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Experiments Shed New Light on Nickel–Fluorine Reactions

The problem:

To obtain a better understanding of the mechanism and kinetics of the nickel–fluorine reaction. This reaction may aid in the development of new fluorine chemical processes for industrial products.

The solution:

Fluorine was found to be the migrating species through the nickel fluoride scale formed during the fluorination of nickel. This is in contrast to nickel oxide scales, where nickel is the migrating species. The reaction rates of the process did not depend upon the type of nickel, but were a function of scale thickness and pressure.

How it's done:

Marker (isotopic tracer) experiments were conducted in which radioactive nickel-63 was used, as well as scale-impingement experiments in which two scales formed during the reaction were forced to impinge upon each other. These experiments helped to determine whether nickel or fluorine migrated through the nickel fluoride scale formed during the fluorination of nickel. Similar experiments were performed with the nickel–oxygen system, a reaction of known mechanism, to verify the experimental method used in the nickel–fluorine study.

The radioactive tracer experiments indicated that fluorine migrates through the growing fluoride scale. The migration of fluorine was evidenced by the lack of movement of the radioactive tracer, which was located at the nickel fluoride scale–fluorine gas interface.

In the nickel–oxygen experiments, the radioactivity was found to be distributed through the oxide scale in a manner predicted from the known mechanism, i.e., that nickel migrates through the nickel oxide scale to the nickel oxide–gas interface.

In the fluoride scale-impingement experiments, the existence of an interface between the two scales growing from opposing surfaces, indicated that fluorine is the migrating species. In the oxide scale-impingement experiments, a continuous scale was formed, thereby indicating that nickel is the migrating species.

Notes:

1. The kinetics of the nickel–fluorine reaction have been studied between 300° and 600°C, using high purity and commercial nickel. The parabolic rate constants for the reaction with high purity nickel were found to be 9.8, 81, 461, and 1860 ($\mu g\ F^2/sq\ cm)^2$ per minute at 300°, 400°, 500°, and 600°C, respectively. No significant difference in reaction rates for the two types of nickel was noted except in the initial portion (less than 500 min) of the reaction period. The parabolic rate was found to be independent of the pressure of fluorine over the range of 100 to 700 mm Hg when the thickness of the nickel fluoride scale was 10^4 Å or less. After a scale having thickness of about 10^5 Å had been deposited, the rate of scale formation was found to vary with the one-half power of the fluorine pressure.
2. Additional details are contained in *The Mechanism and Kinetics of the Reaction between Nickel and Fluorine*, by R. L. Jarry, W. H. Gunther, and J. Fischer, Argonne National Laboratory, Report No. ANL-6684, August, 1963. This report is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151; price $3.00; microfiche $0.65.

(continued overleaf)

3. Inquiries concerning this innovation may be directed to:

Office of Industrial Cooperation
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439
Reference: B67-10397

Source: R. L. Jarry, W. Gunther, and J. Fischer
Chemical Engineering Division
(ARG-10008)

Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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