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Surface Protection of Niti- Shape Memory Alloy by Colgate Visible White Toothpaste

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Abstract : To regulate the growth of teeth people are implanted with orthodontic wires made of different materials. They clean their teeth with different types of toothpastes. During this process the materials may undergo corrosion. The main objective of this work to evaluate corrosion behavior of NiTi shape memory alloy in artificial saliva in the absence and presence of an aqueous solutions of toothpaste Colgate Visible White.

The corrosion parameters have been measured by electrochemical studies such as potentiodynamic polarization and AC impedance spectra. The surface morphology has been analysed by Fourier transform infrared spectroscopy and UV-Visible absorption spectra.

The electrochemical measurements reveal that the corrosion resistance is offered by the toothpaste due to formation of protective film. The corrosion resistance of NiTi shape memory alloy in various solutions decreases in the following order: AS+ toothpaste> toothpaste>AS. It confirmed that the active principles of the ingredients of the toothpaste have coordinated with the corroding metal atoms (their ions) Ni^{2+} and Ti^{2+} through their polar atoms and formed an insoluble complex which acts as a protective film.So people implanted with orthodontic wire made of NiTi shape memory alloy need not hesitate to use Colgate Visible White toothpaste to brush their teeth.

Keywords: Orthodontic, Ingredients, Electrochemical.

Introduction

Nowadays, Nickel–titanium nearly equiatomic possessing unique properties such as shape memory effect, super elasticity and good biocompatibilityconsidered as one of the best biomaterials for use in biomedical implant devices[1-4]. Currently, they are widely used indental appliances, self expanding cardiovascular and urological stents, bone fracture fixation plates and staples, etc[5-7].

Titanium-based alloys exhibit high corrosion resistance because of the formation of a thin, stable oxide layer. But thetitanium-based orthodontic wires undergo corrosion in the presence of fluoride-containing prophylactic agents [8]. TiO_2 based oxides are readily formed when the metal is exposed to the air or moisture as titanium possesses high affinity for oxygen.When NiTi is used as implant material, its corrosion behaviour has to be closely examined and monitored in various simulated physiological fluids. Due to the Ni ion release, the corrosion of NiTi alloy has adverse effect on surrounding tissue [9-10]causing allergenicity, toxicity and carcinogenicity[11-12] as well as allergic contact dermatitis, the incidence of which is as high as 20–30% [13-14]. The leached metal ions during corrosion not only influence the mechanical properties of the metal appliances, but also may affect the body[15-16].

Fluorides are widely introduced into the oral environment by means of toothpastes, mouth rinses, orthodontic gels and other therapeutic dental products to maintain hygienic health of the oral cavity, especially prevent the tooth decay[17-18].In addition to this, tea, dietary supplements and fluoridated bottled water are other sources of fluoride in the oral environment. Therefore, NiTi orthodontic wires are readily exposed to fluoride medium.

The possible danger associated with the use of NiTi archwire for orthodontic treatment is its biologically harmful effects of the released Ni ion during corrosion. Therefore, NiTi archwire with a good corrosion resistance is essential to its biocompatibility during orthodontic treatment.

The present work aimed to investigate the distinctive corrosion characteristics of NiTi orthodontic wires in artificial saliva in the absence and the presence of aqueous solutions of Colgate Visible White toothpaste (CVWT).

Experimental

Materials

The metal specimen chosen for the present study was NiTi shape memory metal alloy and the toothpaste was Colgate Visible White.

Composition of Colgate Visible White toothpaste (CVWT)

Silica, sorbitol, glycerin, polyethylene, glycol, sodium tripolyphosphate, tetra potassium pyrophosphate, sodium lauryl sulphate, flavour, cocamidopropyl betaine, sodium carboxy methyl cellulose, sodium saccharin, sodium fluoride, xanthan, sodium hydroxide, sorbosil BFG 51 blue, titanium dioxide in aqueous base.

Fusayama artificial saliva

Fusayama was used as an electrolyte medium (Table 1)[19]. Fusayama artificial saliva solution constituents closely resemble those of natural saliva. During the study, the artificial saliva solution temperature was maintained at room temperature[20].

Table 1. Chemical composition of artificial saliva (Fusayama Meyer)

Content	Quantity gL^{-1}
KCl	0.4
NaCl	0.4
$CaCl_2.2H_2O$	0.906
$NaH_2PO_4 2H_2O$	0.690
$Na_2S.9H_2O$	0.005
Urea	1

Potentiodynamic polarization

Polarization studies were carried out in a CHI-Electrochemical workstation with impedance, Model 660A. A three electrode cell assembly was used. The working electrode was one of the metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (LPR) and Tefel slopes (anodic =b_a and cathodic=b_c) were calculated.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated from Nyquist plots. Impedance log (Z/ohm) was calculated from Bode plots. During AC impedance spectra were recorded the scan rate (V/s) was 0.005; Hold time at Ef(s) was zero and quite time (s) was 2. The value of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were calculated from Nyquist plot.

$R_t = (R_s + R_t) – R_s$

Where R_s = Solution resistance, R_t =Charge transfer resistance

$$Cdl = \frac{1}{2 \times 3.14 \times R_t \times f_{max}}$$

Where f_{max}= frequency at maximum imaginary impedance.

Surface characterization studies

The specimen was immersed in an inhibitor system, for a period of one day, taken out, dried and the nature of the film formed on the surface was analysed by surface analysis techniques to confirm the results obtained by electrochemical measurements.

Surface analysis by FTIR spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBR. The FTIR spectra were recorded for the pure CVWT and for the film by using Perkin –Elmer 1600 FTIR spectrophotometer with a resolving power of 4 $cm^{-1.}$

UV- Visible absorption spectra of solutions

The possibility of the formation of metal – inhibitor complex in solution was examined by recording their UV-Visible absorption spectra for the blank, the inhibitor and the best system solution using Analytic Jena Specord S-100, UV –Visible spectrometer.

Results

Analysis of potentiodynamic polarization study

Polarization study has been used to evaluate the corrosion resistance of metals and alloys during the corrosion inhibition process[21].The polarization curves of NiTi shape memory alloy immersed in various test solutions are shown in figure1.The corrosion parameter namely, E_{corr}, Tafel slopes (b_c =cathodic; b_a = anodic), LPR and I_{corr} derived from polarization curves are given in table 2.

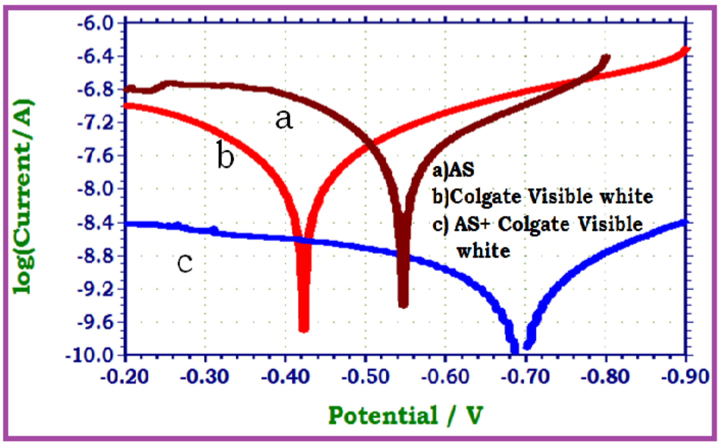

Figure 1. Polarization curves of NiTi shape memory alloy immersed in AS in the absence and presence of CVWT(1%) (Tafel plot)

Table 2. Corrosion parameters of NiTi shape memory alloy immersed in various test solutions

System	E_{corr} mVvs SCE	b_c mV/decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/cm^2
AS	-547	254	184	1299843	$3.574x10^{-8}$
Colgate Visible White	-423	182	176	2531801	$1.537\ x10^{-8}$
AS + Colgate Visible White	-696	179	260	67386056	$0.0686\ x10^{-8}$

It is observed from figure1and table 2 that when NiTi shape memory alloy is immersed in AS, the E_{corr} is -547 mV vs SCE, the LPR value is 1299843 ohm $cm^2$and the I_{corr} is 3.574 x 10^{-8} A/cm^2. When NiTi shape memory alloy is immersed in aqueous solution of CVWT (1%), the E_{corr} is shifted to anodic side (-423 mV vs SCE). The LPR value increases from 630154 to 657372 ohm cm^2 and the I_{corr} decreases from 6.872 x 10^{-8} to 6.730 x 10^{-8} A/cm^2. These observations indicate that corrosion resistance increases in the presence of CVWT and it controls the anodic reaction predominantly.

Further , it is noticed that when NiTi shape memory alloy is immersed in AS containing CVWT (1%), the E_{corr} is shifted to the cathodic side (-696 mV vs SCE) controlling the cathodic reactions predominantly. Further, the LPR value increases from 1299843 to 67386056 ohm $cm^2$and I_{corr} decrease from 3.574 x 10^{-8} to 0.0686 x 10^{-8} A/cm^2.

These observations bring to conclusion that the corrosion resistance is enhanced in the presence of the inhibitor system. So people implanted with orthodontic wire made of NiTi shape memory alloy need not hesitate to clean their teeth with tooth paste Colgate Visible White.

Analysis of AC impedance spectra

AC impedance spectra have been used to analyse the formation of protective film on the surface of metals and alloys in various test solutions[22].The AC impedance spectra of NiTi shape memory alloy immersed in various test solutions are shown in figure 2 (Nyquist plot) and figure 3(a,b,c) (Bode plot). The corrosion parameters derived from these plots are given in table 3. The equivalent circuit diagram is shown in figure4.

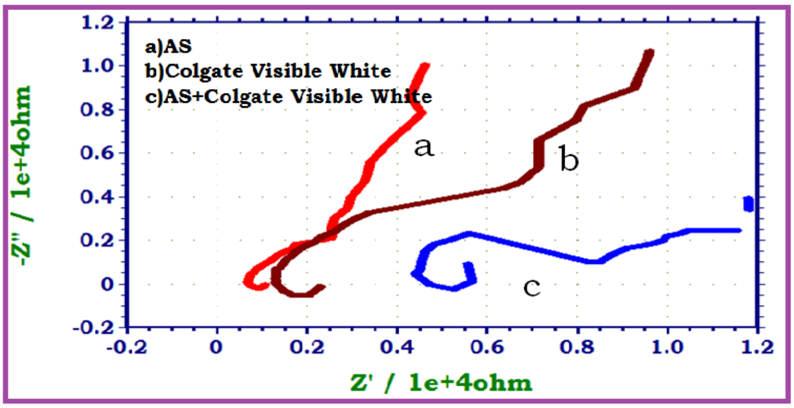

Figure 2. AC impedance spectra of NiTi shape memory alloy immersed in AS in the absence and presence of CVWT (1%) (Nyquist Plots)

Table 3. Corrosion parameters of NiTi shape memory alloy immersed in various test solutions

System	Nyquist plot		Bode plot
	R_t Ohm cm^2	C_{dl} F/cm^2	Impedance value Log z/ohm
AS	3548	$14.374\ x10^{-10}$	4.042
Colgate Visible White	9565	$5.3319\ x10^{-10}$	4.303
AS + Colgate Visible White	19354	$2.6351\ x10^{-10}$	4.522

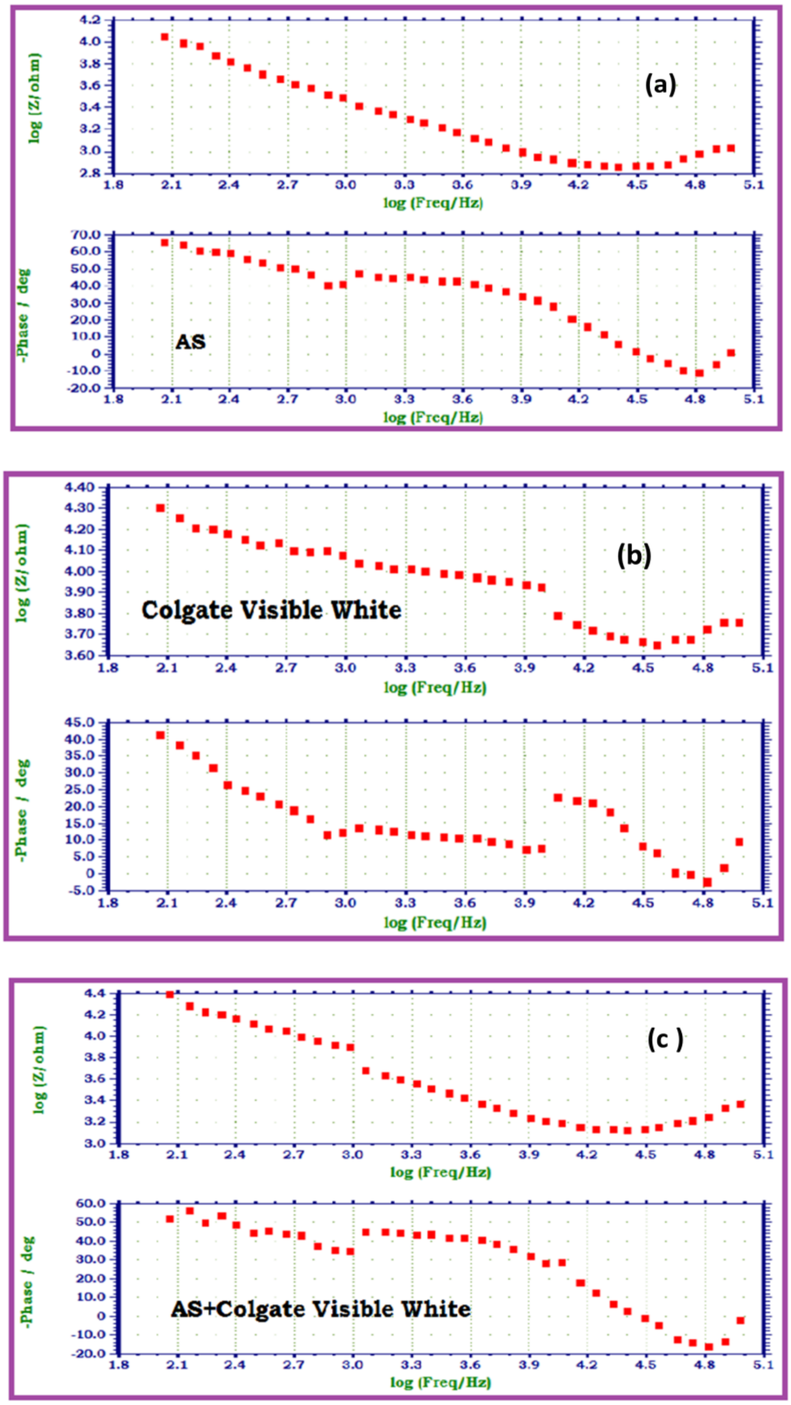

Figure 3(a,b,c) AC impedance spectra of NiTi shape memory alloy immersed in various test solutions

It is observed that when NiTi shape memory alloy is immersed in AS, the charge transfer resistance (R_t) value is 3548 ohm cm^2, the double layer capacitance (C_{dl}) value is 14.374 x10^{-10} F/cm^2 and the impedance(log z/ohm) value is 4.042. When NiTi shape memory alloy is immersed in aqueous solutions of CVWT(1%), the R_t value increases from 3548 to 9565 ohm cm^2, the C_{dl} value decreases from 14.374 x 10^{-10} to 5.3319 x 10^{-10} F/cm^2 and the log (z/ohm) increases from 4.042 to 4.303.

Further, it is observed that when NiTi shape memory alloy is immersed in AS containing CVWT(1%), the R_t value increases from 3548 to 19354 ohm cm^2, the C_{dl} value decreases from 14.374 x 10^{-10} to 2.6351 x 10^{-10} F/cm^2, the log (z/ohm) value increases from 4.042 to 4.522.

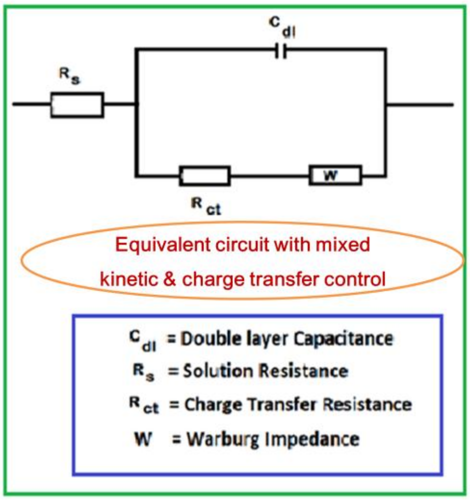

Figure 4. Equivalent circuit diagram for AC impedance spectra

These observations indicate that, a protective film is formed on the metal surface in the presence of AS containing CVWT (1%). This protective film prevents the transfer of electrons from the metal surface to the bulk of the solutions. Hence corrosion resistance increases and the rate of corrosion decreases. The protective film probably consists of Ni^{2+}, Ti^{3+} and the active principle of the ingredients of the tooth paste. It inferred that, in presence of AS containing CVWT, the NiTi shape memory alloy has shown enhanced corrosion resistance.

Analysis of FTIR Spectra

The FTIR (KBr) spectrum of pure toothpaste Colgate Visible White is shown in Fig (5). Analysis of the structures of these compounds reveals that the active principles of the ingredients of toothpaste Colgate Visible White contain functional groups like OH, C=O, N and an aromatic ring. The peak appears at 3383.17cm^{-1}corresponds to O-H stretching frequency and 2926.38 cm^{-1} peak corresponds to C-H stretching frequency. 1644.56 cm^{-1}peak is due to C=O stretching and 1096.90 cm^{-1} peak is due to P-O and C-N stretching. 1213.11 cm^{-1} peak is of P=O stretching. Peak at 1415.47 cm^{-1} indicate the presence of aromatic ring in the compounds present in the toothpaste.

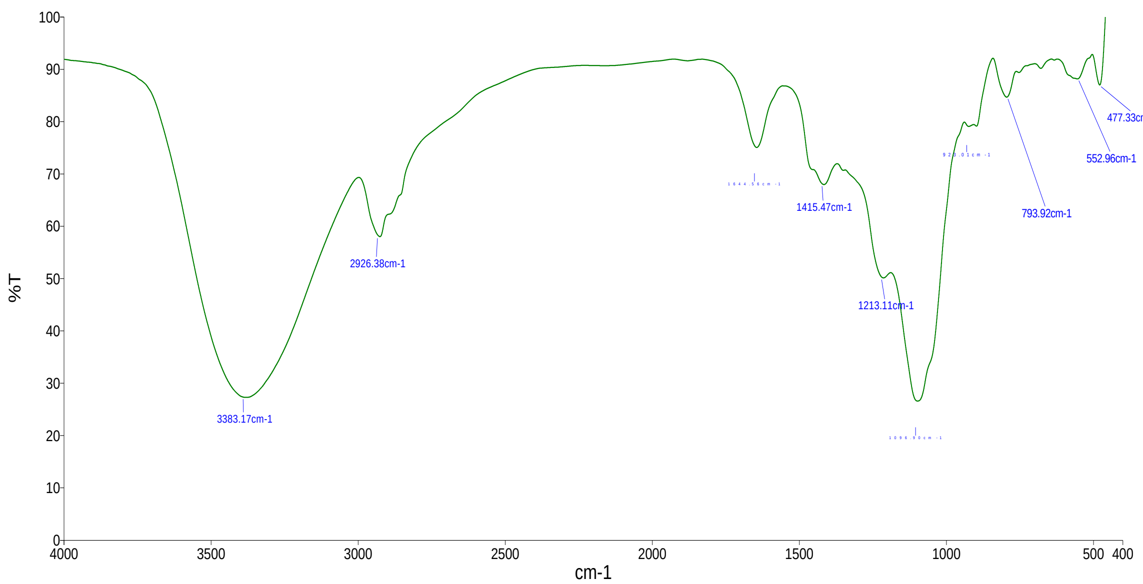

Figure 5. FTIR spectrum of pure CVWT

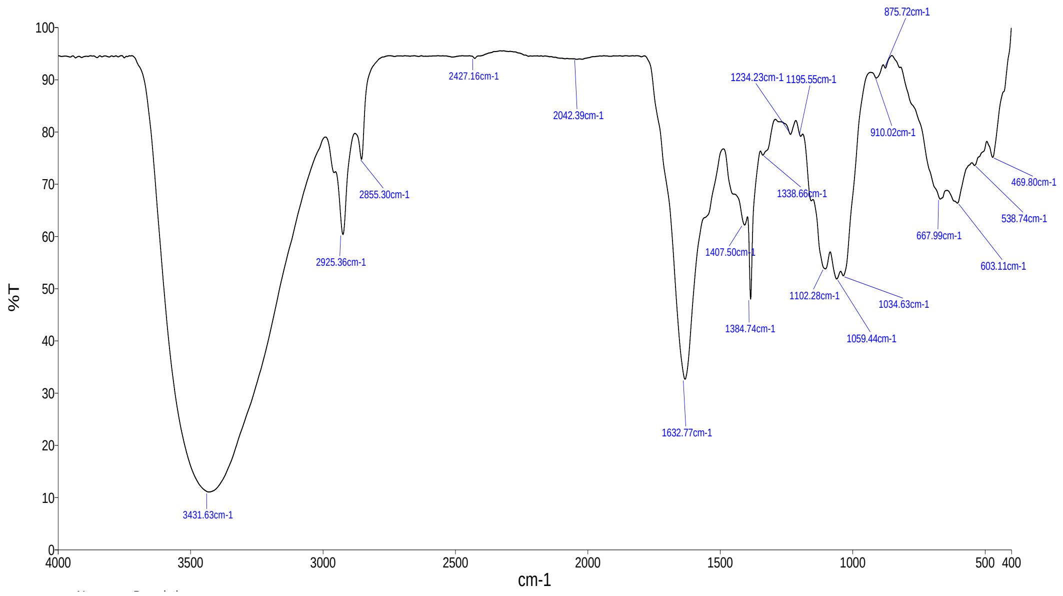

Figure 6. FTIR Spectrum of NiTi shape memory alloy immersed in AS containing CVWT (1%)

The FTIR spectrum of the film formed on the metal surface after immersion in AS containing toothpaste Colgate Visible White is shown in Fig(6) . A shift is observed in the peak due to O-H stretching frequency from 3383.17 cm^{-1} to 3431.63 cm^{-1}. Peak due to C-H stretching frequency has shifted from 2926.38 cm^{-1} to 2925.36cm^{-1}. The shift is observed in the peak for P=O stretching frequency from 1213.11 cm^{-1} to 1234.23 cm^{-1}. Peaks due to P-O stretching frequency has shifted from 1096.90 cm^{-1} to 1059.44 cm^{-1}. Peak for C-N stretching has shifted from 1096.90 cm^{-1} to 1102.28 cm^{-1}. A shift was also observed in frequency from 1415.47 cm^{-1} to 1407.50 cm^{-1} due to aromatic ring. This shift of frequency suggests that the active principles present in ingredients of toothpaste Colgate Visible White has coordinated with Ni^{2+}, Ti^{3+}through oxygen atom of OH group, C=O group and PO group and nitrogen atom of C-N group and forming a protective film of insoluble complex.

Analysis of UV-Visible absorption Spectroscopy

The UV- visible absorption spectrum is used to confirm the protective film formed on the metal surface. The UV- visible absorption spectrum of AS is shown in Fig (7). Peaks appear at 352 nm, 480 nm and 660 nm. The UV- visible absorption spectrum of toothpaste solution is shown in Fig (8). Peaks appear at 320 nm and 388 nm. The UV- visible absorption spectrum of the solution of AS toothpaste system wherein NiTi shape memory alloy was immersed for one day is shown in Fig (9). Peaks appear at 316 nm and 384 nm. A shift in the position of λ_{max} is observed. This is due to the slight dissolution of Ni Ti shape memory alloy in presence of AS- toothpaste system. During this process the metal ions such as Ti^{3+} and Ni^{2+} would have been released. These ions form complexes with the active principles of the ingredients of the toothpaste in solution.

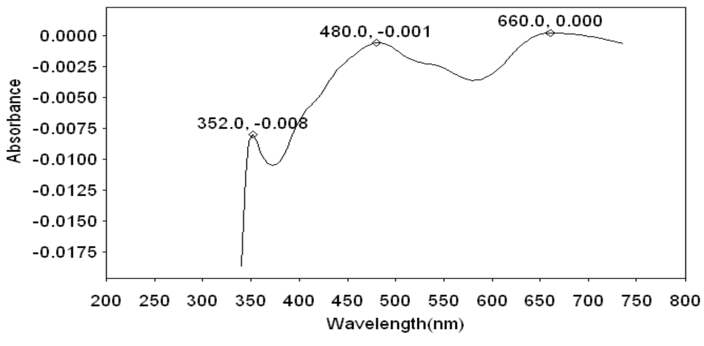

Figure 7. UV-Visible absorption spectrum of AS

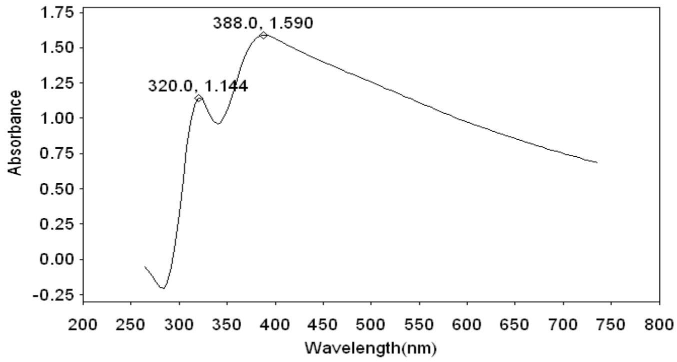

Figure 8. UV-Visible absorption spectrum of solution containing CVWT

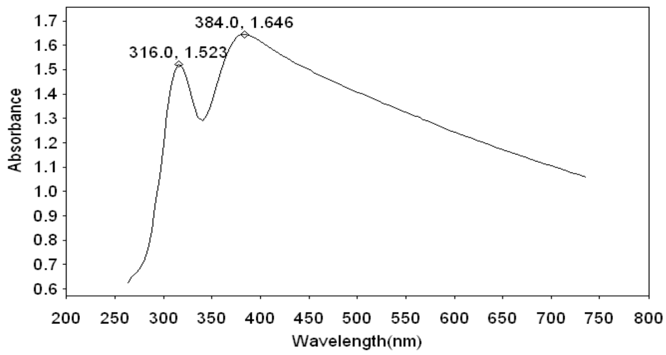

Figure 9. UV-Visible absorption spectrum of solution containing NiTi alloy + AS+ CVWT(1%)

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