EXPERIMENTAL DETAILS AND RESULTS

Aim: The objective of the work is to deposit nickel with diamond on copper disc. The copper disc is phosphor bronze with 92% Cu and 8% Sn. The thickness of the disc is 50, 55 and 65 microns. The diameter of the disc is 3 inch round. Initially the studies were carried out on annealed Cu substrates for ease. Since the Percentage of Sn in Copper discs is very less the properties of Cu substrates in the lab and Cu discs is almost same. Electrodeposition of nanocrystalline nickel was carried on initially by Direct current and Pulsed current. The practical purpose of the work is for polishing (for eg. Polishing of artificial diamond jwellery).

All depositions were carried out in a double walled cell, connected to the constant temperature bath maintained at $50^{O}C$ as shown in the figure.1. The double walled cell was placed on the magnetic stirrer and the electrodes were connected to the DC regulated power supply in case of DC deposition and to the potentiostat for pulsed current deposition. The details of the equipment used are given below:

- Constant temperature bath (Julabo F-32, Germany)
- Magnetic stirrer (SCHOTT, Germany)
- DC regulated power supply (SaiRush Electronic systems SVP 100010, India), which has a voltmeter of resolution of 0.1V and an ammeter of resolution 0.01Amp. This device can supply a maximum current of 10A and a maximum voltage of 100V (for DC deposition)
- Potentiostat/Galvanostat model 263A (Princeton Applied Research, USA) which can supply a maximum of 2A and 10A when connected to the booster.

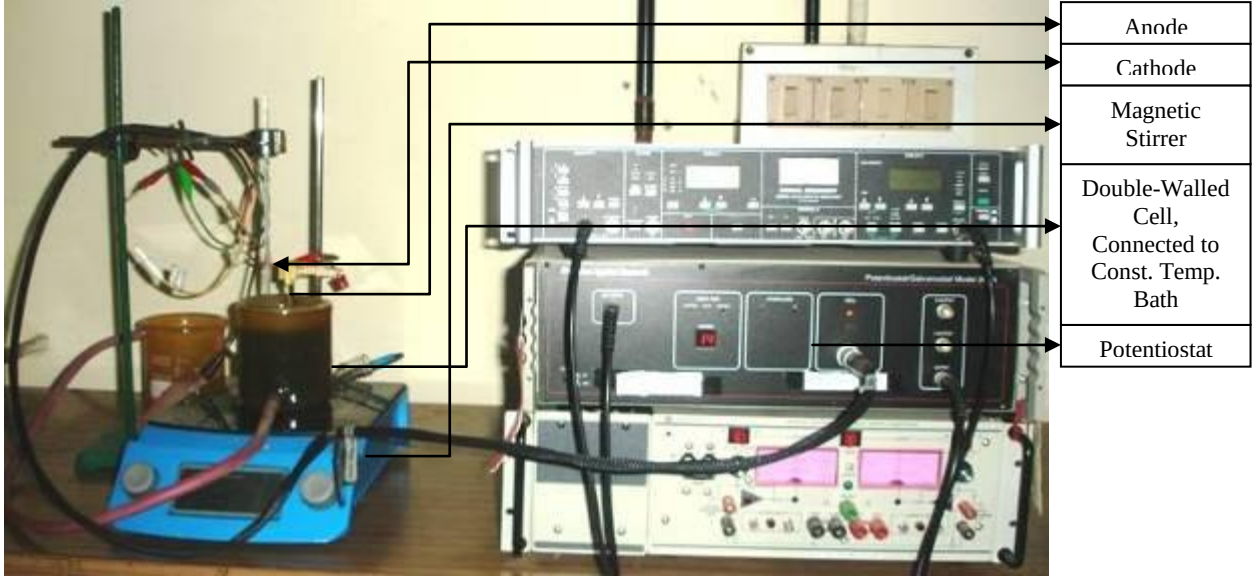


Fig. 1 : Experimental Setup

Cathode

Studies were carried out using copper as a cathode because of excellent adherence of nickel to copper. The substrates used initially were annealed copper samples cut in size of approximately 20 mm by 20 mm(length by height). Before each experiment, the substrate copper was polished using 120P emery papers with grades 1/0, 2/0, 3/0 and 4/0 emery papers, followed by disc polishing using 5µm Alumina suspension and 1 µm alumina suspension and then ultrasonically cleaned in distilled water (or acetone).
Later on the substrates used were thin copper discs (Phosphor Bronze) with thickness 55 µm, 60 µm, 65 µm.

Anode

A cold rolled Ni piece of size approximately 10 cm x 2 cm x 3 mm (length x width x thickness) was used as the anode. It ensured enrichment of the ions in the bulk electrolyte which are used up in the deposition. The anode was polished using P 120 SiC papers followed by ultrasonic cleaning in distilled water before every experiment.

Bath Composition

First few depositions were carried out using Watts Bath for deposition of Ni on Cu. For deposition of diamond along with Ni on Cu, diamond powder was added to the Watts Bath.
Composition of Watts Bath:

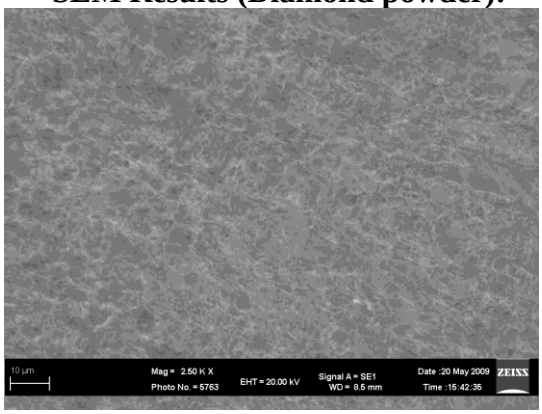
- $NiSO_4\ 6H_2O$ 240g/l
- $NiCl_2\ 6H_2O$ 40g/l
- H_3BO_3 40g/l

All reagents used for the preparation of the Watts bath were of analytical grade and distilled water was used to dissolve the reagents. The temperature of the bath was maintained at 50ºC. Stock solutions were prepared and one bath was used for 4 or 5 depositions. The bath was continuously stirred while the deposition was going on.

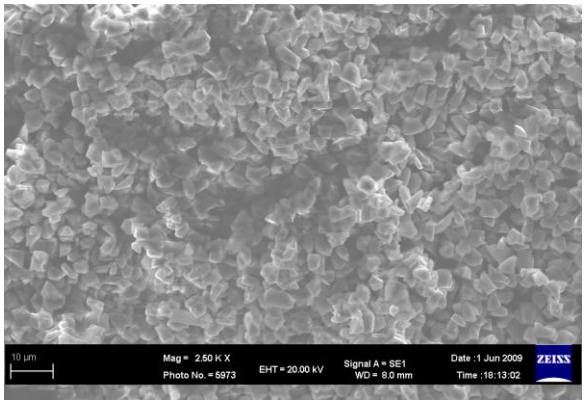
Analysis of the Diamond Powder:

The diamond powder was available in two particle sizes: first one had a particle size of around 0.5 micron and other about 3-6 microns. Both were analyzed using SEM and EDAX to test their contents and nature.

- **SEM Results (Diamond powder):**



250x (SE mode)
(a) 0.5 micron



250x (SE mode)
(b) 3-6 micron

- **EDAX Studies on Diamond Powder:**

1)0.5 micron: The carbon content was found to be around 82.11%. Rest was impurities and oxygen.
2)3-6 micron: The carbon content was found to be around 92.44%. Rest was impurities and oxygen.

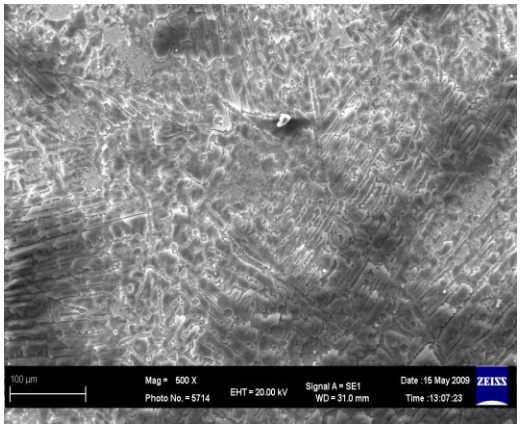
Direct Current Deposition:
Initially direct current depositions were carried out on copper cathode using nickel as anode, with and without diamond addition, at a temperature of 50°C using a current density of 0.05 A/cm^2. The size of the diamond powder was 0.5 microns.

Table 1: Experimental details of initial DC depositions performed at 50^{O}C.

Sample No.	Current density(A/cm^2)	Area Exposed(cm^2)	Deposition Time(min)	Initial Weight (gm)	Final Weight (gm)	Weight Deposited (gm)	Diamond Concentration(if added)	Thickness of deposition (µm)
1	0.05	-	40	-	-	-	No	-
2	0.05	-	40	-	-	-	No	-
9	0.05	-	40	-	-	-	1 g/l	-
*10	0.05	4.2216	40	3.112	3.289	0.177	1 g/l	47.067
11	0.1	2.8864	25	4.535	4.617	0.082	1 g/l	31.8917

*deposition on copper disc

- **SEM Results:**



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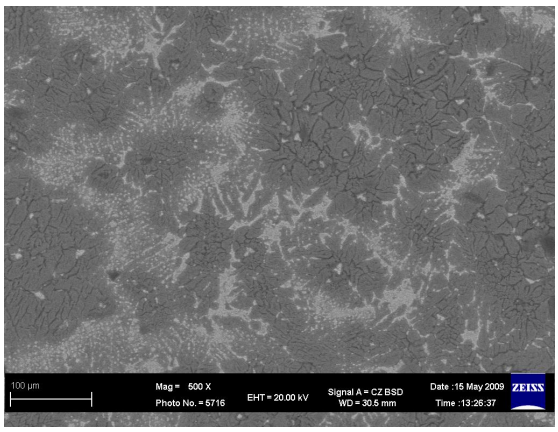
(a) DC, No diamond addition (Sample 1)



500x (BSD Mode)
(b) DC, Diamond added (1 g/l) (Sample 10)

- **Analysis:**

1) The nature of the deposit is non uniform.
2) The DC deposit showed greenish texture after being exposed to air due to Nickel in the deposit. This might be due to the porosity in the deposit.
3) The percentage of Carbon in the deposit when diamond added to the Watts Bath was 1 g/l was found to be quite low (around 5 to 6 %).

Pulse current deposition:

Pulse deposition was performed using a Princeton Applied Research (USA) 263A model potentiostat/galvanostat. Virtual Potentiostat interface allowed in varying the parameters of pulse deposition, such as the on-time (t_{on}), off-time (t_{off}), duty cycle, period, time of deposition using a simple program. Duty cycle is defined as (t_{on}/ t_{on}+t_{off}) given in percentage and the period of deposition is the sum of t_{on} and t_{off} usually mentioned in milliseconds. In present study, a square wave pulse generator program was used. Initial experiments were carried out using a current density of 0.1 A/cm^2 on both annealed copper substrates and Copper disc. The diamond powder used was of two sizes. The particles sizes of the two samples were 0.5 micron and 3-6 microns. The experimental details are given in Table.2. These samples were then characterized by scanning electron microscopy to study the morphology of as-deposited sample.

Table 2: Results of Initial Pulsed Current Depositions performed at 50^{O}C.
(Diamond size: 0.5 micron)

Sample No.	Current density(A/cm^2)	Area exposed(cm^2)	Duty cycle (%)	Time period(ms)	Deposition time(min)	Initial weight(gm)	Final weight(gm)	Weight Deposited(gm)	Diamond Concentration(if added)	Thickness of deposition(µm)
3	0.1	-	20	30	60	-	-	-	No	-
4	0.1	-	20	30	60	-	-	-	No	-
5	0.1	-	20	30	60	-	-	-	No	-
6	0.1	-	20	30	60	-	-	-	No	-

7	0.1	-	20	30	60	-	-	-	No	-
8	0.1	-	20	30	60	-	-	-	No	-
12	0.1	2.8480	20	30	120	4.941	-	-	1 g/l	-
13	0.1	2.8123	20	30	120	4.127	4.227	0.100	1 g/l	39.90
14	0.1	3.0212	20	30	120	4.571	-	-	2 g/l	-
15	0.1	2.8536	20	30	120	4.221	4.254	0.033	2 g/l	12.98
16	0.1	2.7888	20	30	120	4.731	4.847	0.116	2 g/l	46.69
17	0.1	2.0328	20	30	120	4.288	-	-	2 g/l	-
20	0.1	2.1868	20	30	120	4.499	4.505	0.006	1 g/l	3.080
21	0.1	2.6208	20	30	120	4.657	4.685	0.028	1 g/l	11.99
22	0.1	2.4272	20	30	120	4.694	4.845	0.151	1 g/l	69.83

Table 3: Results of Pulsed Current Depositions performed at 50^{O}C.
(Diamond size: 3-6 micron)

Sample No.	Current density(A/cm^2)	Area exposed(cm^2)	Duty cycle (%)	Time period(ms)	Deposition time(min)	Initial weight(gm)	Final weight(gm)	Weight Deposited(gm)	Diamond Concentration(if added)
T1	0.1	2.7888	20	30	180	5.037	5.173	0.136	1 g/l
T2	0.1	2.4920	20	30	180	5.733	5.889	0.156	1 g/l
T3*	0.1	2.9808	20	30	180	5.428	-	-	2 g/l
T4	0.1	2.9072	20	30	180	6.283	6.488	0.205	2 g/l
T5	0.1	2.5896	20	30	180	5.027	5.218	0.191	2 g/l
T6	0.1	2.4804	20	30	180	5.087	5.247	0.160	5 g/l
T7	0.1	3.0046	20	30	180	5.056	5.260	0.204	5 g/l
T8*	0.1	2.6692	20	30	180	5.107	-	-	7.5 g/l
T9	0.1	2.6990	20	30	180	5.693	5.844	0.151	7.5 g/l
T10*	0.1	2.6400	20	30	180	5.084	-	-	7.5 g/l
T11**	0.1	2.6732	20	30	180	5.693	5.793	-	7.5 g/l
T12	0.1	2.6400	20	30	180	6.340	6.501	0.161	10 g/l
T13**	0.1	2.3566	20	30	180	5.281	-	-	10 g/l
T14	0.1	2.5438	20	30	180	6.270	6.431	0.161	10 g/l
T15	0.1	2.4070	20	30	180	6.884	7.040	0.156	5 g/l
T16	0.1	2.7195	20	30	180	5.600			7.5 g/l

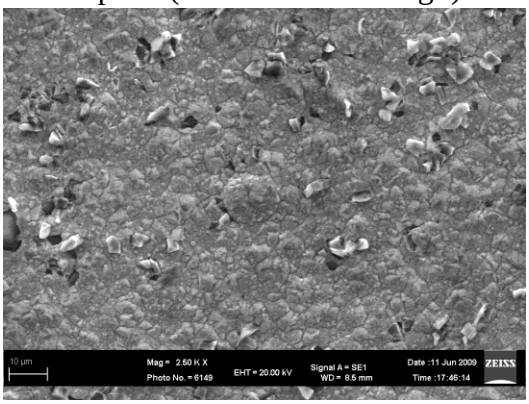
*No Deposition (Due to improper anode activation)
**Deposit came off

- Before every deposition the anode was activated for around 10 minutes using direct current for proper dissolution of Nickel in the electrolyte.
- A major problem that occurred during the deposition was that deposit came off when the concentration of diamond in the electrolyte was increased to 7.5 g/l. To avoid this problem, for the first 15 minutes the deposition was carried out without adding any diamond. Then the diamond was added and deposition continued.

- Finally out of all the samples T1 to T16, a total of 10 samples were selected. SEM and EDAX studies were carried out on these samples to study the nature of the deposit and the % of carbon content in the deposit. To check the surface roughness of the deposits, surface profilometry tests were carried out on these samples.

SEM Studies:

- Sample 1 (diamond conc. =1 g/l)



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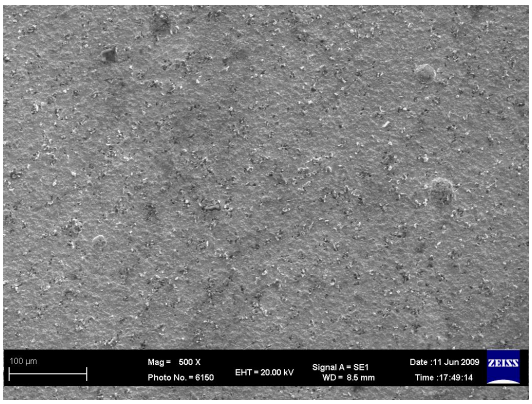

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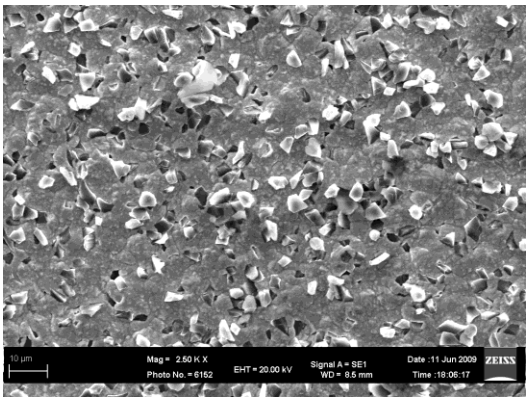
- Sample T2(diamond conc. =1g/l)



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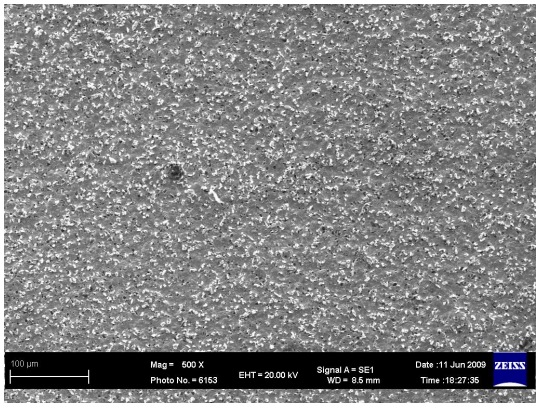

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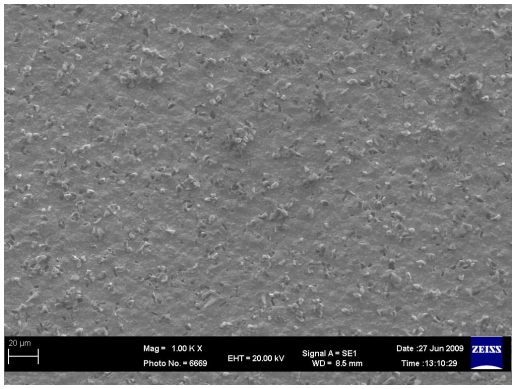
- Sample T4(diamond conc. =2g/l)



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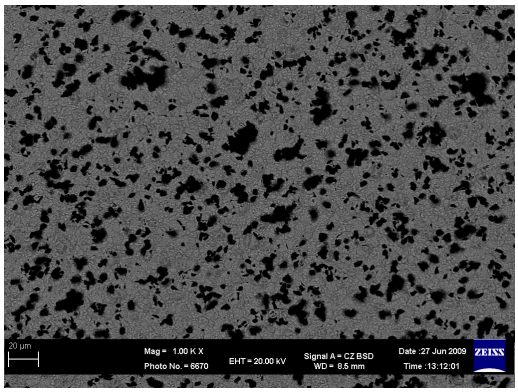

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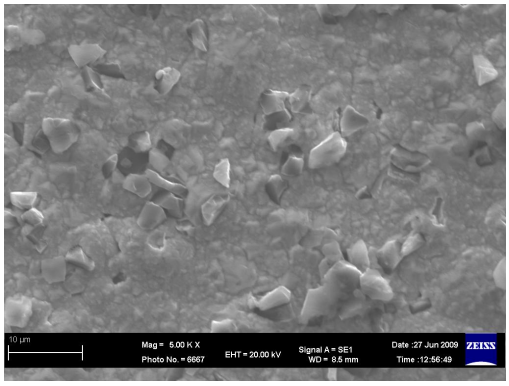

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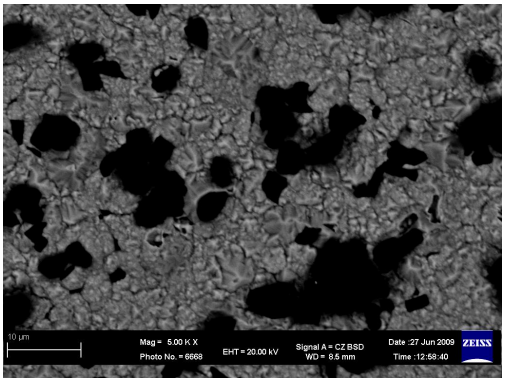

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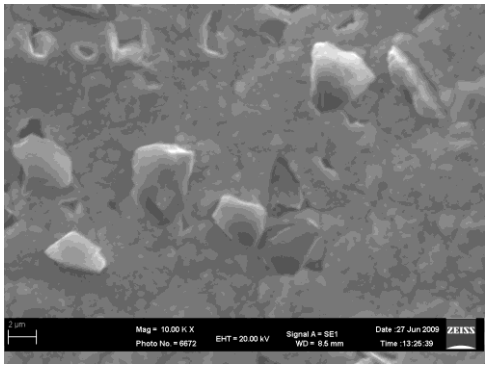
- Sample T5 (Diamond conc. =2g/l)



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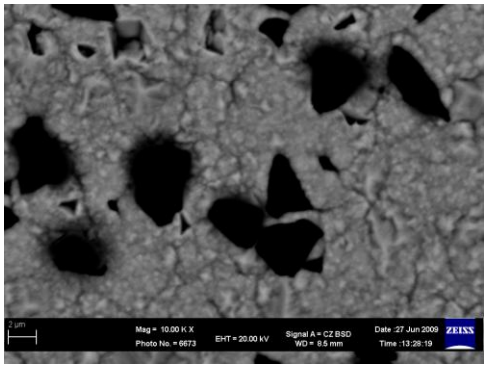

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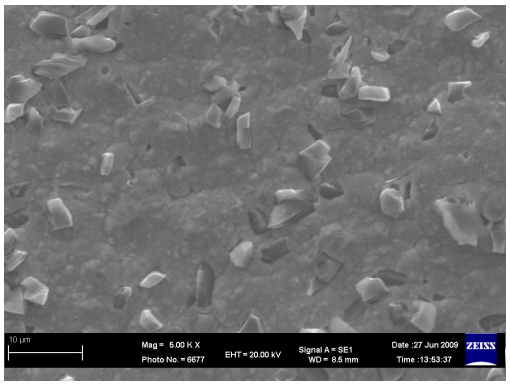

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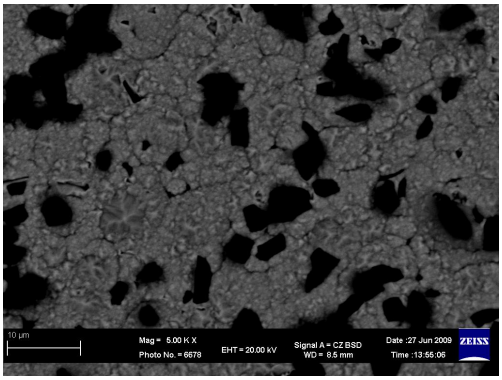

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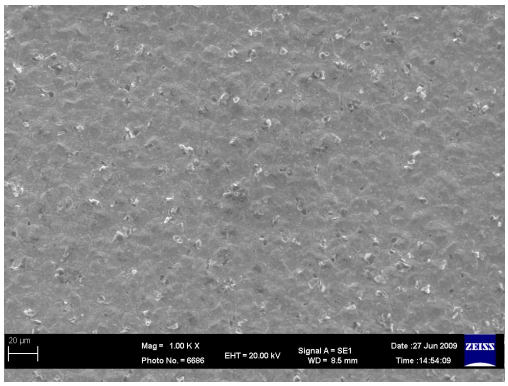
- Sample T6 (Diamond conc. =5g/l)



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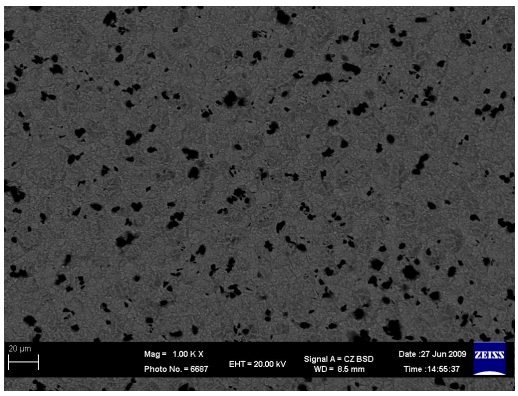

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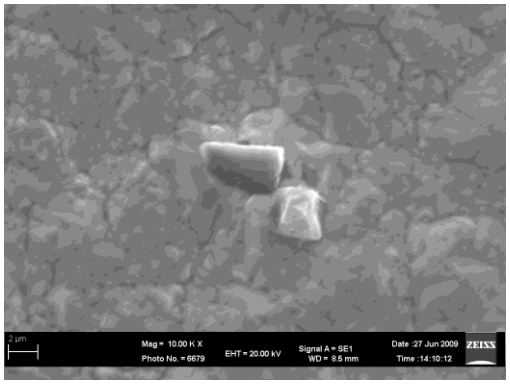

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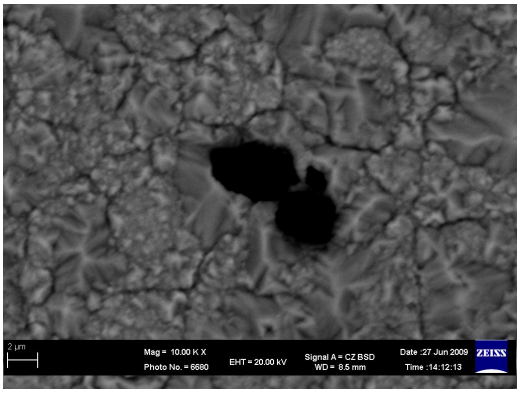

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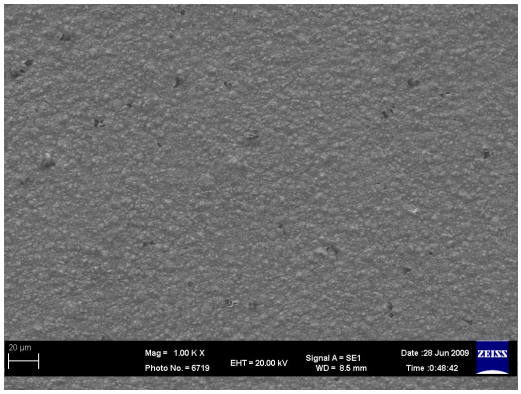
- Sample T15 (Diamond conc. =5g/l)



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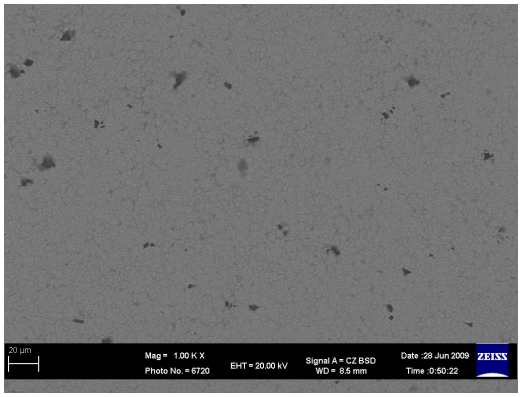

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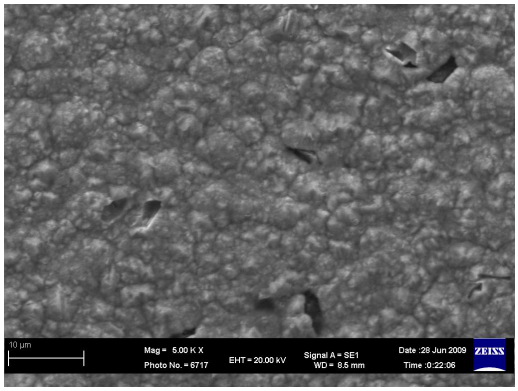

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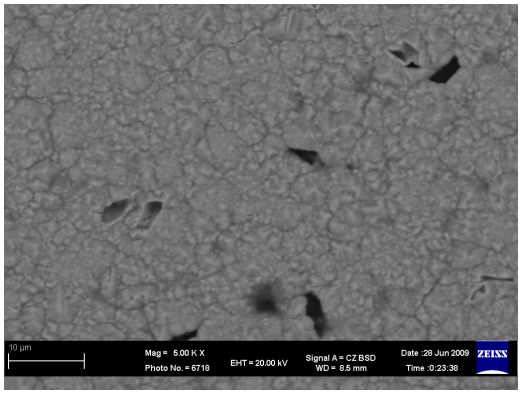

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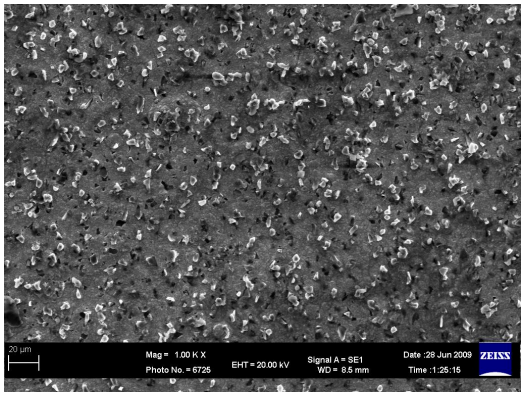
- Sample T9 (Diamond conc. =7.5 g/l)



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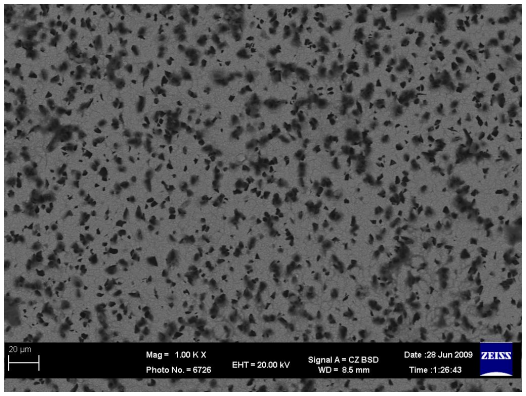

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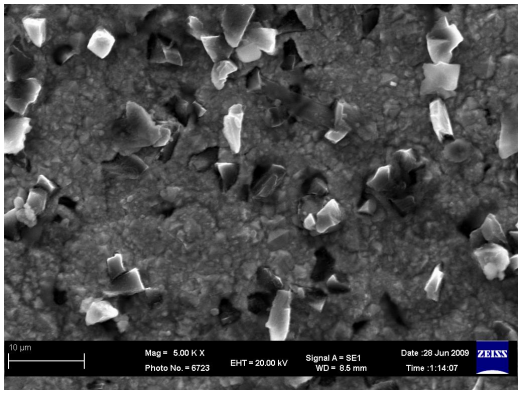

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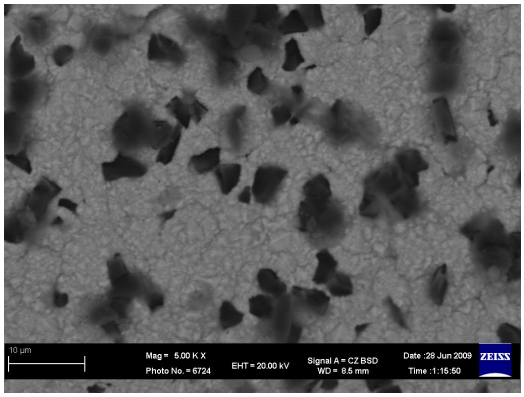

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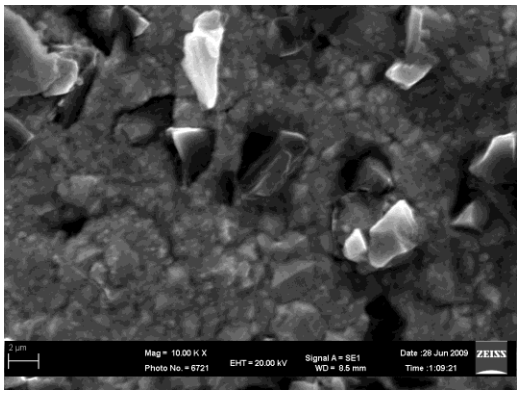

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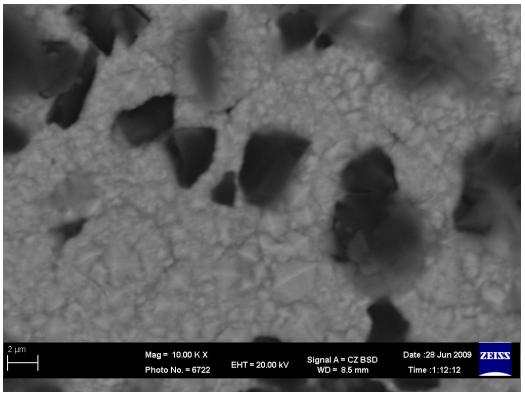

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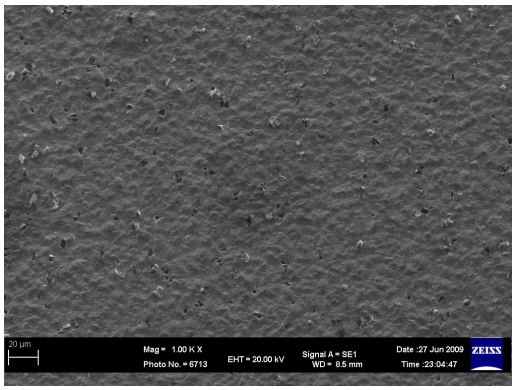
- Sample T16 (Diamond conc. =7.5 g/l)



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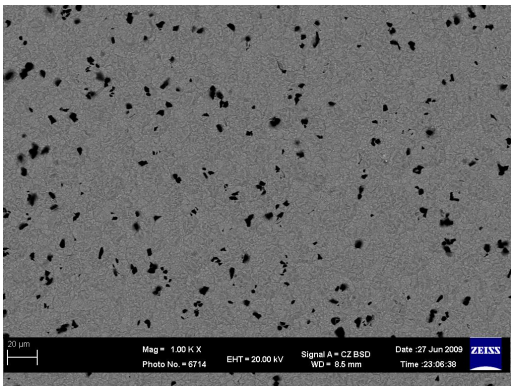

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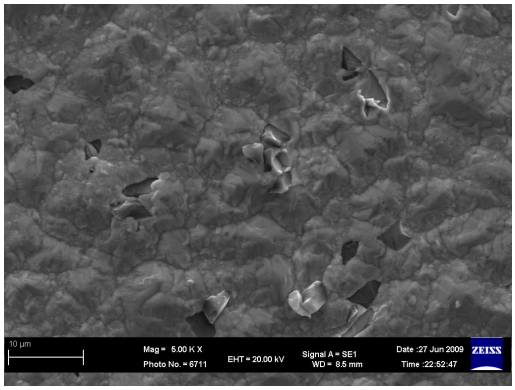

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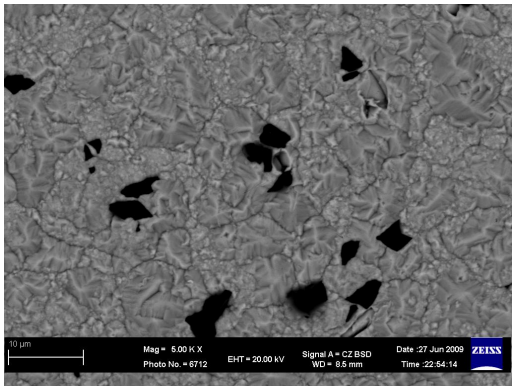

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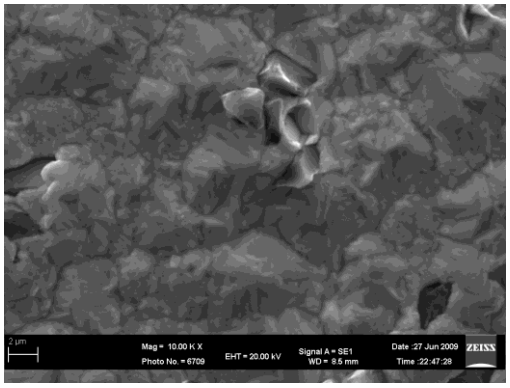

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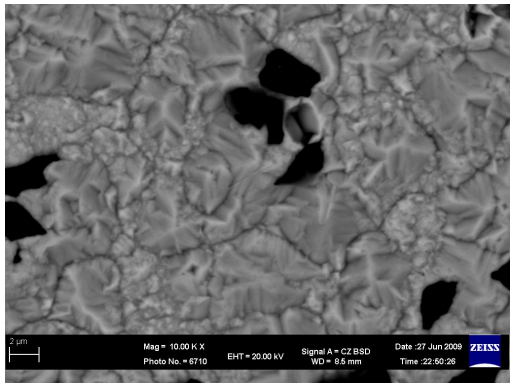
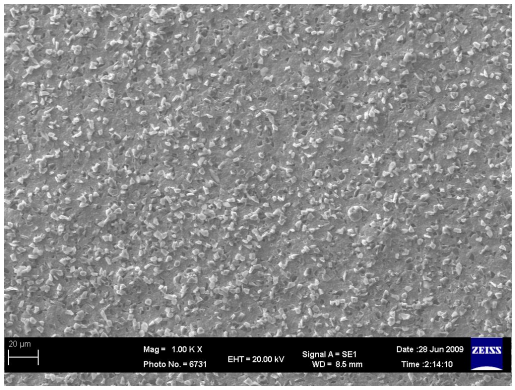
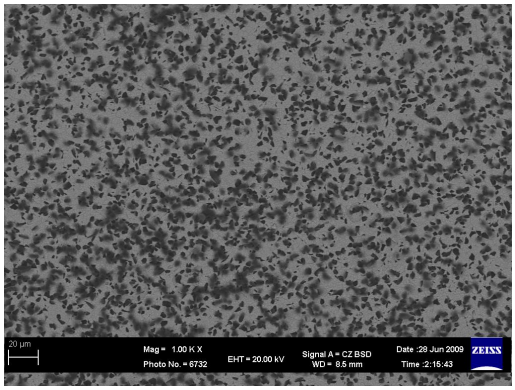


10000x (BSD Mode)

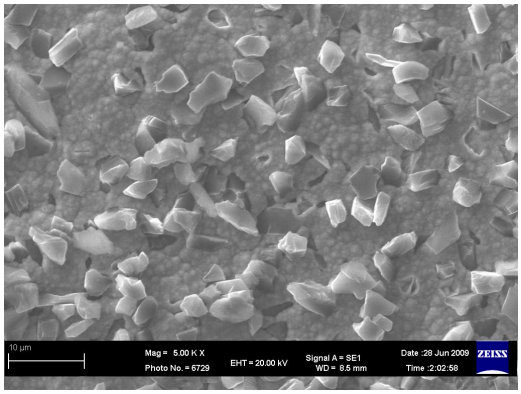
- Sample T12 (Diamond conc. =10 g/l)



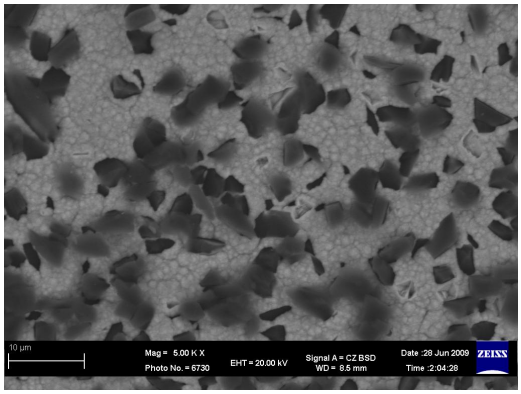
1000x (SE Mode)



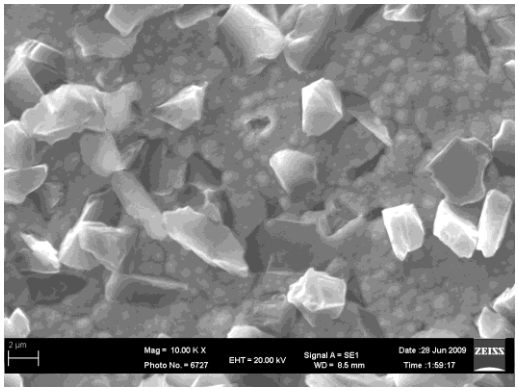
1000x (BSD Mode)



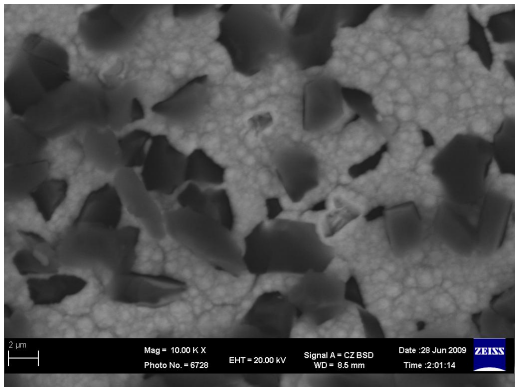
5000x (SE mode)



5000x (BSD Mode)

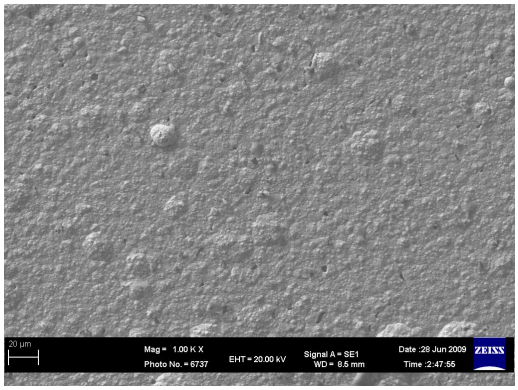


10000x (SE Mode)

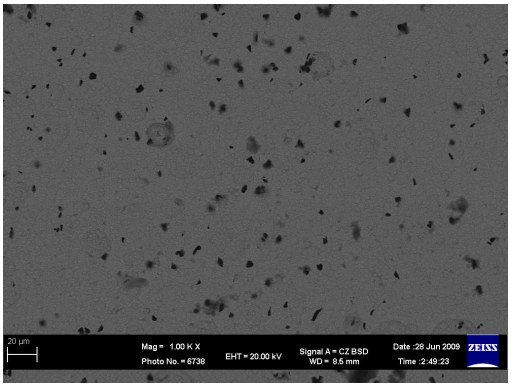


10000x (BSD Mode)

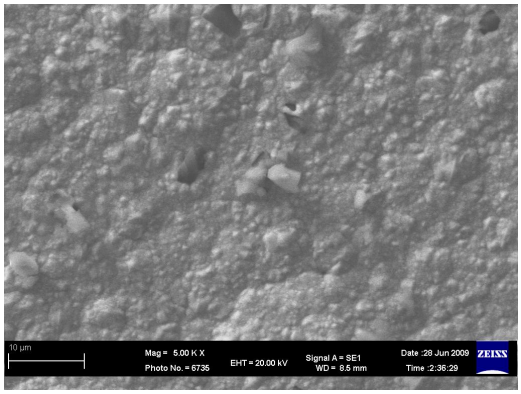
- Sample T14 (Diamond conc. =10 g/l)



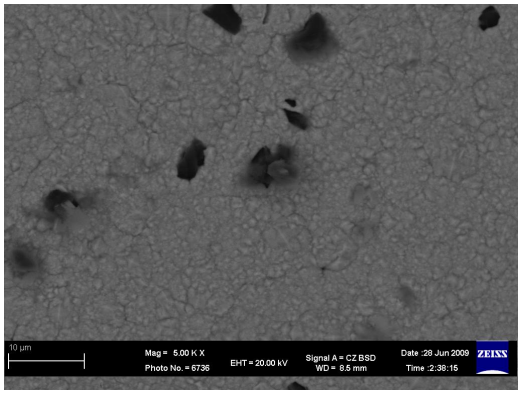
1000x (SE Mode)



1000x (BSD Mode)



5000x (SE Mode)

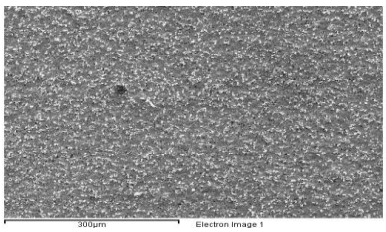


5000x (BSD Mode)

EDAX Studies:

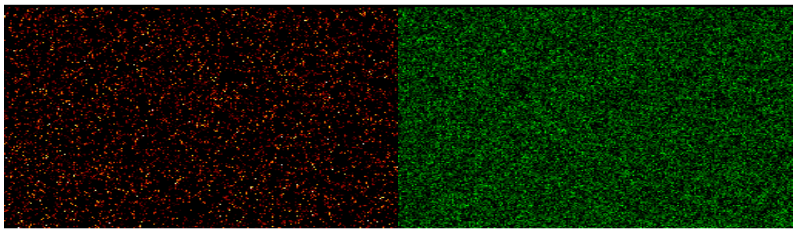
Sample No.	Diamond Concentration	Weight of Deposit(gm)	% C in the deposit (By weight)	% Ni in the deposit (By weight)
T1	1 g/l	0.136	29.465	69.120
T2	1 g/l	0.156	50.567	47.910
T4	2 g/l	0.205	42.435	56.285
T5	2 g/l	0.191	41.823	56.703
T6	5 g/l	0.160	17.233	81.220
T15	5 g/l	0.156	15.600	81.683
T9	7.5 g/l	0.151	41.630	47.330
T16	7.5 g/l		16.880	81.645
T12	10 g/l	0.161	61.675	37.165
T14	10 g/l	0.161	16.460	81.550

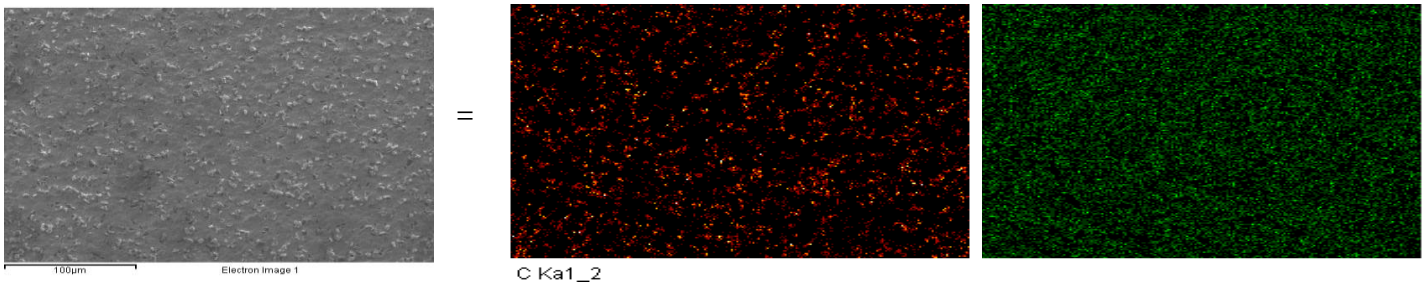
EDAX studies revealed the distribution of carbon and nickel in the deposit. A few of them were as shown in the microstructure below:



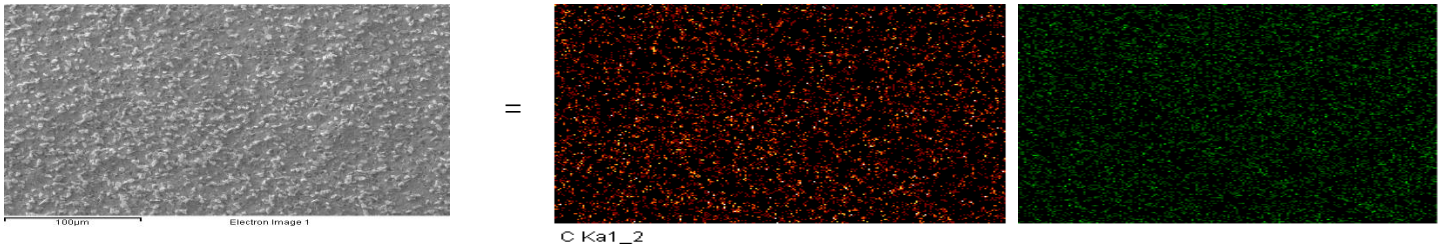
Sample T2 @ 500x
(1 g/l)

=





Sample T5@ 1000x
(2 g/l)



Sample T12 @ 1000x
(10 g/l)