Fig. 14—Dependence of rate on catalytic surface area.

that d , the density, is either constant or can only increase till it reaches the density of solid nickel. A comparison of the number of particles at $i = 1$ and at $i = 5$ gives a ratio of 4. Thus, the process of agglomeration, which results in a decrease in the number of particles at the end of a nickel reduction in which Fe^{++} is used as a catalyst, probably continues in the early densifications when the particles are still fine. The critical size of the particles at which agglomeration ceases depends on many factors, of which degree of agitation is probably very important.

Summary

Both theory and practice show that the reduction of nickel proceeds to completion only when the NH_3/Ni molar ratio is in the range of about 1.5 to 2.5.

The reaction is catalyzed by Fe^{++} , resulting in the formation of metallic nickel nuclei, which further catalyze the reaction, causing an acceleration of the reaction rate (autocatalysis). The acceleration may be explained by assuming a constant rate of formation of the nuclei and a direct proportionality between the rate of reduction and the number of the nuclei.

The nuclei probably not only grow during reduction, but also agglomerate into larger sized particles and gradually assume the spherical form. When a certain critical size is reached, the agglomeration process ceases and the particles grow symmetrically in all directions. At this stage, the rate of reduction is found to be directly proportional to the calculated surface area of the nickel particles.

Apart from the effect of catalysts, the reaction rate is found to be proportional to the H_2 partial pressure to the first order (approximate), to be independent of the nickel concentration in solution, and to have

Fig. 15—Growth of nickel particles (r^3 vs i). Closed circles refer to interpolated values; open circles, experimental values.

an apparent energy of activation of between 5 and 15 kcal.

Acknowledgments

The authors wish to thank Sherritt Gordon Mines Ltd. for providing the opportunity and encouragement to work on this problem and for permission to publish the results. They wish to express their gratitude to F. A. Forward and the late S. Nashner for their interest and support of the work, to thank J. Halpern for his contribution to the treatment of the kinetics of the Fe^{++} catalyzed reaction, R. L. Benoit for his contribution to the treatment of the thermodynamics of the reduction of nickel in ammoniacal solutions, and J. P. Auffray for his part of the work on the nickel particle growth problem.

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Discussion of this paper sent (2 copies) to AIME by Aug. 1, 1957 will appear in *AIME Transactions* Vol. 212, 1958, and in *JOURNAL OF METALS*, October 1958.

Technical Note

Bismuth in Copper Grain Boundaries

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TN 407E. Manuscript, Nov. 30, 1956.

SPECIMENS of five cast Cu-Bi alloys, containing 4.68, 0.53, 0.043, 0.0064, and 0.0025 wt pct Bi and cast pure copper were subjected to a bend test to determine their relative ductility. Using metallographic methods the structures of the fractured surfaces were compared with those of the polished cross sections. Embrittlement was found to be associated with the presence of a second phase in the grain boundaries although, in the lower bismuth