

ELECTRON SPECTROSCOPIC STUDIES OF ION-BOMBARDMENT REDUCTION; L. Yin, T. Tsang*, Code 691.2, Goddard Space Flight Center, Greenbelt, Md. 20771, and I. Adler, University of Md., College Park, Md. 20742.

From many simulated laboratory experiments and from returned lunar samples, it has been established that iron-containing lunar fines may be effectively reduced to metallic iron by solar-wind proton bombardment. The presence of metallic iron is a significant cause of the observed low optical albedo (darkening) of the lunar surface.

Previously (1) in our electron spectroscopic (ESCA) examination of the ion-bombardment reduction mechanism we have established that the reduction is (a) definitely accompanied by the loss of the anion species, (b) relatively insensitive to the mass of the bombarding ion such as He or Ar, (c) dependent only on total ion dosage rather than current density, and (d) not simply related to physical sputtering. Based on these results we have inferred that complete reduction of Fe to the metallic state under solar-wind proton bombardment would require ~ 850 years on the lunar surface, and that the reduction mechanism is probably more chemical than physical in nature and may be governed strongly by the characteristics of the transition metal ion. In a continuing effort to elucidate the reduction mechanism we have chosen to limit ourselves to the simple compounds of the first row transition metals such as the halides and some cyanides rather than the oxides, silicates or minerals in order to avoid the complexity as well as the ubiquitous presence of oxygen in all contaminants.

Ion bombardments were carried out by glow-discharge with Ar ions at 0.2 ma/cm^2 ion current density and 2 keV energy. All samples are in the form of $< 35 \mu$ fine powders. Photoelectron spectra of the core levels of the cation and the anion as well as the valence band region were monitored in all ion-bombardment sequences. Reduction of the cation to the metallic state is evidenced by (a) the loss and near disappearance of the anion core level photoelectron spectral intensity, (b) the shift and alteration of the 2p photoelectron characteristics of the cation which becomes identical to that of the metallic foil sample, and (c) the shift and alteration of the valence region spectra which also becomes identical to that of the metallic foil sample. The experimental results are summarized below.

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1. In the sequence of FeF_2 , CoF_2 , NiF_2 , CuF_2 (electronic configuration $3d^6-3d^9$) the ion-bombardment times needed to achieve complete reduction of the cation to its metallic state are, respectively, 145 min., 120 min., 65 min., and 3 min. The next member, ZnF_2 ($3d^{10}$), shows no reduction even after 145 min. of bombardment. Because our sample layer is extremely thin, after ~ 140 min. of ion bombardment there is very little sample left due to the loss from physical sputtering.

2. With CuCl_2 and CuCl samples, CuCl shows no reduction after ~ 140 min. of ion bombardment. CuCl_2 , on the other hand, reduces to CuCl in about 5 min., but remains as CuCl throughout the rest of the bombardment sequence. This is to be contrasted to CuF_2 which reduces to metallic Cu in 3 min.

3. Although CuCl ($3d^{10}$), does not show signs of reduction, CuCN can be reduced to metallic Cu in ~ 15 min. In general, the cyanides have much higher reduction efficiencies than the halides, e.g. $\text{Ni}(\text{CN})_2$ ~ 5 min., $\text{Co}(\text{CN})_2$ ~ 5 min.

These results may be compared with the recent proposal of Kim et al. (2) where the ion-bombardment reduction rates are correlated with the bulk room-temperature free energy of the compounds. They assume the presence of a "local thermal quasi-equilibrium". We note that thermodynamic parameters deal in general with initial and final states alone, and do not explain the reduction process itself. Furthermore, our results indicate wide ranges of reduction efficiencies (factors of 10 - 100) among compounds with comparable free energies. This raises questions on the existence of local thermal equilibrium and hence, the applicability of thermodynamics to surfaces under low-density, low-energy ion bombardment.

From their experimental results on ion-sputter vaporization, Hapke, Cassidy and Wells (3,4) have recently proposed that under ion bombardment the heavier elements such as Fe more readily re-condense onto the cold surfaces of adjacent grains, whereas the lighter and more volatile elements such as O, with smaller sticking coefficients, tend to escape. Thus an effective fractionation process is established subsequent to physical sputtering which leaves the sample surface enriched in metallic iron. However our results imply that physical sputtering and reduction are in reality two independent mechanisms which occur concurrently under ion bombardment. The linear enhancement according to mass of the species which are sputtered from the sample and then recondensed on another surface as observed by Hapke et al. seems to play only a minor role on the sample surface itself. This is demonstrated by (a) the large differ-

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ence between the reduction efficiencies of CuF_2 (3 min.) and ZnF_2 (> 140 min.) where the mass difference between Cu and Zn atom is only $\sim 3\%$ and the sticking coefficient of F should be identical from both samples, and (b) although CuCl and CuCl_2 involve two identical atomic species, their behavior under ion bombardment is widely different as discussed above. Thus, on the sample surface itself, the enhancement of the metallic species is clearly due to a much more complex reduction mechanism. On the lunar surface, there is a finite probability of return of the sputtered-off species depending on their mass and sputtered velocities (not recondensing until after their return); however, the magnitude of this form of enhancement will become significant only at high sputter temperatures.

Our results imply that ion-bombardment reduction most likely will involve atomic and molecular excitation and charge-transfer processes which depend on the energy available for excitation, transition probabilities, as well as the overlap between the metal 3d and the ligand orbitals.

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