ESF - Exchange Grants – Scientific Report

Exchange Grant:

Reference Number: 371

ESF Activity:

Activity Title: Nanotribology
Activity Acronym: NANOTRIBO

Project:

Title of the research project: Energy dissipation and phase contrast mechanisms in amplitude modulation AFM images of composites materials.
Date of visit: 03/11/2004 – 03/12/2004
Applicant's Name: Eva Natividad, ICMCB-CNRS, Pessac, France

Host Institute:

Prof. Ricardo García, IMM (CSIC), Tres Cantos, Spain

1. Purpose of the visit.

It is known that phase contrast imaging in amplitude modulation AFM (AM-AFM) is a powerful method to obtain compositional contrast in heterogeneous materials [1-4]. However, to develop phase imaging as a quantitative tool for imaging material properties, several tasks must be carried out. First, in order to achieve reliable and precise force values a good calibration method for the force constant (k) of the cantilever is required. Second, a thorough study of the relationship between tip-sample interaction forces, oscillation amplitudes and phase-shift changes is necessary. In fact, phase shifts are influenced by elastic and inelastic processes; however, the phase signal at fixed amplitude is directly related to the energy per cycle dissipated by the cantilever on the sample [5-6]. A consequence of the above is that in many cases topographic contributions also appear in the phase signal [7], making hard to relate a given phase-shift to a single material property.

The aim of the visit was two-fold: on one hand, to find the most suitable cantilever-calibration method for high resonance frequency cantilevers (amplitude modulation AFM cantilevers) and, on the other hand, to study the relationship between tip-surface interactions and phase shifts in amplitude-modulation AFM with composite materials. The obtained results were applied to the study of the sensitisation (Sn adsorption), activation (Pd adsorption) and electroless Cu deposition onto Al_2O_3 [8] (systems Sn/Al_2O_3, $Pd/Sn/Al_2O_3$ and $Cu/Pd/Sn/Al_2O_3$), samples of the kind were used.

2. Description of the work carried out during the visit.

2.1. Force constant calibration.

Cantilever manufacturers usually assign nominal k values to cantilevers, but they are usually calculated or estimated values, and may present errors up to 20%. The commercial software of some AFMs (Nanoscope III Multimode scanning probe microscope (Veeco)), allows calibrating cantilevers by thermal methods (based on the acquisition of the cantilever's thermal distribution spectrum), but presents a strong frequency limitation, and only cantilevers with resonance frequency (f_0) lower than 31 kHz can be measured. We pursued to widen this frequency range by the use of an oscilloscope to register the cantilever fluctuation due to thermal noise, since the oscilloscope has a much wider frequency range. For that purpose, we measured the thermal noise of a commercial cantilever (Bio-Lever from Olympus, cantilever B), of f_0 = 13 kHz and k = 0.006 N/m (nominal), both with the Nanoscope and the oscilloscope, and calculated its k value by three different thermal methods: 1) Hutter and Bechhoefer [9], 2) Butt and Jaschke [10-11] and 3) Burnham et al. [10]. We also evaluated k by 4) Sader's method [12], which is a geometric method based on the cantilevers size and other parameters. Eventually, we used the oscilloscope to measure the thermal fluctuation of a typical AM-AFM cantilever (Olympus) with f_0 = 266 kHz.

2.2. Relationship between tip-sample interactions, oscillation amplitudes and phase-shift changes.

2.2.1. Sample preparation.

The Al_2O_3 substrates used at ICMCB for Cu electroless deposition are commercial polycrystalline plates with a mean roughness (R_a) of 94 nm. These plates were not very adequate to start with, since they are too rough. Then, we decided to use sapphire 00l crystals as substrate for Sn deposition.

Sn deposition was achieved by the immersion of the substrate in a stirred bath containing HCl, $SnCl_2$ and distilled water in adequate proportions. After immersion, the samples were rinsed with distilled water to stop the deposition process and remove loose particles and contamination from the bath. In order to be able to detect phase contrasts between deposit and substrate, it was necessary to leave uncovered one part of the sapphire and to be able to localise the interface. This task became rather difficult due to the small size of sapphire substrates available (less than 1

cm^2). In effect, even if we were able to immerse only half of the substrate into the bath, the water rinsing stage spread the solution over the surface, making the Sn/sapphire interface fade away. This interface was afterwards very hard to find by AFM. After several trials, another solution was applied.

We substituted the small sapphire substrates by glass (SiO_2) sample holders for microscopy, since it allowed us to manage with bigger substrates and, besides, SiO_2 is comparable to Al_2O_3. At the same time, we tried to mask half of the substrate area by sticking a polymeric adhesive before Sn deposition. This adhesive would be removed with ultrasounds in acetone after water rinsing. However, we could observe by AFM that the polymer did not completely disappeared, glass did not show up (the background roughness was greater than that of glass) and we could not distinguish between polymer and Sn. However, at this stage, we started to detect phase contrast due to compositional changes, but it was hard to determine which material gave the contrast.

Finally, we decided to perform the Sn deposition in other way. Instead of immersing the glass into the bath, we deposited a very small drop of Sn solution onto the surface. Then we were able to observe the Sn/glass interface, and we could proceed to the study of AM-AFM phase contrast.

2.2.2. Measurements.

AM-AFM measurements were performed on a Nanoscope III Multimode scanning probe microscope (Veeco) with commercial silicon cantilevers (Nanosensor) of resonance frequency, f_0, of about 75.21 kHz and in ambient conditions. In order to study the relationship between tip-sample interactions, oscillation amplitudes and phase-shift changes, height and phase images of the Sn/glass interface were recorded with the cantilever excited at f_0 and with different drive amplitudes (or free amplitude, A_0) and amplitude setpoints (A_{sp}).

In AM-AFM, the sample is imaged while the feedback adjusts the tip-sample separation to keep the oscillation amplitude at a fixed value A_{sp}. Amplitude variations during measurements are due to the action of short- and long-range tip-sample forces. According to [14-16], there are two elemental tip-sample interaction regimes, attractive and repulsive regimes, in which a net attractive or repulsive force, respectively, controls the cantilever dynamics. This dynamics is determined by the parameters A_0 and A_{sp}. For small A_0 values, the cantilever is in the low-amplitude (LA) or attractive regime. In this case, varying A_{sp} cannot induce a state transition. For intermediate values of A_0, there is a range of A_{sp} values for which the cantilever is in a instable state, that is, small perturbations (such as topographical changes) can easily induce state transitions. These transitions are monitored in the experimental amplitude-distance curves and also reflected in abrupt height or phase changes when imaging a sample. Above this A_{sp} range, the cantilever is in the LA or attractive regime, and below, in the high-amplitude (HA) or repulsive regime. Eventually, for high A_0 values, the A_{sp} range in which the cantilever is in the HA regime increases. It must be mentioned that the A_0 and A_{sp} values for which the cantilever is in repulsive, instable or attractive state depend on the material nature and the tip-sample interactions. For this reason and with the aim of identifying these values, several height and phase images have been recorded for a wide range of A_0 and A_{sp} values. Section analyses were carried out in order to infer the influence of these oscillating amplitudes in the phase-shift changes.

3. Description of the main results obtained.

3.1. Force constant calibration.

From the power spectral density obtained with the cantilever with f_0 = 13 kHz, we calculated the k values through the four methods mentioned above. For the first, second and fourth methods, we obtained k values of 0.0077 ± 0.0001 N/m. For the third method, however, k = 0.0088 N/m. The discrepancy of the Burnham's method comes most probably from the fact that, in this case, only the mean-square amplitude value at the resonance frequency is used to

calculate k, while in the others, the sum of the mean-square amplitudes at all frequencies are used. The error may come from the inaccuracy in the measurement of this single value. However, Burnham's method is very interesting from another point of view: it allows fitting the power spectral density plot and easily obtaining the contribution of the $1/f$ background noise, the white noise, estimating the quality factor (Q) of the cantilever and its f_0.

The measures of the same cantilever performed with the oscilloscope derived a power spectral density with different absolute values, even after calculation of the deflection sensitivity (nm/V). However, from the fit of this curve, we obtained similar Q and f_0 values than with the commercial software. Then, we concluded that there was an error in the estimation of the oscilloscope deflection sensitivity, and that further calibrations should be done.

Eventually, for the high frequency cantilever, we concluded that the thermal fluctuation amplitude at those high frequencies was masked by the electrical noise, and that, in this case, the Sader's method was more adequate to calculate the cantilever force constant k.

3.2. Relationship between tip-sample interactions, oscillation amplitudes and phase-shift changes.

Figure 1 shows the height image of one of the studied areas, together with a cross-section analysis. The glass and the Sn deposit can be observed, the latter presenting maximal height differences of about 40 nm. This image was recorded with A_0 = 200 mV and A_{sp} = 0.2 V. Images of this zone were recorded for A_0 = 200, 400, 800, 1000, 1400 and 2000 mV. For each A_0 value, A_{sp} was varied from the maximal down to the minimal possible values. This study allowed identifying the range of A_0 and A_{sp} values in which the cantilever was in instable, repulsive or attractive regimes.

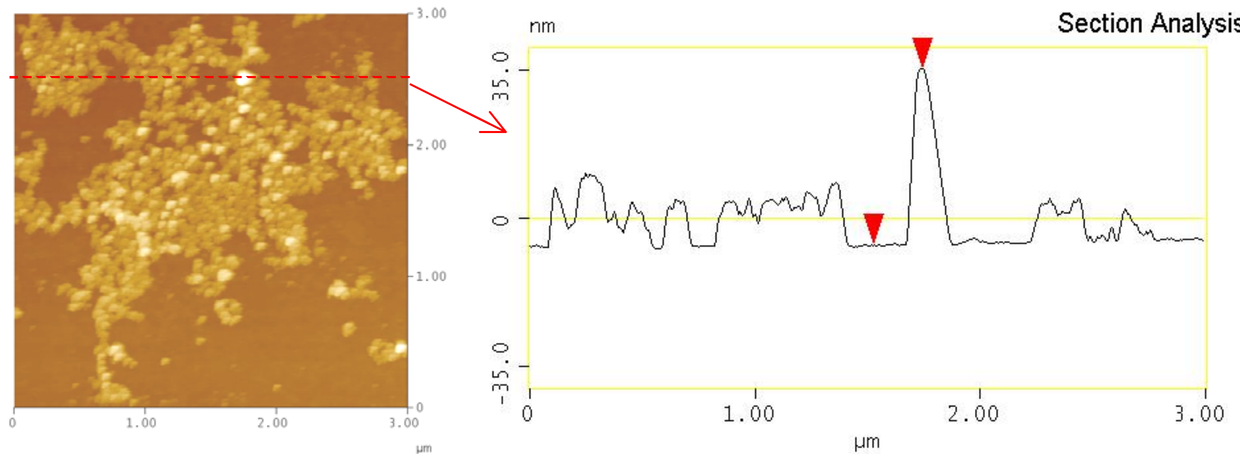

Figure 1. Height image of one of the studied areas, together with a cross-section analysis. A_0 = 200 mV and A_{sp} = 0.2 V.

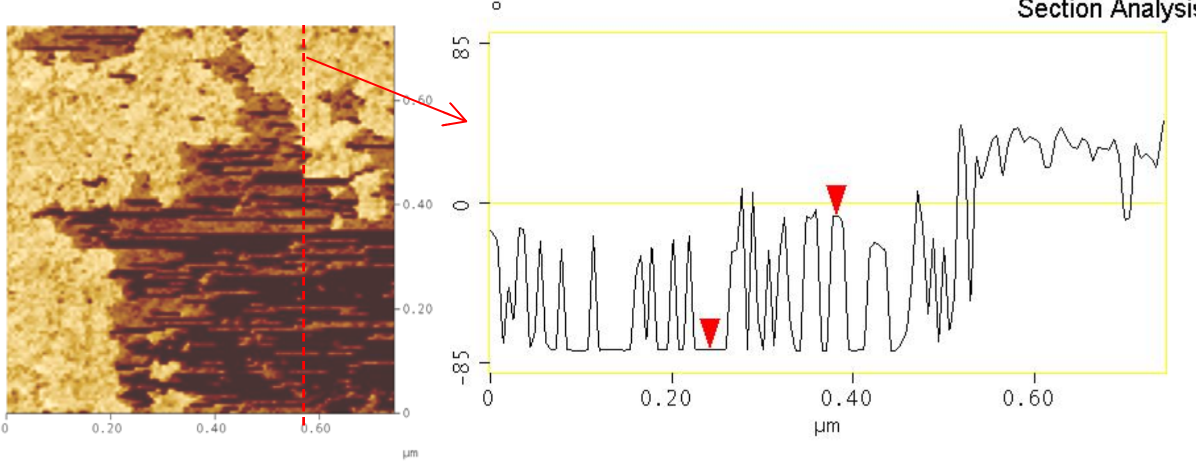

Figure 2. Phase image of one of the studied areas, together with a cross-section analysis. A_0 = 800 mV and A_{sp} = 0.5 V.

The unstable state of the cantilever is reflected in Figure 2, recorded with A_0 = 800 mV and A_{sp} = 0.5 V. In effect, the presence of instabilities is highlighted in the section analysis of the glass part, between 0 and 0.5 μm. In this area, the phase-shift should be constant, since there are neither topographical nor chemical differences but, contrarily, there are strong phase-shifts of about 60-70°. This effect is indicative of transitions between LA and HA states. According to this, the image in Figure 1 has been recorded in attractive or LA regime, which is more adequate for estimate height differences [17].

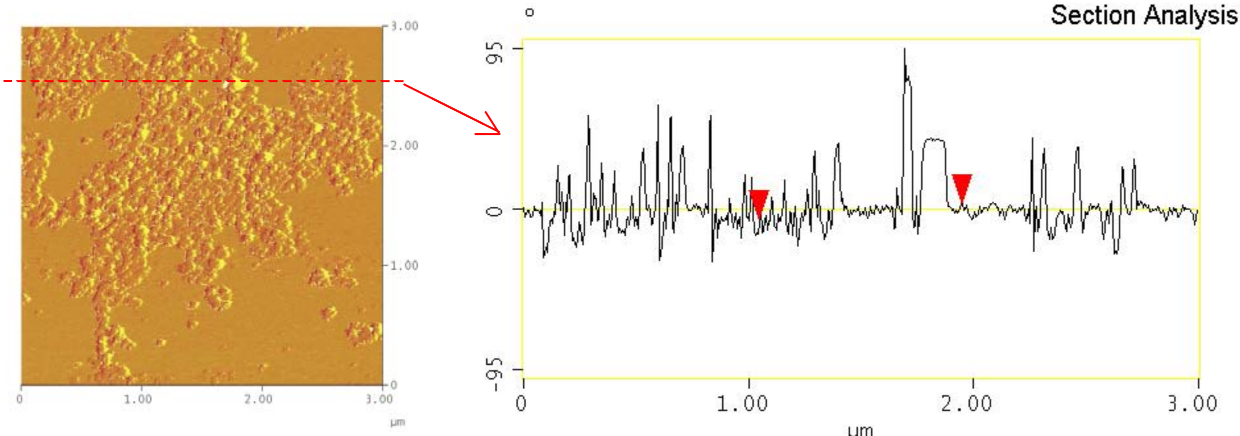

Figure 3. Phase image of one of the studied areas, together with a cross-section analysis. A_0 = 200 mV and A_{sp} = 0.2 V.

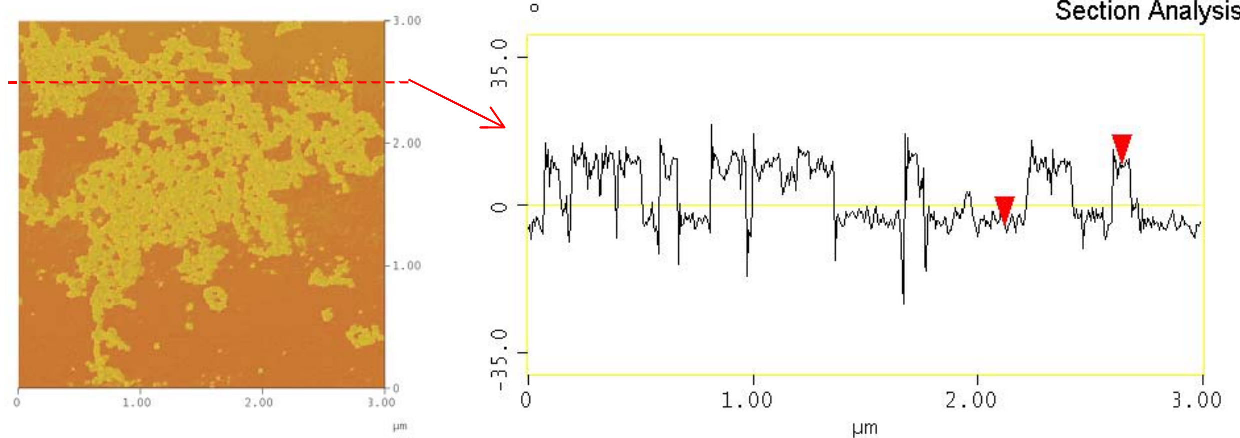

Figure 4. Phase image of one of the studied areas, together with a cross-section analysis. A_0 = 2000 mV and A_{sp} = 1.5 V.

Figures 3 and 4 show phase images recorded in attractive and repulsive regimes, respectively, together with a cross-section analysis. Image 3 was recorded with A_0 = 200 mV and A_{sp} = 0.2 V and image 4 with A_0 = 2000 mV and A_{sp} = 1.5 V. One can immediately see outstanding differences between them. First of all, phase-shift differences in the LA regime are greater than in the HA regime. Secondly, LA image seems to present a strong influence of the topography. If we focus on the highest feature just before 2 μm (see Figure 1), there is a sharp phase shift that corresponds to the positive slope of the feature (tip sweeping from left to right), and a plateau associated to the negative slope. Besides, one cannot clearly distinguish between glass or Sn, due to this strong topography contribution to the phase shift. However, HA image does not present such influence with topography. If we focus on the same feature, we can observe that there is a sharper phase shift at the beginning and at end of the feature, but we can still detect a plateau corresponding to Sn. In this case, Sn and glass are well defined by a phase-shift difference of about 15° (marked with arrows).

To sum it up, the present study derived three main conclusions: i) phase contrast imaging in AM-AFM can be used to obtain compositional contrast in our materials; ii) phase-shift differences increase with decreasing A_{sp} values;

iii) HA or repulsive regime is more adequate to study phase-shift differences due to chemical contrast, since it present less topographical contribution than LA or attractive regime.

4. Future collaboration with host institution (if applicable).

We consider that the work developed in this research visit has produced good results. Therefore, I will keep in contact with Prof. Ricardo García to go on working in the same line.

5. Projected publications/articles resulting or to result from your grant.

We plan to submit a paper to either Surface Science or Ultramicroscopy with the results.

6. Other comments (if any).

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7. References.

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Signed host statement form:

Consejo Superior de Investigaciones Científicas
Centro Nacional de Microelectrónica

INSTITUTO DE MICROELECTRÓNICA DE MADRID

Tres Cantos, 3rd December 2004

To whom it may concern, Prof. Ricardo García certifies that Dr. Eva Natividad has been working at the Instituto de Microelectrónica de Madrid (IMM-CSIC), under his supervision, from 3rd November to 3rd December 2004, for studying energy dissipation and phase contrast mechanisms in amplitude modulation AFM images of composites materials.

Ricardo García.

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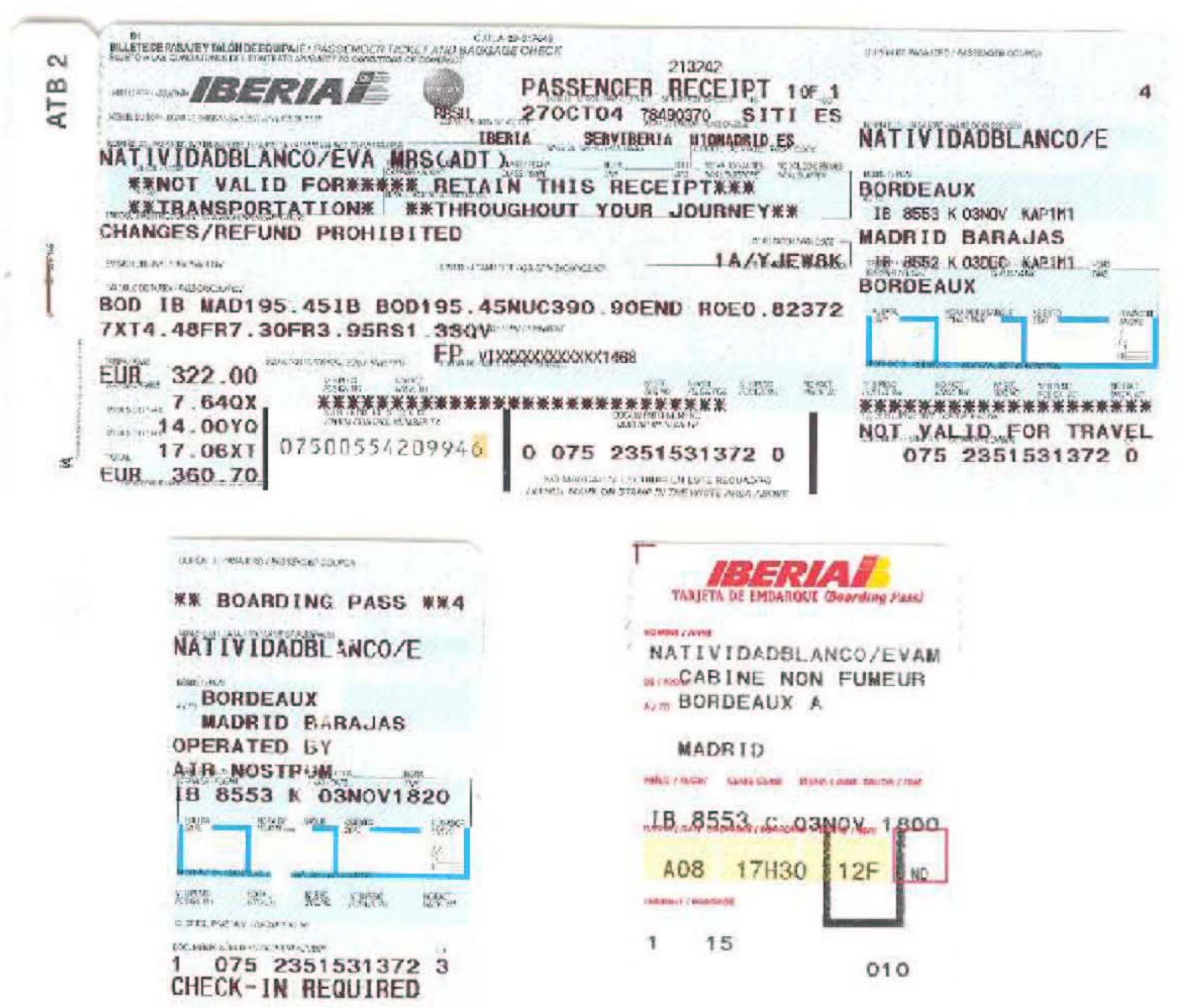

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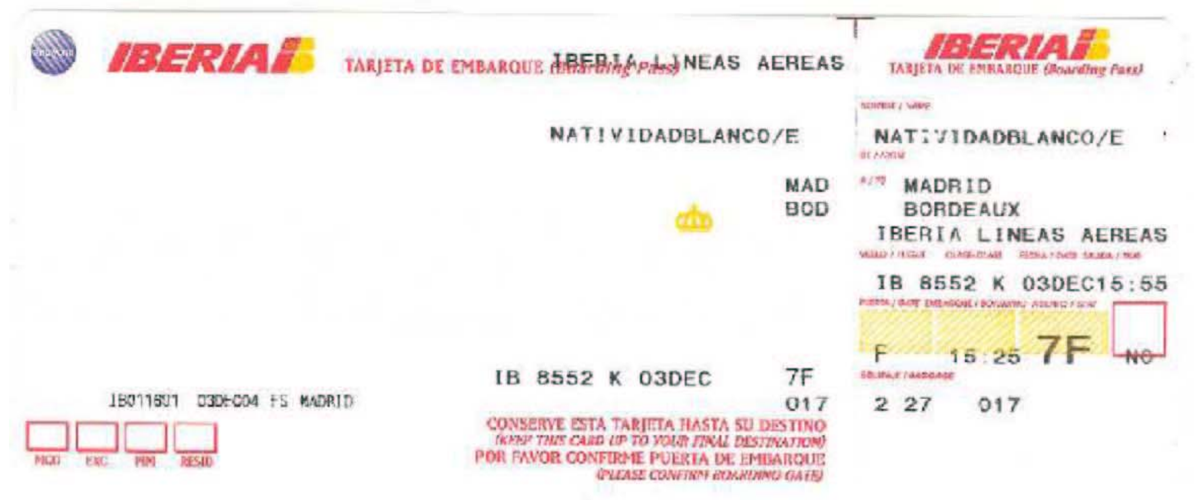

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