properties.

The material obtained according to the invention has different magnetic sources (which was confirmed in EPR examinations). Several magnetic phenomena, such as paramagnetism, ferromagnetism, (anti)ferromagnetism and superparamagnetism were determined in investigated samples. Magnetic ions (Ti ions) are formed in the material obtained according to the invention. The samples contained the phases of (Mo,Ti)C and Ni displaying different magnetic properties.

The powder material is magnetically dense, comprises nanoparticles for whom surface effects are of significance and nanoparticles form agglomerates.

[0008] The invention is presented in more detail in the below examples of synthesis and graphically in Fig. 1 showing EPR spectrum of "A" sample, Fig. 2 showing charts of integrated intensity and its reverse of "A" sample, Fig. 3 showing the total width of EPR line (the line consists of a minimum of two lines) and g, a spectroscopic factor, in the function of temperature for "A" sample, Fig. 4 showing the dependence of magnetic susceptibility on temperature, measured in decreasing temperature conditions with field cooling and with zero field cooling for "A" sample, Fig. 5 showing hysteresis loops taken at 52K and 150K for "A" sample, Fig. 5a showing chart close ups from Fig. 5 which present the values of coercive field and residual, Fig. 6 showing magnetic susceptibility in the function of temperature for "B" sample in FC and ZFC modes, in the magnetic field of 1000 Oe; the insert presents ZFC points in the temperature range of 5-55K with an adjusted Curie - Weiss curve, Fig. 7 showing the magnetic hysteresis of "B" sample, recorded at 160K (blue squares and lines) and at 290K (red squares and lines), the insert presents a close-up of the area in the neighbourhood of zero, Fig. 8 showing the values of coercive field and residual for "B" sample (90K), Fig. 9 showing magnetic susceptibility in the function of temperature for "C" sample in FC and ZFC modes, in the magnetic field of 1000 Oe, Fig. 10 showing the magnetic hysteresis of "C" sample, recorded at 75K, Fig. 11 showing the values of coercive field and residual for "C" sample (75K), Fig. 12 showing the EPR spectrum of "C" sample, Fig. 12a showing the EPR spectrum of "B" sample, Fig. 13 showing integrated intensity in the function of temperature for "C" sample and its reverse (inserts), Fig. 13a showing integrated intensity in the function of temperature for "B" sample and its reverse (inserts) and Fig. 14 showing the width of EPR line and the resonance position of the line in the function of temperature for "B" sample.

[0009] A discussion about the properties of materials according to examples I - III: Fig. 1 showing the EPR spectrum of "A" sample from example I. EPR examination was carried out in the temperature range of 3.75K - 290K. "A" sample is characterised with an asymmetric and wide spectrum, containing signals from different phases. Up to the temperature of ~50 K, the spectrum does not change significantly. However, when temperature increases in excess of 50K, one of its spectral components is shifted, its amplitude [increase] and line width [decrease] are distinctly changed. Fig. 2 shows the dependence of integrated intensity in the function of temperature, which corresponds to the so-called EPR magnetic susceptibility. Up to the temperature of ~20K, a typical behaviour, common to a paramagnetic material, is observed (intensity decreases along with the temperature). The analysis of reverse integrated intensity charts demonstrates that an approximated value of the Curie-Weiss parameter T_{CW} = - 102 K is obtained which reveals strong antiferromagnetic interactions in the sample. Above 20K, integrated intensity increases as temperature goes up to 260K and then suddenly soars above it. As shown, the total width of EPR line undergoes insignificant changes up to the temperature of ~100 K and then it decreases which it characteristic to ions whose rate of relaxation increases along with temperature. A similar change at ~100 K is observed for the dependence of the spectroscopic factor on temperature (g parameter) (Fig. 3). Fig. 4 shows the dependence of magnetic susceptibility on temperature, measured in decreasing temperature conditions with field cooling and with zero field cooling for "A" sample from example I. Fig. 5 shows hysteresis loops taken at 52K and 150K for "A" sample from example I. The magnetic susceptibility of samples was examined in decreasing temperature conditions with field cooling and with zero field cooling. As can be seen in Fig. 1, sample cooling with field cooling causes an increase of the sample's magnetic susceptibility. The spectrum can be divided into three temperature intervals:

- ~2 K-50 K
- ~55 K - 120 K
- ~125 K - 300 K

The three intervals probably reflect three magnetic phases present in the sample. The first phase which affects the shape of magnetic susceptibility in the temperature range up to 50K is paramagnetic in its character [as shown by EPR examinations] (Fig. 2). Strong antiferromagnetic interactions are observed in this phase. The other two phases have superparamagnetic properties. The phase with the largest percentage share and the smallest nanoparticle size provides a strong superparamagnetic signal with the blocking temperature of ~240 K. The other phase provides a superparamagnetic signal in the temperature range of 55K - 120K.

Fig. 5 below shows the close-ups of chart parts which display the values of coercive field and residual for "A" sample from example I. The presence of superparamagnetic phases confirms the presence of coercive field and residual, observed in hysteresis loops taken for the sample at 52K and 150K. The coercive fields were H_c=~48 Oe and H_c=~35 Oe, and residual values were B_r=~$1.8x10^{-3}$ and B_r=~$1.5x10^{-3}$, respectively (Fig. 5). Saturation magnetisation occurs in the temperature range of 52K - 150K. A rapid increase of sample magnetisation (which occurs in a narrow band of 2000 Oe) can provide evidence for very weak dipole-dipole forces among nanoparticles interacting with one another.

Fig. 6 shows magnetic susceptibility in the function of temperature for "B" sample from example II, in FC and ZFC modes, in the magnetic field of 1000 Oe, with the insert presenting ZFC points in the temperature range of 5-55K, with an adjusted Curie - Weiss curve. Fig. 7 shows the magnetic hysteresis of "B" sample from example II, recorded at the temperature of 160K (blue squares and lines) and 290K (red squares and lines), with the insert showing a close-up of the area in the neighbourhood of zero.

Figs. 9-11 show results obtained for "C" sample from example III. Figs. 12-14, for comparison purposes, show measurement results for "C" and "B" samples. The presence of superparamagnetic phases confirms the presence of coercive field and residual, observed in hysteresis loops taken for "B" and "C" samples at 75K and 90K. The coercive fields were H_c=~46 Oe and H_c=~37 Oe, and residual values were B_r=~$4.9x10^{-3}$ and B_r=~$10x10^{-3}$, respectively (Figs. 8 and 11).

The analysis of magnetic susceptibility up to 70K demonstrated that the Curie-Weiss temperature for "C" sample in FC and ZFC modes was respectively -5.12 K and -1.5 K while that of "B" sample was respectively -21.8 K and -6.54 K. The results demonstrate that "C" sample displays weak and "B" sample displays strong antiferromagnetic interactions.

The magnetic properties of "B" and "C" samples are very similar to those of "A" sample. EPR examinations were conducted on obtained materials, using an EPR spectrometer, manufactured by Brucker ELEXSYS E 500 CW (9.4 GHz, 100 frequencies of 100 kHz magnetic field modulation), operating in X band. EPR measurements for "A" sample were performed at temperatures from helium to room, and for "B" and "C" samples at temperatures from nitrogen to room. A helium-nitrogen cryostat, Oxford Instruments, was used in the examinations. The analysis of temperature dependence of EPR spectra was conducted by determining the total insensitivity of EPR line, its width and the value of the spectroscopic parameter g, which determines the location of the middle of resonance line.

[0010] Magnetic measurements were conducted using a SQUID MPMS-7 magnetometer, in the temperature range of 2 - 300K in different magnetic fields, in the following modes: a) with field cooling, b) with zero field cooling.

EXAMPLE I

the synthesis of Mo-Ti-C/Ni powder (marked with "A" code)

[0011] A mixture of anatase-TiO_2 (~30nm), MoO_3 oxide (~20nm) and black coal in the mass content of 0.5; 0.05; 0.45, respectively, was mixed with a nickel microcrystalline powder, with the mass content of 0.03 g/g. To homogenise the powder, the mixture was ground for approximately 5 min and then soaked under argon atmosphere at 1500°C, for approximately 2 h. During soaking, a cermet powder is formed. During soaking, a (Ti,Mo)C-*6 mass*%Ni cermet powder is formed and excess carbon.

[0012] The obtained material is characterised by the content of Mo/Ti=0.10 [g/g].

EXAMPLE II

the synthesis of Mo-Ti-C/Ni powder (marked with "B" code)

[0013] A mixture of anatase-TiO_2 (~30nm), MoO_3 oxide (~20nm) and carbon in the mass content of 0.2; 0.07; 0.73, respectively, was mixed with a nickel microcrystalline powder, with the mass content of 0.4 g/g. To homogenise the powder, the mixture was ground for approximately 5 min and then soaked under argon atmosphere at 1050°C, for approximately 5 h. During soaking, a cermet powder is formed. During soaking, a (Ti,Mo)C-*70 mass*%Ni cermet powder is formed and excess carbon.

[0014] The obtained material is characterised by the content of Mo/Ti=0.40 [g/g].

EXAMPLE III

the synthesis of Mo-Ti-C/Ni powder (marked with "C" code)

[0015] A mixture of anatase-TiO_2 (~30nm), MoO_3 oxide (~20nm) and amorphous carbon in the mass content of 0.35; 0.07; 0.58, respectively, was mixed with a nickel microcrystalline powder, with the mass content of 0.2 g/g. To homogenise the powder, the mixture was ground for approximately 5 min and then soaked under argon atmosphere at 1200°C, for approximately 3.5 h. During soaking, a (Ti,Mo)C-*40 mass*%Ni cermet powder is formed and excess carbon.

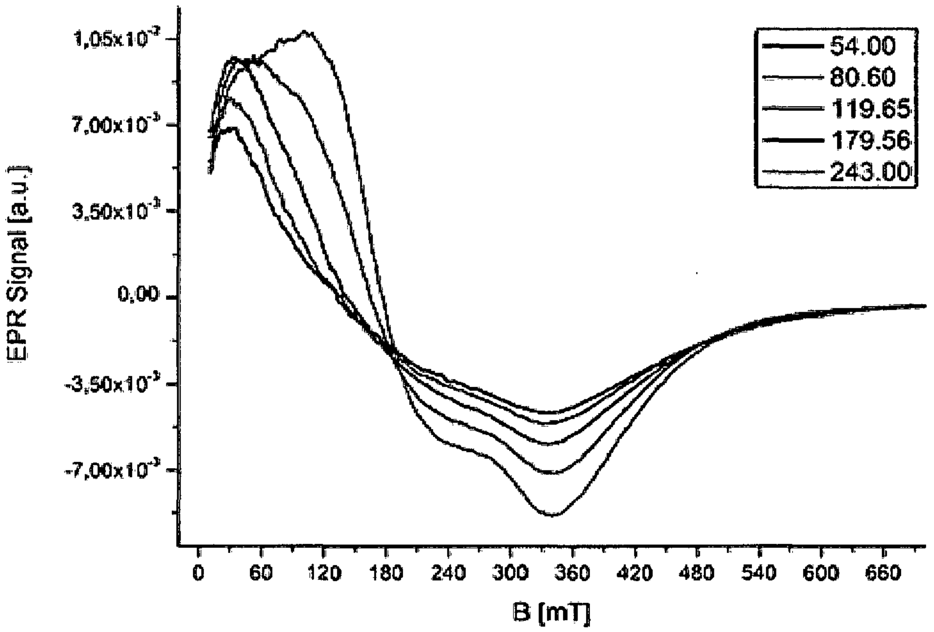
[0016] The obtained material is characterised by the content of Mo/Ti=0.20 [g/g].

Claims

1. A material in the form of a powder with magnetic properties, **characterised in that** it is a nano-structural cermet powder in a Ti-Mo-C-Ni system and it comprises 6-70 mass % nickel in proportion to the sum of the mass of constituent elements containing molybdenum and titanium carbides, with the Mo/Ti ratio varying between 0.1 and 0.4 g/g.

2. The method of preparation of the material in the form of a powder with magnetic properties to produce composite products by mixing and soaking powders, **characterised in that** nano-structural powders of molybdenum oxide and titanium oxide with the MoO_3/TiO_2 mass content of 0.1÷0.4 and a carbon material in the amount of above 45 mass% are mixed, and then a nickel powder is added in the amount of 3÷40 mass%, relative to the mixture mass of titanium and molybdenum oxides and carbon, and then all constituent elements are ground under inert atmosphere, in ambient temperature to homogenise and then the resulting product of grinding is isothermally soaked in the temperature range of 1050 - 1500°C, under inert atmosphere, for 2 - 5 hours to produce a nano-structural cermet powder in the Ti-Mo-C-Ni system.

3. The method of preparation according to claim 2, **characterised in that** activated carbon and/or nano-structural carbon and/or black coal is used as the carbon material.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120
180
240
300
360
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540
600
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B [mT]
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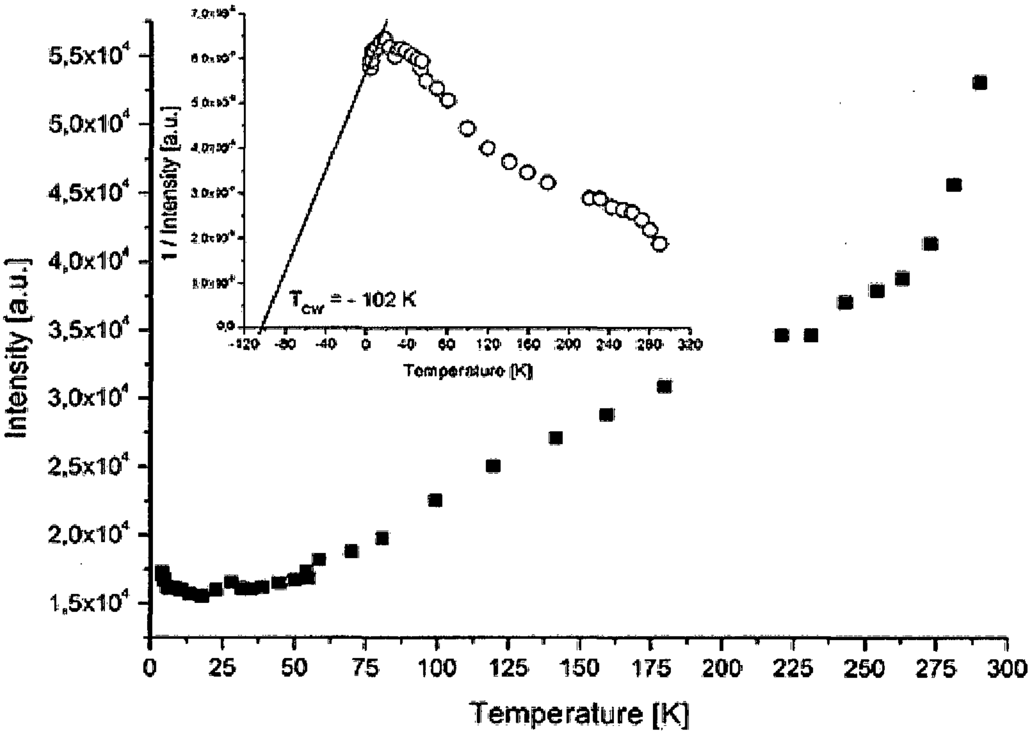
80.60
119.65
179.56
243.00

Fig. 1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2,0x10⁴
1,5x10⁴
Intensity [a.u.]
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25
50
75
100
125
150
175
200
225
250
275
300
Temperature [K]
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1 / Intensity [a.u.]
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240
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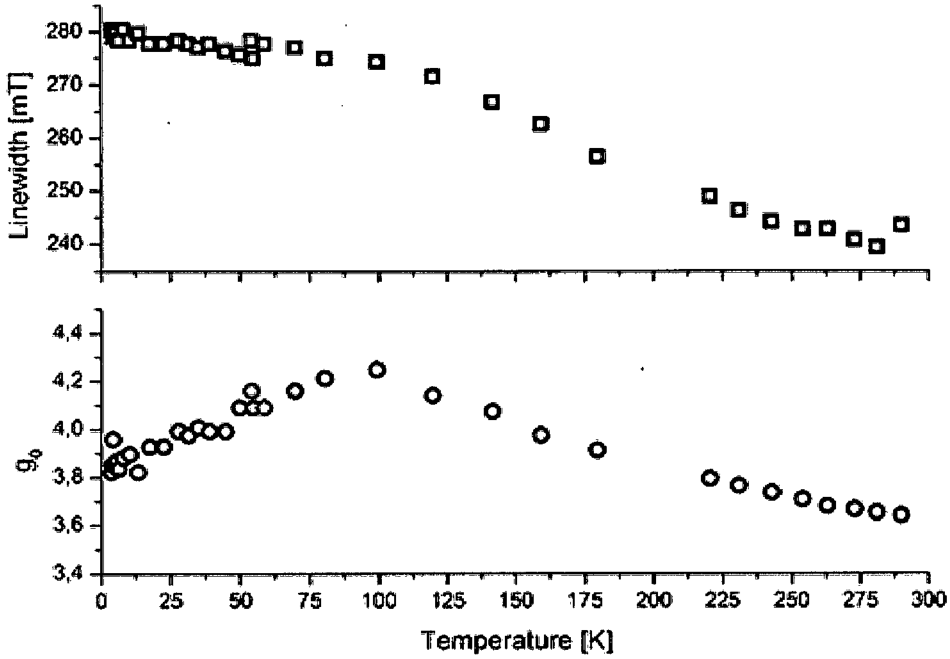
Fig. 2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50
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125
150
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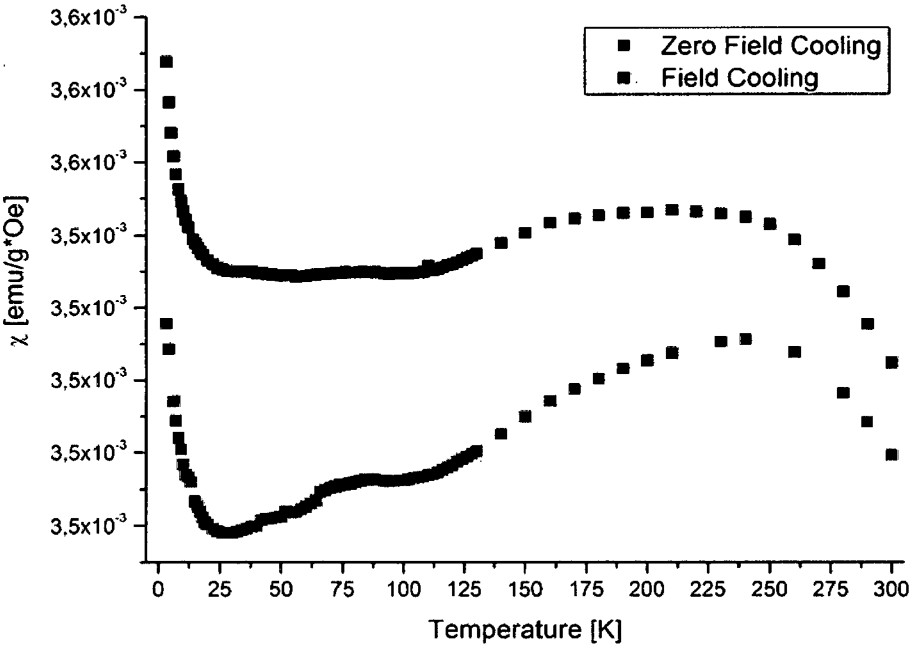
200
225
250
275
300
Temperature [K]

Fig.3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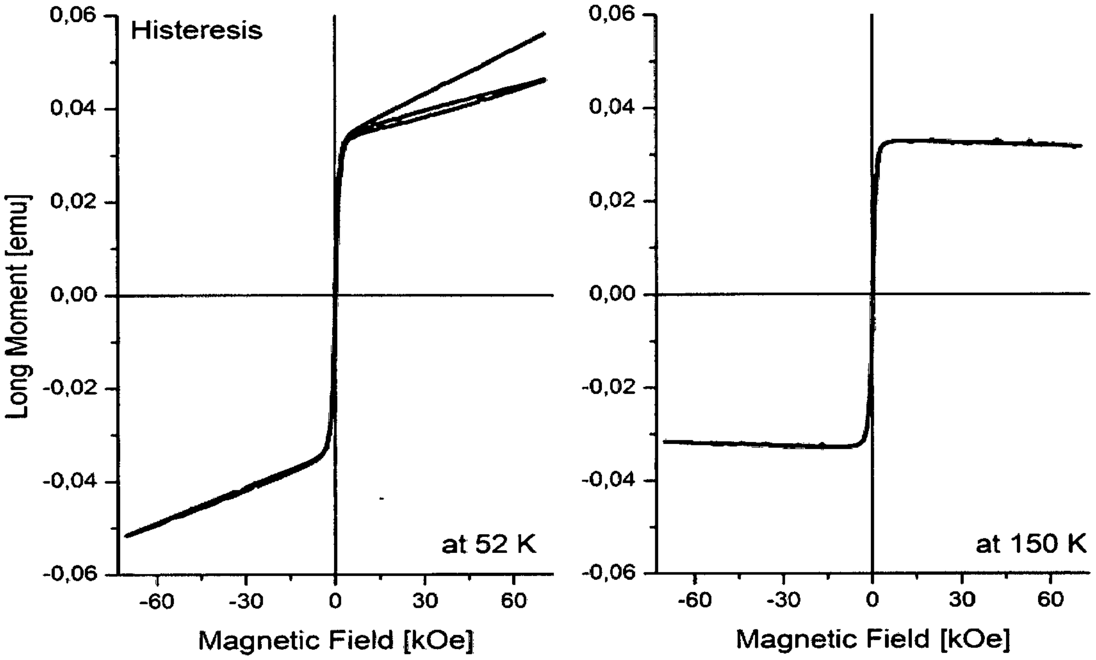
3,6x10-3
3,5x10-3
3,5x10-3
3,5x10-3
3,5x10-3
3,5x10-3
χ [emu/g*Oe]
Zero Field Cooling
Field Cooling
0
25
50
75
100
125
150
175
200
225
250
275
300
Temperature [K]

Fig.4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Long Moment [emu]
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-0,04
-0,06
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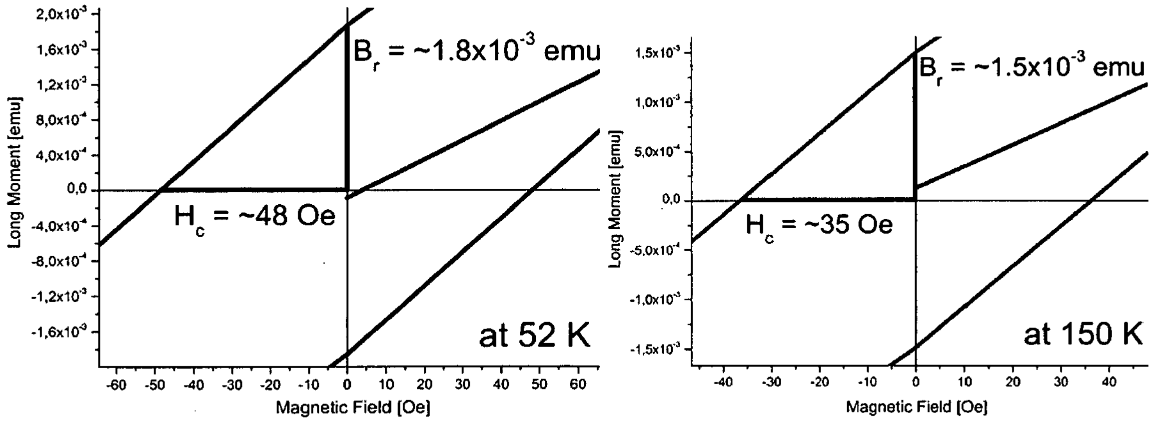
0
30
60
Magnetic Field [kOe]
at 52 K
0,06
0,04
0,02
0,00
-0,02
-0,04
-0,06
-60
-30
0
30
60
Magnetic Field [kOe]
at 150 K

Fig. 5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1,6x10^{-3}
1,2x10^{-3}
8,0x10^{-4}
4,0x10^{-4}
0,0
-4,0x10^{-4}
-8,0x10^{-4}
-1,2x10^{-3}
-1,6x10^{-3}
B_r = ~1.8x10^{-3} emu
H_c = ~48 Oe
at 52 K
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
Magnetic Field [Oe]
Long Moment [emu]
1,5x10^{-3}
1,0x10^{-3}
5,0x10^{-4}
0,0
-5,0x10^{-4}
-1,0x10^{-3}
-1,5x10^{-3}
B_r = ~1.5x10^{-3} emu
H_c = ~35 Oe
at 150 K
-40
-30
-20
-10
0
10
20
30
40
Magnetic Field [Oe]

Fig.5a

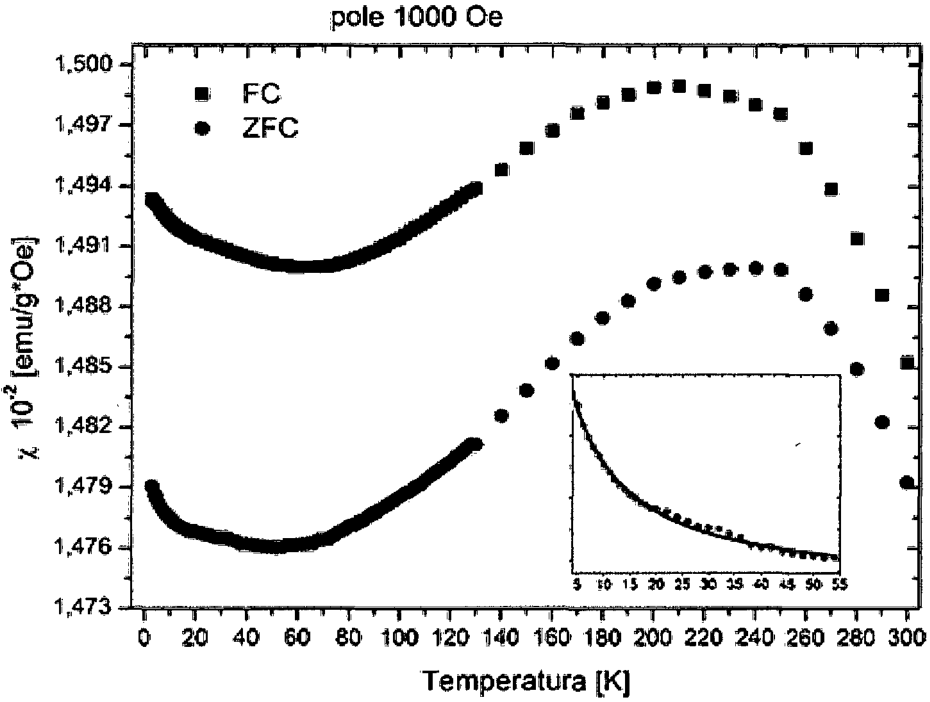

pole 1000 Oe
FC
ZFC
χ 10⁻² [emu/g*Oe]
1,500
1,497
1,494
1,491
1,488
1,485
1,482
1,479
1,476
1,473
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Temperatura [K]
5 10 15 20 25 30 35 40 45 50 55

Fig. 6

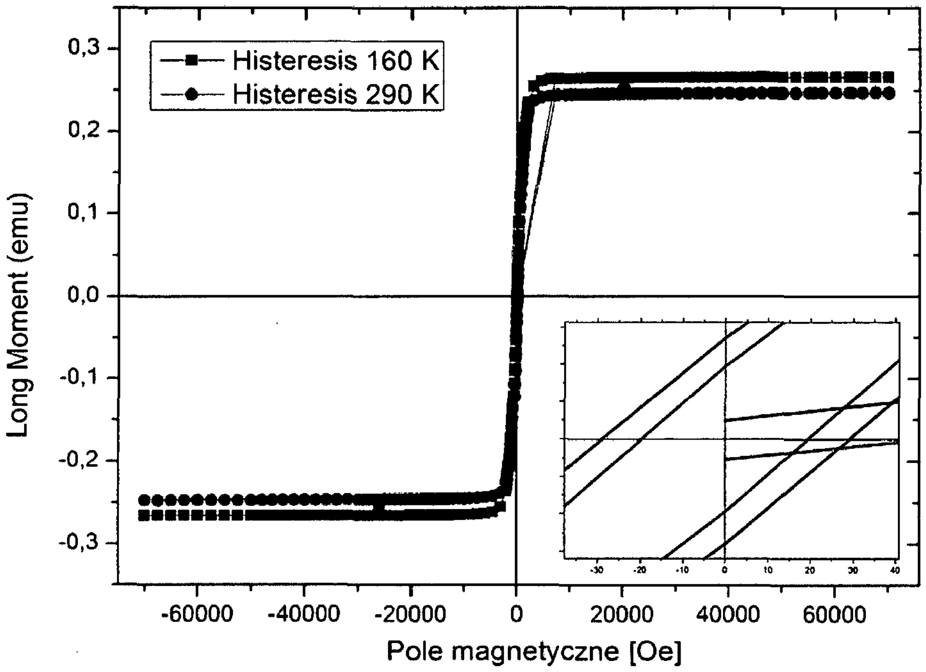

Histeresis 160 K
Histeresis 290 K
Long Moment (emu)
0,3
0,2
0,1
0,0
-0,1
-0,2
-0,3
-60000 -40000 -20000 0 20000 40000 60000
Pole magnetyczne [Oe]
-30 -20 -10 0 10 20 30 40

Fig. 7

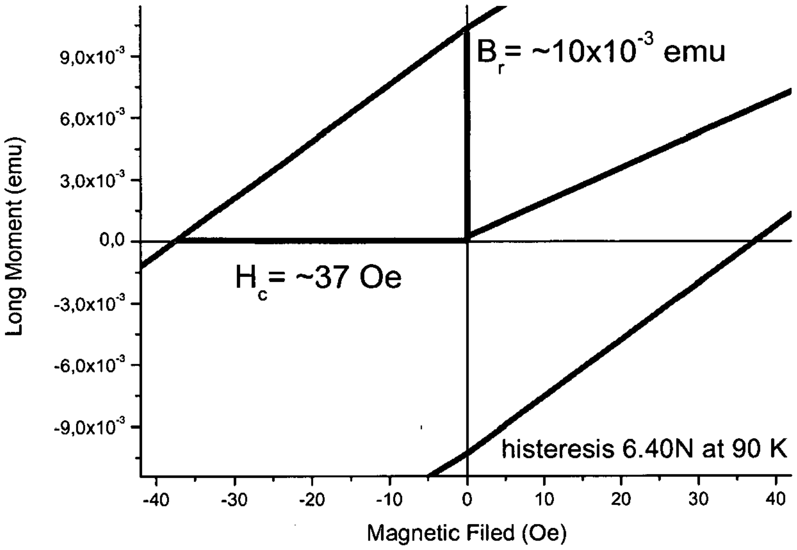

9,0x10^{-3}
6,0x10^{-3}
3,0x10^{-3}
0,0
-3,0x10^{-3}
-6,0x10^{-3}
-9,0x10^{-3}
Long Moment (emu)
-40
-30
-20
-10
0
10
20
30
40
Magnetic Filed (Oe)
B$_r$= ~10x10^{-3} emu
H$_c$= ~37 Oe
histeresis 6.40N at 90 K

Fig.8

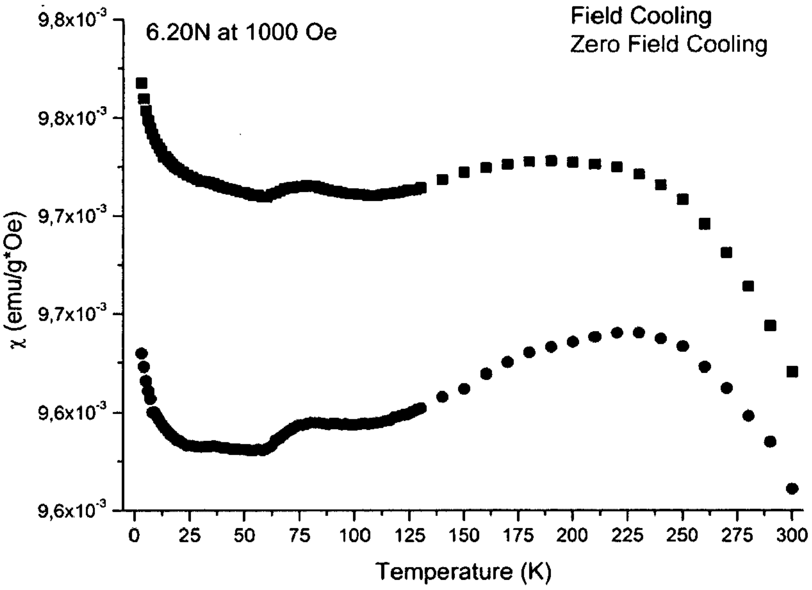

9,8x10^{-3}
9,8x10^{-3}
9,7x10^{-3}
9,7x10^{-3}
9,6x10^{-3}
9,6x10^{-3}
χ (emu/g*Oe)
0
25
50
75
100
125
150
175
200
225
250
275
300
Temperature (K)
6.20N at 1000 Oe
Field Cooling
Zero Field Cooling

Fig.9

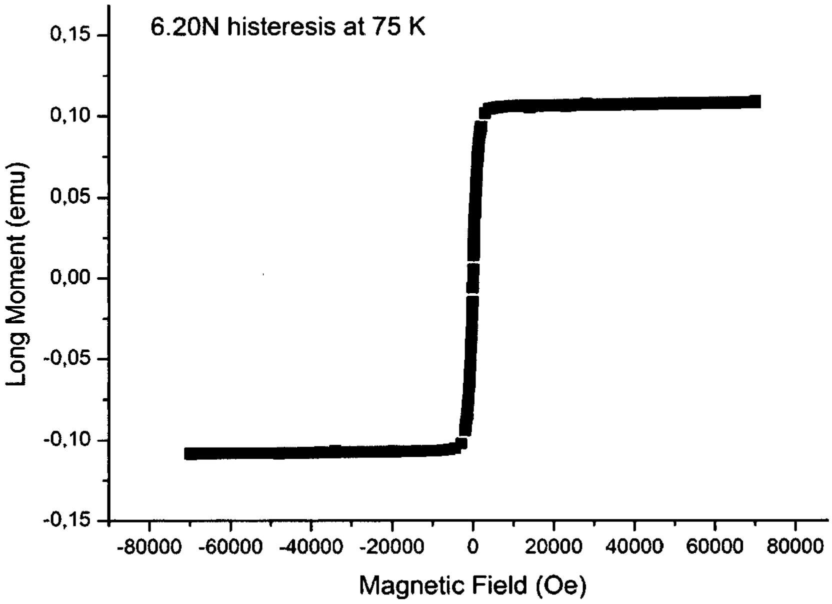

6.20N histeresis at 75 K
Long Moment (emu)
0,15
0,10
0,05
0,00
-0,05
-0,10
-0,15
-80000
-60000
-40000
-20000
0
20000
40000
60000
80000
Magnetic Field (Oe)

Fig.10

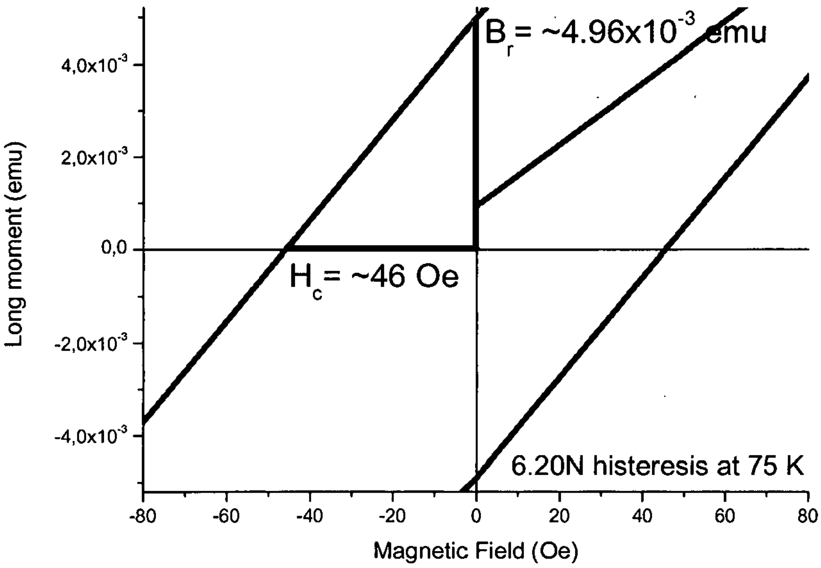

B_r= ~4.96x10^{-3} emu
H_c= ~46 Oe
6.20N histeresis at 75 K
Long moment (emu)
4,0x10^{-3}
2,0x10^{-3}
0,0
-2,0x10^{-3}
-4,0x10^{-3}
-80
-60
-40
-20
0
20
40
60
80
Magnetic Field (Oe)

Fig.11

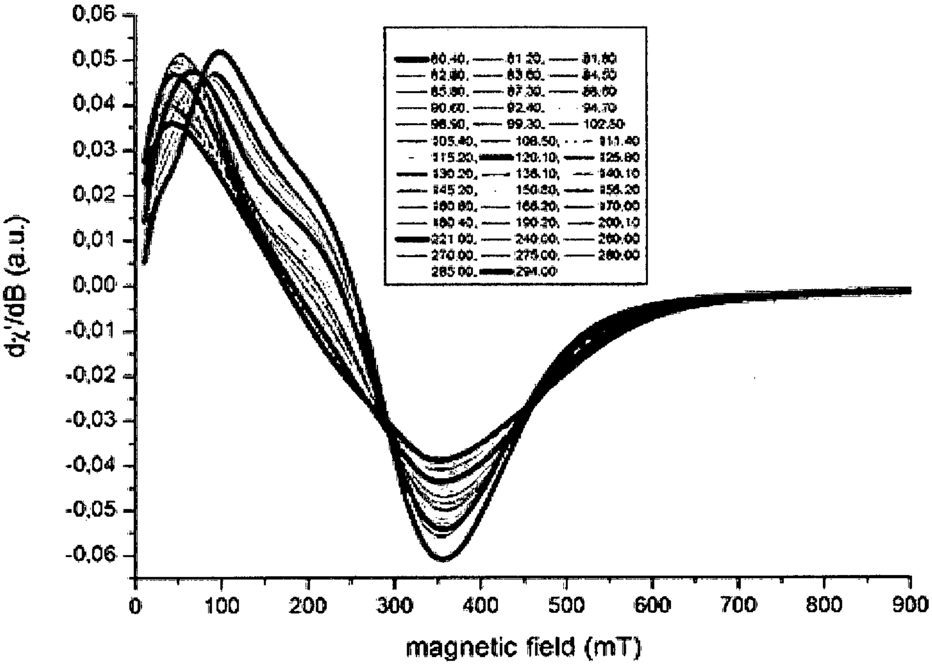


Fig. 12

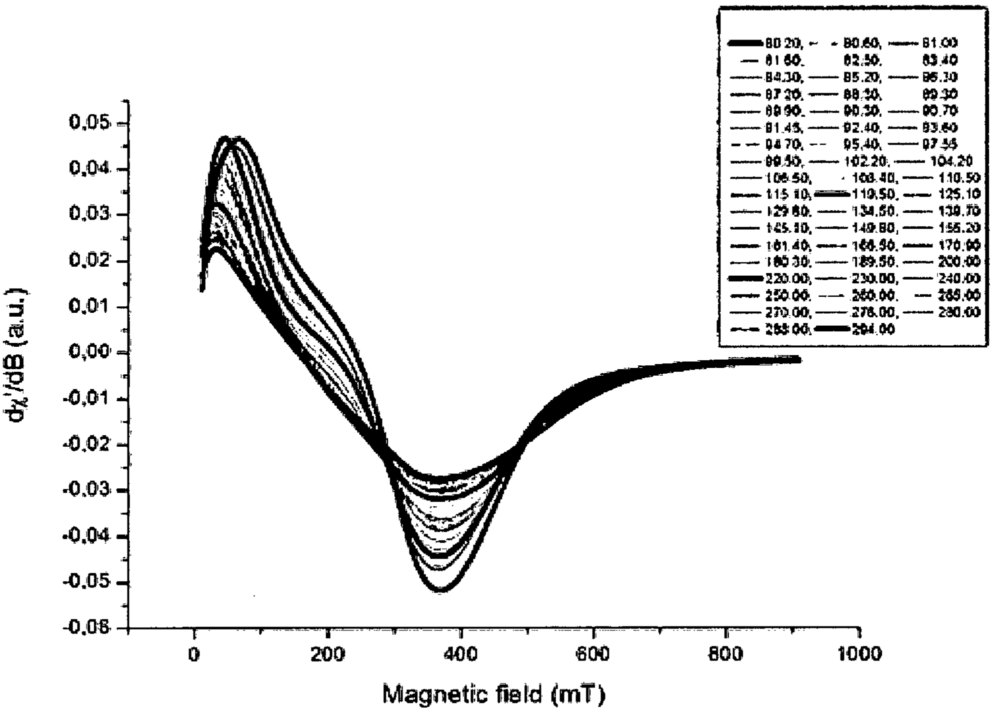


Fig.12a

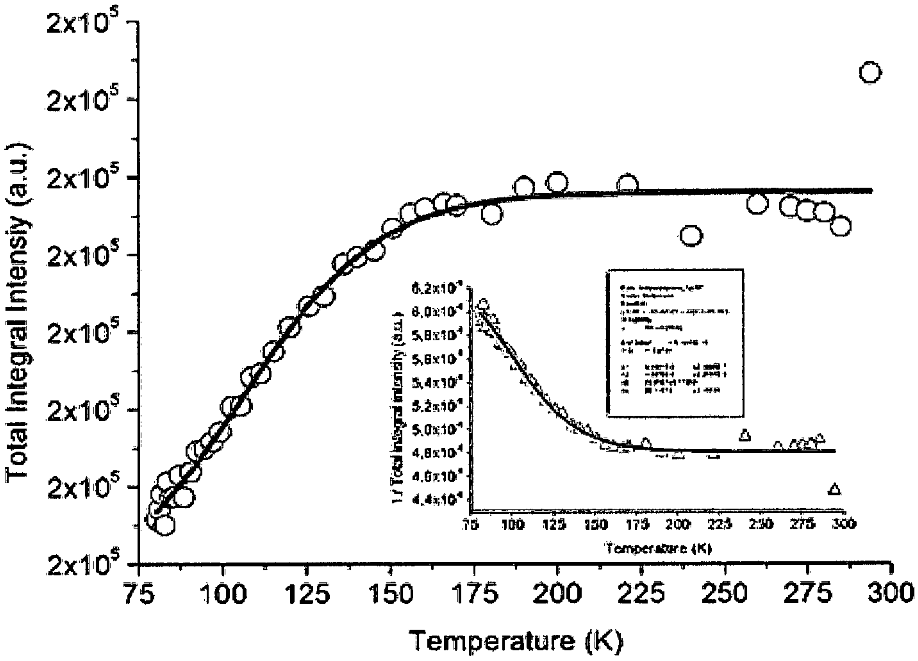
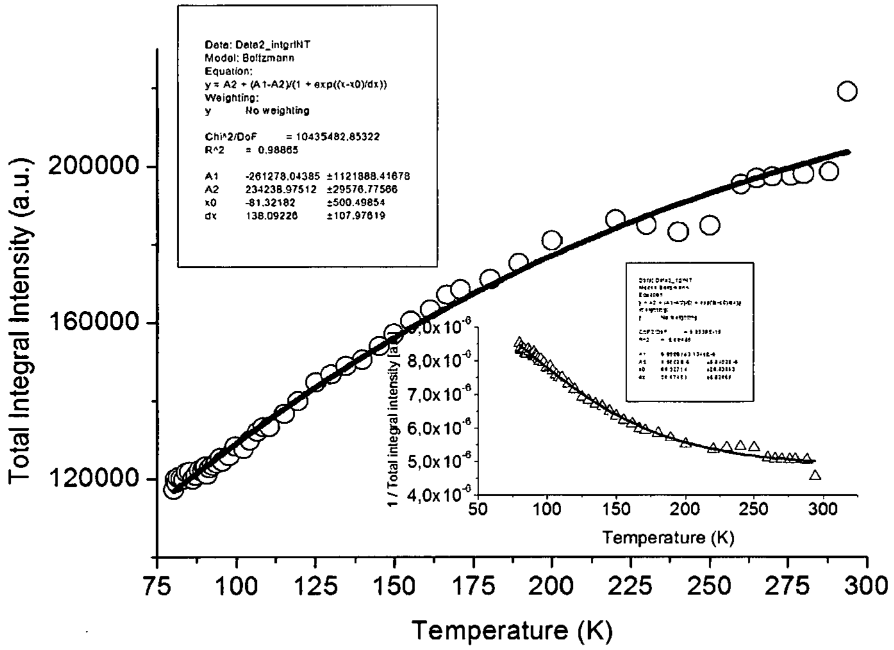


Fig. 13


```
Date: Data2_intgrINT
Model: Boltzmann
Equation:
y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))
Weighting:
y          No weighting

Chi^2/DoF        = 10435482.85322
R^2       =  0.98865

A1        -261278.04385  ±1121888.41678
A2        234238.97512   ±29576.77566
x0        -81.32182      ±500.49854
dx        138.09226      ±107.97619
```

Rys. 13a

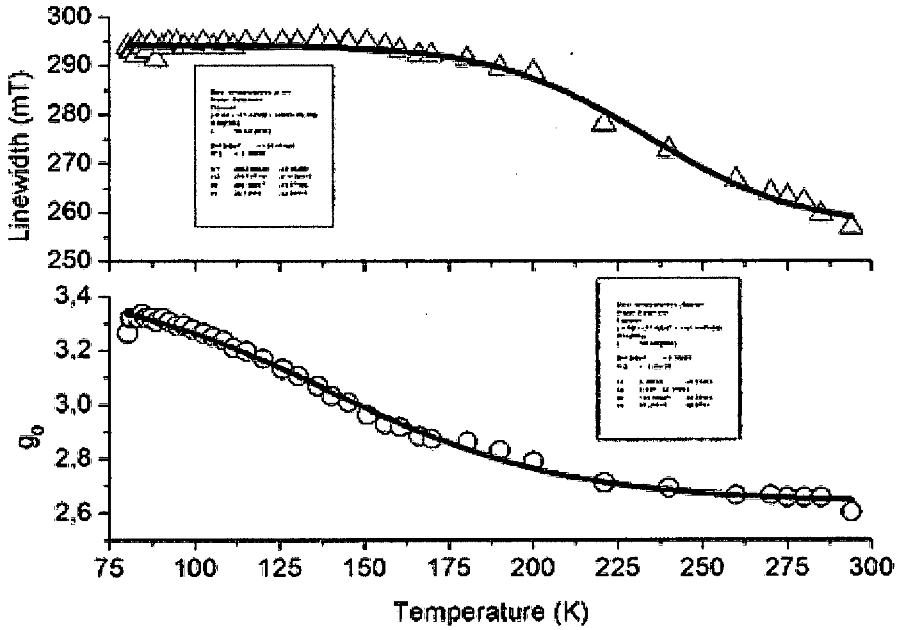


Fig. 14

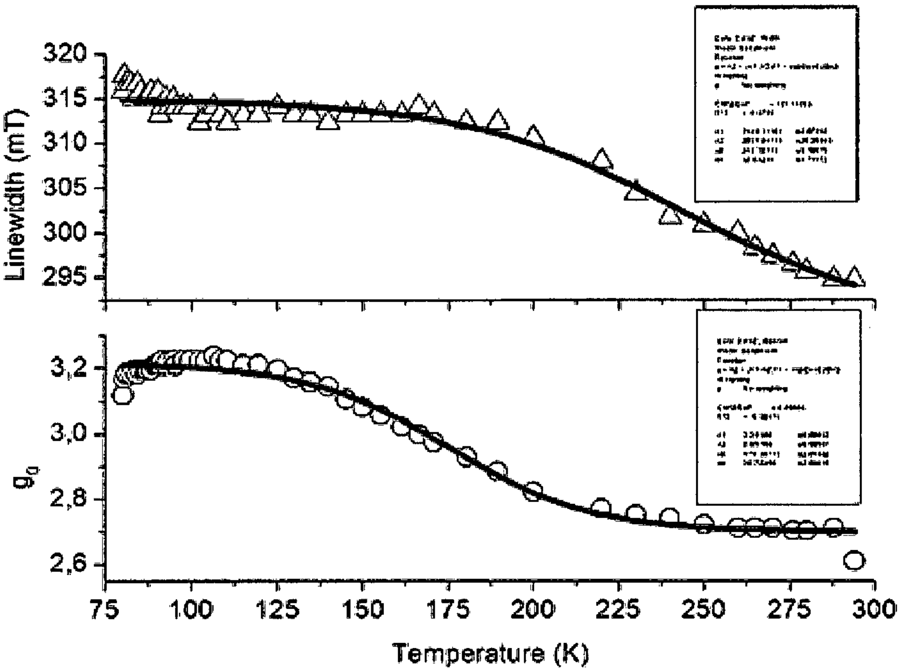


Fig. 14 a

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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 1561

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	KIM Y K ET AL: "Mechanochemical synthesis of nanocomposite powder for ultrafine (Ti, Mo)C-Ni cermet without core-rim structure", INTERNATIONAL JOURNAL OF REFRACTORY METALS AND HARD MATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 22, no. 4-5, 1 July 2004 (2004-07-01), pages 193-196, XP004627898, ISSN: 0263-4368, DOI: 10.1016/J.IJRMHM.2004.06.004	1	INV. C22C29/06 C22C32/00 C22C1/05
A	* abstract * * 2. Experimental * -----	2,3	
X,D	CHEN XIAO ET AL: "Characterization of Ti-based solid solution cermets prepared by mechanically induced self-sustained reaction and subsequent pressureless sintering", JOURNAL OF ALLOYS AND COMPOUNDS, vol. 583, 8 September 2013 (2013-09-08), pages 523-529, XP028747878, ISSN: 0925-8388, DOI: 10.1016/J.JALLCOM.2013.08.120	1	TECHNICAL FIELDS SEARCHED (IPC) C22C B22F
A	* abstract * * 2. Experimental * ----- -/--	2,3	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	25 January 2017	Morra, Valentina

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 1561

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	MAREK JÕELEHT ET AL: "The formation of reactive sintered (Ti, Mo)C-Ni cermet from nanocrystalline powders", INTERNATIONAL JOURNAL OF REFRACTORY METALS AND HARD MATERIALS, vol. 43, 1 March 2014 (2014-03-01), pages 284-290, XP055338906, AMSTERDAM, NL ISSN: 0263-4368, DOI: 10.1016/j.ijrmhm.2013.12.016	1	
A	* table 1 * * 2.Experimental methods * -----	2,3	
A	US 3 981 062 A (MOSKOWITZ DAVID ET AL) 21 September 1976 (1976-09-21) * the whole document * -----	1-3	
A	US 2010/267542 A1 (KANG SHINHOO [KR]) 21 October 2010 (2010-10-21) * claims * * example 7 * -----	1-3	TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	25 January 2017	Morra, Valentina

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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 46 1561

25-01-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3981062 A	21-09-1976	AU 7325074 A	18-03-1976
		CA 1041472 A	31-10-1978
		DE 2446684 A1	03-04-1975
		GB 1470611 A	14-04-1977
		IT 1019445 B	10-11-1977
		JP S5061508 A	27-05-1975
		JP S5551417 B2	24-12-1980
		SE 409743 B	03-09-1979
		US 3981062 A	21-09-1976
US 2010267542 A1	21-10-2010	KR 20100105862 A	30-09-2010
		US 2010267542 A1	21-10-2010
		WO 2009082178 A2	02-07-2009

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2005053881 A **[0002]**
- PL 115937 **[0002]**

Non-patent literature cited in the description

- **ZACKRISSON ; A. LARSSON ; H.-O. ANDREN.** Microstructure of the Ni binder phase in a TiC-Mo2C-Ni cermet. *Micro,* 2001, vol. 32, 707-712 **[0002]**
- **YOUNGKWAN KIM ; JAE-HYEOKSHIM ; YOUNG WHANCHO ; HYO-SEUNG YANG ; JONG-KU PARK.** Mechanochemical synthesis of nanocomposite powder for ultrafine (Ti, Mo)C-Ni cermet without core-rim structure. *International Journal of Refractory Metals & Hard Materials,* 2004, vol. 22, 193-196 **[0002]**
- Solid Lubrication Mechanisms in Laser Deposited Nickel-Titanium-Carbon Metal Matrix Composites. **JON-ERIK MOGONYE.** Master of Science. University of North Texas, December 2012 **[0002]**
- **JASMINE IMANI KEENE.** Characterization of a Ti(Mo)C-Ni Cermet for Use in Impact Resistant Sandwich Panels. *School of Engineering and Applied Science University of Virginia,* December 2013 **[0002]**
- **M. M. KULAK ; B. B. KHINA.** Selfpropagation high-temperature synthesis in the Ti-C-Ni-Mo system on application of powerful ultrasound. *Journal of Engineering Physics and Thermophysics,* 2014, vol. 87 (2), 333-343 **[0002]**
- **Y. F. YANG ; S. B. JINB ; Q. C. JIANG.** Effect of reactant C/Ti ratio on the stoichiometry, morphology of TiCx and mechanical properties of TiCx-Ni composite. *Cryst Eng Community,* 2013, vol. 15, 852-855 **[0003]**
- **T. VIATTE ; T. CUTARD ; G. FEUSIER ; W. BENOIT.** High Temperature Mechanical Properties of Ti(C, N)-Mo2C-Ni Cermets Studied by Internal Friction Measurements. *Journal de Physique IV, Colloque C8, supplement au Journal de Physique 111,* vol. 6 **[0003]**
- **MA QIAN ; L.C. LIM.** On the disappearance of Mo2C during low-temperature sintering of Ti(C,N)-Mo2C-Ni cermets. *Journal of materials science,* 1999, vol. 34, 3677-3684 **[0003]**
- **J.C. LASALVIA ; D.K. KIM ; R.A.LIPSETT ; M.A. MEYERS.** Combustion Synthesis in the Ti-C-Ni-Mo System: Part I. *Micromechanisms, Metallurgical and materials transactions A,* 1995, vol. 26A, 3001-3009 **[0003]**
- **MART VILJUS, JÜRI PIRSO, KRISTJAN JUHANI AND SERGEI LETUNOVIT.** Structure Formation in Ti-C-Ni-Mo Composites during Reactive Sintering. *Materials science (MEDZIAGOTYRA),* 2012, vol. 18 (1), 62-65 **[0003]**
- **HIROYUKI HOSOKAWA ; KIYOTAKA KATOU ; KOJI SHIMOJIMA ; RYOICHI FURUSHIMA ; AKIHIRO MATSUMOTO.** Effect of Ni Contents on Microstructures and MechanicalProperties for (Ti0.8Mo0.2)C-Ni Cermets. *Materials Transactions,* 2014, vol. 55 (9), 1451-1454 **[0003]**