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CHARACTERIZATION OF IMPURITIES IN 304 STAINLESS STEEL CABLES USED IN THE ASSEMBLY OF MEDICAL DEVICES

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RESUMEN

Esta investigación muestra el estudio realizado sobre partículas presentes en cables de acero inoxidable 304 utilizados en el ensamblaje de dispositivos médicos. El estudio se realizó para desarrollar una caracterización superficial, química y térmica, que permita conocer la naturaleza de las impurezas. Se utilizó un análisis complementario utilizando diferentes técnicas como microscopía electrónica de barrido (SEM), espectroscopía dispersiva de energía (EDS), análisis termogravimétrico (TGA), calorimetría diferencial de barrido (DSC) y difracción de rayos X (XRD), para caracterizar las partículas, y concluir sobre su origen y su posible tratamiento. Los mejores resultados para el análisis se obtuvieron a partir de las imágenes generadas en el SEM, ya que, la naturaleza de la impureza resultó ser de carácter superficial, por lo que se pudo recomendar, como método de limpieza, el uso de solventes orgánicos.

ABSTRACT

This research shows a study of particles present in 304 stainless steel used in the assembly of medical devices. The study was performed in order to develop a superficial, chemical and thermal characterization, which allows to know the nature of the impurities. A complementary analysis using different techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction Analysis (XRD) was used to characterize the particles, and to conclude on their origin and possible treatment. The best results for the analysis were obtained from the images generated in the SEM, since the nature of the impurity was superficial, so it was possible to recommend as a cleaning method the use of organic solvents.

Palabras Clave:

Dispositivos médicos, impurezas, caracterización, espectroscopía EDX, termogravimetría, calorimetría, microscopía, difracción de rayos-X.

Keywords:

Medical devices, impurities characterization, EDX spectroscopy, thermogravimetry, calorimetry, microscopy, X-ray diffraction.

Introduction

The stranded wire tube is a component used for assembly of guidewires subsequently applied to manufacturing of some medical devices. Their assembly process is complex because it involves a wire drawing process and during this procedure, the chance of adding organic contaminants is quite high [1]

Due to the use of this material in the assembly of medical devices, it is extremely important that these components present low traces of any contaminants. Today there are a wide variety of characterization techniques that allow to gather information about a material. By scanning electron microscopy (SEM) it is possible to obtain information about the material structure and composition. It is also a good technique for analyzing a sample in terms of its topography doe to its large depth of field, which allows one to keep in focus much of the sample [2]. In the atomic interactions with the electron beam, some atoms of the sample are ionized, but this is an unstable energy state, so that the energy must be released as characteristic X-rays, with a determined wavelength for each element, which are collected in Energy Dispersive Spectroscopy (EDS).

Thermogravimetric analysis (TGA), provides a quantitative technique to determine the weight change of a material with temperature under heating. In dynamic processes, the weight change with respect to time (DTG) also provides valuable data for evaluating degradation [3]. In thermal degradation, it is logical to assume that the rate of decomposition is directly proportional to the amount of material present on the sample. Differential scanning calorimetry analysis (DSC), can show processes where an enthalpy variation occurs. This is appropriate to determine some physical characteristics in any material, for example determination of specific heats, boiling and melting points, purity in crystalline compounds and reaction enthalpies [4].

Chemical analysis by X-ray diffraction (XRD) is based on the fact that a crystalline substance always produces a characteristic diffraction pattern, a phenomenon that consists of the dispersion of X-rays by electron clouds surrounding crystal atoms, following a pattern that depends on the type of atom, the crystal structure and the wavelength of the X-rays. The observed pattern is the result of constructive and destructive interference of radiation scattered by all atoms [5].

The XRD technique is one of the most important in characterizing crystalline materials such as metals. This technique can be used to identify the phases present in the sample, as well as providing accurate information on the structure of materials. The quality of the diffraction pattern is usually limited by the nature and energy of radiation available for the resolution of the instrument and the physical and chemical conditions of the sample. Since many materials can be prepared only in a polycrystalline form, XRD becomes the only realistic option for a determination of the crystal structure of materials, and for this reason is that it offers an excellent platform to measure and identify complex phase mixtures that it can compare with a database.

In this technique, the most important phenomenon is that described by the Bragg Law, which indicates that if the wavelength of the X-rays is known and the diffraction angle (Theta) is measured, it is possible to determine the spacing of different atomic planes, and from them the crystalline structure for the diffracting material [5].

For the characterization analysis, the first step was a topographic visualization using the SEM to define the metallic surface and analyze if the impurity was part of the metallic structure, or otherwise a surface particle. Then, thermal analysis was carried out to show behavior differences between the metal and particles. The EDS and XRD analyses were used for the chemical and structural characterization of the unknown particles.

For this purpose, metallic cable samples were used, these samples presented problems during their incoming inspection and during their manufacturing process. This situation is of concern, because this material is used for medical device assembly. The purpose of this research was to use the various techniques described above to characterize the impurities present in the metallic cable, and determine whether this contamination is organic or of another nature.

Materials and Methods:

For the determination of the nature of the impurity particles, the following characterization techniques were performed:

Scanning Electron Microscopy

Tabletop Hitachi TM-3000 and TM-1000 microscopes (Institutional Microscopy Laboratory, Costa Rica Institute of Technology) were used. The latter was coupled with an Energy Dispersive Spectroscopy (EDS) system. Images from the surface of samples were obtained at magnifications from 80X to 500X. For this purpose, an acceleration voltage of 15 KV was used. Samples with clean and dirty sections of the cable were analyzed by EDS, generating a chemical species spectrum.

Thermal Analysis

For the thermogravimetric analysis, a TA Q500 (National Nanotechnology Laboratory LANOTEC-CeNAT) instrument was used. A sample of the metallic cable of 15 mg was weighed in an alumina crucible for the analysis.

For differential scanning calorimetry (DSC) analysis a TA Q200 (National Nanotechnology Laboratory LANOTEC-CeNAT) was used. The measured mass of sample was ~30 mg on an aluminum pan. It was processed using a flow of Nitrogen gas of 50 mL/min and a temperature ramp of 20 °C/min from -89.98 °C to 396.98 °C.

X-Ray Diffraction Analysis

For the XRD technique, the sample was prepared by grinding so that multiple planes of the metallic structure are present in different angles when mounted on the holder, as shown in Figure 1.

Figure 1. Sample placement on the silicon sample holder for the x-ray diffractometer.

The XRD was carried out in a Panalytical Empyrean powder diffractometer (School of Materials Science and Engineering, Costa Rica Institute of Technology). The parameters for analysis are shown in Table 1. The obtained spectrum was compared with the crystal structure databases in order to know the chemical nature of the sample and analyze its structure.

Table 1. *Parameter for X-Ray analysis*

Parameter	Value
Initial Position	5.0117 [°2Th.]
Ending Position	69.9857 [°2Th.]
Step size	0.0130 [°2Th.]
Scanning Time	3.5700 s
Generator setting	40mA, 45 KV
Scan Type	Continuous
Specimen Length	10.00mm
Measurement temperature	25 °C
Anode material	Cu

Results

Scanning Electron Microscopy

In the SEM analysis, the sample was observed at lower magnifications for a general visualization of the cable, then the image was magnified near to the sample surface and this allowed a detailed analysis of the sample topography. Besides it could be seen that the impurities show an irregular surface, as shown in Figures 2 a, b and c.

Figure 2a shows the cable has a high density of particles in dark contrast, and most of them are not visible to the human eye. The wire contains a lot of particles with different sizes and shapes and only the bigger ones are visible without a SEM. The particles become visible when they accumulate in the space between the wires of the coil.

Figure 2b shows a higher magnification view and allows to visualize that the particles are not part of the cable, and are rather external to the metal of the wire. The image also allows to determine that the size of impurity particles is not larger than 500 mm in length, most of them are in the order of 100 mm or less and it is observed that the impurity has not a regular form. Figure 2c shows a high magnification image of one such particles with a size of approx. 200 mm. Moreover, it confirms that the particle is of irregular shape.

Energy Dispersive Spectroscopy Analysis

The EDS analysis allows to make a scan on the sample, to determine the chemical elements presents in the material, this procedure can be performed during the SEM analysis, and generates a quasi-quantitative criteria about the composition differences between the samples. Figure 3 shows a comparison of the chemical composition of samples with and without impurities, in order to know their chemical nature.

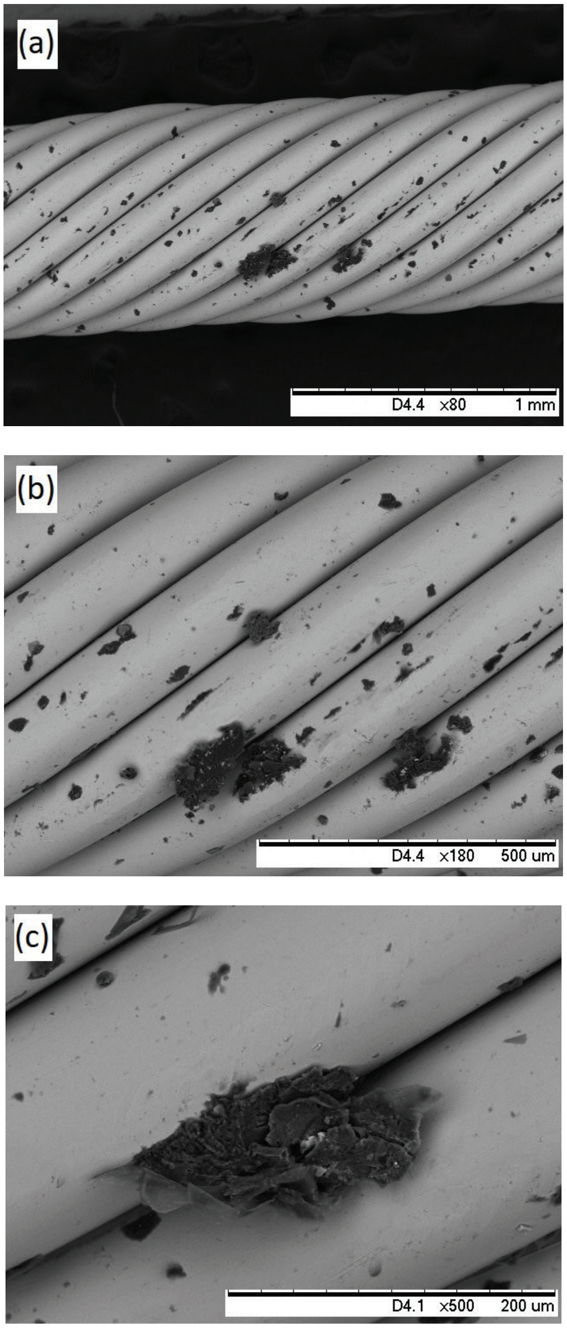

Figure 2. SEM image of the sample cable, at a) 80X, b) 180X and c) 500X.

The result shows that the contaminated sections of the wires have a major percentage of carbonic charge (6.5%) and in contrast to the clean section, it contains 0.5% of Chlorine, among other differences in the percentage of the components corresponding to the metal matrix.

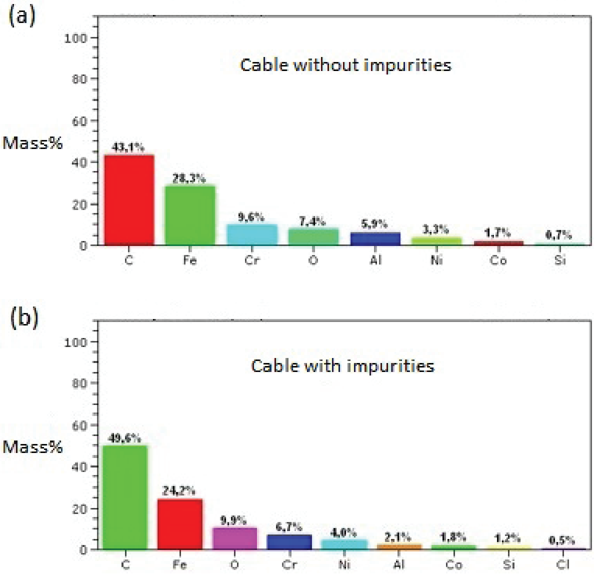

Figure 3. Comparison of the elemental composition in mass percent, between the cables (a) without and(b) with impurities by EDS Analysis

Thermal Analysis

For this analysis only cables with impurities were used. In the TGA instrument, the sample was heated in continuous way, from room temperature until 1000 °C, and the curve that exhibits the change of the sample mass versus of the heating temperature is recorded, as shown in Figure 4. The curve shows information of the reactions occurring in the sample involving loss or gain of mass. A slight decrease in the mass of 0.36% was recorded up to 400 °C, which indicates that some matter foreign to the cable is decomposing (volatiles), since the melting temperature of the cable is much higher. After this point, there is some gain in the mass of 0.9912% after 600 °C, possibly due to oxidation in the cable. There is some abnormal noise after 750 °C, but this is perceptible as product of the oxidation reaction, but also could be due to an external disturbance (noise) in the instrument.

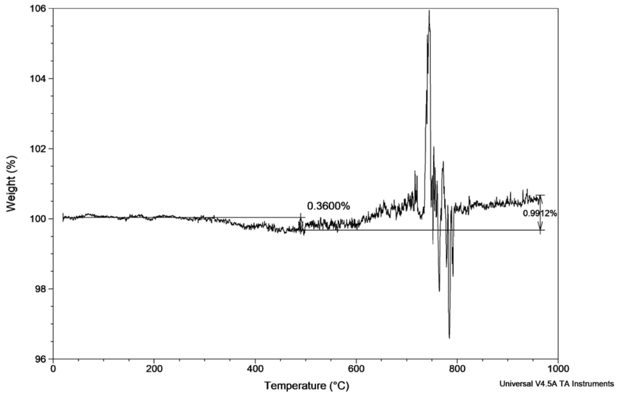

Figure 4. Thermogram of the sample cable by TGA analysis.

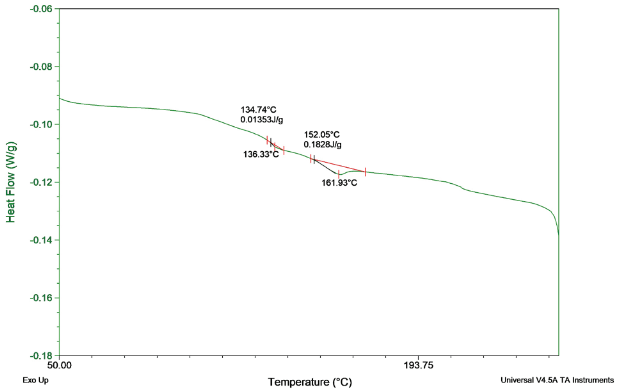

Figure 5. Calorimetric curve of the sample cable by DSC analysis.

The DSC analysis was carried out to measure the change in the reaction heat (enthalpy) with temperature. For this purpose, the instrument increases the sample temperature from room to 250 °C and calculates the reaction heat necessary to keep the sample at the furnace temperature, which is affected by the reactions occurring in the sample. This allows analysis of the different processes that alter the sample that don't involve changes in its mass.

It can be seen in Figure 5 that at least two endothermic reactions occurred at ~136 °C and ~162 °C, which is consistent with reactions in organic matter.

X-Ray Diffraction Analysis

The diffractogram in Figure 6 shows the results of a scan over the sample and registers the signals from X-rays that return to the detector versus the diffraction angle 2 θ.

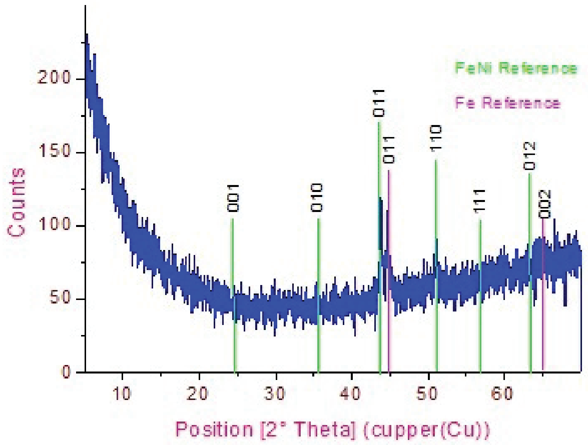

Figure 6. Spectrum for the sample cable by X-Ray Diffraction analysis.

In this spectrum, it is shown that the diffraction for the sample has a high noise signal that acts like interference in the results obtained, because the wavelength of Cu tube produces a high noise signal with ferrous samples. It has two maxima, which are near of the 45° and 50° (2Theta) respectively. The intensities for the rest of the diffraction peaks are low, and indeed it is difficult to distinguish between the signal of the sample and the noise signal. Nonetheless, diffraction from the Fe and $Fe_{0.612}Ni_{0.388}$ solid solution phases was detected by the XRD. The Miller indices (hkl) for the corresponding phases are shown in Figure 6, so that direct comparison can be made between the lines of maximum diffraction of the sample and the reference pattern. Table 3 shows the diffraction maxima from the reference patterns as extracted from the database, with the peak list of the "h", "k" and "l" values for the corresponding diffraction peak.

Table 3. *Comparison between the degrees and the orientation for the sample, and the $Fe_{0.612}Ni_{0.388}$ and Fe reference patterns.*

Sample	Orientation	2 Theta (deg)
Reference 98-010-8555 of $Fe_{0.612}Ni_{0.388}$	(001) (010) (011) (110) (111) (012)	24.858 35.438 43.772 50.987 57.531 63.630
Reference 98-063-1724 of Fe	(011) (002)	44.680 65.033

Through the characterization made by x-ray diffraction it can be said that the crystalline phases present in the wire are in agreement with the crystallographic references 98- 010-8455 for FeNi, with a tetragonal structure, and 98-063-1724 for Fe, with a body-centered cubic structure. However, other phases could be present that are not detectable by the XRD analysis due to the low signal to noise ratio.

Discussion

The SEM images in Figure 2 show that contamination can be distinguished, because the production of back-scattered electrons involved in forming the image vary according to atomic number, in that elements with different atomic number produce different amounts of backscattered electrons, so that the detectors pick greater intensity on substances with higher atomic number, such as the metal in the wire, and therefore display a bright contrast. Organic contamination is formed by low atomic number elements, such as in hydrocarbons, and they produce a darker contrast [6].

In the SEM technique, the radiation used is a monochromatic electron beam of high frequency, which generates good resolution at high magnification, and large depth of focus, and this allows perceive the impurity particle surface and volume in the analysis [2]. With the SEM analysis, it is noted that the contamination is present around all wires, and it is probably composed of organic compounds, because their contrast is different of that from the metallic compounds in the wire.

The EDS analysis shown in Figure 3 indicates that the wires had a large fraction of carbon, and this amount increased in the contaminated area of the sample. Therefore, considering the SEM results it is correct to assume carbon is associated with the particles. In the EDS analysis, the incident radiation penetrates the sample and interacts with its atoms. For this reason, it is possible to detect emission spectra from both metallic and organic elements [7]. The elements present in the wire such as Fe, C, Cr, Ni, Al and Co were detected, so that others such as excess C and Cl are possibly due to external contamination. The composition results from EDS analysis, are not absolute, because O, C and Si are common elements present in the metal itself. From these elements, it is difficult to indicate with certainty what is the composition of the contaminant particles. A complimentary analysis such as FTIR spectroscopy could determine the specific composition [8].

In the thermogravimetry shown in Figure 4, it was possible to detect a loss of 0.36% mass after 300 °C, which although small, could be attributed to decomposition of organic particles, since this temperature is too low for the metal to show any transitions. After 600 °C there is a slight increase in mass, followed by a transition at 750 °C, probably produced by an oxidation reaction that occurs at elevated temperatures with the residual humidity in the sample chamber, resulting in an increase of ~1% in weight. It is important to mention that the TGA analysis may be affected by different error sources, so the sharp peak at 750 °C could also be due to buoyancy effects produced by the heat on gas or by the formation of foam, or a fluctuation in the flow gas [9].

Figure 5 shows the calorimetric curve for the metallic cable. It can be observed that there is a decrease in the heat flow with respect to the temperature steadily. This phenomenon occurs by a constant loss of heat capacity in the sample. Besides this, two endothermic transitions are observed at 134.74 °C and 152.05 °C (onset temperature), corresponding to enthalpies of 0.01353 J/g and 0.1828 J/g, respectively.

In general, the DSC can work in a temperature range ranging from liquid nitrogen temperature to about 600 °C, therefore this analytical technique is used to characterize materials that undergo thermal transitions in that temperature range. The type of materials that show all thermal transitions in this interval are polymers and organic materials. For example, the melting point for the stainless steel is around of 1400 °C [10]. Therefore, it is assumed that the transitions in Figure 5 are due to the organic particles on the wires.

From the diffraction pattern in Figure 6 it can be said that the phases detected by the XRD are characteristic of stainless steel [8]. The wavelength of the characteristic radiation depends on the material from the tube, and this has an important effect on the signal noise depending on the nature of the material to be analyzed. To work with most materials, Cu is recommended as the source, however, for ferrous materials such as Fe, Co is preferred because it generates less fluorescent scattering from the sample. Since for this analysis the sample was tested with a Cu tube and the material of the sample is stainless steel 304, there is a significant fluorescence from the sample getting into the detector. Although it was possible to obtain a spectrum, relatively high background radiation was produced, as shown in Figure 6. Nevertheless, the XRD showed results only about of the structure of the metal, but not from any other crystalline compound. Thus, it can be inferred that the structure of the particles is not crystalline, which is common for organic particles to have an amorphous structure [10].

It must be mentioned that most of the characterization techniques used in this research, indicate that the impurity is of organic nature, so that it is recommended to apply a cleaning process to the wire with an organic solvent, in order to remove the impurities. These particles could be produced by remnants of lubricants or debris in the manufacturing process, which is then passed on to the coiling operation, it could come from a previous process, before putting all the wires into a coil.

Conclusions

- Using the SEM technique, the most important visual information was collected. This analysis confirmed that the impurities have a low molecular weight and that they are at a superficial level, not embedded in the material.
- By the TGA analysis a slight decrease in the mass at low temperatures confirms the decomposition of some matter foreign to the wire. This was confirmed by endothermic reactions in the temperature range below 300 °C.
- The XRD did not show crystalline components besides those corresponding to the stainless steel. According to the analysis, the wire has a FeNi phase with a tetragonal structure, and an Fe phase with a cubic structure.
- In general, the characterization indicated that the impurities in the cable are of organic nature and are not part of the metal structure. An FT-IR analysis is recommended to isolated particles because the metallic matrix is an interference.
- It is recommended to clean the cable with some organic solvents or mild acids to remove the contaminants from the metal surface.

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