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On the theoretical description of the early oxidation stages of copper by cw CO₂ laser irradiation

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Résumé. — On étudie l'application des interprétations théoriques disponibles à l'analyse de nouvelles données expérimentales obtenues en étudiant les premières étapes de l'oxydation de cibles en cuivre sous irradiation laser CO₂ continu.

Abstract. — An analysis is performed concerning the application of the available theoretical interpretations in analysing the new experimental data obtained in the study of the early stages of the cw CO₂ laser oxidation of copper targets.

1. Introduction.

The oxidation of metallic surfaces under the action of powerful laser radiation, in competition with the « cleaning effect » and at the same time with the induction of new defects, presents both current scientific interest and particular technological significance. Indeed, the coming out and the development of oxides leads to a substantial modification of the thermal and optical properties (first of all of the absorptivity and reflectivity) strongly determining the behaviour of the metallic components (mirrors, deflectors, etc.) when used in powerful laser systems. After several qualitative investigations [1-3], we have recently succeeded in measuring the thickness of the oxide layer induced during the early stages of the oxidation of copper monocrystalline targets by cw CO₂ laser irradiation [4, 5]. We have also recorded the irradiation time, the incident laser power and determined the temperature that is reached on the target surface.

To this end, we used a new, jet polishing method, proceeding from the unirradiated face of the target and protecting the oxide layer with a sticky tape [4].

We have recently developed a new method for determining the thickness of the oxide layer. Thus, as previously reported [3, 4], the oxide layer grown on the copper samples surface as a result of cw CO₂ laser irradiation shows a poor adherence to the metallic support and is rather likely to break. Therefore, when scratching the oxidized target surface with a fine needle, the oxide cracks in small plates (like ice on the water). By scanning electron microscopy at high magni-

fication and a proper tilting of the sample we determined the thickness directly by measuring the edge width of the oxide plates. Further details on this technique will be given in a next paper of ours [5].

In this Letter, we consider the possibility of applying the available theoretical interpretations in analysing such new quantitative results on the evolution of the oxidation process induced and controlled under the action of laser radiation.

2. Laser heating.

Small plates of polycrystalline Cu of $(5 \times 5 \times 0.3)$ mm³ mechanically or electrochemically polished; freshly cleaned with alcohol were irradiated with a TEMoo power stabilized cw CO₂ laser. The laser output beam of ≈ 30 W was practically covering the whole surface of the plates. The variation of the samples' temperature and its derivative were followed with the aid of built-in chromel-alumel thermocouples. The targets absorptivity variation of the 10.6 μ m radiation was then inferred according to the procedure described in [7]. If the thermal constants of copper are considered, one can check out that the temperature inside the samples gets uniform in a time interval which is negligible as compared to the irradiation durations of hundreds and thousands of seconds. In any case, the recorded values of the temperature are in good keeping with the inferred evolution of the absorptivity.

A typical recording of the sample temperature evolution during irradiation is given in figure 1. As one may see, the temperature saturates rather rapidly (a few seconds) and remains almost constant for the rest of the irradiation.

3. Laser oxidation.

The oxide thickness, x , as established by the earlier mentioned techniques [4, 5], is given in table I, together with the corresponding irradiation times, t , and the value of the temperature reached in the target as a result of laser irradiation, T .

On the other hand, SAD studies pointed Cu₂O as the only oxide grown onto the irradiated target surface.

We emphasize from the beginning that the mere application of the available theoretical treatments to the initial stages of the laser oxidation of copper appears to be quite unsatisfactory.

Thus, the Wagner theory [6] according to which the thickness of the oxide layer, x , is evolving as

$$\frac{dx}{dt} = \frac{d_0}{x} \exp\left(-\frac{T_D}{T}\right), \quad (1)$$

Fig. 1. — Typical recording of the temperature (1), its derivative (2) and of the laser power (3), during the irradiation of the Cu plates.

Table I. — *Experimental and calculated oxide thickness values.*

Nr.	Sample's surface state [3]	t (s)	T (°C)	x (Å)	x_1 (Å)	x_2 (Å)
1	mechanically polished	660	155	400-600	285	60
2	electrochemically polished	660	195	500-680	660	275
3	mechanically polished	1 140	210	600-800	1 050	610
4	mechanically polished	1 140	210	600-1 000	1 050	610
5	electrochemically polished	1 200	228	800-1 000	1 465	1 110
6	mechanically polished	1 440	220	1 000-1 300	1 360	945
7	mechanically polished	1 540	260	1 200-1 800	1 870	1 885

where d_0 and T_D are thermodiffusive constants, applies only for $x \gtrsim 1\,000$ Å, while we mainly recorded in the (500-1 000) Å range [4, 5]. Therefore when evaluating x from equation (1) using the « non laser » constants $d_0 \simeq 0.299$ cm²/s, $T_D \approx 18\,800$ K and assuming a constant temperature during the irradiation process (as pointed before), one obtains a value of x 30 times smaller than the experimental one.

On the other hand, the Wagner-Valensi approach [6] which takes the complex structure of the oxide film into account is also unsuitable as it predicts the advantageous growth of CuO during the early oxidation stages, which sharply contradicts our experimental evidence [4].

However, if in equation (1) we use the « laser » values of the thermodiffusive constants which we established in [7], by processing the variation curves of the sample's temperature and its derivative during laser irradiation, i.e. $d_0 = 1.4$ cm²/s and $T_D = 15\,500$ K, a much better agreement with the experimental results is to be pointed out, as one can notice from table I (x_1 values).

Finally we stopped at the Cabrera-Mott theory [6, 8], which is known to refer to the thin oxide film growth, covering a rather large thickness range for the oxide layer from (50-100) Å up to several hundreds of Å (as recorded in our case). Thus, as experimentally confirmed by « classical » oxidation experiments [9], a cubic growth rate law seems to be most appropriate in describing copper oxidation in the (100-250)°C range

$$\frac{dx}{dt} = \frac{d_1}{x^2} \exp\left(-\frac{T_1}{T}\right). \quad (2)$$

The values calculated with the above equation, where $d_1 = 10^{-7}$ cm²/s, $T_1 \simeq 12\,755$ K, were also given in the table (x_2 values).

Upon studying table I, one can conclude that there is a generally good agreement between the experimentally inferred values of the oxide layer thickness grown in early stages onto the surface of copper targets as a result of cw CO₂ laser irradiation, and the predictions of equation (1) and (2). More particularly, values of x_1 appear to describe better the experimental evidence corresponding to the shortest irradiation durations in our experiments, while values of x_2 grow more and more appropriate as the irradiation time rises.

Further developments are therefore necessary in our opinion in order to get a unitary, fully adequate theoretical description of the early oxidation process evolution of copper (and generally metallic) samples under laser irradiation. To this effect a much larger set of direct experimental data should be available. New experiments devoted to this aim are now in progress, including a comparison of the oxide growth kinetics under laser irradiation with the kinetics associated with a furnace heating under identical conditions.

References

- [1] URSU, I., MIHĂILESCU, I. N., NISTOR, L. C., TEODORESCU, V. S., PROKHOROV, A. M., CHAPLIEV, N. I., KONOV, V. I., RALCHENKO, V. G., TOKAREV, V. N., *Appl. Phys. A* **29** (1982) 209.
- [2] URSU, I., APOSTOL, I., MIHĂILESCU, I. N., NISTOR, L. C., TEODORESCU, V. S., PROKHOROV, A. M., KONOV, V. I., CHAPLIEV, N. I., in *Surface Studies with Lasers*, Springer Series in Chemical Physics, vol. 33 ; Eds., Aussenegg, F. R., Leitner, A., Lippitsch, M. E. (Springer Verlag, Berlin, Heidelberg, NY, Tokyo) 1983, p. 234.
- [3] URSU, I., APOSTOL, I., CRĂCIUN, D., DINESCU, M., MIHĂILESCU, I. N., NISTOR, L. C., TEODORESCU, V. S., PROKHOROV, A. M., CHAPLIEV, N. I., KONOV, V. I., *J. Phys. D* **17** (1984) 747.
- [4] URSU, I., NISTOR, L. C., TEODORESCU, V. S., MIHĂILESCU, I. N., APOSTOL, I., NANU, L., PROKHOROV, A. M., CHAPLIEV, N. I., KONOV, V. I., TOKAREV, V. N., RALCHENKO, V. G., 1983 SPIE Technical Conference Geneva, paper 398-69, published in *Industrial Applications of Laser Technology* (SPIE Eds.) 1983, p. 398.
- [5] URSU, I., MIHĂILESCU, I. N., APOSTOL, I., NISTOR, L. C., TEODORESCU, V. S., NANU, L., PROKHOROV, A. M., KONOV, V. I., CHAPLIEV, N. I., RALCHENKO, V. G., TOKAREV, V. N., to be published in *Appl. Phys. A* (1984).
- [6] KUBASCHEWSKI, O., HOPKINS, B. E., *Oxidation of Metals and Alloys* (Butterworth, London) 1962.
- [7] ARZUOV, M. I., KARASEV, M. E., KONOV, V. I., KOSTIN, V. V., METEV, S. M., SILENOK, A. S., CHAPLIEV, V. I., *Sov. J. Quantum Electron.* **8** (1978) 892.
- [8] CABRERA, N., MOTT, W. F., *Rep. Progr. Phys.* **12** (1948/1949) 163.
- [9] CAMPBELL, W. E., THOMAS, U. B., *Trans. Electrochem. Soc.* **91** (1947) 623.

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