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RECTANGULAR WAVE CURRENT EFFECT ON PLATED NICKEL HARDNESS

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***Abstract*— Effects of frequency, average current density and duty cycle on hardness of electroplated nickel were studied in Watts and sulphamate solutions by mean of direct and rectangular pulse current. The results in Watts solutions show high hardness values at low duty cycles, high average current density and high frequency of the pulse current. Hardness in nickel sulphamate solutions shows a low variation with duty cycle and frequency changes. Hardness values obtained in the Watts bath with rectangular pulse current are higher than those achieved with direct current at the same average current density. In the sulphamate bath this difference has not significance.**

***Keywords*— Pulse current, Hardness, electroplating, Nickel.**

I. INTRODUCTION

Nickel is a metal with good abrasion and corrosion resistance. This characteristic allows its electro-deposits to have applications in the engineering field where the functional behavior, rather than the appearance, is the main required attribute

Early, nickel deposits applications were associated with works of art replicas manufacture, but at the present time they are used in the aerospace industry, in the manufacture of intricate guides, in production of compact and video disks and micro-components for the electronics industry.

Recently, research has begun to focus over these electro-deposits hardness and grain size. It is broadly accepted that the hardness is a parameter that provides an appropriate indication of the material strength, wear and abrasion resistance.

One recently proposed way to increase the nickel deposits hardness is the use of pulse current waveforms. This has driven remarkable improvements in properties like internal stress, elongation, corrosion resistance and hardness, among others. Additionally, it was been found that this technique decreases the energy costs as well as the raw material quantity needed to improve the deposits hardness (Chen and Wan, 1989).

It is known that the waveform, frequency, duty cycle and the peak current density produce remarkable changes in the electro deposits properties (Durney, 1984).

Most of the published works with pulse current waves for nickel electro deposits have been made using nickel sulphate baths (commonly referred as Watts baths) and in nickel sulphamate baths. Initially, Ping *et al.* (1979), established that with higher peak current densities, greater over potentials are generated, which favors the new nuclei formation, instead of the crystals growth, therefore producing deposits with finer grain size in nickel sulphamate baths when using pulse waves. They also report increases in the hardness when increasing the frequency in Watts baths.

Later on, El-Sherik *et al.* (1996) obtained nickel deposits with grain size below 100 nanometers obtained from Watts solutions free of organic additives using pulse current.

Devaraj and Seshadri (1996) report that using rectangular pulse current in nickel sulphate baths, deposits with soft surfaces that contain smaller pores, free of fractures, with decreased grain size and reduced tension stress are obtained with the hardness improvement at low duty cycles (10%) and low frequencies (smaller than 10Hz).

Improvements in the hardness of nickel electrodeposits were obtained in sulphamate solutions using several types of current waveforms: rectangular, rampup, ramp-down and triangular (Wong *et al.*, 2000), being achieved the highest hardness values with the ramp-down waveform and the lowest with continuous current.

It has also been reported that the deposits hardness using pulse current is significantly higher than the one obtained with direct current, at the same average current density (Qu *et al.*, 2003).

Tang *et al.* (2004) found that electrodeposition with pulse current produces deposits with more fine, more compact grain sizes, of lower porosity and with better substrate adherence. Additionally they show an increase in the plating rate and in the current efficiency with this technique. These experimentations in Watts baths showed an improvement in the hardness with the use of pulse current with frequencies above 40 Hz.

It is interesting to note that although there is an agreement about the benefit of using pulse current, there is not a clear conclusion about whether the hardness of deposits improves with high frequencies or not. Some propose low frequency (smaller than 10 Hz) and others propose high frequency (greater than 40Hz).

This article aims to study the effect of the rectangular current waveform on the nickel deposits hardness. Specifically, the article seeks to determine the effects associated to the pulse frequency, the average current density and the duty cycle, in Watts and nickel sulphamate solutions.

II. EXPERIMENTAL PROCEDURE

Experimentation was carried out using direct current and rectangular pulse current. For the latter, the average current density, the pulse frequency and the duty cycle was changed. The form of this wave is shown in Fig. 1.

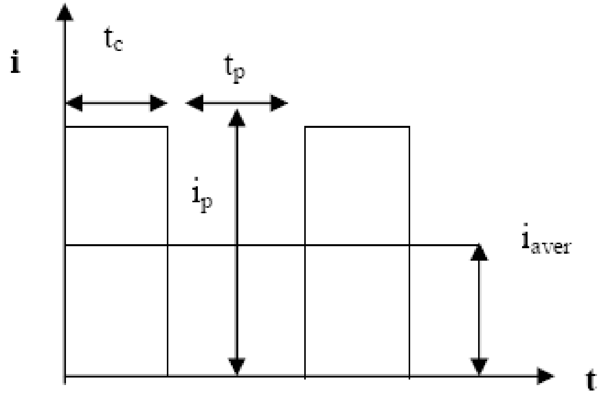

Fig. 1. Rectangular pulse current with relaxation time.

The parameters that characterize the rectangular pulse current waveform are described by Eqs. 1 to 3:

$$\lambda = \frac{t_c}{t_c + t_p} * 100 \quad (1)$$

$$i_{aver} = \frac{t_c}{t_c + t_p} * i_p \quad (2)$$

$$f = \frac{1}{t_c + t_p} \quad (3)$$

where t_c and t_p are the pulse and pause times, respectively, i_{aver} and i_p are the average and peak current densities, respectively, A is the duty cycle and f is the pulse frequency.

The variation of parameters for the rectangular pulse current was carried out by means of a factorial experimental design, conformed by three factors, each one with three levels, as is specified in Table 1. The deposit hardness was considered as the output variable.

1.6 cm side copper square sheets, with a 0.5 mm thickness were used as substrate for plating. The copper pieces underwent a conventional pre-treatment in order to guarantee appropriate surface preparation to achieve good plating (Table 2). Between each stage, intermediate rinses were placed to minimize reagents mixing between stages.

The plating was carried out in Watts baths without additives and in nickel sulphamate solutions. Composition and operation conditions for each bath are listed in Tables 3 and 4, respectively. In both cases deposits thickness was 50 μm.

Table 1. Experimental design.

Level	Factor		
	f (Hz)	λ (%)	i_{aver} (A/dm^2)
1	10	20	12
2	25	50	8
3	50	80	4

Table 2. Substrate pre-treatment stages.

Stage	Operation conditions	Reactants
Chemical degrease	70 -90 °C 3-10 minutes	Alkaline degrease
Strip	Room temperature	H_2SO_4 50 % V HCl 50 % V
Electrolytic Degrease	60 -70 °C 4-10 A/dm^2 5-9 Volt 1-5 minutes	Alkaline degrease for wear electrolytic
Activate	Room temperature	HCl 5 %V

Table 3. Operation conditions for nickel Watts bath.

Parameter	Value
$NiSO_4.7H_2O$ (Nickel sulphate)	312.5 g/l
$NiCl_2.6H_2O$ (Nickel chloride)	45 g/l
Metallic nickel equivalent	73.75g/l
H_3BO_4 (Boric acid)	37.44g/l
PH	4-4.6
Temperature Mechanical mixer	55 – 60 °C 70 rpm

Table 4. Operation conditions for nickel sulphamate bath.

Parameter	Value
$Ni(SO_3NH_2)_2$ (Nickel sulphamate)	327g/l
Equivalent of metallic nickel	75.0g/l
H_3BO_4 (Boric acid)	45g/l
pH	3.5-4
Temperature	55 – 60 °C
Mechanical mixer	70 rpm

High purity electrolytic nickel coins (Inco, S-round®) submerged in titanium baskets were used as anodes. Anodes superficial area was kept higher than the cathode area to avoid polarization problems.

Hardness testing was made according the ASTM E384 standard with 0.5 μm resolution. Five hardness measures were made for each sample. The measure was conducted in the center of the piece with a load of 50 gf. The reported value is an average trimmed to ten percent (10%).

A Scanning Electronic Microscope (SEM) following the ASTM E112 standard was used to obtain morphological photographs of deposits.

III. RESULTS

A. Deposits obtained from Watts solution.

Average hardness values obtained from the Watts bath are reported in Table 5.

Based upon the averages and standard deviations, the factors profiles can be built. Profiles for the pulse frequency, duty cycle and average current density are shown in Fig. 2, 3 and 4, respectively.

An increase in the hardness of deposits appears when increasing the pulse frequency from 10Hz to 25Hz as can be seen in Fig. 2. However, when moving from 25Hz to 50Hz, although the tendency is slightly growing, statistically speaking the difference among levels is not considerable (according to the Duncan statistical test).

In Fig. 3 a small increase in hardness is observed when diminishing the duty cycle from 80% to 50%, but this increase is not significant. However, a duty cycle of 20% causes a considerable increase in the hardness.

Table 5. Deposit hardness from Watts solution

	10 Hz		
Duty cycle (%)	**$12A/dm^2$**	**$8A/dm^2$**	**$4A/dm^2$**
	Hardness (Vickers)		
20	341.6	250.8	233.0
50	214.9	181.3	169.5
80	230.3	140.7	207.9
	25 Hz		
20	304.6	280.6	258.2
50	284.9	186.3	200.7
80	231.8	197.3	188.5
	50 Hz		
20	342.8	370.9	223.9
50	271.0	230.7	212.4
80	231.8	220.9	215.1
Direct current	226.8	196.8	198.7

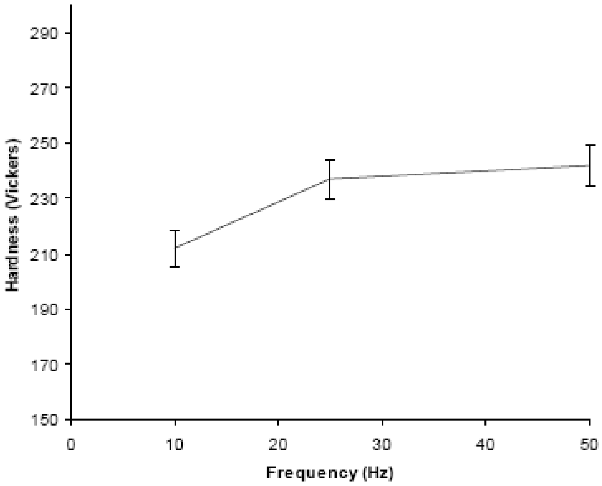

Fig. 2. Frequency effect on deposit hardness from Watts bath.

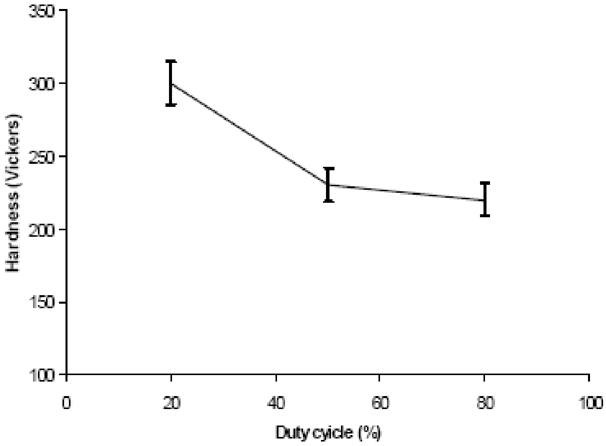

Fig. 3. Duty cycle effect on deposit hardness from Watts bath.

In Fig. 4, a notable increase in the harness of deposits is observed when increasing the average current density from 8 A/dm^2 to 12 A/dm^2. Passing from 4 A/dm^2 to 8 A/dm^2 does not produce statistically different results.

The highest nickel deposits hardness values were reached at low duty cycles and high average current densities. These two characteristics imply high peak currents in order to guarantee the same average current. High peak currents favor the nuclei formation instead of the crystal growth. This is due to a tremendous reduction in the time for diffusion of nickel adatoms at the surface, living them no time to find lower energy sites that favor its growth.

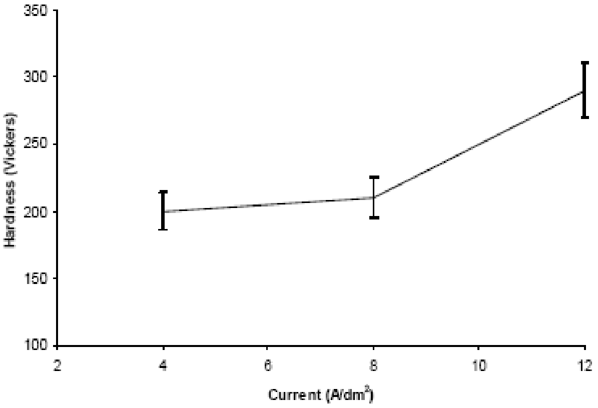

Fig. 4. Average current density effect on deposit hardness from Watts bath.

A comparison between the hardness values obtained when using rectangular pulse current and when using conventional direct current is made in Fig. 5. It is observed that the rectangular pulse current hardness values overcome those obtained with conventional direct current.

Low duty cycles are associated with shorter electrolysis times in comparison with pause times. The pause time in pulse current, allows reestablishing the species concentration near the electrode, which causes a decrease in the diffusive layer. That is to say, diminishes the concentration over-potential. This guarantees that, at the beginning of a current pulse, more species exist in the electrode proximities compared to the existent species when plating with direct current.

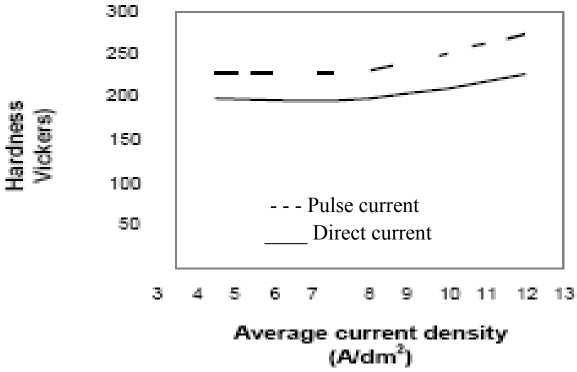

Fig. 5. Hardness obtained with direct and rectangular pulse current from the Watts bath.

To use very high duty cycles, it is similar to use conventional direct current since the pause times are too short and do not allow the reestablishment of conditions near the electrode. When using a direct current, the hardness of the deposit is affected in a negative way (it diminishes) due to the pause time absence. It seems to be that the pause time, that is to say, the species concentration reestablishment in the electrode proximity, has favorable effects in the deposit hardness.

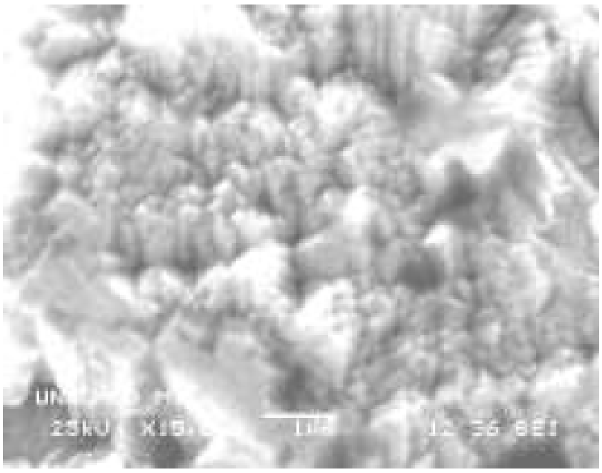

Fig. 6. Morphology associated with the lowest deposit hardness (140.7 Vickers) from Watts bath.

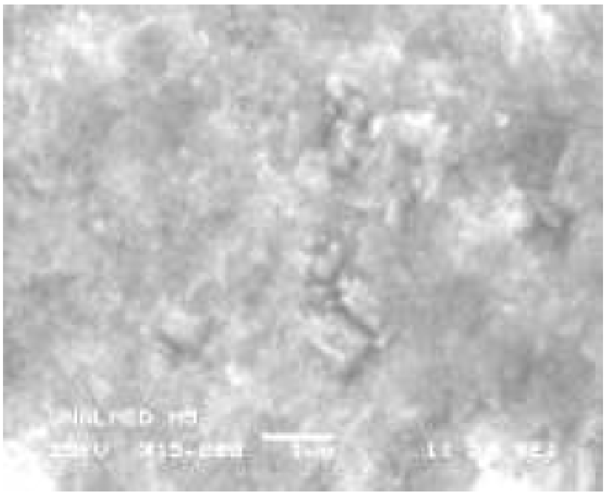

Fig. 7. Morphology associated with the highest deposit hardness (370.9 Vickers) from Watts bath.

Generally speaking, nickel plating carried out in Watts baths exhibited a shining appearance. The deposits morphology obtained at low duty cycles shows differences with those obtained at higher duties. This supports the expected relationship between hardness and grain size. That is to say, smaller grain size deposits have a higher hardness.

The maximum and minimum hardness values reached were 370.9 and 140.7 Vickers, respectively. The difference between the morphologies for each deposit is shown in the Figs. 6 and 7.

B. Deposits obtained from nickel sulphamate baths. The average hardness values obtained from the nickel sulphamate solution are shown in Table 6.

The pulse current effect is not significant and the hardness values with direct current are very close to those obtained with rectangular waveform.

Base upon the averages and standard deviations, each factor profile was built. Figures 8 through 10 shown the current density, frequency and duty cycle effects on the hardness of deposits, respectively.

Table 6. Deposit hardness from sulphamate bath

	10 Hz		
Duty cycle (%)	**12A/dm^2**	**8A/dm^2**	**4A/dm^2**
	Hardness (Vickers)		
20	241.6	233.0	230.7
50	210.2	216.8	225.7
80	200.2	230.4	250.8
	25 Hz		
20	198.0	237.5	231.8
50	223.9	234.0	239.4
80	218.6	234.3	251.8
	50 Hz		
20	218.6	268.3	233.0
50	249.3	222.9	233.0
80	199.1	229.6	221.3
Direct current	218.6	226.5	236.9

An appreciable difference for the current density factor levels can be seen in Fig. 8. A remarkable deposit hardness decrease when increasing the average current density from 8 A/dm^2 to 12 A/dm^2 is observed. The change from 4 to 8 A/dm^2 does not produce results statistically different.

A small increase is observed in the deposit hardness when increasing the pulse frequency (Fig. 9), but without obtaining significant differences.

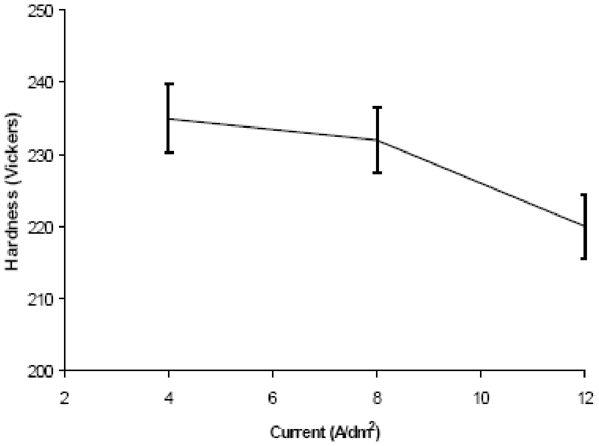

Fig. 8. Average current density effect on deposits hardness from nickel sulphamate bath.

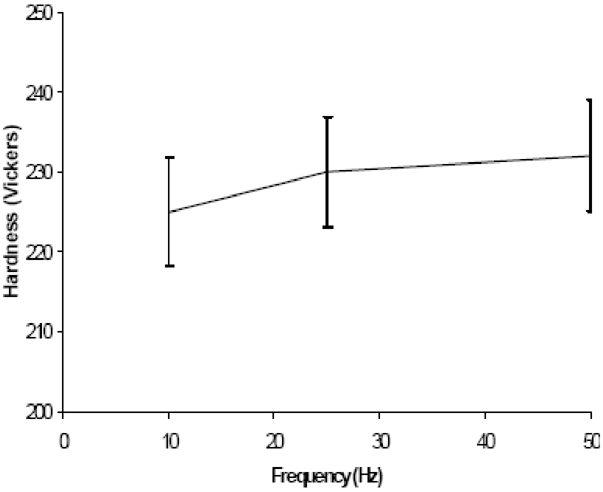

Fig. 9. Frequency effect on deposits hardness from nickel sulphamate bath.

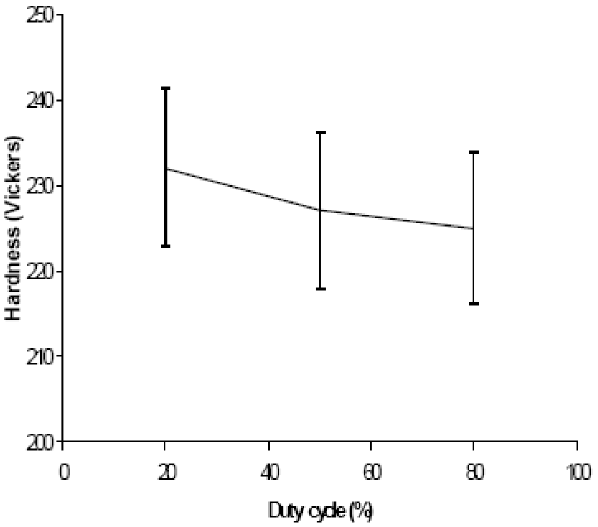

Fig. 10. Duty cycle effect on deposit hardness from nickel sulphamate bath.

In Fig. 10, a slight decrease is noticed in the deposit hardness when increasing the duty cycle. However, the statistical difference among levels is not considerable.

A comparison between the hardness obtained when using rectangular pulse current and those obtained when using direct current is made in Fig. 11. It is observed that the hardness is practically the same.

Deposits obtained in the sulphamate bath presented a dull appearance and greater deposit uniformity, in contrast with those obtained in the Watts bath where the deposits had a shining surface.

The maximum and minimum hardness values obtained were 268.3 and 198.0 Vickers, respectively. The grain size appearance is shown in Figs. 12 and 13, for both values.

A grain size refinement is observed in Figs. 12 and 13 for the highest hardness value in comparison with the minimum value

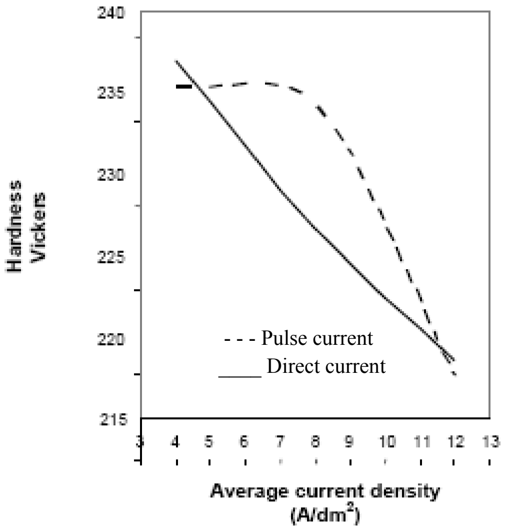

Fig. 11. Hardness for direct and rectangular pulse current from nickel sulphamate bath.

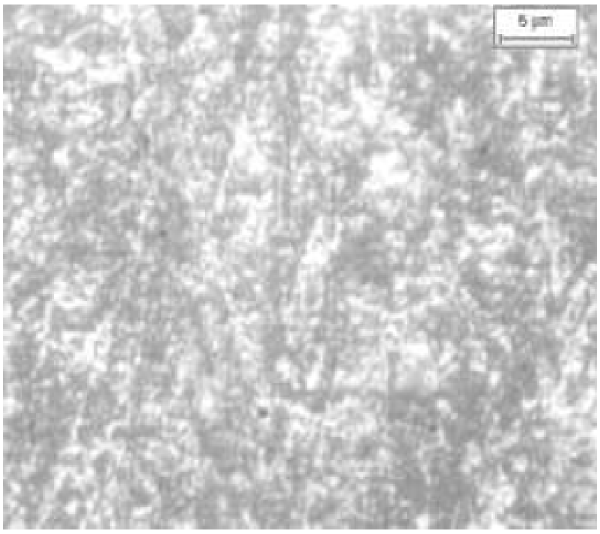

Fig. 12. Morphology associated with the minimum deposit hardness (198.0 Vickers) from nickel sulphamate solutions.

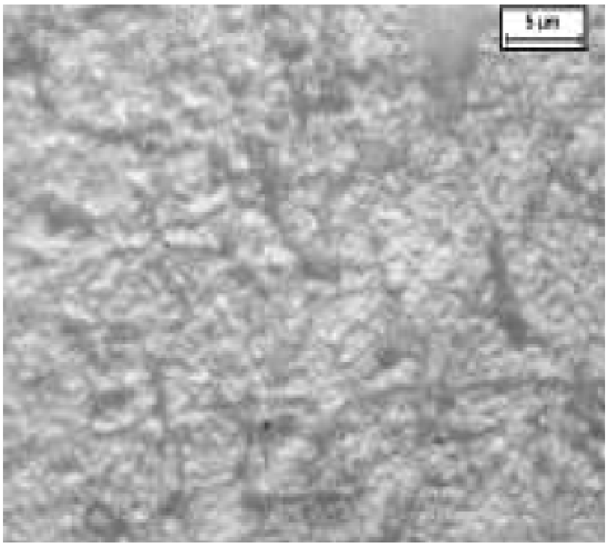

Fig. 13. Morphology associated with the maximum deposit hardness (268.3 Vickers) from nickel sulphamate solutions.

IV. CONCLUSIONS

When studying the duty cycle effect in Watts baths, it is observed that the highest hardness were reached at a 20% duty cycle. A considerable hardness decrease was observed when increasing the duty cycle percentage.

The current density effect on the deposit hardness in Watts baths, produces higher values at 12A/dm^2. When diminishing the average current density the nickel deposit hardness diminishes.

With regard to the pulse frequency, higher frequencies increase the deposit hardness in Watts baths.

The hardness values obtained from the Watts bath with rectangular current waves overcome the values reached with conventional direct current at the same average current densities.

The deposits obtained from the nickel sulphamate bath are very slightly affected by the pulse frequency and the duty cycle. The factor having incidence it is the average current density.

The deposit hardness for the nickel sulphamate bath is higher at 4A/dm^2 and diminishes when increasing the current density.

The deposit hardness difference from the nickel sulphamate bath when using rectangular current wave and direct current is not significant.

The plating carried out in the sulphamate bath presented a dull appearance. The morphological differences are harder to appreciate than in the Watts solution, since the deposits are more uniform.

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