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Splitting of Platinum Crystallites Supported on Thin, Nonporous Alumina Films

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Direct observation in the transmission electron microscope of the behavior of metal crystallites supported on thin films of alumina is reported. Nonporous substrates of alumina have been prepared by anodizing thin aluminum foils in tartaric acid solutions. A sputtering technique was used to deposit platinum crystallites on the anodized aluminum foil. The remaining aluminum was dissolved by amalgamation. The specimens annealed in air at 600°C showed strong sintering of the crystallites. Reheating these specimens at 500°C in air lead, because of splitting, to a large decrease in the average size of the crystallites.

INTRODUCTION

Supported metal catalysts are widely used for important industrial processes involving, for instance, hydrogenation and dehydrogenation, hydrogenolysis, oxidation, and petroleum reforming. The exposure of the supported metal catalyst to high temperatures and to the impurities of the chemical atmosphere leads to a decrease in catalytic activity. Among the causes is the loss of exposed surface area of metal resulting from the sintering of metal crystallites. The redispersion of crystallites of aged supported metal catalyst is therefore an important problem. The following regeneration procedures have been suggested in the literature:

(1) Heating the aged catalyst in an oxygen-containing atmosphere.
(2) Heating the aged catalyst in an oxygen-containing atmosphere followed by reduction in a hydrogen atmosphere.
(3) Heating the catalyst to high temperatures followed by rapid cooling.
(4) Chemical dissolution and redispersion of the metal.

Johnson and Keith (*1*) reported a redispersion of platinum metal in a commercial platinum on alumina catalyst when heated in dry air between 510 and 580°C. Higher temperatures than 580°C caused sintering of the metal crystallites. Kraft and Spindler (*2*) noticed an increase in the exposed area of metal in a Pt-on alumina catalyst prepared by impregnation when heated in air at 500°C. Jaworska-Galas and Wrzyszcs (*3*) found that the initial dispersion of the metal is restored in an aged platinum on alumina catalyst when heated in air at 480°C.

Schwarzenbek and Turkevich (*4*) reported that heat treatment at 480°C, in an oxygen-containing atmosphere with a partial pressure of at least 5 psia, followed by reduction in hydrogen, caused reactivation of the sintered catalyst. Weller and Montagna (*5*) reported that the cyclic exposure to oxygen and hydrogen at 550°C caused redispersion of the metal only during

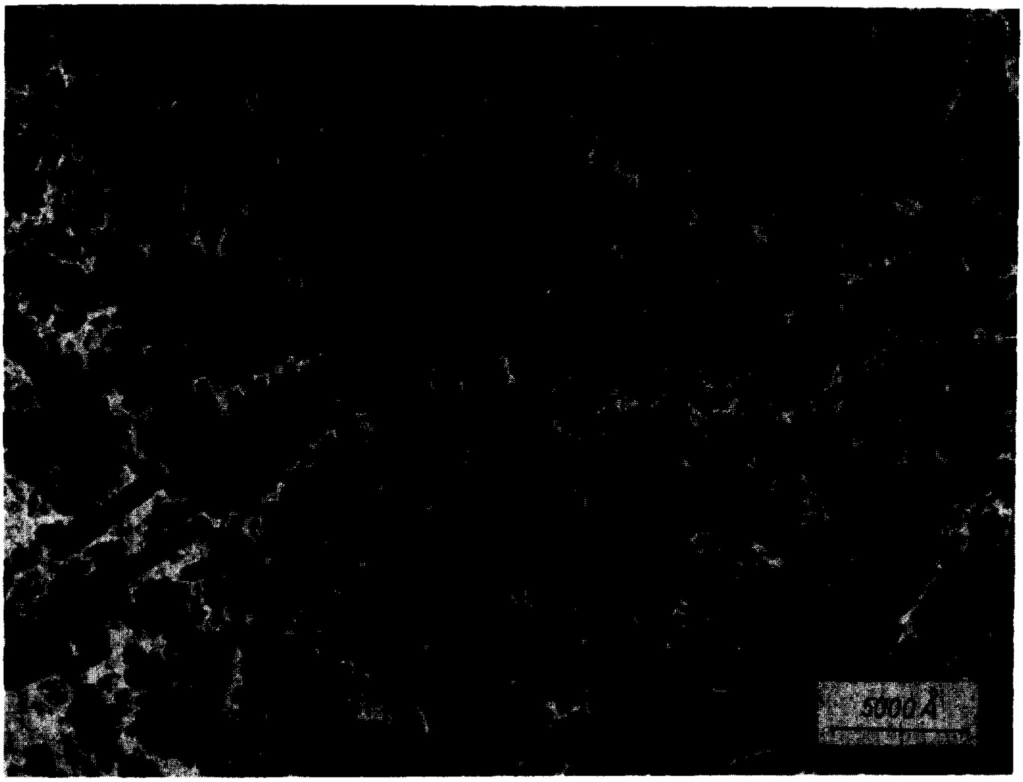

FIG. 1. Transmission electron micrograph of a nonporous alumina substrate film (~300 Å thick) prepared by anodization and heated in air at 600°C for 20 hr. Grains of γ-alumina are separated by sharply defined grain boundaries.

the reduction step. During the oxidation step, sintering was observed. Emelianova and Hassan (*6*) observed that splitting of sintered crystallites occurred on rapid cooling of the catalyst.

Kogler and Queck (*7*) proposed a regeneration procedure which dissolves the sintered crystallites chemically and redisperses the metal phase on the support. The method consists in impregnating the aged catalyst with a solution of NH_4Cl and NH_4NO_3, heating at 170°C, slowly raising the temperature to about 280°C, and heating in air at 450°C. The regenerated catalyst exhibited the same activity as the fresh catalyst in the conversion of cyclohexane to benzene. Weidenback and Furst (*8*) reported that the activity for the isomerization of *n*-hexane and the aging behavior are essentially the same for the fresh and regenerated catalysts.

Another regeneration procedure based upon chemical dissolution and redispersion, commonly used, consists of the treatment of the aged catalyst with steam and chlorine.

The increase of the exposed surface area of metal caused by regeneration was detected in the above-mentioned experiments indirectly by selective adsorption of H_2 or O_2. The main goal of this work was to observe directly, using transmission electron microscopy, the splitting of the crystallites on a model catalyst. To achieve this, platinum crystallites have been deposited on thin films of alumina of less than 1000 Å thickness. The electron micrographs have demonstrated that heat treatment of the specimens at 600°C in air produces strong sintering. Reheating at 500°C of the specimens previously heated at 600°C leads to splitting of the crystallites.

EXPERIMENTAL PROCEDURES

Anodic Oxidation Procedure to Prepare Thin Films of Nonporous Alumina

Various procedures are available to prepare thin substrates of less than 1000 Å thickness which can be used in the transmission electron microscope. They are based on ion milling, on the use of the microtome, or on the sputtering technique. We have tried the sputtering technique, but the resultant films have ruptured when heated for a long time at high temperatures. In the experiments reported here, methods developed for producing protective coatings of nonporous alumina (*9*) have been adapted to prepare thin, nonporous alumina films which are stable when heated at high temperature for long intervals of time (*10*).

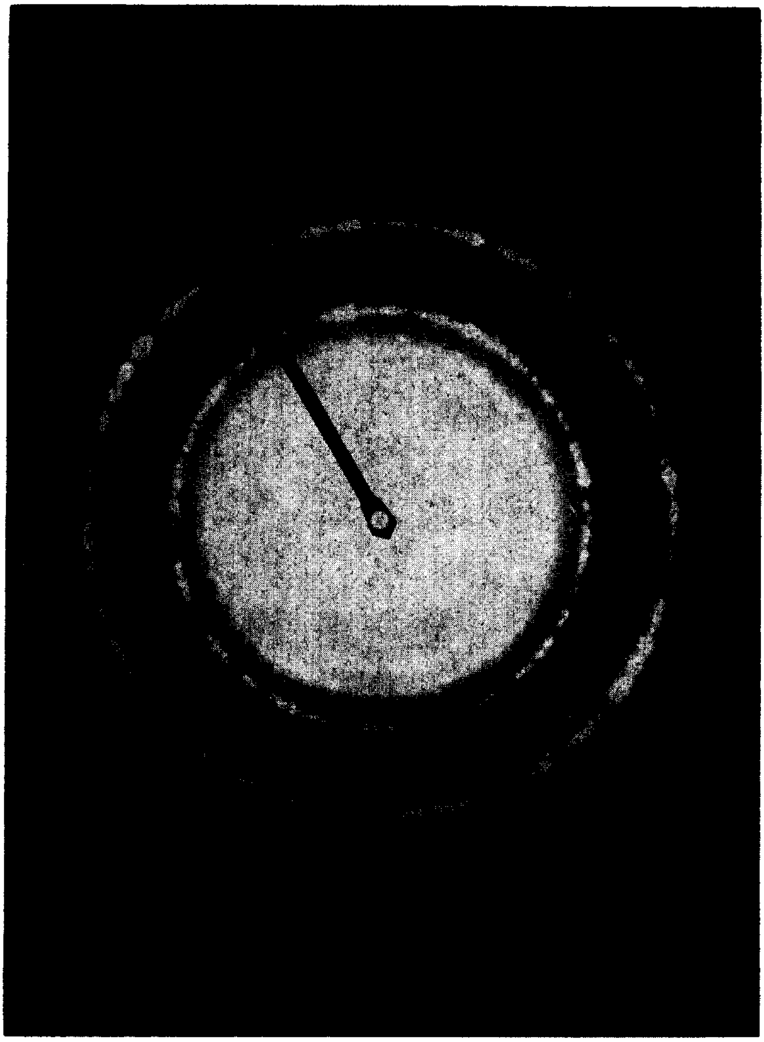

FIG. 2. Selected area electron diffraction pattern of the substrate from Fig. 1, which shows that the substrate is γ-alumina.

A pure thin aluminum foil (purity 99.999%) was polished chemically prior to anodic oxidation. The polishing solution consisted of 100 ml of 85% wt orthophosphoric acid to which 4 ml of nitric acid (70.4% wt) and 20 ml of distilled water was added. The polishing of the aluminum foil was achieved in about 4 min when the solution was warmed to ~80°C. The polished aluminum foil was washed in distilled water and dried. The aluminum oxide was prepared by anodization of the polished aluminum foil at 20 V in a 3% wt tartaric acid solution (adjusted to a pH of 5.5 with ammonium hydroxide). This produced a nonporous layer of alumina of about 300 Å thickness (~15 Å/V).

Deposition of Metal Islands onto Oxide Films

Metal islands were deposited onto the oxide films supported on aluminum using a Mini-Coater (supplied by Commonwealth Scientific Corporation), which is basically a small dc glow discharge sputtering system. The thickness of the film deposited depends upon the intensity of the current and the duration of deposition. In this case low currents (3–5 mA), low pressures (75–100 μm Hg) and short intervals ($\sim\frac{1}{2}$ min) have been used to obtain metal islands over the oxide film. Chemically inert argon gas was used in the chamber in order to avoid any oxidation of metal during sputtering.

The supported metal–alumina film on aluminum foil was calcinated in a quartz crucible. Only after heat treatment and cooling, the remaining aluminum metal was removed by amalgamation.

The specimen was immersed in a concentrated mercuric chloride solution. When amalgamation started, the specimen was

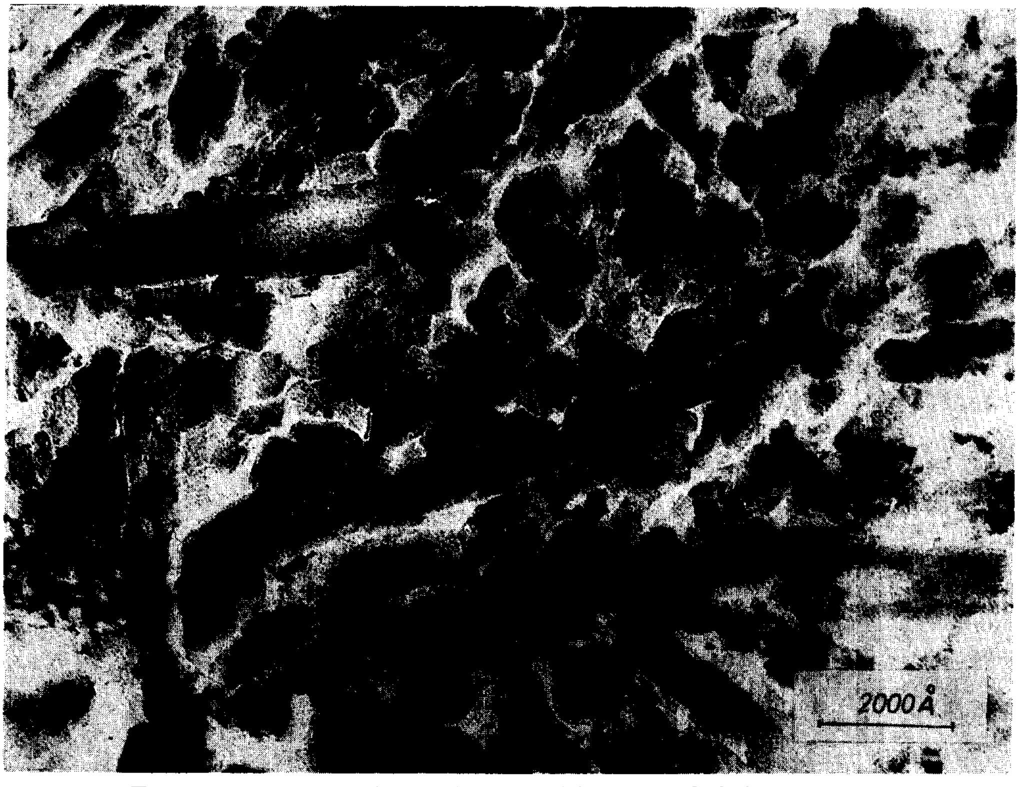

FIG. 3. Transmission electron micrograph of a model catalyst of platinum supported alumina at ambient temperature. The metal islands of 31 Å average size are uniformly scattered all over the γ-alumina substrate film.

FIG. 4. Transmission electron micrograph after the model catalyst from Fig. 3 was annealed in air at 500°C for 24 hr and slowly cooled to room temperature. The average size of the metal crystallites is 39 Å.

transferred into distilled water and amalgamation allowed to continue until the oxide film supporting the crystallites separated from the aluminum. The films were again transferred into fresh distilled water, then picked up on the electron microscope screens, allowed to dry, and kept in high vacuum for several hours before introducing in the TEM to avoid contamination of the microscope.

TEM Examination

Model specimens of supported metal catalyst were examined in a transmission electron microscope (TEM-JEOL 100 U) operated at 100 kV. The small islands of platinum crystallites which were scattered over the alumina substrate film could be easily detected due to contrast differences and to the high resolution of the microscope (~5 Å).

RESULTS AND DISCUSSION

Characterization of Alumina Substrate Films

Thin films of alumina prepared by anodization of aluminum in tartaric acid solutions are nonporous and stable (i.e., do not rupture) when heated at elevated temperatures. At ambient temperature the structure is amorphous, as demonstrated by the lack of sharp diffraction rings in the electron diffraction pattern. On heating the specimen at 400°C for several hours the amorphous alumina transformed into the crystalline γ-alumina. To avoid the occurrence of such a transformation during the annealing of the specimen containing platinum crystallites on alumina, the amorphous

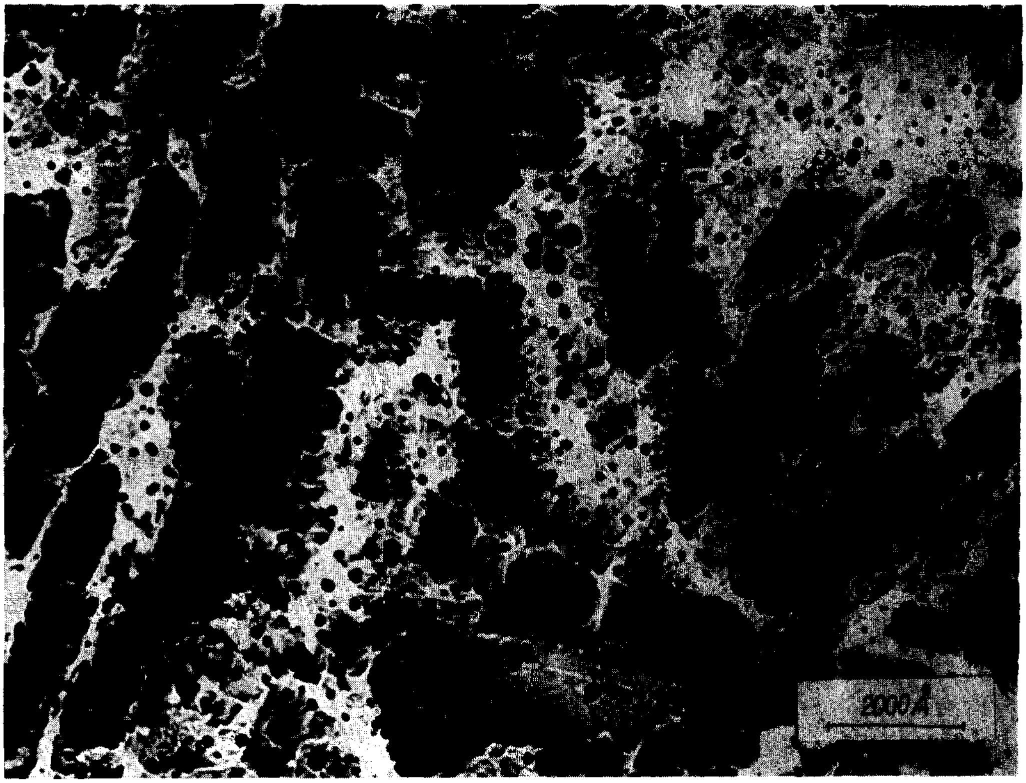

FIG. 5. Transmission electron micrograph after the model catalyst from Fig. 3 was heated in air at 600°C for 24 hr and slowly cooled to room temperature. Sintering of platinum crystallites occurred during heating and the average crystallite size grew to 107 Å.

alumina film was annealed at 600°C for 20 hr to ensure complete transformation of the amorphous alumina into the crystalline γ-alumina. Figure 1 shows a transmission electron micrograph after the amorphous alumina film was heated at 600°C for 20 hr. The grains of γ-alumina are well resolved and separated from each other by sharp grain boundaries. Contrast in different grains shows different orientations of the grains. Selected area electron diffraction pattern shown in Fig. 2 confirms that the material is γ-alumina.

Observation of Sintering and Splitting of Platinum Crystallites on Alumina Substrate Film

The results of heating the specimens in air at various temperatures are shown in Figs. 3–7. Figure 3 shows a transmission electron micrograph of platinum islands deposited by sputtering, at room temperature, onto a stable γ-alumina film. Metal islands of 31 Å average size are scattered all over the substrate film. Figure 4 presents an electron micrograph after the specimen shown in Fig. 3 was annealed in air, at 500°C, for 24 hr and then slowly cooled to room temperature. A small increase in the average size was observed. The average size of the metal crystallites increased from 31 Å (Fig. 3) to 39 Å. The size distribution is, however, nonuniform, with most of the crystallites in the range from 25–44 Å. Figure 5 shows a transmission electron micrograph when the specimen shown in Fig. 3 was heated in air at 600°C for 24 hr and then slowly cooled to room temperature. Strong sintering of the crystallites occurred and the average size of the particles grew to 107 Å.

A decrease of the average size of the crystallites was obtained in the following experiment. The specimen prepared by sputtering, containing small islands of platinum, was first heated in air at 600°C for 24 hr and after slow cooling was cut into two parts. One of the parts was further heated at 500°C, also in air, for 24 hr and slowly cooled to room temperature. The corresponding electron micrograph (Fig. 6) shows that the size of the crystallites decreased from an average of 107 Å (Fig. 5) to an almost uniform distribution of 41 Å average size. The second part was heated at 400°C, also in air, for 24 hr and again cooled slowly to room temperature. The corresponding electron micrograph (Fig. 7) shows a decrease of the average size of the metal crystallites to 83 Å. Experiments also have been carried out heating the specimens in air for 4 and 8 hr. A large decrease in the average size always occurred after reheating in air at 500°C the specimens previously heated in air at 600°C. A much smaller decrease in the average size occurred by reheating in air at 400°C the specimens previously heated in air at 600°C. Splitting probably occurs when the decrease in the average size is large, and just only contraction when the decrease is small.

After an initial heating at 400°C, some specimens were cooled rapidly to liquid nitrogen temperature. After the rapidly cooled specimen had returned to ambient temperature, it was examined in the transmission electron microscope. No platinum however, could be, identified on the surface of the specimen. Either the platinum had

FIG. 6. Transmission electron micrograph of the specimen from Fig. 5 after it was further heated in air at 500°C for 24 hr and cooled to room temperature. The average metal crystallite size was found to decrease from 107 Å (Fig. 5) to 41 Å.

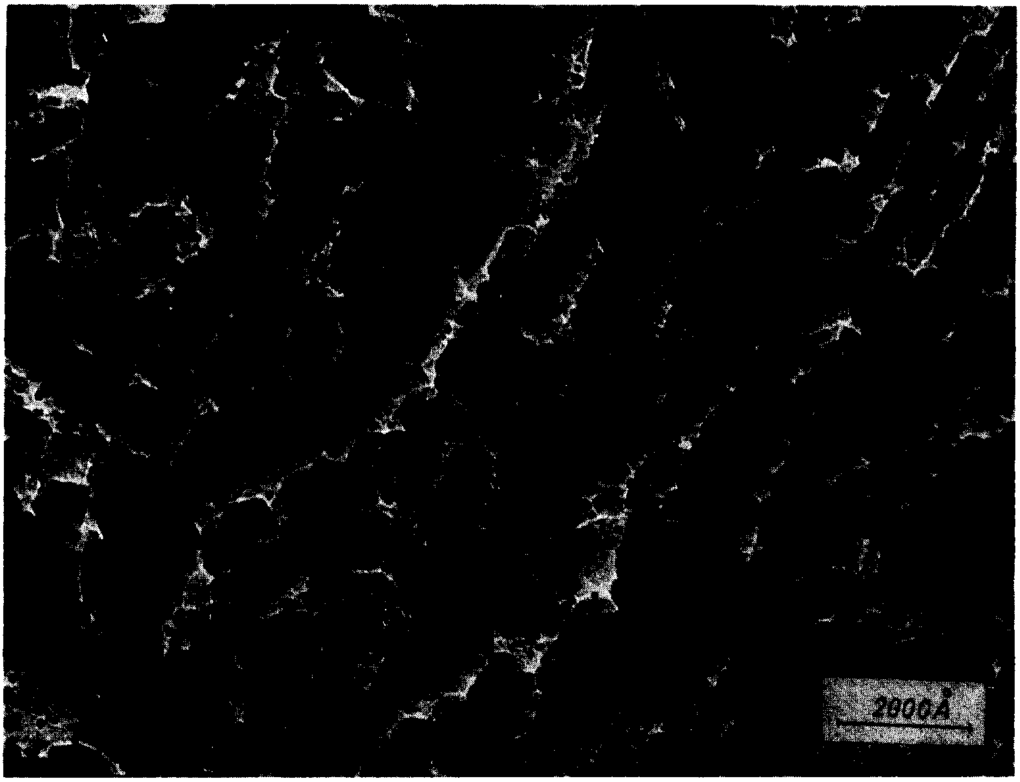

FIG. 7. Transmission electron micrograph of the specimen from Fig. 5 after it was further heated in air at 400°C for 24 hr and cooled to room temperature. The average metal crystallites size was found to decrease from 107 Å (Fig. 5) to 83 Å.

fragmented drastically into atomic particles which were not resolved by the microscope, or the platinum had completely vaporized due to fragmentation.

Strain energy caused by Pt–alumina complex formation as possible cause of splitting. Johnson and Keith (*1*) postulated that a Pt–alumina complex existing in an oxidized state is responsible for the redispersion of the metal in supported metal catalysts. A Pt(IV)–alumina complex was first postulated by McHenry *et al.* (*11*) to account for the "soluble Pt" in aqueous HF. Because no soluble platinum is found in the absence of oxygen, Kluksdahl and Houston (*12*) rejected the existence of a metal–substrate complex. Johnson and Keith reported that by increasing the severity of the oxygen treatment (by increasing the pressure of air and the temperature), both the amount of soluble platinum and the degree of dispersion of the metal increased. They concluded that in the oxidized state a platinum–alumina complex does exist. On increasing the temperature, a condition will be reached at which the decomposition pressure of the complex equals the partial pressure of oxygen. Above this temperature the complex is no longer stable. This critical temperature is near 510°C at 0.21 atm and near 580°C at 1.0 atm. If indeed splitting is associated with formation of the complex, one may expect that it will occur only below the critical temperature. Of course, for the formation of the complex a sufficiently large temperature is necessary.

Why does the complex split the crystallites? A possible explanation might be the following. The complex formed at the substrate–metal interface has a structure that induces in the metal a strain energy which is relaxed in part by the fracture of the crystallite. In other words, the free energy of the system composed of complex and crystallite is greater (because of the strain energy) than the free energy of the system composed of several small crystallites (in which the strain energy is partially relaxed) and substrate, although the surface area is increased. The internal stresses which always exist in the sintered crystallites facilitate the splitting. An argument in support of the above explanation is the behavior of thin films on a substrate. The interfacial mismatch due to the differences in the lattice parameters is accommodated in this case by a parallel sequence of misfit dislocations at the interface (*13,14*). The mismatch induced by the presence of the mentioned compounds is much more complex and may lead to rupture.

It is interesting to observe that this mechanism can explain some of the contradictory results reported in (*1,5*). In the work reported in (*1*), the temperature was near the critical one and redispersion occurred, whereas in the latter the temperature was above the critical temperature of stability of the complex and consequently sintering occurred.

In some conditions, due to surface tension effects, a contraction of the particles may occur. Perhaps the relatively small decrease in the average size from 107 to 83 Å obtained by reheating at 400°C a previously heated specimen at 600°C can be explained in this manner.

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