# Reports of the Academy of Sciences of the USSR

1960

## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 132, No. 5

## PHYSICAL CHEMISTRY

**M. S. BELETSKII and M. I. ERUSALIMSKII**

# ON THE MECHANISM OF PROTECTION OF MAGNESIUM FROM OXIDATION

*(Presented by Academician G. V. Kurdyumov, February 13, 1960)*

Pure magnesium, after being in air for a long time at room temperature, becomes covered with an oxide film that prevents oxygen from penetrating into the metal. As the temperature is raised, the thickness of the oxide film increases. Upon reaching a certain limiting temperature, Mg ignites and burns.

The reason for this behavior of magnesium and for its interaction with oxygen is explained by the specific structure of its electron shell. In the magnesium atom, its two valence electrons, having oppositely directed spins, in the free state fill the $3s$ subgroup. When in a crystal, both valence electrons of each atom are placed in $3s3p$-hybrid orbitals; their spins acquire the same directions. In magnesium atoms located on the surface of a solid, some of the bonds are uncompensated and they are under the influence of a weaker potential field created by the surrounding atoms. Therefore it may be considered that their properties (those of the surface atoms) are closer to the properties of free atoms than to those of internal atoms. Thus, the valence electrons of the surface layer of magnesium atoms, being mainly in the $3S$ state, should readily form an exchange bond with the $p$-electrons of oxygen.

The concepts set forth regarding the mechanism of magnesium oxidation have been confirmed experimentally by introducing neodymium into the surface layer of magnesium; apparently, this transferred the valence $3s$-electrons of the magnesium atom to a higher $3p$-level, shielding them, in accordance with the "selection rule," from exchange bonding with the valence electrons of oxygen. Consideration of the structure of the electron shells of atoms made it possible to establish that not only neodymium, but also certain other elements, are suitable for this purpose.

The oxidation behavior of magnesium was judged from the change in the character of the electron-diffraction pattern obtained from the corresponding specimens.

Specimens for electron-diffraction studies were prepared in a vacuum evaporation chamber providing a pressure on the order of $5—7 \cdot 10^{-6}$ mm, which excluded

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the possibility of oxidation of the metal in it. A very thin collodion film stretched over brass washers was used as the substrate for the evaporated metals. The starting materials for evaporation were: 98% neodymium and a magnesium-neodymium alloy containing 45% neodymium. Magnesium of 99.98% purity was subjected to oxidation.

The conditions for evaporation of the metals were kept, as far as possible, identical. The distance from the collodion film to the molybdenum spiral was 95-97 mm. For sputtering magnesium and the magnesium-neodymium alloy, the heating current of the spiral, inside which one of them was placed, was slowly brought to 5 A, and then rapidly increased to 7-8 A and maintained at this value for 3-5 sec. Neodymium was sputtered at a higher temperature. For this purpose the current of the spiral was slowly increased to 10 A, then rapidly to 18-20 A, and maintained at this value for 10-15 sec.

**Fig. 1.** Electron diffraction pattern of a magnesium film immediately after transfer from the evaporation chamber (a), after being exposed to air for 24 hours (b), and the same after 72 hours (c).

**Fig. 2.** Electron diffraction pattern of a magnesium film with a small amount of Nd, obtained immediately after evaporation (a), and the same after one month of exposure to air (b).

The metallic films obtained under the indicated conditions, after cooling in vacuum, were removed from the evaporation chamber and quickly placed in an electron-diffraction apparatus prepared for operation. After the first recording of the electron diffraction patterns, the films were kept in air at room temperature for various periods of time, after which they were again subjected to electron-diffraction examination at a voltage of 40 kV.

In Fig. 1a, b, c are shown electron diffraction patterns of evaporated magnesium films that had been in contact with air for different intervals of time. It turned out that the rate of oxidation of pure magnesium is very high. Magnesium oxide formed even during a very short interval of time (1-2 min), while the film was being transferred from the evaporation chamber to the electron-diffraction apparatus.

Figure 1a shows the electron diffraction pattern of such a specimen. In it, in addition to the interference rings with indices (100) and (101), characteristic of magnesium, weak rings (002) and (022), belonging to magnesium oxide, are also visible.

In the electron diffraction pattern of the same film after being kept in air for 24 hours (Fig. 1b), the interference rings of magnesium oxide are of considerably greater intensity, whereas the intensity of the corresponding rings from magnesium has decreased.

With a further increase in the duration of the magnesium film' s exposure to air, more complete oxidation takes place. From the electron diffraction pattern (Fig. 1c) it is evident that the amount of magnesium in the specimen is considerably smaller than before. The amount of magnesium oxide, on the contrary, has increased.

The oxidation of neodymium proceeds in an entirely different way. In the electron diffraction pattern of neodymium that had not been exposed to air, distinct interference rings with indices (100), (102), (103), (006), etc. are visible. After neodymium has been in contact with air at room temperature for one hour, changes occur in it as a result of which, in the electron diffraction pattern, some interference rings disappear while others become blurred. Such a character of the change in the diffraction pattern may indicate the onset of the oxidation process of neodymium and a decrease in the degree of long-range order in the arrangement of atoms in its crystal lattice.

A similar investigation was also carried out with magnesium films that had interacted with neodymium. In this case the task consisted in evaporating onto the surface of magnesium such an amount of neodymium that the intermetallic compound $Mg_9Nd$, whose properties differ significantly from those of magnesium, would not be formed. This task was successfully solved by experimental selection of the evaporation regime.

Figure 2a contains an electron diffraction pattern obtained immediately after the evaporation of magnesium and a very small amount of neodymium. Interpretation of the electron diffraction pattern showed that all intense interference rings belong to magnesium. Only one weak ring belongs to magnesium oxide. The formation of oxide in this case is possible owing to the small amount of oxygen remaining in the evaporator despite the maintenance of a high vacuum in it ($10^{-5}$ mm).

Figure 2b shows an electron diffraction pattern obtained from a magnesium film with neodymium after it had been kept in air for one month at room temperature. As is evident from this electron diffraction pattern, the character of the interference rings of magnesium has not changed, despite the prolonged action on it of oxygen from the air. This circumstance indicates a significant influence of neodymium atoms on the inhibition of the oxidation process of magnesium. This influence of neodymium is undoubtedly connected with the structural features of the electron shell of its atom and that of the magnesium atom. As is known, in the neodymium atom one valence electron is located in the 5d shell and two electrons in the 6s shells. According to the selection rule, the 5d shell can contain 10 electrons.

The presence, on the last electron diffraction patterns, of interference rings only

from magnesium indicates very small amounts of neodymium in the specimens. Therefore it may be assumed, in accordance with the theory of the structure of semiconductors ([2]), that in the neodymium atoms present in the specimens under study the existing energy bands do not overlap, and that the distribution of electrons in them is the same as in free atoms.

All-Union Scientific Research
Aluminum-Magnesium Institute

Received
6 II 1960

## CITED LITERATURE

[1] Yu. M. Rozenri, *Atomic Theory for Metallurgists*, Moscow, 1954. [2] A. F. Ioffe, *Theory of Semiconductors*, Publishing House of the Academy of Sciences of the USSR, 1957.

*Note: Figure translations are in progress. See original paper for figures.*