Metal Surface Analysis with Agilent 4300 FTIR

Introduction

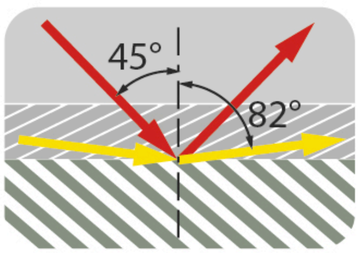
In many industrial fields the metal surface is subjected to physical and chemical processes which vary the composition of the surface layer. In some cases these transformations are intentional but other times they are considered unwanted. The need to characterize surfaces is fundamental to ensure a proper control of the production process.
Fourier Transform Infrared Spectroscopy (FTIR) is a highly appreciated analytical technique in the study of materials and, thanks to the high precision and speed, it is a prime choice for the characterization of a material at a molecular level.
The Agilent 4300 FTIR System is a high performance portable FTIR spectrometer that allows to operate ion-site with the precision and quality of a benchtop instrument. Featuring an ultra-compact ergonomic design, it is the perfect tool for analyzing large samples directly on field avoiding laborious preparations. Equipped with several easily interchangeable sampling technologies (ATR-D, ATR-Ge, External Reflectance, Diffuse Reflectance and 82° Grazing Angle) it is the perfect tool for multiple applications.

Analysis of the thickness of oxide on aluminum sheets

The metallurgical processes, concerning brazing, connect metal pieces with the aid of a third metal, called filler, thus avoiding melting the starting metals. The brazing process is based on the intimate contact between the three materials and it is very sensitive to the presence of surface contaminants on the metals to be brazed. In many cases "dirty" surfaces strongly influence the mechanical characteristics of the product, making it unsuitable for molding or painting.

In the case of aluminum in sheets, the most common surface contaminant is its oxide, Al_2O_3, which forms layers with a thickness of less than μm that are difficult to remove. The extent of the thickness follows an increasing, but not linear, trend as a function of temperature and can vary from 4 nm (200° C) to 15 nm (500° C).
Even materials kept at a lower temperature can develop an appreciable thickness of oxides and create difficulties.
The aluminum oxide has characteristic absorption bands that are appreciable in the infrared and, through the Grazing Angle accessory, it is possible to analyze even such thin layers.

The Grazing Angle is part of the family of specular reflectance accessories and differs only in the angle of incidence which is very close to normal (82°), in order to increase the length of the optical path within the material.



The oxide formed at low temperatures (T <450° C) is found in the amorphous form and has a characteristic absorption peak at 933 cm^{-1} attributable to the molecular vibration of the bond Al-O-Al, useful for quantifying the thickness layer. This band tends to increase up to a temperature of 450-500° C where instead we observe the increase of a secondary band at 733 cm^{-1} probably due to a morphological rearrangement[1].

In the case considered, the analyzed samples show only the absorption peak at 933 cm^{-1}.

The measurements are carried out without performing any pretreatment of the sample, simply by placing the FTIR on the sampling area of interest. In the spectrum it is possible to identify the peak relative to the oxide (933 cm^{-1}) as well as the stretching group C-H around 2900 cm^{-1} attributable to a lubricating oil that is not properly cleaned.

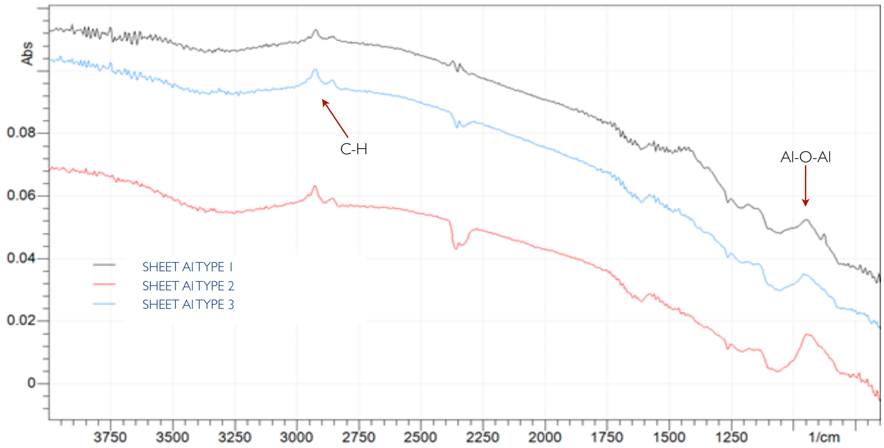


Figure 1 - FTIR Grazing Angle spectra of aluminum sheets

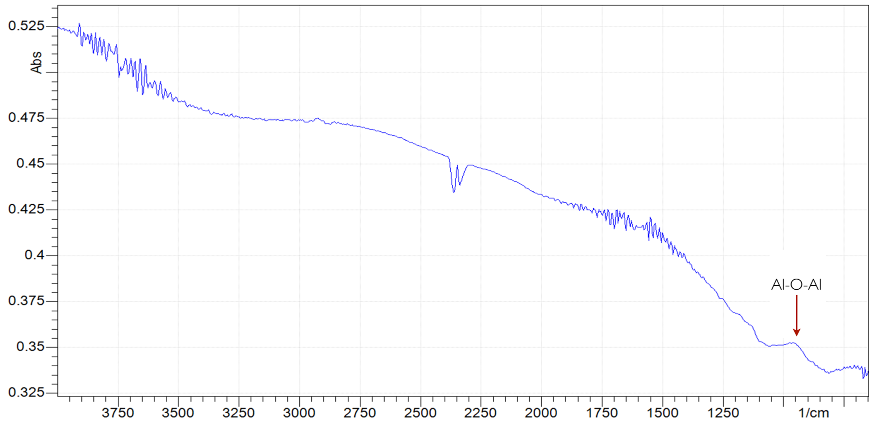
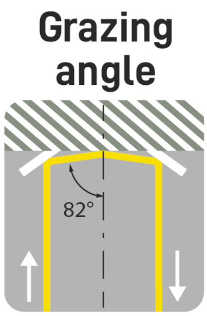


Figure 2 - FTIR Grazing Angle spectrum of an aluminum tube



Thanks to the geometry of the Agilent Grazing Angle accessory, it is possible to measure on curved surfaces such as pipes without the aid of other accessories.

The quantitative data obtained are extrapolated using a PLS1 chemometric method that correlates the intensity of the oxide band with the temperature to which an aluminum sample should be subjected to obtain the corresponding oxide layer. The data obtained is therefore a temperature data that allows to know the oxidation state of the surface of the material.
This way of proceeding was chosen to be the fastest to be built even if it is possible to obtain the same results by correlating the thickness (in Å) found with a complementary technique such as the XPS[2].

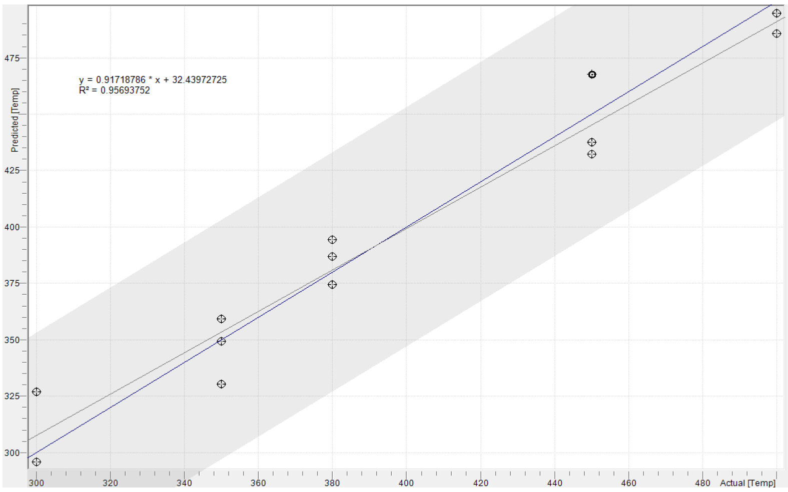


Figure 3 - Chemometric method PLS1 correlating Absorbance vs Temperature

Results

The data indicate that the three slabs have oxide thicknesses neither very marked nor very distant from each other (T 275° C) but the SHEET Al TYPE2 sample has the most advanced oxidative layer. This is in line with the material production certificate which indicates a higher temperature used to made it than the other two batches.

The aluminum tubes were simply placed on the Grazing Angle interface and present the oxide layer with the thinnest thickness among all the samples analyzed. From the spectrum it is also possible to exclude the presence of organic contaminants.

SHEET Al TYPE 1	
Test number	T/°C
1	315
2	264
3	267
4	238
5	272
6	263
7	282
8	271
9	256
10	254
T avg/°C	268
STD/°C	20,3
%STD	7,57

SHEET Al TYPE 2	
Test number	T/°C
1	285
2	278
3	269
4	235
5	287
6	296
7	298
8	296
9	289
10	301
11	299
12	301
13	283
T avg/°C	286
STD/°C	18,1
%STD	6,34

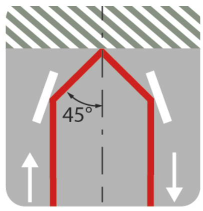
SHEET Al TYPE 3	
Test number	T/°C
1	287
2	267
3	262
4	276
5	256
6	272
7	289
8	280
9	275
10	275
T avg/°C	274
STD/°C	10,3
%STD	3,76

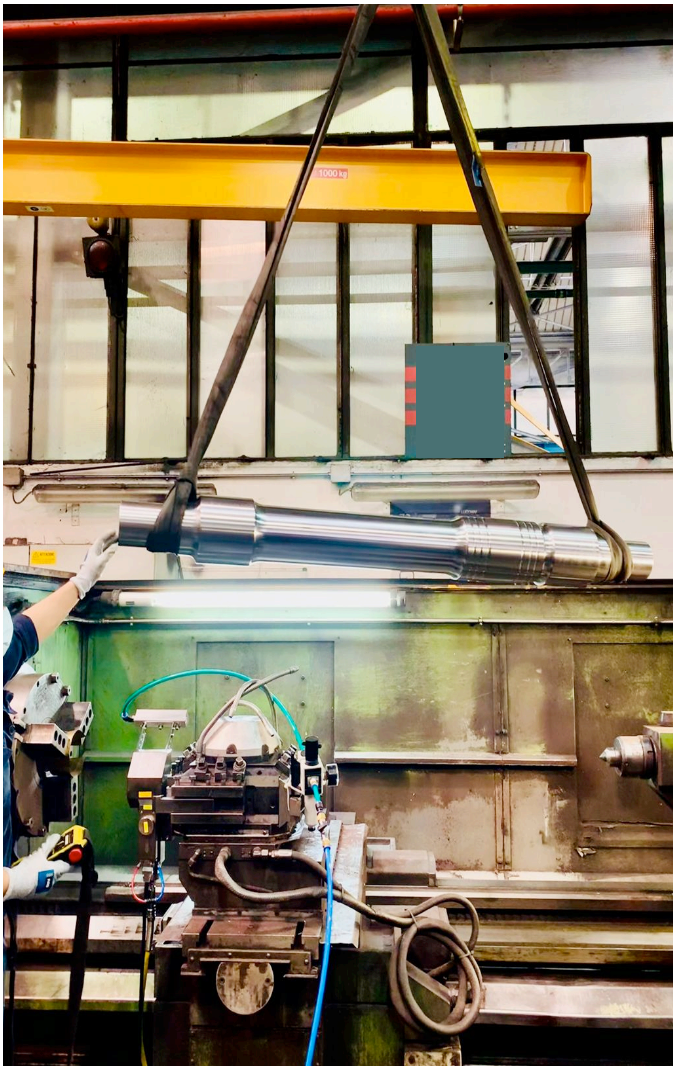
ALUMINUM TUBE	
Test number	T/°C
1	245
2	215
3	242
4	240
5	239
6	234
7	241
8	198
9	249
10	261
11	289
12	226
13	219
14	236
15	212
16	208
17	230
18	230
T avg/°C	234
STD/°C	20,9
%STD	8,92

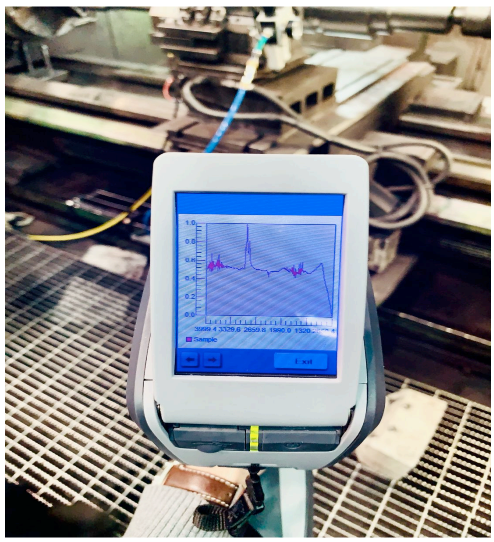
Analysis of the state of contamination of metal surfaces before painting

The painting of metal materials is an operation of more chemical than aesthetic interest. This is because, thanks to the paint, the metal surface is isolated from external contaminants that could corrupt the mechanical strength and chemical inertia of the material. It is important to consider that the adhesion of the paint to the metal surface occurs correctly only if the metal is perfectly clean and free of contaminants, such as residues of lubricants, inks and coarse material.
In the case considered, the analytical solution developed was to evaluate the cleanliness of a railway axle before painting and after laser cleaning. The size of the sample and its weight required to use a portable FTIR without which it would have been impossible to achieve the expected result.
The main contaminants present are organic in nature (oils, greases, inks, dust) and the evaluation of the intensity of the stretching C-H (3000 cm^{-1}), attributable to residual hydrocarbons, has been identified as a discriminant between material suitable for painting or not.
To appreciate the infrared signal on a shiny and specular surface, such as that of an axle, specular reflectance is the most suitable accessory. The specular reflectance is based on the irradiation of the sample surface with an angle of 45° which is collected at the same angle. In this way it is possible to analyze even very thin layers.

External reflectance







Thanks to the geometry of the Agilent External reflectance accessory, it is possible to measure on curved surfaces without the aid of other accessories.

Results

From the acquired data it can be highlighted that the laser cleaning performed on moderately dirty axles (low C-H stretching signals even before the Laser treatment) is very effective. On the other hand, when the initial quantity of oils and fats is very high, signals of the aliphatic component are observed even after the Laser treatment and carbon black deposition occurs.

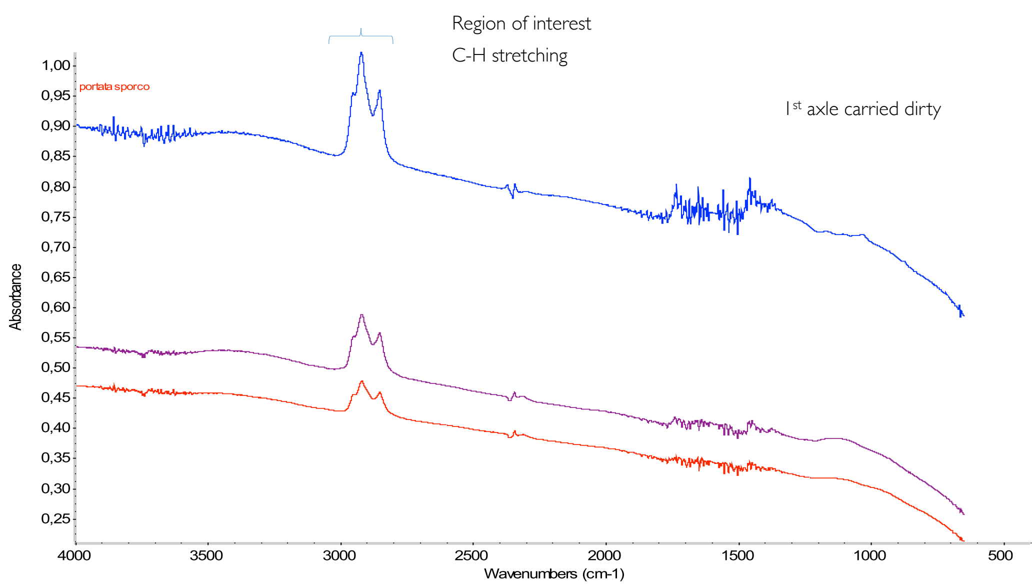


Figure 4 - Specular reflectance analysis of a dirty axle before treatment. The analysis was performed in three points.

After Laser cleaning

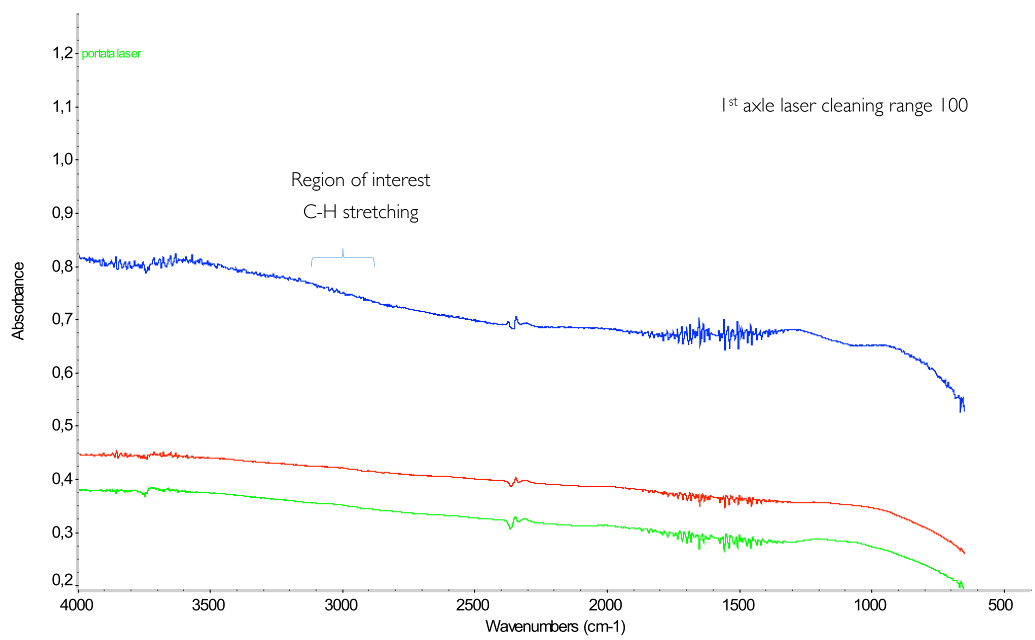


Figure 5 - Axle analysis following laser cleaning in the same sampling points as in Figure 4.

The analysis of the surface is therefore fundamental to the production process since it allows you to identify whether the surface of the axle is suitable or not to be painted. For example, the analysis of the underlying axle allowed to identify traces of organic contaminants, even after cleaning, resulting in the piece being rejected as it is not suitable for painting. Thanks to the Agilent 4300 FTIR it was possible to carry out this control directly on-site without the need to treat the sample in advance.

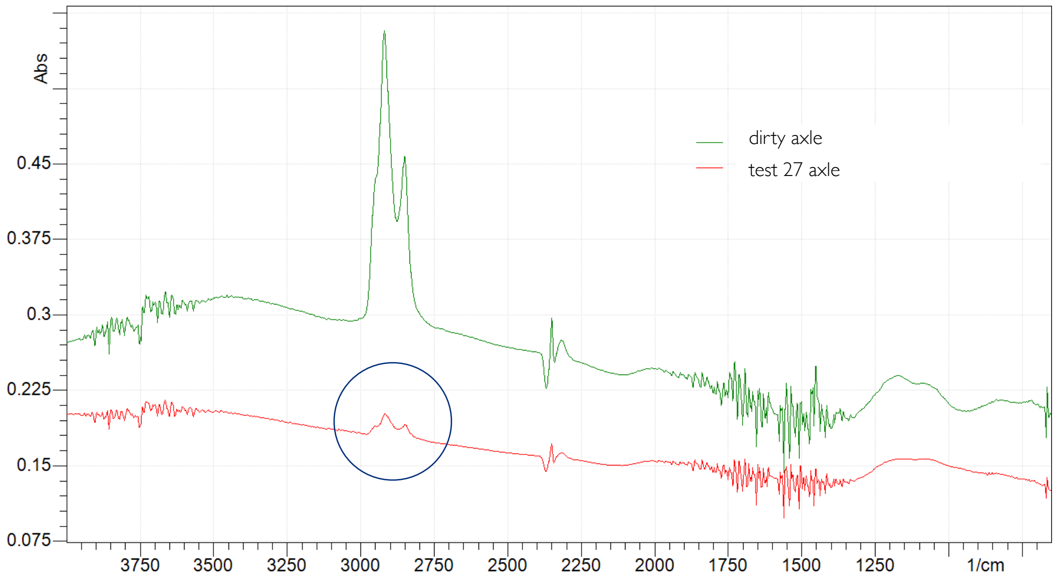


Figure 6 - Comparison of the cleanliness level of a heavily soiled axle. It is possible to notice traces of organic contaminants also following the cleaning process (detail circled in blue) which leads to the piece being rejected as it is not suitable for painting.

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References

1 Koichi Nishikida and R. W. Hannah, "Kramers-Kronig Calculation of the Grazing Angle Reflection Spectrum of Barrier Oxide Layer on Aluminum," Appl. Spectrosc. 46, 999-1001 (1992)

2 Uçar, Özlem & Meşe, Ayten Ekin & Birbaşar, Onur & Dündar, Murat & Özdemir, Durmuş. (2017). Determination of Aluminum Oxide Thickness on the Annealed Surface of 8000 Series Aluminum Foil by Fourier Transform Infrared Spectroscopy. 10.1007/978-3-319-51541-0_36.

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