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Chemical Evolution of SiC Particles Surface in Salt Solution

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Abstract: WATT bath solution is constituted of NiCl₂, NiSO₄ with a pH value fixed to 3 with H₃BO₃. This solution is used as electrolyte for SiC co deposition from Ni/SiC system. The very good embedment of the particles noticed with this solution is due to particles' surface state at this pH value. Particles' surfaces are constituted of chemical groups which, interacting with solutions, play a role in the surface state. The experimentations undertaken pulled out that the interaction between the electrolyte and groups such as SiO₃C and SiC₂O₂ for example present at the particles' surface, governs zeta potential, which control SiC particles embedment in the nickel matrix. At pH 3 particles are neutral by adsorbing positive and negative species. When they are transported to the reduction pole, the negative adsorbed species are vanished; the particles become positively charged by the silanol protonated groups. As the kinetic of proton reduction is slower than nickel ions one at pH 3, the particles are stuck at the cathode surface and embedded in nickel electrodeposited matrix.

Key words: SiC, codeposition, pH, zeta potential

INTRODUCTION

Silicon carbide SiC particles present more and more interest in many material processes. In ceramic elaboration, particles or whiskers are incorporated to melts. This component got advantages such as a low pressing temperature; it also improves mechanical properties and confers super elasticity to composite at high temperature (Sakka *et al.*, 1995; Vassen and Stober, 1999; Shinoda *et al.*, 1999). But in solution, SiC particles tend to agglomerate causing then non homogeneity in the ceramic microstructure leading to a low density and bad mechanical properties.

Elaboration of new composite constituted of metallic matrix with dispersed inert particles is a wide investigation field (Tomaszewski *et al.*, 1969; Snaith and Groves, 1972). Nickel electroplating process consisting in Ni²⁺ ions reduction from Watt bath is very well established (George, 1992). This electrochemical process is used to embed inert

particles into the metallic matrix being electrodeposited for composite elaboration.

The Ni/SiC system has widely been studied (Guglielmi *et al.*, 1972; Lavanant, 1991). Presence of SiC particles in the coats improves mechanical properties and prevents 50 times from corrosion compared to only Ni coat after heating at 400°C (Wang *et al.*, 1999). The Ni/SiC co deposition is also applied in car industry mainly for engines coating.

Investigations undertaken on similar systems led to diverse results. Co deposition of alumina powder in copper matrix has revealed a better incorporation of α -Al₂O₃ in contrary to γ -Al₂O₃ particles (Lee *et al.*, 1988). This was attributed to the negative zeta potential of γ -Al₂O₃ particles in CuSO₄ acidic solutions. The same approach with a nickel matrix pulled out γ -Al₂O₃ particles incorporation level to depend on Ni reduction current density and a competition between charge transfer controlled by Ni²⁺ ions reduction and mass transfer of

γ - Al_2O_3 particles for high current (Webb and Neil, 1994). Silica co deposition in Ni matrix compared to SiC one showed a very low incorporation level for SiO_2 (Nowak *et al.*, 2000). SiO_2 particles were supposed to enhance specific capacitance of the electrode while this should decrease in presence of SiC particles in the electrolyte. Thus for a given metal, incorporation may depend on particles and even on its allotropic forms. A physicochemical activity between particles surface and the electrolyte may exist and could explain those changes. The interactions between particles surface, electrolyte and the metal in reduction may so be responsible of incorporation level. Particles surface may chemically advance according to different parameters such as electrolyte composition, pH values (Diakova *et al.*, 2002; Hashiba *et al.*, 1988; Snaith and Groves, 1977) and presence of refracting agents in the colloidal phases (Beebhas *et al.*, 1990; Wang and Wei, 1995).

The experimental or process parameters also play an important role in the co deposition state (Snaith and Groves, 1978; Feng *et al.*, 2006). The best incorporation level for SiC particles in nickel matrix may be related to its surface state during plating (Kaisheva and Fransær, 2004). SiC surface may present particular chemical groups that interact with the electrolyte to favour incorporation in the metallic matrix. In the present study, we try to establish SiC surface evolution in Watt bath constituted of $NiSO_4$ and $NiCl_2$ and also, the effect of chloride and per chlorate ions at different pH values in order to find out an explanation to the good incorporation of these particles in the nickel matrix.

MATERIALS AND METHODS

Solution of $NaCl$, $NaClO_4$ and of watt bath salt that are $NiCl_2$ and $NiSO_4$ were elaborated at $10^{-2}M$ concentration with $2 g L^{-1}$ SiC particles. The pH of the solution was fixed in the range of 1.5 to 4 with the counter ion acid. The samples were kept shacked for 10 days and then left to sediment during 24 h at least. Then two pH values are measured with a pH meter PH M210 type METERLAB of TACUSSEL-ELECTRONIC.

Foundation of these experiments is based on that, pH values fixed when elaborating samples represent the liquid phase one, when no interaction did occur with the SiC particles. So, pH_1 corresponds to the supernatant liquid after dismissing, while pH_2 is determined for the stirred phases. Two variables are then established from experimental data according to the following relations:

$$\Delta pH_1 = pH_1 - pH_{init} \quad (1)$$

$$\Delta pH_2 = pH_2 - pH_1 \quad (2)$$

ΔpH_1 may inform on the reaction that takes place during interaction between solution and particles' surface while ΔpH_2 gives indication on the kind of chemical species that are fixed on the surface. Zeta potential that represents charges moving with particles through an electric field is also determined with a zetasizer 3000HS coupled to zetasizer software. Zeta potential values in accordance with pH variation should permit to propose a chemical reaction scheme that leads to changes noticed and the surface state. Consciousness of the surface state may thus permit to understand the good incorporation of SiC particles and also agglomeration phenomenon in ceramic melts.

RESULTS AND DISCUSSION

Measurements of pH values show that they change confirming thus a chemical activity between particles' surface and solutions. Zeta potential also indicates variation revealing evolution of particles surface state.

Analysis for chloride and per chlorate solutions:

Figure 1a and b that, respectively represent changes in chloride and per chlorate solution indicate that ΔpH_1 is negative until pH 3.15 for chloride and 3.8 for per chlorate. On these scales, interaction has caused acidification of the supernatant liquid phase. The difference of pH scale on which acidification occurs for both anions reveals their implication in this evolution. For higher pH values in both cases, ΔpH_1 becomes positive; the interaction on these pH ranges may cause proton consuming. The pH of some chloride samples have been readjusted to initial values.

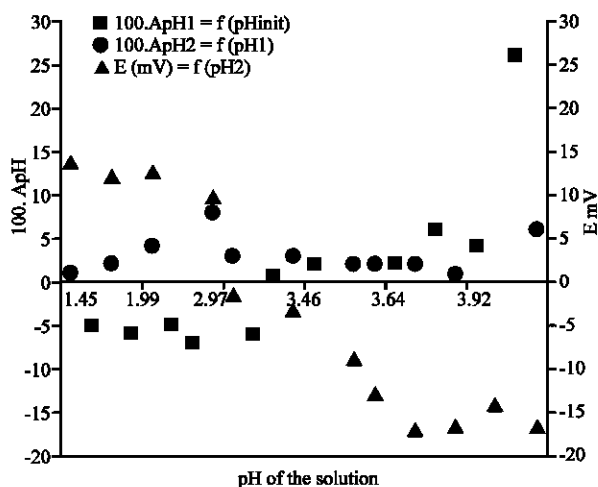


Fig. 1a: ΔpH and zeta potential evolution versus pH in chloride solution

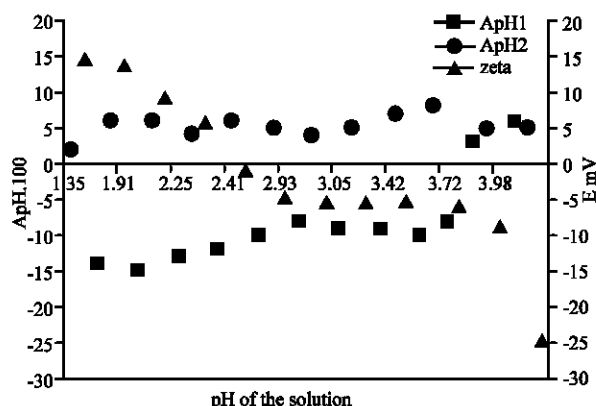


Fig. 1b: ΔpH and zeta potential evolution versus pH in per chlorate solution

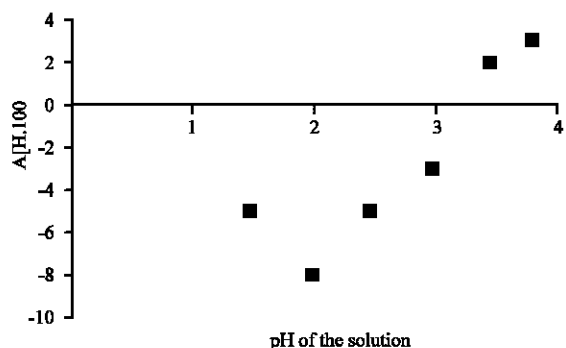


Fig. 1c: ΔpH change of supernatant liquid after pH adjustment

Figure 1c shows that ΔpH₁ still varies with the same shape on the main pH scale. ΔpH₁ variation may so be the result of an equilibrium state between SiC particles surface and the solutions. ΔpH₂ variations on the same scale show that stirred solution is least acidic.

This means that basic species are released into the solution and react with proton making pH increase. These basic species may necessary come from particles surface. Acidification is widely higher for per chlorate solutions then chloride's one. ClO₄⁻ may activate the interaction that produce proton and this also confirm one more time that the anions present in solution are implicated in the pH evolution.

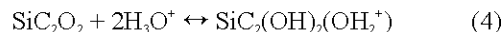
Zeta potential values for both solutions show that particles got positive surface charges in high acidic solutions and decrease to attain the isoelectric pH point which values are, respectively around 3 for chloride and 2.5 for per chlorate. Surface charges for both become negative for higher pH values. Positive zeta potential values may be relied to protons activity. Protons may adsorb on a specific chemical group at particles surface producing positive charges.

Charges values thus decrease as proton activity decrease. The iso electric pH value (pH_{iep}) in both solutions are much closed to the silica one as determined elsewhere (Yeh and Van, 1994). In aqueous solution, SiO₂ creates silanol group that are protonated and make zeta potential positive according to reaction 3:

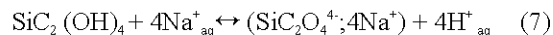
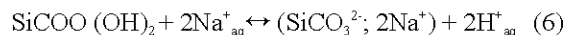


Reaction 3 does not free proton; so acidification necessary implies another reaction. Other chemical groups may so be responsible of the supernatant liquid acidification. Silicon carbide powder have been analysed by XPS (Binner and Zhang, 2001). These investigations pulled out presence of bonds such as C-C, Si-O, O-O-Si. In another work, oxycarbides SiO₂C₂ and SiO₃C have been found on SiC particles surfaces (Mejean *et al.*, 1995). The developed formula of these chemical groups can be represented as on Fig. 2a and b.

Those two species are characterised by all prevailing different bonds. Thereby, they can be considered as being the major components at the particles' surface. For both components, reaction with water leads to silanols formations that are protonated in acidic middle and confer positive charges to particles:



During sedimentation, Na⁺ ions that are very badly solvated are spurned to the SiC particles surface to form soda salts and release protons in the supernatant phase that becomes more acidic:



Acidification level is higher in per chlorate solution then chloride one. This means that the anions are implied in reaction 4 and 5. By its oxygen atoms, ClO₄⁻ ions easily

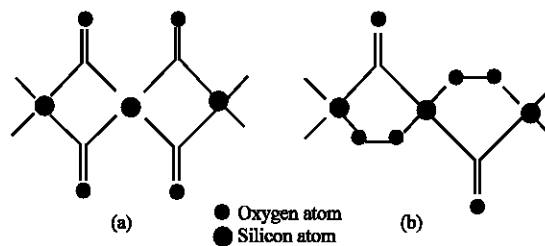
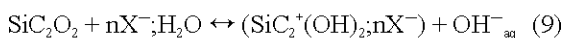


Fig. 2: a) SiC₂O₂ and 2b) SiO₃C

adsorb on more silicon atoms. This favours a better protonation leading to reaction 4 and 5 to form more silanol groups. Chloride ions that are bigger hardly adsorb in the same condition limiting then the reactions. Acidification becomes less in both solutions when pH increases; this shows that protonation step is decisive. As proton activity fails, reactions 4 and 5 hardly take place reducing by the same way acidification of the supernatant phase.

Difference between the pH_{lep} for chloride and per chlorate solution is to be relied to their adsorption capacity. The pH_{lep} in per chlorate is more acidic then in chloride one. Per chlorate ions do adsorb more so that charge neutralization occurs in more acidic solution. From pH 3.15 in chloride solution and 3.8 in per chlorate one, supernatant liquids become less acidic. And on the same pH range, particles are negatively charged. A reaction that consumes proton occurs. Hydroxide ions may so be released in the liquid phase. Proton activity becomes so feeble that protonation does no longer occur. The main reaction that can produce hydroxides can be schemed as follow:



For reaction 8, a molecule of water reacts with the basic α position oxygen to free an hydroxides. The positive charge variation $+\delta$ on the bond linking silicon and the α oxygen protonated is stabilized by the anion X-through its free electrons doublet on the surface and make zeta potential equal to zero.

For reaction 9, the isomeric form of the carbonyl function prevails; the positive charge appearing on the carbon is stabilized by anion adsorption. Then oxygen anion reacts with a molecule of water releasing the hydroxide. Adsorption of other X-anions and hydroxides give a negative charge to the particles. Reactions 4 and 5 still prevail in per chlorate solution until pH 3.8 because its adsorption mode favours these reactions. For SiO_3C , it may render the oxygen at silicon atom α position more basic so that despite a feeble proton activity, protonation still occurs. For SiC_2O_2 , adsorption of chlorate ion may stabilize the isomeric form that guide reaction 4, while these no longer exist in chloride solutions after pH 3.15. The molar quantity of protons free by reactions 6 and 7 or consumed by reaction 8 and 9 is calculated by relation 10:

$$[H^+]_{free} = [H^+]_{final} \cdot [1 - 10^{-\Delta pH}] \quad (10)$$

Decimal logarithm representation of free or consumed protons versus pH of the solution is taken positive when

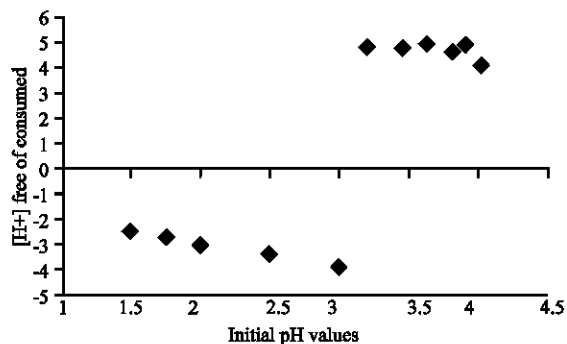


Fig. 3a: Logarithmic representation of proton produced and consumed versus pH in chloride solutions

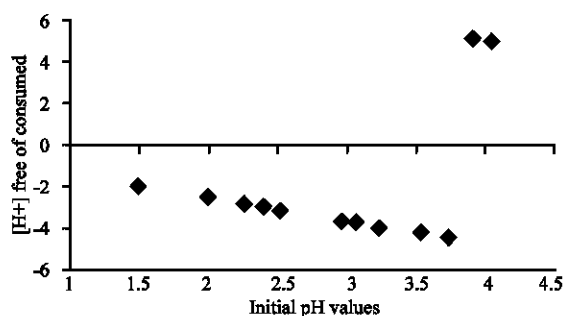


Fig. 3b: Logarithmic representation of proton produced and consumed versus pH in per chlorate solutions

consumed. Figure 3a and b representing, respectively chloride and per chlorate solutions show that the reaction that consumes protons does not depend on the pH solution and this confirms reaction 8 mechanism. The molar quantity of proton consumed in both solutions is almost equal to $10^{-5} \text{ mol L}^{-1}$. This constancy indicates that the origin of this phenomenon is something constant. In our cases, this can be relied to SiC particles quantity that is constant.

On the other hand, proton production decreases with the same slop and this indicates that the same reaction occurs in the solutions on respective pH scales. This shows that sodium ion is lest spurned at the particles' surfaces when pH increases. This is in accordance with the fact that as proton activity fails, sodium ions are better solvated in the solution by molecules of water. Reactions 6 and 7 are no longer favored.

Analysis for Nickel chloride solution: Chloride ions effect has already been established. The experiments undertaken here with nickel chloride solutions is to pull out whether nickel ions adsorb at the particles surface as written elsewhere (Wang and Cheng, 2001; Grosjean *et al.*, 1998). In case of nickel ions adsorption, zeta potential values should be very different form what

found in the case of chloride solutions. Figure 4 shows that zeta potential also decreases with almost the same shape on the same scale with chloride solutions ones. This means that no nickel ion adsorbs at the particles surface. The pH of isoelectric point in nickel chloride solution is somewhat more acidic; 2.42 in other of 2.8 in chloride solutions.

This change is due to the fact that Nickel chloride solution contains twice more chloride ions so that absorption is higher inducing a more acidic pH_{iep} . Nickel ion seems not to adsorb. It simply remains in the acidic solution to form $Ni(H_2O)_6^{2+}$ specie very stable in contrary to Na^+ that is spurned at particles surfaces.

Analysis for Nickel sulphate solutions: As in the case of chloride and per chlorate solutions, Fig. 5 also shows an acidification of supernatant liquid. Except this similarity, Fig. 5 presents a particular behavior for zeta potential values which are all negative for any pH values and the stirred solutions that stays more acidic in contrary to what

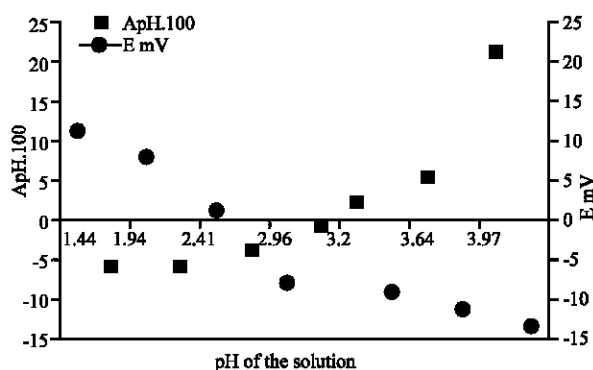


Fig. 4: ΔpH_i and zeta potential in nickel chloride solution

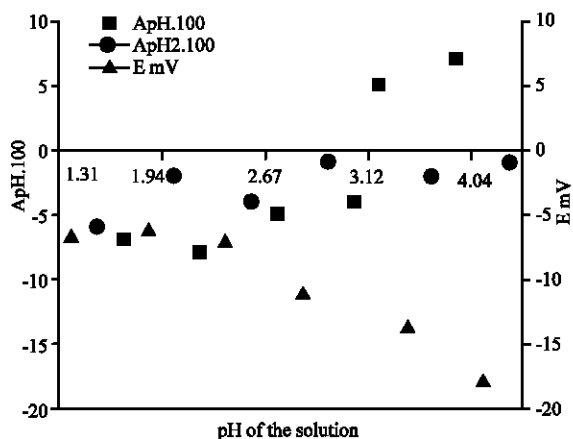


Fig. 5: ΔpH and zeta potential evolution versus pH in nickel sulphate solution

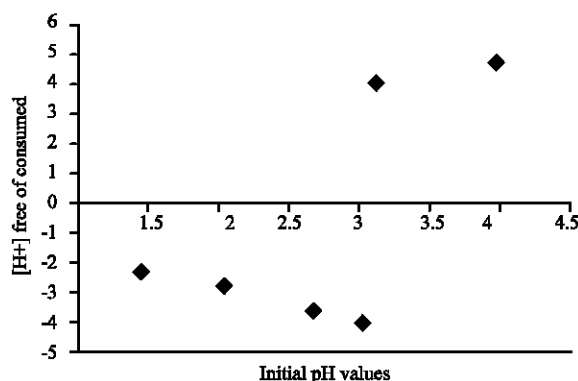
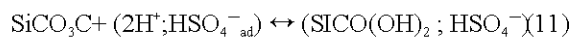


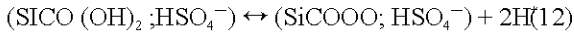
Fig. 6: Logarithmic representation of proton produced and consumed versus pH in sulphate solutions

was noticed for the other solutions. These particularities are necessary relied to sulphate ions in the solutions. Sulphuric acid used to fix pH values, presents a second acidity for pH 2.99. First acidity is characterised by dissociation that leads to hydro sulphate ion; HSO_4^- . From pH 2.99 the second acidity free sulphate ion SO_4^{2-} . Zeta potential values in solution of pH values inferior to second acidity stays constant around -6 mV and strongly decreases after pH 3. The high decreasing of zeta values indicates that ions adsorbing are more negative. For pH less than 3, the SO_4^{2-} -ions coming from nickel sulphate salt dissociation react with water to form HSO_4^- that adsorbed for a zeta value equal to -6 mV. The constancy of this value shows that it only depends on $NiSO_4$ concentration that is fixed. After pH 3, sulphuric acid second acidity occurs so; more sulphate ions with higher negative charge are disposal to adsorb leading to zeta potential decreasing (Fig. 6). This particularity shows that the origin of supernatant acidification in the case of nickel sulphate solutions is different from that takes place with chloride and per chlorate where spurning of sodium ions to the particles surface permit. One more time, this indicates that nickel ions do not adsorb on the pH range of investigation.

For nickel sulphate solutions, sulphate ions adsorb on the nucleophilic silicon sites of the components present at the particles' surface. Then, protonation of the oxygen at silicon α position occurs. The silicon positive charge is so stabilized and can react with a molecule of water to release the proton conformal to reaction schemed as follows:



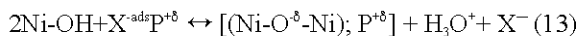
Then during sedimentation, the two-OH functions supported by the silicon form a peroxide link and release two protons that acidify the supernatant phase.



Reaction 12 takes place during sedimentation and some protons may so be retained in the dismiss and are released during stirring making the phase more acidic in contrary to what is noticed in chloride en per chlorate solutions. After pH 3, supernatant phase is also more basic. Reactions 8 and 9 may then take place, with SO_4^{2-} adsorbing. Hydroxides are released in the middle and zeta potential becoming more negative because of SO_4^{2-} charge. Relation 10 applied to these data; Fig. 5 also presents the same shape. This confirms the hypothesis of reactions that occur at the particles' surface.

CONCLUSIONS

Experimentations undertaken in this study have revealed that SiC particles surface evolves in zeta potential values according to solution pH and ions present in the middle. Nickel ion does not seem to adsorb and may stay solvated in $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ form in the solution for the pH range considered. In the papers pretending adsorption of nickel ions, the working pH was superior to 4.5. In such condition, $\text{Ni}^+\text{-OH}$ may form and adsorption of this specie can occur by oxygen free electrons. Chloride, per chlorate and sulphate ions adsorb on specific function such as SiO_2C_2 and SiO_3C that exist at the surface. Their adsorption is effective on Si electrophilic site. SO_4^{2-} -when present in the middle adsorbs independently of pH, while Chloride and per chlorate ions adsorb when activity of protons that adsorb on silanol groups fails. The SiC particles embedment in the metallic matrix so depends on the pH of the solution. In acidic middle; pH inferior to 3, particles are positively charged by protons adsorption on the silanol group. So near the reduction pole, they disadsorbed to form hydrogen. Hydrogen forming on the surface prevents particles embedment. For pH around 3, particles are neutralized by adsorption of negatives species on electrophilic site of the components on their surfaces. Near the reduction pole, the negative species are vanished; the electrophilic site charge $+\delta$ prevailing so, favours sticking of the particles on the cathode for a good embedment. According to this process, particles are taken to the cathode surface, only by hydrodynamic forces and are not affected by the electric reduction field. During reduction, nickel matrix surface is formed by Ni-OH. An interaction that can occur between Sic particles' surface as described and Ni-OH can stand as follows:



With P designing the particle; X-the negative specie adsorbed on its electrophilic site. The partial charges $+\delta$ on the particle and $-\delta$ on the oxygen stabilize the particle in the metallic matrix.

The worst embedment of SiO_2 noticed may so be due to none present of positive charge or nucleophilic site ion Si-OH_2^+ so that near the reduction pole, protons are reduced in hydrogen and the SiO_2 particle rejected into the solution. Concerning the worst embedment for $\gamma\text{-Al}_2\text{O}_3$ noticed, this could be relied to the oxide steric form that may not allow a good sticking by its aluminium electrophilic site. Watt baths are constituted by a same molar quantity of NiCl_2 and NiSO_4 for a pH value fixed to 3 with H_3BO_3 . In such conditions, for pH value inferior to 3, protonation of silanol groups leads to positive zeta potential values according to what noticed from chloride solutions. Adsorption of hydro sulphate ions present in the middle is up to neutralise the particles' charges. For pH equal to 3 the kinetic of protons reduction into hydrogen is slower than nickel ion one. Thereby, when the particle approaches the reduction pole, the hydro sulphate is vanished, the positive charge so prevails to favour sticking and the particle is so embedded in the nickel matrix. For ceramic elaboration, particles agglomeration is to be avoided. Therefore, they must stay charged to assure repulsive forces between them. The isoelectric pH value has to be defined to permit determination of working pH range.

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