cross section within which the ion must pass if it is to incur at least the percentage energy loss indicated as abscissa. It is believed that the curves will lend themselves in a very satisfactory manner to analysis of the forces existing between the particles.

The author wishes to acknowledge gratefully the guidance and valuable suggestions of Doctor Robert N. Varney who directed this problem by correspondence from the Naval Proving Ground at Dahlgren, Virginia; also the courtesies extended by Professor A. L. Hughes, Professor G. E. M. Jauncey, and Doctor Joseph Keller of this department.

PHYSICAL REVIEW VOLUME 63, NUMBERS 11 AND 12 JUNE 1 AND 15, 1943

Diffusion Rates of Carbon in Iron-Molybdenum and Iron-Tungsten Alloys

R. SMOLUCHOWSKI
Research Laboratory, General Electric Company, Schenectady, New York
(Received March 24, 1943)

Measurements are reported of the influence of tungsten and molybdenum on the diffusion rate of carbon in face-centered iron at 1000°C. Both of these elements slow down the diffusion of carbon, the influence of tungsten being more than twice that of molybdenum. These results are compared with previous measurements on iron-cobalt alloys and other known data. No connection seems to exist between the variation in lattice parameter of face-centered iron and the variation in diffusion rate of carbon.

IN a previous paper[1] a strong accelerating influence of cobalt on the diffusion rate of carbon in face-centered iron was reported.* In continuation of this study, experiments were made with iron-molybdenum and iron-tungsten alloys.

There are relatively few binary systems in which measurements of this type can be made conveniently. The main condition is the existence of a sufficiently wide range of homogeneous face-centered solid solution. It should be possible to vary the concentration of carbon and of the alloying element, within relatively wide limits, to suit the accuracy of the measurements. Both in tungsten-iron and in molybdenum-iron alloys no single phase region with face-centered lattice exists beyond a few percent of the added element. Carbon, however, increases this range somewhat. Accordingly, experiments were made with the following alloys; the tungsten pair: 1.1 atomic percent (about 3.5 wt. percent) tungsten with 2.6 atomic percent (0.58 wt. percent) carbon and with 0.22 atomic percent (0.05 wt. percent) carbon; the molybdenum pair: 1.1 atomic percent (about 1.9 wt. percent) molybdenum with 3.1 atomic percent (0.7 wt. percent) carbon and without carbon, and finally a pair of alloys with the same molybdenum content but with 4.2 atomic percent (about 0.9 wt. percent) carbon, and without carbon. The first two groups of alloys, the tungsten alloys and the molybdenum alloys with lower carbon content, fall within the region of homogeneous face-centered lattice at 1000°C.[2] The third group, the molybdenum alloys with higher carbon, fall into the region where at 1000°C some of the carbides do not dissolve. These alloys were included in the experiments in order to see to what extent the presence of carbides affects the observed diffusion.

The experimental method was essentially the same as that used in the previous investigation. The welded samples were heated for three days at 1000°C and the concentration of carbon in layers parallel to the interface was determined.

[1] R. Smoluchowski, Phys. Rev. **62**, 539 (1942).

* *Note added in proof:* Mr. Malcolm F. Hawkes and Dr. Robert F. Mehl of the Carnegie Institute of Technology kindly informed me that their experiments do not show this strong accelerating influence of cobalt. This point needs thus further experimental clarification in particular in view of reference 6 quoted in reference 1 of this paper.

[2] S. Takeda, Tech. Rep. Sendai **9**, 483 (1930); **9**, 627 (1930); and **10**, 42 (1931). E. C. Bain, *The Alloying Elements in Steel* (Am. Soc. Metals, Cleveland, Ohio, 1939).

An interesting phenomenon was observed in the case of tungsten alloys. In order to prevent decarburization, all samples were enclosed in quartz tubes filled with argon. In each tube were two samples; one with iron containing molybdenum or tungsten and another with pure iron, in order to be able to compare the diffusion rates in iron and in iron alloy under identical conditions. Determination of the carbon concentration in the first heat-treated tungsten-iron samples showed that the carbon-rich side was somewhat decarburized and the carbon-poor side was carburized on the surface. There was a radial gradient of carbon concentration. No such effect was observed on the pure iron sample which was enclosed in the same quartz tube and thus underwent the heat treatment simultaneously with the iron-tungsten sample. An explanation of this effect, on the assumption that the argon used was impure, is difficult to accept because of the absence of this decarburization and carburization in the pure iron sample. Such an effect is, of course, very undesirable because it affects the concentration gradient due to volume diffusion and thus falsifies the results. In order to prevent it, the samples were covered electrolytically with a 0.3-mm thick layer of copper before heat treatment. This protective measure was applied to all samples, and it eliminated the occurrence of these surface phenomena. The computation of the diffusion coefficients was made by the usual Grube method. Because of the presence of the alloying elements on both sides of the interface, the computations were simple, and the use of the corrective formulae derived in the previous paper was not necessary.

The numerical results at various carbon concentrations are given in Table I.

The decelerating influence of both tungsten and molybdenum on the diffusion rate of carbon is clearly seen. For the same atomic percentage of added element, tungsten is much more effective than molybdenum. In Fig. 1 are plotted the diffusion coefficients of carbon in various iron alloys at 1000°C. Former measurements on iron-cobalt alloys[1] are included, also Wells and Mehl's data on iron-nickel alloys and iron-manganese alloys[3] and the recent measurements of Ham, Parke, and Herzig on iron-molybdenum alloys.[4] The latter were made with 0.47 atomic percent (0.80 wt. percent) molybdenum at various temperatures. The corresponding points in Fig. 1 were obtained by interpolation from Table III in Ham, Parke, and Herzig's paper at 1.1 and 2.2 atomic percent carbon. We see that the agreement is satisfactory, the influence of molybdenum being somewhat stronger than that reported here. The difference easily may be due to experimental errors and interpolation inaccuracies.

The diffusion coefficients given in Table I

TABLE I. Diffusion coefficients of carbon in iron-molybdenum and in iron-tungsten alloys at 1000°C. $D \times 10^7$ cm^2 sec.$^{-1}$.

Atomic percent carbon	Pure Fe	Solvent 1.1 at. percent Mo	1.1 at. percent W
0.6	2.9	2.5	1.1
1.1	3.2	2.6	1.2
2.2	3.7	2.8	1.25

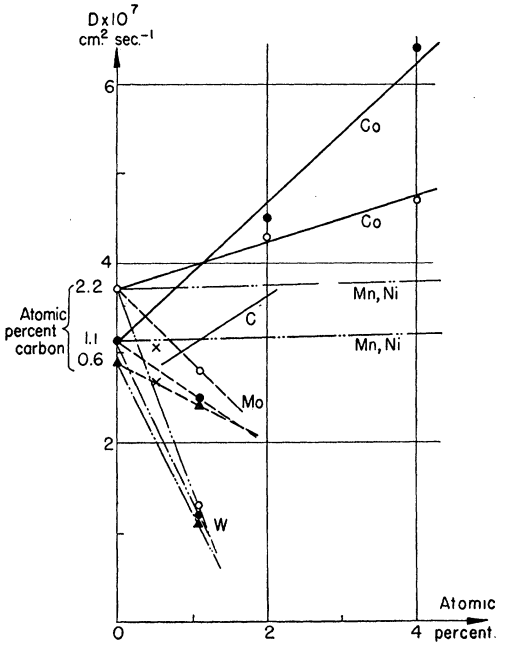

FIG. 1. Diffusion coefficients of carbon in various iron alloys at 1000°C. (Data for Mn and Ni were obtained from reference 3. Crosses indicate values for Mo based on reference 4.)

[3] C. Wells and R. F. Mehl, Trans. A. I. M. E. **140**, 279 (1940).

[4] J. L. Ham, R. M. Parke, and A. J. Herzig, Am. Soc. Metals, Preprint, 1942.

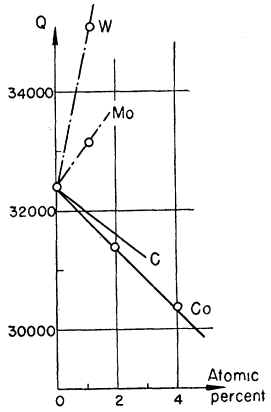

FIG. 2. Activation energies of the diffusion of carbon in various iron alloys.

and Fig. 1 were obtained with alloys which form solid solutions at 1000°C. As mentioned before, experiments were made also with another molybdenum alloy which had a little more carbon than the solubility limit at that temperature. The diffusion coefficients obtained from this alloy were within 15 percent of those given in Table I. This shows only that the few carbides present were quickly dissolved when the concentration of the surrounding solid solution decreased and thus they did not affect appreciably the total diffusion rate. In general, one would expect deviations from the simple concentration distribution law and other complicating effects.

In the previous paper, it was shown that the Dushman-Langmuir equation gives values of the activation energy Q in good agreement with experimental data in the case of iron-cobalt alloys. The same formula was applied here, and we assumed as before that the "free path" δ was 1.8A. We shall not repeat the details and discussion of the limitations of this procedure. The results for 1.1 atomic percent carbon are shown in Fig. 2 where the values for various iron alloys, including those investigated earlier, are plotted against the composition. A strong increase of the activation energy due to the presence of tungsten and molybdenum is apparent. It should be stressed that it is perfectly justifiable not to take into account the variation in δ with composition. A change in the lattice constant of one percent changes the value of Q by about 50 calories, which is, of course, entirely negligible as compared with the effects here observed.

It seemed interesting to see if there is any correlation between the changes in the lattice of iron brought about by the dissolved elements and the change of the rate of diffusion of carbon. Practically no data are available on the lattice constants in the face-centered lattice range of the iron-tungsten and iron-molybdenum alloys. In order to obtain a rough estimate of the influence of these two elements on the lattice of face-centered iron, measurements were made of the density and thermal expansion in the proximity of 1000°C. It turned out that both tungsten and molybdenum expand the iron lattice at a rate which is close to that computed from atomic radii, that is, about 2 percent per 10 percent of added element. Let us compare the change in the diffusion rate of carbon in iron due to the presence of other metallic elements as pictured in Fig. 1 on the one hand, and the change in lattice constants on the other. It turns out that there is no simple relation: cobalt, which leaves the iron lattice constant practically unaltered,[5] accelerates the diffusion markedly. On the other hand, carbon, which accelerates its own diffusion almost as effectively as cobalt, increases the lattice constant of iron rapidly, because of its interstitial location. Molybdenum and tungsten, which both have practically identical atomic radii, decrease this rate to a very different extent. The influence of tungsten is more than twice as strong as that of molybdenum. Nickel has practically no influence on the rate of diffusion, but it decreases the lattice constant of the face-centered iron.[6] Manganese, like nickel, leaves the diffusion rate practically unchanged, but increases the lattice constant of face-centered iron.[7] In the previous paper it was stated that the simple model of carbon atoms diffusing through the crystal lattice of iron, in which only the geometrical factors play a role, is untenable and that only a study of the influence of the alloying elements on the electronic interactions between the iron lattice and the carbon atoms can correlate the observed facts. The results here reported add support to this conclusion.

[5] A. Osawa, Sci. Rep. Tohoku **19**, 109 (1930).
[6] E. A. Owen, E. L. Yates, and A. H. Sully, Proc. Phys. Soc. **49**, 315 (1937): H. Esser and G. Müller, Arch. f. d. Eisenh. **7**, 265 (1933–1934).
[7] E. Öhman, Zeits. f. physik. Chemie **B8**, 81 (1930).