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Pore structure in nickel created by ammonia at 873 K

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Abstract Nickel spheres (of 0.76-mm diameter and purity 99%) were exposed to ammonia at 873 K for 140 h. The spheres were removed and examined using FEGSEM (Field Emission Gun Scanning Electron Microscopy) and compared with a fresh sample. Formation of a porous layer, several microns thick, was observed at the surface with a pore size distribution concentrated in the range 50–200 nm. Additionally, cracking occurred along the grain boundaries, in some cases reaching the centre of the spheres. Particles of alumina were also observed embedded in the surface of the spheres. Similar experiments with high purity nickel wire (99.999%) showed the same type of pore formation indicating that the observations for the spheres were not likely to be caused solely by impurities in the nickel.

Introduction

This work originates from an attempt to find a suitable catalyst to give reproducible performance for testing the Flux Response method [1] for in situ monitoring of heterogeneous catalysis. It was thought that catalytic decomposition of ammonia at a nickel surface would be a good system to test a model being developed for the Flux Response of a catalytic reactor. Unfortunately it was found that, instead of giving reproducible results at unchanged conditions, the activity of the catalyst increased with repeated use. This increase in activity was believed to be due to structural changes in the nickel, so a systematic study of the effect of exposure of nickel to ammonia at high temperature was begun.

Recently published work [2, 3] concerning the interaction of ammonia with nickel has used inlet gas mixtures of ammonia and steam or hydrogen and mainly used alloys rather than pure nickel. This work looks at a simpler system, where the metal is nickel and the gas phase contains only ammonia and its decomposition products.

Experimental

Nickel spheres (Goodfellow, 99%) were exposed to pure ammonia (BOC, nitride grade) at 873 K for approximately 140 h. The apparatus (see Fig. 1) used was a simplified version of that used for earlier flux response experiments [1]. The spheres were placed in a 4 mm ID quartz tube reactor and held in place with plugs of quartz wool.

The tube was placed in a furnace and the spheres were kept under flowing argon until a temperature of 873 K was reached, the argon was then replaced with

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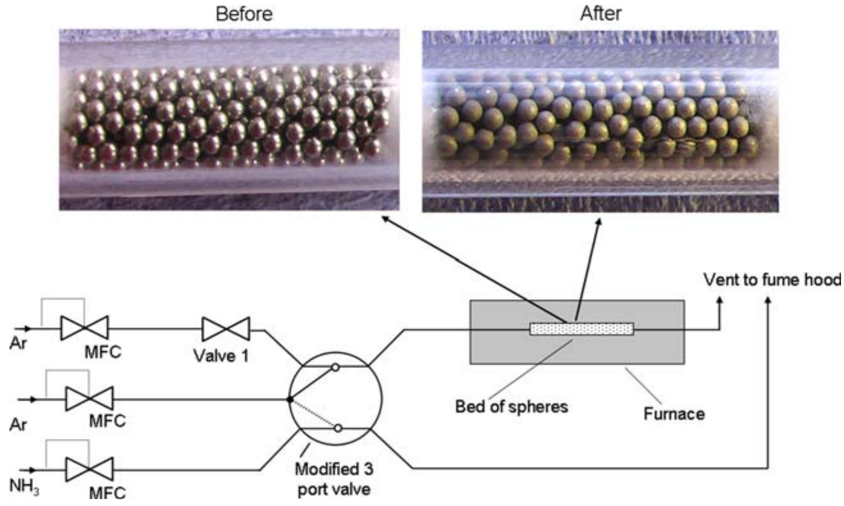


Fig. 1 Experimental set up, also showing photographs of the bed of spheres before and after the experiment

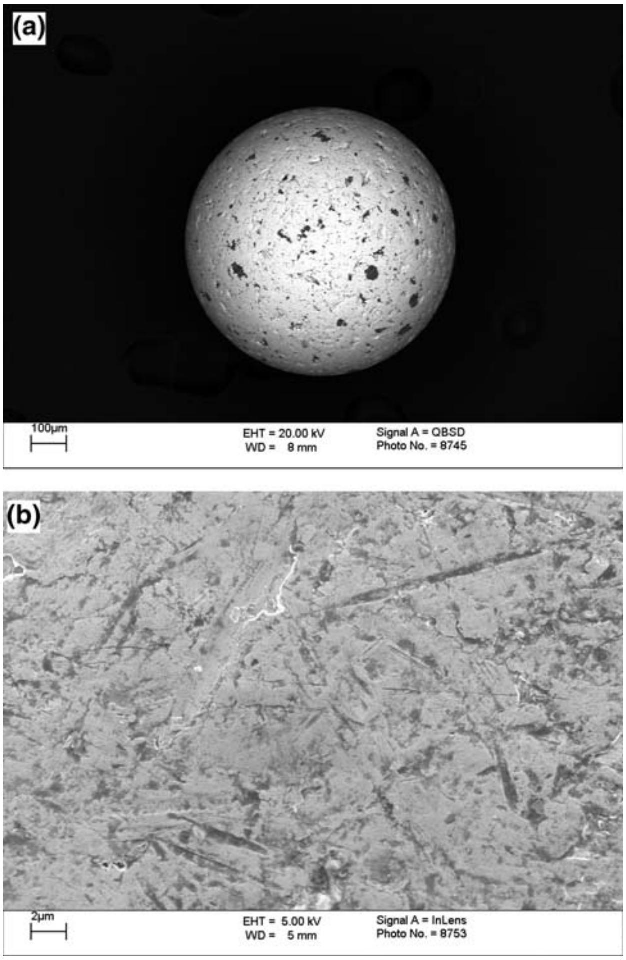


Fig. 2 Fresh sphere: (**a**) Whole sphere, with alumina particles visible as black regions; (**b**) a higher magnification view of the surface

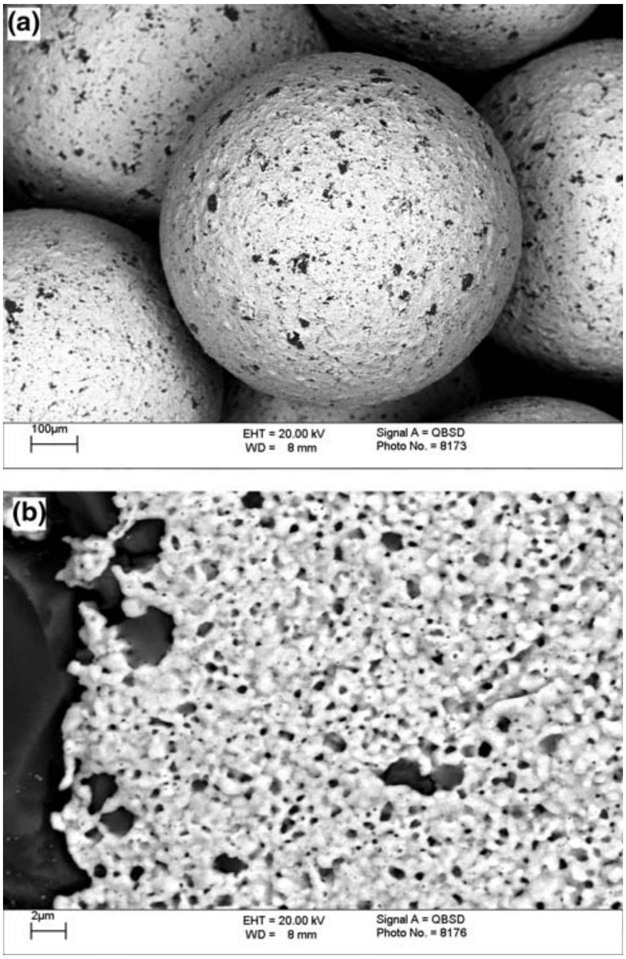


Fig. 3 Spheres removed from reactor at end of experiment: (**a**) At the same magnification as Fig. 2a, some roughening of the surface is just discernible; (**b**) The nickel surface has become porous but the alumina (black area) is not affected

pure ammonia flowing at 2 ml min^{-1} by first adding ammonia to the flow by switching the 3-port valve, then closing valve 1. Before removing the spheres, the flow was switched back to argon and the tube was rapidly cooled to near room temperature by removing it from the furnace.

Results and discussion

On removal from the tube, the spheres were found to be stuck together. They had also lost their shine as can be seen from the photographs in Fig. 1. On closer inspection, the end nearer the inlet appeared darker than the outlet. Some spheres were removed from the two extreme end sections of the bed and examined with an electron microscope. The first observation, seen more clearly using a back scattered electron detector, is the presence of particles of alumina which are seen as black spots on a fresh sphere in Fig. 2 and on the used spheres in Fig. 3. They appear to be unaffected by the exposure to ammonia. The alumina particles are introduced by the final polishing process which the spheres undergo during manufacture. The second, more significant, observation from the electron microscope pictures of the sphere surfaces is the development, seen in Fig. 3, of porosity near the surface.

In order to see how far the porous layer penetrated below the surface, spheres from each end of the reactor were then mounted in conducting Bakelite and sectioned by grinding and polishing, finishing with a 1-micron polish. Further images were then obtained using a backscatter detector. Figure 4 demonstrates that the spheres near the inlet have been more severely attacked and shows that the depth of the porous layer is irregular and only a few microns deep.

Finally, one of the samples was further polished with colloidal silica and an EBSD (Electron Backscattering Diffraction) image was taken showing the orientation of the exposed nickel surfaces. This confirmed that cracking occurred at the grain boundaries as shown by Fig. 5.

Further tests were done exposing spheres to nitrogen, hydrogen and a mixture of the two gases under conditions which were otherwise similar to those for the ammonia experiments. Exposure to ammonia itself has a much larger effect than a nitrogen:hydrogen mixture, as can be seen from Fig. 6. This confirms the role of ammonia in the pore formation.

During ammonia decomposition, atomic nitrogen is produced as an intermediate species at the nickel surface giving a much higher nitrogen fugacity than the presence of molecular nitrogen. Hence the inlet spheres are the most severely attacked because they are exposed to pure ammonia, which is decomposed on the nickel surface. The spheres near the outlet are exposed to a considerably lower concentration of ammonia, mixed with molecular nitrogen and hydrogen.

Both the pores and the cracking are believed to be due to the release of nitrogen at high pressure below the surface of the nickel. Due to the extremely high nitrogen fugacity at the surface, significant amounts dissolve in the nickel but, as the dissolved nitrogen diffuses away from the surface, its fugacity decreases very rapidly and it comes out of solution as nitrogen gas which forces its way back to the surface. This mechanism will produce an open pore structure.

It is also possible that there is transient formation of some nickel nitride. Nickel nitride may be synthesised from nickel and ammonia but is not stable above approximately 680 K [4]. However, Grabke et al. [2] reported observing

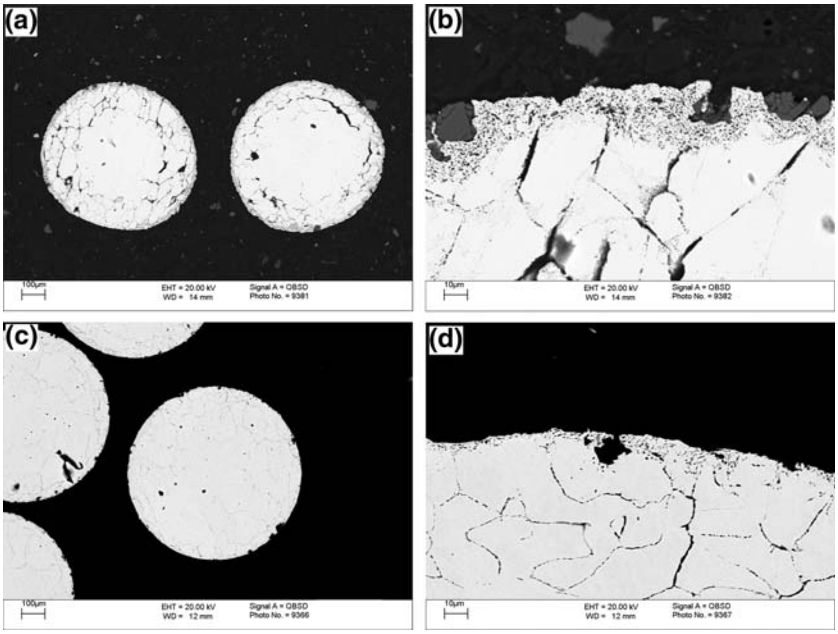


Fig. 4 Cross section of used spheres: (**a** and **b**) A sphere near the inlet of the bed; (**c** and **d**) A sphere adjacent to the outlet. The particles embedded in the surface seen in (**b**) were identified as alumina using EDX (Energy Dispersive X-ray micro-analysis). The pore size can be seen to be of the order of 100 nm

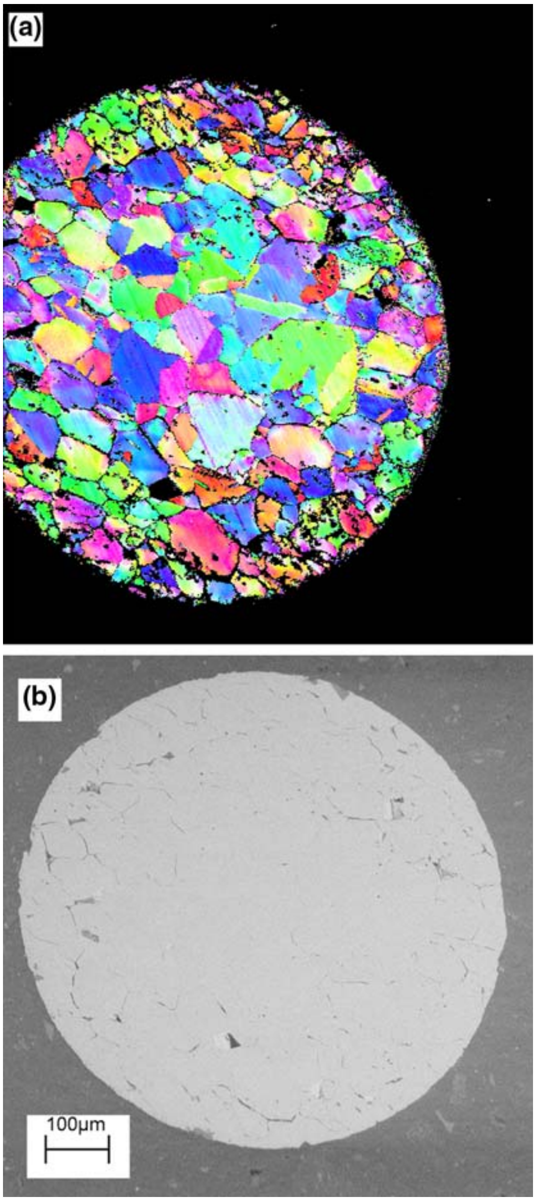


Fig. 5 (**a**) EBSD image showing the orientation of exposed crystal planes for a sectioned sphere and cracks at grain boundaries; (**b**) SEM image of the same sphere

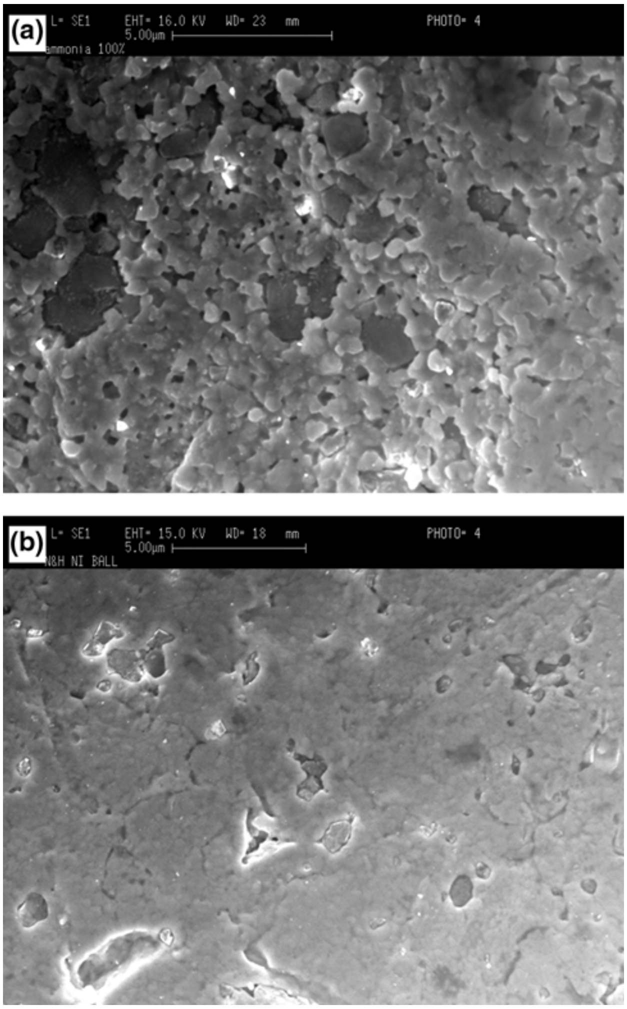


Fig. 6 Comparison of (**a**), a sphere exposed to ammonia, with (**b**), one exposed to a mixture of nitrogen and hydrogen

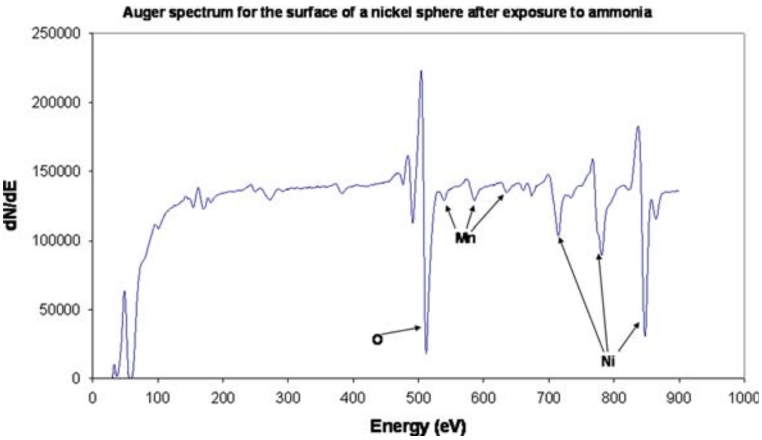
unstable nickel nitride at 773 K in the presence of steam and ammonia. Formation of the nitride was said to lead to internal stresses thus causing the cracking. The rapid decomposition of the nitride, produced nitrogen gas at high pressure which forced its way to the surface creating pores. At the temperature used in our work (873 K), nickel nitride is thermodynamically unstable but could be formed as an intermediate species. However, this could not be confirmed experimentally.

Impurities in the nickel may also react to form other, more stable, nitrides and make a contribution to the crack and pore formation e.g. iron and titanium are both listed by the manufacturer as impurities in the nickel spheres. (Kodentsov et al. [3] have published a detailed study of the deformation phenomena occurring in nickel alloys of titanium and chromium when nitrided with an ammonia hydrogen mixture.)

AES (Auger Electron Spectroscopy) analysis of the surface of a sample of our exposed spheres showed up to 1 at% nitrogen, compared with zero for unused spheres. The AES analysis also showed the presence of manganese (average 2.4 at%) for all the used spheres compared to none for the new spheres. An example spectrum is shown in Fig. 7. Manganese is another listed impurity in the nickel and may have migrated to the surface. No iron or titanium was observed.

Other than the work of Grabke et al. [2] (who did not specify the purity of their nickel) the great majority of previously published experimental work [3, 5–7] looking at nickel nitridation and the resulting morphology was performed using alloys rather than pure nickel. The AES

Fig. 7 Auger Electron Spectrum for surface of a nickel sphere exposed to ammonia at 873 K. For this particular spectrum, the atom percentages for the labelled peaks were: Ni 45.0, O 40.7, Mn 3.1



results suggest that the porous structure seen in Figs. 3 and 4 were composed of relatively pure nickel. To further confirm that the effects seen in the experiments with the spheres were not mainly caused by formation of nitrides of impurities (such as manganese) a test with nickel of much higher purity was carried out. The experiment, using 99.999% nickel wire, once again showed pore formation, as seen in Fig. 8. Therefore, the changes seen previously to the spheres could not be attributed exclusively to the presence of impurities.

Conclusions

In summary, the surface of nickel exposed to ammonia at high temperature becomes porous due to interaction with the atomic nitrogen species produced as an intermediate in the decomposition of the ammonia. By controlling the reaction conditions it may be possible to regulate the thickness and pore size of the porous layer and produce useful, that is to say high surface area, porous layers of nickel [8]. There are a variety of possible applications for this type of nickel, for example as catalysts or electrode materials. Further work will be done to study the development of the structure with time, this will allow evaluation of the surface area created and the strength of the material produced.

Under the conditions and time scales reported here, the surface area of the nickel continued to increase but the stability of the porous structure outside of these conditions is not known and would need to be investigated under any proposed environment of use for the material. One concern would be sintering at high temperature, other than that there is no reason to suppose that the structure would be unstable. If the pore structure were lost due to sintering, it is anticipated that it could be regenerated by repeated exposure to ammonia.

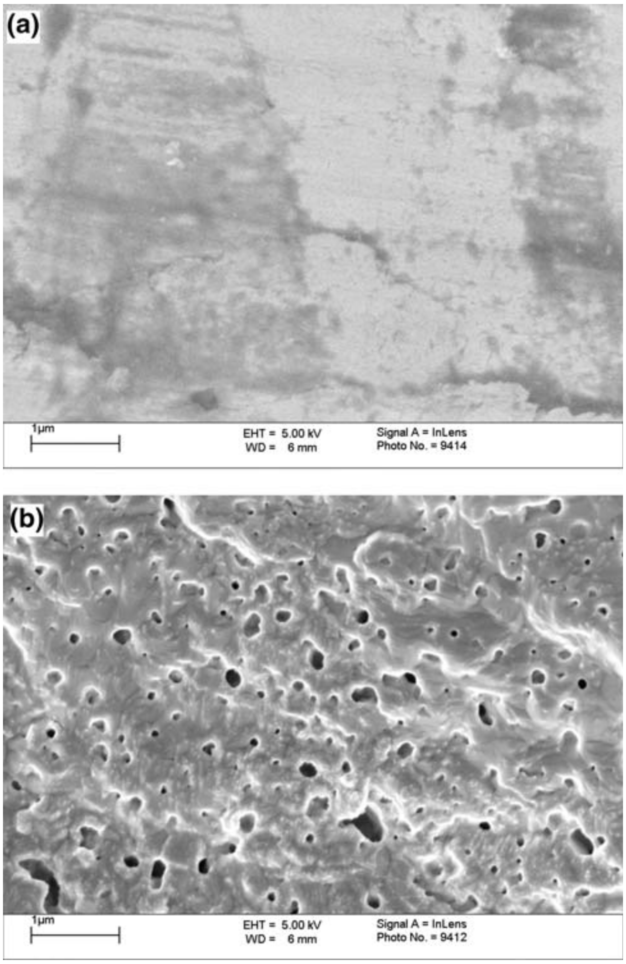


Fig. 8 High purity [Alfa Aesar 99.999% (metals basis)] nickel wire, (**a**) before and (**b**) after exposure to ammonia for 18 h at 873 K

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