3D-AFM Mapping Surface Investigations and Micro-Structural Surface Features of Some Inorganic Materials

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The present investigations introduce new trend of applying AFM-microscopy together with SE-microscopy to visualize real complete characterized three and two dimensional images for samples surface’s under investigations. Nickel superalloy and (Ni, Mn) Single metal of cyclotetraphosphates were selected to be target for these investigations due to their importance as surfaces in industrial applications and ceramics. Furthermore optimizing of synthesis conditions specially sintering temperatures in which monoclinic crystal is formed with high degree of stabilization. Microstructural features of the surface were also investigated via both of SE-microscopy and X-ray diffraction.

Keywords: Ni-superalloy, Inorganic-cyclophosphate; 3D-AFM-mapping; Surface; Microstructure; SEM; XRD

1. Introduction

Inorganic metals cyclophosphates have great attentions at micro- or nanoscale levels because of their strong varieties on the chemical and physical properties of materials. The topology and morphology of these metals cyclophosphates qualify it to play an important roles in optical, catalytic reactions specially if it synthesized in the micro-/nanoscalemetal phosphates, [1-4].

Transition metals cyclotetraphosphates have great attentions in last decade due to its huge applications in micro-/nanoparticles as potential pigments, selective catalysts, phosphors, materials for corrosion-resistant coatings and biocompatible matters applied in tissue of human or animals [5–10]. Several divalent including 3d metals, namely, Mn, Co, Fe,Zn, Cu, and Ni, are known to form the single metal cyclotetraphosphate M₂P₄O₁₂, where M(II) stands for a divalent metal. The binary metal cyclotetraphosphates M₂−xAxP₄O₁₂ (M and A=Mg, Ca, Mn, Co, Ni, Zn, or Cu; x=0–2), isostructural with the single metal cyclotetraphosphates M₂P₄O₁₂, were prepared by [6–11]. All these compounds have very similar x-ray diffraction patterns and close unit cell parameters, which crystallize in monoclinic space group C12/c1 (Z=4) [12]. Various methods have been employed to synthesize binary metal cyclotetraphosphates, including two-step thermal method [5–8], hydrothermal synthesis [5] and the decomposition of binary metal (II) dihydrogenphosphates [9–11].

Many researchers [13-20] have investigated different physical properties of metalized cyclotetraphosphates such as luminescence, thermal decomposition and kinetics rates of thermal decompositions. Furthermore effect of synthesis condition on the particle size [15]. Nickel-based superalloy possess excellent corrosion and oxidation resistance in addition to high strength and ductility at high temperature, ranging from 873 to 1673 K.

The major goal of the present investigations is applying both 3D-AFM and SEM together to draw complete characterized micro-image with complete microanalysis features for the surface’s of Ni-superalloy, metals cyclotetraphosphates samples under investigations.

2. Experimental

2.1. Synthesis of Metal-cyclotetraphosphate:
The single nickel and manganese cyclotetraphosphate were synthesized via three step reactions as shown in equations 1,2 and 3 respectively. These steps of synthesis procedures are in partial agreement with data reported in references [5,6,10].

\[ M^{II}CO_3 + \text{few drops of HNO}_3 \rightarrow M(NO_3)_2 \] \hspace{1cm} (1)

\[ M(NO_3)_2 + 2H_3PO_4 \xrightarrow{\Delta 220^\circ C} M(H_2PO_4)_2 + H_2O + NO_2 \] \hspace{1cm} (2)

\[ M(H_2PO_4)_2 \xrightarrow{\Delta 1100^\circ C} M_2P_4O_{12} \] \hspace{1cm} (3)

The powders of pure (Ni, Mn ) cyclotetraphosphate were ground in agate mortar for 25 min., then the resulted powders forwarded to perform the different structural measurements starting with x-ray diffraction analysis. The details of synthesis and thermal analysis studies were discussed in references [5,6,7,10].
2.2. Nickel Superalloy Sample:

The Ni-based alloy used in this work was received as turbine blade scrap supplied from a gas turbine power plant. 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.

2.3. Structural measurements:

The X-ray diffraction (XRD): Measurements were carried out at room temperature on the fine ground samples using Cu-Kα radiation source, Ni-filter and a computerized STOE diffractometer/Germany with two theta step scan technique. Rietveld and indexing of structure were made via Fullprof package and Gesas program.

Scanning electron microscopy (SEM): measurements were carried out along ab-plane using a small pieces of the prepared samples by using a computerized SEM camera with elemental analyzer unit Shimadzu (Japan). Atomic force microscopy (AFM): High-resolution Atomic Force microscopy (AFM) is used for testing morphological features and topological map (Veeco-di Innova Model-2009-AFM-USA). The applied mode was tapping non-contacting mode. For accurate mapping of the surface topology AFM-raw data were forwarded to the Origin-Lab version 9 -USA program to visualize more accurate three and two dimension surface of the sample under investigation. This process is new trend to get high resolution 3D-mapped surface for very small area reach to (0.01 μm²).

3. Results and discussion

3.1. Structural Identification:

Figs.1a–d, 2a–c show different x-ray diffraction patterns of both of nickel and manganese cyclotetraphosphate synthesized and treated at different elevated sintering temperatures (600, 800 and 1100°C) respectively.

The accurate analyses of these patterns were performed by using rietveld and indexing via both of Fullprof package and Gesas program. The analyses are focused on the main intense reflection peaks (Fingerprint of structure) and indicated that metalized M₂ cyclotetraphosphate (where M= Ni ,Mn) are mainly belong to single monoclinic phase with C12/c1 space group as indexed and symbolized by pink cycles in Fig.1a–d and blue squares in Fig.2a–c. Only very few percentage of unreacted metal oxides are detected as secondary phase in minor. It was observed that the impurity phases are decreasing as sintering temperatures are increasing as shown in Fig.1, Fig.2. The comparisons of most intense reflections peaks in all patterns (fingerprint reflections represent monoclinic –phase) indicated that both patterns of Ni and Mn - cyclotetraphosphate which are sintered at 1100°C is the best fitted one achieving high degree purity than others which sintered at temperatures 600, 800 and (1000°C in case of Ni only) respectively.

In the hypothesis of iso-structural, due to existence of Ni(II) and Mn (III) the spectrum peaks (X-ray profile ) for the system of Ni and Mn- cyclotetraphosphate (solid solution) which is including single metal within the lattice of
cyclotetraphosphate (M₂P₄O₁₂, M= Ni , Mn ) are quite similar because of the equivalent electronic charges and the close radii of cations (Ni²⁺=0.69 and Mn³⁺=0.46Å). Consequently, all of characteristic diffraction peaks in the Fig.1 and Fig.2 are nearly typical and found to be in agreement with monoclinic M₂P₄O₁₂ and space group C12/c 1 without violation. Only few characteristic peaks of other impurities (e.g. Ni, Mn- Oxides) were clearly observed at lower sintering temperatures (600, 800°C).

From XRD analysis (Figs. 1, 2), grain size evaluated and calculated twice according to the Scherrer’s formula: 

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where D is particle diameter, K= 0.89 (the Scherrer’s constant), \( \lambda \) =1.5406 (wavelength of the X-ray used), \( \beta \) is the width of line at the half-maximum intensity and \( \theta \) is the corresponding angle. The average crystallite size of product is estimated from the strongest three diffraction peaks below 40° for 2\( \theta \) and found to be 87 and 96 ±11nm for Ni and Mn- cyclotetraphosphate respectively.

This crystallite size of the prepared Ni- and Mn- cyclotetraphosphate is smaller than those data estimated from SEM and AFM-investigations in the present which confirm that the powder mixture of Ni- and Mn- cyclotetraphosphate are not possess unified grain sizes and grain sizes are fractionated in the bulk than surface’s layers. The lattice parameters of the prepared Ni- and Mn- cyclotetraphosphate were calculated from the XRD spectra and found to be \( a =11.8321 \), 11.7909(2), \( b = 8.3121 \),8.2753(1), \( c = 9.8893 \),9.823(2) Å respectively, which are very close to those of the standard data file (ICSD #300027) and the literatures [5,6,8,9,10 and 14]. These results support and confirm that the grain size is not unified in size within the materials bulk and it is in most probably contains different gradient of sizes.

3.2. Atomic Force Microscopic Investigations:

3.2.1. AFM investigations for Ni- cyclotetraphosphate (Ni₂P₄O₁₂):

Fig.3a displays 3D-AFM-micrograph tapping mode image captured for scanned area 0.5 \( \mu \)m\(^2\) of Ni- cyclotetraphosphate (Ni₂P₄O₁₂). The image was constructed by application tapping mode with slow scan rate and high resolution imaging with 1024 line per 0.25 nm .The tapping amplitude current was monitored as a function of line drawing heights. For more accurate surface analysis AFM-raw data was forwarded to Origin Lab program version 9 and the data are converted into matrix then 3D-contour surface mapping is constructed as shown in Fig.3a.

Fig.3b shows 3D-visualized-contour plot of AFM-micrograph captured for scanned area 0.5x0.5 \( \mu \)m\(^2\) of surface imaging captured for scanned area 0.5x0.5 \( \mu \)m\(^2\) of Ni-cyclotetraphosphate (Ni₂P₄O₁₂).

Fig.3a: 3D-AFM-micrograph tapping mode

Fig.3b: 3D-visualized-contour plot of AFM-micrograph captured for scanned area 0.5x0.5 \( \mu \)m\(^2\) of surface imaging captured for scanned area 0.5x0.5 \( \mu \)m\(^2\) of Ni-cyclotetraphosphate (Ni₂P₄O₁₂).
The second zone represents ~ [dark green zone (12%) + pale green zone (11%)] which represents ~ 23 % (0.0575 μm²) from the whole scanned area with heights gradient ranged in between 4.225 - 4.30 μm. The 3rd zone occupies ~ 53% = 0.1325 μm² from the whole scanned area with heights gradient lies in between 4.0 - 4.22 μm. This gradient in the blue color is ordered according to the following dark blue (8% = 0.02 μm²) , pale blue represents (12% = 0.03 μm²) and the rest is represented by cyan zone color ~33% of the scanned area = 0.0825 μm². Fig.3d displays AFM- deflection points centers existed in scanned area 0.5x0.5 μm² of nickel cyclotetraphosphate. As clear in Fig.3d these deflections centers dispersed regularly throughout the whole scanned area as hemi spiral -shape. These deflections dots centers can be connected together to contour the deflection plans within scanned area 0.25 μm².

The average particle size was estimated for Ni-cyclotetraphosphate from AFM-analysis and found in between 72-91 nm which is nearly matched with that calculated from XRD through applying Scherrer’s formula ~ (87 nm). The differences in the values of average grain sizes calculated via SEM, AFM and Scherrer’s formula are good evidence for existence gradient in the grain sizes in the bulk which are completely different than those on the surface layers.

Fig.4 displays gray scale of AFM-tapping mode image recorded for Ni-cyclotetraphosphate showing the surface profile topology for cartesian coordinates of yellow line. The gray scale was built up via origin lab program version 9 depending on the input data raw file exported from AFM-instrument. As clear in Fig.4 the topology of the surface through the cartesian coordinates of line (yellow line) resembles stairs like structure but the heights of each step is differ than next step as clear in the Fig.4. The horizontal view of the surface topology of Ni-cyclotetraphosphates indicated that the surface is not smoothed and has a lot of different morphological heights with minimum height ~ 4.09 μm and maximum height ~ 4.455 μm. By the same vertical sector was analyzed and indicated that the minimum height ~ 4.2 μm and maximum height ~ 4.52 μm.
This topology of Ni-cyclotetraphosphate increase the suitability and validity of these materials as coating colorant materials with high performance due to its large surface area.

3.2.2. AFM investigations for Mn-cyclotetraphosphate (Mn₂P₄O₁₂):

Fig.5a displays 3D-AFM-micrograph tapping mode image captured for scanned area 0.04 μm² of Mn-cyclotetraphosphate (Mn₂P₄O₁₂). The image was constructed by application tapping mode with slow scan rate and high resolution imaging with 1024 line per 0.20 μm. The tapping amplitude current was monitored as a function of line drawing heights. The gradient of red coloration in Fig.5a indicates that the surface not smoothed and has a lot of roughness heights gradient.

Fig.5b shows 3D-visualized-contour plot of AFM(660,261),(902,726) micrograph surface imaging captured for scanned area 0.2x0.2 μm² of Mn-cyclotetraphosphate (Mn₂P₄O₁₂), the tapping current amplitude was adjusted at minimum rate of frequency scan to raise image resolution.

To increase the accuracy of analysis of this image the data were forwarded to plot Fig.5c which is 2D-visualized-contour plot for the same image of Mn- cyclotetraphosphate (Mn₂P₄O₁₂).

The analysis of the surface morphology enhance us to understand application of these materials metalized cyclotetraphosphate (M₁P₄O₁₂) as colorant materials in coating and ceramic industry. The minimum height observed in the scanned surface was ~ 4.46 μm and maximum was 4.64 μm for red zone as shown in key of the Fig.5b. To be able to calculate ratios of each heights gradient Fig.5a was constructed. As clear it shows 2D- AFM-captured image applying tapping mode which can be divided into three zones 1st zone include (yellow, orange and red color) this zone represents ~ 16% (0.0064 μm²) of the whole scanned area which is equal ~ 0.04 μm², the surface heights in this zone ranged in between 4.57-4.64 μm as clear in the key-image. The maximum height in the whole image is red zone which represents 1% = 0.0004 μm² which have the highest height in the scanned area with height max. = 4.64 μm, the second partition is orange color with ratio ~ 5% of the whole area = 0.002 μm² and the third part is yellow coloration zone with area percent ~ 0.004 μm² which represents (10%) with heights ranged in between 4.57-4.59 μm.
The second zone represents ~ [dark green zone (12%) + pale green zone (11%)] which represents ~ 23 % (0.0092 \mu m^2) from the whole scanned area with heights gradient ranged in between 4.52 - 4.57 \mu m. The 3rd zone occupies ~ 51% = 0.0204 \mu m^2 from the whole scanned area with heights gradient lies in between 4.48 -4.52 \mu m. This gradient in the blue color is ordered according to the following dark blue (6% = 0.0024 \mu m^2), pale blue zone represents (21% = 0.0084 \mu m^2) and the rest is represented by cyan zone color ~23% of the scanned area = 0.0092 \mu m^2. Fig.5d displays AFM- deflection points centers exist in scanned area 0.1x0.1\mu m^2 of Mn- cyclotetraphosphates. As clear in Fig.5a these deflections centers dispersed regularly throughout the whole scanned area as hemi spiral -shape. These deflections dots centers can be connected together to contour the deflection plans within scanned area 0.04 \mu m^2. These notifications on the deflections plans could be informative if the investigated materials have optical applications as different kinds of metalized phosphates glasses [21-23].

The average particle size was estimated for Mn-cyclotetraphosphate from AFM-analysis and found in between 88-112 ±9 nm which is nearly matched with that calculated from XRD through applying Scherrer’s formula ~ (96 ±11). The differences in the values of average grain sizes calculated via SEM, AFM and Scherrer’s formula are good evidence for existence of gradient in the grain sizes in the bulk which are completely different than those on the surface layers.

Fig.6 displays gray scale of AFM-tapping mode image recorded for Mn-cyclotetraphosphate showing the surface profile topology for cartesian coordinates of yellow line. The gray scale was built up via origin lab program version 9 depending on the input data raw file exported from AFM-instrument. As clear in Fig.6 the topology of the surface through the coordinates of yellow lines resembles stairs like structure but the heights of each step is differ than next step as clear in the Fig.6.
The analysis of the horizontal sector of the surface topology of Mn-cyclotetraphosphates indicated that the surface is not smoothed and roughness has a lot of different morphological heights with minimum height \( \sim 1.75 \mu m \) and maximum height \( \sim 1.9 \mu m \). By the same vertical sector was analyzed and indicated that the surface morphology has minimum height \( \sim 1.755 \mu m \) and maximum height was found to be \( \sim 1.98 \mu m \).

This topology of Mn-cyclotetraphosphate recommends using of these materials as coating colorant materials with high performance due to its large surface area as detected in AFM-investigations.

3.3. SEM investigations for Metalized- cyclotetraphosphate:

Fig.7a-f shows the different micrographs recorded for metalized cyclotetraphosphates with general formula \( M_2P_4O_{12} \), where \( M=\text{Ni and Mn} \) respectively which synthesized at sintering temperature = 1100°C with different magnification factors. The average grain sizes were estimated and found to be 2.14\( \mu m \) and 3.5\( \mu m \) for Ni- and Mn-cyclotetraphosphates respectively. These values are bigger than those reported in literatures [9, 16]. The raising in average of grain size is attributable to the precipitation or co-precipitation techniques used in synthesis could yield to higher grain sizes since crystal growth is time factor dependent. Accordingly the raising in average of grains for both Ni- and Mn-cyclotetraphosphates is due to two factors 1\( ^{st} \) is synthesis procedures specially step 2 in which metalized dihydrogenphosphates is formed and 2\( ^{nd} \) is the digestion time of the precipitated Ni- and Mn- dihydrogenphosphates which control in the nucleation of aggregative particle sizes.

Fig.7a-f: SE-micrographs captured for Ni-and Mn-cyclotetraphosphates synthesized at 1100°C respectively.
3.4. AFM-Investigations of Ni-superalloy surface:

Fig.8a, b: displays 2 and 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) [24, 25] and only ~ 10% has the heights higher than 6.5 µm. From these results, one can indicate that as strengthen phase ratio (ɳ-phase) increases these heights will be increased.

These notifications are clear in Fig.8a since the ratio of heights area dark zones (roughness zones) to the homogeneous Ni-surface blue coloration is nearly equal to ~ 10-12%.

4. Conclusions

The present 3D-AFM and SEM investigations succeeded to draw complete characterized micro-image with complete microanalysis features for the surface’s of Ni-alloy and metals cyclotetraphosphates under investigations. This process introduced new trend of AFM-microscopy to get high resolution 3D-mapped surface for very small area reach to (0.01 µm²).

References