
Khaled M. Elsabawy¹,²,* , N. H. Elbagoury²,³

¹Materials Science Unit, Chemistry Department, Faculty of Science, Tanta University, Tanta 31725, Egypt
²Metallurgy Laboratory, Advanced Materials Department, Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87, Helwan, Cairo, Egypt
³Chemistry Department, Faculty of Science, Taif University, 888 Alhawyah, Taif City, Saudi Arabia

*E-mail address: khaledelsabawy@yahoo.com , ksabawy@hotmail.com

ABSTRACT

The synthesized Ni-alloy was prepared via conventional casting technique under vacuum and highly superheated treatment route. The casting parameters such as solidification cooling rate (SCR) was monitoring by both of AFM and SEM. Micro-structural investigations within different spots in the same sample indicated that γ matrix is the domain phase besides minor phases as MC carbides, σ phase and η phase which was observed to solidify in two forms as plate-like and blocky shape. The volume fraction (Vₜ) of σ and η phases was increased as the solidification cooling rate decreases. 3D-microstructural imaging map of the Ni-based super-alloy was constructed depending upon AFM-data evaluating that the morphology of the alloy-surface is a function of casting parameters. Furthermore, raman spectra of highly superheated casted Ni-based super-alloy was performed to confirm existence of different phases recorded via SEM and EDX-elemental analysis with their corresponding different vibrational modes such as Ni-O vibrating modes in the region 360-510 cm⁻¹ and Mo-O vibrating mode which lies at 1005 cm⁻¹.

Keywords: Synthesis; Casting; Raman Spectra; SEM; AFM; 3D-microstructure
1. INTRODUCTION

The Ni-base super-alloy has a great attention of researchers and investigators due to their industrial and manufacturing application as blades of powerful gas turbines (over 125 MW).

These blades work at critical conditions of creep, corrosion, and fatigue for more than 70,000h. Many of additives specially refractory elements like Mo, W, Ta, Cr and Co were added to prevent local hot corrosion [1-3]. In spite of important role of most of Ni base super-alloy in the high temperature performance, limited data on microstructure and material characterization are reported, therefore a complete description of the effect of casting parameters on the Ni base alloys is required [4-7]. Ni base super-alloy is known to have a multiphase microstructure consisting of a solid solution strengthened austenitic nickel γ matrix, bimodal γ’ precipitate, γ / γ’ eutectic, carbides and a small amount of deleterious phases such as: δ, σ, η and laves [8-11]. In some cases, minor phases like η phase and σ phase which usually form at solid state in super-alloys may form at the end of solidification owing to the influence of composition. The η phase has a hexagonal close-packed (hcp) structure and has the basic stoichiometry of Ni$_3$Ti, while σ phase has a tetragonal topologically close-packed (TCP) structure. Both η and σ phases are generally considered as deleterious minor phases by alloy designers as they usually pose negative impact on superalloys’ mechanical properties. Previous studies are focused in analyzing the precipitation mechanism of η and σ phases in solid state in superalloys. η phase may form either during casting or thermo exposure process in nickel based superalloys. Bouse has reported that η phase or platelet phases formed in the as cast microstructure of alloys containing high percentages of Ti, such as IN792 Hf, IN939, GTD111 and IN6203 [12]. Other studies also reported the occurrence of η phase at the periphery of the γ / γ’ eutectics [13-15].

Many researchers through laser raman spectroscopy (LRS) investigations suggest that probability of existing species like oxides, hydroxides, oxy hydroxides, nitrates, nitrides, sulphates, chlorides and oxy chlorides of Fe, Cr and Ni could be present in the passive film and surface layers of synthesized M-based-alloy [16-25]. The contributions of other elements apart from Ti, W, Al, Mo and Co, were not expected to be detected in surface layer, since their content in the alloy was very low to be detectable.

The major goal of the present article firstly is investigating the effect of high superheating treatment and cooling rates on the micro-structural parameters of different phases existed (even those with low content) on the alloy bulk and their vibrational modes detectable thoroughly raman spectroscopic analysis and secondly implementation of LRS raman spectroscopy as qualitative tool to identify different phases which are present in the nickel alloy matrix.

2. EXPERIMENTAL

The Ni-based alloy used in this work was received as turbine blade scrap supplied from a gas turbine power plant. Table 1 shows the chemical composition of as-received alloy. This scrap was double melted and cast under vacuum using an induction vacuum furnace. In the second melt some amounts of alloying elements such as Ti, Co, Ta, W were added to adopt the chemical composition, then a third melting was made to ensure melting and homogenous
distribution of all alloying elements in the heat. Heats were made by melting 10 kg of turbine blade scrap. Pouring was carried out into an investment casting ceramic mold.

The chemical composition of the prepared experimental polycrystalline Ni base superalloy is shown in Table 1. Optical emission apparatus, ARL3560OES as well as Ni base software were used to determine the chemical composition of as-cast alloys.

Table 1. Chemical composition of as cast Ni base superalloys.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ti</th>
<th>Co</th>
<th>Al</th>
<th>Nb</th>
<th>Ta</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Based-Alloy</td>
<td>0.13</td>
<td>15.01</td>
<td>1.97</td>
<td>2.81</td>
<td>3.63</td>
<td>7.67</td>
<td>4.52</td>
<td>1.07</td>
<td>1.27</td>
<td>Bal.</td>
</tr>
<tr>
<td>As cast (H)</td>
<td>0.54</td>
<td>16.95</td>
<td>2.45</td>
<td>4.36</td>
<td>5.88</td>
<td>10.48</td>
<td>1.49</td>
<td>0.10</td>
<td>1.86</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1. The schematic Skelton of the produced castings indicating different solution treatment/solidification conditions.
The microstructure of as-cast specimens was investigated by Zeiss light optical microscope fitted with Hitachi digital camera as well as JOEL JSM-5410 Scanning Electron Microscope (SEM). The specimens for microstructure examination were cut from the cast ingots then ground, polished and etched with 100 ml H₂O + 50 ml HCl + 50 ml H₂SO₄ + 4 g CuSO₄ solution. Studying the microanalysis and segregation for alloying elements was performed using EDS in JEOL JSM5410. Samples were scanned on Analytical Scanning Electron Microscopy for the Jeol JSM-63OLA and VEECO INNOVA -AFM with multimodes function USA. Raman laser of samples were measured on the Bruker FT Raman with laser source 50 mW.

Figure 1 shows the schematic skelton of the produced castings indicating different solidification conditions. There are 2 castings, the first one has high superheat, named coarse casting giving symbol (H), and the other one has low superheat, called fine casting giving symbol (L). Additionally, each one consists of three sections; thin, intermediate and thick referring to fast, medium and slow cooling rates, respectively.

3. RESULTS & DISCUSSION
3.1. SEM/3D-AFM-Microstructure Analysis of Casted-Ni-Alloy

3.1. A. At High Solidification Cooling Rate (HSCR)

Fig. 2a: displays the optical microscope image captured for casted Ni-super-alloy with high solidification cooling rate (HSCR). It was observed that it consists of primary γ, eutectic γ/γ’, MC carbides and minor phases in the interdendritic zones such as σ-phase and η-phase that has plate-like form with Ti-rich content (Ni₃Ti) phase which symbolized by orange squares. These observations of existence of multi-phases are in full agreement with data reported in [9-11].

It can be seen from Fig. 2b the nodular and plate-like of σ, and η-phases that found in interdendritic regions near eutectic γ/γ’. The plate-like phase existed at the eutectic periphery was found to be rich in both Ti and Ni and lower in both Cr and W as detected in EDX analysis results given in Table 3. This plate-like phase is identified as Ti-rich (Ni₃Ti) phase.

The eutectic γ/γ’ colonies found at the interdendritic zones in the as cast microstructure specimen. It is clear that the γ/γ’ eutectic is distributed at dendrite boundaries, often near micro-pores, showing that they are formed during the last stages of solidification. The approximate ratios (area/area ratios) Vf of η-phase that represented in orange squares was found to be in between ~ 12-18 % of captured image area in the case of high solidification cooling rate (HSCR). Furthermore the average grain size of Ni-super-alloy was estimated from Fig. 2b and ranged in between 2.3-5.4 μm which is fully consistent with those reported on literature [4,5]. Fig. 2c: shows high resolution three dimensional AFM-image recorded for Ni-super-alloy surface with HSCR applying tapping mode. For hyperfine 3D-structure of the surface the experimental data supplied from AFM-device was forwarded to visualize the 3D-surface to be able to map the surface with maximum accuracy as possible see Figs. 2d,e.

Fig. 2d: displays 3D-mapping structure for very small area 0.35x0.35 μm of nickel-superalloy. It was noticeable that ~ 50 % of the surface morphology has z-axis (heights) ranged in between (0.26-6.5 μm represented by dark and pale blue) and only ~ 10 % has the heights higher than 6.5 μm. One can indicate that as strengthen phase ratio increases these heights will be increased and consequently increasing of η- phase will lead to corresponding
increase in these heights. This notification is confirmed as clear in Fig. 2e such that the ratio of heights area dark zones to the homogeneous Ni-surface blue coloration is nearly equal to ~10-12% which is identical to the estimated ratio of $\sigma$, and $\eta$-phases as confirmed from SE-micro-structural investigations with EDX-analyses see Table 2.

![Fig. 2(a-c).](image)

(2a) Optical micrograph captured for Ni-alloy with HSCR.
(2b) SE-micrograph showing $\sigma$ and $\eta$-phases and $\gamma'$ eutectic zone at HSCR.
(2c) 3D-AFM tapping mode image of Ni-super-alloy.

EDX analysis was used to investigate the micro-segregation of the as cast specimens as shown in Table 2. The partitioning coefficient, $k'$, was calculated to characterize the degree of micro-segregation between dendrite core and interdendritic areas represented by eutectic $\gamma'/\gamma'$. $k'$ is the ratio between the element composition in dendrite core and the composition of the same element in eutectic $\gamma'/\gamma'$ zone.
Fig. 2d. 3D-AFM-visualized image of Ni-super alloy at HSCR.

Fig. 2e. 2-D-vertical view image to map heights ratio of Ni-alloy.
Table 2. EDX-elemental analysis of the micro-constituents in as cast alloys.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ti</th>
<th>Co</th>
<th>Al</th>
<th>Nb</th>
<th>Ta</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>η in as cast fine</td>
<td></td>
<td>0.19</td>
<td>4.31</td>
<td>0.84</td>
<td>1.17</td>
<td>15.94</td>
<td>7.19</td>
<td>1.53</td>
<td>0.34</td>
<td>3.00</td>
<td>Bal.</td>
</tr>
<tr>
<td>η in as cast coarse</td>
<td></td>
<td>1.89</td>
<td>5.72</td>
<td>1.90</td>
<td>2.37</td>
<td>14.07</td>
<td>8.33</td>
<td>2.08</td>
<td>0.13</td>
<td>6.46</td>
<td>Bal.</td>
</tr>
<tr>
<td>σ in as cast fine</td>
<td></td>
<td>0.31</td>
<td>33.85</td>
<td>9.73</td>
<td>4.68</td>
<td>5.05</td>
<td>11.15</td>
<td>0.70</td>
<td>0.04</td>
<td>1.20</td>
<td>Bal.</td>
</tr>
<tr>
<td>σ in as cast coarse</td>
<td></td>
<td>0.78</td>
<td>36.75</td>
<td>20.37</td>
<td>10.01</td>
<td>2.29</td>
<td>9.68</td>
<td>0.47</td>
<td>--</td>
<td>3.45</td>
<td>Bal.</td>
</tr>
<tr>
<td>MC in as cast fine</td>
<td></td>
<td>6.84</td>
<td>0.35</td>
<td>1.63</td>
<td>7.63</td>
<td>23.35</td>
<td>0.17</td>
<td>--</td>
<td>0.23</td>
<td>56.99</td>
<td>Bal.</td>
</tr>
<tr>
<td>MC in as cast coarse</td>
<td></td>
<td>6.35</td>
<td>1.26</td>
<td>1.93</td>
<td>8.01</td>
<td>20.32</td>
<td>0.63</td>
<td>0.15</td>
<td>0.36</td>
<td>56.71</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2 shows the partition coefficient of important elements in the experimental Ni base superalloys used in this study. There are two groups of alloying elements according to the portioning coefficient. The first group of elements symbolized (G1) has $k'$ higher than one such as W, Mo, Co and Cr. These elements segregate to the dendrite core during solidification.

However, the other group of elements symbolized as (G2) has $k'$ lower than one like Al, Ti and Ta. These elements of this group are preferably segregated to the liquid during solidification process ultimately solidifying in interdendritic zones.

3. 1. B. At Medium Solidification Cooling Rate (MSCR)

Fig. 3a: displays the optical microscope image captured for casted Ni-super-alloy with medium solidification cooling rate (MSCR). The same notifications was also observed such as existing of multi-phases as primary $\gamma$, eutectic $\gamma/\gamma'$, MC carbides and minor phases in the interdendritic zones such as η-phase that has plate-like form with Ti-rich content (Ni$_3$Ti) phase which symbolized by orange squares. The differences between HSCR and MSCR could be summarized in the following points as clear in Fig. 3b that $V_f$ the plate-like form of σ, and η-phases represented by yellow squares increase slightly to record ~ 22-28 % area ratio at expense of eutectic $\gamma/\gamma'$ zones. The increasing in the approximate ratios (area/area ratios) $V_f$ of σ and η-phase that represented in yellow squares was found to be ~ 10 % extra than of that found under HSCR. Furthermore the average grain size of Ni-super-alloy was estimated from Fig. 3b and ranged in between 3.2-6.1 µm which is remarkably higher than with those reported on literature [4,5]. Fig. 3c: displays 3D-mapping structure for very small area 0.35x0.6 µm of nickel-superalloy. It was noticeable that ~ 70 % of the measured surface morphology has z-axis (heights) with the following division (~ 40 % of heights has 1 – 3 µm and the rest 30 % higher than 3 with maximum height 7 µm represented by orange and dark orange color as clear in Fig. 3c. The increasing in the area ratio with heights is due to the previously mentioned increasing of strengthen phases as σ and η-phases plus M-carbides phases.
Fig. 3(a-b).

(3a) Optical micrograph captured for Ni-alloy with MSCR.

(3b) SE-micrograph showing \( \eta \)-phase and \( \gamma/\gamma' \) eutectic zone at MSCR.

Fig. 3(c). 3D-AFM-visualized image of Ni-super alloy at MSCR.
3.1. C. At Low Solidification Cooling Rate (LSCR)

Fig. 4a: displays the optical microscope image captured for casted Ni-super-alloy with low solidification cooling rate (LSCR). The same trend was also observed such as existing of multi-phases as primary $\gamma$, eutectic $\gamma/\gamma'$, MC carbides and minor phases in the interdendritic zones such as $\eta$-phase that has plate-like form with Ti-rich content ($\text{Ni}_3\text{Ti}$) phase which symbolized by orange squares.

The differences between HSCR and LSCR could be formulated in the following points as clear in Fig. 4b that area ratio ($V_f$) the plate-like form of $\sigma$, and $\eta$-phases represented by yellow squares increase slightly to record maximum $\sim 43\%$ area ratio at expense of others phases zones.

The increasing in the approximate ratios (area/area ratios) $V_f$ of $\sigma$ and $\eta$-phase that represented in yellow squares was found to be $\sim 33.6\%$ extra than of that found under HSCR. Furthermore the average grain size of Ni-super-alloy was estimated from Fig.4b, and ranged in between 0.5-5.2 $\mu$m which is remarkably variated according to the casting parameters specially cooling rates.

Fig. 4c: shows 3D-mapping structure for small area 0.6x0.6 $\mu$m of nickel-superalloy. It was noticeable that $\sim 100\%$ of the measured surface morphology has z-axis (heights) with the following features ($\sim 26\%$ of heights has 0.1-1.9 $\mu$m, 28% from 1.9-3.56 $\mu$m, 19% from 3.56 to 4.37 $\mu$m and the rest 27% higher than 4.37 with maximum height 6 $\mu$m respectively as clear in Fig. 4d, and as a result the increasing in the $V_f$ with heights is due to increasing of strengthen phases as $\sigma$ and $\eta$-phases plus M-carbides phases which are maximum with low solidification cooling rate (LSCR).

Fig. 4a. Optical micrograph captured for Ni-alloy with LSCR.
Fig. 4b. SE-micrograph showing $\eta$-phase and $\gamma/\gamma'$ eutectic zone at LSCR.
Fig. 4c. 3D-AFM-visualized image of Ni-super alloy at LSCR.

Fig. 4d. 2-D-vertical view image to map heights ratio of Ni-super-alloy.
In all Figs. 2b, 3b and 4b that show SE-micrograph there are two types of carbides; the MC blocky type carbides which are located inside the γ matrix as well as at the grain boundaries. The MC agglomerated carbides mainly consist of (Ta, Ti) C in addition to lower percentages of Nb and W as presented in Table 3. The other type of carbides is the fine M23C6 carbides as with Cr in which Cr(III) is the basic element (Cr23C6), which can be observed only at the grain boundaries, as indicated in Table 3.

### Table 3. Partition coefficient of major elements in cast Ni base superalloys.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Ta</th>
<th>W</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>k' in as cast G1</td>
<td>0.95</td>
<td>0.50</td>
<td>1.24</td>
<td>1.21</td>
<td>1.16</td>
<td>0.52</td>
<td>1.65</td>
<td>1.013</td>
</tr>
<tr>
<td>k' in as cast G2</td>
<td>0.81</td>
<td>0.53</td>
<td>1.09</td>
<td>1.15</td>
<td>1.26</td>
<td>0.57</td>
<td>1.78</td>
<td>0.997</td>
</tr>
</tbody>
</table>

### 3. 2. Laser Raman Spectroscopy

Fig. 5a shows the laser raman spectra recorded for non-smoothed casted Ni-alloy inside the range 300-550 cm\(^{-1}\) to identify different vibrational modes of nickel as major constituent of Ni-alloy. It was observed that the most common vibrating modes of Ni-O lie at 364, 400 and 510 cm\(^{-1}\) by additional to vibrating mode appears at 476 cm\(^{-1}\) which is revealed to Ni3O4-phase. These results are in full agreement with those reported by [18]. Furthermore there are some extra bands appear in Fig. 4a like those lie at 309, 379, 446, 461 and 519 cm\(^{-1}\) which are assigned as α- or β-Ni-OH vibrating modes as reported in [26].

To identify some of minor phases constituent in the interfacial layers of Ni-base superalloy another scanning of raman spectra was constructed in the range in between 800-1200 cm\(^{-1}\) as clear in Fig. 5b. It was obviously that there are multi-mixed vibrational modes assigned as the following sequence,

(i) blue circles assignment which lie at 819, 858, 875, 940 and 952 cm\(^{-1}\) are attributable to CrIII-CrVI-O vibrational modes.
(ii) vibrational mode lies at 451,701 and 920 cm\(^{-1}\) is corresponding to Ti-O mode as confirmed by Ramya et al. [26].
(iii) vibrational mode lie at 667,716,751,765 and 935 cm\(^{-1}\) is corresponding to W-O modes.
(iv) vibrational mode lies at 1005 cm\(^{-1}\) is corresponding to Mo-O vibrating mode and finally (v) vibrational mode lie at 364, 499, 510, 1085 cm\(^{-1}\) which are belonging to Ni-O modes.

These results are consistent with those reported by [18-21] who investigated nickel-stainless alloy namely 316LN SS alloy by laser raman spectroscopy and they characterized different vibrating modes existed in the corroded interfacial surface of Ni-alloy.

The present results can be understood on the basis that Ni-based alloy could be passivated and form some metal-oxides according to the composition of the interfacial layers which means that Ni-based-alloy vibrating modes are preparative conditions dependent.
Fig. 5a. Raman spectra recorded for casted–non-smoothed Ni-superalloy showing different vibrational modes of Ni-O moiety.

Fig. 5b. Raman spectra recorded for casted–non-smoothed Ni-superalloy showing different vibrational modes of Cr-O, Ti-O and Mo-O moieties.
Fig. 5c. Raman spectra recorded for casted –non-smoothed Ni-superalloy showing different vibrational modes of W-O moiety.

In the case of compounds of chromium on the passivated surface of Ni-alloy, they will exist as Cr(III) or Cr(VI). The moderate intensity peak at 860 cm\(^{-1}\) was attributed to Cr(III) and Cr(VI) mixed phase [27-32], which was slightly red shifted by a few wave numbers (around 871-885 cm\(^{-1}\)). Also, a weak peak around 520-570 cm\(^{-1}\) was due to Cr\(_2\)O\(_3\) [29], which was diminished and overlapped with the frequencies of nickel oxides, thus indicating the possibility of existing in the form of NiCr\(_2\)O\(_4\).

Apart from the presence of chromium and Titanium oxides, one could expect contributions of Ni as NiO at the surface layer. The reported value for the heat of formation of NiO was found to be equal \(-243.19\) kJ mol\(^{-1}\) [33]. Cr\(_2\)O\(_3\) has more negative heat of formation, i.e., \(-1058.58\) kJ mol\(^{-1}\). Hence, Cr would preferentially get oxidized and nickel was expected to be segregated at the oxide interface [34].

Garke et al. [35] showed that there was only a small amount of nickel in the oxide/metal interface, where there was no change in the nickel concentration and the nickel was in elemental state in the segregated zone. Since LRS cannot trace out individual elements [36], the presence of elemental Ni could not be detected. Even if all the Ti, W and Cr get oxidized, paving way to nickel oxidation, still it was difficult to sense the presence of traces of elemental-nickel due to the limited sensitivity of LRS. Fig. 5c shows the raman spectra recorded in specific range 660-780 cm\(^{-1}\) to identify the vibrational modes of W-O.
**Fig. 6a.** Raman spectra recorded for casted–smoothed Ni-superalloy showing diminishing of most common vibrational modes.

**Fig. 6b.** Raman spectra recorded for casted–smoothed Ni-superalloy in specific range of measurements 2000-2300 cm\(^{-1}\) showing hydroxylated metals vibration modes.
As clear in Fig. 4c there are bands lie at 668, 713, 745 and 772 cm$^{-1}$ by additional to that appears in Fig. 4b at 935 cm$^{-1}$ these bands were observed also with Frost at al. with some wavenumbers shift [37] who reported that W-O vibrating modes includes $v_1$ symmetric stretching mode of the W-O units at around 926 cm$^{-1}$. And two bands at 765 and 751 cm$^{-1}$. These bands are thought to be associated with the antisymmetric and symmetric A$_g$ modes, respectively, of the WO$_2$. Multiple low intensity bands are observed in the 740-780 cm$^{-1}$ region. The bands observed at 767 and 747 cm$^{-1}$ are assigned to be $v_3(B_g)$ and $v_3(E_g)$ modes.

Fig. 6a,b show the raman spectra recorded for smoothed Ni-alloy sample. It was noticeable that most of common raman vibration modes throughout the whole range were diminished as clear in Fig.6a only few vibration modes appeared in the range (2000-2300 cm$^{-1}$) as showed in Fig. 6b these bands did not previously published in literature and in our speculations it could be attributable to hydroxylated metal oxide while metal could be Ni, W, Ta, Al or Ti according to the chemical constitution of Ni-alloy.

4. CONCLUSIONS

The conclusive remarks inside this article could be briefed in the following points:

1- The casting parameters such as solidification cooling rate (SCR) has very important role in microstructure features such that as the volume fraction ($V_f$) of $\sigma$ and $\eta$ phases increased as the solidification cooling rate decreases and vice versa.

2- Volume fraction ($V_f$) of the plate-like form of $\sigma$, and $\eta$-phases are recording maximum $\sim$ 43 % area ratio at expense of others phases zones at LSCR.

3- SE-microscopy proved that Metal carbide (MC) blocky type carbides are located inside the $\gamma$ matrix as well as at the grain boundaries.

4- Laser Raman spectroscopy (LRS) could be used as qualitative technique to identify different phases constituents that present in the interfacial layer of the Ni-alloy surface since

a- Ni-O vibrational modes lie at 364, 499, 510, 1085 cm$^{-1}$.

b- vibrational mode lies at 1005 cm$^{-1}$ is corresponding to Mo-O vibrating mode.

c- vibrational modes lie at 451,701 and 920 cm$^{-1}$ are corresponding to Ti-O modes.

d- vibrational mode lies at 819, 858, 875, 940 and 952 cm$^{-1}$ are attributable to CrIII-CrVI-O vibrational modes.

e- vibrational mode lie at 667, 716, 751, 765 and 935 cm$^{-1}$ is corresponding to W-O modes.

References


(Received 14 December 2015; accepted 28 December 2015)