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Geometric surface relief and the allotropic transformation in iron

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Geometric surface relief effects have been observed in association with the $\gamma \rightarrow \alpha$ allotropic transformation in iron. The selected-area electron channelling pattern technique has been used to establish that tent shaped geometric relief effects, common to single α precipitate plates in Fe–C and Fe–C–X alloys, are also associated with similar single crystal morphologies in pure iron. These experimental observations extend to the allotropic transformation in iron the same rationale for the relationship of interfacial structure to surface relief effects that is known to apply in the instance of precipitation reactions. In addition it provides support for an earlier proposal that "massive" transformations can be subject to the same crystallographic constraints as precipitation processes.

1. Introduction

Surface displacements that accompany solid-state phase transformations are of two general types. One is the non-crystallographic rumpling that accommodates a difference in specific volume between parent and product phase [1] and the other is the "geometric" relief that is characterized by one or more planar surface tilts [2]. Although the two kinds of surface relief in general cannot be used to distinguish mechanistically between modes of transformation, it is observed operationally that the migration of a disordered interphase boundary usually leads to non-crystallographic rumpling, whereas structured interface motion often produces geometric relief [3, 4]. The geometric surface tilts that are easiest to understand and to describe quantitatively are those that accompany the invariant plane strains (IPS) of martensitic transformations [5, 6] However, it has been shown recently that certain diffusional transformations also can produce equivalent surface-relief effects [3, 7–9]. In other words, the propagation of structured interfaces, whether by co-operative atom movements or by diffusion, can lead to similar surface tilts and thus to superficial ambiguity concerning the transformation mechanism. Regardless of surface relief, it can be argued that composition differences between parent and product phases effectively distinguish diffusional transformations from martensitic, but this then leaves open the issue of non-martensitic transformations without composition differences, involving short range diffusion, as for example massive transformations in alloys and alloptropic (massive) transformations in pure metals.

The allotropic $\gamma \rightarrow \alpha$ transformation in unalloyed iron, when it occurs during cooling at rates less than $\sim 5000^\circ C\ sec^{-1}$ [10], is usually cited as an example of the non-crystallographic surface-rumpling mode. The surface features reflect the "massive" development of predominantly equiaxed ferrite crystals, presumably through the agency of disordered interface migration. These relief effects ought to be related to the crystallographic details of α growth from γ in much the same way as they are in iron–carbon [3] or iron–carbon–X alloys [11] (leaving aside for the moment the morphological consequences, through kinetics, of satisfying the necessity for partition of alloying elements). That is, there is no *a priori*

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reason why allotropic α cannot develop by way of anisotropic shapes such as rods or plates, and if nearly coherent interfaces are involved to some degree, then to that degree there should be geometric surface relief on an originally planar surface. It is the purpose of this note to present experimental evidence in support of this suggestion.

2. Experimental procedures

Bulk samples of electrical grade Armco iron and a high purity Battelle (0.003%C) iron [12] were prepared as 1 cm x 1 cm x 0.1 cm wafers. To ensure a strain-free initial structure with large grain size, the samples were annealed in vacuo for 4h at 1200° C, furnace cooled to 700° C, then cooled more rapidly to ambient. Sample surfaces were next mechanically polished and finished with an electropolish. Each of the samples was then sealed individually in quartz capsules that had been evacuated to 10^{-5} Torr. After the specimens were re-austenitized for 2 h at 1200° C, the capsules were removed from the furnace, set on a refractory brick and allowed to cool slowly to room temperature, whereupon the capsules were broken and the specimens retrieved.

Surface relief associated with the allotropic transformation was observed and recorded photographically by both conventional and (thallium) light interference microscopy. Areas of geometric relief so located were re-examined in a Cambridge Stereoscan scanning electron microscope equipped with a dynamically corrected spherical abberation unit for the selected-area electron channelling mode [13]. This instrument can obtain a crystallographic pattern from an area as small as 1 μm diameter, with a sensitivity of better than 0.3 degree variation in orientation. Selected-area channelling patterns, typified by the example shown in Fig. 1, were taken throughout the areas of observed geometric surface relief. An accurate mapping was achieved both of the positions of α/α grain boundaries and of the relation of surface features to underlying structure.

3. Results

A number of examples of the observed geometrical relief effects are shown in Fig. 2. While some seem more strikingly "martensitic" in appearance than others, all can be characterized as exhibiting relatively planar facets, in contrast to the far more irregular rumpling found in adjacent areas. In (a) the relief appears indistinguishable from that commonly associated with highly symmetrical proeutectoid ferrite plates in Fe–C alloys [3, 14]. The geometrical surface distortions in (b) are somewhat less obviously planar, and the result in (c) is identical to the appearance of the "sawtooth" morphology of proeutectoid ferrite on the as-transformed surface [3, 15]. Prior austenite grain boundaries, thermally etched at 1200° C, dominate the background structure. Regions such as these were not typical of each entire pre-polished surface area; most of the surface was rumpled in the "traditional" way, but several such examples could be found on each specimen.

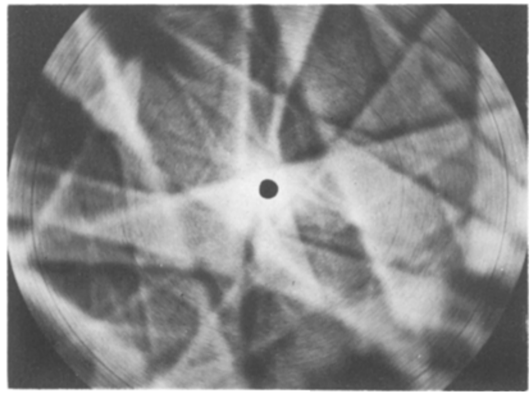

Figure 1 Selected-area electron channelling pattern from ferrite (grain α_1 in Fig. 4) indicating the pattern quality obtained in this study from 2μm diameter areas.

The results of the selected-area orientation analyses by electron channelling patterns can be simply stated: single crystals often exhibited multifaceted geometric relief effects. It turned out that there is little relation between the details of the geometric surface distortions and the underlying structure, except that it is common for grain boundaries to lie along the outer edges of the geometrical areas. Parallel bundles of "tent" relief, as in Fig. 2a, invariably produced channelling patterns of just one crystal orientation, and frequently regions of relief with multiple trace directions, as in Fig. 2b and c, occurred on the surface of a single crystal.

Examples of the relation of surface relief to disposition of underlying crystals are shown in Figs. 3 and 4. Crystal boundaries in Fig. 3 are sketched in (b) and (d), corresponding to the photomicrographs (a) and (c), respectively. Fig. 3a and b show the location of α/α boundaries that are associated with tent-shaped ridges and other linear features. Boundary BC parallel to the ridge is a

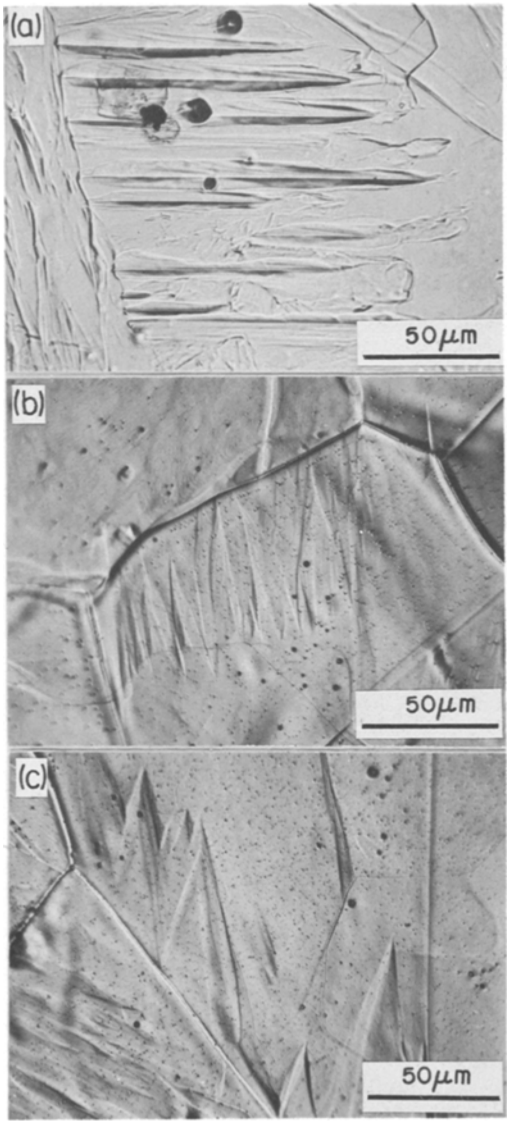

Figure 2 Geometric surface relief effects resulting from the allotropic transformation of (a) ARMCO iron and (b) and (c) Battelle iron, chosen to illustrate the range in appearance observed in this study.

low-angle (2°) interface, while the boundary AC involves a misorientation of 4.8° plus a 130° rotation. In Fig. 3c and d the grain boundary BC defines the lower extent of the sawtooth surface-relief morphology, and aligns with the boundary of the anisotropic morphologies at the BC boundary on the right and the BA boundary on the left. In between, the direction of post-transformation grain-boundary "adjustment" in the vicinity of the dominant geometric relief is indicated by arrows. Fig. 4 affords comparison between geometric surface relief effects as normally viewed and as quantified by light interferometry. The dominant grain-boundary groove marks the extent of the prior austenite grain. The seemingly arbitrary disposition, with regard to the anisotropic relief features, of the α grain-boundary only becomes apparent in the scanning electron micrographs in Fig. 4c and d.

4. Discussion

The genesis of geometric relief effects in iron can be deduced by analogy to the way that similar structures are generated in alloyed iron. Therefore, we first enumerate the mechanisms that are appropriate to Fe–C and Fe–C–X alloys, and then account for the differences between alloyed and unalloyed iron.

In Fe–C (and Fe–C–X) alloys, ferrite nucleates and grows within the crystallographic constraints of an orientation relationship to austenite. The relationships deduced from habit-plane measurements [8, 16] appear to be in the range from Kurdjumow–Sachs [17] to Nishiyama [18]–Wasserman [19]. Since the lattice parameters of austenite and ferrite are fixed, there are relatively few spatial orientations of the interface that produce nearly coherent interphase boundaries [3, 20, 21]. When these do occur [22], they constitute a structural barrier to growth [3, 15, 23] so that the shape of ferrite crystals is biased in the direction of motion of the disordered segments of the interphase boundaries. The portion of the interface that forms the structural barrier can be moved only through the agency of ledge passage [15], which is usually a much slower process than the migration of disordered interfaces. Of importance here is that geometric surface relief effects are associated with these structural barriers to growth [3], whereas transformation by the motion of disordered interphase boundaries leads to non-geometric surface rumpling. Moreover, when a competing disordered interface replaces a nearly coherent (dislocation) boundary, the nature of the surface relief changes accordingly, so that the resulting ferrite grain can exhibit a complex mixture of geometric and non-geometric surface features [3, 14, 24]. Presumably, then, the disposition of such relief effects can be used to deduce at least the qualitative nature of the α/γ interface at any point in the growth sequence. A possible sequence for proeutectoid ferrite is shown schematically in Fig. 5a to c.

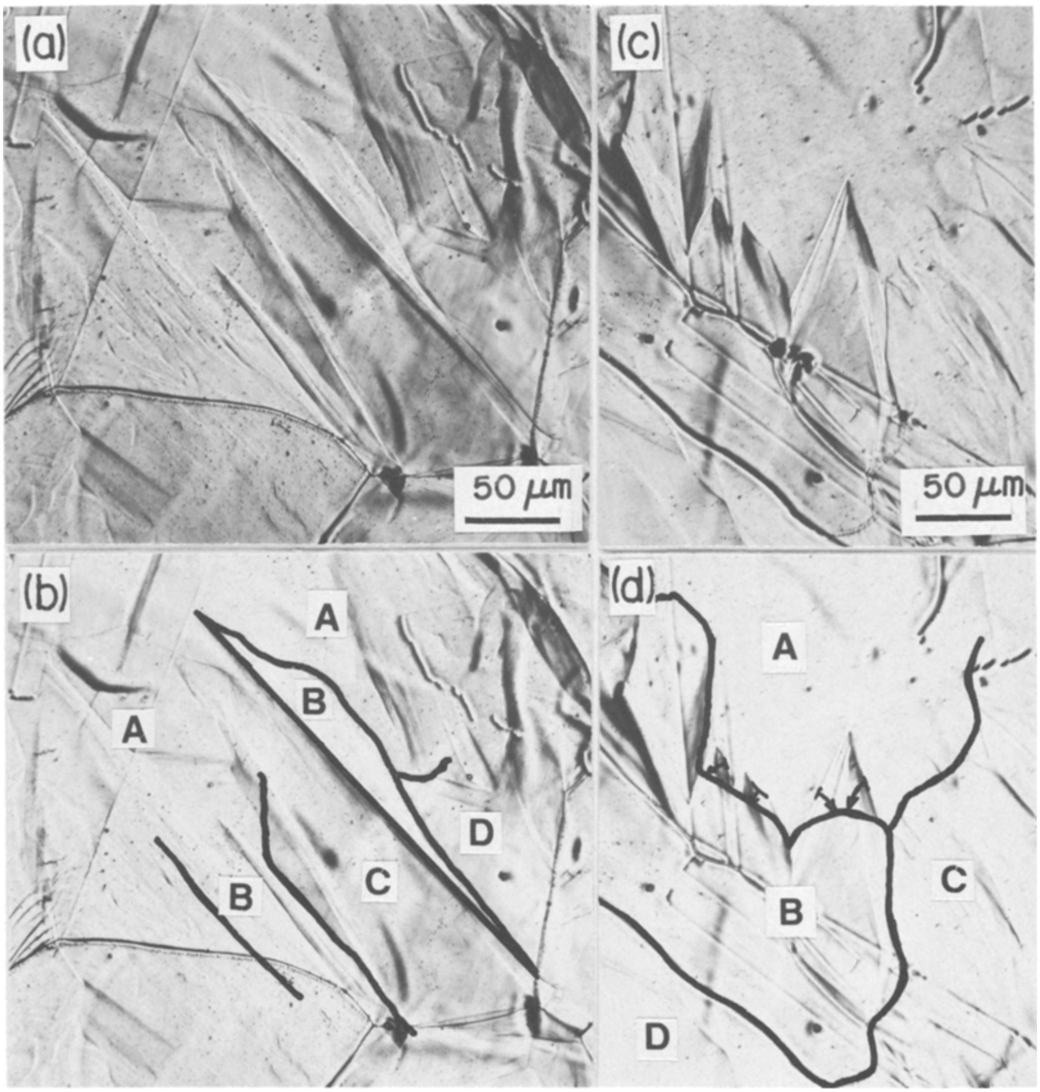

Figure 3 Geometric surface relief effects correlated with grain-boundary placement chosen to illustrate (a) and (b) commonly observed relation of lineage structure to grain boundary (previous α-γ interface) and (c) and (d) results of grain-boundary adjustment following transformation of α_1-γ interphase interface into α_1-α_2 grain boundary.

Surface relief effects should provide a similarly translatable record of structural evolution for the allotropic formation of ferrite in pure iron. Although geometric relief effects are not the most prevalent, they have not gone unnoticed in the published literature [25]; the consequent conclusion that the "Widmanstatten transformation" was somehow "inherent" to pure iron was based on the observation that W_s temperatures extrapolate to the vicinity to 900° C as carbon content approaches zero [26]. There are, however, two important differences between ferrite formation in alloyed and unalloyed iron. One is that interstitial, and occasionally also substitutional [27], alloying elements partition between γ and α during transformation. A "chemical" stability, with respect to local reverse transformation, is thereby conferred on the transforming structure. Moreover, ferrite regions are usually bounded by decomposition products (pearlite or bainite) of austenite in which the solute level had built up, by partition, to supersaturation. The interfaces so defined are essentially immobile. Not only is chemical partition absent in unalloyed iron, but even more important, the final structure is all ferrite. This means that all former γ/α boun-

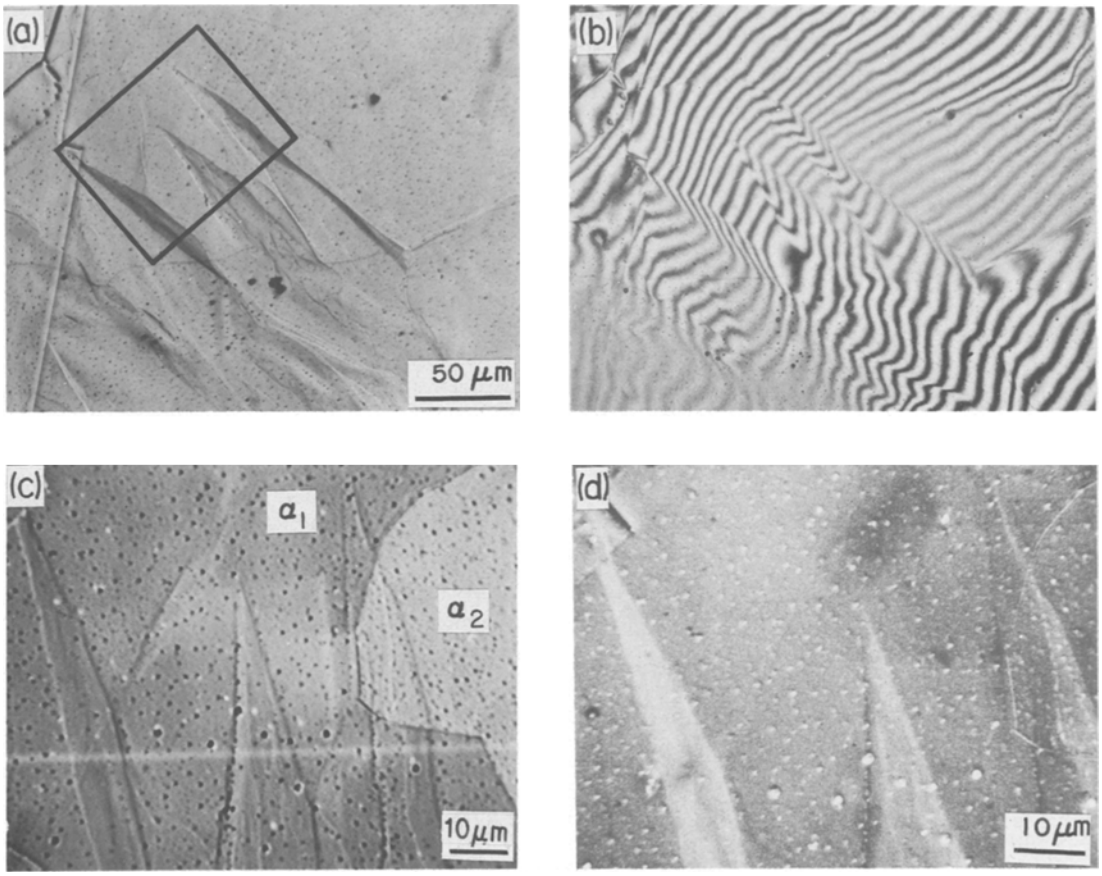

Figure 4 Light optical (a) and light interference micrographs (b) characterizing anisotropic surface relief effects in high purity Battelle iron. Scanning electron micrographs in (c), specimen current modulation, and (d), secondary electron imaging mode, reveals the location of the α grain boundary in the area outlined in (a).

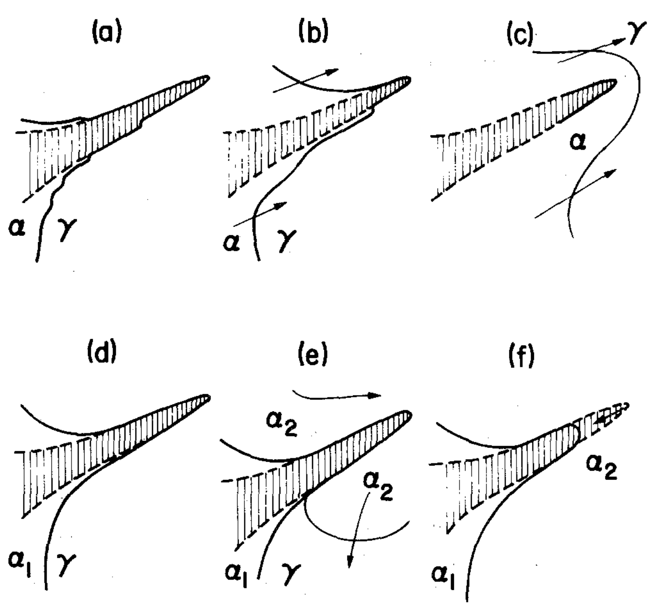

Figure 5 Schematic portrayal of possible growth sequences leading to structures observed in pure iron. Shaded portions are areas of geometric surface relief.

daries, some of which were special (nearly coherent), end up as α/α boundaries; α/α homophase boundaries will almost invariably be more mobile than the complex interfaces between α and α-Fe_3C composite phases.

The result of the foregoing is that in alloyed iron continued transformation tends to stabilize the ferrite grains at their furthest extent of growth and once γ transformation is complete, any subsequent changes in the structure can be relatively slow. But in pure iron, any γ which has a special interfacial relationship with a developing α_1 morphology (an interface that generates geometric surface relief as it propagates) may complete the transformation via a different, α_2, ferrite orientation. Then, post-transformation grain-boundary movement may cause some areas of geometric surface relief to end up with two or more crystals underneath, even though each of the areas overlaid a monocrystal at the time of transformation. Illustration of such a growth sequence is shown schematically in Fig. 5d to f. In similar fashion, transformation of $\gamma \to \alpha$ might be accomplished by nucleation of the same variant, α_1, in different parts of the γ grain. Subsequent impingement of the separate α_1 crystals could lead to a low-angle boundary in the final ferrite structure, as for example the 2° boundary shown in Fig. 3a and b.

Another important difference between alloyed and unalloyed iron is that the former transforms over a range of temperatures, and the latter transforms at one relatively high temperature. The $\gamma \to \alpha$ transformation is complete in iron at 900°C, a temperature at which grain boundaries can be quite glissile. In order to pre-empt all possibility of martensitic transformation, our experiments emphasized slow cooling through the transformation, a situation which would encourage post-transformation grain-boundary adjustments. That this seems a factor in the apparent relation of surface relief to ultimate grain structure is shown by example in Fig. 3c and d. In these instances the replacement of γ by α_2 (Fig. 5e and f) destroys the structural identity and function of the previous α_1/γ interface, and thence the α_1/α_2 boundary mobility is, to first order, influenced by boundary curvature and responds as indicated in Fig. 5e. Such grain-boundary migration leaves previous macroscopic surface distortions invariant since only crystal orientation changes. Essentially the same result obtains upon the reverse ($\alpha \to \gamma$) transformation, leaving geometric reliefs in recognizable form if the transformation is accomplished by disordered interface motion [28].

In view of the comparatively few examples of pronounced geometric surface relief found, the conclusion is that α/γ dislocation interfaces (structural barriers) are either rare or not very tenacious relative to disordered interfaces in pure iron. The rapid increase in driving force with even slight undercooling favours a high nucleation rate and encourages rapid conversion of austenite to ferrite. Under these conditions only the most singular structural barriers are able to be sustained long enough during growth to establish geometric surface relief characteristics extensive enough to be clearly detected by optical inspection. The perhaps more common (composite) structural interfaces comprised of segments of dislocation interfaces, slightly misoriented with respect to each other and joined by comparatively large (disordered) ledges [3], break down with more facility and are easily replaced by largely disordered interfaces. Support for the suggestion that ledge motion to circumvent barriers of this sort are more common during growth than would appear from (surface) vestigal remains can be garnered from growth kinetic date of Eichen and Spretnak [29] which are believed to be indicative of ledge passage. In the case of pure iron the crystallographic factors (orientation relationships, lattice parameter, etc) do not provide for distinctly strong structural barriers [21]. This, taken with the high mobility of disordered interfaces (with very little undercooling), encourages even slightly disordered interface segments to be replaced with structures favoring sustained and rapid growth.

5. Conclusion

Geometric surface relief effects accompanying the ($\gamma \to \alpha$) allotropic transformation in pure iron have been correlated with the underlying crystal structure. A rationale has been constructed which lends credence to the proposition that the role of structural barriers to growth, both with regard to morphological influence and effect on surface relief, established for alloyed iron and other precipitation reactions [15, 23], can be directly extented to include the allotropic transformation in pure iron. Significant also is the tacit support lent to the earlier suggestion [30] that the role of interfacial structure in the growth of "massive" transformations, of which the allotropic transformation in iron is but one (albeit special) example, is mechanistically the same as in precipitation reactions.

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