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ADSORBATE INDUCED VIBRATIONS MEASURED BY EELS ON A CuZn α 75/25 (110) SURFACE DURING ITS EARLY STAGE OF OXIDATION

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Abstract.- Using high resolution electron energy loss spectroscopy (EELS), we have measured three vibrational bands on a clean CuZn α 75/25 (110) surface after O₂ exposure. The band at 420 cm⁻¹ is related to the metal-O stretching vibration. The band around 3630 cm⁻¹ is interpreted as the O-H stretching vibration arising from water contamination. At higher coverages, a third band emerges (550 cm⁻¹). It is attributed to an optical surface phonon and associated with a preliminary stage of bulk oxide formation.

1. Introduction.- Brass alloys of Cu/Zn are largely used for industrial applications. There is great interest in understanding the reaction of such materials with oxygen. In order to start from a fundamental point of view, the experiments reported here were performed on a single crystal of CuZn, a brass 75/25. Although it crystallizes in the f.c.c. lattice, it is a solid substitutional solution of Zn in Cu.

2. Experimental.- EELS experiments were carried out with an hemispherical RIBER-SEDRA spectrometer, capable of an energy resolution of 35 cm⁻¹ (4 meV) /5/. The analyzer is rotatable in the plane of incidence. All spectra were taken with 4 eV impact energy, a monochromator current of 3 x 10⁻¹⁰ A, and an energy resolution of 60 cm⁻¹. The spectrometer is mounted in an UHV chamber (10⁻¹¹ Torr range), where other techniques are available, such as LEED, AES using retarding field analyzer, Kelvin probe for work function measurements and quadrupole mass analyzer.

Water contamination in oxygen (nominal purity : 99,998 %) was measured to be lower than 0.5 %. Pressure indications are uncorrected gauge readings. The polished crystal was cleaned by cycles of Ar⁺ bombardment and annealing up to 430 K. The consecutive Auger spectra showed no observable contamination. Sharp LEED patterns were observed in agreement with the (110) face. During O₂ admission, LEED did not reveal any superstructure. A maximum of the work function was found at 20 L (1 Langmuir = 10⁻⁶ Torr.s).

3. EELS results and interpretation.- EELS results are summarized in fig. 1. One peak (420 cm⁻¹) was observed to grow regularly without

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any frequency shift. It is attributed to the stretching vibration of atomic oxygen adsorbed on the surface. Dissociative adsorption is inferred from the absence of molecular O$_2$ vibration. This frequency (420 cm$^{-1}$) lies in the range of atomic oxygen vibrations measured on other metallic substrates /1,2/. Off specular experiments (10$^\circ$, 20$^\circ$ and 30$^\circ$) indicate clearly that it is excited by dipole scattering, because its intensity peaks strongly in the specular direction. The observation of only one vibration imposes that only one site is activated. Four sites are available: on-top, short bridge, long bridge and the deep center site where the oxygen may have 5 nearest neighbours. Following a general rule, the atom is most likely to choose the site offering the highest coordination. This would favour the center site, although for O–Cu(110) a long bridge site /1/ and for O–Ni(110) a short bridge one have been reported.

From the very beginning of O$_2$ exposure, a peak at 3630 cm$^{-1}$ was observed. It is assigned to the stretching vibration of OH species adsorbed on the surface. Separate measurements were made with exposure to H$_2$O: on the clean surface, they did not reveal any loss feature; if the surface was previously dosed with O$_2$, a small increase was observed for the OH peak. It is believed that some amount of H$_2$O contaminant in the admitted gas can interact with the surface only during the adsorption of O$_2$ itself. A similar mechanism of assisted selective adsorption has been reported for stainless steel /3/. The OH is adsorbed on the same...
site as the atomic oxygen, since only one adsorbate-metal vibration is observed at low exposure. The relatively low frequency with respect to the free OH is an indication of the existence of H-bonding with oxygen adsorbed on adjacent sites.

When the $O_2$ exposure varied from 10 L to 100 L, the EELS spectra changed substantially. The relative intensity of the OH vibration saturated and its frequency shifted from 3630 cm$^{-1}$ to 3680 cm$^{-1}$. A third peak emerged at 550 cm$^{-1}$, very close to the frequency of the surface optical phonon of ZnO /4/. It is interpreted as the vibration of oxygen incorporated in the surface during a preliminary stage of oxide formation. The decrease of the 3630 cm$^{-1}$ peak intensity indicates that the mechanism of $H_2O$ assisted selective adsorption must then be inhibited: this is explained as an incorporation of the oxygen atoms ($\Delta\Phi$ decrease), relaxing the H-bonding, as the OH frequency shifts by 50 cm$^{-1}$.

Annealing of the sample after $O_2$ adsorption lead to the following observations (Fig. 2): the oxide-like peak at 550 cm$^{-1}$ was enhanced and its intensity became higher than the 420 cm$^{-1}$ one, that shifted to low energy; the OH vibration vanished. This is consistent with our interpretation: the occupation of the 550 cm$^{-1}$ site inhibits the OH- and the 420 cm$^{-1}$ vibrations at the same time.

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