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017991143

AN INVESTIGATION OF SECONDARY HARDENING OF A 1% VANADIUM - 0.2% CARBON STEEL

01-7991143

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Reprinted from the Acta Metallurgica, Vol. 14, 1966

Reprint Series **RS 61**

Price 25 cents

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Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1968

AN INVESTIGATION OF SECONDARY HARDENING OF A 1% VANADIUM-0.2% CARBON STEEL*

E. SMITH†

Steel samples were quenched into oil, tempered and examined by transmission electron microscopy. The structure of the quenched steel was very similar to that of plain carbon steels of similar carbon content. Most of the ferrite grains were needles or large untwinned plates. Within the grains was a very high density of dislocations and also a Widmanstätten precipitate of iron carbide, formed during the quench. This structure was resistant to tempering up to about 20 hr at 500°C when the secondary hardening reaction appeared to begin. Peak hardness coincided with the formation of coherent platelets of vanadium carbide only a few unit cells in thickness and about 100 Å in diameter. The dislocation network was stable under these conditions and appeared to be held by the precipitates.

The fall from peak hardness was accompanied by increase in size and reduction in number of the vanadium carbide particles. At the same time the dislocation network cleared from the grains accompanied by polygonization and recrystallization of the ferrite.

Attempts were made to correlate measurements of strength and particle density with various theories for precipitation hardening. Moderate agreement was found with theories dependent on particle strength and spacing, but not for hardening based on coherency strains.

ETUDE DU DURCISSEMENT SECONDAIRE D'UN ACIER A 1% VANADIUM, 0,2% CARBONE

Des échantillons de l'acier, après trempe à l'huile et revenu, ont été examinés par transmission au microscope électronique. La structure de l'acier trempé ne diffère pas sensiblement de celle des aciers au carbone de même teneur en carbone. La plupart des grains de ferrite sont sous forme d'aiguilles, ou de larges plaquettes, sans macle. A l'intérieur des grains, on observe une densité élevée de dislocations ainsi qu'une précipitation de carbure de fer en structure de Widmanstätten, qui proviennent de la trempe. Cette structure résiste au revenu jusqu'à environ 20 heures à 500°C; à partir de là débute le processus du durcissement secondaire. Le pic de dureté coïncide avec l'apparition de petites plaquettes cohérentes de carbure de vanadium de quelques plans atomiques seulement d'épaisseur et d'environ 100 Å de large. Le réseau de dislocations reste stable à ce stade, sans doute du fait des précipités.

La diminution de dureté, au delà du pic, s'accompagne d'une augmentation de la dimension et d'une réduction du nombre de particules de carbure de vanadium. Simultanément, le réseau de dislocations disparaît des grains, en même temps que la ferrite polygonise et recristallise.

Les tentatives faites pour relier les mesures de résistance et la densité des précipités à diverses théories sur le durcissement de précipitation ont révélé une concordance raisonnable lorsque la théorie utilisée fait intervenir la résistance et l'espacement des particules, mais non lorsqu'elle base le durcissement sur les tensions de cohérence.

UNTERSUCHUNG DER SEKUNDÄRVERFESTIGUNG EINES STAHLES MIT 1% VANADIUM UND 0,2% KOHLENSTOFF

Stahlproben wurden in Öl abgeschreckt, getempert und im Elektronenmikroskop durchstrahlt. Die Struktur des abgeschreckten Stahles war ähnlich der Struktur von einfachem Kohlenstoffstahl mit gleichem Kohlenstoffgehalt. Die meisten Ferritkörner waren Nadeln oder große nicht verzwillingte Plättchen. Innerhalb der Körner war die Versetzungsdichte sehr hoch. Ferner beobachtete man während des Abschreckens gebildete Widmannstätten-Ausscheidungen von Eisenkarbid. Diese Struktur war beim Tempern stabil bis zu 20 Std. bei 500°C. Dann schienen Prozesse der Sekundärverfestigung einzusetzen. Die größte Härte fiel zusammen mit der Bildung von kohärenten Plättchen aus Vanadiumkarbid, wenige Elementarzellen dick und etwa 100 Å im Durchmesser. Unter diesen Bedingungen war das Versetzungsnetzwert stabil und schien durch die Ausscheidungen festgehalten zu werden.

Die Abnahme von der Maximalhärte war verbunden mit einer Zunahme der Größe und einer Verminderung der Anzahl der Vanadiumkarbidteilchen. Gleichzeitig löste sich das Versetzungsnetzwerk von den Körnern, verbunden mit polygonisation und Rekristallisation des Ferrit.

Es wurden Versuche unternommen, die Messungen von Festigkeit und Teilchendichte mit verschiedenen Theorien der Verfestigung durch Ausscheidung zu korrelieren. Eine mäßige Übereinstimmung wurde gefunden für Theorien, die auf Teilchenfestigkeit und Teilchenabstand aufbauen, nicht aber für Verfestigung auf Grund von Kohärenzverzerrungen.

INTRODUCTION

Secondary hardening has been studied extensively by extraction replicas[1–5] and also by thin foil techniques.[6,7] Secondary hardening is coincident with the formation of vanadium carbide, V_4C_3, and the simultaneous dissolution of the cementite formed earlier in the tempering process. At peak hardness extraction replicas show a cloud-like precipitate that gives a diffraction pattern corresponding to that of vanadium carbide, but with some lines absent or weak and showing broadening due to very small particle size. The shape of the particles was not clear. They were reported as plates, threads or needles.[1–3] On overageing a Widmanstätten precipitate of vanadium

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carbide is seen. More recent work with foils has shown that the particles are platelets lying on {100} planes of the iron.

The purpose of the present work was to investigate more thoroughly the secondary hardening reaction and to try to correlate the hardening mechanism with some of the current theories on precipitation hardening.

EXPERIMENTAL

The steel was made as a 500 lb arc furnace melt. The percentage composition is shown below. The

C	V	Mn	Si	P	S	N_2
0.23	1.0	1.2	0.24	0.004	0.01	<0.01

ingot was hot forged to 1 in. bar, which was ground to remove the oxidized layers and rolled to 0.025 in. strip with a minimum of annealing in controlled atmospheres to prevent further decarburization. One inch square samples of the strip were heated to 1050°C in a salt bath and quenched into oil. They were tempered in a salt bath or inert atmosphere. Vickers hardness measurements were made on these samples.

Tensile specimens with a gauge length 1 in. long and $\frac{3}{16}$ in. dia. were roughly machined from the 1 in. bar, heat treated and ground to proper dimensions.

For electron microscopy the sheet samples were thinned to about 0.005 in. in a solution of 50% water, 40% HNO_3, 10% HF. This solution, described by Keown and Pickering,[8] was most effective in thinning large areas uniformly with very little attack at the edges. Final preparation was by a modified Bollmann technique.[9] The foils were examined in a Siemens Elmiskop 1 electron microscope.

Mechanical tests

Vickers hardness measurements were made on the 0.025 in. sheet samples with a 10 kg load. Values are shown in Table 1. A plot of hardness against tempering time at 600°C is shown in Fig. 1.

TABLE 1

hr	°C	VPN	hr	°C	VPN
Quenched		400	100	500	418
5	400	405	½	650	427
20	400	403	5	700	266
4	500	405	100	700	250

See Fig. 1 for 600°C tempering.

Yield point and U.T.S. measurements were made on the $\frac{3}{16}$ in. tensile specimens, quenched and tempered 2 hr at 600°C. An Instron tensile machine was used at a strain rate of 0.02 in/min, and samples were

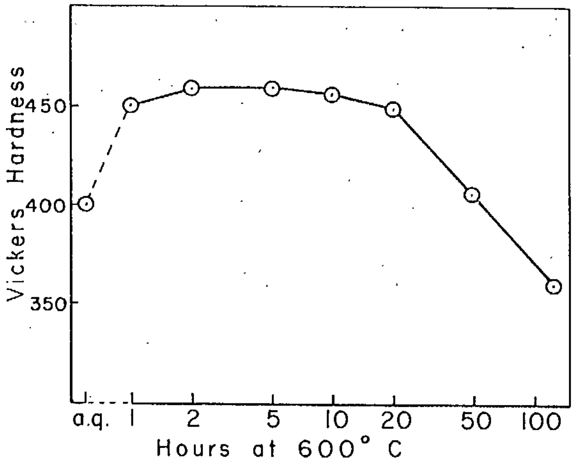

FIG. 1. Plot of Vickers hardness and time of tempering at 600°C.

tested at −186°C, −78°C, 0°C, 26°C, 100°C and 200°C. Three or four samples were tested at each temperature and variation of yield point and U.T.S. between test bars was less than 2 per cent at all temperatures. There was no sharp yield point and the values for yield were taken at the onset of plastic flow. Values of yield point and U.T.S. are shown in Table 2.

TABLE 2

All samples tempered 2 hr at 600°C		
Test temp. °C	Yield klb/in²	U.T.S. klb/in²
−186	Broke in grips at about 175	
−80	217	225
+23	199	211
+100	180	200
+200	173	193

Microstructure

Quenched into oil from 1050°C. The microstructure of the quenched steel, Fig. 2, was similar to that of low carbon steels as found by Kelly and Nutting.[10] Two types of martensitic grains were present, plates and needles, A and B in Fig. 2. No retained austenite was detected. The plates were about 5 μ long and 1–2 μ across. A few contained twins 500–1000 Å thick, with a (211) twinning plane and a [111] type twinning direction as is normal for iron. No very fine twins, as seen in high carbon martensites, were observed. The martensitic needles, each about 1 μ by $\frac{1}{4}$ μ were grouped in bundles. Electron diffraction showed that in many bundles, all the needles had the same orientation within about five degrees rotation about a [111] axis. Many of the boundaries of the former austenite grains were well defined, C in Fig. 2, and it could be seen that plates and needles had formed within individual austenite grains. All the needles in any bundle had

FIG. 2. Specimen oil-quenched from 1050°C—all micrographs from thin foils.

formed in the same austenite grain. The very high contrast of the martensitic and former austenitic grain boundaries seems to be due to a high density of dislocations very close to the boundary. No grain-boundary carbide could be detected although after tempering it is often possible to extract thin sheets of carbide from the grain boundaries.(2)

The electron diffraction patterns were not accurate enough to detect any tetragonality of the martensitic grains.

Within the martensitic grains were small acicular or blade-like particles, of rather ragged appearance, about 1000 Å long. The particles within the plates formed a Widmanstätten array. At least three directions of growth were observed. The particles within the needles were generally more sparsely distributed with fewer directions of growth observed. In some needles there was only one set of particles, usually perpendicular to the long axis of the needles. Most of the large plates gave electron diffraction patterns showing reflections from both matrix and precipitates. The lattice spacings of the precipitates derived from the patterns corresponded most closely to the values given by Jack(11) for cementite in which the Laue condition for X-ray reflection is fulfilled only in the (001) planes of the lattice, that is, from essentially two-dimensional particles. It was assumed, therefore, that the particles were thin blades of cementite and their orientation in the iron lattice corresponded with that found by Bagaryatskii(12) in high carbon steels:

Fe_3C		Fe
[100]	$\|\|$	$[\bar{1}10]$
[010]	$\|\|$	[111]
[001]	$\|\|$	$[\bar{1}\bar{1}1]$

An alternative relationship has been given by Isaichev(13) as

$$(\bar{1}01)_{Fe} \,||\, (103)_{Fe_3C}$$

and

$$[111]_{Fe} \,||\, [010]_{Fe_3C}.$$

In one pattern, a direction corresponding to (103) of the cementite was found to be about six degrees away from a (110) direction of the iron. This would seem therefore to preclude Isaichev's relationship at this stage of formation of the precipitates. The particles were found to be lying in the {110} planes of the iron. The long axis of the particles appeared to be along a $[111]_{Fe}$ direction but the possibility of $[211]_{Fe}$ could not be eliminated.

Attempts to extract the particles from the quenched samples were unsuccessful.

In a few patterns from the needles, however, it was not possible to find a fit between the two lattices on the assumption that the particles were cementite. However, if it was assumed that the particles were epsilon carbide in the orientation found by Jack,(11) i.e. $(011)_{Fe} \,||\, (0001)_\varepsilon$, $(101)_{Fe} \,||\, (10\bar{1}1)_\varepsilon$, then the following directions should be coincident to within ten degrees: $[\bar{1}\bar{1}1]_{Fe}$ and $[1\bar{2}10]_\varepsilon$, $[001]_{Fe}$ and $[1\bar{1}02]_\varepsilon$, $[110]_{Fe}$ and $[01\bar{1}1]_\varepsilon$. These coincidences were found in one pattern, which suggests that epsilon-carbide is present, probably in the needle-shaped martensitic grains. The particles appeared to be lying in a $(100)_{Fe}$ plane with their long axes in a [110] direction.

Also, throughout all the martensitic grains was a very dense network of dislocations all highly jogged and tangled (Fig. 3). The contrast of the dislocations was very sensitive to the orientation of the foil. At maximum contrast the dislocations obscured the precipitates, shown by arrows in Fig. 3. There was no evidence

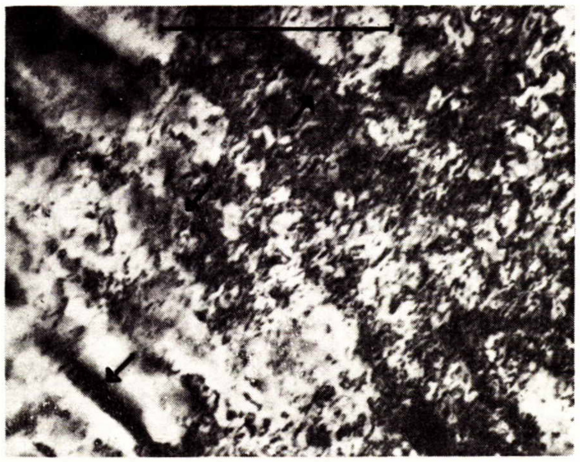

FIG. 3. Dislocations and cementite particles (arrowed) in quenched samples.

of a definite interface between the matrix and the precipitates. The dislocation network seemed unaffected by the presence of the particles, suggesting that the dislocations passed through them. It seems probable that the particles were coherent with the matrix, which would account for their ragged appearance and also for the difficulties in extracting them.

Tempering at 400°C. Throughout the tempering range up to 50 hr at 400°C the microstructures were very similar to those of the quenched structure except that more carbide particles were observed and they became progressively more sharply defined with increased tempering (Fig. 4). The particles were found to be cementite in the orientation of Bagaryatskii,[12] although no evidence was found in these samples to exclude Isaichev's[13] relationship. The sharpening of their outlines was probably due to their becoming non-coherent.

The dislocation network within the grains appeared unchanged.

Tempering at 500°C. In the early stages of tempering at 500°C, up to about 20 hr, the structures were very similar to those found in the specimens tempered at 400°C, except that the needles of cementite were thicker. The high density of dislocations was still present. After 100 hr, the cementite particles appeared much more ragged than at shorter times and a few grains contained no particles at all. This is believed to be due to the dissolution of the cementite. After 180 hr very few cementite particles could be seen within the grains. Also, in diffraction patterns from thin grains at the edge of the foil, having a $(100)_{Fe}$ or $(110)_{Fe}$ in the plane of the foil and showing a strong $(200)_{Fe}$ reflection, streaking of the iron matrix spots, parallel to the $\langle 200\rangle_{Fe}$ directions was clearly visible

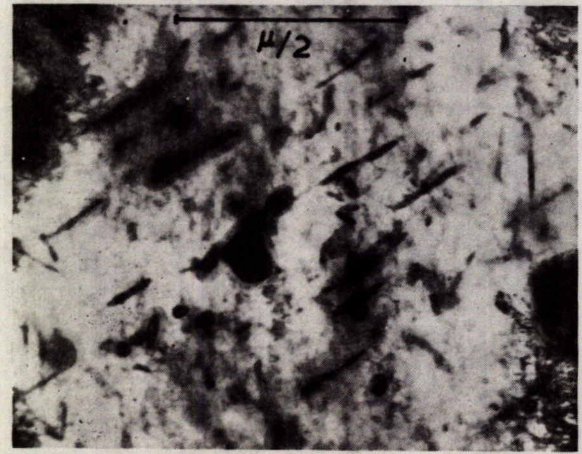

Fig. 4. Cementite particles after tempering 5 hr at 400°C.

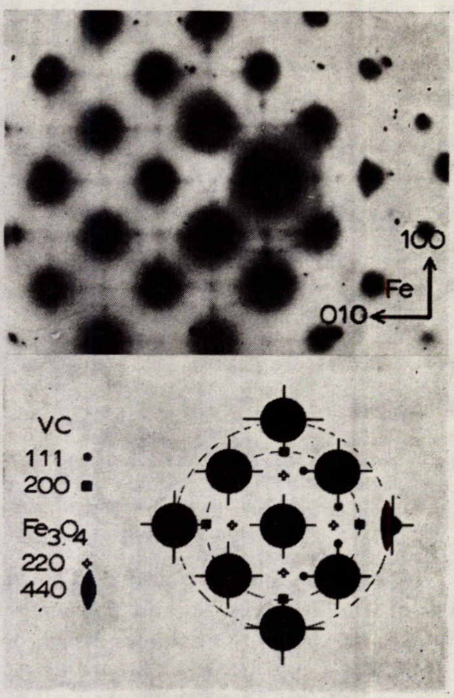

Fig. 5. Electron diffraction pattern from sample tempered 180 hr at 500°C.

(Fig. 5). Patterns from grains with $(110)_{Fe}$ or $(210)_{Fe}$ in the plane of the foil showed fainter streaking of Fe {200}, {110} and {211} spots in the $\langle 200\rangle_{Fe}$ directions while in grains of $(111)_{Fe}$ orientation, the Fe {110} and {211} spots showed slight streaking parallel to $\langle 211\rangle_{Fe}$ directions, i.e. normal to the traces of the {100} planes. This streaking appears to be similar to that found in Al–Cu alloys by Nicholson and Nutting[14] and is believed to be due to the existence of platelets of vanadium carbide a few atoms thick on the $\{100\}_{Fe}$ planes of the iron lattice, probably analogous with the θ' phase of Al–Cu alloys. The possibility of the formation of Guinier–Preston type zones of vanadium on the {100} planes of the iron is considered unlikely because of the high affinity of vanadium for carbon. Since most of the cementite had dissolved before the streaking was clearly seen, it is thought that the carbon had already been taken by the vanadium in the very first stages of formation of vanadium carbide. The vanadium carbide, however, is probably deficient in carbon since even after severe tempering V_4C_3 rather than VC is found.[15]

Most of the electron diffraction patterns show one or more faint rings besides spots and streaks. The rings correspond to those of vanadium carbide, the {200} being the strongest, followed by the {220}. These rings may be due to random precipitation of vanadium

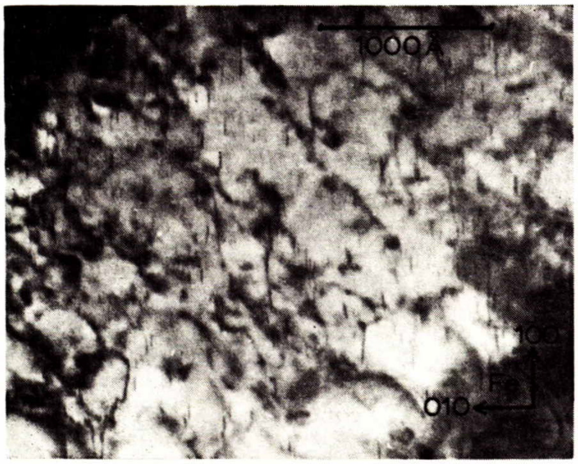

FIG. 6. Particles in sample tempered 2 hr at 600°C.

carbide, possibly at grain boundaries or on dislocations. However, since replicas can pull particles of V_4C_3 off the electropolished surfaces of the specimens, it is possible that the rings are produced by loose particles of vanadium carbide on the surfaces.

The images of grains giving streaked patterns showed numerous short streaks 50–100 Å long and 5–10 Å wide, perpendicular to the ⟨100⟩ directions of the iron (Fig. 6). It was sometimes possible to tilt the foil to give a second strong (200) reflection at 90° to the first. When this was done, the image showed a second set of short streaks at right angles to the first. Usually the first set disappeared, but in one or two specimens both sets were seen together (Fig. 7). These streaks are assumed to be the images of the precipitates of vanadium carbide. A third set of platelets in the plane of the foil could not been seen because the particles were too thin.

Strain contrast around the particles was a minimum for a strong (200) reflection and a maximum for (110) reflections.

After these effects had been found in the 175 hr specimen, the 100 hr specimen was examined again and faint streaking of $(100)_{Fe}$ patterns was found only in a few grains that did not show cementite particles. No short streaks were seen in the bright field micrographs.

Tempering at 600°C. At 600°C the rise in hardness is rapid, the peak being reached after about 1 hr. Very little cementite was seen even in the sample tempered for half an hour. The most striking observation was that the dislocation network was still present within the ferrite grains, although the dislocations appeared less jogged than at lower tempering temperatures.

At certain orientations the dislocations appeared spotty (Fig. 8). This may be due to the presence of vanadium carbide particles along the dislocations either nucleating on them or being connected by moving dislocations as discussed below. As stated above, the rings observed in diffraction patterns may be due to random nucleation of vanadium carbide which could occur at dislocation sites. The orientations that showed spotty dislocations did not give good contrast for particles or dislocations so that it is difficult to determine the reason for the spotiness.

The dislocations showed up in very strong contrast when the diffraction pattern showed a strong (110) reflection. The counting of these dislocations was easier than for the highly jogged dislocations in the specimens tempered at lower temperatures. The method of counting was that of Ham[16] and values between 0.5×10^{11} and 1.5×10^{11} lines/cm^2 were

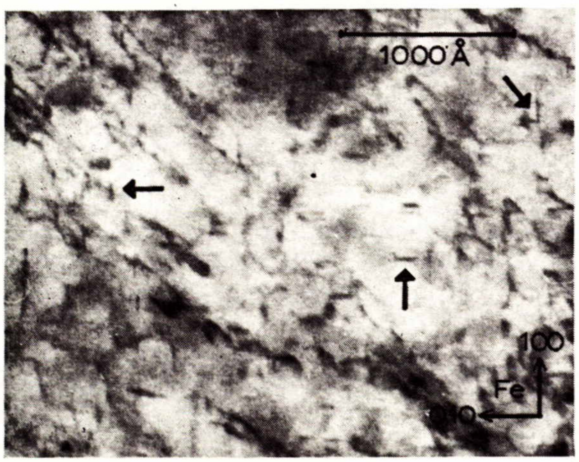

FIG. 7. Image of two sets of particles at 90° in specimen tempered 1 hr at 600°C.

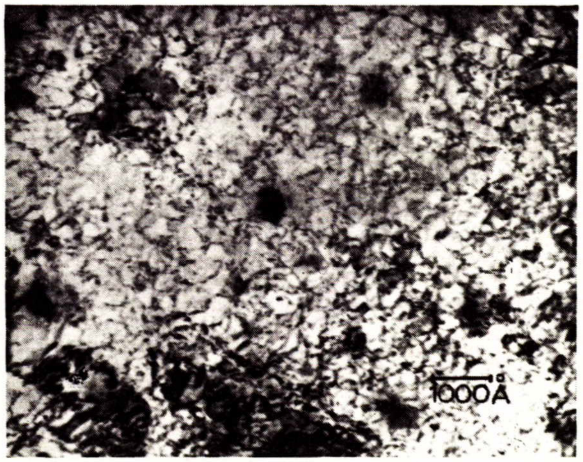

FIG. 8. Dislocations in specimen tempered 1 hr at 600°C.

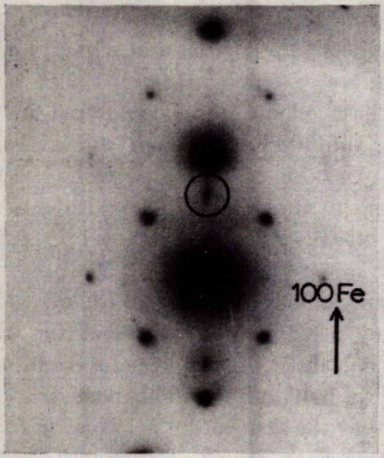

FIG. 9. Diffraction pattern after ½ hr at 650°C showing development of maxima in streaks.

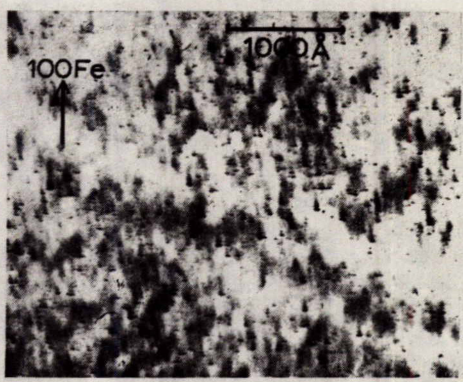

FIG. 10. Dark field picture of V_4C_3 particles taken using ringed spot in Fig. 8, a (200) V_4C_3 spot. Negative print.

obtained for samples tempered at 600°C for up to 5 hr.

The diffraction patterns from grains in a $(100)_{Fe}$ orientation again showed streaking parallel to the $\langle 100\rangle_{Fe}$ directions, and the bright field images showed short streaks about 10 Å wide by 100–150 Å long. Again two sets of streaks could be seen as in the 500°C specimens. The images of the particles were sharper than at 500°C and it was easier to count them. The average particle density was about 10^{17} cm^3.

The streaks on the electron diffraction patterns were not continuous but showed modulations that developed into sharp maxima as tempering progressed (Fig. 9). After 100 hr the maxima were spots corresponding to the (111) and (200) interplanar spacings of vanadium carbide. The development of the maxima appears to be due to the growth of the particles from a thickness of one or two unit cells and consequent loss of coherency. In specimens tempered for 2 hr and longer it was possible to obtain dark field pictures from the maxima, showing that they were being produced by diffraction from individual particles (Fig. 10).

After 100–120 hr at 600°C, when the hardness had fallen to about the quenched hardness, the precipitates of vanadium carbide had grown in size to about 50 Å thick by 200 Å across (Fig. 11). The particles were thick enough so that in foils of (100) orientation the particles lying in the plane of the foil could be seen as well as those lying in the (010) and (001) planes. It was also found that about 10 per cent of the particles were lying in {110} planes. However, the distribution of particles and of dislocations was no longer uniform. There were regions in the foils where the dislocation network had disappeared. These areas seemed to be sub-grains or parts of the acicular ferrite grains in which polygonization had begun and which had cleared of dislocations or had the dislocation density greatly reduced (Fig. 12). Some of the polygonized regions were as small as 2000 Å across. Also, in some regions dislocations had begun to clear from the larger platelike grains (Fig. 13), and in a few areas there had been recrystallization with growth of new grains into the original structure (Fig. 14). In the areas of low dislocation density the particles of vanadium carbide were larger and fewer than in the areas of high dislocation density. They were up to 500 Å across and numbered 10^{14}–10^{15}/cm^3 (centre of Fig. 12 has 10^{14}/cm^3), many of which were in grain boundaries. The development of grain boundary precipitates seemed to be typical of long tempering at 600°C. At peak hardness there were very few grain boundary precipitates.

Further tempering produced a gradual disappearance of the regions of high dislocation density and growth and decrease in number of the vanadium carbide particles. The number of particles remained

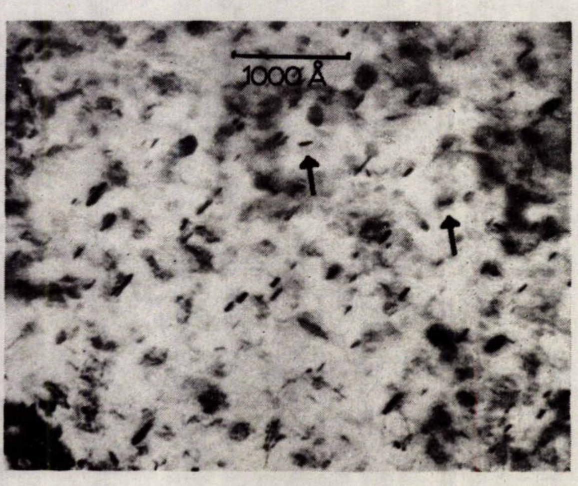

FIG. 11. V_4C_3 particles after 100 hr at 600°C. Particles lying in $\{110\}_{Fe}$ planes are arrowed.

Fig. 12. Specimen tempered 120 hr at 600°C showing polygonized areas.

Fig. 13. Specimens tempered 120 hr at 600°C, showing dislocations clearing from centre of large plate-like grain.

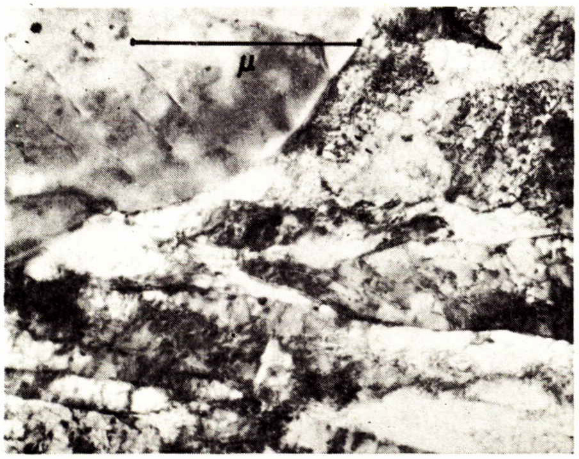

Fig. 14. Tempered 120 hr at 600°C showing large recrystallized grain and unrecrystallized region.

Fig. 15. Tempered $\frac{1}{2}$ hr at 650°C. Particles lying in $\{110\}_{Fe}$ planes shown by arrows.

at about $10^{14}/cm^3$ inclusive of grain boundary particles.

Tempering above 600°C. Above 600°C the time to peak hardness and subsequent fall was faster with increasing temperature. Nucleation of the vanadium carbide particles was more rapid than at 600°C and the polygonization of the ferrite and growth of carbide particles were accelerated. Also nucleation on planes other than $\{100\}_{Fe}$ was observed after shorter tempering times. Figure 15 shows the sample tempered for $\frac{1}{2}$ hr at 650°C. About 1 per cent of the particles were lying in $\{110\}_{Fe}$ planes and others appeared to be lying in planes a few degrees off $\{100\}_{Fe}$. It seems that up to about 10 per cent of the particles can eventually form on $\{110\}_{Fe}$ planes. The electron diffraction pattern of Fig. 15 showed streaking parallel to $\langle 200\rangle_{Fe}$ directions, but the maxima in the streaks corresponding to $\{111\}$ and $\{200\}$ VC were already well developed and gave good dark field pictures of the precipitates (Figs. 9 and 10).

Although tempering at up to 700°C accelerated the growth of precipitates and the clearing of the dislocation network, the density of the particles remained at about $10^{14}/cm^3$ and the polygonization process was still incomplete even after 100 hr at 700°C (Fig. 16).

DISCUSSION

Precipitation of vanadium carbide

The microstructure of the steels at peak hardness consisted of a fine dispersion of platelets of vanadium carbide, about 10 Å thick and 100–150 Å across and numbering about $10^{17}/cm^3$. The platelets were lying in $\{100\}$ planes of the iron such that

$$(100)_{Fe} \parallel (100)_{VC}$$
$$(011)_{Fe} \parallel (010)_{VC}$$

as suggested by Baker and Nutting.[4]

FIG. 16. Tempered 100 hr at 700°C, showing region from which dislocations have not cleared.

In this orientation the lattice misfit between the VC and the iron in the $(100)_{Fe}$ planes and [010] and $[001]_{VC}$ directions is about 2.5 per cent, assuming that the particles are VC. If, as is probable, the carbide is deficient in carbon the misfit would be less. Thus, the carbide particles could grow to about 20 unit cells in diameter before the total strain exceeded half a lattice spacing and could be reduced by insertion of an extra plane of iron atoms, that is, an interface dislocation. Twenty unit cells give a diameter of about 80 Å, which agrees very well with the observed sizes. However, in the $(010)_{VC}$ plane (parallel to $(011)_{Fe}$), the misfit along the $[010]_{VC}$ direction, normal to the plane of the carbide platelet, is 22 per cent for VC and 14 per cent for vanadium atoms only. Hence, the misfit in this plane would reach 50 per cent at a thickness of only three or four unit cells, 10–15 Å, which again agrees with observation. It seems likely therefore that at peak hardness, the particles are at the limit of the size at which they can be coherent and the formation of interfacial dislocations is just beginning. This condition would give maximum interfacial strain.

After 100 hr at 600°C, although the particles were too big to be coherent, no dislocations were seen at the interfaces between the matrix and particles. Strain contrast was still observed after 120 hr. Where the dislocations had cleared, however, the particles, which were generally about 500 Å in diameter rarely showed strain contrast effects.

The particles appeared to nucleate independently in the matrix although nucleation on dislocations cannot be ruled out, since some particles were seen to be lined up along dislocations. However, at 600°C, where the structure was formed, the dislocations would be mobile and, in trying to move to form sub-boundaries or to anneal out, they would be held up by the growing particles. Thus, whether the particles nucleated in the matrix or not, they would quickly become connected by dislocations that might be paths of easy diffusion of vanadium and carbon.

Besides the particles, there was throughout the grains a uniform dense network of dislocations numbering about 10^{11} lines/cm^2, which remained stable at peak hardness, as compared to a plain carbon steel in which the dislocations began to anneal out after 1 hr at 400°C. This density is equivalent to that of a highly work-hardened metal but the dislocations were not arranged in cells. The arrangement was similar to those found in aluminum–3–7% magnesium alloys deformed to fracture and described by Waldron,[7] who ascribes the lack of cells to the prevention of cross-slip by solute atoms. In the steel the dislocations are probably prevented from forming cells or sub-boundaries by the particles.

Mechanisms of hardening

Numerous theories have been evolved to account for hardening by precipitation. Mott and Nabarro's[18] theory is based on strain fields around particles, Orowan's[19] on the force required to bow a dislocation loop between hard particles, and Kelly and Fine's[20] theory depends upon the work required to force a dislocation through the particles. Evidence from electron micrographs for any of these theories is difficult to obtain unless tests can be carried out in the microscope. Further, dislocations, precipitates and strain fields each show up best at different orientations of the foil, so that micrographs showing one do not have optimum conditions for all. No evidence was found for dislocations bowing out between particles, but some micrographs (such as Fig. 17) showed particles apparently lined up with dislocations passing through them (arrowed). Individual particles, not on dislocations, can also be seen. The evidence from the micrographs, therefore, points to the cutting of the particles by the dislocations.

Since the experiments show that there is a fall in strength when the number of particles falls from 10^{17} to 10^{16}, any theory of hardening that relates hardness only to volume fraction of precipitate and neglects the spacing of the particles must be discounted. Mott and Nabarro's theory was developed for spherical particles and predicts a critical particle spacing for maximum hardness. If, however, the critical resolved shear stress, $\tau = 2G\varepsilon f$ is calculated, where G is the shear modulus for iron (11.7×10^6 lb/in^2), ε the lattice strain and f the volume fraction of the precipitate, a value of about 40,000 lb/in^2 is obtained. This is surprisingly

FIG. 17. Tempered 1 hr at 600°C. Arrows show particles aligned along dislocations.

close to the value obtained for the flow stress which was about 70,000 lb/in^2 assuming that the measured yield stress of the polycrystalline specimen is about three times the flow stress for the single crystal, as found by Taylor.[21] Further, the critical particle spacing, given by $d = b/4\varepsilon f$, where b is the Burgers vector of a dislocation, was found to be about 350 Å, which is again in good agreement with experiment (see below). However, attempts to estimate flow stress by assuming true disc shaped particles, as described by Nicholson and Kelly[22a] and using the principle of dislocations cutting a forest after Saada,[23] gave values of less than 15,000 lb/in^2 for a particle spacing of 240 Å.

Three other theories considered were those of Orowan,[19] Ansell and Lenel,[24] and Kelly and Fine,[20] The first two theories give a dependence of flow stress upon particle spacing, d; Orowan's theory gives $\tau = Gb/d$ and Ansell and Lenel $\tau = (G'Gb/2dK)^{1/2}$ where G' is the shear modulus of the particle and K a constant. An expansion of the Orowan equation,[22b]

$$\tau = \tau_0 + \frac{2Gb\phi}{4\pi d} \ln \frac{d}{2b}$$

where $$\phi = \tfrac{1}{2}\left(1 + \frac{1}{1-\nu}\right)$$

was also considered.

The values for particle spacing on the (110) slip plane of the iron were calculated assuming the particles to be lying in $\{100\}_{Fe}$ planes. At peak hardness, with 10^{17} particles/cm^3, 150 Å long and 10 Å thick, the average density on $(110)_{Fe}$ is 1.2×10^{11}/cm^2. All the particles would appear as needles of average length about 115 Å. Two thirds of the needles would be parallel to the [100] direction and one third with [110]. The planes in the precipitates, parallel to the slip plane of the iron are, $\{233\}$ and $\{100\}$ respectively, neither of which are slip planes of the vanadium carbide.

The mean particle spacing along a random dislocation line in the slip plane was found to be about 1000 Å, but the shortest distance between the particles about 250 Å. Thus, if a dislocation with particle spacing of 1000 Å began to move, it would bow out and soon come into contact with other particles so that the effective spacing would be reduced. Hence, the values 1000 Å and 250 Å represent lower and upper limits for particle spacing along dislocations. Since dislocations will have moved before the yield point can be detected on the tensile machine, the particle spacing along dislocations at the measured yield point is not known. The only known spacing, 250 Å, represents the loop length of dislocations held up by as many particles as possible. This condition would seem to correspond more nearly with the ultimate tensile stress than with the yield point, since work hardening is rapid and plastic extension small, about 2 per cent. Further, as stated above, since the structure is formed at 600°C, the dislocations would be mobile and would tend to move and become held up by more particles than would be on the random line, giving a loop length less than 1000 Å even before plastic flow. Figure 17 seems in agreement with this.

To test the theories of Orowan, and Ansell and Lenel, the calculated yield stress was plotted as a function of particle spacing (Fig. 18). Measured values of U.T.S. and particle spacing are plotted for specimens tempered for 2 hr at 600°C, $\frac{1}{2}$ hr at 650°C and 120 hr at 600°C. For Ansell and Lenel's equation a value of 16×10^6 lb/in^2 was used for G', $b = 2.5 \times 10^{-8}$ cm, and $G = 11.7 \times 10^6$ lb/in^2. The value of K can vary between 30 and 10^4, depending upon whether the particles are hard or soft. The true value of K is not known, but for these steels must be about 100 to obtain any reasonable agreement. This lack of knowledge of K greatly reduces any usefulness of this theory in predicting flow stress.

The value G'/K in Ansell and Lenel's equation is to some extent a measure of the strength of the particle. Kelly and Fine[20] attempt to equate the flow stress with the strength of the particle that is cut by the dislocation. The particles will be cut if the stress to cut them τ_c is less than the Orowan stress, τ_0. That is

$$\tau_c = \gamma a/bd < \tau_0 = \frac{Gb}{d}$$

i.e. if $$a < \frac{Gb^2}{\gamma}$$

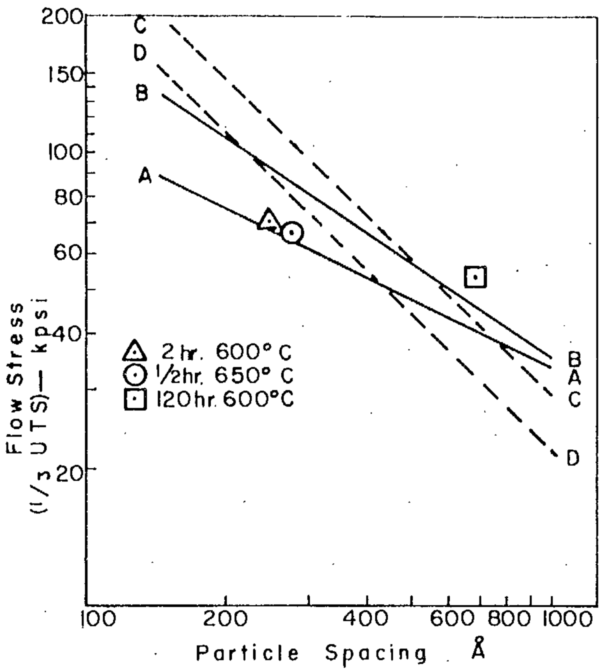

FIG. 18. Log–Log plots of calculated flow stress against particle spacing as given by theories of A, Ansell and Lenel with $K = 200$,[24] B and C, Orowan[22b,19] and D, Kelly and Fine[20].

where, a, is the particle width along the dislocation and, γ, the interfacial energy between particle and matrix. Nicholson and Kelly[22c] use van der Merwe's[25] treatment of grain boundaries to obtain $\gamma \simeq 0.03\ G'b'$ where G' and b' are shear modulus and smallest lattice translation vector of the particle. Using this value for γ gives $a < 25b$, i.e. about 60 Å.

It is possible to estimate, a by assuming that $\gamma = \Delta E/3s^2$ where s is the nearest neighbour separation.[22d] The value of ΔE was estimated from values of free energy of formation of vanadium carbide. The free energy of formation of VC, ΔG, was taken as 27,000 cal/mole[26] and, from Richardson's[27] values for variation of ΔG with activity of vanadium, a value of 17,000 cal/mole was assumed for an activity of vanadium of 1%. The heats of solution of vanadium and carbon in iron[28] are about -3500 and $+5000$ cal/mole respectivley, so it was assumed that the value of 17,000 cal/mole would also be reasonable for the free energy of formation of vanadium carbide in iron containing 1% vanadium. From this value, ΔE is about 0.75 eV/mole. The value then found for, a, is about 50 Å. Both these values are smaller than the diameter of the particles but larger than the thickness, so that the dislocations could probably cut the particles perpendicular to their long axes. This seems to be confirmed by the few micrographs that show both particles and dislocations (Fig. 17). In any case it seems likely that a dislocation approaching parallel with the long axis of a particle could swing around so as to cut the particle along a narrower front, so that provided the thickness of the particles remained small the dislocations could always cut through them.

The equation of Kelly and Fine used to calculate the flow stress was

$$\tau = \frac{\Delta E \cdot n}{2b^2 d}.$$

Nicholson and Kelly give a more complete version of this formula, but this could not be used owing to lack of knowledge of various parameters in the equation. The value for ΔE in this equation was taken as 17,000 cal/mole as above. The average length of a dislocation in a particle on the slip plane is about $3a$, where a is the thickness. This gives about 30 Å which is equivalent to about 8 unit cells of V_4C_3, so that n was assumed to be about 16. These values were used to calculate τ, which was then plotted against d on Fig. 18.

The agreement of all curves of Fig. 18 with the measured values is surprisingly good but needs to be tested further by examination of other alloys with different vanadium and carbon contents to obtain different particle densities. Samples near to peak hardness are preferable, since in overaged samples the particle distribution is not uniform.

All the theories predict rather lower strengths than actually observed after long tempering when the particle density is about $10^{16}/cm^3$. The simple theory of Orowan also predicts higher strengths at peak hardness than those observed. The agreement of Ansell and Lenel's equation is determined by the value used for K. With a value of about 200, this equation gives the best fit of all the curves, suggesting that for these steels, in the relation between strength and particle spacing, $\tau \propto 1/d^n$, the value of n is nearer to one half than to one.

Agreement of Kelly and Fine's equation may also be fortuitous since ΔE and n are only estimates. Further, no account is taken of the difference in slip planes of the iron and vanadium carbide, which would necessitate a misfit dislocation.

Although the simple Orowan equation, $\tau = Gb/d$ predicts strengths at peak hardness well above those measured, the expanded equation (Curve B) gives a reasonable fit so that the curves give no real indication of which mechanism of hardening may be operating. The agreement of the Orowan equation suggests that the particles may be approaching the state in which dislocations will bow between them rather than cut them. It appears, however, that the contribution of coherency strains is too small to account for the hardness. The main significance of coherency may be that the mechanism of formation of the particles makes it impossible to form enough (about 10^{17}) particles which are not coherent, to give sufficient strengthening.

The effect of the dislocation forest is not known and has been neglected, but with 10^{11} dislocations per cm^2 the forest probably would not add appreciably to the flow stress, since the dislocations would provide less effective barriers than the particles.

The dependence on temperature of measured and calculated flow stresses was plotted, but, although the measured flow stress appeared to be more temperature dependent than the Orowan stress and less so than the Kelly and Fine values, the differences in slopes were too small to be significant.

Overageing

The number of particles seems to control the overageing of the steel and when there are fewer than about $10^{16}/cm^3$ the dislocations, can anneal out at 600°C, forming many sub-grain boundaries. There also appears to be recrystallization as well as polygonization. Clearly, the time for which high hardness is retained is dependent upon the rate of growth of the carbide particles and could be extended if a more stable carbide such as NbC were used.

The increase with tempering of the percentage of particles growing on $\{110\}_{Fe}$ planes and other planes besides $\{100\}_{Fe}$ is in agreement with nucleation theory, since the strain on $\{100\}_{Fe}$ planes is a minimum and the reaction should follow the path of least activation energy. It also appears that particles are freshly nucleated on $\{110\}_{Fe}$ planes after several hours at 600°C when most of the vanadium carbide has already precipitated on $\{100\}_{Fe}$ planes. At higher temperatures nucleation takes place simultaneously on several sets of planes. Nucleation on grain boundaries seems to be part of the overageing rather than the ageing process.

CONCLUSIONS

1. In a 1% V, 0.2% C steel, quenched and tempered, the rise in hardness on tempering at 500°C or above is due to the formation of coherent plates of vanadium carbide in the $\{100\}$ planes of the iron. There are about 10^{17} particles/cm^3 at peak hardness.

2. A dense network of dislocations numbering about $10^{11}/cm^2$, formed during the transformation on quenching, is held stable by the particles for up to about 50 hr at 600°C.

3. When the number of particles falls below a certain value, about $10^{16}/cm^3$, the dislocations can anneal out. This is the stage of overageing.

4. The initial carbide, formed on quenching was found to be cementite with possibly a small amount of epsilon carbide.

5. Attempts to correlate results with theories of hardening indicated that coherency stresses are inadequate to explain all the hardening. While agreement with theories based on dislocations cutting particles or bowing out between them was fairly good, it was not possible to determine conclusively which mechanism was responsible for the hardening. The microscopic evidence favours the cutting of the particles by the dislocations.

6. Whether the particles are nucleated in the matrix or on dislocations would not affect their strengthening of the steel since, at the tempering temperature, the dislocations would always tend to move to the particles and be held by them.

REFERENCES

1. K. Kuo, *J. Iron Steel Inst.* **184**, 258 (1956).
2. E. Smith and J. Nutting, *J. Iron Steel. Inst.* **187**, 314 (1957).
3. A. K. Seal and R. W. K. Honeycombe, *J. Iron Steel Inst.* **188**, 9 (1958).
4. R. G. Baker and J. Nutting, *Iron Steel Inst. Sp. Report* 64, "Precipitation Processes in Steels," pp. 1–22 (1959).
5. F. B. Pickering, *Iron Steel Inst. Sp. Report* 64, pp. 23–43 (1959).
6. E. Smith, *Proc. 5th. Conf. Elec. Micro.*, Paper CC10. Academic Press, 1962.
7. E. Tekin and P. M. Kelly, *AIME Symposium on Precipitation from Iron Based Alloys*, Cleveland 1963. To be published.
8. S. R. Keown and F. B. Pickering, *J. Iron Steel Inst.* **200**, 757 (1962).
9. F. W. Boswell and E. Smith, *ASTM Symposium on Advances in Electron Metallography*, Tech. Publ. No. 245.
10. P. M. Kelly and J. Nutting, *Proc. R. Soc.* **A259**, 203 (1960).
11. K. H. Jack, *J. Iron Steel Inst.* **169**, 26 (1951).
12. A. Yu. Bagaryatskii, *Dokl. Akad Nauk SSSR* **73**, 1161 (1950).
13. I. V. Isaichev, *Zh. Tech. Fiz.* **17**, 835 (1947).
14. R. B. Nicholson and J. Nutting, *Phil. Mag.* **3**, 531 (1958).
15. H. J. Goldschmidt, *J. Iron Steel Inst.* **160**, 345 (1948).
16. R. K. Ham, *Phil. Mag.* **6**, 1183 (1960).
17. G. W. J. Waldron, *A Study by Transmission Electron Microscopy of the Tensile and Fatigue Deformation of Al–Mg Alloys*. To be published.
18. N. F. Mott and F. R. N. Nabarro, *Proc. Phys. Soc. Lond.* **52**, 86 (1940).
19. E. Orowan, *Symposium on Internal Stresses in Metals and Alloys*, p. 451. Inst. of Metals (1948).
20. A. Kelly and M. E. Fine, *Acta Met.* **5**, 365 (1957).
21. G. I. Taylor, *J. Inst. Metals* **62**, 307 (1938).
22. R. B. Nicholson and A. Kelly, *Prog. Materials Science*, 1963, vol. 10, No. 3, ch. 15–17. (a) p. 327, (b) p. 338, (c) p. 373, (d) p. 335.
23. G. Saada, *Acta Met.* **8**, 200 (1962).
24. G. S. Ansell and F. V. Lenel, *Acta Met.* **8**, 612 (1962).
25. J. H. Van Der Merwe, *Proc. Phys. Soc. Lond.* **A63**, 616 (1950).
26. C. J. Smithells, *Metals Reference Book* Vol. 2, p. 587. Butterworths, London (1955).
27. F. D. Richardson, *J. Iron Steel Inst.* **175**, 33 (1953).
28. *Electric Furnace Steelmaking*, Vol. 2 p. 133. AIME Publication, C. E. Sims, Editor. Interscience (1963).