82. A Study on the Structure of Cementite.

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Cementite, iron carbide Fe_3C, is an extremely hard and brittle substance and generally assigned to rank $6 \sim 6.5$ in Mohs' scale of hardness. It occurs as microscopic crystals in steel or pig iron.

By the existence of manganese, cementite unites with manganese to form "Spiegeleisenkristall" and becomes very stable and grows from microscopic to single crystals of about $5 \sim 30$ m/m long, $3 \sim 5$ m/m and 1/2 m/m thick. As the atomic weight of manganese is nearly the same as that of iron, if we assume that manganese unites with cementite by the replacement of iron atoms, it so happens that the presence of manganese in cementite affects but very little its carbon content, and was confirmed, by means of the chemical analysis.

Cementite has the magnetic transformation point at 210° C, but this is not an allotropic change, so the crystal structure is not altered at this point.

The crystal structure of cementite was röntgenographically investigated by Westgren and Phragmén,[1] Polaniyi, Wever,[2] and Bain,[3] but the atomic arrangement in crystal lattice was not determined.

Results obtained by these authorities are:

(1) Manganese does not affect the atomic arrangement of cementite, that is the crystal structure of Spiegeleisenkristall is equal to that of cementite.

(2) Cementite or Spiegeleisenkristall belongs to the orthorhombic system and the dimension of the unit cell is:

By Westgren & Phragmén	$a=4.53$ Å	$b=5.11$ Å	$c=6.77$ Å
„ Wever	$a=4.48_1$ Å	$b=5.03_9$ Å	$c=6.70_8$ Å
„ Polanyi	$a=4.52$ Å	$b=5.01$ Å	$c=6.74$ Å

(3) The number of Fe_3C molecules in a unit cell is 4.

In the present experiment both cementite and Spiegeleisenkristall

1) Jour. of Iron & Steel Inst. **105** (1922), p. 241.
2) Mitt. Kaiser-Wilhelm-Inst. für Eisenforschung. **4** (1922), p. 67.
3) Chem. & Met. Eng. II (1921), p. 657.

were studied by the X-ray-spectrometric-method, Laue-method, Powder-method, and Rotation-crystal-method.

In the first place, it was reconfirmed that manganese does not affect the crystal structure of cementite except a slight contraction of lattice constants.

The dimension of the unit cell determined is:

For cementite..... $a=4.51_1$ Å $b=5.04_6$ Å $c=6.73_8$ Å
„ Spiegeleisenkristall $a=4.50_4$ Å $b=5.03_8$ Å $c=6.72_8$ Å

For all practical purposes, the values $a=4.51$ Å, $b=5.04$ Å, $c=6.73$ Å were used for both cementite and Spiegeleisenkristall.

In the next place, it was found that cementite and Spiegeleisenkristall belong to the simple orthorhombic lattice "Γ_0" and the space group "V_h^{16}."

Lastly, the distribution of each atom for 4 Fe_3C in the unit cell was determined to be as follows:

4 carbon atoms at (c_2):

$u_2,\ v_2,\ 0\ ;\ \bar{u}_2,\ \frac{1}{2}-v_2,\ \frac{1}{2}\ ;\ \frac{1}{2}-u_2,\ v_2+\frac{1}{2},\ 0\ ;\ u_2+\frac{1}{2},\ \bar{v}_2,\ \frac{1}{2}.$

4 iron atoms at (c_1):

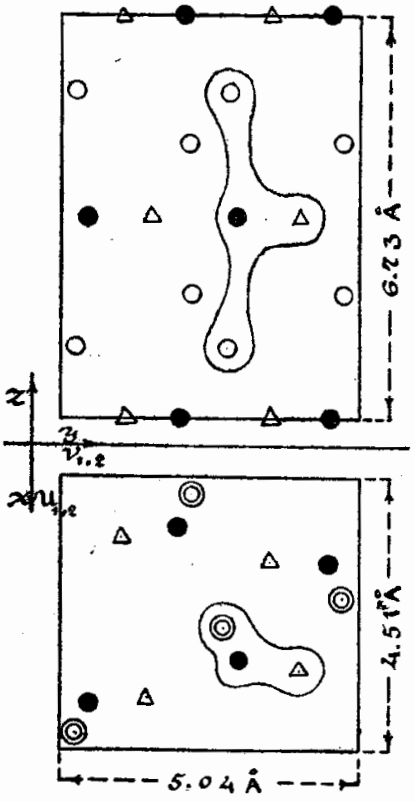
$u_1,\ v_1,\ 0\ ;\ \bar{u}_1,\ \frac{1}{2}-v_2,\ \frac{1}{2}\ ;\ \frac{1}{2}-u_1,\ v_1+\frac{1}{2},\ 0\ ;$
$u_1+\frac{1}{2},\ \bar{v}_1,\ \frac{1}{2}.$

8 iron atoms at (d):

$x,\ y,\ z\ ;\ \bar{x},\ \frac{1}{2}-y,\ z+\frac{1}{2}\ ;\ \frac{1}{2}-x,\ y+\frac{1}{2},\ \bar{z}\ ;$
$x+\frac{1}{2},\ \bar{y},\ \frac{1}{2}-z\ ;\ \bar{x},\ \frac{1}{2}-y,\ \frac{1}{2}-z\ ;\ x,\ y,\ \bar{z}\ ;$
$x+\frac{1}{2},\ \bar{y},\ z+\frac{1}{2}\ ;\ \frac{1}{2}-x,\ y+\frac{1}{2},\ z.$

The parameters for iron atoms being $u_1=.2050$, $v_1=.1987$, $x=.0550$, $y=.4325$, $z=.3156$, and those for carbon atoms $u_2=.181$, $v_2=.415$. Parameters for carbon atoms could not be determined so accurately as those for iron atoms, because the diffraction effect of the former is very small compared with that of the latter.

The atomic arrangement is illustrated in the figure. Three iron and one carbon atoms in the closed curve can be considered to form the cementite molecule.



Atomic Arrangement of Cementite and Spiegeleisenkristall.
Where: ● Carbon at (c_2)
△ Iron " (c_1)
○ " " (d)

A molecule of cementite consists of one carbon at (c_2), one iron at (c_1), and two iron at (d), and moreover it was found thatir on which is replaced by manganese in the case of Spiegeleisenkristall should be atoms at (d) but not those at (c_1).

These atomic arrangements are in conformity with all properties of cementite and Spiegeleisenkristall, such as the hardness, brittleness, mode of crystal occurrence, etc. From these results, it can be concluded that carbon is contained as neutral atoms in austenite, but comes to take the configuration of the cementite molecule with neighbouring iron atoms as austenite changes to martensite, and segregate out always as cementite at the A_1 transformation point. Carbon metastably contained in α-iron (this is less than 0.03%) also takes the cementitic arrangement.

Details of this paper will be published by a forth coming number of the Journal of the Faculty of Engineering, Tokyo Imperial University.

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