

(19)



(11)

EP 2 803 736 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

19.11.2014 Bulletin 2014/47

(51) Int Cl.:

C21D 6/00 (2006.01)

C21C 7/06 (2006.01)

C22C 1/02 (2006.01)

C22C 38/04 (2006.01)

C22C 38/28 (2006.01)

C22C 38/38 (2006.01)

(21) Application number: **13167522.5**

(22) Date of filing: **13.05.2013**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

(71) Applicant: **Sandvik Intellectual Property AB**
811 81 Sandviken (SE)

(72) Inventors:

- **Ekengård, Johan**
216 22 Limhamn (SE)
- **Ehrlin, Niklas**
SE-211 44 Malmö (SE)

(54) **Wear resistant manganese steel**

(57) A wear resistant manganese steel and a method for producing the same having a composition by weight carbon: 0.4 t: 10 to 16%; silicon: 0.2 to 1.0%; tungsten:

0.5 to 5%; chromium: less than or equal to 1.0%; wherein the balance comprises iron and impurities; wherein powdered tungsten is added to the steel melt.

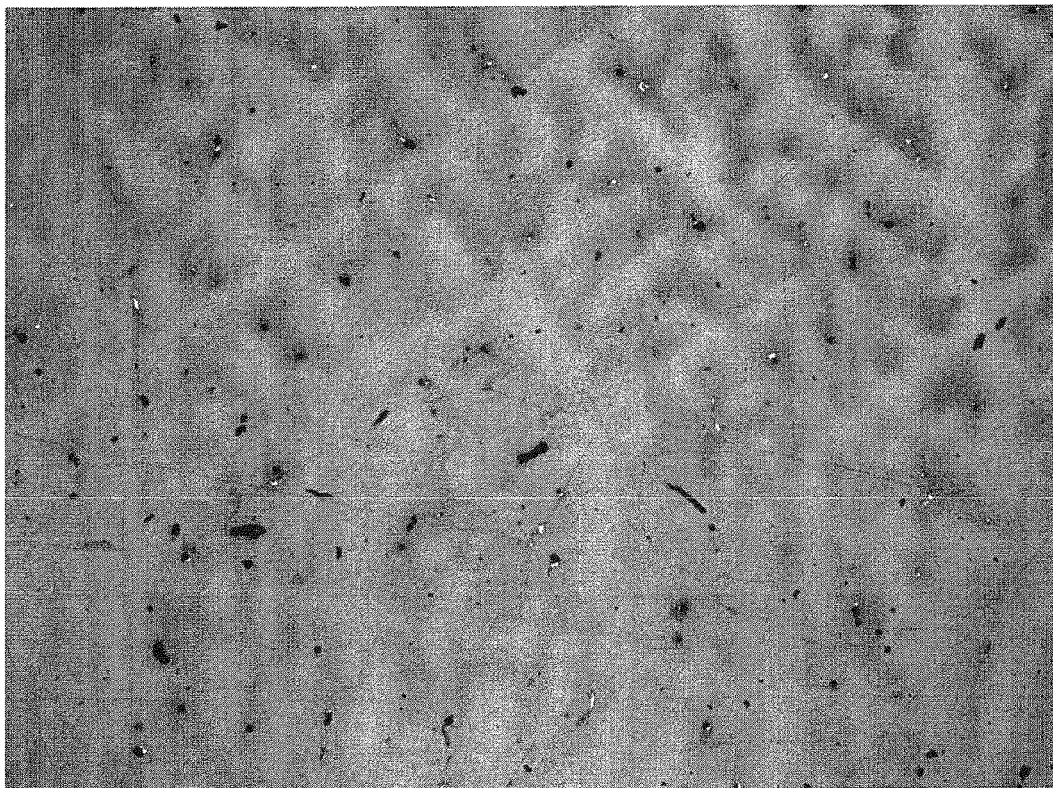


Figure 33

EP 2 803 736 A1

DescriptionField of invention

[0001] The present invention relates to a wear resistant manganese steel and its method of production.

Background art

[0002] A particular category of wear resistant steels are typically referred to as Hadfield, manganese or austenitic manganese steels. These materials are suitable for applications where a high toughness and a moderate abrasion resistance are required including for example use as wear parts for crushers that are subjected to strong abrasion and dynamic surface pressures due to the rock crushing action. Abrasion results when the rock material contacts the wear part and strips-off material from the wear part surface. Additionally, the surface of the wear part is subjected to significantly high surface pressures that cause wear part fatigue and breakage.

[0003] Manganese or Hadfield steel is typically characterised by having an amount of manganese usually above 11% by weight. The ratio of carbon and manganese is typically adjusted such that the ratio by weight of manganese is typically of the order of 10-11 times the weight of carbon. Such steels commonly comprise 0.8 to 1.25% carbon and 11 to 15% manganese by weight as their fundamental composition. However, fully austenitic (carbide-free) Hadfield steel is typically too ductile for wear parts in modern crushers that are subject to extreme operating conditions. Accordingly, attempts have been made to improve the work hardening characteristic of manganese steels from the fundamental composition by using additional alloying components. In particular, chromium, molybdenum, vanadium and tungsten are alloying elements that form strong carbides within the resulting alloy. Hardened manganese alloys are disclosed in US 5,308, 408; RU 2009116306; US 2009/123324; CN101736658; HU197775; CN1271028; CN101831590 and CN101638753. However, existing manganese steels exhibiting enhanced wear resistance are typically energy inefficient to produce, due largely to the very high processing temperatures involved (typically above 1000°C for extended holding times). There is therefore a need for a manganese steel that is energy efficient to produce and exhibits enhanced wear resistance and hardeners so as to find a particular application as a crusher wear part.

Summary of the Invention

[0004] It is an objective of the present invention to provide a manganese steel exhibiting enhanced wear resistance for use as a crusher wear part that is energy efficient to produce whilst optimising the toughness and deformation hardening properties of the resulting alloy.

[0005] The objectives are achieved by providing a manganese steel alloy having a microstructure that provides a high hardness of the steel matrix whilst keeping the impact toughness at a desirable level. This is achieved by forming highly dispersed carbides, and in particular tungsten carbides, within the austenite phase (the matrix of the alloy). In particular, the solubility of tungsten and carbon in the grain boundaries and within the matrix of the material is achieved by introducing a powdered form of tungsten to the initial base charge steel melt. In particular, and in one implementation, the tungsten comprises a particle size of less than 200 μm , 150 μm , or more preferably less than 100 μm . The inventors found this advantageous to significantly decrease the dissolution time of the tungsten into the melt and also to provide a homogenous matrix that includes high concentrations of tungsten and carbon within the austenite phase. Accordingly, when cast and heat treated, the elemental tungsten and carbon are present in sufficient concentrations to allow carbide formation within the matrix. The enhanced solubility of tungsten and carbon within the matrix ensures the carbide does not diffuse to the grain boundaries thereby increasing the micro hardness of the matrix. Accordingly, the present manganese steel comprises highly dispersed small tungsten carbides precipitated within i) the matrix and optionally ii) within the matrix and at the grain boundaries. A high degree of dispersion is achieved as the small particulate size of the powdered tungsten is dispersed homogeneously within the melt. The tungsten may be added in a form of powder-pressed Fe and W (that may be referred to as ferrotungsten). Accordingly, wear parts formed from the present alloy and method do not exhibit segregated physical and mechanical properties to provide a highly wear resistant part whilst maintaining toughness and deformation hardening properties.

[0006] The present method of producing the manganese steel alloy advantageously comprises a heat treatment phase in which the cast alloy is heat treated at a temperature above a predetermined level. By heat treating the cast at the required temperature, undesirable phases (such as a cementite phase of the alloy) are dissolved completely to achieve the desired phase composition. In particular, optimising the heat treatment is important so as to not exceed a predetermined temperature threshold to maintain and not dissolve the phase comprising tungsten carbide. The present method for producing an alloy is configured to establish an equilibrium in the alloy so as to achieve only two desired phases: an austenite phase and a phase comprising tungsten carbide. Preferably, the present method comprises quenching immediately after heat treatment to ensure these phases are retained and persist at room temperature. Accordingly, a wear

part having significant wear resistance is provided.

[0007] By heat treating the cast alloy at the appropriate temperature, any carbides present at the grain boundaries are dissolved with the tungsten being then solubilised with the matrix. Accordingly, the inventors have identified uniform and generally homogenous precipitation of tungsten carbide clusters within the austenite phase. A such, the present alloy comprises uniformly dispersed carbide (preferably tungsten carbide) precipitates throughout the microstructure which, in turn, may be considered to increase the micro hardness of the matrix. Additionally, the carbide is precipitated homogeneously at the different grains such that the microscopic hardness of the alloy is optimised.

[0008] According to a first aspect of the present invention there is provided a method for producing a wear resistant manganese steel comprising: creating a steel melt having a chemical composition by weight: carbon: 0.4 to 2.0%; manganese: 10 to 22%; silicon: 0.2 to 1.0%; tungsten: 0.5 to 5%; chromium: less than or equal to 1.0%; wherein the balance comprises iron and impurities; wherein powdered tungsten or a powdered tungsten containing material is added to the steel melt.

[0009] Optionally the method comprises creating a steel melt having a chemical composition by weight: carbon: 0.4 to 2.0%; manganese: 10 to 16%; silicon: 0.2 to 1.0%; tungsten: 0.5 to 5%; chromium: less than or equal to 1.0%; wherein the balance comprises iron and impurities; wherein powdered tungsten or a powdered tungsten containing material is added to the steel melt.

[0010] Preferably, the powdered tungsten is added in the form of ferro tungsten containing pressed powder of Fe and W. In particular, briquettes of pressed Fe and W powder are added to the initial base charged melt so as to dissolve readily within the melt to provide homogenous dispersion of tungsten. As will be appreciated, other forms of powdered tungsten may be suitable optionally in depressed composite form with other elements of the present alloy.

[0011] Preferably, a particle size of the powdered tungsten is within the range 2 to 150 μm . More preferably, the particle size of the powdered tungsten is in the range of 10 to 100 μm . Preferably, the powdered tungsten is added to the steel melt following an initial melting process of the various other starting materials of the present alloy. Alternatively, the powdered tungsten is added to the starting material components prior to the initial melting process to create the base melt. Preferably, the method further comprises casting the steel melt to produce a cast. Preferably, the method comprises heat treating the cast at a temperature between a liquidus temperature of the cast and a precipitation temperature of tungsten carbide within the manganese steel. Preferably, the method further comprises heat treating the cast at a temperature high enough to dissolve a cementite phase within the manganese steel and below a precipitation temperature of a tungsten carbide within the manganese steel.

[0012] Preferably, the method comprises heat treating the cast at a temperature in the range 800 to 1400°C. More preferably, the heat treatment is within the temperature range 950 to 1200 °C; 1000 to 1200 °C and more preferably 1050 to 1150 °C. Preferably, the heat treatment at this elevated temperature represents a final heat treatment of the cast.

[0013] Preferably, the method comprises heat treating the cast at the heating temperature for a holding time of 1 hour/25mm thickness of the cast. Preferably the heating rate may comprise heating in the order of 100 °C/h. Preferably, the method further comprises quenching the heat treated cast directly from the heat treatment temperature.

[0014] Preferably, the manganese steel comprises a chemical composition by weight: carbon: 1.1 to 1.4%; manganese: 11 to 14%; silicon: 0.4 to 0.8%; tungsten: 2.5 to 3.5%; chromium: less than or equal to 0.5%.

[0015] According to a second aspect of the present invention there is provided a wear resistant manganese steel having a chemical composition by weight: carbon: 0.4 to 2.0%; manganese: 10 to 22%; silicon: 0.2 to 1.0%; tungsten: 0.5 to 5%; chromium: less than or equal to 1.0%; wherein the steel comprises dispersed carbides within a matrix of the steel.

[0016] Optionally, the chemical composition by weight comprises manganese at 10 to 16%. Preferably, the steel comprises dispersed carbide precipitates within an austenite matrix of the steel. Preferably, the carbides are tungsten carbides. Reference within the specification to 'dispersed' encompasses a generally uniform dispersion of the carbide precipitates within the resulting cast alloy so as to represent carbide islands within the austenite matrix. The carbides are therefore spatially separated from one another in a randomly arranged manner within the austenite grains of the alloy.

[0017] According to a third aspect of the present invention there is provided a method for producing a wear resistant manganese steel comprising: creating a steel melt having a chemical composition by weight: carbon: 0.4 to 2.0%; manganese: 10 to 16%; silicon: 0.2 to 1.0%; tungsten: 0.5 to 5%; chromium: less than or equal to 1.0%; wherein the balance comprises iron and impurities; casting the melt and then heat treating the cast at a temperature: between a liquidus temperature of the cast and a precipitation temperature of tungsten carbide within the manganese steel; at a temperature high enough to dissolve a cementite phase within the manganese steel and below a precipitation temperature of a tungsten carbide within the manganese steel and/or at a temperature in the range 800 to 1400°C; 950 to 1200 °C; 1000 to 1200 °C or 1050 to 1150 °C.

[0018] According to a third aspect of the present invention there is provided a crusher wear part configured to crush material within a crusher comprising manganese steel as claimed herein.

Brief description of drawings

[0019] A specific implementation of the present invention will now be described, by way of example only, and with reference to the accompanying drawings in which:

Figure 1 is a schematic illustration of a step geometry model in which a tungsten manganese steel was cast;

Figure 2 is a Thermo-Calc™ diagram showing the phases at equilibrium and at infinite time;

Figure 3 is an LOM image of a sample 4460, heat treated under v1;

Figure 4 is an LOM image of a sample 4460b, as-cast;

Figure 5 is an LOM image of a sample 4462, heat treated under v1;

Figure 6: is an LOM image of a sample 4462b, as-cast;

Figure 7 is an LOM image of a sample 4490, heat treated under v2, 4h/inch;

Figure 8 is an LOM image of a sample 4495, heat treated under v2, 1h/inch;

Figure 9 is an LOM image of a sample 4460, heat treated under v1;

Figure 10 is an LOM image of a sample 4460b, as-cast;

Figure 11 is an LOM image of a sample 4490, heat treated under v2, 4h/inch;

Figure 12 is an LOM image of a sample 4495, heat treated under v2, 1h/inch;

Figure 13 is an LOM image of a sample 4462, heat treated under v1;

Figure 14 is an LOM image of a sample 4462b, as-cast;

Figure 15 is an LOM image of a sample 4490, heat treated under v2, 4h/inch;

Figure 16 is an LOM image of a sample 4495, heat treated under v2, 1 h/inch;

Figure 17 is an LOM image of a sample 4477, reference M1;

Figure 18 is an XEDS analysis of the matrix in the as-cast sample;

Figure 19 is an XEDS analysis of the lamellar structure in the as-cast sample;

Figure 20 is an XEDS analysis made by point analysis of a triangular carbide in the as-cast sample;

Figure 21 is an XEDS analysis made by point analysis on a carbide close to the triangular carbide in the as-cast sample;

Figure 22 is an XEDS point analysis on a carbide in the heat treated v1 sample;

Figure 23 is an XEDS area analysis of the matrix in the heat treated v2 sample;

Figure 24 is an area XEDS analysis on the dissolved lamellar structure of the heat treatment v2 sample;

Figure 25 is an XEDS point analysis on the matrix within the dissolved lamellar structure in the heat treated v2 sample;

Figure 26 is an XEDS analysis showing a triangular like structure with high concentration of W in the heat treated v2 sample;

EP 2 803 736 A1

Figure 27 is a point XEDS analysis on the small carbide phases within the dissolved lamellar structure;

Figure 28 is a LOM image of three different phases in an as-cast sample of the tungsten alloyed manganese steel;

Figure 29 is the plotted results from the Brinell test, 5 strikes at each sample;

Figure 30 is the micro hardness measurements on the matrix of the different samples;

Figure 31 is the micro hardness measurements on the carbide centre of the different samples;

Figure 32 is the micro hardness measurements on the lamellar or dissolved lamellar structure of the different samples;

Figure 33 is a LOM image of a heat treated v3 sample.

Detailed description of preferred embodiment of the invention

[0020] A specific implementation of the present invention is described with reference to the following examples. As will be appreciated, the examples are specific to particular implementations that are intended to be non-limiting with other examples and variations being possible within the definition of the invention according to the present claims.

[0021] Two of the most significant mechanisms that affect the physical and mechanical properties of a casting are heat transfer and atomic diffusion. The main heat transfer mechanisms in a foundry and heat treatment plant are radiation, conduction and convection. The atomic diffusion both in the melt and in the solid state is closely dependent on temperature, with higher diffusion rates at higher temperatures. Diffusion also is dependent on the rate of temperature change. Any solidification starts by the heat transfer from the melt, and when enough heat has been transferred, the melt starts to solidify at nucleation points, from where the grains start to grow. If the casting is done by pouring the melt into a mould, the nucleation and solidification usually starts at the mould-melt interface. The casting is kept in the mould until it is completely solidified, before it is removed and the casting continues to cool in ambient atmosphere. This gives a slow cooling rate which enables the growth of lower temperature phases in the cast material. In the manganese steel this is usually the growth of carbides. In order to redress the effects of the slow cooling rate, the present casting is heat treated. The present heat treatment is optimised by temperature, temperature rates and holding times. The heat treatment is followed by a quenching step known to those skilled in the art and comprises submersion of the cast in water, oil or liquid salts with the purpose of attaining a high cooling rate to suppress undesired growth of the lower temperature phases.

Example one

[0022] One objective of the experimental investigation was to identify the relative weight % of the various starting materials to determine an optimum manganese steel alloy composition. In general, the inventors have identified a particular target composition as detailed in table 1 below with respect to the overall elemental composition of the alloy expressed with respect to carbon, manganese silicon, tungsten and iron.

Table 1- Charge calculation:

element	Target	scrap	FeMn	FeSi	Fe+W	
C	1,3	0,2	6		1	
Mn	13	0,8	68			
Si	0,5	0,5		70		
W	3				78,3	
Fe		98,5	26	30	20,7	
Added material	kg	190	44	2	9	245

[0023] The inventors have identified that using powdered tungsten (e.g., in the form of pressed Fe and W) followed by a characterised heat temperature and quenching process, an alloy is produced with highly dispersed carbides within the primary phase of the metal (austenite matrix). In particular, pressed briquettes of W and Fe powder were used with a particulate size of the W and Fe being in the range 10 to 100 μm . Whilst the specific composition of the briquettes

may vary (according to the present example), the objective W composition of the present alloy is between 2.5 to 3.5 wt.%. This concentration range is correlated to the maximum solubility of W in the austenitic matrix which is approximately 3.5 wt.% in the present alloy at and around the present heat treatment process. Additionally the objective amounts of other selected components of the present alloy (both in the initial melt and final alloy stages) are Mn 11-14 wt.%, Cr ≤ 0.5 wt.%, C 1.1-1.4 wt.%, Si 0.4-0.8 wt.%.

Sample Casting

Melt furnace and casting

[0024] The melt is prepared with an electric arc furnace which is loaded with scrap iron and alloying elements. The temperature of a tap ready melt should be around 1550 °C, before it is poured into a preheated ladle. The ladle is a bottom pour ladle and the temperature of the melt when in the ladle is around 1510° C. The melt is poured in vacuum moulds of sand and the temperature of the melt is around 1465° C when casted. The cast material is removed from the mould shortly after it has solidified.

Heat treatment

[0025] Heat treatment of the solidified cast is then undertaken at a predetermined temperature, heating rate and holding time. In particular, the heating rate should be of the order of 100° C/h. The holding temperature of approximately 1100° C should be kept for at least 1 hour/25 mm (1 hour/inch) casting thickness. The subsequent quenching is to be performed in water down to room temperature.

[0026] A steel melt was prepared according to table 1. In particular, iron scrap (190 kg) was combined with 44 kg of FeMn and 2 kg of FeSi. This was melted and analysed and when the melt had a temperature of 1508° C, 9 kg of pressed briquettes of Fe and W powder was added and after 35 minutes the samples were casted. No Cr was added in order to keep the Cr concentration low in the alloy, with the intention of not letting the formation of Cr carbides compete with the formation of tungsten carbide. The moulds comprised furan sand. The sample was casted as a step casting with three different thicknesses; 25, 50 and 100 mm (Figure 1). The different thicknesses were obtained to give different cooling and heating rates at different sections of the casting to assess the microstructure of the material.

Table 2 - Starting material amount:

		Kg added	Wt-% of element
Fe		201,053	82,38189
C		3,11	1:27
Mn		31,44	12,88
Si		1,4	0,57
W		7,047	2,89
		244,05	

Heat treatment v1

[0027] A holding temperature of approximately 950 to 980° C and a holding time of 1 h/25 mm was chosen initially in order to try and fully dissolve any carbides in the material. The heating rate of 'laboratory oven' as used is much higher than the heat treatment oven used in typical production and has an average heating rate of about 13.5 °C/min. Then the temperature was lowered to about 850°C in order to find the equilibrium where the only carbide forming is the tungsten carbide. The holding time at 850°C was again 1 h/25 mm, before the material was quenched in water. The casted step were cut and separated in its different thicknesses prior to the heat treatment.

Spectroscopy and density measurement

[0028] Table 3 lists chosen elements of the present cast as prepared and described above expressed as wt.%.

Table 3: Composition of the cast tungsten alloyed manganese steel:

Element	Mn	W	c	Si	Cu	Cr	Ni	V	P	S
wt. %	13.5	3.5	1.4	0.6	0.22	0.1	0.1	0.028	0.05	0.008

[0029] The targeted percentages of Mn, C and W are fairly close to the result, but the 0.22 wt.% of Cu is higher than one could expect and probably a result of the iron scrap used. The concentrations of Ni, V, P and S are considered normal when using scrap metal.

[0030] A Mettler Toledo ML6001E was used to measure the density of the material. In the setup, the density is measured by weighing the sample first in air, then in water. A bigger piece of the cast tungsten manganese steel (1192.6 g) was used to measure the density of the material. The density of the cast material was assumed to be homogenous on the different thicknesses. Five measurements were made on the same sample and in order to homogenize the measurements, the samples were soaked in water prior to the first weighing, to get all of the measurements on wet material.

Heat treatment v2

[0031] Theoretical calculations indicated that the previous holding temperature of 850°C was too low for the objective to avoid cementite formation. Accordingly, a second heat treatment cycle was performed with the 'laboratory oven', in order to try and reach equilibrium where the only stable carbide should be WC. The first sample measured 25x25 mm (1x1 inch) and 13 mm in thickness and was kept at 950 to 980° C for 4 h, before it was water quenched. This gave a 4 times longer heat treatment than the usual 1h/25 mm.

[0032] To get a reference that more corresponds to the actual process when heat treating production wear parts, a heat treatment at the same temperature (at holding time of 1h/25 mm) was also performed. This was also quenched from the holding temperature of 950 to 980° C. The intention was also to see if the holding time of 1h/25 mm is sufficient to reach equilibrium.

Reference Material, M1

[0033] The M1 quality reference material came from a scrapped wear part (mantle) manufactured at a foundry in China. The M1 piece was assumed to have been heat treated according to a standard heating rate 100° C/h and; a heating temperature of 1100° C at a holding time of 1h/25 mm.

Spectroscopy measurement

[0034] Spectroscopy analysis of the reference casting is shown in Table 4.

Table 4: The composition of the used M1 reference material:

Element	Mn	Cr	c	Si	Cu	P	Ni	V	Mo	S
Wt. %	11.07	1.65	1.11	0.6	0.0617	0.0542	0.0379	0.0115	0.0109	0.0103

Microscopy, LOM and SEM

[0035] To prepare the samples for light microscopy a small piece of the material, preferably with the dimensions of 20 x 20 x 20 mm was cut. This was followed by an embedding in a thermosetting resin, done in a Struers LaboPress-3. The produced pellet with the embedded metal sample was then polished in a pre-set polishing program including 5 different steps, all with different polish material. This was done with a Struers TegraPol-15. After the polishing was done, the sample pellet was rinsed in ethanol and dried with a blow dryer. In order to better reveal the microstructures in the sample, the material was etched with 2 % nital (2 wt.% nitric acid, HNO₃ in alcohol, in the present case, ethanol). Before the samples were run in the SEM, the resin had to be removed to make the sample conducting again and to avoid charging the sample. An XEDS analysis was performed in order to determine the elemental composition within the different phases in the samples.

Mechanical TestingStone barrel

[0036] The test undertaken was a standardized test used typically to determine the abrasive index, AI, of a rock material. The metal barrel is 120 mm deep barrel with the diameter of 300 mm. Inside the barrel is a holder to mount a piece of tool steel for testing (standard QRO 90 material) conventionally in the shape of a paddle. When the test is run, the barrel rotates with 72 rpm. At the same time the holder with the paddle inside the barrel is rotating 9 times faster, 648 rpm, in the same direction as the outer barrel. The barrel is filled with 400 ± 1 grams of the rock material and run for 15 min. Then the barrel is emptied of rock material and the rock product is collected, before filling it again with 400 ± 1 grams and run for another 15 min. This is repeated in total 4 times, before the collected rock product is analysed with respect to particle size distribution. At the same time the QRO 90 paddle is weighed both before the run and after, in order to fully conclude the abrasive index of the rock material. The purpose is to give an idea on how the rock material will behave in the crushing plant.

[0037] In the present method, samples called "thumbs" were prepared, with the intended geometry of 25 x 25 x 6.2 mm. A thickness of 6.2 mm was selected and in further testing by this method, the thickness can be selected as either 6 or 7 mm. These samples were weighed and measured, before placed one by one, unattached within the barrel together with 400 ± 1 grams of rock material. The standardized steel (QRO 90) paddle was weighed and mounted in the holder in the barrel. By placing the samples unattached within the barrel together with the rock material, the idea is that the wear will be homogenous on all of the surface areas of the sample. The wear resistance of the samples is most likely lower on the edges of the sample why the total length of the edge preferably should be similar between samples. Once again the wear resistance is related to the volume loss of the sample. Measurements have been made in order to determine the densities of the two materials, the M1 reference and the cast tungsten manganese steel which can be used to calculate a thought volume loss. A statistical test of significance was performed on the obtained data in order to evaluate if there is a material dependent difference in the wear of the tested materials. Brinell hardness tests were performed on the samples after the run in the stone barrel in order to determine if the stone barrel test had induced any deformation hardening of the material. The weight loss of the mounted paddle (QRO 90) was measured in order to facilitate the comparison of the wear between different runs.

Sample preparation

[0038] Samples originated from two sections of the cast tungsten manganese steel. Five samples from the thickest step section (referred to as work nr 47602 and heat treated with v1) and five of the middle step section (referred to as work nr 47601 and heat treated with v1) of the test casting as well as five samples that were heat treated with v2 (referred to as work nr 47635) were cut. In order to make a comparative test, five samples from the M1 quality, was also prepared (referred to as work nr 47617).

Running the test

[0039] First the sample was weighed and placed together with 400 ± 1 grams of dry rock material in the barrel. A 11-16 fraction material, mainly gneiss, with about 10 % diabase and quartz and taken from the quarry in Dalby outside of Lund. The paddle (QRO 90) was also weighed before it was mounted in the barrel.

[0040] The barrel was then closed and run for 15 minutes, before the rock material was emptied and replaced with 400 ± 1 grams of unused rock material. Before filling the barrel again it was brushed to remove as much dust material as possible. Also the sample was brushed. The procedure was done 4 times, giving a total running time of 60 minutes, thru 1600 ± 4 grams of rock material for each sample. The sample was then removed and washed first in water and then with 30 % HCl for about 10 seconds before it was rinsed with water again. Then the sample was dried and weighed again. The paddle was dismounted and washed in the same manner as the sample and it too was dried and weighed again. In order to minimize any possible corrosive wear, the rock material was kept dry.

Hardness, Brinell test

[0041] For testing metals and alloys, a force of around 30 kN or = 3000 kg is applied to a steel ball (usually 10 mm to the diameter) for 20-30 s. The diameter of the residual impression, d, is measured and a hardness number can be calculated.

[0042] The test was made with a steel ball with the diameter of 10 mm. The load of 3000 kg or = 30 kN was applied for about 20+10 seconds (20 seconds of continuous load and 10 seconds of applying and releasing the load). 20 tests were done on material that had not been run in the stone barrel, so called unaffected material, 5 tests on the reference

M1 material (work nr 47617), 5 tests on the thickest section (work nr 47602 - heat treated with v1) and 5 on the mid-section (work nr 47601 - heat treated with v1) of the cast tungsten manganese steel as well as 5 tests on a sample heat treated according to v2 (work nr 47635).

5 Micro hardness

[0043] Micro hardness test is based on the same principle as the Brinell test, but performed with a much smaller indenter and with a load (F) of between 0.01 kg and 2 kg and denoted in Newtons. In order to identify the different phases in the sample, polished and etched samples were used. The loads used in the test varied depending on the examined phase. On smaller phases, such as the different morphologies of the carbides in the samples, a smaller load was used in order to exclusively measure the intended area. The load was held for 30 seconds in every case.

[0044] Five indentations were made on the matrix of the M1 reference material (work nr 47617) using a polished and etched piece with the metallographic nr 4477. The carbides were too small to measure in this sample. On two samples (one heat treated sample with heat treatment v1, with metallographic nr 4462 and one non-heat treated sample, with metallographic nr 4462b) of the tungsten manganese steel 5 tests were done on the matrix and 10 tests were done on two different morphologies of the carbides in the samples. The two morphologies in these samples are the centre, dense metallic looking part of the carbide and the pearlite looking, lamellar structure of the carbide (Figure 28). Measurements were also made on a sample that was heat treated according to heat treatment v2. Three different phases were measured; the matrix, the small metallic carbide core and the residual phase of the dissolved lamellar structure.

20 Deformation hardening measurement

[0045] No direct and standardized method of measuring the samples ability to harden by deformation was available during this work. However, two methods were discussed in order to see if any significant deformation hardening could be noted. The first method was to perform a Brinell test on the samples that were run in the stone barrel. The idea was that the deformation subjected to the samples in the stone barrel should result in a thin layer of deformation hardened material. In order to measure this probably small effect, no machining of the sample could be performed prior to the Brinell test as this could remove all of the material that actually hardened. The second method considered was to first perform a Brinell test on a machined and smooth surface, and follow this with micro hardness measurements both within the Brinell indentation and outside of it and hopefully a difference in hardness of the matrix inside the deformed area and outside, could be noted. The purpose of these tests would not be to get a value on how much the material harden on deformation, but to examine both if the material has the ability to deformation harden and if the stone barrel induces any deformation hardening on the material.

35 Other mechanical testing

[0046] A Charpy V impact test, (to evaluate the brittleness of a material) with sample preparation, was ordered from Exova Materials Technology. A comparative test between the M1 quality and the present tungsten manganese sample heat treated v2 was obtained. The choice of the sample that were heat treated with v2 was motivated with the micro-structure analysis and the result from the hardness tests as it seemed to show a better ductility than the sample that were heat treated with v1.

Results and Discussion

45 Evaluation of the Current Conditions

[0047] The calculated diagram (Figure 2) with the correct composition of our test alloy using Thermo-Calc™ prediction model (a computational thermodynamics software that uses different database packages) is the best prediction available for the present complex alloy. As will be noted, the 13 wt.% of Mn in the alloy will stabilize the austenite phase (2: FCC_A1#1) down to 600° C, before the bcc phase (1: BCC_A2) start to form. Given the diagram for Fe-W system, the Fe-rich austenite show a maximum solubility of W at about 1.3 at.%, which is about 3.5 wt%. If the austenite phase in the present alloy is stable down to 600° C, this could mean that there will not be any precipitation of metallic W. And no metallic W phase is shown in the diagram. But one should be aware of the fact that this diagram is for equilibrium at infinite time and no information regarding the dissolution times of the added W particles is given. At temperatures above 600° C, the only two carbides predicted to form is WC (6: MC_SHP) and Fe₃C (8: CEMENTITE). At the temperatures below 1250° C the only stable W carbide is WC. So regarding the theoretical prediction, the tungsten carbide will precipitate, but due to the nucleation difficulties of WC, the thermodynamically less advantageous phase M6C (possibly as Fe₃W₃C in the test alloy) could form instead. Since this phase is not favourable in any binary and ternary phase

diagrams of the involved systems, the phase does not show in the Thermo-Calc™ diagram.

[0048] The other carbides presented in the Thermo-Calc™ are 4: M_5C_2 and 5: M_7C_3 , both at temperatures below 550°C . These carbides could be Mn_5C_2 , Mn_7C_3 , and Cr_7C_3 but the probable reason that they are present, as shown in figure 2, is the fact that the calculation is done at full equilibrium and infinite time. In reality a very long holding time at about 550°C and below would have been required if these carbides should form. And since the material is quenched from temperatures well above, these phases can be disregarded.

LOM

[0049] The light microscope analysis was done at three different magnifications, 25, 100 and 500 times magnification. The samples examined:

Sample nr 4460: Tungsten alloyed manganese steel, cut from the thinnest section. Heat treated according to heat treatment v1.

Sample nr 4460b: Tungsten alloyed manganese steel, cut from the thinnest section. Not heat treated.

Sample nr 4462: Tungsten alloyed manganese steel, cut from the thickest section. Heat treated according to heat treatment v1.

Sample nr 4462b: Tungsten alloyed manganese steel, cut from the thickest section. Not heat treated.

Sample nr 4462: Tungsten alloyed manganese steel, cut from the mid- section. Heat treated according to heat treatment v2 at 4h/inch.

Sample nr 4495: Tungsten alloyed manganese steel, cut from the mid- section. Heat treated according to heat treatment v2 at 1h/25 mm.

Sample nr 4477: Reference M1 quality.

[0050] The grain boundaries and carbide structures are very similar in structure in samples 4460, 4460b, 4462 and 4462b, why all of the images taken at a higher magnification are not reported here. The differences between the mentioned samples are more easily detected at overview images at lower magnification.

[0051] The LOM examination reveals that the heat treatment v1 (Figure 3, 5) just slightly decreased the lamellar like carbide structure at the grain boundaries compared to the as-cast samples (Figure 4, 6). The difference between the thickest section and thinnest section, regarding the carbides sizes are negligible for the samples that were subjected to heat treatment v1. Both the samples that were heat treated with v2 (Figure 7, 8) but with different holding times show a change in the lamellar carbide phase. The structure has become more metallic and looks like it has dissolved. The M1 reference (Figure 17) show small ($<100\mu\text{m}$) carbides and pores and a grain size of about $100\text{--}300\mu\text{m}$ and no big grain boundary carbides. At 100X magnification there are hardly any difference between the sample that was heat treated according to v1 (Figure 9) and the as-cast sample (Figure 10). The carbide structure with the carbide centre and a mixture phase between the carbide centre and the matrix is very similar. But a clear difference can be noticed in the samples that were heat treated according to v2 (Figure 11, 12). The lamellar structure has been partly dissolved and this phase is seen as a light shadow along the grain boundaries and other areas that previously consisted of the lamellar structure. Also the grain boundary carbides have decreased and the grain boundary itself is more easily revealed. In a comparison between the samples with different holding times in heat treatment v2, hardly any difference in the microstructure was seen. This indicates that a holding time of 1h/25 mm is sufficient in order to reach the equilibrium in the heat treatment cycle.

[0052] The 500X magnification clearly reveals the lamellar structure around the carbide centre in both the heat treated v1 (Figure 13) sample and the as-cast sample (Figure 14). The matrix in the two samples looks about the same when examined in the light optical microscope. In both samples that were heat treated with v2 (Figure 15, 16), the lamellar structure has dissolved into smaller point phases. These small phases are also spread in the matrix, but at a lower concentration. The areas of the metallic carbide centre also look smaller after heat treatment v2. The M1 quality (Figure 17) show quite a different microstructure with small spheroidal shaped carbides and an overall smaller total area of visible carbides than by the samples heat treated with v2. At the same time the concentration of C in the M1 is only 0.3 wt.% lower than the concentration within the tungsten alloyed manganese sample.

SEM

[0053] The SEM examination was mainly performed to make an X-ray Energy Dispersion Spectroscopy (XEDS) on the different areas and phases of the samples. The SEM and XEDS were performed using a Hitachi S-3700N. Three different samples of the tungsten alloyed manganese steel were examined; one as-cast sample, one with heat treatment v1 and one with heat treatment v2.

As-cast sample

[0054] The XEDS on the matrix of the as-cast sample (Figure 18) show a composition as expected for Fe and Mn. The high wt.% of C most likely comes from surface contamination or polishing residues and will probably be higher when performing an area scan as the area/volume ratio is slightly bigger than when performing a point analysis. The wt.% of W is higher than the total added to the alloy. This could mean that the concentration of W in the matrix is not homogenous and is higher at the examined area, or it could be an uncertainty regarding the quantification as the signal detecting W is from the M-peak of W with a less intense signal.

[0055] The composition of the lamellar structure (Figure 19) shows a higher concentration of both W and Mn than in the matrix. Also the wt.% of C is higher. The lamellar structure is probably a mixture of the matrix and different carbides. The carbides could be M₆C (either as Fe₃W₃C, Fe₃Mn₃C or a combination of the both) but could also be a complex of Mn₇C₃ and Fe₃C together with either metallic W or WC. At higher magnification, point XEDS analyses were performed in order to more precisely determine the composition of the different carbides. In Figure 20 an interesting phase is shown. The composition has a stoichiometric relationship between W and C that could indicate WC and the shape of the phase is triangular, also an evidence that point towards WC. The Fe and Mn signal is probably from the matrix beneath the carbide. When performing a point analysis on a different carbide (Figure 21) near the triangular carbide, a different composition is revealed. The composition in the phase indicates a complex carbide.

Heat treated v2 sample

[0056] The sample that were heat treated with v1 showed very little difference in structures and composition in both the matrix and the lamellar structure compared to the as-cast sample. A structure that resembled the structures reported in the literature as M₆C type carbides were examined (Figure 22). The stoichiometric relationship between Fe and W allow the carbide to be a M₆C type carbide in the form of Fe₃W₃C. Although the concentration of C is very high, this could be either a contamination effect or possibly an effect of the visible pore to the right of the carbide, which could contain residues with high carbon content.

Heat treated v2 sample

[0057] The XEDS analysis of the sample that were heat treated with v2 showed a higher concentration of C than was added to the melt and has to be a result of surface contamination and cannot be completely quantified. Examining the matrix of the sample (Figure 23) gave similar results on all examined areas. And the composition in the matrix is close to the composition of the matrix in the as cast material and most likely as in the heat treated v1 sample. The reported concentration of W is higher than the added wt.% and it is higher than the theoretical solubility of W within the austenite phase. An area XEDS was also performed on the phase that used to be lamellar structure, referred to the dissolved lamellar phase (Figure 24). The area show a higher concentration of C, Mn and W compared to the matrix in Figure 23. At the same time the concentrations of Mn and W is lower in the dissolved area than in the lamellar structure of the sample heat treated with v1, which could indicate that the total volume of carbides in the area is lower in the dissolved lamellar phase. A visual inspection also leads to the probable conclusion that this phase is in fact matrix material, with small carbides spread in the phase. A point analysis on the thought matrix at the dissolved lamellar area (Figure 25) show that the composition in fact is very close to the matrix of the sample, which supports the above conclusion regarding the dissolved area. The carbide centre mainly has the same composition as the examined area in Figure 26. As revealed in the light optical microscope, the phase is usually located in the centre of a dissolved lamellar structure and usually also along grain boundaries. The concentration of W in these phases are typically between 25-30 wt.% or 64-69 wt.%.

[0058] The examined phase also show a triangular like structure that can be found in alloys containing WC. The signals from Fe and Mn could either come from the underlying matrix or the fact that the phase is a carbide complex of the identified elements (i.e. M₆C carbide). It should be mentioned that some of the structures examined showed a concentration of W up to about 45 wt.% or 70 wt.% which could indicate that the phase also contain metallic W or an undissolved particle of the Fe-W powder.

[0059] At a higher magnification a point analysis was performed on the small carbide phases contained in the dissolved lamellar area (Figure 27). The lower concentration of W compared to the bigger carbide centre could be a result of the excitation volume of the electrons being bigger than the examined phase, meaning that the examination is not only performed on the small carbide, but on the surrounding and underlying matrix as well. But it is clear that the phase has a higher concentration of W than the matrix of the sample.

Mechanical TestingStone barrel

[0060] Measurements on the geometry of the samples were done before they were run in the stone barrel. But due to the abrasion and deformation of the samples in the barrel it was difficult to identify the correct area after the run was completed, and a measurement of the geometry would have been erroneous. The only parameter that was measured before and after the run was the weight, from which the volume loss was calculated. The calculated volume loss of work nr 47617, the M1 quality follows the normal distribution:

$$X_i \in N(\mu_1, \sigma_1^2), i = 1, \dots, n_1 \quad \text{Equation 1}$$

and have a mean value of $\bar{x} = 0.014$ and a calculated sample variance of $s_1^2 = 4.8 \cdot 10^{-6}$.

[0061] The calculated volume loss of work nr 47601, the mid-section of the cast tungsten manganese steel follows the normal distribution:

$$Y_i \in N(\mu_2, \sigma_2^2), i = 1, \dots, n_1 \quad \text{Equation 2}$$

and have a mean value of $\bar{y} = 0.025$ and a calculated sample variance of $s_2^2 = 9.7 \cdot 10^{-6}$.

[0062] The calculated volume loss of work nr 47602, the thickest section of the cast tungsten manganese steel follows the normal distribution:

$$Z_i \in N(\mu_3, \sigma_3^2), i = 1, \dots, n_1 \quad \text{Equation 3}$$

and have a mean value of $\bar{z} = 0.020$ and a calculated sample variance of $s_3^2 = 2.3 \cdot 10^{-6}$.

[0063] The calculated volume loss of work nr 47635, the cast tungsten manganese steel heat treated with v2, follows the normal distribution:

$$XX_i \in N(\mu_4, \sigma_4^2), i = 1, \dots, n_1 \quad \text{Equation 4}$$

and have a mean value of $\bar{xx} = 0.017$ and a calculated sample variance of $s_4^2 = 9.9 \cdot 10^{-6}$.

[0064] Both series of the tungsten manganese steel that were heat treated with v1 (work nr 47601 and 47602) have a higher expected mean of the volume loss than the reference material (work nr 47601). The series with the tungsten manganese steel that were heat treated with v2 (work nr 47635) have the same expected mean of the volume loss as the reference material. At the same time, the expected mean of the volume loss can be the same for work nr 47635 and work nr 47602. This gives an indication (if the stone barrel test can be considered to test the wear resistance) that the heat treatment v2 was a step in the right direction as the reason for the higher volume loss for the samples that were heat treated according to v1 probably is that the material was brittle due to large carbide areas.

Brinell test

[0065] Due to uncertainties in the tilt of the sample while performing the test, the underlying structure of the measured surface, the difficulty in precisely measuring the diameter of the indentation and the fact that the measurement table is quantified in steps of about 4 HB, the present measurements should be considered as qualitative assessment of the hardness rather than an absolute quantitative measurement. The results of the test are shown in figure 29.

[0066] The spread of the measurements, the variance, could tell something about the homogeneity of the material and by this one can conclude that the M1 quality (nr 47617) and the sample heat treated with v2 (nr 47635) show a better homogeneity than the other two samples.

5 Micro hardness test

[0067] The three different phases that were measured with the micro hardness tester was defined as pictured in Figure 28. In the micro hardness tester, the magnification is 400 times, compared to the magnification of 500 times. Samples that were heat treated with heat treatment v2 had almost no lamellar structure as it had dissolved and the carbide metallic centre had decreased in size. The M1 reference had carbides that were too small to measure. In order to only measure the desired phase, lower forces were used to produce smaller indentations on the smaller carbide centres. HV 1 is the force of 9.89 N giving the load of 1 kg, HV 0.1 is 0.99 N and HV 0.05 corresponds to 0.49 N. On the M1 reference sample (metallographic/sample nr 4477) the carbides were too small to measure, why only the matrix of this sample was measured.

[0068] The sample nr 4477 and nr 47617 were cut from the M1; the sample nr 4462 and 4462b were cut from the cast tungsten manganese test alloy, where 4462 was heat treated with heat treatment v1 and 4462b was as-cast without any heat treatment. The sample nr 4495 was cut from the tungsten manganese test alloy with sample nr 47602 that was heat treated according to heat treatment v2. Due to the surprisingly high hardness of the matrix in sample 4495, a second test run was performed after the tester was calibrated again to verify the result. The results are shown in figures 30 to 32.

[0069] The metallic looking carbide centre of sample 4495 was much smaller than prior to heat treatment v2 and a smaller load had to be used in order to only measure the desired phase. Sample nr 4477, the M1 reference, had carbides too small to measure. The sample nr 4477 does not have any lamellar structure between the carbide centre and the matrix that is detectable and measurable with this method. The structure between the carbide centre and the matrix in sample nr 4495 is no longer lamellar and looks like a dissolved lamellar structure, and this was the phase that was examined.

[0070] The large spread in hardness when measuring the different areas of the carbides is most likely due to the fact, that the phases are not completely homogeneous and the measure will not only measure the desired, the indentation could be on more than one phase in the same measurement. This is also true for the other phases with a smaller spread, it can never be concluded that only the desired phase is measured. And as stated in the literature, WC shows a wide anisotropic hardness, giving different values based on the measured direction. Since all measurements of the diagonals are performed with the same magnification of 400X, a smaller load hence a smaller indentation will be more difficult to precisely measure, and this too could result in a larger spread. The reported high values of the different carbides that could be present in the samples was never found, but this could be an effect of the fact that the reported values are on single phase carbides and the measurement with micro hardness is done on a carbide imbedded in a softer, elastic matrix.

[0071] A conclusion regarding the matrix of the samples with significance level of $\alpha = 0.05$ or a 95% confidence can be concluded; the addition of tungsten with heat treatment v1 or no heat treatment gave a softer matrix than the matrix of the M1 quality. But the tungsten alloyed manganese steel subjected to heat treatment v2 gave a significantly harder matrix than the other samples. But as with the Brinell measurement, the big spread indicates that these results should not be considered as absolute values of the hardness.

40 Other mechanical testing

[0072] The Charpy test performed by Exova AB gave an average value of the absorbed energy for the tungsten alloyed manganese steel (heat treatment v2) of 35 J. The reference M1 material gave an average value of 110 J. The tungsten alloyed material show a much lower ductility than the M1 material.

45 Conclusions

[0073] A comparison of the tungsten alloyed manganese steel with different heat treatment cycles, show a better result for the heat treatment v2. The big grain boundary carbides found in heat treatment v1 samples and the as-cast samples, have partly been dissolved with heat treatment v2. This is accompanied with a hardening of the matrix verified by micro hardness measurement. A higher temperature should enable a higher concentration of W dissolved in the matrix, which could make the matrix harder, but the XEDS does not show any significant difference in concentration of W in the matrix for the samples with different heat treatments. But the XEDS show a higher concentration of C in the matrix of the heat treated v2 sample, and the only carbide predicted by Thermo-Calc™ is tungsten carbide. It is therefore likely that the very small, finely dispersed tungsten carbides have been precipitated in the matrix during heat treatment v2. Additionally, the good solubility for tungsten carbide in the austenite also enables this.

[0074] The heat treatment v2 made the material more ductile as expected since the grain boundary carbides had

decreased in volume, than by heat treatment v1. This manifested in a lower Brinell hardness and a better result from the stone barrel test. However, even with heat treatment v2 there is a metallic/carbide phase in the grain boundaries that is not completely dissolved and most likely still makes the material more brittle than the M1 quality. The phases are not present in the M1 quality, although the difference in carbon concentration is not that large. These metallic/carbide phases are probably a mixture of metallic W and complex carbides such as M₆C, which is indicated by the XEDS analysis. If the concentration of W was to be lowered in the alloy and/or a higher holding temperature provided, these phases could be decreased.

Heat treatment v3

[0075] In order to test the above conclusion, a third heat treatment cycle was undertaken at a higher holding temperature of approximately 1100° C. The sample was kept at 1100° C according to a holding time of 1h/25 mm. The cast was then quenched from the holding temperature as before. Light microscope analysis of the sample heat treated via v3 is shown in figure 33. As can be seen from figure 33, homogeneously dispersed carbides are precipitated in the matrix. Figure 33 confirms the complete dissolution of the grain boundary carbides and the precipitation of the finely dispersed carbides within the grains (and to some extent within the grain boundaries).

[0076] Following micro hardness (within the matrix) assessment on the sample heat treated according to v3 it was observed that the sample remained ductile and did not exhibit higher brittleness than the referenced material. The micro hardness (matrix) was found to be approximately 268 HV and a macro hardness of approximately 230 HB. This is to be contrasted with a micro hardness for v1 of around 230 HV; a macro hardness for v1 of approximately 230 HB; a micro hardness for v2 being approximately 370 HV and a macro hardness for v2 being approximately 203 HB.

[0077] It is noted that the v3 heat treated sample did not show improvement in mechanical properties based on the above hardness measurements as compared with the reference material. However, the v3 heat treated sample provided a ductile material with finely dispersed carbides within the grains. As indicated, an objective of the present invention is to provide small carbides dispersed within the grains that act as dislocation 'lock up' that will enable fast deformation hardening. These carbide precipitates are most likely tungsten carbide in the form of WC (with a hardness of up to 2400 HV) or a carbide with a high concentration of W such as M₆C (with a hardness of approximately 1400 HV) and hence reportedly being a harder carbide than a Cr carbide. The fact that the carbides, as confirmed by figure 33, are evenly dispersed within the matrix will accordingly improve the abrasive wear resistance of the resulting material.

Claims

1. A method for producing a wear resistant manganese steel comprising:

creating a steel melt having a chemical composition by weight:

carbon: 0.4 to 2.0%
manganese: 10 to 22%
silicon: 0.2 to 1.0%
tungsten: 0.5 to 5%
chromium: less than or equal to 1.0%;

wherein the balance comprises iron and impurities;

wherein powdered tungsten or a powdered tungsten containing material is added to the steel melt.

2. The method has claimed in claim 1 wherein a particle size of the powdered tungsten is within the range 2 to 150 μm.

3. The method as claimed in claim 2 wherein the particle size of the powdered tungsten in the range of 10 to 100 μm.

4. The method as claimed in any preceding claim further comprising casting the steel melt to produce a cast.

5. The method as claimed in claim 4 further comprising:

heat treating the cast at a temperature between a liquidus temperature of the cast and a precipitation temperature of tungsten carbide within the manganese steel.

6. The method as claimed in claim 4 further comprising:

heat treating the cast at a temperature high enough to dissolve a cementite phase within the manganese steel and below a precipitation temperature of a tungsten carbide within the manganese steel.

7. The method as claimed in claim 4 further comprising:

heat treating the cast at a temperature in the range 800 to 1400°C.

8. The method as claimed in claim 7 further comprising:

heat treating the cast at a temperature in the range 1000 to 1200°C.

9. The method as claimed in anyone of claims 5 to 8 further comprising:

heat treating the cast at the heating temperature for a holding time of 1 hour/25mm thickness of the cast.

10. The method as claimed in anyone of claims 5 to 9 further comprising:

quenching the heat treated cast directly from the heat treatment temperature.

11. The method as claimed in any preceding claim wherein the manganese steel comprises a chemical composition by weight:

carbon: 1.1 to 1.4%
manganese: 11 to 14%
silicon: 0.4 to 0.8%
tungsten: 2.5 to 3.5%
chromium: less than or equal to 0.5%.

12. A wear resistant manganese steel having a chemical composition by weight:

carbon: 0.4 to 2.0%
manganese: 10 to 22%
silicon: 0.2 to 1.0%
tungsten: 0.5 to 5%
chromium: less than or equal to 1.0%;
wherein the steel comprises dispersed carbides within a matrix of the steel.

13. The manganese steel as claimed in claim 12 comprising a chemical composition by weight:

carbon: 1.1 to 1.4%
manganese: 11 to 14%
silicon: 0.4 to 0.8%
tungsten: 2.5 to 3.5%
chromium: less than or equal to 0.5%.

14. The manganese steel as claimed in claims 12 or 13 comprising dispersed tungsten carbide within an austenite matrix of the steel.

15. A crusher wear part configured to crush material within a crusher comprising manganese steel as claimed in anyone of claims 12 to 14.

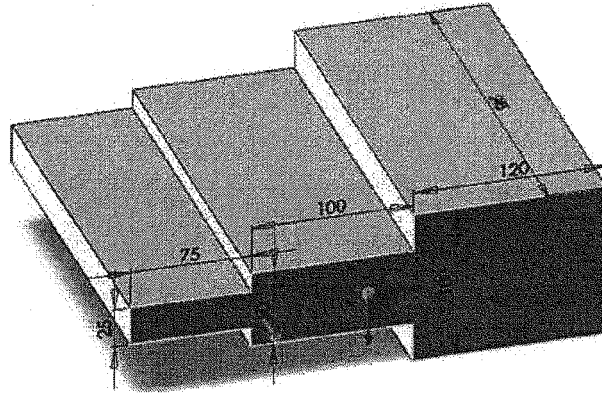


Figure 1

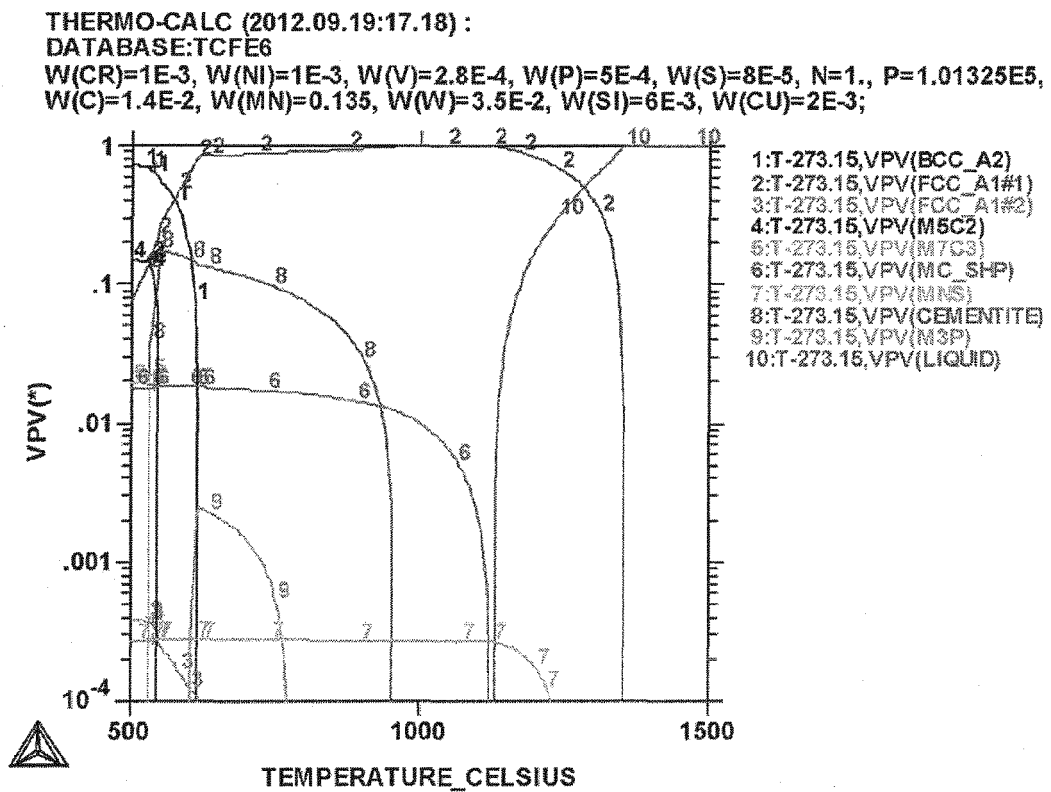


Figure 2

Magnification 25X

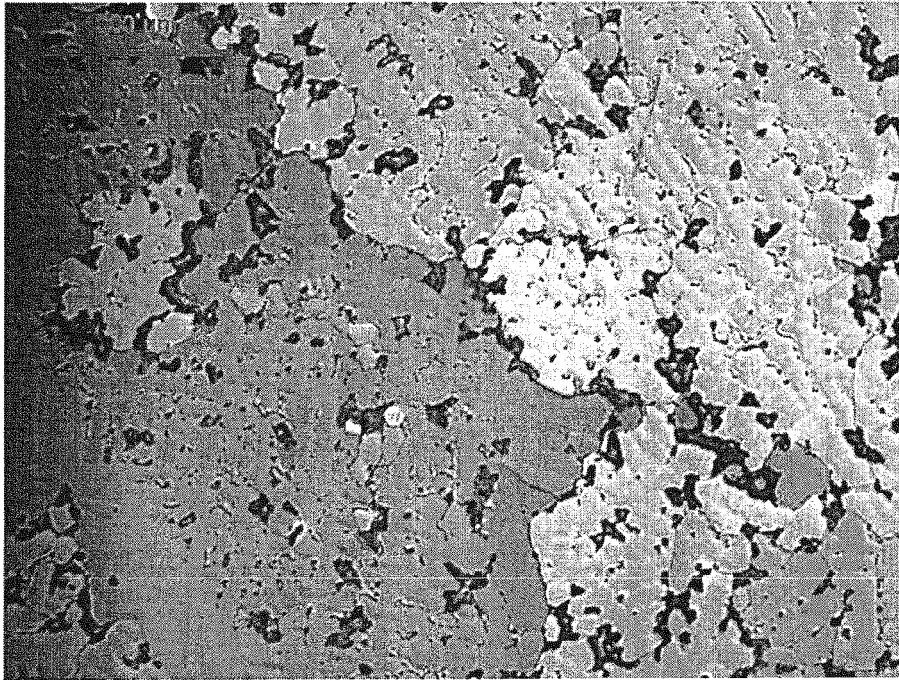


Figure 3

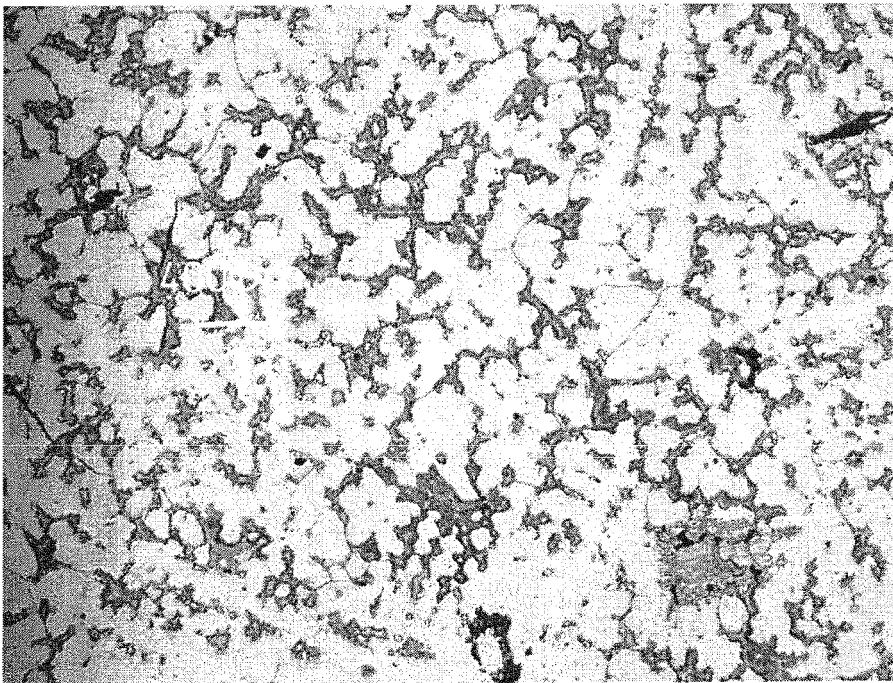


Figure 4

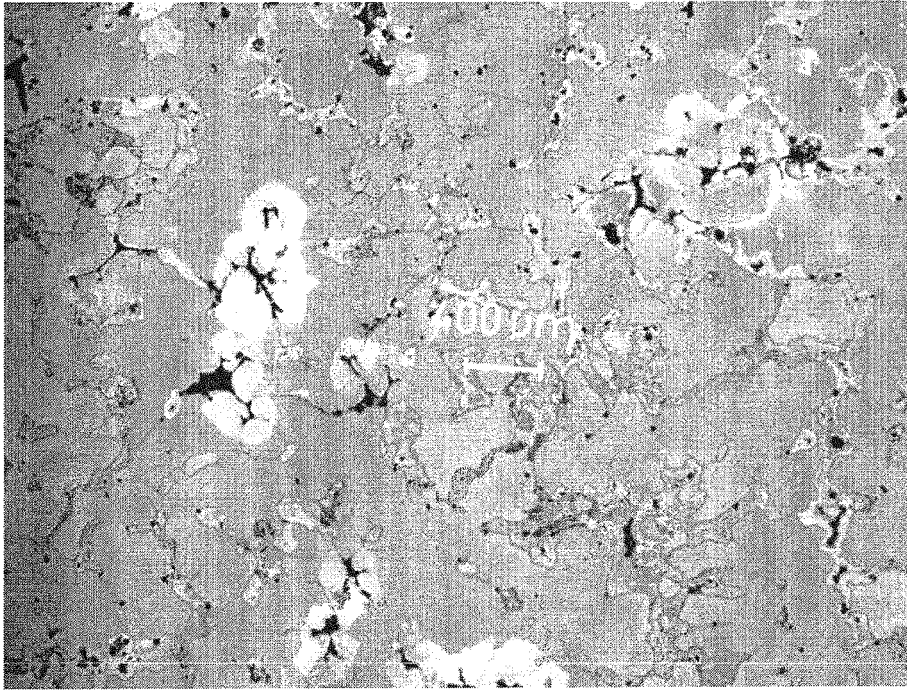


Figure 5

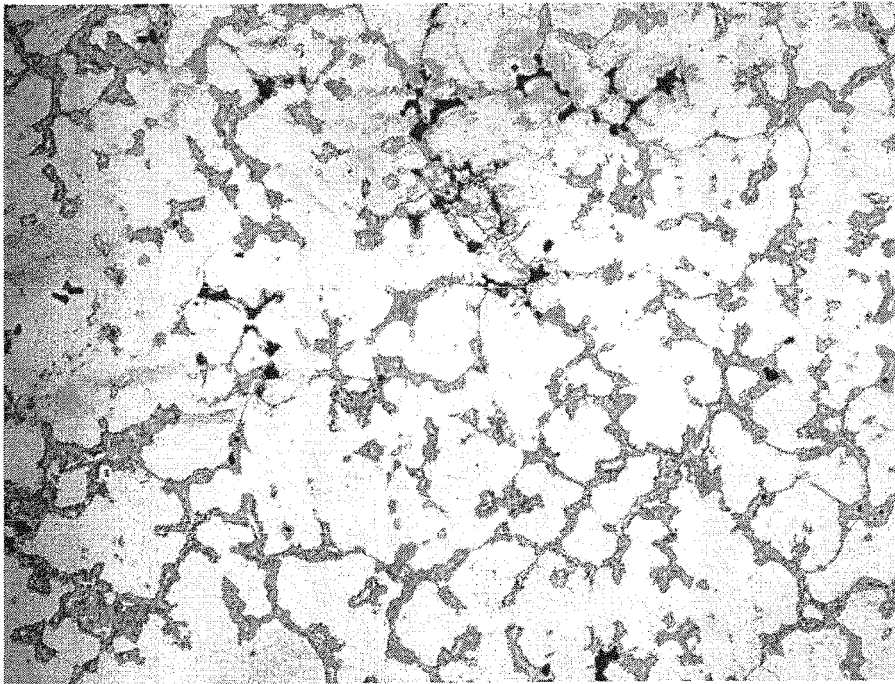


Figure 6

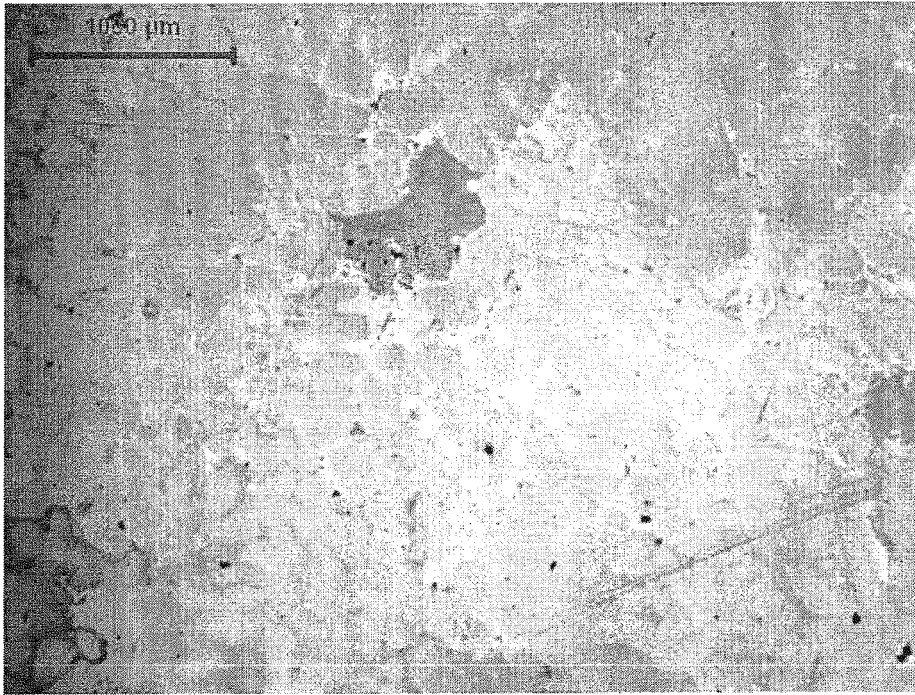


Figure 7

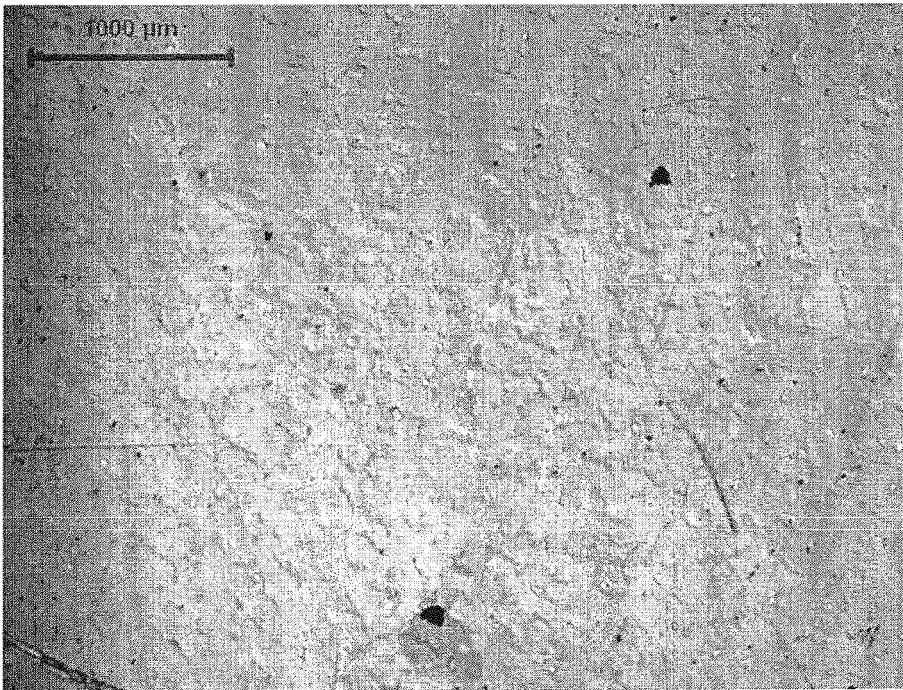


Figure 8

Magnification 100X

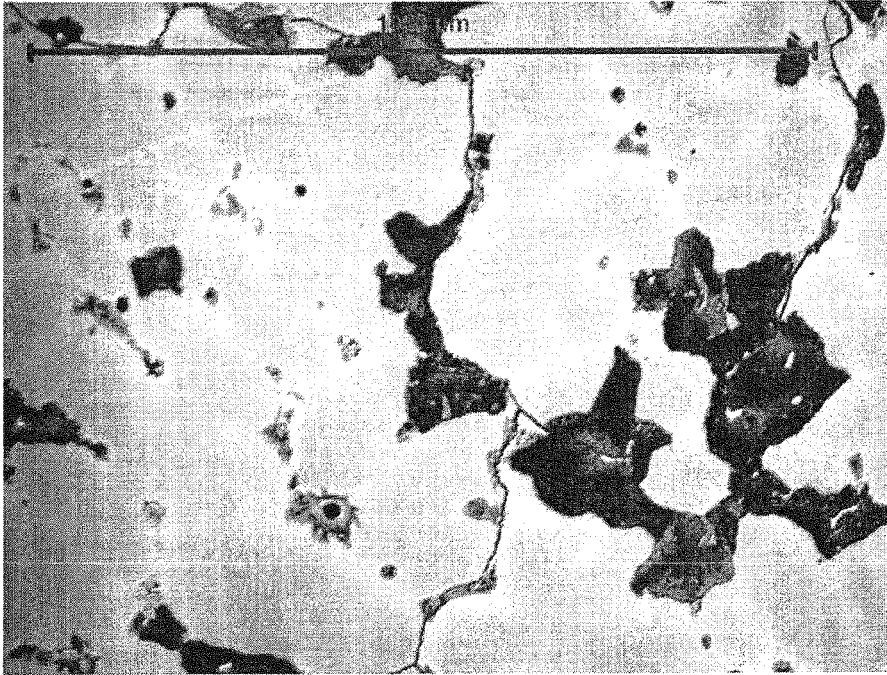


Figure 9

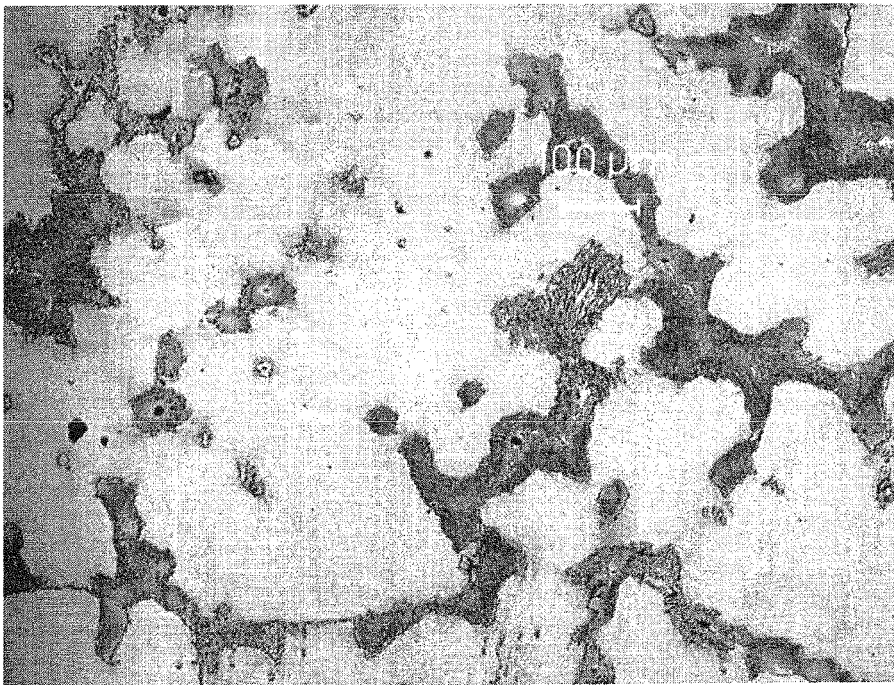


Figure 10

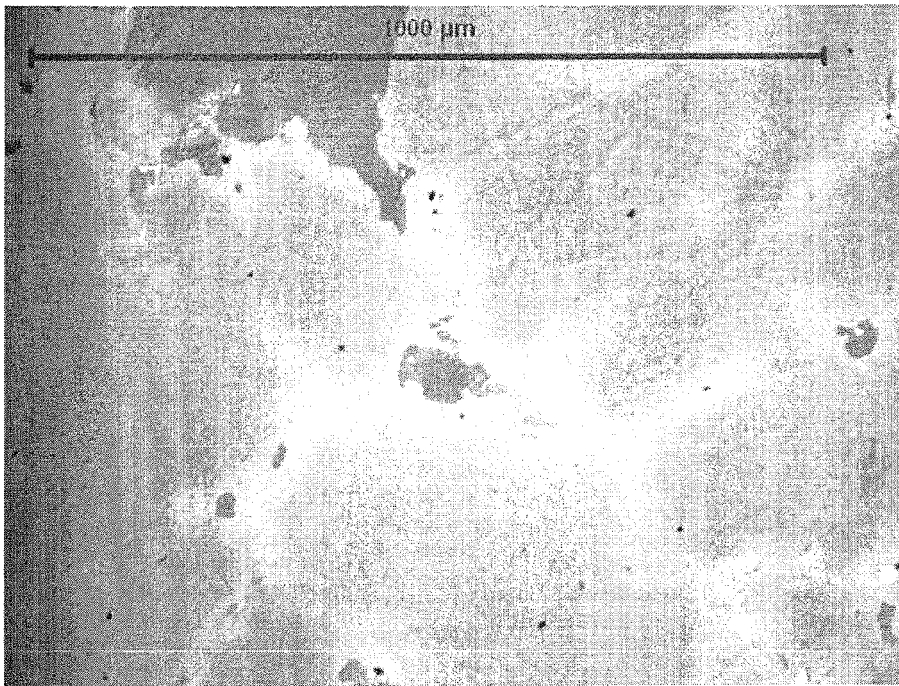


Figure 11

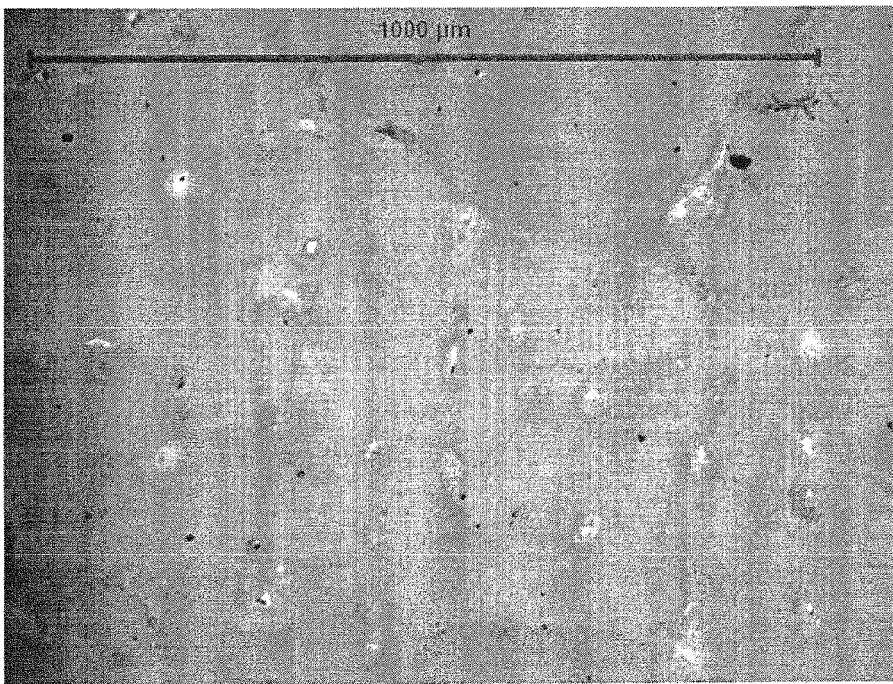


Figure 12

Magnification 500X

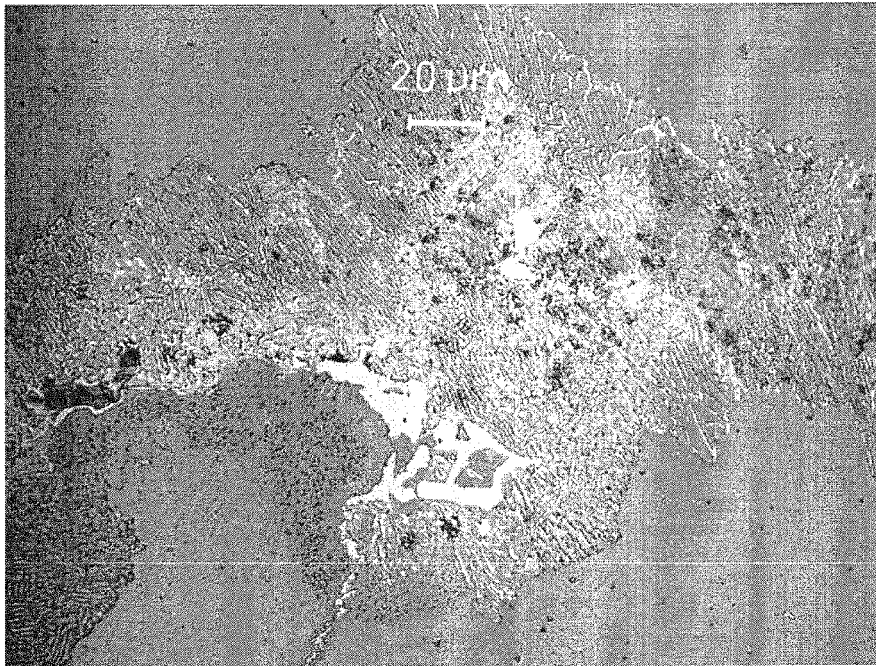


Figure 13

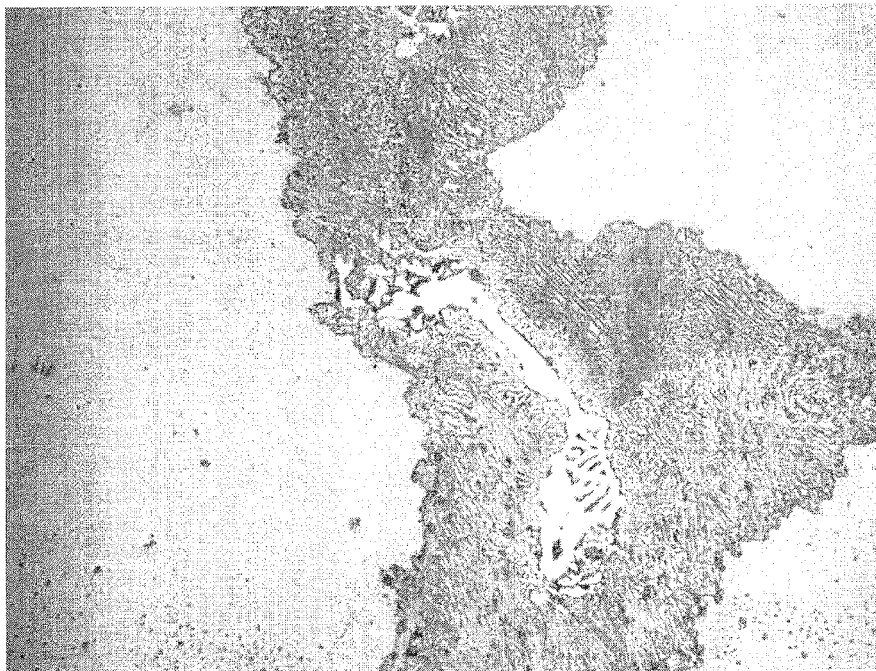


Figure 14

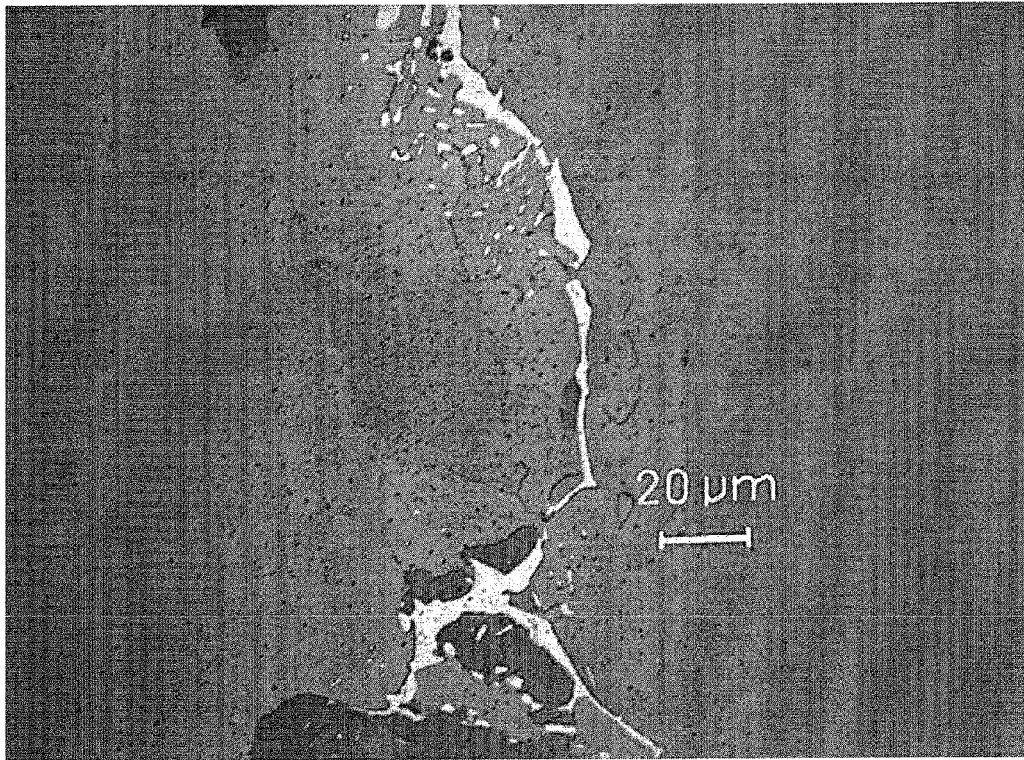


Figure 15

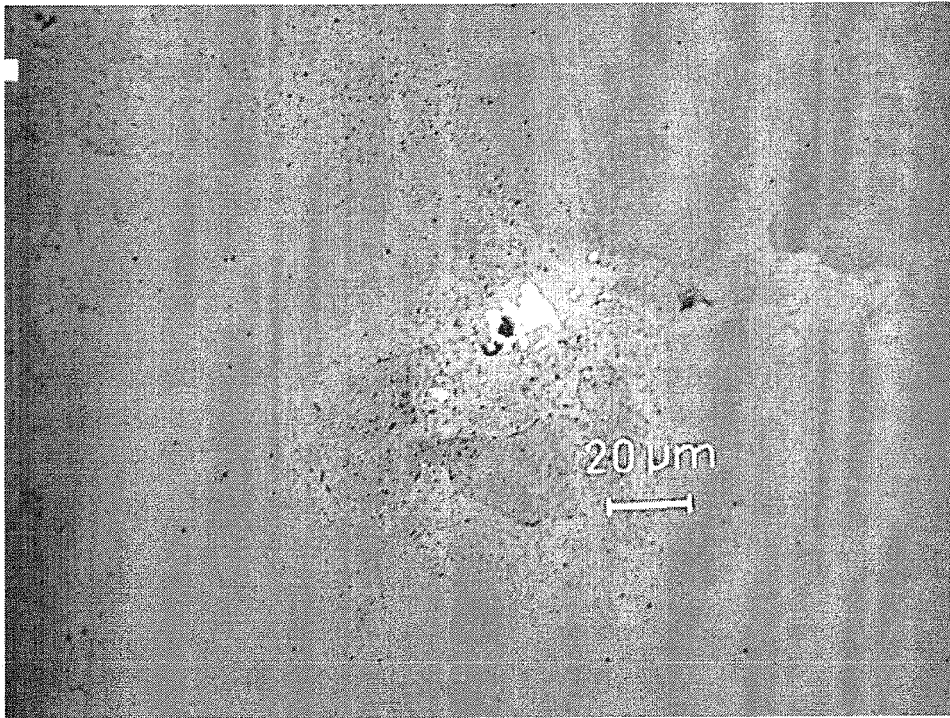


Figure 16

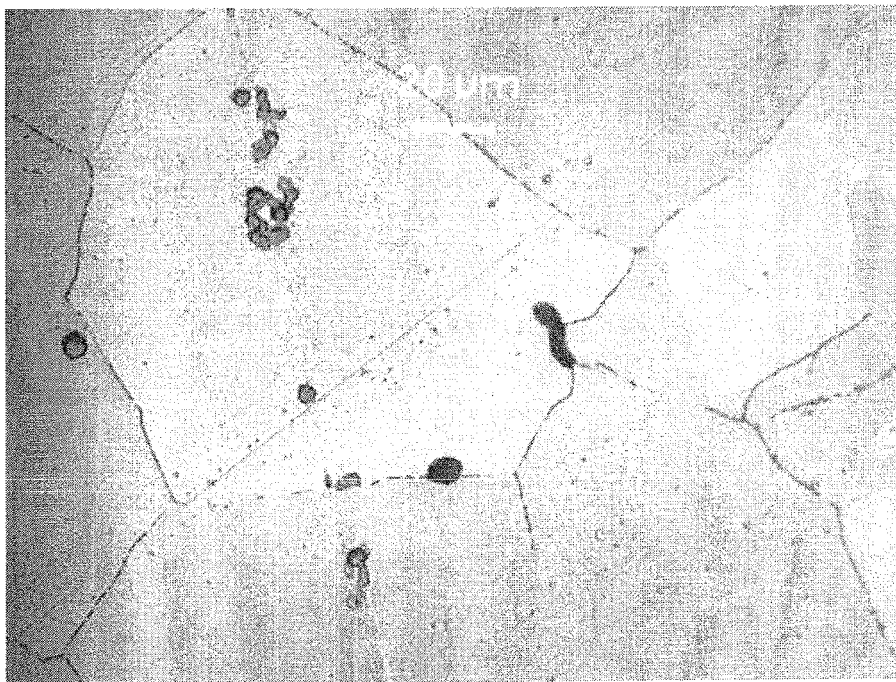
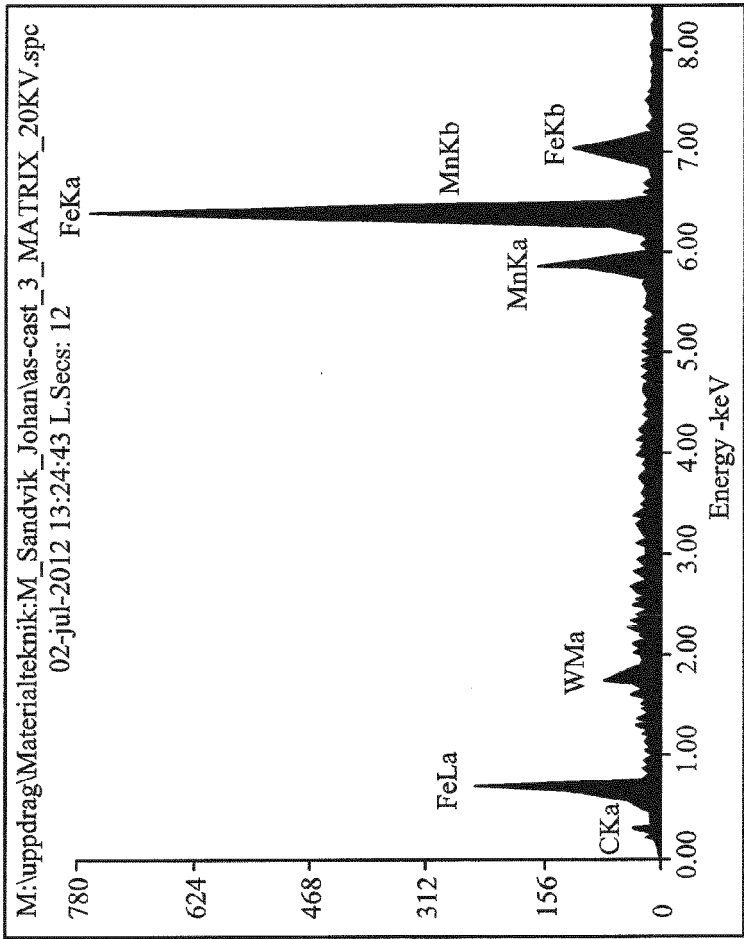


Figure 17

Element	Wt %	At %
CK	04.44	18.33
WM	05.30	01.43
MnK	11.56	10.42
FeK	78.70	69.82



KV: 20.00. TILT: 0.00 TAKE-OFF: 52.55 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

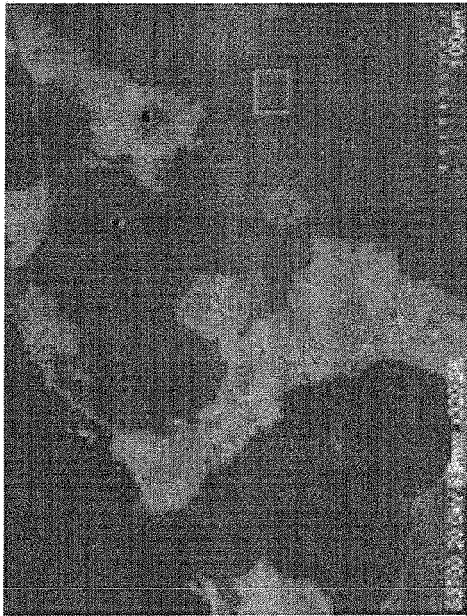


Figure 18

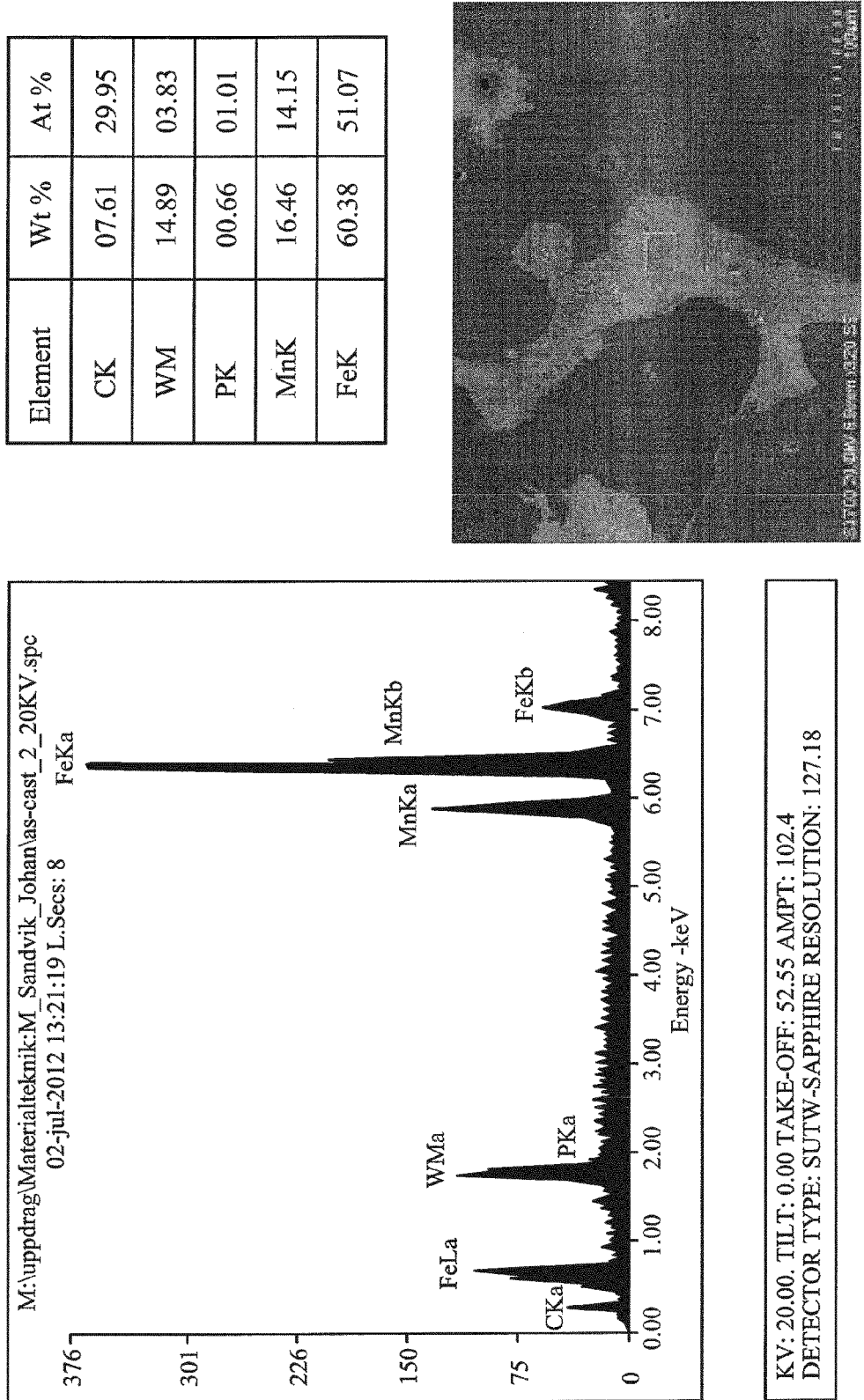
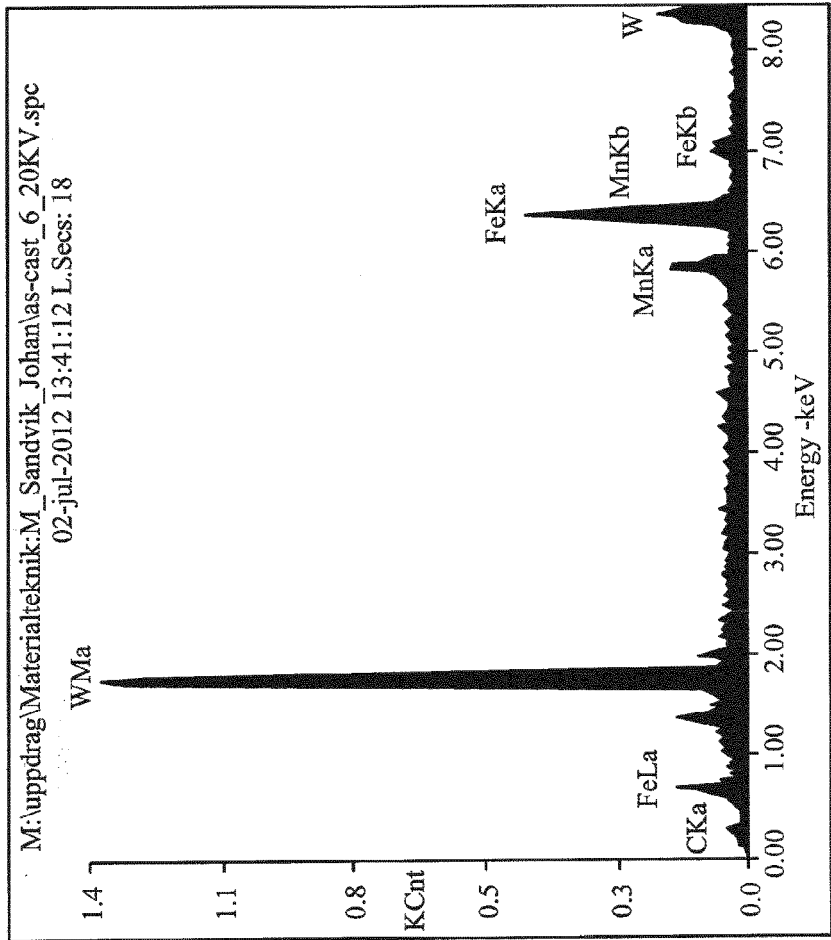
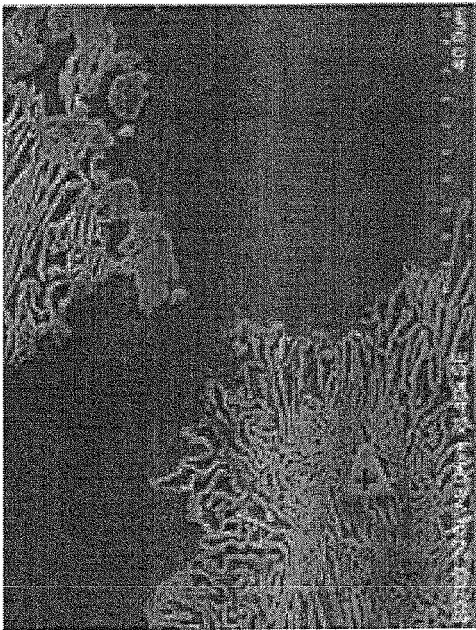


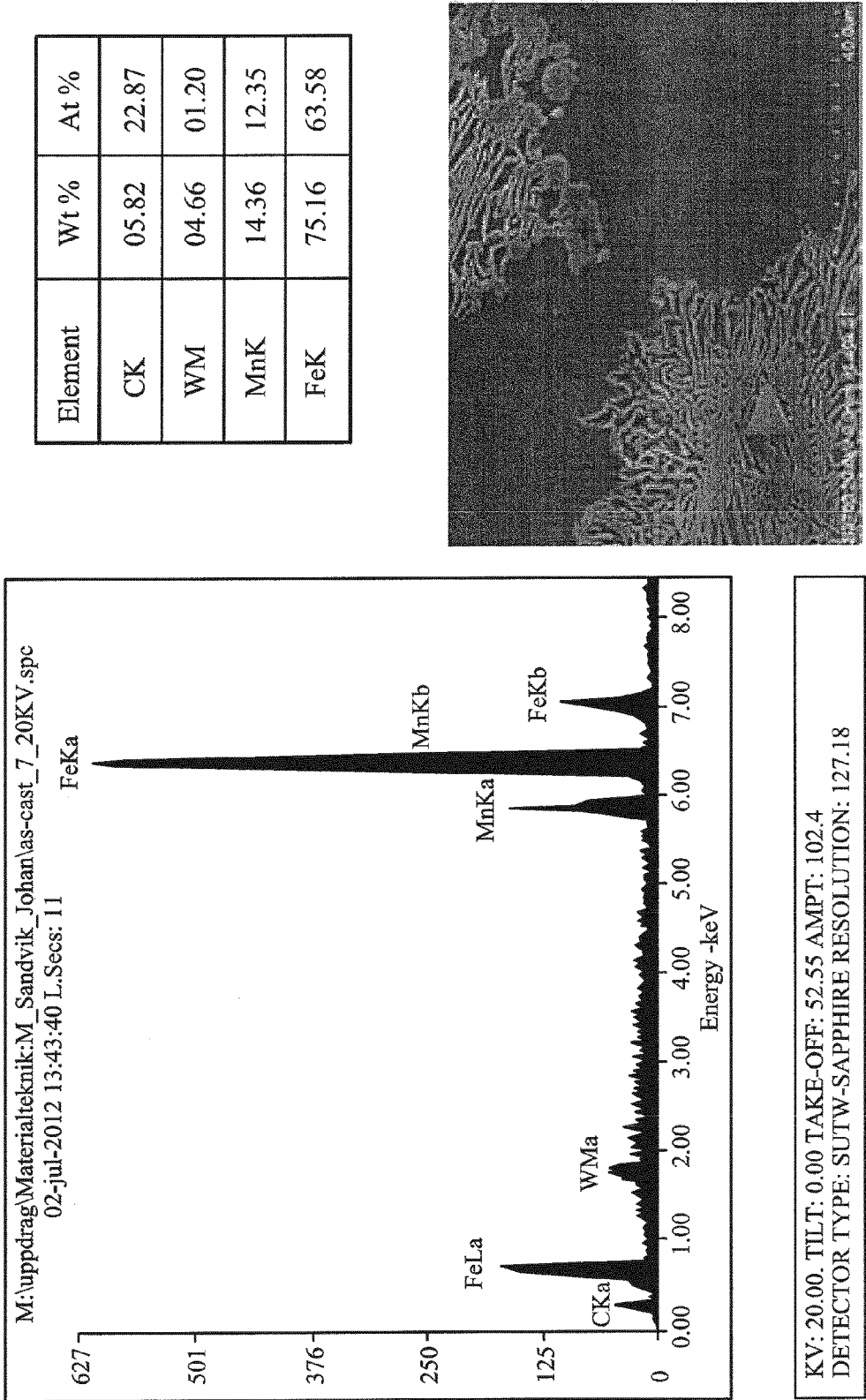
Figure 19

Element	Wt %	At %
CK	03.85	26.04
MnK	06.35	09.39
FeK	24.59	35.76
WL	65.21	28.81



KV: 20.00. TILT: 0.00 TAKE-OFF: 52.55 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

Figure 20



KV: 20.00. TILT: 0.00 TAKE-OFF: 52.55 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

Figure 21

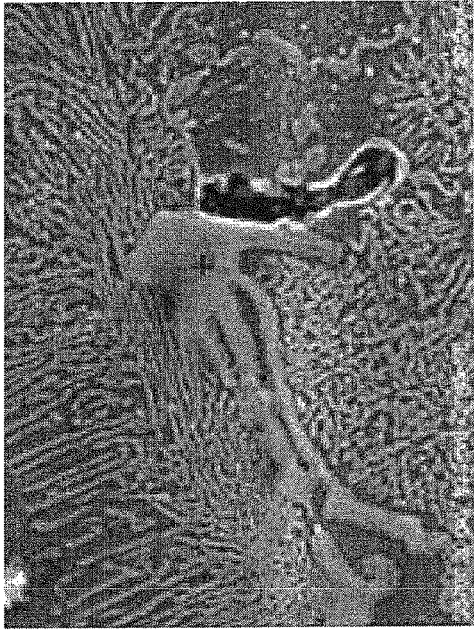
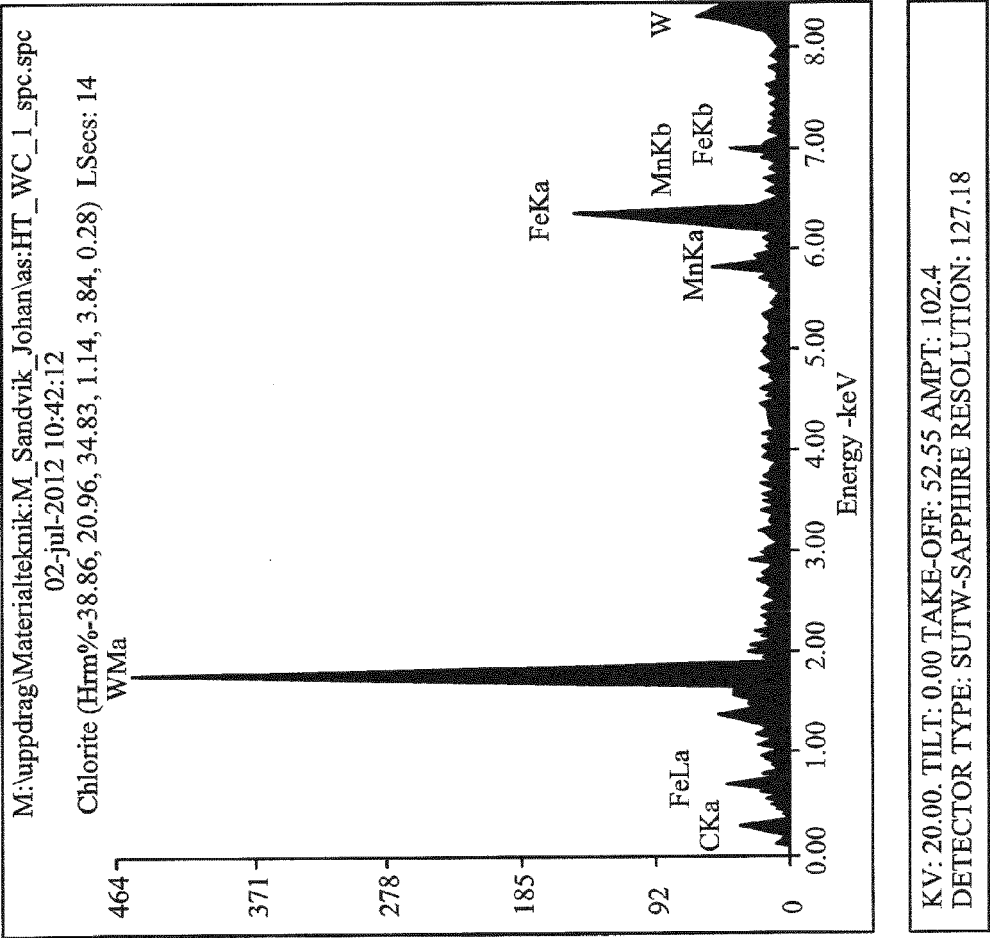
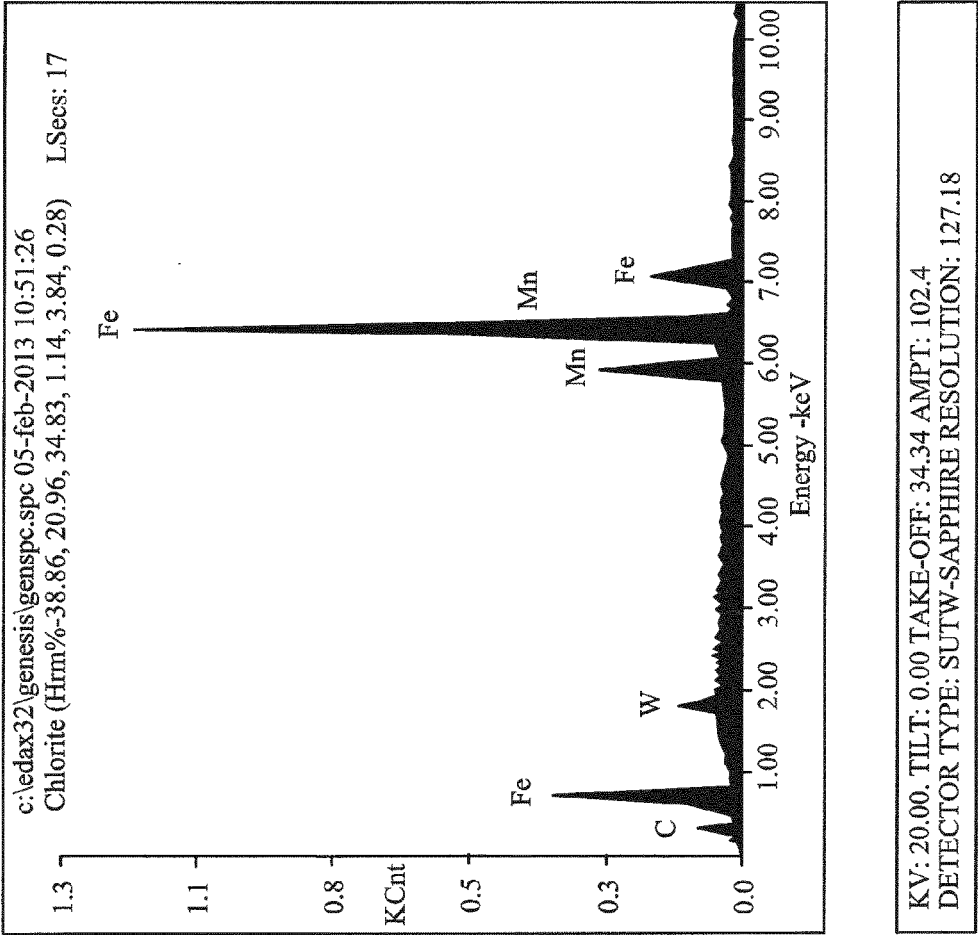


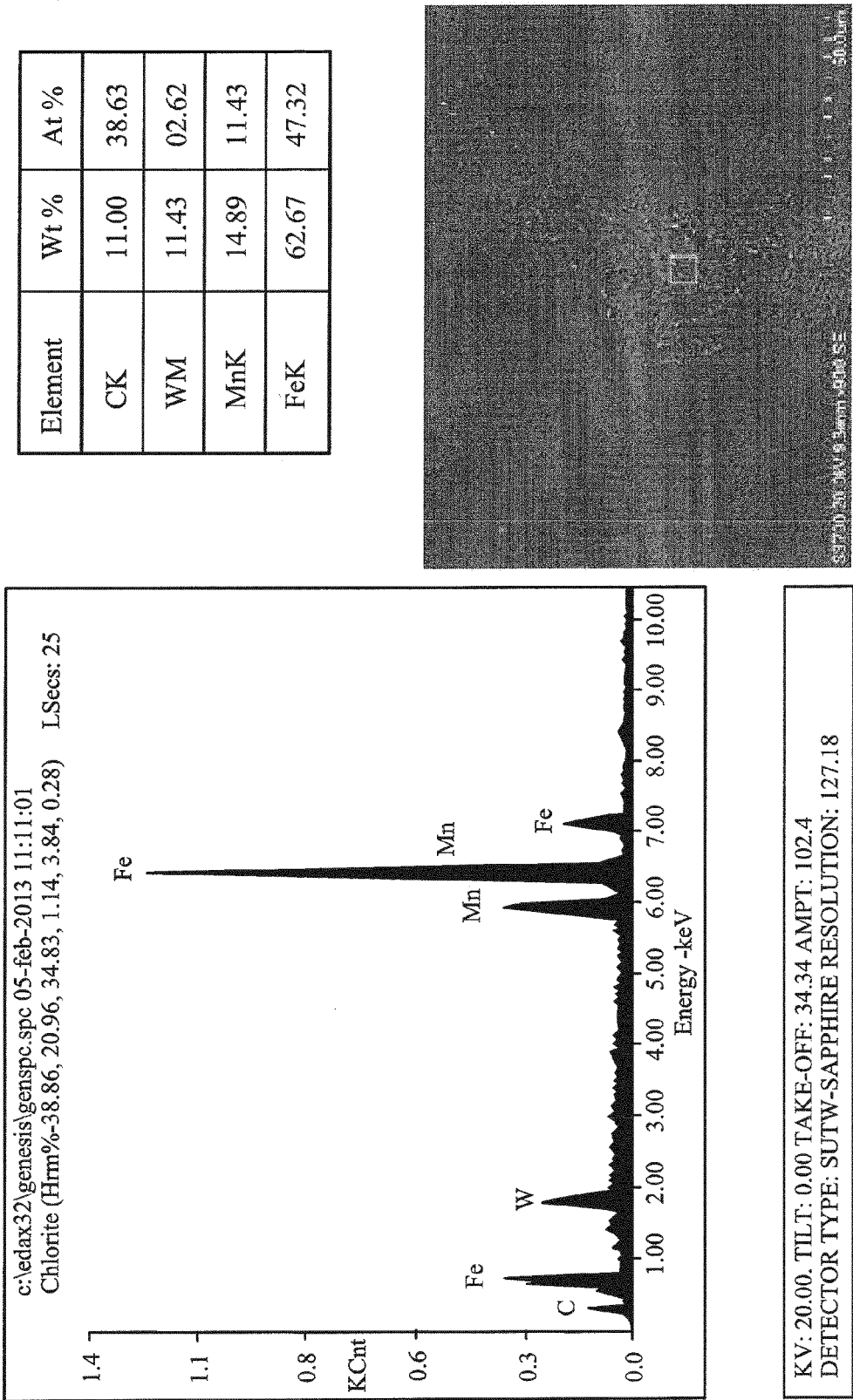
Figure 22



Element	Wt %	At %
CK	08.55	31.22
WM	05.84	01.39
MnK	12.25	09.78
FeK	73.36	57.60

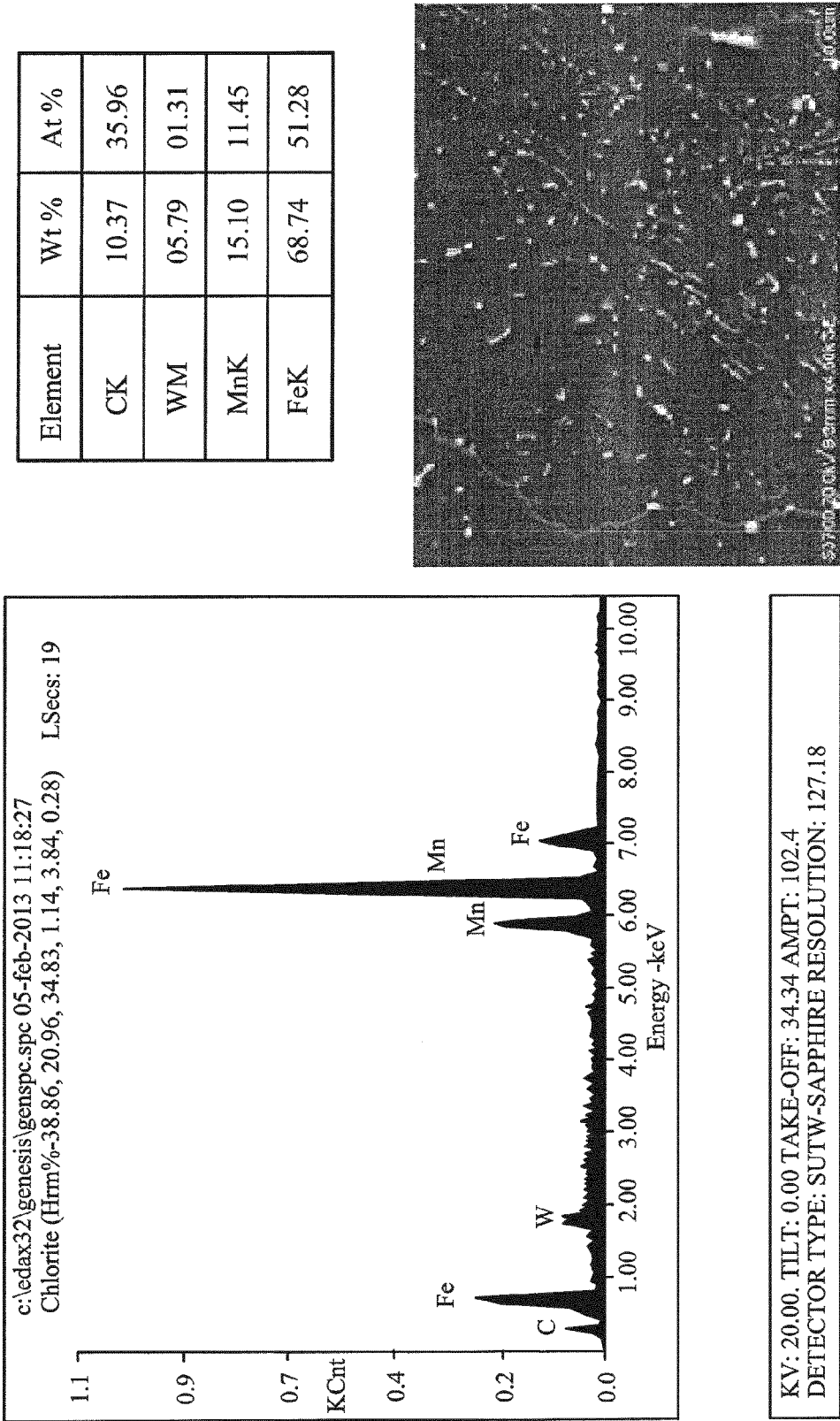


Figure 23



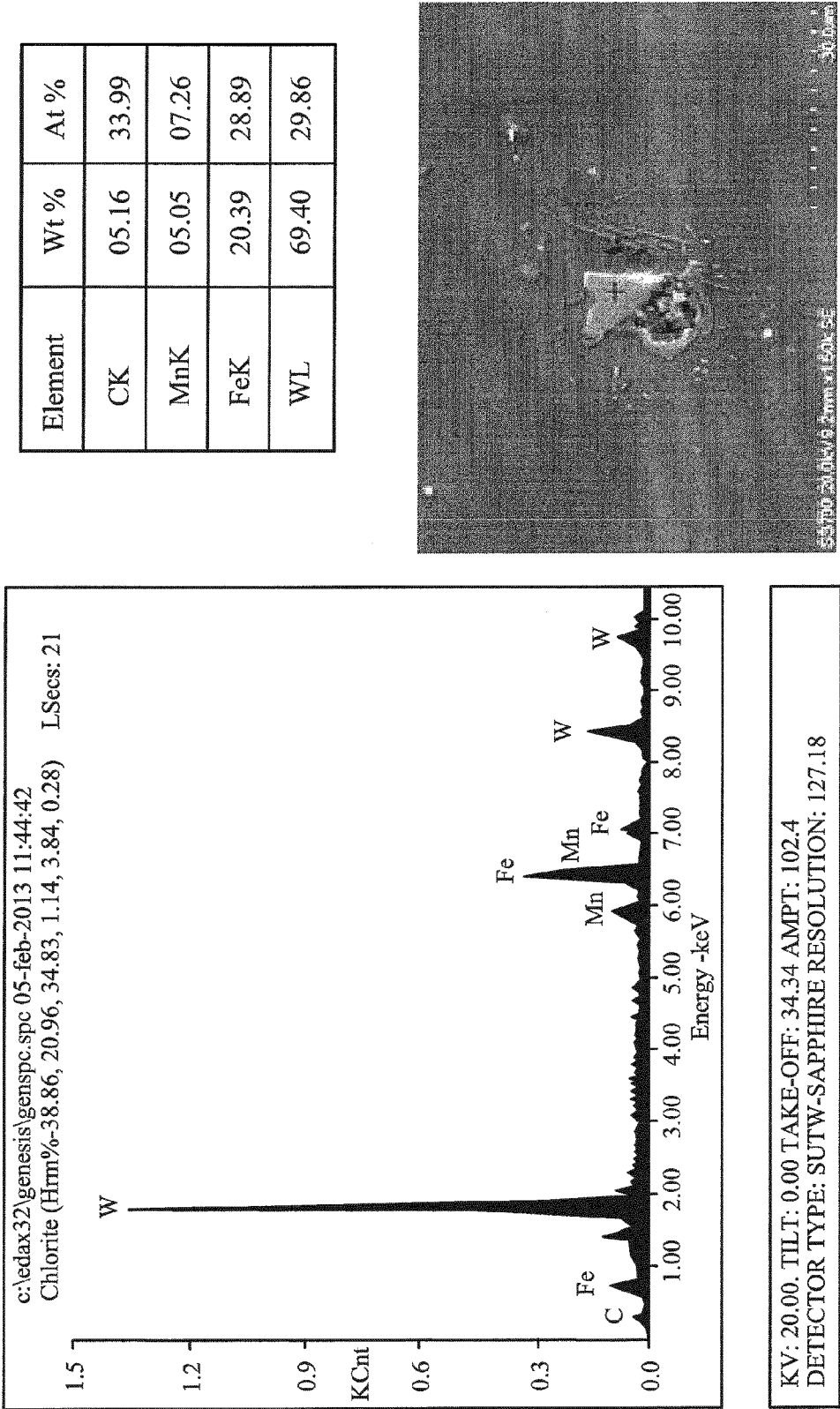
KV: 20.00. TILT: 0.00 TAKE-OFF: 34.34 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

Figure 24



KV: 20.00, TILT: 0.00 TAKE-OFF: 34.34 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

Figure 25



KV: 20.00. TILT: 0.00 TAKE-OFF: 34.34 AMPT: 102.4
DETECTOR TYPE: SUTW-SAPPHIRE RESOLUTION: 127.18

Figure 26

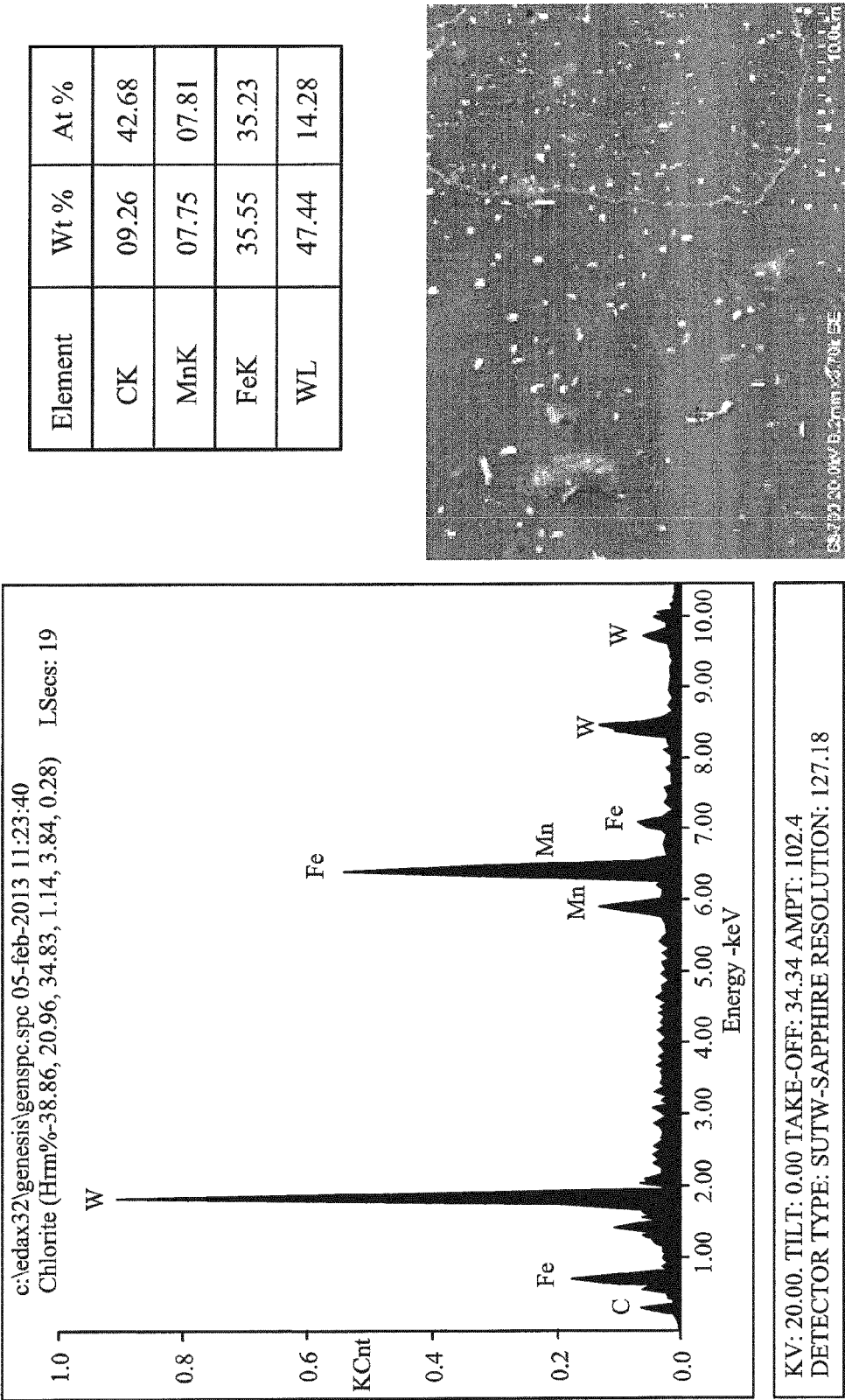


Figure 27

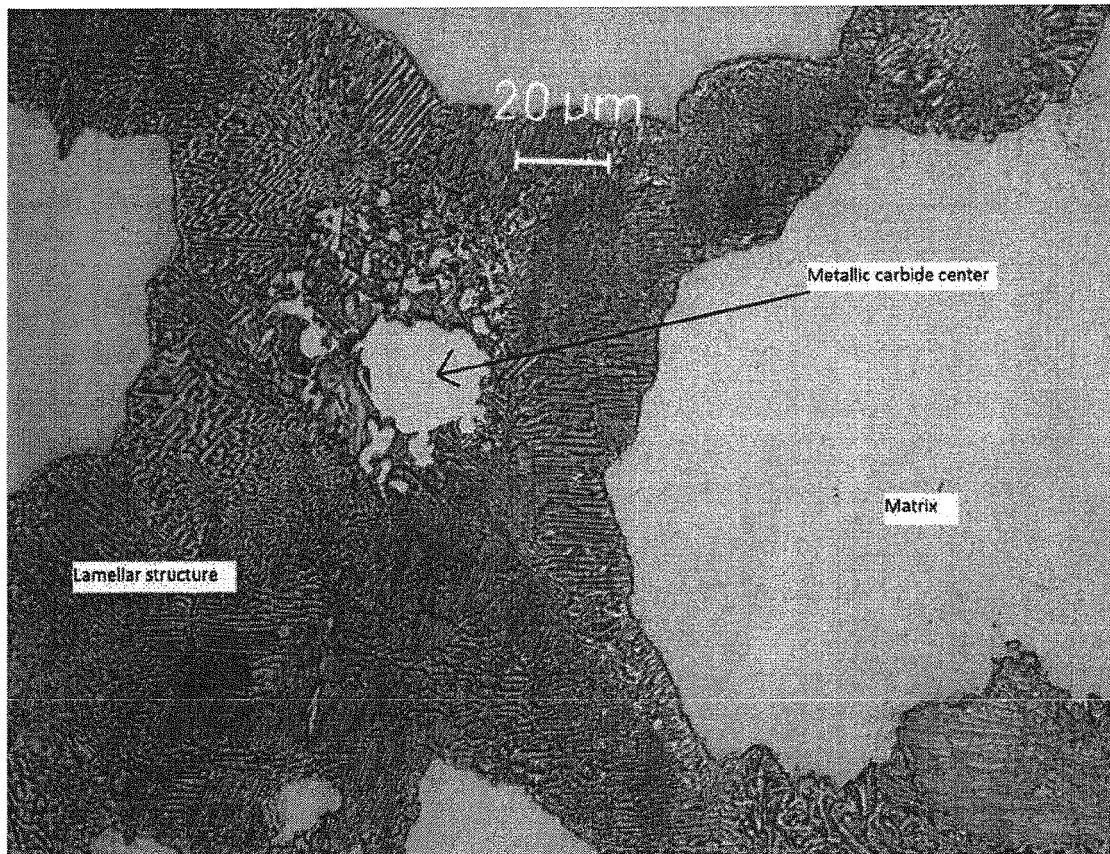


Figure 28

Brinell

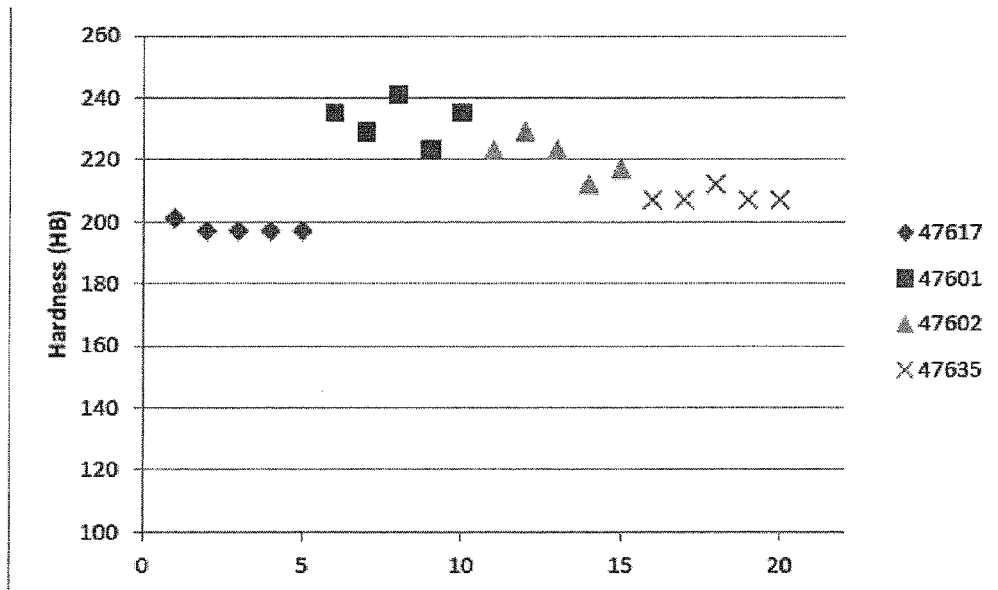


Figure 29

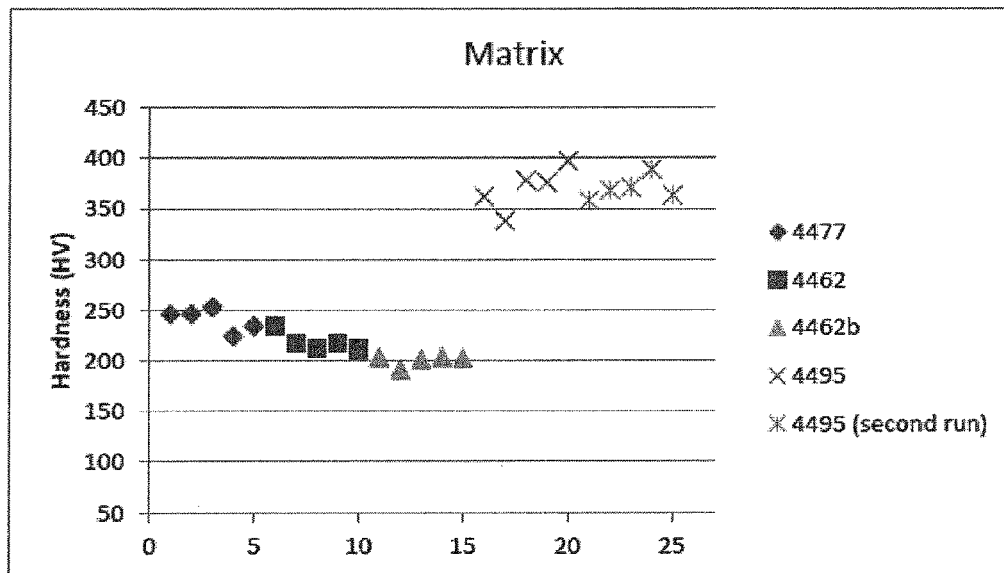


Figure 30

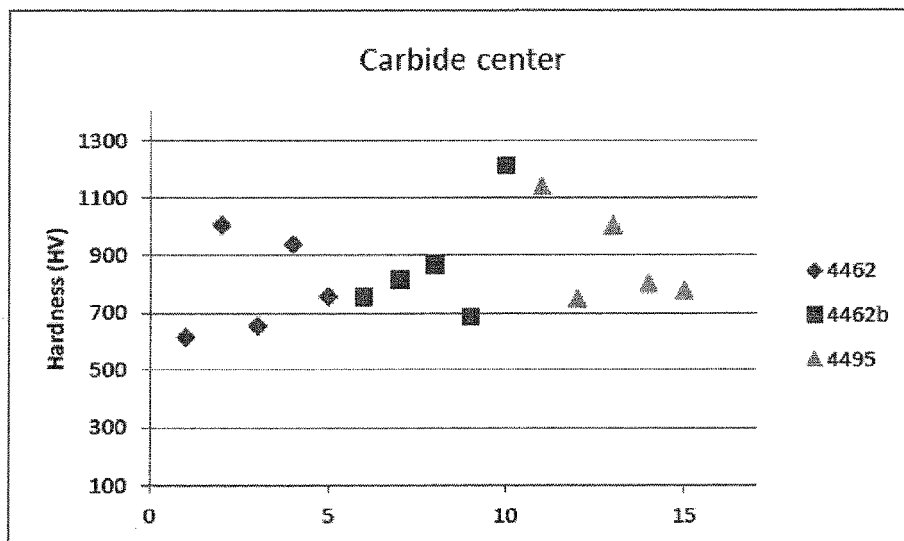


Figure 31

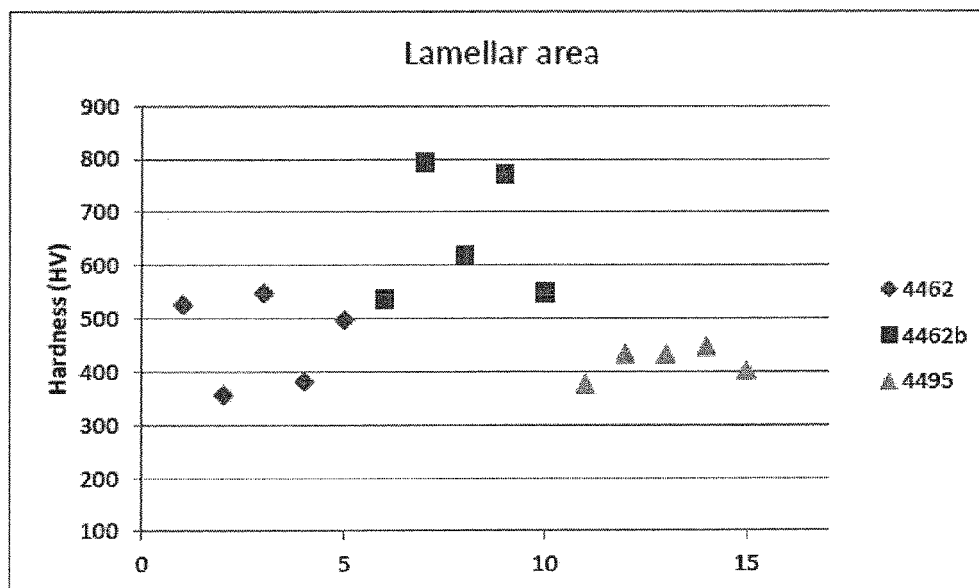


Figure 32

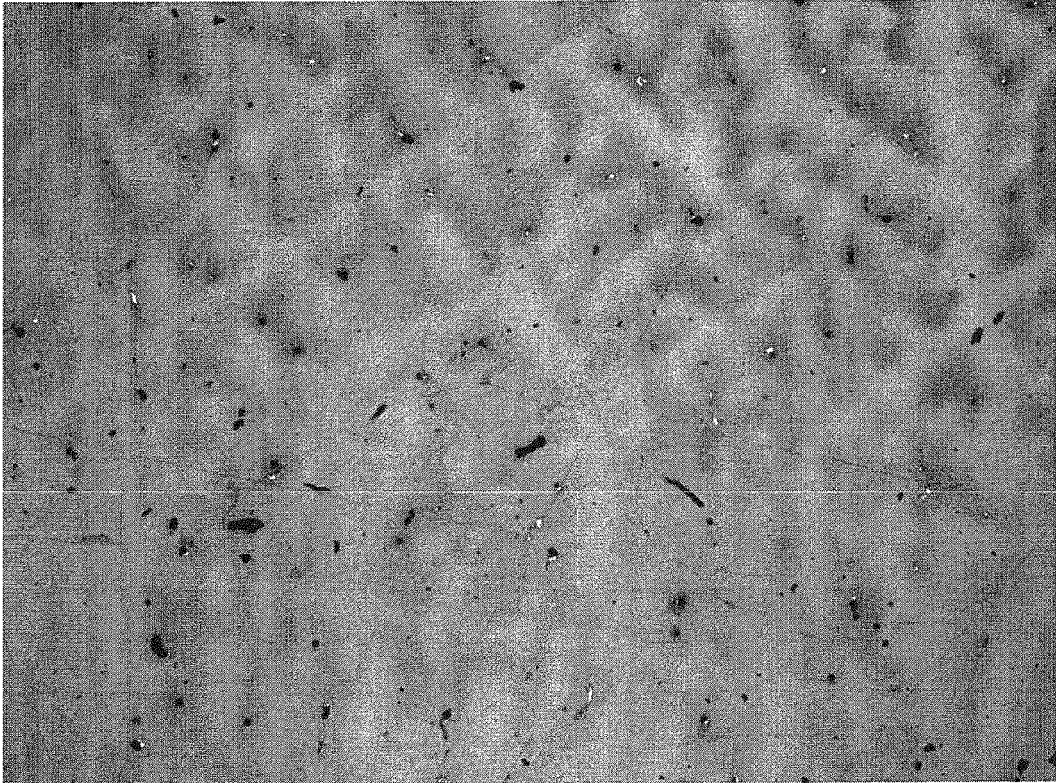


Figure 33



EUROPEAN SEARCH REPORT

 Application Number
EP 13 16 7522

5

10

15

20

25

30

35

40

45

50

55

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	"Tungsten in Steel", ITIA NEWSLETTER, INTERNATIONAL TUNGSTEN INDUSTRY ASSOCIATION, 1 December 2008 (2008-12-01), pages 1-8, XP002715339, Brussels, Belgium * pages 1-8 *	1-15	INV. C21D6/00 C21C7/06 C22C1/02 C22C38/04 C22C38/28 C22C38/38
A	US 5 308 408 A (KATILA REIJO [FI]) 3 May 1994 (1994-05-03) * paragraphs [0002] - [0005]; claims 1-6 *	1-15	
A,D	CN 101 736 658 A (UNIV YANSHAN) 16 June 2010 (2010-06-16) * abstract *	1-15	
A,D	RU 2009 116306 A (UCHREZHDENIE ROSSIJSKOJ AKADEMII NAUK INST FIZ PROCHNOSTI I MATERIALOV) 10 November 2010 (2010-11-10) * abstract *	1-15	
A	EP 2 465 964 A1 (FUNDACION INASMET [ES] FUNDACION TECNALIA RES & INNOVATION [ES]) 20 June 2012 (2012-06-20) * pages 2-4; claims 1-4 *	1-15	TECHNICAL FIELDS SEARCHED (IPC) C21D C21C C22C
A	WO 01/88213 A1 (PROENGCO AB [SE]; ANDERSSON CARL HAAKAN [SE]; NILSSON ANDERS [SE]; STA) 22 November 2001 (2001-11-22) * pages 4-14; claims 1-34 *	1-15	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 24 October 2013	Examiner Chebeleu, Alice
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 13 16 7522

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-10-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5308408 A	03-05-1994	AU 8437891 A	30-03-1992
		EP 0548119 A1	30-06-1993
		FI 904500 A	13-03-1992
		JP H06500825 A	27-01-1994
		US 5308408 A	03-05-1994
		WO 9204478 A1	19-03-1992

CN 101736658 A	16-06-2010	NONE	

RU 2009116306 A	10-11-2010	NONE	

EP 2465964 A1	20-06-2012	CN 102534361 A	04-07-2012
		EP 2465964 A1	20-06-2012
		US 2012145286 A1	14-06-2012

WO 0188213 A1	22-11-2001	AU 5898201 A	26-11-2001
		AU 2001258982 B2	03-02-2005
		BR 0110886 A	08-05-2007
		CA 2409124 A1	22-11-2001
		CN 1429280 A	09-07-2003
		EP 1409755 A1	21-04-2004
		JP 2003533593 A	11-11-2003
		MX PA02011197 A	19-08-2004
		NO 20025499 A	16-01-2003
		SE 522667 C2	24-02-2004
		UA 75593 C2	17-03-2003
		US 2004028548 A1	12-02-2004
		US 2009123324 A1	14-05-2009
		WO 0188213 A1	22-11-2001
		ZA 200209057 A	07-11-2003

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5308 A [0003]
- US 408 A [0003]
- RU 2009116306 [0003]
- US 2009123324 A [0003]
- CN 101736658 [0003]
- HU 197775 [0003]
- CN 1271028 [0003]
- CN 101831590 [0003]
- CN 101638753 [0003]