

# Photodegradation Effects in Materials Exposed to High Flux Solar and Solar Simulated Radiation

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## INTRODUCTION

The stability of materials under high flux solar radiation ( $\sim 1 \text{ MW/m}^2$ ) has recently been a point of interest in materials research. Usually, this high solar flux environment has been connected with high temperatures (350 - 600 °C), however, this enhanced temperature regime is not the sole factor in degradation of materials under high flux irradiation. Under high flux irradiation, a material is exposed to concentrated radiation of wavelengths from  $\sim 0.3 \text{ }\mu\text{m}$  to  $\sim 2 \text{ }\mu\text{m}$ . Radiation from this spectrum is by and large absorbed over a shallower depth ( up to a factor of 100 to 1000 times shallower) than infrared radiation; this surface localized absorption can lead to a surface temperature much higher than the measured bulk temperature. In addition, the ultraviolet and near ultraviolet components of the solar radiation may induce various chemical changes at the surface of the material. Such changes are based in the energetic nature of the photons associated with solar radiation ( $\sim 0.5 \text{ eV}$  to  $4 \text{ eV}$ ).

Both such surface localized and photon specific effects have been observed and characterized in the study of the interaction of high flux solar and solar simulated radiation with materials. The results of these studies will be enumerated in this report.

## HISTORICAL PERSPECTIVE

The first indications of photoeffects in solar energy relevant materials were in the Black Chrome solar absorber system studied by us in the early part of this research program. The Black Chrome system is an absorber system that has its basis in the solar selective nature of its optical absorption due to the particulate nature of the Black Chrome material. The composition of the coating is principally chromium particles with  $\text{Cr}_2\text{O}_3$  skins. The high temperature ( $T > 400^\circ\text{C}$ ) degradation of the coating is based in the further oxidation of the particles, changing the composition of the coating and as a result changing optical response.

High flux solar irradiation ( $\sim 1 \text{ MW/m}^2$ ) of the coatings to elevated temperatures of from  $350$  to  $550^\circ\text{C}$  resulted, however, in reduction of the optical degradation of the coating. Subsequent analysis of the chemical composition of the coating indicated major reduction of oxidation of the chrome particles. Further studies determined that this reduction was the direct result of the photodesorption process. Within this mechanism, solar photons of energy greater than a certain threshold (usually of the order of 2 to 3 eV) can excite a surface complex causing it to no longer be bound to the surface. This complex then desorbs from the surface and changes the chemical composition of the surface. Within the Black Chrome system, the surface complexes were principally  $\text{CO}$  and  $\text{CO}_2$ , and their photodesorption caused a reduc-

tion of the oxygen content of the surface. This reduction, therefore, reduced the rate of oxidation of the Black Chrome under high flux solar irradiation, with the flux intensity (the number of photons/cm<sup>2</sup>sec) defining the extent of oxidation reduction in the material.

As noted, this was the first observation of the effect of high solar fluxes on the stability of materials, and in fact indicated a beneficial component to high flux irradiation. The studies were, however, on solar absorber materials and it was of interest to determine the effect of high solar fluxes on the stability of other solar relevant materials.

#### HIGH FLUX EFFECTS IN METALS

Aluminum has been significantly used in solar technology both as a reflector material and as a structural material. Its response to high flux solar irradiation was critically investigated in our studies and resulted in rather interesting conclusions.

As shown in Fig. 1, oxide thicknesses between infrared heated and high flux irradiated aluminum samples are quite different. However, the variances seem different than expected. As previously discussed, solar radiation is expected to be preferentially absorbed in the surface region of a material (especially a metal which has a high imaginary component of the index of refraction). As a result, a material should experience a surface

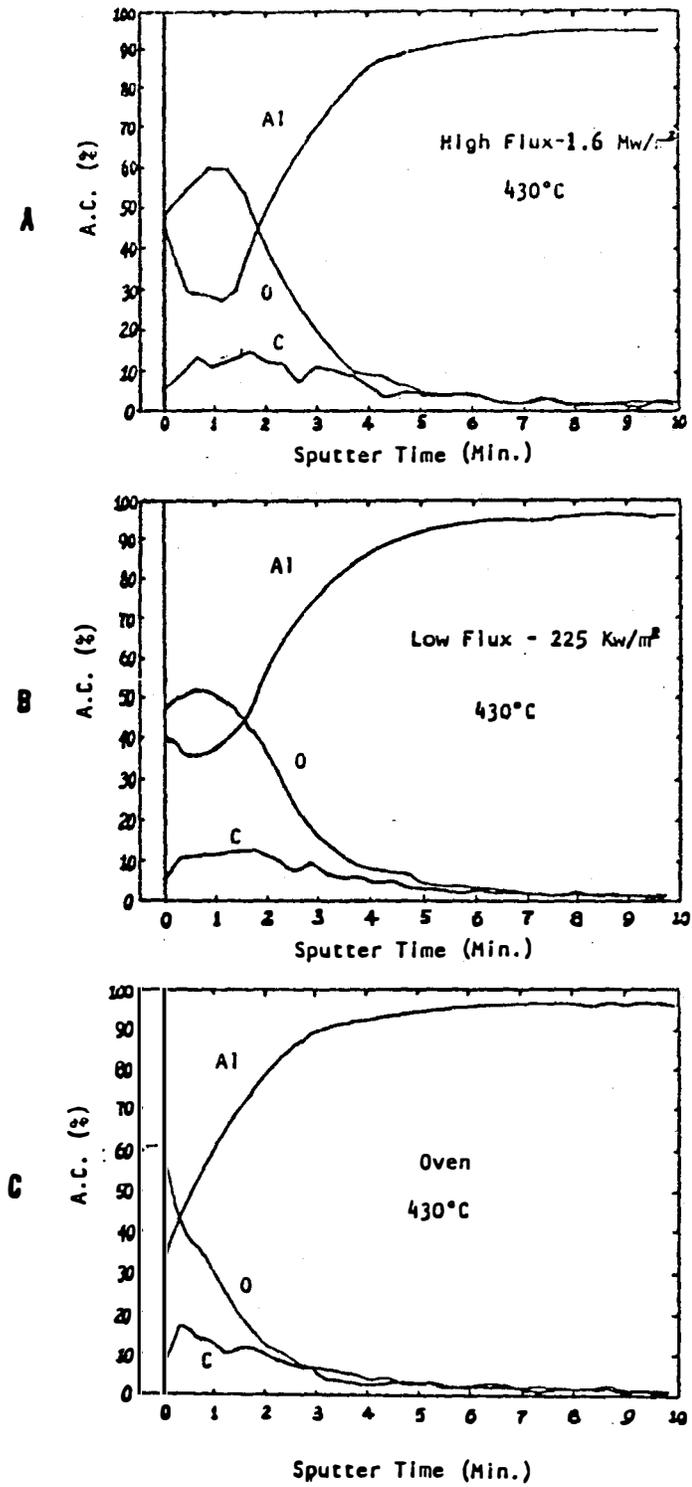


Fig. 1. AES depth profiles giving the atomic concentrations of oxygen, aluminum and carbon for aluminum samples heated for 135 minutes at 430°C using different techniques.

temperature that is higher than that of the bulk, and hence in the case of a metal, should exhibit greater oxidation when irradiated in air. Fig. 1 shows just the opposite - that the oxide thickness of the high flux irradiated ( $> 1\text{MW}/\text{m}^2$ ) aluminum sample is less than that of the infrared irradiated sample. This paradox was rectified through the study of aluminum oxidation kinetics which showed that the rate of oxidation of aluminum decreases above  $550^\circ\text{C}$ . The measured decrease of oxide thickness at  $500^\circ\text{C}$  (bulk measured temperature) under solar irradiation as compared to infrared irradiation, therefore, indicates surface temperatures under solar irradiation as being higher by about  $100^\circ\text{C}$  than the bulk measured temperatures. This was however, an indirect measure of surface temperature difference under high flux irradiation. More quantitative measure will be seen in the report of the high flux work on nickel.

Additional high flux studies on aluminum have shown that photodesorption of surface localized oxygen and carbon in the forms of CO and  $\text{CO}_2$  also occurs. This process not only further reduces the surface oxide thickness, but also increases the aluminum content at the surface thereby increasing the absorptance of the surface region further enhancing the surface absorption of the high flux solar radiation.

Since photodesorption of surface localized species was observed on the aluminum surface, the photodesorption process was further studied to determine the exact desorption mechanism. CO,  $\text{CO}_2$ ,  $\text{O}_2$

and H<sub>2</sub>O were adsorbed on the aluminum surface and the system exposed to high flux solar simulated radiation. It was determined that a threshold for photodesorption on aluminum was ~3.65 eV, and that solar photons significantly affect surface chemistry. As an example, it was determined that CO<sub>2</sub> was desorbed from a surface under photo-irradiation when only CO was adsorbed, i.e., the solar photons were effective in catalyzing the surface adsorbed CO molecules to CO<sub>2</sub> and desorbing that specie. This was the first observation of high flux photo-enhanced catalysis active at a surface and formed the basis for significant follow-on work in high flux enhanced catalytic reactions.

Stainless-type steels form the basis for a major category of materials utilized in the solar industry. The stainless steels are, however, relatively complex alloys, and as a result, the individual components of the alloys were studied as to their response to high flux solar irradiation.

Both chromium and iron showed minor oxidation enhancements under high flux irradiation. Iron showed oxide thickness enhancements of the order of 8 to 30% under irradiation of from 0.6 to 1.6 MW/m<sup>2</sup> and temperatures of 300 to 500 °C. Chromium showed very similar behavior with the additional complication of significant photodesorption of CO and CO<sub>2</sub>. The desorption yields were relatively large for Cr<sub>2</sub>O<sub>3</sub> which had carbon contamination present (~6 x 10<sup>-4</sup> to 1 x 10<sup>-3</sup> mol/photon). This behavior is quite similar to that observed initially for Black Chrome where the

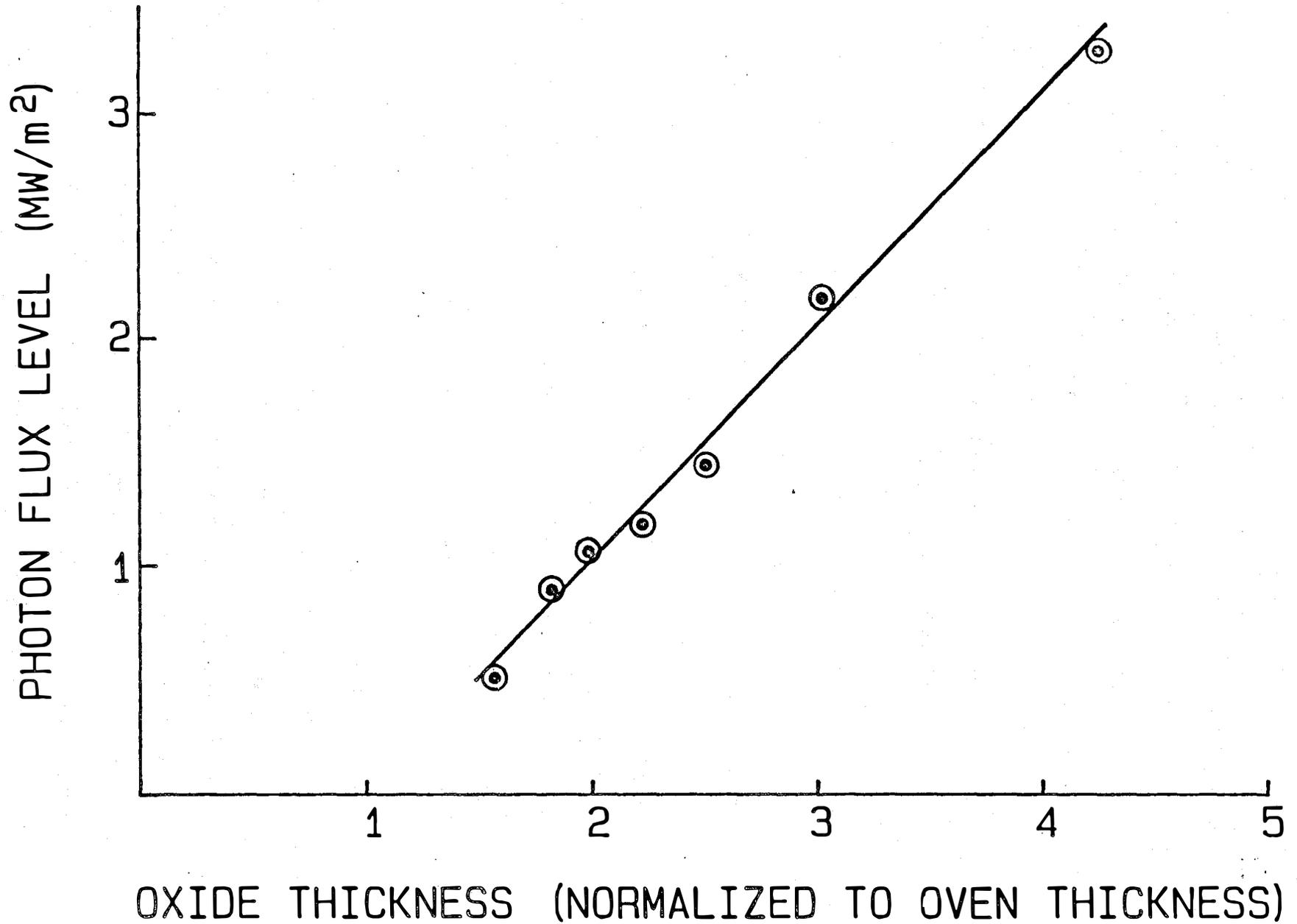


Fig. 2. Dependence of oxide thickness on photon flux for nickel samples.

large desorption yields resulted in reduced oxidation of the chromium. It will be shown later how this will play a role in defining the high flux stability of stainless steels.

Nickel high flux studies led to one of the major discoveries of the program - high flux enhanced oxidation of materials. Nickel, when exposed to high flux irradiation (0.5 to 3.6 MW/m<sup>2</sup>) at elevated temperatures (350 to 550 °C) undergoes significantly enhanced oxidation. Samples were tested over the above noted range of fluxes and temperatures and have shown oxidation enhancements of up to 450% (Fig.2).

Such enhancements could be the result of increased surface temperatures under solar irradiation as observed indirectly in the aluminum system. To test for this possibility, detailed experiments were undertaken utilizing low energy electron diffraction (LEED) to critically measure the surface temperature of a nickel single crystal exposed to high flux irradiation. LEED measures the average temperature of the top three or so atomic layers of the surface. Therefore, the LEED technique does not suffer from the depth uncertainty associated with infrared pyrometer or thermocouple measurements of surface temperature. It is also well to note that a material interacts with its environment through its atomic surface and that processes like oxidation occur in the top atomic layers of the material.

Figure 3 shows the experimental apparatus for the LEED measure-

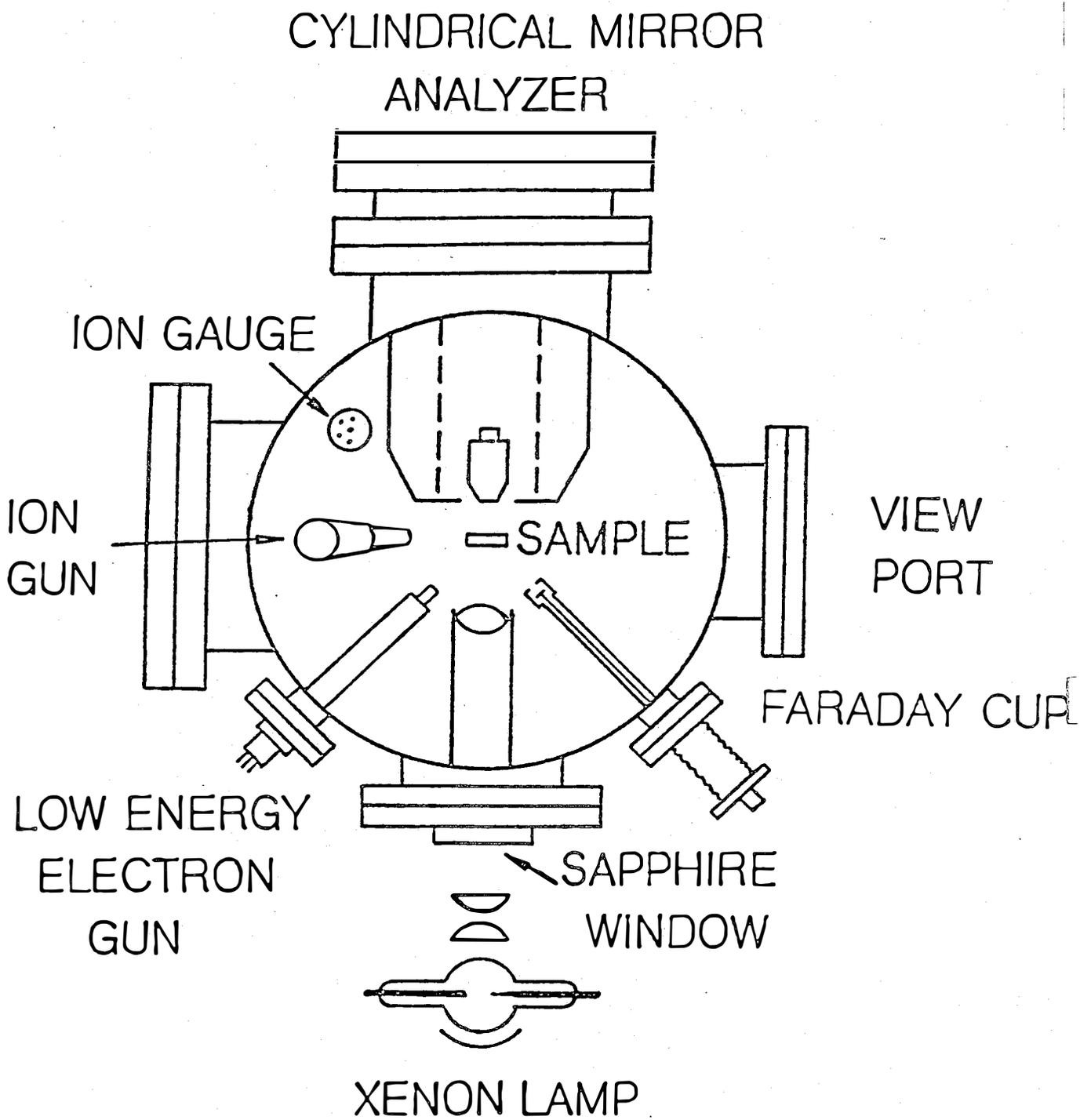


Figure 3. The experimental set-up used for the LEED experiments for the determination of surface temperature under high flux irradiation. The low energy electron gun and the Faraday cup are used for the experiments with the sample irradiated by the high power xenon lamp.

ments. LEED intensity-energy profiles were measured as a function of temperature under infrared, equilibrium heating conditions. These 'temperature standards' were then used to define the temperature of the surface of the high flux solar irradiated sample. Table I lists the surface temperatures and bulk temperatures of an irradiated nickel sample under different levels of solar simulated flux. It should be noted that the data shows that the temperature difference between the actual surface temperature and the bulk sample temperature as measured by a thermocouple can be as large as  $60^{\circ}\text{C}$  at sample temperatures of  $\sim 500^{\circ}\text{C}$  and fluxes of  $\sim 2 \text{ MW/m}^2$ . This data well corroborates the work on aluminum which approximated a  $100^{\circ}\text{C}$  temperature difference between surface and bulk at a solar irradiation of  $1.7 \text{ MW/m}^2$ .

The surface temperature difference of the order of  $60^{\circ}\text{C}$ , however, can not account for the several hundred percent increase of oxide thickness in the nickel. Nickel oxidation kinetics indicate that for nickel to have a  $\sim 400\%$  increase in oxide thickness at a bulk temperature of  $400^{\circ}\text{C}$ , the surface temperature must be at least  $600^{\circ}\text{C}$ . This is outside the acceptable range of surface temperature enhancement under high flux irradiation, and as a result, another mechanism must be responsible for the major enhancement in nickel oxidation.

Wavelength threshold measurements were subsequently undertaken in attempts to determine the mechanism responsible. An eximer laser was used for this purpose as the solar simulator/monochrometer

Table I. Surface and bulk temperatures as a function of flux as measured by low energy electron diffraction from a nickel surface.

SOLAR FLUX	1.0	1.0	1.3	1.6	1.9
SURFACE TEMP. (C)	346	351	407	468	566
BULK TEMP. (C)	323	326	373	420	503
DELTA TEMP (C)	23	25	34	48	63

system used in the previous work did not yield adequate flux for oxidation enhancement measurements as a function of wavelength. Laser experiments yielded the data of Table II. Significant enhancement of oxidation was observed over the whole wavelength range with, however, decreased enhancement noted above 647nm. This decrease in high flux enhanced oxidation occurs near the excitation of the oxygen singlet sigma excited state, and points to the possibility of excited state chemistry playing a role in the observed photo-enhancement.

A singlet sigma excited state for the oxygen could make it more conducive to dissociation on the surface of the nickel/nickel oxide and result in a higher surface density of atomic oxygen yielding greater oxidation. The singlet sigma state at 762nm (1.63 eV), however, is not expected to be optically active with a cross section approaching  $10^{-9}$ . This is for the singlet state in molecular gas phase oxygen, and it may be affected by the chemisorptive character of the bonding of the molecule at the surface. The possibility is, therefore, strong that this excited state of oxygen, excited by the incident high flux solar radiation is responsible for the observed high flux oxidation enhancement in nickel.

With completion of the testing of the major elemental components of stainless-type steels, a series of stainless steel samples were subjected to high flux solar irradiation at elevated temperatures (Table III). All of the samples showed major enhance-

Table II. Laser enhanced oxidation of nickel as determined by AES depth profiling. Sputter time relates to the thickness of the oxide on the surface. The % increase has been normalized to the number of photons at each wavelength.

Wavelength (nm)	Energy (eV)	Flux (W/cm <sup>2</sup> )	# Photons per cm <sup>2</sup> -sec	Sputtering Time (min.)	% Increase Over Oven
308	4.02	50	7.76E+19	19	691
350	3.54	50	8.83E+19	20	644
413	3	66.8	13.91E+19	19.4	395
647	1.83	41.4	14.14E+19	10	173

High Flux	2.8
Infrared Oven	2.4

## Composition of Stainless Steels (%)

	C	Mn	Si	Cr	Ni	Fe	P	S	Mo	Cu	N	Co	Ti
304	0.08	2	1	18.2	8	70.72	-	-	-	-	-	-	-
310	0.06	1.55	0.47	24.88	19.62	52.798	0.03	0.002	0.32	0.27	-	-	-
316	0.054	1.38	0.67	17.21	11.16	66.951	0.03	0.005	2.21	0.33	-	-	-
321	0.042	1.63	0.59	17.46	10.18	68.697	0.025	0.016	0.33	0.42	0.02	0.13	0.46
347	0.6	1.74	0.75	17.77	10.45	67.912	0.029	0.009	0.27	0.22	-	0.25	-
410	0.15	1	1	12.5	-	85.35	-	-	-	-	-	-	-
440C	1.06	0.44	0.58	16.79	0.3	80.809	0.019	0.002	-	-	-	-	-

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Table III.

Composition of stainless steels investigated in this study of photo-degradation.

ments of oxidation under high flux irradiation. This was quite unexpected for the stainless steels since they were supposed to be high temperature stable systems. Detailed studies of the exposed samples through Auger electron spectroscopy depth profiling showed steels with the expected surface localized  $\text{Cr}_2\text{O}_3$  oxidation barrier destroyed. The result was stainless steel which oxidized up to 1000% more under high flux irradiation than under infrared irradiation in equivalent conditions.

The mechanism for the "loss" of the surface  $\text{Cr}_2\text{O}_3$  layer was studied in detail and was determined to be the photodesorption of CO and  $\text{CO}_2$  species from the stainless steel's surface under high flux irradiation. The yields were measured to be in the range of  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  atoms per photon, and were similar to that found for CO and  $\text{CO}_2$  photodesorption from chrome oxide. The photodesorption, therefore, chemically reduced the surface localized chrome oxide thus removing the  $\text{Cr}_2\text{O}_3$  anti-diffusion barrier present in the stainless steels and inducing high temperature oxidation of the iron underlayers.

A critical evaluation of the oxidation enhancement with flux was undertaken for the 304 stainless steel system. Samples were exposed at the Sandia Solar Furnace over a range of flux ( from 0.6 to  $2.6 \text{ MW/m}^2$ ) at  $500^\circ\text{C}$  for a period of 1/2 hour. The data is shown in Figure 4. The data was analyzed for an analytic expression defining the oxidation behavior under high flux oxidation. An extremely good fit to the data was obtained for the

# Oxide Thickness vs Flux

Stainless Steels, Type 304

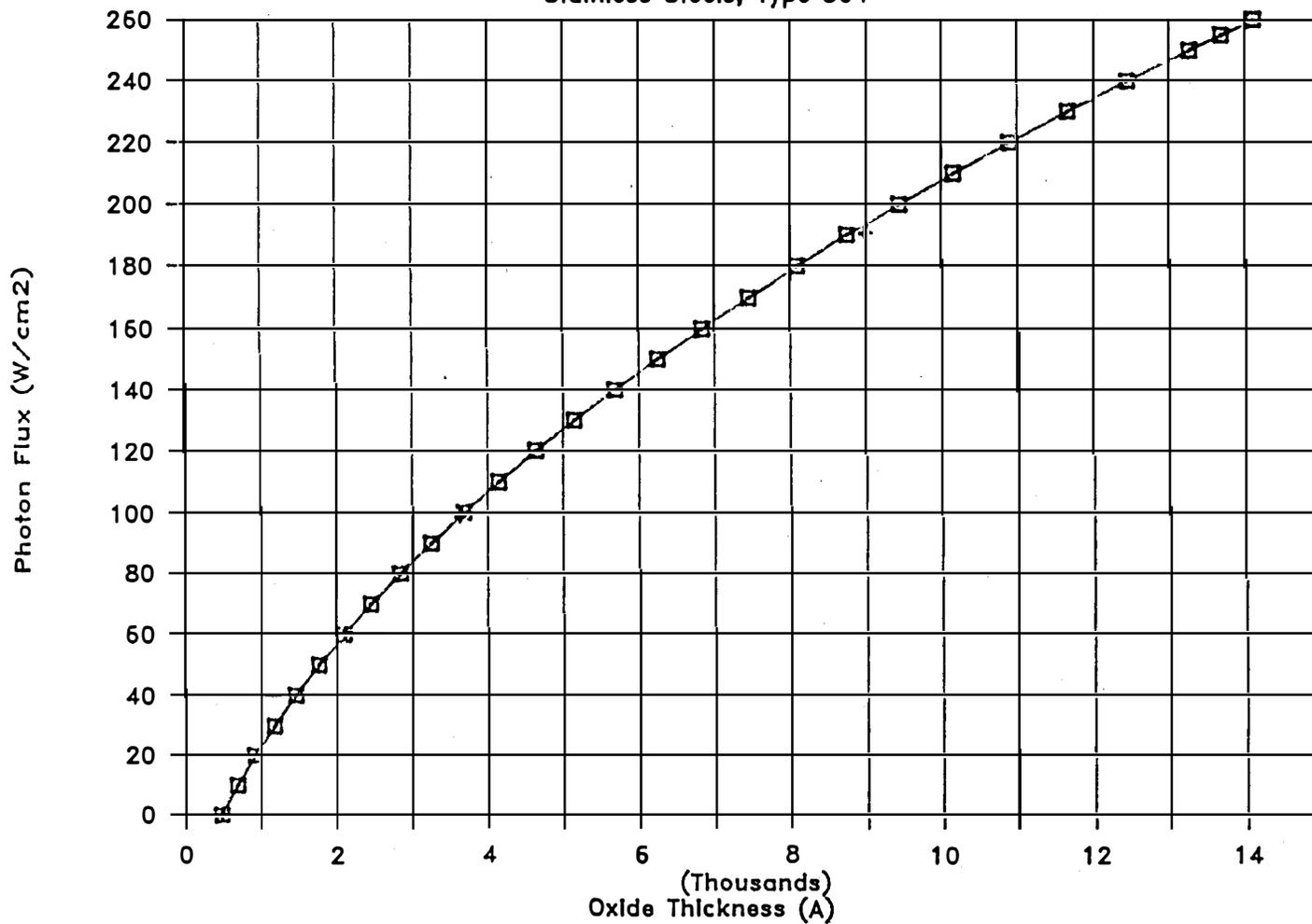


Figure 4. Oxide thickness for # 304 stainless steel as measured by Auger electron spectroscopy depth profiling.

expression:

$$X = X_0 + B F + A F^2$$

where  $X_0 = 480 \text{ A}$

$B = 19.4 \text{ A cm/W}$

$A = 0.13 \text{ A cm}^2/\text{W}^2$

The behavior is non-linear in flux and clearly indicates the major problems to be expected in the use of stainless steels under high flux levels. Note that even at nominal fluxes of  $1 \text{ MW/m}^2$  ( $100 \text{ W/cm}^2$ ), the enhancement in oxidation can be up to 900%, and that operation at flux levels can lead to oxidation enhancements of over 5000%.

#### SUMMARY

In summary, the above noted studies have conclusively shown that high flux photo-irradiation of materials can result in significant changes in the stability of the materials. The major mechanisms have been determined to be photodesorption and photo-enhanced oxidation. These mechanisms have been shown to affect, in extremely adverse ways, the expected thermal stability of solar relevant materials, especially stainless steels (it is expected that related high temperature alloy steels will be similarly affected), and an analytical expression has been generated to predict the flux behavior of the steels using #304 as a

prototypical stainless steel system.

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11. "Photodesorption from Stainless Steels", A. Mesarwi and A. Ignatiev; J. Vac. Sci. Technol. (in print).

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