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Multilayer Surface Films Coexisting with Crystallites in Model Fe/Al_2O_3 Catalysts

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In the case of iron on alumina model catalysts, contiguous patches of multilayer surface films have been observed to coexist with three-dimensional crystallites, following high-temperature oxygen treatment. The films are clearly visible around the particles in the electron micrographs. The film is likely to exist also farther away from the particles, but it is too thin to be directly observed. The existence of such a film on the substrate away from the crystallites is, however, inferred indirectly from the diminished sharpness of the substrate grain boundaries in oxygen as compared to that in hydrogen, and also from the formation of a large number of new particles on subsequent hydrogen treatment. In some instances, the visible films extend out farther and contact those around other crystallites thus generating patches of thick films which interconnect a few separated, neighboring crystallites. Following oxygen treatment, thermodynamic and kinetic conditions for wetting are so favorable that relatively small crystallites of the spectrum, but as large as 500 Å, have been observed to have almost completely spread out, leaving only a patch behind. When such spreading occurs, the subsequent high-temperature reduction leads to the formation of a large number of new particles on the substrate even in the regions where particles were not present. The new particles form probably as a result of either the rupture of a contiguous multilayer surface film and the subsequent contraction of the resulting patches, or by the contraction of unconnected, extended patches of film present on the substrate. Thermodynamic considerations are employed to explain the stability of the thin surface film in an oxidizing atmosphere and its instability and rupture during subsequent reduction.

INTRODUCTION

The phenomenon of wetting has major consequences in supported metal catalysts, since it influences the shape and size distribution of the metal crystallites, which in turn affect the activity and selectivity. While discussing the role of wetting on the particle size distribution and on the redispersion of the sintered catalysts in an oxygen atmosphere, Ruckenstein and Pulvermacher (*1*) pointed out that the interplay between the strong metal–support interactions and the interfacial free energies plays a significant role in the behavior of the crystallites. They also examined the role of additives on the wetting characteristics of the crystallites. Subsequently, experimental results were presented and the role of wetting in the observed redispersion of Pt on Al_2O_3 was again emphasized (*2*). Direct evidence for the extension of metal crystallites on substrates has been obtained using electron microscopy in a number of model, supported metal catalysts (*3–9*). Derouane *et al.* reported on the wetting behavior of iridium particles on graphite (*7*) as well as on the wetting of copper particles on MgO (*8*). Extended shapes were also observed in the case of Pt/TiO_2 in hydrogen (*9*). Chen and Ruckenstein observed wetting-related phenomena at different temperatures in the case of Pd/Al_2O_3, including pit formation, toroidal shapes, and "tearing" of the crystallites (*4, 6, 10*). Nickel (*11, 12*) and iron (*13, 14*) on alumina were shown to give rise to unusual toroidal shapes and to the rupture of the crystallites.

Recently (*14*), results were presented regarding the behavior of Fe/Al_2O_3 model catalysts in oxidizing and reducing atmospheres. The effect of the strong in-

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teractions between the crystallites and the support on the wetting behavior and consequently on the shape of the crystallites was emphasized. In an oxidizing atmosphere at 700°C, thick films were detected around the crystallites and, in addition, the possible presence on the support of a thin multilayer film, of either iron oxide or iron aluminate, coexisting with the three-dimensional crystallites was inferred from the electron micrographs. This undetectable film on the substrate is not necessarily continuous but is most likely composed of interconnected patches extending out from around the crystallites, their thickness decreasing farther away from the latter. This inference was based on the detection of the visibly thick film around the particles, as well as on the diminished sharpness of the grain boundaries of the support. The expectation that at temperatures greater than 700°C, the film would be thick enough to be clearly seen in the micrographs, not just around the particles but over a larger area, prompted the present high-temperature experiments.

EXPERIMENTAL

The experimental procedure is similar to that described in Refs. (*2*, *14*). High-purity iron (99.998%, Alfa Products Inc.) evaporated onto electron-transparent films of planar, nonporous, crystalline alumina served as the specimen for the electron microscopic studies. The model iron/alumina catalysts were heated in purified hydrogen and in oxygen at or above 800°C inside a 2.5-cm-diameter quartz tube. The ultrahigh pure hydrogen supplied by Linde Division, Union Carbide Corporation (99.999% pure, <1 ppm O_2 and <2 ppm moisture), was further purified by flowing it through a Deoxo unit (Engelhard Industries) followed by an indicating type silica gel column and then through a bed of 15% MnO on SiO_2 (*15*) and finally through 13X and 5A molecular sieve beds immersed in liquid nitrogen. Ultrahigh pure oxygen (99.99%, <3 ppm moisture) was used without further purification. Ultrahigh pure helium (99.999%, <3 ppm moisture) was passed through the 5A molecular sieve bed immersed in liquid nitrogen. The flow rate of the gases was about 150 cm^3/min and was held constant during the heat treatment. Several specimens were investigated, but the results for two of them are presented here. The specimen of 7.5 Å initial film thickness corresponding to Fig. 15e in Ref. (*14*), which was previously used for alternate heating in oxygen and hydrogen at and below 700°C (specimen A), was further used to observe the changes following the higher temperature treatments. In addition, results are presented for a fresh specimen having the same initial loading as A. This specimen was first heated in hydrogen successively at temperatures between 500 and 800°C. The specimen thus obtained (specimen B) served as the initial state for the subsequent alternate oxidizing and reducing treatments. All the samples were gradually heated from room temperature to the desired value in a helium atmosphere and, following the specified duration of heating in hydrogen or oxygen, were again slowly cooled to the room temperature in a helium atmosphere. A JEOL 100U transmission electron microscope was used to observe the changes in the same regions of the specimen following different heat treatments. Electron diffraction patterns were obtained after each heat treatment to learn about the chemistry of the process.

RESULTS AND DISCUSSION

Evidence for a Thick Surface Film

The heating sequence and the events observed are listed in Tables 1 and 2. Fig. 1a represents the initial state of specimen A. Heating this specimen at 800°C in hydrogen for 1 h caused the particles to grow in size (Fig. 1b). In addition, a few pairs of neighboring particles coalesced and concurrently a number of small particles appeared on the substrate. The small particles which formed might have resulted (i) by the rupture of a contiguous film and/or contrac-

TABLE 1

Sample A

Heating conditions	Events observed
800°C, H_2	
1 h	Increase in size of all particles, coalescence of a few neighboring crystallites, and appearance of new small crystallites (Fig. 1b)
2 h	Crystallite rotation and/or reconstruction, increase in size of some small particles, disappearance of other small crystallites, and coalescence of neighboring pairs of crystallites (Fig. 1c)
5 h	Increase in size and contrast of all particles. Coalescence of a few particles. A few of the smaller particles disappeared and others grew in size (Fig. 1d)
800°C, O_2	
1 h	Patches of thick film around the crystallites interconnecting a few neighboring crystallites. Decrease in the particle size (Fig. 1e)
5 h	Apparent increase in the thickness of the visible film. Substrate grain boundaries less sharp compared to those after heating in H_2 (Fig. 1f)
500°C, H_2	
1 h	Decrease in the thickness of the visible film
5 h	Further decrease in the thickness of the visible film. Substrate grain boundaries much sharper (Fig. 1g)
800°C, H_2	
1 h	Almost complete withdrawal of the visible film to merge with the neighboring crystallites
5 h	Coalescence of a few nearby particles (Figs. 1h, h′)
800°C, O_2	
2 h	Reappearance of the thick, interconnected, patches of film (Fig. 1i)
900°C, O_2	
1 h	An increase in the thickness of the film. Disappearance of a few small crystallites (Figs. 1j, j′)
15 h	Disappearance of smaller crystallites, or their considerable extension and loss of molecules to result in traces of relatively thin patches. The particles are faceted (Figs. 1k, k′)
900°C, H_2	
1 h	Complete contraction of the thick film to merge with the crystallites. Coalescence of nearby particles. A substantial increase in particle size and a corresponding decrease in their number (Fig. 1l)
800°C, H_2	
5 h	Particle reconstruction. Formation of a few small particles (on contraction of residual surface film) (Fig. 1m)
800°C, O_2	
4 h	A narrow ring of film around the particles and a thin film also on the substrate. The film appears to spread in stages. At least, 2 layers can be differentiated in the film around the particles (A in Fig. 1n)
900°C, O_2	
5 h	An apparent film on the substrate, more uniform and thinner than before. A narrow ring of thick film around the crystallites (Fig. 1o)
800°C, H_2	
4 h	Withdrawal of the visible film (Fig. 1p)
800°C, H_2	
3 h	(After a few months of storage in desiccator). Residual film around crystallites.
900°C, O_2	
12 h	Thick patches of film interconnecting neighboring particles (Fig. 1q)
800°C, H_2	
4 h	Contraction of the film. There is still a thin residual film on the substrate (Fig. 1r)
900°C, H_2	
3 h	Further contraction of the residual film around the particle to form very small crystallites (Fig. 1s)

TABLE 1—*Continued*

Sample *A*

Heating conditions	Events observed
800°C, H_2	
4 h	Partial recontraction of the patches of film. The films appear thinner
900°C, O_2	
12 h	Extension of the newly formed small crystallites and reappearance of thick interconnected patches of film. Some relatively large particles also extend out completely (Fig. 1t)

TABLE 2

Sample B

Heating conditions	Events observed
500–800°C, H_2	Initial state. Very large particles (~1000 Å) and small particles (~100 Å) present on the substrate (Fig. 2a)
800°C, H_2	
5 h	A number of small particles grew in size to 300 Å or larger. Some of the small particles vanished and others remained. Some large particles appear to have formed by the coalescence of the detectable and undetectable small particles. The previously existing large particles changed little in size (Fig. 2b)
500°C, O_2	
1 h	A visible film forms around the particles interconnecting the neighboring crystallites. A number of small particles of 150 Å or less remain (without extending out completely) with a large cavity and a small remnant particle within
19 h	Very little change (Fig. 2c)
500°C, H_2	
8 h	A complete withdrawal of the film. Decrease in the number of particles as a result of the coalescence of some small particles with the large ones. A number of small particles remain and most of them are dark and compact (Fig. 2d)
800°C, H_2	
4 h	A decrease in the number of small particles. A few small ones grow while others nearby decrease, disappear, or remain as such. The large particles are unaffected (Fig. 2e)
600°C, O_2	
2 h	Little change
800°C, H_2	
4 h	Very little change
700°C, O_2	
5 h	A narrow ring of film around the particles. No other change
800°C, H_2	
4 h	No change
800°C, O_2	
4 h	A narrow ring of film around the particles. Very little change (Fig. 2f)
900°C, O_2	
4 h	A few small particles lost their particle character and thick patches were left in their places. The substrate grain boundaries are less sharp. The substrate appears modified or covered by patches of thick film (Fig. 2g)
800°C, H_2	
2 h	A number of new particles of 150–300 Å appeared in all the regions. The substrate grain boundaries are sharper.
Up to 8 h	Very little change (Fig. 2h)
800°C, O_2	
4 h	Reconstruction of large particles. A narrow ring of film around most particles

TABLE 2—*Continued*

Sample *B*

Heating conditions	Events observed
900°C, O_2	
4 h	Most of the small particles are replaced by thick patches of film. The large particles are unaffected (Fig. 2i)
800°C, H_2	
4 h	The extended patches recontract to form small particles with a large cavity, and some cavities have a small particle within (Fig. 2j)
900°C, O_2	
8 h	(After a few months of storage in desiccator). Film around the particles and extension of small particles to patches (Fig. 2k)
22 h	Thick films around particles. A decrease in the particle size. The small particles decrease in size or disappear leaving patches of film behind
40 h	Additional small particles lose their particle character and leave patches of thick film behind. A few small particles disappear (Fig. 2l)
800°C, H_2	
3 h	Formation of a number of small particles both in regions where patches were left behind as well as in other regions. The particles formed are much smaller than the ones which lost their particle appearance before (Fig. 2m)
7 h	Some small particles decrease in size while other small particles increase in size
900°C, H_2	
3 h	Decrease in size or disappearance of smaller particles and growth of others. A considerable decrease in the number of small particles
900°C, O_2	
12 h	A decrease in size or disappearance of smaller particles. Small patches of film on the substrate (Fig. 2n)
800°C, H_2	
4 h	A few small particles on the substrate. Very little change except for an increase in the sharpness of the substrate grain boundaries

tion of undetectable patches of film on the substrate, (ii) by migration and coalescence of small undetectable particles, and (iii) by nucleation and subsequent growth by the capture of atoms or molecules diffusing on the substrate. Another hour of heating led to further sintering. Some small particles grew in size while other small particles vanished (Fig. 1c). Some large particles rotated and/or coalesced with their neighbors and/or underwent shape modifications. Subsequent heat treatment in hydrogen for 3 additional hours caused an increase in the size of all the crystallites (both small and large) without a decrease in the number of smaller particles (Fig. 1d). Some of the relatively small crystallites increased to as much as two or three times their original size, and some of the larger particles in contact coalesced. All the particles were dark and compact. Since the particles increased in size considerably and no detectable particle disappeared, the observed growth could either be apparent, because of extension and reorganization, or real. If the growth were real, which is more likely, the crystallites must have increased in size either by the capture of unresolved particles or atoms, or by the contraction and merging with the crystallites of surrounding, undetectable films. Electron diffraction provided *d*-values which did not correspond to any particular stoichiometric compound of iron. The major *d*-values were larger than those of the iron aluminate, $FeAl_2O_4$. A nonstoichiometric Fe_xO, or more likely, its solid solution with Al_2O_3, might have formed.

The subsequent heat treatment in oxygen gave rise to interconnected films on the substrate surrounding the crystallites (Fig.

1e). The latter were faceted. Following further heating in oxygen, the films around the particles appeared to have become thicker (Fig. 1f). In the regions away from the particles, where the film is not clearly visible, the substrate grain boundaries appear considerably less sharp as compared to those observed after heating in hydrogen. Therefore, it appears that a film extends over a large part of the support, its thickness being larger closer to the particles and substantially smaller sufficiently away from them. The film may not be continuous throughout, but may be composed of interconnected patches. It does not appear to be extended symmetrically around the particles, perhaps because of substrate heterogeneities. In the diffraction pattern recorded following the above heating in oxygen, the rings detected earlier after the hydrogen treatment remained, but with their *d*-values now larger and approaching those of γ-Fe_2O_3. In addition, a number of new rings appeared. The most intense of them correspond to the major *d*-values of $AlFeO_3$. These additional rings were less bright and were spotted, indicating that only a finite set of orientations of crystallites or patches of thick film, more likely the latter, were diffracting. Since the film and the additional spotted rings appear only following the oxygen treatment, it is very likely that the film is composed of $AlFeO_3$. The particles themselves may also be covered by such a film. This compound could be formed either by the diffusion of iron oxide from the particles to the substrate (the bulk as well as the surface), or by the diffusion of Al_2O_3 to the crystallites. The particles in contact did not coalesce on prolonged heating in oxygen, indicating that perhaps a protective layer of $AlFeO_3$ was present on the crystallites which hindered coalescence.

Heating this specimen further in hydrogen at the lower temperature of 500°C for 5 h did not affect the chemical composition but marginally decreased the apparent thickness of the film around the particles (Fig. 1g). However, heating in hydrogen at 800°C for 1 h caused almost a complete withdrawal of the films around the particles, which, very likely, coalesced with the latter. Some of the particles, which were close together or already in contact, coalesced (probably as a result of the reduction and consequent elimination of the protective layer), leading to a small decrease in the number of distinct crystallites Figs. 1h, h′). Correspondingly, the additional diffraction rings observed under the oxidizing conditions were almost completely eliminated and the *d*-values of the other rings reverted in time to the values prior to oxidation. As inferred from the diminished sharpness of the grain boundaries, the substrate still appeared to be covered with a very thin film. Probably, because of the strong interaction between γ-Al_2O_3 and iron oxide, a thin residual film which is not completely reduced, still remains on the substrate even after heating in hydrogen.

Thick films interconnecting several neighboring particles reappeared on heating for only 2 h in oxygen at 800°C (Fig. 1i). The micrographs appear to indicate that the thick film "flows" over the particles. There is a marginal decrease in the size of the particles. On increasing the temperature to 900°C and heating in oxygen for 1 h, the

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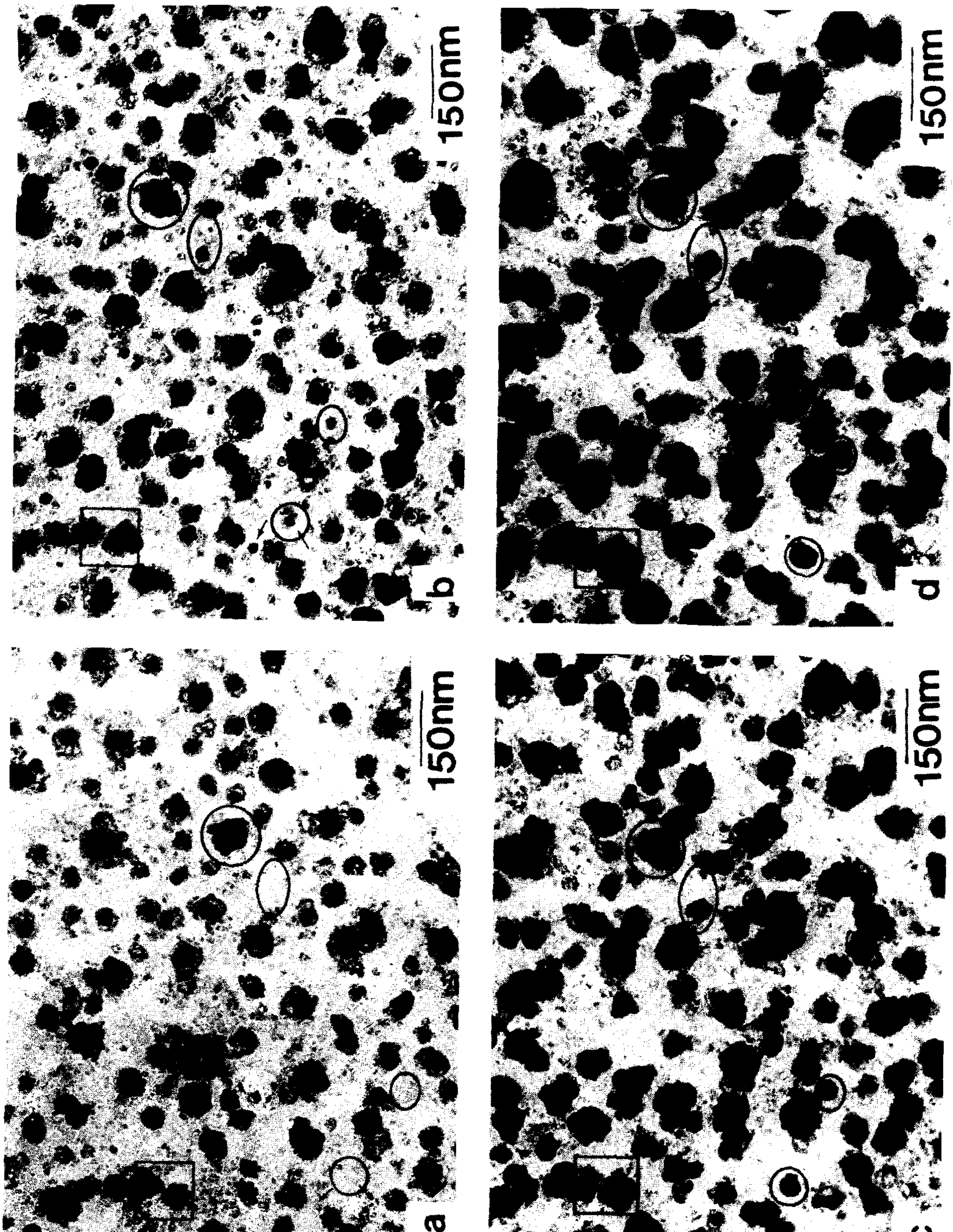
FIG. 1. Sequence of changes in the same region of a model Fe/Al_2O_3 catalyst. The same specimen was previously used to investigate the behavior during alternate oxidation and reduction at temperatures between 500 and 700°C (specimen A). (a) 1 h, H_2, 700°C. Initial state (it corresponds to Fig. 15e of Ref. (*14*)). (b) 1 h, H_2, 800°C, (c) 2 h, H_2, 800°C (d) 5 h, H_2, 800°C, (e) 1 h, O_2, 800°C, (f) 5 h, O_2, 800°C, (g) 5 h, H_2, 500°C, (h) 5 h, H_2, 800°C, (i) 2 h, O_2, 800°C, (j) 1 h, O_2, 900°C, (k) 15 h, O_2, 900°C, (l) 1 h, H_2, 900°C, (m) 5 h, H_2, 800°C, (n) 4 h, O_2, 800°C, (o) 5 h, O_2, 900°C, (p) 4 h, H_2, 800°C. The following micrographs correspond to a different region of the same specimen: (q) 12 h, O_2, 900°C, (r) 4 h, H_2, 800°C, (s) 3 h, H_2, 900°C, (t) 12 h, O_2, 900°C. Micrographs h′, j′, and k′ are from a different region of the sample, but correspond to the same heat treatment as h, j, and k, respectively.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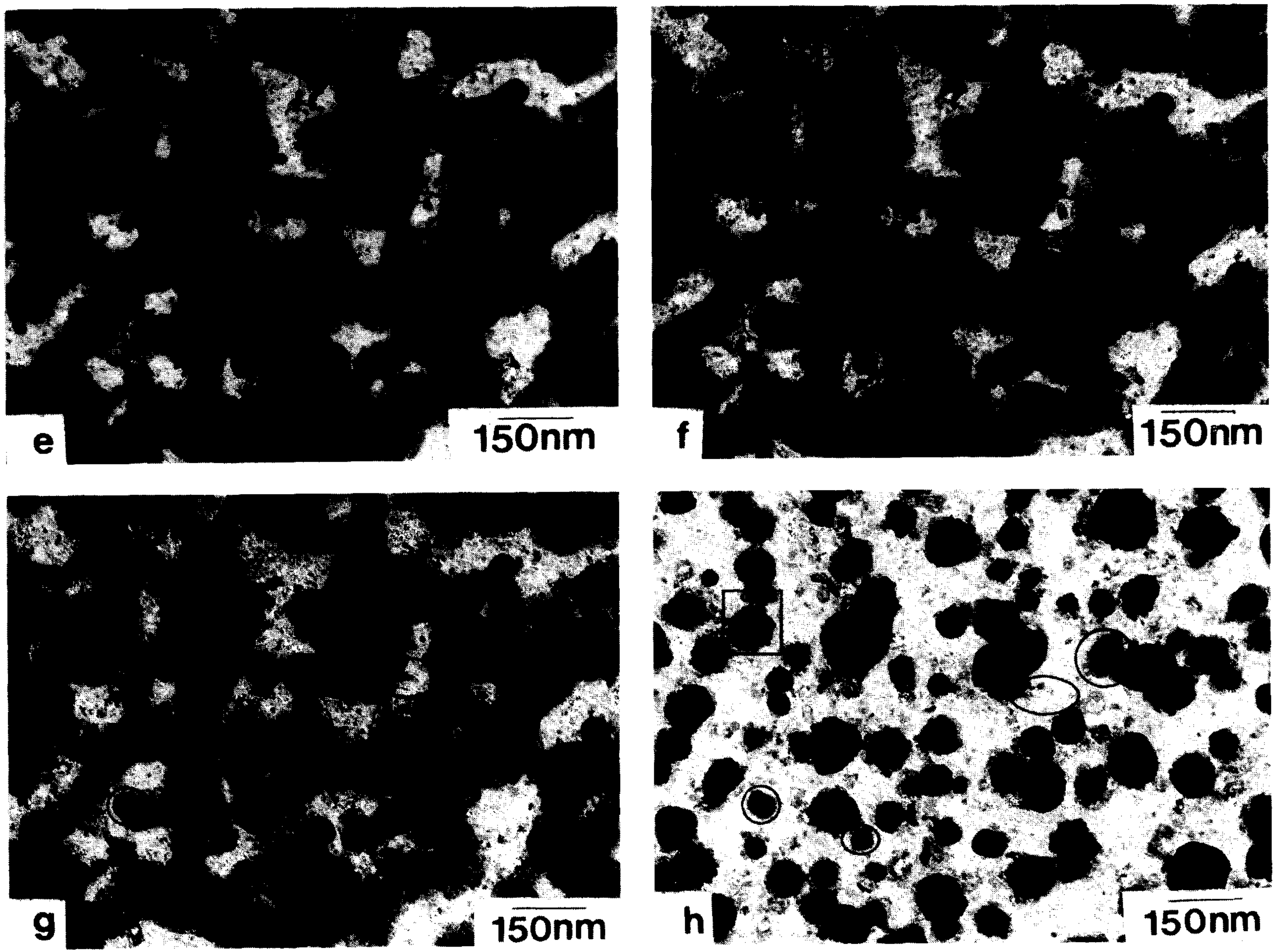
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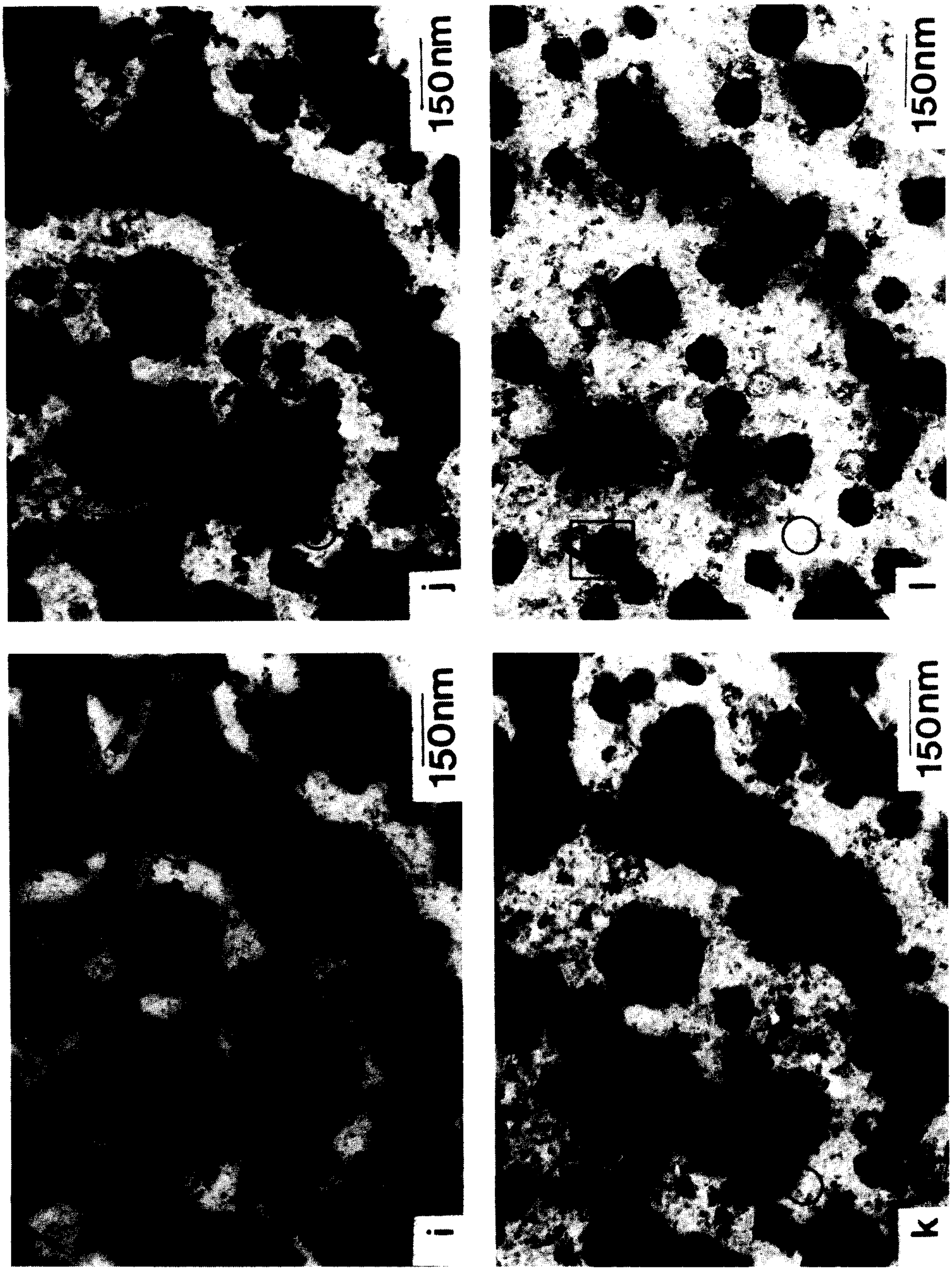

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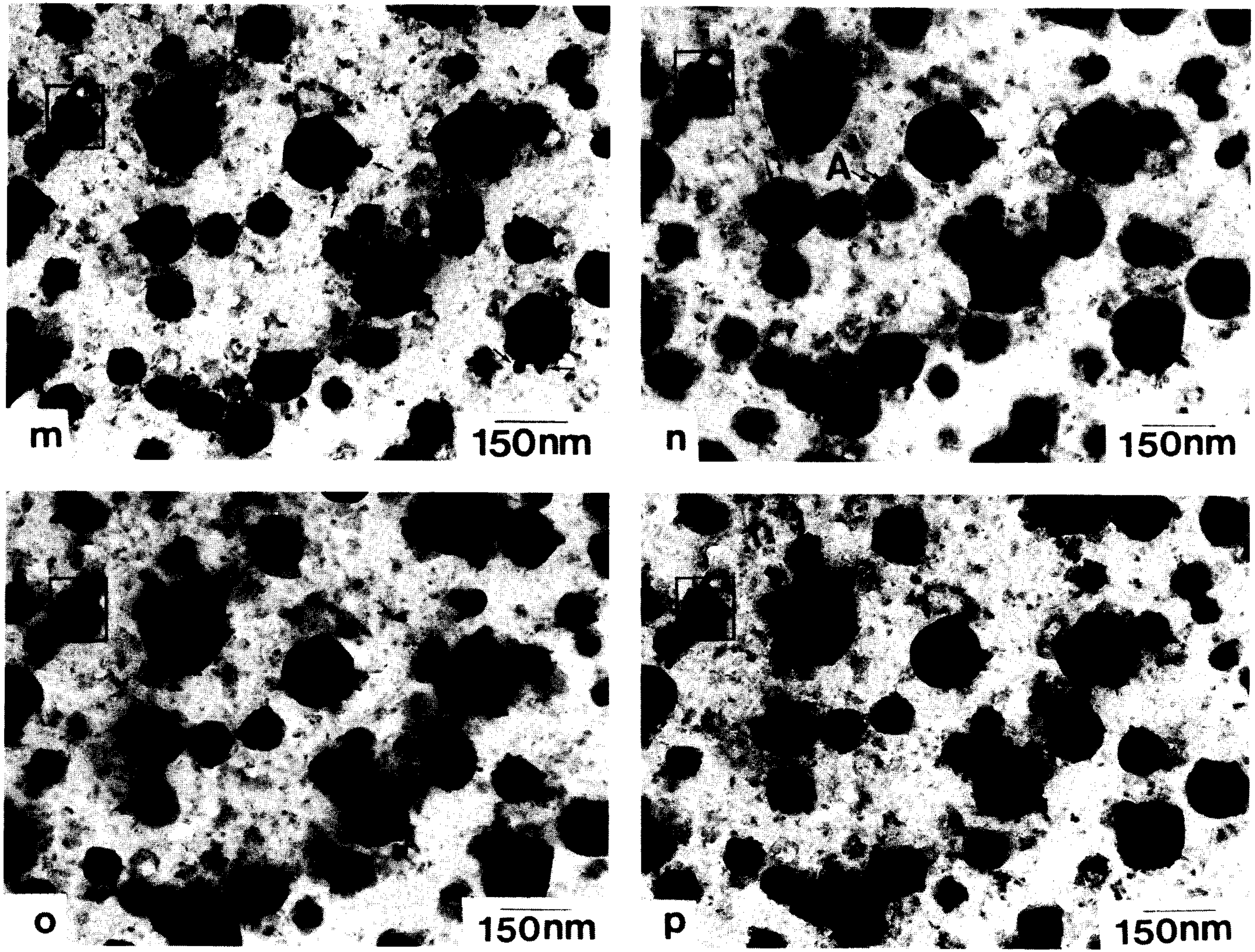
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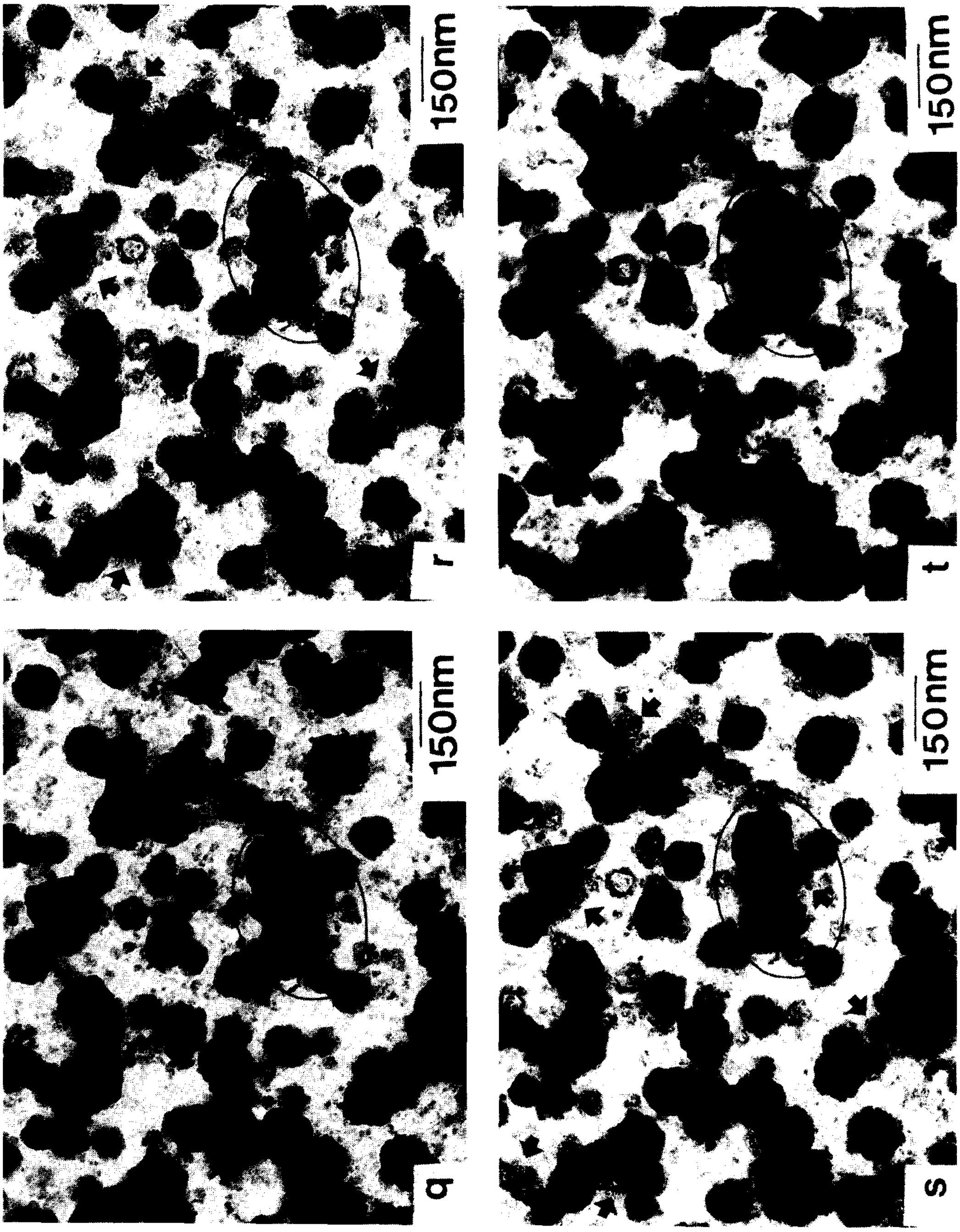

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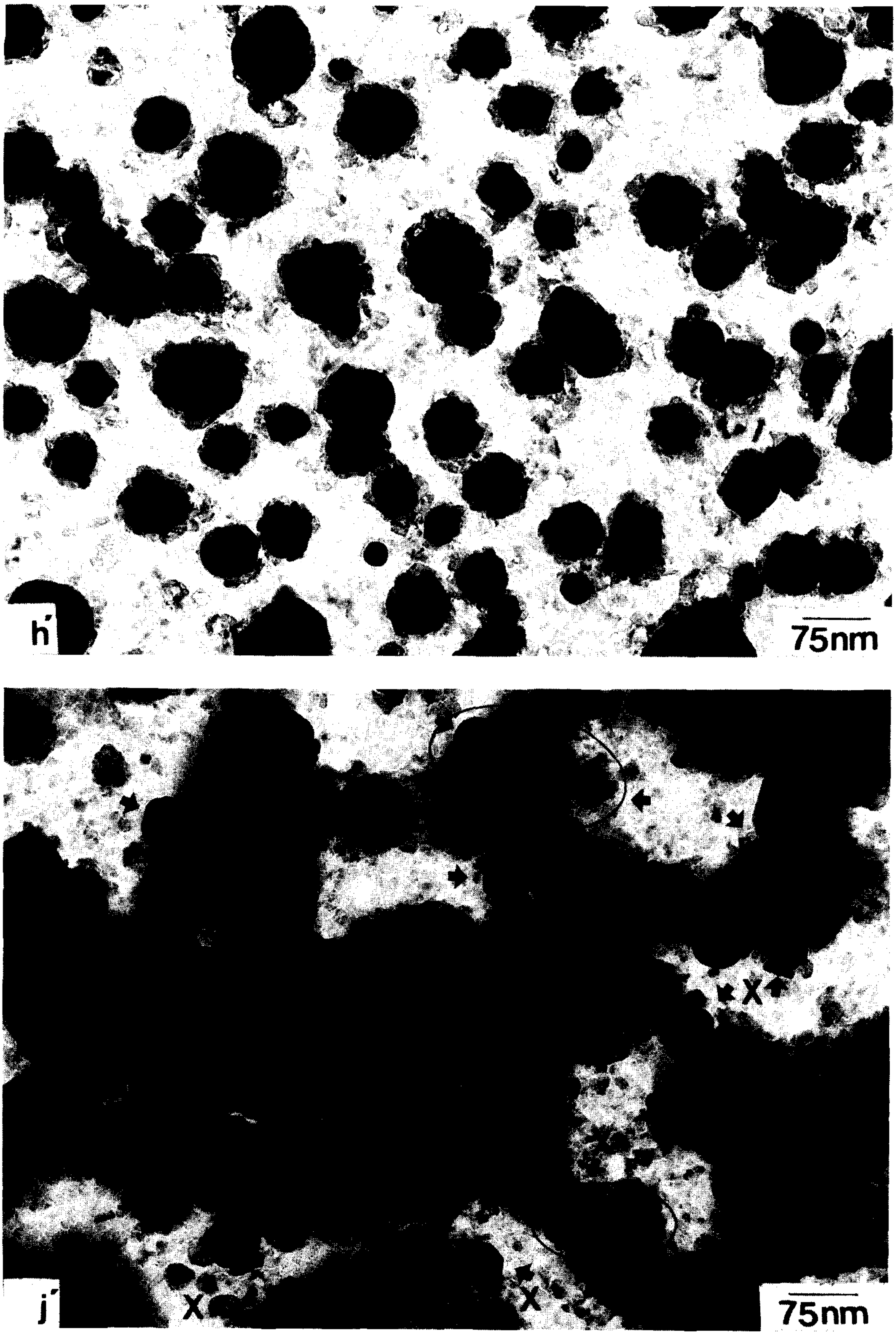

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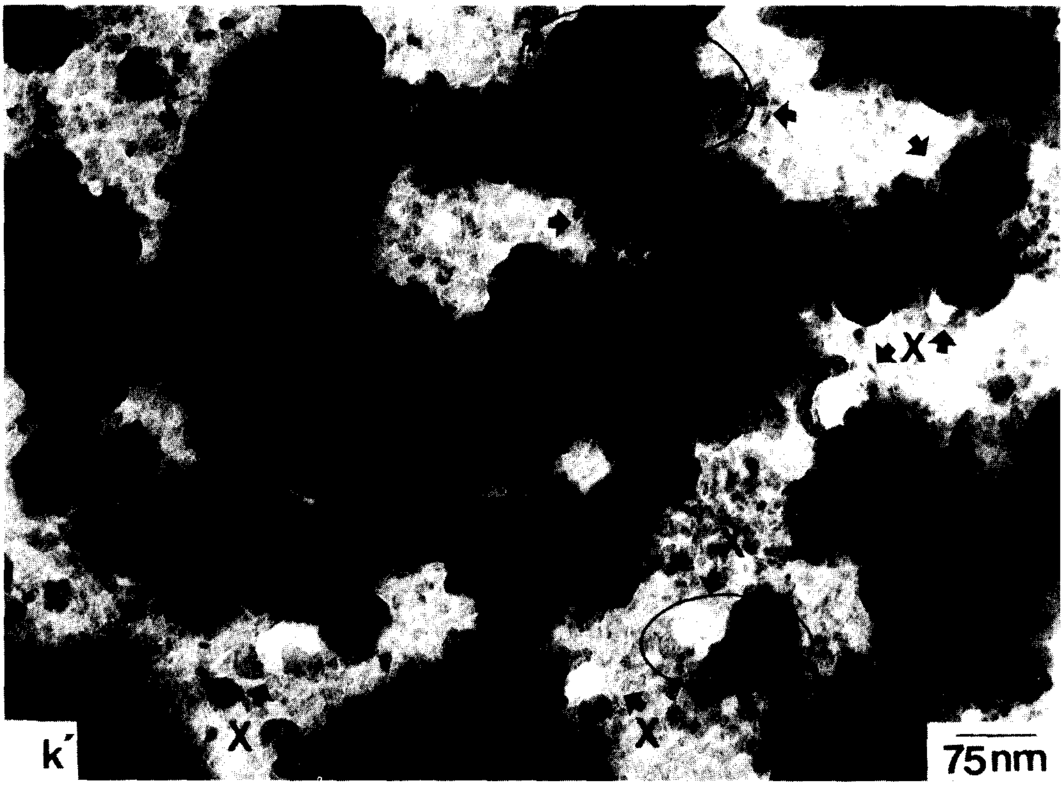


FIG. 1—*Continued.*

smaller particles of the size spectrum (but as large as ≈300 Å) either decreased in size or vanished (Figs. 1j, j'). On continued heating for 4 more hours, a number of additional particles (up to ≈500 Å in size) disappeared or decreased in size, most likely because of their spreading and merging with the surface film (Figs. 1k, k'). The film on the substrate appeared to be thicker. Electron diffraction indicated the presence of the same compounds as those detected during the previous oxidation step.

On a cursory observation of the micrographs, one may be tempted to attribute the disappearance of a large number of crystallites to ripening. However, there was very little change in the size of the larger particles and, in fact, there was a marginal decrease in size. The rapid and total disappearance of large particles (up to about 500 Å in size, some of which left white traces on the micrographs (X in Figs. 1j' and k')) suggests another possibility, namely, the loss of material by evaporation. This is not likely, because the melting temperatures of iron and its oxides are much higher than the heating temperature and, in addition, the material is essentially recovered during subsequent heating in H_2.

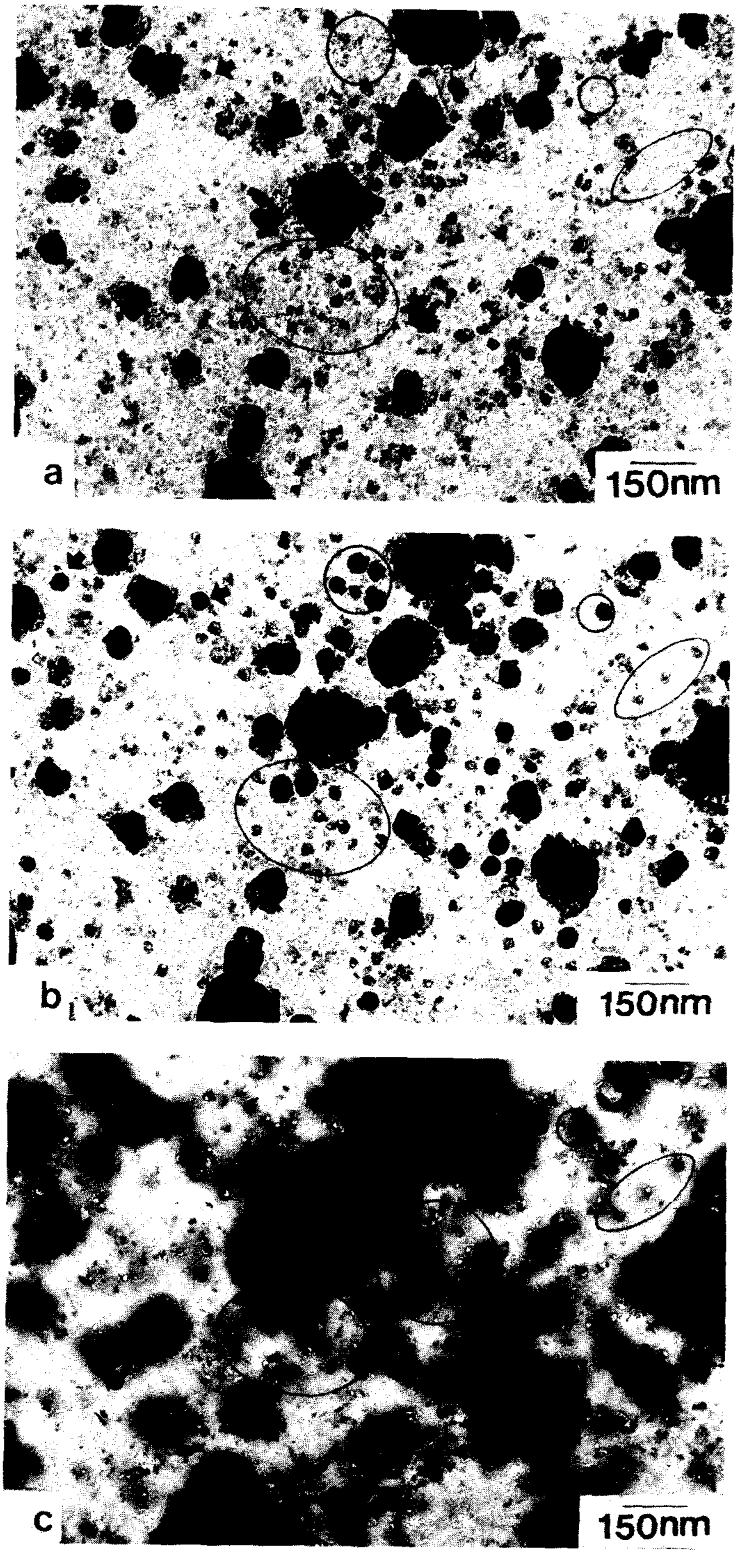
Only an hour of heating in hydrogen at 900°C caused the withdrawal of the films. The films must have merged with the particles, since all the particles increased in size significantly (Fig. 1l). Only a few pairs of neighboring crystallites coalesced. A comparison of the micrographs before and after heating in oxygen (Figs. 1d and h; h and l) indicates that there is very little, if at all, decrease in the amount of material on the substrate. The drastic decrease in the amount of material present as crystallites, observed following heating in oxygen, is essentially recovered during subsequent reduction. The net effect is excessive sintering accomplished via establishment of a contact between the crystallites through the thick surface film in an oxidizing atmosphere and their coalescence, because of the contraction of the interlinking surface film, in a reducing atmosphere. There is, therefore, a drastic decrease in the number of crystallites, but not of the total number of atoms or molecules. The higher temperature reduction yielded $FeAl_2O_4$ (and possibly also some α-Fe), instead of an "in-between" compound detected earlier on reduction at 800°C. Another such oxidation–reduction cycle yielded similar results (Figs. 1m–p), though the film following oxidation appeared substantially thinner and more uniformly extended around the particles than in the previous cases. The appearance of a thinner film may be a result of the fact that the driving force for spreading is substantially smaller for the larger and faceted particles, than for the smaller particles. In addition, the substrate might have undergone modifications and its wettability might have been changed.

Subsequent cycles of heat treatment give rise to thick patches of films around the particles in oxygen at 900°C, as before. However, in hydrogen, there is a decrease in the thickness of the film at 800°C, while on further heating at 900°C, this residual film ruptures to generate new, small crystallites (Figs. 1q–t).

Rupture of the Surface Film and Generation of New Particles (Redispersion)

Figure 2a represents the initial state of specimen B, before it was heated alternately in oxygen and hydrogen. It was obtained by heating the evaporated iron film in hydrogen, first at 500°C and then gradually at higher temperatures upto the temperature of interest, 800°C. Heating at 800°C in hydrogen led to the formation of large particles due to excessive sintering. Continued heating in H_2 caused considerable growth of some small crystallites, while other small crystallites either disappeared or remained unaffected. In addition, a number of new, small, as well as large particles appeared on the substrate (Fig. 2b). Electron diffraction indicated the presence of α-Fe and of a solid-solution of iron oxide with alumina (the d-values are smaller than those of the stoichiometric aluminate $FeAl_2O_4$, but larger than those of γ-Al_2O_3). The specimen was subsequently heated in oxygen for 1 h at 500°C to verify if the surface film detected at the higher temperature forms also at lower temperatures. A film indeed forms around and probably even on the particles, as seen in Fig. 2c. A number of small particles disappeared and a few relatively large particles appeared. Some of these new particles resulted from the growth of detectable, small particles, while others appeared in places where there were no detectable particles before. $FeAl_2O_4$ could clearly be detected in the electron diffraction pattern. The subsequent hydrogen treatment for 8 h at 500°C, led to a complete withdrawal of the film (Fig. 2d). A few particles disappeared, some coalesced with the neighboring crystallites and a number of smaller particles appeared on the substrate. $FeAl_2O_4$ could still be detected as the major compound in the electron diffraction patterns. When the specimen was heated again in hydrogen for 4 h at the higher temperature of 800°C, to ensure a more complete reduction, a few of

FIG. 2. Sequence of changes in a fresh specimen (B) with the same initial loading as specimen A (7.5 Å initial film thickness). The specimen was heated in hydrogen successively between 500 and 800°C. Changes in the same region on subsequent heating are shown here. (a) 2 h, H_2, 800°C, (b) 5 h, H_2, 800°C, (c) 1 h, O_2, 500°C (there is very little change between 1 and 19 h of heat treatment), (d) 8 h, H_2, 500°C, (e) 4 h, H_2, 800°C (the specimen was heated in the following sequence prior to (f): 2 h, O_2, 600°C; 4 h, H_2, 800°C; 5 h, O_2, 700°C; 4 h, H_2, 800°C), (f) 4 h, O_2, 800°C, (g) 4 h, O_2, 900°C, (h) 3 h, H_2, 800°C, (i) 4 h, O_2, 900°C, (j) 4 h, H_2, 800°C. The following micrographs correspond to a different region of the specimen. (k) 8 h, O_2, 900°C, (l) 40 h, O_2, 900°C, (m) 3 h, H_2, 800°C, (n) 12 h, O_2, 900°C.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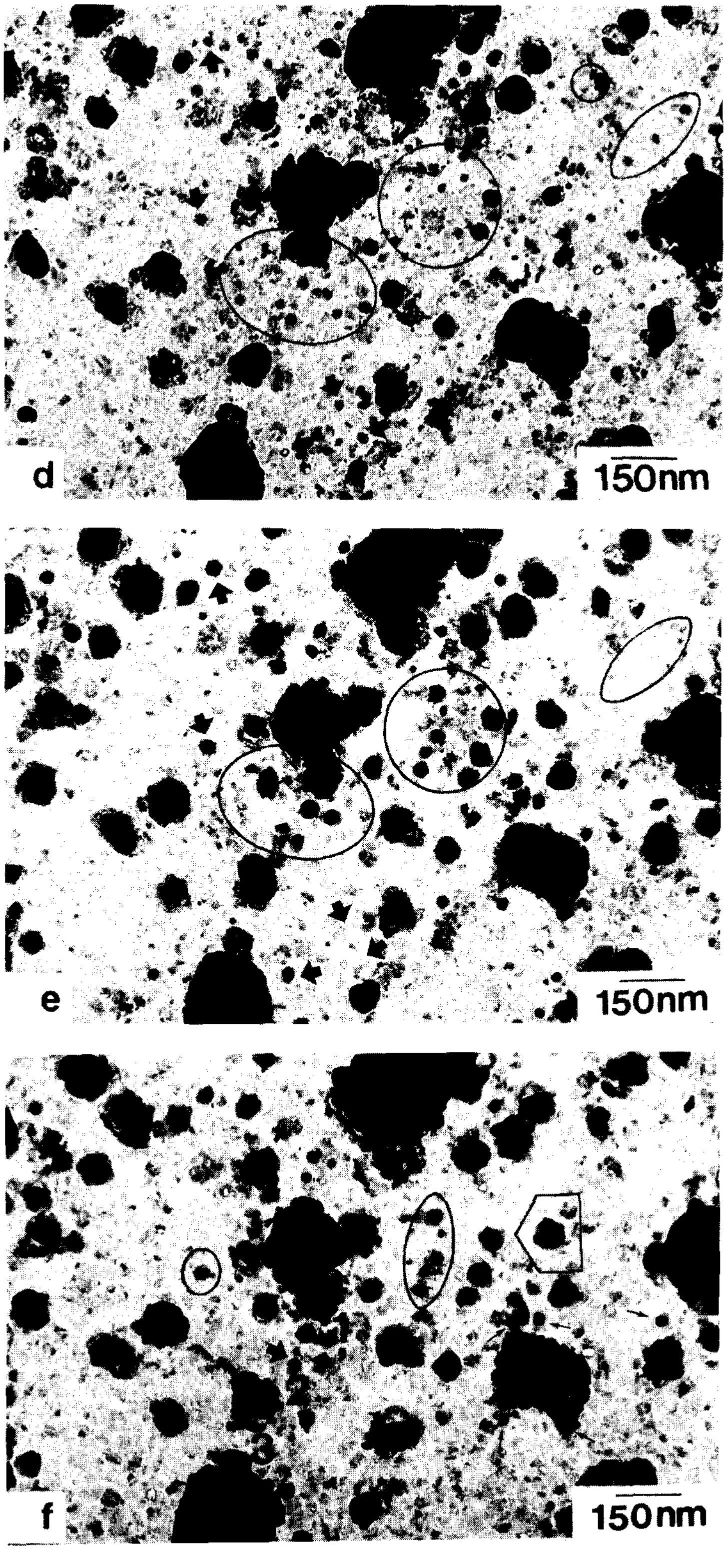
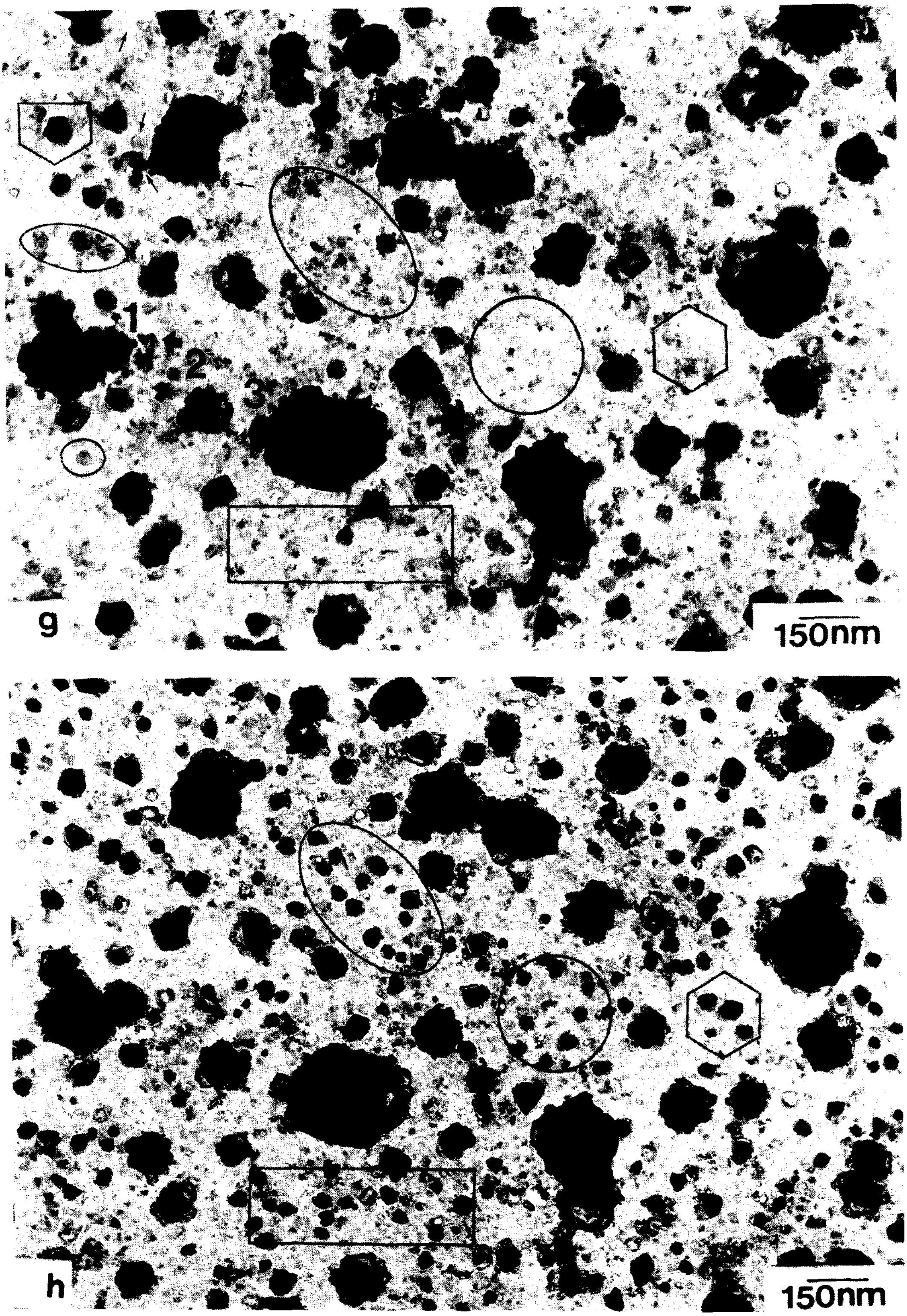


FIG. 2—*Continued.*



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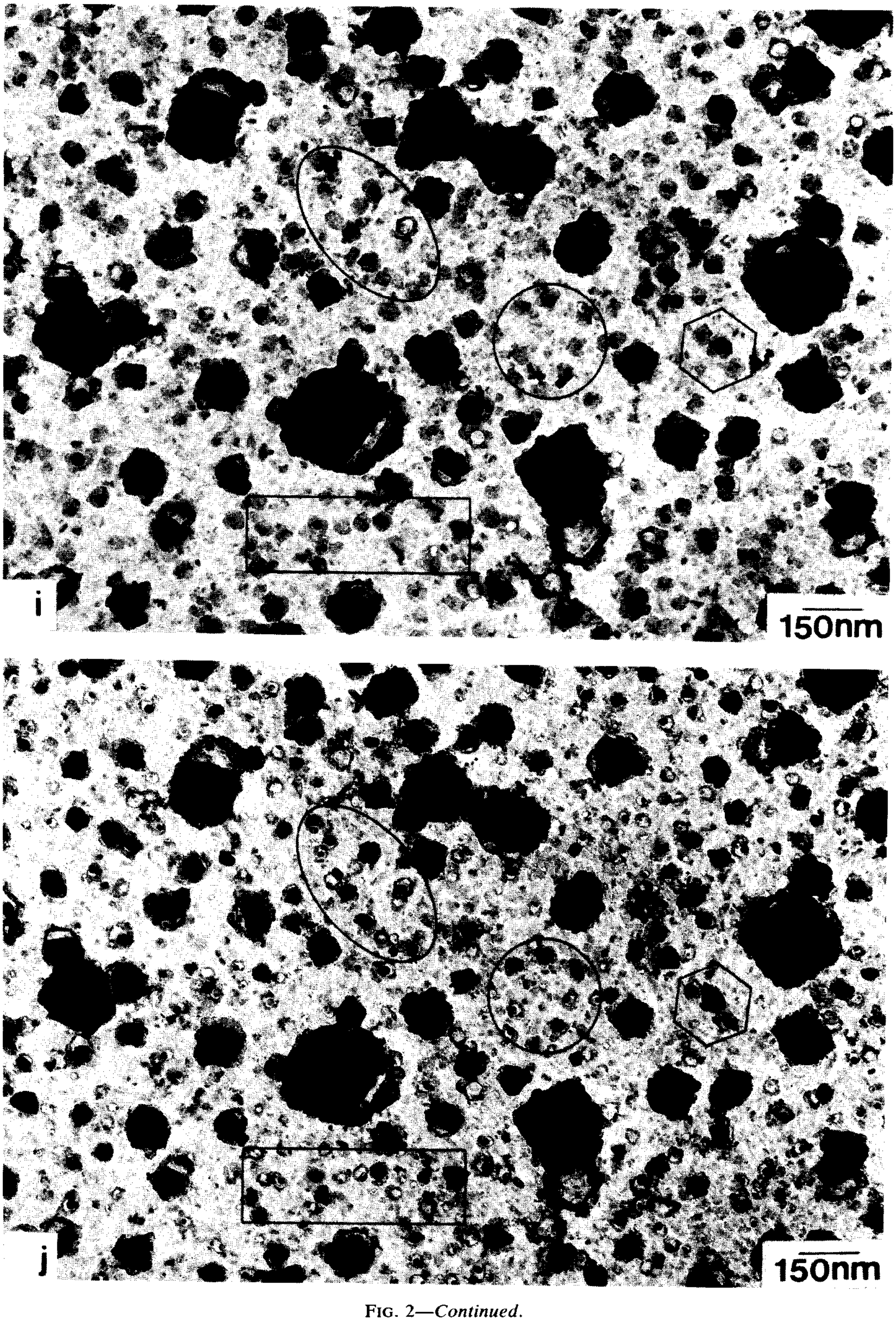

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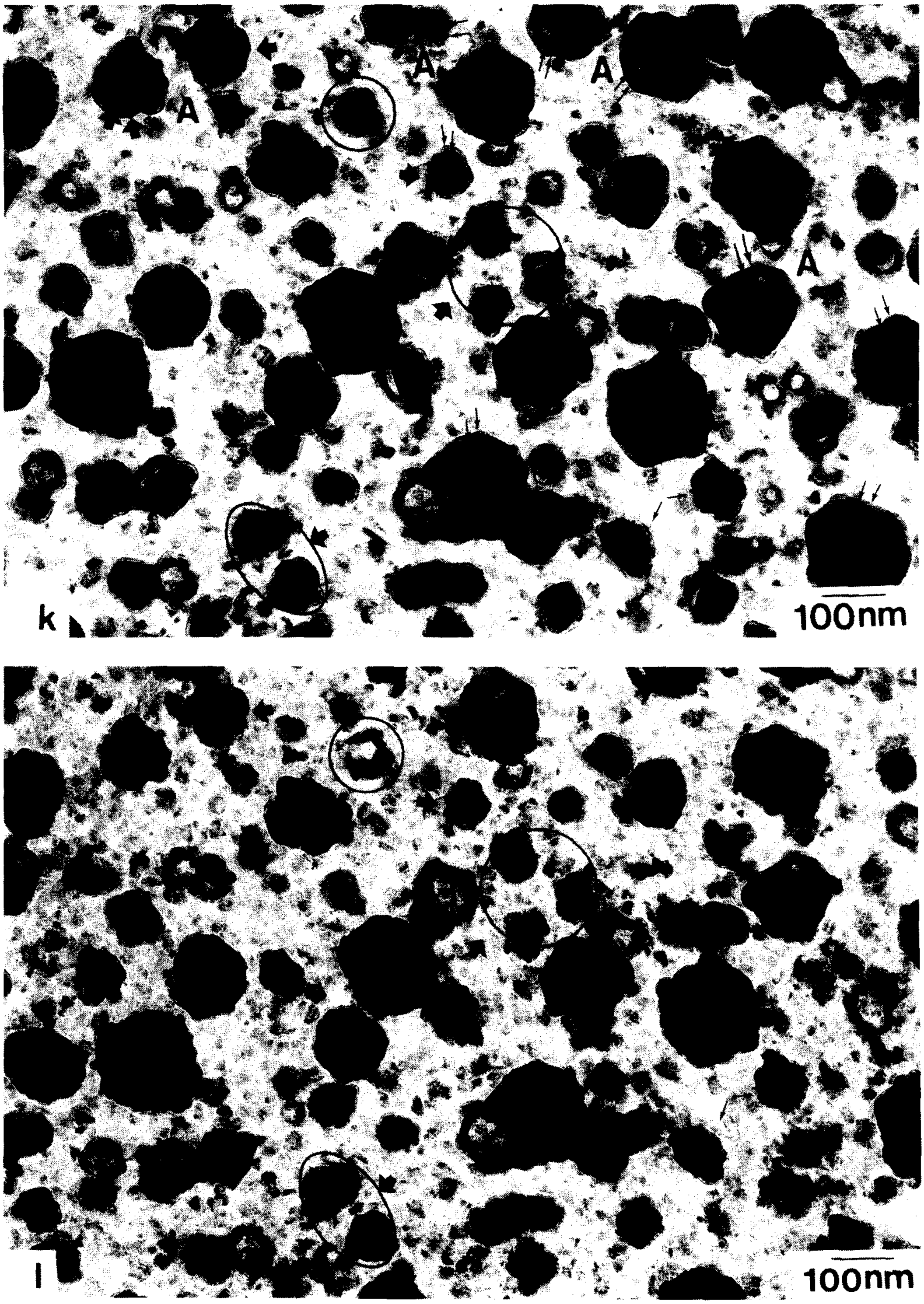

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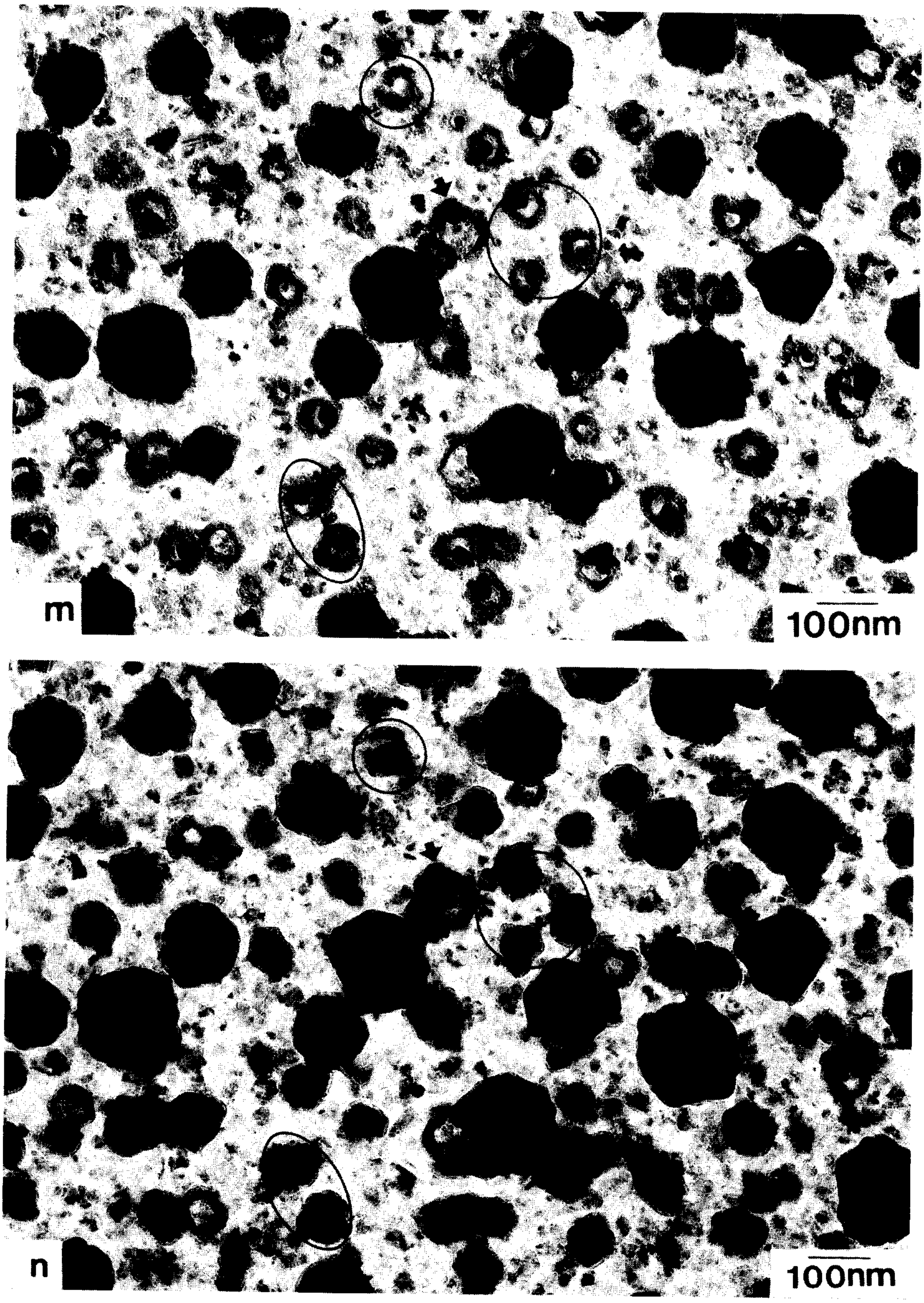

FIG. 2—*Continued.*

the small crystallites grew in size considerably while other small as well as larger crystallites vanished (Fig. 2e). Subsequently, the wetting behavior of the crystallites in O_2 was investigated at progressively higher temperatures of 600, 700, and 800°C. Prior to each oxidation step, the specimen was reduced in H_2 at 800°C. There was practically no change in the particle size or shape after any of these stages of heating. Regarding the surface film, however, only a narrow ring of lower contrast film around the particles could be observed after oxidation at 700 and 800°C (Fig. 2f). There was also a decrease in the sharpness of the grain boundaries of the support. Only $FeAl_2O_4$ could be detected by electron diffraction after heating in hydrogen, whereas after heating in oxygen, the *d*-values increased to values in between those of $FeAl_2O_4$ and γ-Al_2O_3. One may note that the first heating in O_2 at 500°C, after a high-temperature reduction at 800°C, led to the formation of a detectable film; the subsequent heat treatments in O_2 at 600, 700, and 800°C did not, however, generate such detectable films. It is likely, that either an undetectable film spread out on the substrate at the higher temperatures, or/and the wetting characteristics of the substrate were modified during the previous heat treatments.

Sample B, which was heated in oxygen at 800°C, as mentioned above, was further heated in oxygen at 900°C without a hydrogen treatment in between. A number of small particles extended out considerably, leaving behind detectable patches (Fig. 2g). The presence of a film covering the substrate surface could easily be inferred from the micrograph. No change in the chemical composition could be detected by electron diffraction.

An interesting change was noted on heating specimen B subsequently in hydrogen for 2 h at 800°C. A number of relatively small particles (of about 150 Å or larger) appeared all over the substrate, especially in regions devoid of particles before (Fig. 2h). Since the previously existing particles grew very little in size and the substrate grain boundaries became much sharper, it appears that contiguous patches of multilayer films coexisted with the three-dimensional crystallites prior to the reduction treatment. The films probably ruptured to generate the new, three-dimensional crystallites. Of course, the new particles could have formed also by Ostwald ripening or coalescence of undetectable crystallites. If Ostwald ripening had occurred, the larger crystallites should have grown in size and at least a few of the small crystallites should have decreased in size or even disappeared. On the other hand, if the growth were a result of the coalescence of migrating, undetectably small crystallites, all the particles, small and large, should have grown in size. However, since so many new, relatively large particles formed everywhere, while the previously existing three-dimensional crystallites (both small as well as large) changed very little, it is very likely that the new particles formed by the rupture of a surface film and/or by the contraction of undetectable surface patches. On prolonged heating in H_2, for additional 6 h in steps, no decrease in size or disappearance of particles was observed. On the contrary, a handful of additional, much smaller particles, was formed, very likely by the contraction of some undetectable patches which were reduced relatively slowly.

A few particles were observed to sinter but obviously only by coalescence with the nearby particles. That the particles originated most likely from a surface film was additionally verified, indirectly, by heating specimen B again in oxygen at 800°C and subsequently at 900°C. At 800°C, the particles extended marginally, and narrow rings of films appeared around them, but the number of particles remained practically the same. However, after heating in oxygen at 900°C, most of the small particles extended considerably, losing their particle appearance. Only thick extended patches could be seen where particles were present before (Fig. 2i). The extended patches contracted, tending to form particles again, on heating subsequently in hydrogen at 800°C (Fig. 2j). The extension to patches of film and recontraction to particles were observed to repeat during the subsequent cycles of treatment in O_2 and H_2 at 900°C (Figs. 2k–n).

The heating history appears to affect the specimen behavior. Following heating in oxygen at 900°C, either visibly thick patches of interconnected films (specimen A) or thin, undetectable films (specimen B) form on the substrate. In the former case, the films contract and merge with the neighboring crystallites on subsequent heating in H_2, while in the latter new particles are formed on the substrate.

DISCUSSION

The results presented above as well as in Refs. (*1, 2, 6, 13, 14, 16*) exemplify the role of wetting on the shape, sintering, and redispersion behavior of the supported metal crystallites, along the lines suggested in Ref. (*1*). The possibility of the coexistence of three-dimensional crystallites with thin films of the oxide either as a two-dimensional fluid (monolayer or less) (*2, 17*) or as a multilayer film (*2*) have been suggested in the past. As pointed out above repeatedly, the present results suggest that, in the case of Fe/Al_2O_3 model catalysts, there is a surface film rather than a surface phase of single molecules which coexists with the three-dimensional crystallites. The results indicate that the degree of extension of the crystallites increases with temperature (*14*), leading to even almost complete wetting of the substrate by the smaller crystallites at high temperatures. This may happen because the small crystallites are more completely oxidized than the larger ones. The micrographs (Figs. 1e–g, i–k, j′, and k′) clearly show the presence of thick patches of film around each particle, the patches around neighboring particles being interconnected. The micrographs indicate that the extension and film formation occurs in a few stages. Regions of at least two different contrasts in the film surrounding the particles (A in Figs. 1n; 2k, l) suggest that initially a basal film extends, over which subsequent layers spread. Indirect evidence (the diminished sharpness of the grain boundaries of the substrate, for example) appears to indicate that the films around the particles extend farther than their immediate surroundings but with decreasing thickness. Since the films farther away from the particles are too thin they are not seen in the micrographs. A film could be present even at lower temperatures, but again it may be too thin to be seen in the micrographs. At higher temperatures (800 or 900°C) the films are thicker and are clearly seen. This is both because of the higher mobility of the atoms/molecules (these temperatures being above the Tammann temperature for iron as well as for its oxides) as well as the more favorable conditions for the formation of interoxide compounds (such as $FeAl_2O_4$ and $AlFeO_3$), which better wet the substrate (and perhaps even the surface of the particles). One may note that these temperatures are above the Curie point of iron (770°C) (and also above the Curie and Neel points of its oxides) (*18, 19*). The drastic decrease in the interactions between the atoms of these magnetic materials above the Curie or Neel points may render them more mobile and aid in the extension of the crystallites.

The formation of new crystallites on heating in hydrogen subsequent to heating in oxygen indicates that, under reducing conditions, the surface film becomes unstable, ruptures, and contracts to form new particles.

A discussion of the wettability of the support by the crystallites in oxidizing and reducing atmospheres is provided in Refs. (*1, 14*). In reducing conditions the particles assume larger wetting angles and hence contracted shapes. In contrast, in oxidizing atmospheres the wetting angle is smaller and the particles assume more extended shapes. The film–gas (σ_{fg}) and film–substrate (σ_{fs}) interfacial tensions are larger under reducing conditions than under oxidizing conditions. When the sum of the above two interfacial tensions exceeds the substrate–gas interfacial tension, σ_{sg}, the film will not wet the substrate, but will contract to form a particle since $\cos\theta = (\sigma_{sg} - \sigma_{fs})/\sigma_{fg} < 1$, in such a case. ($\theta$ is the wetting angle.) The film will wet the substrate when the above inequality is reversed and therefore will remain as such (since, when $\sigma_{fg} + \sigma_{fs} < \sigma_{sg}$, $\cos\theta > 1$). The above considerations are valid for thick films, while the undetectable surface films discussed above are thin. In what follows thermodynamic arguments are adduced to demonstrate that these thin films can rupture under the action of dispersion interactions.

While in a thick film, the molecules located at its free surface do not feel the presence of the substrate, in a thin film they interact with the substrate. In addition, the range of the interaction forces of a majority of the molecules of a thick film is smaller than the thickness of the film. In contrast, the range of the interaction forces for all the molecules of a thin film is greater than the thickness of the film. As a result, the free energy of formation of a thin film depends on its thickness. Assuming for illustrative purposes London dispersion forces between molecules, the following expression can be derived for the interaction potential, ϕ, acting on a unit volume located at the planar free surface of the film (*20*):

$$\phi = \phi_0 + \frac{A}{h^3}. \qquad (1)$$

Here, ϕ_0 is a constant, h is the thickness of the film, and A is a constant related to the strength of the interactions between the molecules of the film among themselves and with those of the substrate. To be more specific, $A = A_1 - A_2$, A_1 characterizing the strength of the interactions among the molecules of the film and A_2 of those between the molecules of the film and of the substrate. Because ϕ_0 is negative and A is positive, expression (1) shows that the potential energy of interaction is less negative when the thickness h is smaller.

Let us consider a planar film and perturb this planarity to a simple wave shape. Perturbations arise naturally in systems such as ours from thermal fluctuations as well as from nonuniform surface reduction. The dynamics of the system can either amplify or cause the decay with time of this initial perturbation. When the perturbation is amplified, the film will rupture. Let us identify the conditions under which such an amplification is thermodynamically favored. First, one may note that the perturbation increases the surface area and hence increases the contribution to the free energy of the system due to the film–gas surface tension. However, the perturbation displaces some molecules from distances nearer to the film–substrate interface to greater distances (Fig. 3). Even though Eq. (1) is valid only for molecules located at the planar free surface, it suggests nonetheless that this increase in distance decreases the potential energy of the displaced molecules (makes their potential energy more negative). It is true that the molecules below the cusp (A in Fig. 3) have now fewer molecules above them than before and this makes their interaction potential less negative. However, the molecules beneath the crest and below the previous planar surface (B in Fig. 3) now have a larger number of molecules above them and this makes their interaction potential more negative. It is likely that the latter two effects largely compensate each other. However, the molecules moved from the cusp (X in Fig. 3) to the crest (Y in Fig. 3) have been moved farther away from the film–substrate interface and therefore there will be a net de-

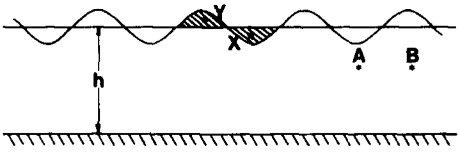

FIG. 3. Schematic of the perturbation of the free surface of a thin film.

crease in the total free energy due to the dispersion interactions. The perturbation will grow if this free energy change exceeds in absolute value that due to the increased surface area. This can happen when the thickness of the film is small and the constant A is sufficiently large, because only then the above effect of the dispersion interactions becomes sufficiently important. In an oxidizing atmosphere, both the film and the substrate being oxides, the difference between A_1 and A_2 is relatively small and the film is stable. In a reducing atmosphere, however, the substrate and film compounds being different, A can become sufficiently large and as a result the film can become unstable. One may also note that some internal stresses generated during the formation of the film can be relaxed by its rupture and this also favors the breakup. For these reasons a film may exist in an oxidizing atmosphere, but will rupture to form patches and further particles in a reducing atmosphere.

Of course, the above thermodynamic argument can only provide some insight into the onset of the instability, but not on its dynamics. Ruckenstein and Dunn (*20*) have developed and discussed in more detail the theory behind the dynamics of the above process.

CONCLUSIONS

The experimental results indicate that in the case of model Fe/Al_2O_3 catalysts, the degree of extension of the crystallites over the substrate in an oxidizing atmosphere increases as the temperature is increased. Patches of interconnected, thick, multilayer films extending from around the particles could be observed at 800 and 900°C. It is suggested that the surface film may be present even at lower temperatures, but because of its very small thickness is not detectable by electron microscopy. When the films around the particles are thick, they contract completely and merge with the crystallites during subsequent heating in hydrogen at high temperatures. However, if after heating in oxygen the film is thin, it becomes unstable during subsequent heating in hydrogen, ruptures, and generates new three-dimensional crystallites. A number of new crystallites of 250 Å or larger were generated on heating an oxidized specimen in hydrogen at 800°C. These particles were observed to extend again almost completely on heating in oxygen at 900°C.

REFERENCES

1. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29,** 224 (1973).
2. Ruckenstein, E., and Chu, Y. F., *J. Catal.* **59,** 109 (1979).
3. Sushumna, I., Ph.D. dissertation. SUNY, Buffalo, 1985.
4. Ruckenstein, E., and Chen, J. J., *J. Catal.* **70,** 233 (1981).
5. Tatarchuk, B. J., and Dumesic, J. A., *J. Catal.* **70,** 308 (1981).
6. Chen, J. J., and Ruckenstein, E., *J. Phys. Chem.* **85,** 1606 (1981).
7. Derouane, E. G., Baker, R. T. K., Dumesic, J. A., and Sherwood, R. D., *J. Catal.* **69,** 101 (1981).
8. Derouane, E. G., Chludzinski, J. J., and Baker, R. T. K., *J. Catal.* **85,** 187 (1984).
9. Baker, R. T. K., Prestridge, E. G., and Garten, R. L., *J. Catal.* **56,** 390 (1979).
10. Ruckenstein, E., and Chen, J. J., *J. Colloid Interface Sci.* **86,** 1 (1982).
11. Ruckenstein, E., and Lee, S. H., *J. Catal.* **86,** 457 (1984).
12. Nakayama, T., Arai, M., and Nishiyama, Y., *J. Catal.* **79,** 497 (1983).
13. Sushumna, I., and Ruckenstein, E., *J. Catal.* **90,** 241 (1984).
14. Sushumna, I., and Ruckenstein, E., *J. Catal.* **94,** 239 (1985).
15. Onal, I., and Butt, J. B., *J. Chem. Soc. Faraday Trans. 1* **78**(p6), 1887 (1982).
16. Baker, R. T. K., *J. Catal.* **63,** 523 (1980).
17. Yao, H. C., Sieg, M., and Plummer, Jr., H. K., *J. Catal.* **59,** 365 (1979).
18. Weast, R. C., Ed., "Handbook of Physics and Chemistry," 62nd ed. CRC Press, Boca Raton, Fla., 1981.
19. Blackman, M., and Kaye, G., *Proc. Int. Conf. Magn. Crystallogr. 1961* **II,** 289 (1961).
20. Ruckenstein, E., and Dunn, C. S., *Thin Solid Films* **51,** 43 (1978).