RESEARCH ARTICLE

EFFECT OF CIGARETTES SMOKING YIELDS ON CORROSION BEHAVIOR OF AMALGAM IN ARTIFICIAL SALIVA AT PH= 6.2 AND 37°C

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ABSTRACT

This work involves study the effect of cigarettes smoking yields on the corrosion behavior of amalgam in artificial saliva at pH = 6.2 and 37°C using potentiodynamic measurements at scan rate 3 mV.sec^{-1} by saturation the saliva with smoking yields of 3, 6, 9, 12 and 15 cigarettes. The corrosion parameters indicate than corrosion potential value shifts to active direction with increasing the saturation of cigarettes smoking yields. Corrosion current density became higher after saturated with 3, 6, and 9 cigarettes yields, i.e. increases in corrosion rate due to increasing of heat and decreasing of pH to 5.51, while after continuously saturated with 12 and 15 cigarettes yields the corrosion current density decreases due to adsorption of some molecules from composition of cigarettes smoking such as poly aromatic hydrocarbons and amines on amalgam surface leading to behave as inhibitor to make a barrier between amalgam and saliva as shown from FTIR spectra of cigarette compositions and for adsorption film on amalgam surface. While the microstructure investigation indicate that the corrosion will increase after remove the formed film by cleaning the teeth or by eating and drinking, e.i. the smoking increase the corrosion of amalgam even after long period time of exposure to smoking yields.

INTRODUCTION

Tobacco smoke is comprised of thousands of chemical compounds whose health implications are understood to varying degrees. The smoke is made up of a visible mist of micron-sized liquid particles suspended in a colorless gas. The mist, which typically accounts for approximately 10% of the weight of the smoke, consists of condensed water, tar, and nicotine (Kerosuo *et al.,* 1995). Tar is a mixture of thousands of compounds and is primarily responsible for the cancer-causing potential of tobacco smoke. It contains powerful carcinogens such as benzo-pyrene (one member of the class of compounds known as polycyclic aromatic hydrocarbons, PAH), nitrosamines, and aromatic amines, as well as a host of carcinogenic heavy metals such as arsenic, chromium, and lead. Nicotine is the most powerful addictive agent in tobacco smoke. It is thought to contribute to coronary heart disease. While not a proven carcinogen, recent studies indicate that nicotine interfere with the body's defenses against cancer. The gas phase accounts for roughly 90% of the weight of tobacco smoke. It consists mainly of nitrogen, oxygen, and carbon dioxide (these three account for approximately 85% of the gasses in the smoker), carbon monoxide, water vapor, volatile

hydrocarbons, carbonyls, and other materials. From a health perspective, carbon monoxide is the most significant component as it has been implicated in coronary heart disease, atherosclerosis and sudden death, and chronic respiratory disease.

The volatile hydrocarbons include known carcinogens such as benzene, but because of their low concentrations they are not deemed important in comparison to the compounds present in tar fraction (Kerosuo *et al.,* 1995). Despite the difference in structure between narghile and cigarettes, which include the difference in burning temperature, they both involve the consumption of tobacco. Therefore, it is expected that some of the chemical compounds identified in cigarette smoke would also be found in the smoke of a narghile, albeit at different concentrations due to the differences between the two smoking methods. While very few studies have been conducted on the chemical composition of narghile smoke, what has been found thus far suggests that this smoking method poses significant health hazards. It was found that the mainstream smoke of a single narghile smoking session contains many times the CO and nicotine found in the mainstream smoke of a single cigarette. A single narghile smoking session yields 20 times the amount of carcinogenic polycyclic aromatic hydrocarbons found in mainstream cigarette (Iijima *et al.,* 2001). Aldehydes

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have been established as a major group of compounds emitted from cigarettes. Hoffmann et al. showed in their review on the chemical composition of mainstream cigarette smoke, that the amounts of formaldehyde, acetaldehyde and acrolein, which are primarily found in the gas phase, vary within the ranges 20–100, 400–1400 and 60–240 µg/cigarette, respectively (Department of Health and Human Services 2000).

Other studies show that the addition of sugars and flavors to cigarette tobacco results in an increase (up to 60%) in the amounts of aldehyde compounds produced and in altering the chemical composition of the smoke (Kamal Chaoachi 2006). The importance of assessing aldehyde compounds in narghile smoke lies in the fact that these compounds are known to be toxic, carcinogenic and hazardous (Iijima *et al.,* 2001). Brain *et al.* (2006) studied association of cigarette smoking and media literacy about smoking among adolescents (Brian *et al.,* 2006). While Alan Sihadeh and Sima Azar generated dry particulate matter and carbon monoxide yields using the playback and equivalent periodic puffing regimens are compared for a single smoking session by a 26-year-old male narghile water-pipe smoker. It was found that the periodic puffing regimen yielded 20% less carbon monoxide than the played-back smoking session, indicating that steady periodic smoking regimens, which are widely used in tobacco smoke research, may not produce realistic smoke aerosols (Alan Sihadeh and Sima Azar 2006). Rashidi *et al.* (2008) studied aldehydes in the mainstream smoke of the narghile waterpipe which generate using a popular type of flavored ma'ssel tobacco mixture. This study performed by using smoking machine connected to chromatography to estimate aldehyde yields (Al. Rashidi *et al.,* 2008). Kamal C. (2009) studied cigarette environment tobacco smoking which classically understood as a combination of side – stream smoke and exhaled main – stream smoke. He studied specific chemicals in smoking such as nicotine, CO, aldehydes, polycyclic aromatic hydrocarbons, phenols, benzene and toluene, nitric oxides, heavy metals, nitrosamines, acetone and 2-butanone, radiotoxic elements, and other materials (Kamal Chaouachi 2009). Nancy Daher *et al.* (2009) studied the comparison of carcinogen, carbon monoxide, and ultrafine particle emissions from narghile waterpipe and cigarette smoking; side stream smoke measurements and assessment of second – hand smoke emission factors by using smoking machine (Nancy Daher *et al.,* 2009). Odeh *et al.* (2009) showed that the practice of narghile smoking is reviewed in terms of it is effect on general health and oral health particularly its effect on periodonttium and oral mucosa (Odeh *et al.,* 2009). In addition to study the corrosion of amalgam by many authors (Jaro Pleva 1989; Chang *et al.,* 2003; Maruthamuthu 2005; Zhang *et al.,* 2009; Mareci *et al.,* 2010) in the presence of many materials in saliva medium.

Experimental Procedure

Materials and Chemicals

The used alloy in this study was amalgam; with chemical composition wt% (56.7 Ag, 28.6 Sn and 14.7 Cu) which prepared by amalgamator. And then cold mounted using pyrax polymers to obtain only surface area. The open side was polished mechanically to a mirror finish, rinsed in distilled water and stored in desiccators. The electrolyte reference used was modified Fusayama artificial saliva (Geis *et al.,* 1985), which closely resembles natural saliva, with composition of (0.4 g/L KCl, 0.4g/L NaCl, 0.906 g/L $CaCl_2.2H_2O$, 0.69 g/L $NaH_2PO_4.2H_2O$, 0.005g/L $Na_2S.9H_2O$ and 1g/L urea). pH of this electrolyte was 6.2 . For the analysis of organic compounds in smoking yields, FTIR spectra were obtained on a Shimadzu spectrophotometer, using a KBr disk for dray tobacco in cigarette and for film forming on amalgam surface after exposed to 15 cigarette smoking yields in artificial saliva.

Corrosion Test

Polarization experiments were performed in WINKING M Lab 200 Potentiostat/Galvanostat from Bank-Elektronik with electrochemical standard cell with provision for working electrode (amalgam), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with saturated calomel electrode SCE reference electrode. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec^{-1}. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method.

Microstructure

The microstructure evolution was investigated by means of optical microscope using (BEL photonics) microscope was connected to computer.

RESULTS AND DISCUSSION

Corrosion Behavior

Fig. (1) shows the variation of open circuit potential (E_{oc}) with time, from which several deductions can be made. The first is that the initial potential in artificial saliva vs. SCE. This could be due to the mixed potential resulting from the ionic constitution of the solutions. This figure indicates that through the time the E_{oc} shifts to more active values with increasing the saturation of saliva with smoke of cigarettes. In this work, artificial saliva was saturated with 3, 6, 9, 12, and 15 cigarettes. The polarization curves, Fig. (2), show the anodic and cathodic region, the lower section represents reduction reaction which includes evolution of hydrogen molecules because acidity of electrolyte (artificial saliva) as follows:
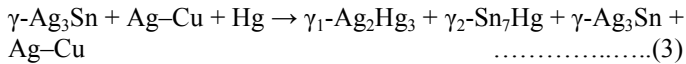
$$2H^+ + 2e \rightarrow H_2 \text{ .....(1)}$$
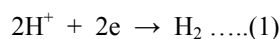
In addition to reduction of oxygen to water molecules:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \text{ ....(2)}$$
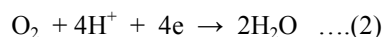
While at anodic sites dissolution of metals in amalgam can occur such as Ag, Sn and Cu. Mercury diffuses into the alloy particles and reacts with silver, tin and copper, forming various compounds. The exact compounds formed depend on the chemical composition of the powder and on particle shape (which can be spherical or irregular) but are mainly phases of

the systems Sn–Hg, Ag–Hg, with Ag–Cu and Ag–Sn phases remaining from the reactants. For the currently used, high copper amalgams, the main reaction is (Acciari *et al.,* 2001):

$$\gamma\text{-Ag}_3\text{Sn} + \text{Ag–Cu} + \text{Hg} \rightarrow \gamma_1\text{-Ag}_2\text{Hg}_3 + \gamma_2\text{-Sn}_7\text{Hg} + \gamma\text{-Ag}_3\text{Sn} + \text{Ag–Cu} \quad \ldots\ldots\ldots\ldots\ldots..(3)$$

The Sn–Hg phase, which has a relatively low corrosion resistance, then undergoes further reaction, according to

$$\gamma_2\text{-Sn}_7\text{Hg} + \text{Ag–Cu} \rightarrow \acute{\eta}\text{-Cu}_6\text{Sn}_5 + \gamma_1\text{-Ag}_2\text{Hg}_3 \quad \ldots\ldots\ldots..(4)$$
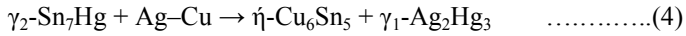
at the amalgam electrode surface as well as the influence of surface oxide. Hypothesis has also been proposed, that the released mercury may partly react with Ag_3Sn, to produce additional Sn_7Hg, so that the corrosion cycle can continue. The filling becomes porous and can lose most of its strength. Absorption of released mercury by Ag_3Sn requires the absorbing phase in close vicinity of the corroding Sn_7Hg-phase, otherwise there is no thermo dynamical reason for mercury to diffuse into the filling with high mercury content. Rather, it will evaporate. The content of Ag_3Sn may vary depending on amalgam composition and working methods of
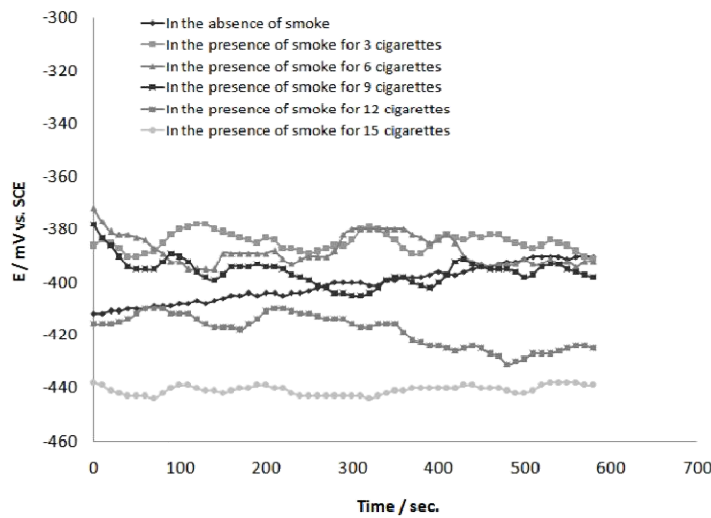

Fig. 1. Variation of open circuit potential with time for amalgam in artificial saliva at 37ºC in the presence of cigarettes smoking yields
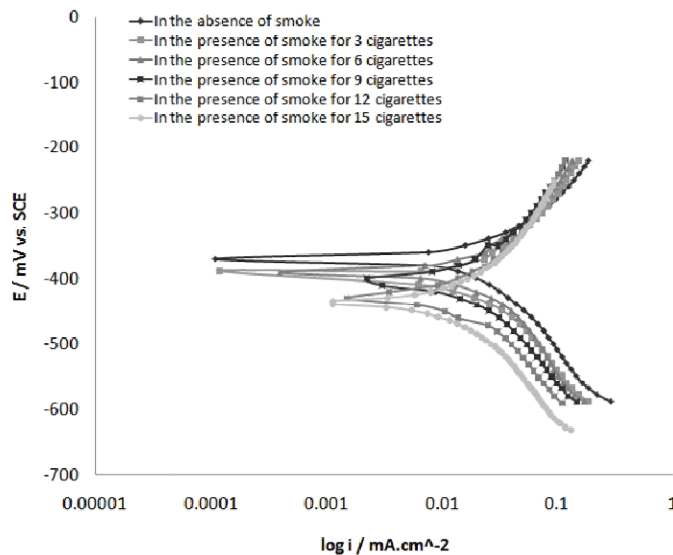

Fig. 2. Linear polarization of amalgam in artificial saliva at pH=6.16 and 37ºC in the presence of cigarettes smoking yields

The microstructure of the dental amalgam is complex, consisting of new microphases, as produced in the reactions above, and the remains of the powder alloy particles, within the $\gamma_1\text{-Ag}_2\text{Hg}_3$ matrix phase (Acciari *et al.,* 2001). For this reason, and in order to understand better the role of the various phases, individual phases have electrochemical measurements can lead to an improved understanding of the processes that take place

the particular dentist. As the amount and distribution of Ag_3Sn cannot be controlled, the hypothesis about Ag_3Sn as a sink for all mercury released by corrosion is not substantiated.

In particular, surface corrosion will result in evaporation and abrasion of major part of free mercury, rather than its diffusion into the filling. The partial pressure of mercury over amalgam

is 11–25% of that over pure liquid mercury, and increases with increasing mercury concentration and temperature (Brecht-Bergen *et al.,* 1933). The corrosion products found on amalgam surfaces are mainly tin oxide and hydroxichloride (Sarkar *et al.,* 1975) and silver chloride (Guthrow *et al.,* 1967). Instead, silver has been found in the solution already after a few days exposure to artificial saliva (Brune and Evje 1984). Though ionized mercury also has been found among the dissolved corrosion products by radioactive tracer method (Brune and Evje 1985) the main part is released as metallic mercury, which can be found as droplets on freshly corroded amalgam surfaces (Fredin 1985). The evaporated mercury can be measured in expired air (Sware *et al.,* 1981; Patterson *et al.,* 1985).

These data of corrosion for amalgam in artificial saliva in the presence of smoke of cigarettes with different saturation indicate that the presence of smoking yields in artificial saliva shift the corrosion potentials values (E_{corr}) in active direction. This means that the potential of the galvanic cell becomes more positive or negative and hence the Gibbs free energy change (ΔG) for the corrosion process becomes more negative or positive respectively. The corrosion reaction is then expected to be more or less spontaneous on pure thermodynamic ground and vice versa. It is thus shown that (E_{corr}) value is a measure for the extent of the feasibility of the corrosion reaction on purely thermodynamic basis (Ronald L. Bianchetti 2001).

While the corrosion current densities values (i_{corr}) shift to higher values for amalgam after continuously saturated with smoking yields of 3, 6, and 9 cigarettes. It is known that any factor that enhances the value of (i_{corr}) results in an enhanced value of the corrosion rate on pure kinetic ground. The rate (C_R mm/y) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation (Lawrence *et al.,* 1992):

$$C_R(mm/y) = 3.27 \frac{e}{\rho} i_{corr}.$$

where $C_R(mm/y)$: corrosion rate in millimeter per year, e: equivalent weight of alloy (gm), and ρ: density of alloy (gm/cm^3). The data of corrosion rate which listed in Table (1) show increasing of rate up to saturate with 9 cigarettes due to increasing the temperature which increases the dissolution of metals at anodic sites in addition to decreasing in pH from 6.16 to 5.51. While after continuously saturation with 12 and 15 cigarettes can be seen that the rate of corrosion decreases because of adsorption of some organic molecules from the composition of main stream smoke of cigarettes. These molecules may be aldehydes, polycyclic aromatic hydrocarbons, and aromatic amines. Figs. (3) and (4) show FTIR spectra of cigarette composition and the adsorption film on amalgam surface after saturated with 15 cigarettes yield respectively. FTIR spectrum of cigarette in Fig. (3) indicates the presence of C—H stretch in vinylic, aromatic and

Table 1. Corrosion parameters of amalgam in artificial saliva saturated with cigarettes smoking yields at 37ºC

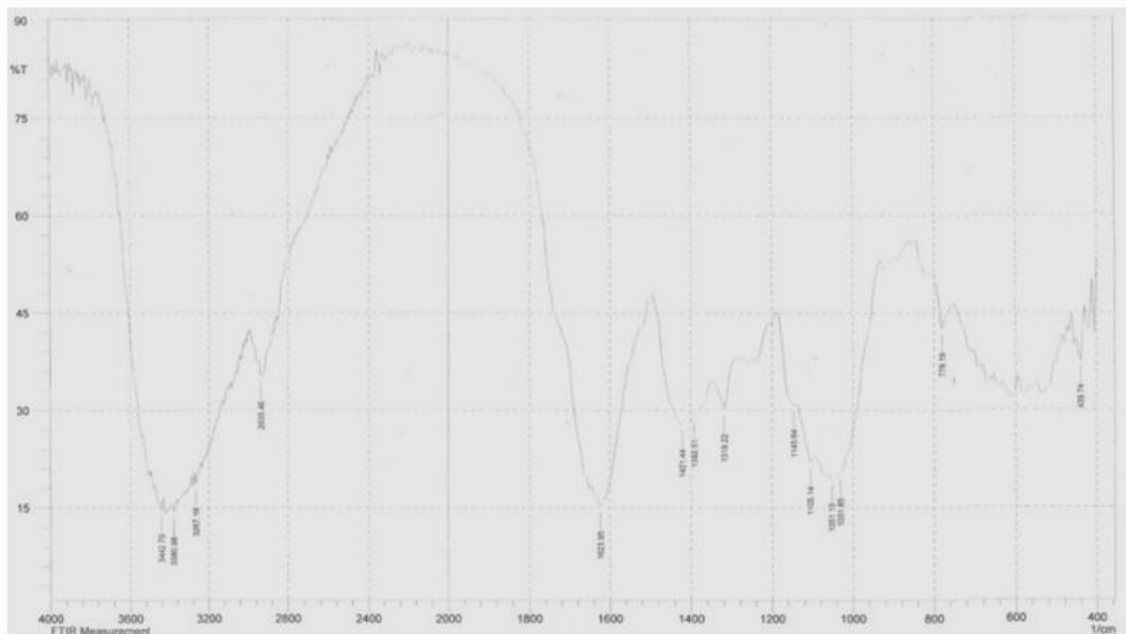| No. of cigarette	-E_{oc} mV	-E_{corr} mV	$i_{corr} \mu A.cm^{-2}$	-b_c mV.dec^{-1}	b_a mV.dec^{-1}	C_R mm/y
0	390	368.3	13.13	130.1	91.7	0.4416
3	391	388.0	13.16	130.7	118.1	0.442
6	392	390.0	13.93	141.5	124.4	0.468
9	398	400.1	14.28	169.1	152.8	0.480
12	425	428.1	13.32	146.2	175.0	0.447
15	439	437.1	9.89	144.2	136.7	0.332

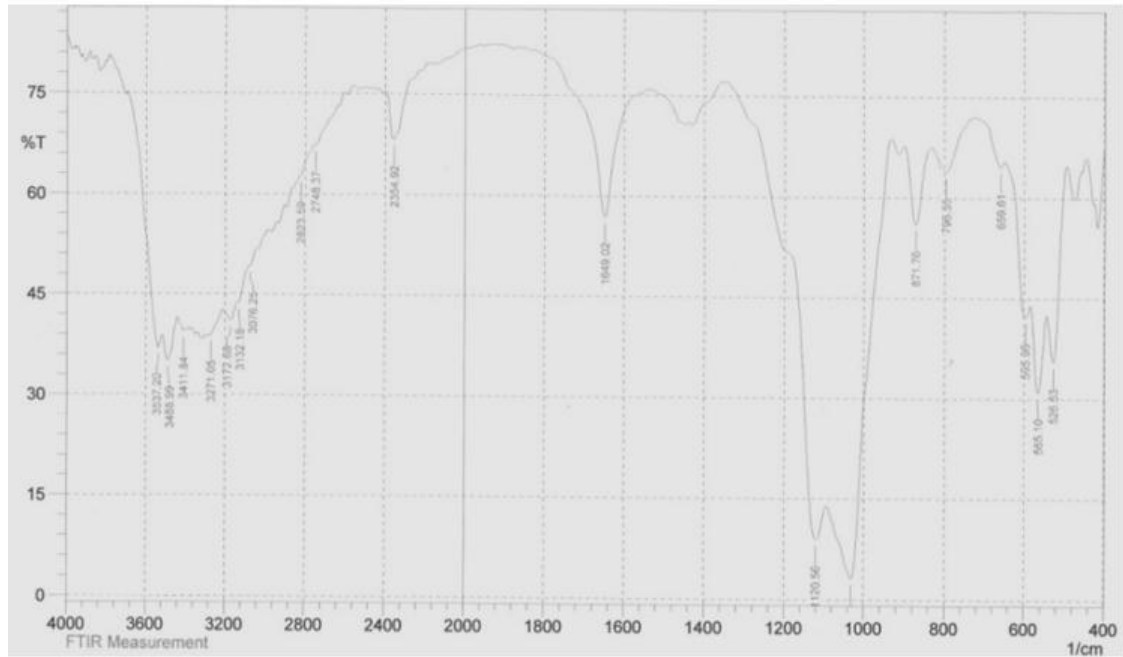**Fig. 3. FTIR spectrum of cigarette compositions**

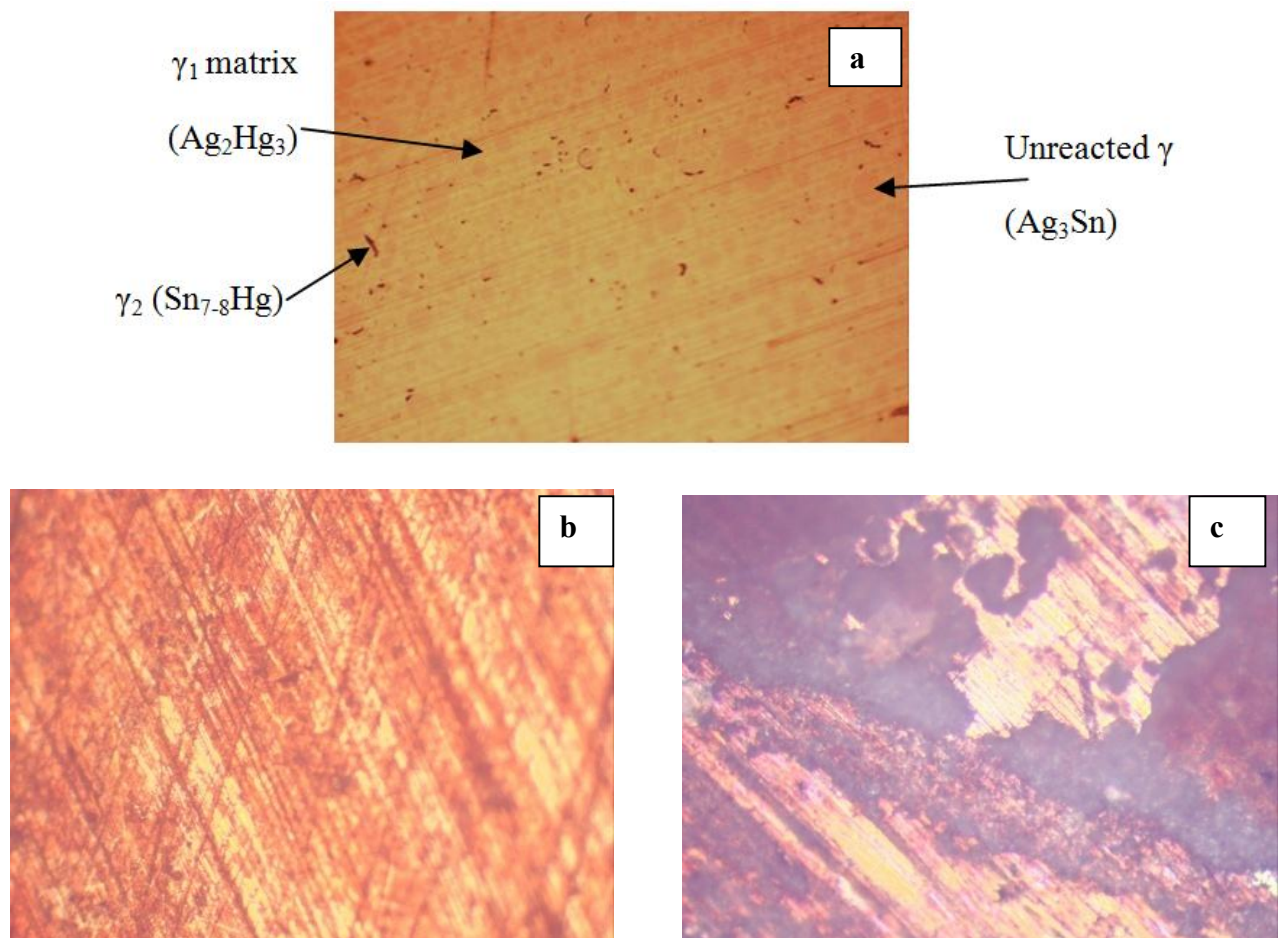**Fig. 4. FTIR spectrum of cigarette compositions after deposit on amalgam surface**

Fig. 5. Optical microscope for amalgam: (a) before corrosion, (b) after remove adsorbed film, and (c) after expose to smoke of 15 cigarettes with corrosion products

hydrocarbons at 3380.98cm^{-1}, C═O stretch for aldehydes at 1623.95cm^{-1} and C—H stretch of aldehyde(—CHO) at 2935.46cm^{-1}. In other hand, can be seen N—H stretch of amine at 3442.7cm^{-1}, N—H bend at 1623.95cm^{-1}, N—H out of plane bending at 779.19cm^{-1} and C—N stretch at 1319.22cm^{-1}. While in Fig. (4), the most intensity of band decreases due to the interaction with metal ions at amalgam surface especially the band of C═O group.

The Tafel slopes were very much influenced in the presence of cigarettes smoking yields, the cathodic Tafel slopes (b$_c$) anodic Tafel slopes (b$_a$) were increased for amalgam. It is inferred that the rate of charge of current with change of potential was increases during cathodic anodic polarization. Fig. (5) shows the optical microscopic test for amalgam. In Fig. (6-a) can be seen the phases in microstructure of polished amalgam before corrosion which consist of unreacted particles surrounded by a matrix of the reaction products. The reaction is principally a surface reaction, and the matrix bonds the unreacted particles together.

The initial diffusion and reaction of mercury and alloy are relatively rapid and the mass changes rapidly from a plastic consistency to a hard mass. Completion of the reaction may take several days to several weeks, which is reflected by the change in mechanical properties over this time (Robert *et al.,* 2002). Fig. (6-c) shows the adsorption of cigarettes smoking yields on amalgam surface especially nicotine (3-((2S)-1-methylpyrrolidin-2-yl) pyridine, with formula $C_{10}H_{14}N_2$) and PAH. After carefully remove this adsorbed film, corroded surface can be observed as shown in Fig. (6-b), this means that corrosion of amalgam in the presence of cigarettes smoking yields may be continuous because of the filling (amalgam) in the mouth exposed to change the environment by eating, drinking and cleaning, i.e. cigarettes yield continuously increases the corrosion of amalgam.

Conclusion

The effect of cigarettes smoking on the corrosion behavior of amalgam in saliva may be positive effect or may be not depending on the time and amount of saturation with smoking yields. When saturated with 3, 6 and 9 cigarettes smoking yields the corrosion rate increases because of increasing in temperature of medium and decreasing in pH to 5.51. while increases the continuously saturation with 12 and 15 cigarettes smoking yields lead to inhibit the corrosion of amalgam due to adsorption of poly aromatic hydrocarbons and amines from cigarettes compositions as shown from FTIR spectra.

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