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# Martensitic transformation in iron-arsenic alloys

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A study was conducted into the structural features of martensitic transformation in four iron–arsenic alloys, ranging between 0.22 and 1.68% As. The structures produced by quenching these alloys from a suitable austenitizing temperature into iced brine were studied systematically by optical and electron microscopy. The martensitic substructural units were lath shaped. The orientation relationships between adjacent laths were determined using selected-area electron diffraction techniques, and the observed orientation relationships were consistent with the theory that adjacent laths adopt different variants of the Kurdjumov–Sachs orientation relationship. Single surface trace analyses established that the laths have a habit plane close to $\{1\,1\,0\}\alpha$ and a long direction parallel to $\langle 1\,1\,1\rangle\alpha$. The results are compared with the prediction of recent phenomenological theories of martensitic transformation.

## 1. Introduction

In iron-base alloys, two major types of martensite form as a result of the shear-type, diffusionless martensitic transformation of high-temperature solid solution austenite [1]. In the martensite that forms in dilute alloys of iron, the basic transformation unit is lath-shaped. It is suggested that each lath is the result of a homogeneous shear, and that successive shears produce a packet of parallel laths containing a high density of tangled dislocations. The other type, plate martensite, differs in shape by a transformation unit and its transformation sequence is characterized by non-parallel plate formation.

Elements alloyed with iron form two types of binary systems: those with $\gamma$-loops (Cr, Mo, Sn, V, W) and those with stabilized $\gamma$(C, Ir, Mn, N, Pt, Ru). The $\gamma$-stabilized systems form lath martensite and, with sufficient additions also form plate or hexagonal $\epsilon$-martensite, whereas the $\gamma$-loop systems usually transform into lath martensite.

In contrast to the plate martensite which has been well investigated, the crystallography of the martensite formed in low-carbon steels and in dilute binary substitutional systems is not well understood. The shape change of lath martensite is certainly accompanied by extensive plastic deformation of the parent and previously formed martensitic lattices near to the habit plane. The extensive self-accommodation is probably the reason why the transformation to lath martensite in chemically homogeneous crystals goes to completion. Since retained austenite is not generally found in conjunction with lath martensite, it is not possible to determine directly the crystallographic features of the transformation.

Arsenic and iron form the phase diagram with a $\gamma$-loop [2]; the maximum solubility of arsenic in the $\gamma$-phase is 1.75% As at 1150° C. In the literature available, only the data of Svechnikov and Grindnev [3] on quenched iron-arsenic alooys, which are optically similar to martensitic structure, were known up to early 1938.

In view of this uncertainty about Fe–As martensite, the purpose of the present work was undertaken to determine the morphology and crystallographic characteristics of martensite in iron–arsenic alloys. The structures observed in this investigation were similar to those previously observed in low-carbon steels and dilute binary ferrous alloys.

## 2. Experimental procedure

### 2.1. Materials

The alloys investigated were made from carbonyl-iron (C < 7 ppm, O < 100 ppm, S < 1 ppm) and metallic arsenic (99.9% As). Melting was carried out in a beryllia crucible in an argon atmosphere. Four alloys were prepared as 200 g laboratory heats; the compositions of the binary iron alloys were: Fe–0.22% As, Fe–0.85% As, Fe–1.31% As and Fe–1.68% As. It was hoped that by studing different alloys, the results obtained would permit the comparison of the effect of arsenic content on the structure of lath martensite. The ingots were machined initially to 3.0 mm thick plates and subsequently cold-rolled to various section sizes, ranging from 0.2 to 1.0 mm, and finally homogenized by vacuum annealing at 1160° C for 24 h.

### 2.2. Heat-treatment

The austenitizing treatments (1150° C, 15 min) were performed in a vertical tube furnace containing a nitrogen atmosphere. A rapid quench rate was achieved by dropping the specimens through the bottom of the furnace (sealed by a rubber envelope) into iced brine. Specimens of different cross-sections were employed, resulting in considerable differences in cooling rate.

### 2.3. Specimen preparation

The specimens for transmission electron microscopy were quenched in the form of a 0.2 mm thick strip. These specimens required only light grinding on metallographic paper to produce a flat, smooth sheet from which thin foils could subsequently be obtained. Considerable difficulty was experienced initially in the preparation of suitable thin-foil specimens. Various techniques were tested; the best success was achieved by means of opposed-jet thinning [4], in a solution of 5% perchloric acid in glacial acetic acid at a 150 V potential. After formation of the hole, the specimens were immediately removed from the jet thinning unit and well rinsed in high purity methanol in order to avoid the formation of an oxide film on the specimen surface. The transmission electron microscopy was conducted on both a Siemens Elmiskop IA and a JEM 200 B, operating at 100 and 200 kV, respectively.

## 3. Results and discussion

### 3.1. Morphology

All four Fe–As alloys exibited similar microstructure when quenched from the austenite range. Metallographic examination of specimens, after polishing and etching, revealed the typical microstructure of lath martensite (Fig. 1). Packets were the predominant feature of these microstructures, and the individual martensitic laths were visible as a fine substructure within the packets. The laths often appeared in groups of parallel arrays (Fig. 2), within which the boundaries between the laths were usually fairly straight and quite well defined. The laths were long and

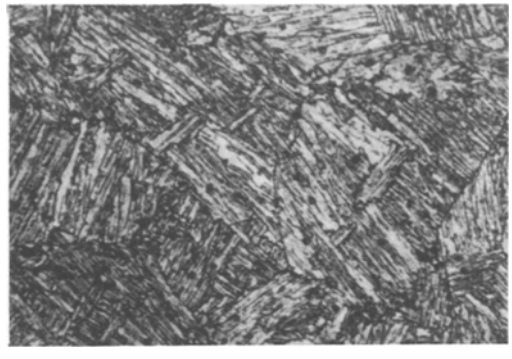

*Figure 1* Light micrograph showing lath martensite in an iced brine quenched Fe–1.31% As alloy. Etched with 1 g picric acid, 10 ml hydrochloric acid and 10 ml nitric acid in 50 ml ethanol, × 740.

*Figure 2* Thin-foil electron micrograph of Fe–1.31% As alloy, showing array of laths. Within the laths high densities of tangled dislocations (cell walls) can be resolved, × 40 000.

approximately 0.4 $\mu$m wide. However, arrays of laths were observed where the boundaries were not always straight and where adjacent laths apparently merged together. One explanation for the observation of irregular laths is that they had become distorted as a result of impingement and deformation accompanying the transformation [5]. Evidence of the existence of this deformation was apparent within the laths as a high density of tangled dislocations. Some of these form cell walls (Fig. 2), a substructure similar to cold-worked iron. The dislocation density is too high to measure by transmission electron microscopy, but Speich [6] has shown it to be between 0.3 and $0.9 \times 10^{12}\,cm^{-2}$ by electrical resistivity measurements.

The complete absence of internal twinning was confirmed in two ways. First, a large number of martensitic laths were studied, but none of the diffraction patterns showed twin spots. Second, dislocations were readily visible in the interior of the martensitic laths, which is not the case when internal twinning is present. This observation is in agreement with the morphology of lath martensite in the Fe–V, Fe–W, Fe–Sn, Fe–Mn and Fe–Mo alloys [1], although fine internal twins were noticed in lath martensite of Fe–C alloys and steels [7, 8].

### 3.2. Results of measurements of orientation relationships between adjacent laths

The analyses of the orientation relationships between laths were confined to those cases in which the lath boundaries were fairly straight and well defined. Selected-area diffraction patterns were obtained either from an area enclosing the boundary between laths and then determining which zone belonged to each lath by using dark-field techniques, or from individual adjacent laths in order to determine their orientations. Speich and Swann [5] and Chilton *et al.* [9] indicated that if adjacent regions of martensite adopted different variants of the Kurdjumov-Sachs orientation relationship, then the occurrence of both twin-related laths and laths that are separated by low-angle boundaries, would be expected. In addition, they stated that large-angle rotations should exist across adjacent laths in certain cases.

The Kurdjumov–Sachs relation is

$$\{1\,1\,1\}\gamma \parallel \{0\,1\,1\}\alpha \text{ with } \langle 0\,1\,1\rangle\gamma \parallel \langle 1\,1\,1\rangle\alpha.$$

This relationship is associated with a total of 24 variants. However, comparison of these theoretical predictions with experimental observations is difficult, except for exactly twin-related cases. Owing to this, it is convenient to express predicted orientation relationships of pairs of variants by measuring the deviation from the twinning orientationship. If adjacent laths are assumed to adopt different variants, the results of such an analysis fall into four separate groups, as described in [9]. In practice, it was not possible to distinguish between all four theoretical predictions, because of crystallographic and electron diffraction limitations. In view of this, the experimental observations were divided into three groups as follows:

(1) those cases in which adjacent laths were off twin orientation by less than 5°;

(2) those cases in which adjacent laths were off twin orientation by between 5° and 20°;

(3) those cases that were misoriented in standard orientation by less than 10° (about a $\langle 1\,1\,0\rangle\alpha$ direction).

It should be emphasized that the reference to twinning orientation does not imply a physical twinning process. The twinning orientation relationship is merely a convenient way of describing the orientation relationship between the laths, which is dictated by the Kurdjumov–Sachs relationship.

From all four iron–arsenic alloys, out of 25 cases analysed, 2 were assigned to group 1, 7 to group 2 and 8 to group 3. None of the groups were observed to be restricted to cases from any one particular alloy. Composite diffraction patterns from the adjacent laths, assigned to group 1, revealed zones of either two $\langle 1\,1\,0\rangle\alpha$ or $\langle 1\,1\,2\rangle\alpha \parallel \langle 1\,2\,2\rangle\alpha$, parallel to the electron beam. The combination of two $\langle 1\,1\,0\rangle\alpha$ patterns arose from exact twin orientations between adjacent martensitic laths, i.e. all the principal poles in one lath were 15° away from the nearest $\{1\,1\,1\}\alpha$ pole in the other [9]. The zones $\langle 1\,1\,2\rangle\alpha$ and $\langle 1\,2\,2\rangle\alpha$ are not quite twin related. The twin relation is not exact, because a twinning operation would result in $\langle 1\,1\,2\rangle\alpha$ and $\langle 1\,2\,2\rangle\alpha$ poles which are misoriented by 4° 28′ rotation about a $\langle 1\,1\,0\rangle\alpha$ direction. In group 2, diffraction patterns showed that adjacent laths have an orientation relationship of $\langle 1\,0\,0\rangle\alpha$ and $\langle 1\,1\,1\rangle\alpha$. These two zones are 54° 44′ apart in standard orientation and thus obviously do not belong to the small angle group (group 3); they are, however, 15° off twin orien-

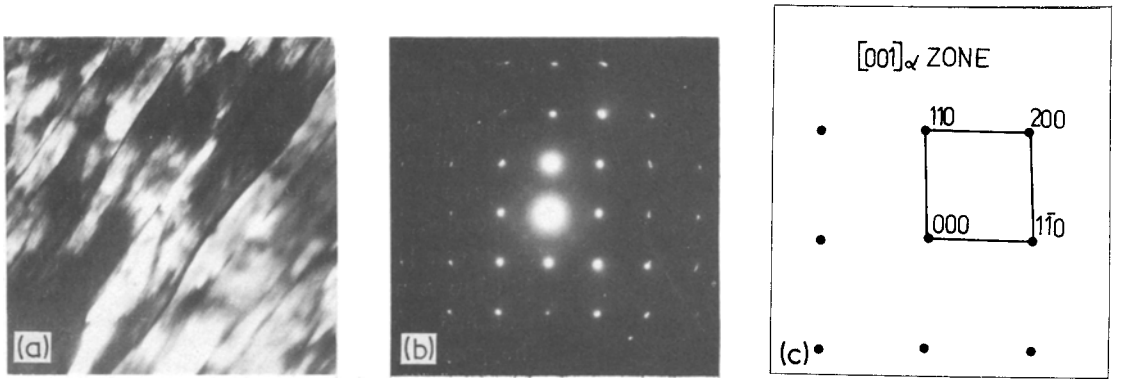


*Figure 3* Small-angle laths in quenched Fe–O.85% As alloy. (a) Thin-foil micrograph, × 20 000; (b) diffraction pattern; (c) analysis of diffraction pattern.

tation and were therefore assigned to group 2.

An example of a case that could be unambiguously assigned to group 3 is illustrated in Fig. 3. The electron diffraction pattern obtained from essentially the entire field shown in Fig. 3a is presented in Fig. 3b. The pattern analysed in Fig. 3c reveals a ⟨1 0 0⟩α zone. Because the intensity distribution of the reflections from single laths differs considerably, and the cells observed within the laths were excluded from the analysis, it was concluded that the laths were misoriented by a few degrees.

A fairly frequent observation was that a diffraction pattern taken from two adjacent laths would exhibit a single ⟨1 1 1⟩α zone. This situation could, in principle, arise from one of three cases: the laths could be exactly twin-related (group 1), or they could be misoriented about a ⟨1 1 0⟩α axis (group 3); a third possibility is that the boundary was not a true lath boundary but a low-angle cell wall. Since the possibility that the boundary was a very low-angle cell wall could not be ruled out, these cases were not included in the computation of the number of cases belonging to each group.

Twin-related laths were observed in plain-carbon steels [7, 10], iron–chromium–nickel alloys [11] and iron–ruthenium [12], but investigators of the iron–carbon [13], iron–nitrogen [14] and iron–chromium [15] systems reported finding no evidence of twin orientation between laths. Our results are consistent with the previous works [7, 10–12].

The accepted, and in this study confirmed, assumption [5, 9] that adjacent laths adopt different variants of the Kurdjumov–Sachs orientation relationship is not consistent with the orientation relation in Fe–C and Fe–Ni–C alloys which has been found to be nearly, but not exactly, the Nishiyama orientation relationship [16]. However, it is obvious that at this stage, a satisfactory understanding of all aspects of {1 1 1}α martensite must await the conclusion of further experimental work in addition to this and other formal analyses.

On the basis of limited sampling, it is not possible to make any detailed conclusion as to whether or not there was a tendency for particular combinations of variants to form side by side. However, it is significant that the cases where the inhomogeneous shears are complementary (adjacent laths exactly twin-related) [17] were not in the majority. The observation of a relatively high number of small-angle cases may indicate that these particular variants are effective in minimizing strain energy. It is postulated that the laths result from accommodation relaxation in either the parent austenite [18] or product martensite [15, 19].

### 3.3. Habit-plane determination

Selected-area diffraction patterns of the laths established the long axis of the laths. Only those laths with long directions lying approximately in the metallographic surface were analysed; otherwise the laths would appear foreshortened and consequently trace measurement would be difficult. The results obtained are plotted on the stereogram shown in Fig. 4.

In agreement with the previous works [7, 10, 16, 20, 21] the long direction of these martensitic laths always passed through, or very near to ⟨1 1 1⟩α. Single-surface trace analyses were made for the normals to the lath boundary to establish of a habit plane and, if so, to determine that plane. From a study of the corresponding traces of the normals for these laths, it was observed that the

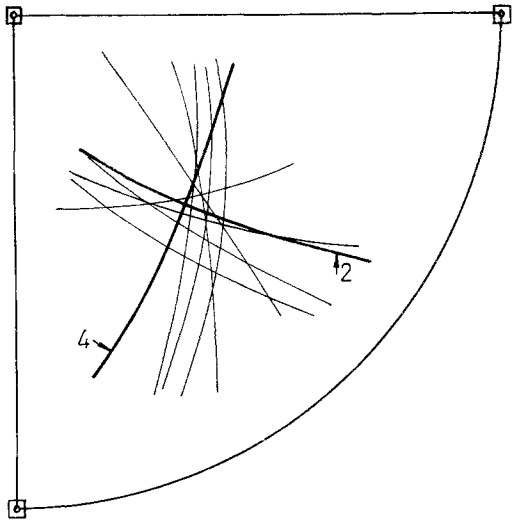


*Figure 4* Traces of long directions of laths showing that long directions of laths are parallel to ⟨1 1 1⟩α (numbers indicate coincident traces).

normal direction to the lath boundaries passed, within experimental scatter, through a particular point (1 1 0)α of the stereogram. Some of the results obtained are shown in Fig. 5. The observation of both a consistent habit plane and a long direction directly imply that the structural unit has a shape such that if $a$, $b$ and $c$ are the three principal dimensions, then $a \gg b > c$, i.e. the structural unit has the shape of a lath, but not that of a needle. There was no systematic variation of the habit plane with composition, which is in agreement with the data (for the lath martensite with the habit plane {1 1 1}γ) of Marder and Krauss [13] for Fe–C alloys andSchoen *et al.* [21] for Fe–Ni–C alloys.

It was shown previously [16] that the crystallographic parameters of lath martensite with a habit plane near to {1 1 1}γ are reasonably compatible with the assumption that the lattice invariant shear is (0 1 1) [0 $\bar{1}$ 1]α (which is equivalent to (1 1 1) [$\bar{1}\,\bar{1}$ 2]γ, "system II" [17]) as suggested by Wechsler *et al.* [22]. The predicted habit plane is 7.5° from ($\bar{1}$ 1 1)γ or (1 $\bar{1}$ 1)γ. However, no dilatation parameter (δ) has been incorporated; if a small δ is allowed, the discrepancy disappears [16]. The invariant shear (0 1 1) [0 $\bar{1}$ 1]α is not an observed deformation mode of b c c metals and, thus, it is reasonable to consider the possibility that this shear is the resultant of equal shear on (0 1 1) [$\bar{1}$ $\bar{1}$ 1]α and (0 1 1) [1 $\bar{1}$ 1]α. This is the only pair of commonly observed shears which satisfies the necessary condition that the two sets of dislocations must have the same shear plane and be parallel [23]. Through the analysis of the double shear concept proposed by Acton and Bevis [24], the amounts of shear on these two component systems may be varied with a consequent change in the resultant total lattice invariant shear, which is now equivalent to an invariant plane strain on (0 1 1) [$h$ $k$ $l$] α where $h$, $k$, $l$ are irrational numbers. It can be deduced that there is a range of reasonable shear magnitude [21] which gives good agreement with the experimental habit plane in the iron–arsenic alloys.

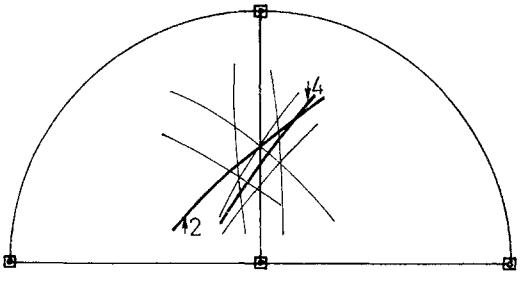


*Figure 5* Trace analyses of normals to lath boundaries showing that habit plane of martensitic lath is close to {1 1 0}α (numbers indicate coincident traces).

## 4. Conclusions

(1). It was found that the lath martensite in the iron–arsenic alloys is made up of packets of parallel laths.

(2) The substructure of the iron–arsenic martensite has the form of laths and within the lath boundaries a network of dislocation cell walls exists.

(3) Adjacent laths may be separated by low- or high-angle boundaries or may be twin-related, which is consistent with the theory that adjacent laths adopt different variants of the Kurdjumov–Sachs orientation relationship.

(4) It is established that the long direction of the laths was parallel to ⟨1 1 1⟩α and the habit plane was close to a {1 1 0}α plane.

(5) The present observations were consistent with the transformation of low-carbon lath martensite occurring by the system II [17] as one of the two possible inhomogeneous systems.

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