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Surface segregation in commercial nickel-iron alloys

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The paper describes the various factors which influence the segregation of silicon-rich compounds at the surface of commercial nickel-iron reed substrates when these are annealed at high temperatures (~1000° C) in hydrogen atmospheres. The mechanism of formation of these "minor-phases" is still a matter of speculation although results indicate a diffusion controlled selective oxidation process.

1. Introduction

Substrate surface condition has long been recognized as one of the most important factors influencing the quality of electroplated gold; this becomes of prime importance when subsequently the gold is to be used for electrical contact purposes. The manufacture of reed contact units is a well-established industry where the quality of electroplated gold has to be maintained at a high standard to ensure reliability and long service life in telecommunications equipment. In recent years, scanning electron microscopy and transmission electron microscopy have enabled substrate surfaces and gold electrodeposits to be examined in very great detail. These techniques have enabled an unexpected surface phenomenon to be revealed for the 51 wt % nickel-iron alloy, which is used as the substrate material for reeds, when this is annealed at temperatures of the order of 1000° C in hydrogen atmospheres. This phenomenon undoubtedly affects the quality of the gold which is subsequently electroplated onto these surfaces.

During annealing at about 1000° C, the surface of the nickel-iron substrate becomes thermally etched as thermally activated mass transport processes occur under a driving force derived from the need for the surface to attain a minimum energy configuration. A network of grain- and twin-boundary grooves is established, sharp surface irregularities (e.g. scratches) become smoother and a certain amount of grain surface faceting takes place. However, in addition, for commercial 51 wt % nickel-iron alloy, a surface distribution (both at grain boundaries and on grain surfaces) of small mounds can be observed [1, 2]. Although scanning electron microscopy has characterized the physical form of these surface discontinuities, there appears to be some doubt regarding their exact nature. One author [1] has described them as "minor-phases" and attributes their formation to the migration of impurity elements present in the nickel-iron to the surface along grain boundaries and particularly through the "holes" which occur at grain-boundary intersections. It is also claimed that certain of these "minor phases" can be of an insulating nature. However, another author [2] has described what appears to be exactly the same phenomenon as "blistering" caused by temperature-dependent evolution of gases (e.g. CO_2, CO) formed as a consequence of reaction between the hydrogen, the water vapour in the hydrogen, and the substrate material, and in particular with the carbon content of the nickel-iron. In the present work, an attempt has been made, using scanning electron microscopy coupled with electron microprobe analysis and transmission electron microscopy, to clarify this situation.

2. Experimental programme

Various commercial 51 wt % nickel-iron alloy wires of suitable diameter for reed manufacture, annealed in both wet and nominally dry hydrogen atmospheres at temperatures between 850 and 1150°C, were examined using scanning electron microscopy (Stereoscan instrument, ex Cambridge Instrument Co) and electron microprobe analysis (Microscan 5 instrument, ex

Figure 1 Sample no. 2 (× 1000).

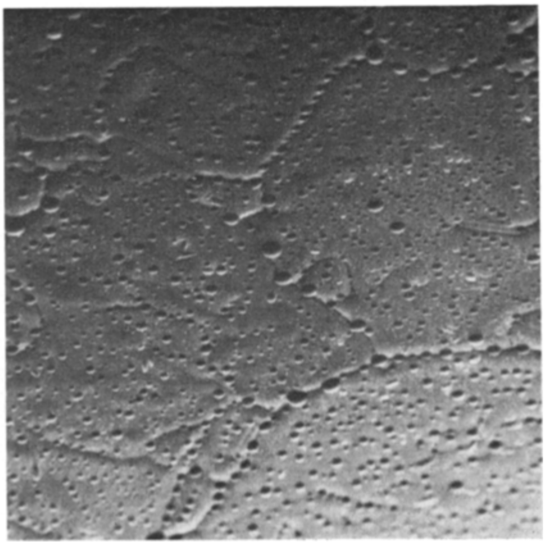

Figure 2 Sample no. 4 (× 1000).

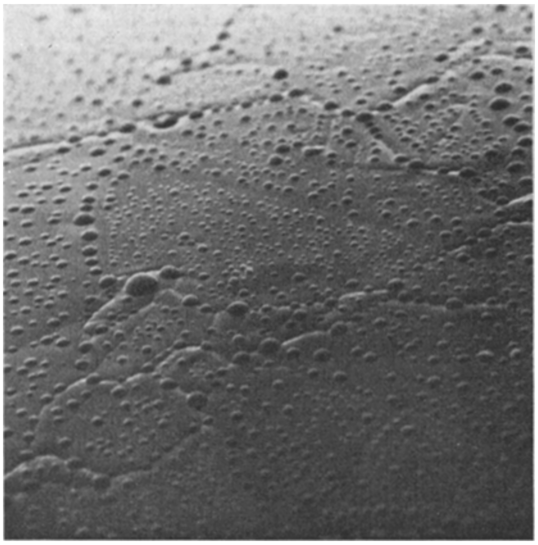

Figure 3 Sample no. 5 (× 1000).

Figures 1 to 3 Scanning electron micrographs of commercial Ni/Fe wires annealed in nominally dry hydrogen for $\frac{1}{2}$ h at 1150°C.

Cambridge Instrument Co). Both nickel-iron wire "as-received" from the supplier and reeds formed from wire were used in the investigation and each sample of material was carefully characterized regarding chemical composition and metallurgical condition. Transmission electron microscopy of carbon extraction replicas was also carried out.

3. Results

Five samples of nickel-iron wire, "as-received" from the suppliers, were heat-treated simultaneously in the same hydrogen atmosphere for $\frac{1}{2}$ h at 1150°C. No special precautions were taken to dry the hydrogen which was drawn from a cylinder of high purity gas (ex BOC). The quantity of "minor-phases" produced on the nickel-iron surfaces varied for the different samples. Scanning electron micrographs were used to arrange the five materials in order of increasing quantity of "minor-phase" and with respect to this order the materials were numbered one to five. The SEM micrographs of Figs. 1 to 3 show, at the same magnification, representative surface areas of three different samples of wire. The carbon, silicon and manganese contents of the five samples of wire are given below.

These results indicate that the quantity of minor-phase (for a given annealing time, temperature and atmosphere) is not critically dependent on the carbon content of the nickel-iron but seems to vary directly with silicon and inversely with manganese content. It was not surprising, therefore, that electron microprobe analysis revealed the minor-phase to be rich in silicon and that this was associated with manganese; in all probability it was some form of manganese silicate. Fig. 4 is a secondary electron micrograph of part of the surface of wire no. 5 and Figs. 5 and 6 are the corresponding X-ray images for silicon and manganese. Electron

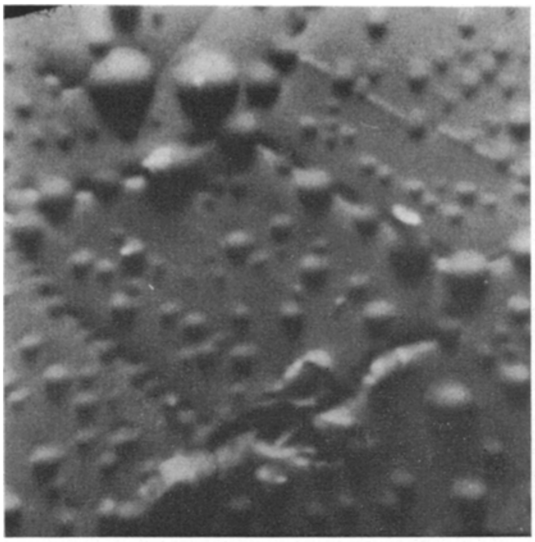

Figure 4 Electron microprobe analysis. Secondary electron image. Sample no. 5 (× 2000).

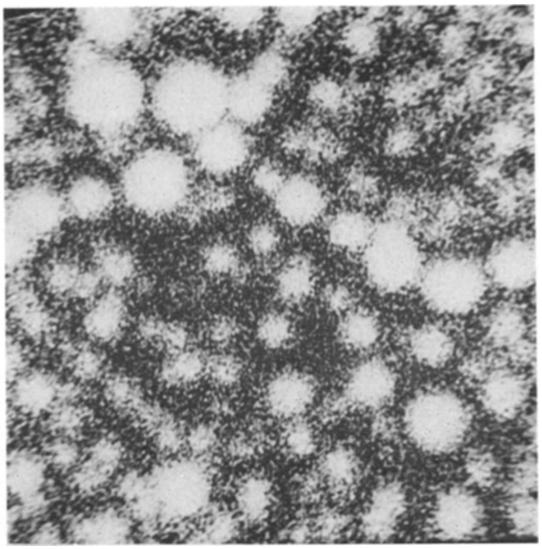

Figure 5 Electron microprobe analysis. Silicon X-ray image (× 2000).

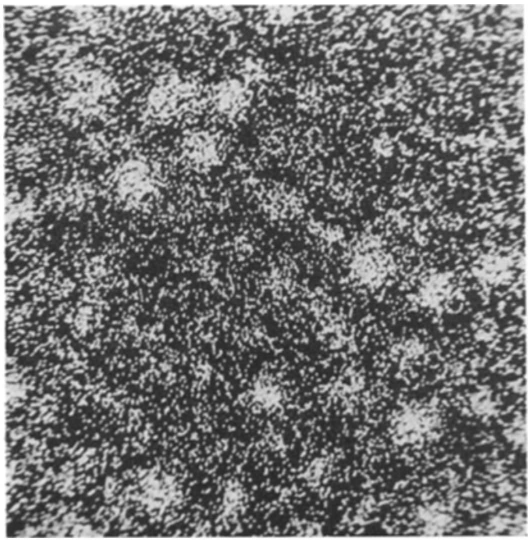

Figure 6 Electron microprobe analysis. Manganese X-ray image (× 2000).

microprobe analysis also revealed that the minor-phase was very much depleted in nickel and iron with the iron and nickel X-ray images showing only a background signal in regions consisting of minor-phase. However, it should be stressed that silicon and manganese are not the only elements which have been detected in these surface mounds. Oxygen, aluminium, magnesium, potassium, sodium, chromium and calcium have also been detected. Whereas few of the elements detected seem to occur simultaneously in significant quantities in any given mound, one element, silicon, is always a major constituent of these minor-phases. Although the dew-point of the hydrogen atmosphere used in this work has not been closely controlled (either nominally dry or deliberately moistened hydrogen has been used), the results are in agreement with the work of Richards [2] in so far as the occurrence of the minor-phases is directly dependent on the presence of water in the hydrogen. Richards showed that at low water levels (less than 100 ppm by volume) the quantity of minor-phase appearing on the surface is severely reduced in comparison with surfaces annealed in wetter atmospheres. Thus, it would appear that the phenomenon is dependent upon a number of variables. These are listed below and their individual effects are given (other variables being kept constant).

3.1. Temperature

For a given annealing time, a more well-developed minor-phase distribution occurs at higher temperatures. This effect is demonstrated very markedly in the scanning electron micrographs of Figs. 7 and 8 which show, at the same high magnification, the surfaces of the flattened ends of two reeds taken from one sample of material after annealing in nominally dry hydrogen for ½ h at 850 and 950° C respectively. Fig. 7 shows that, after treatment at 850° C,

Figure 7 ½ h at 850°C (× 5000).

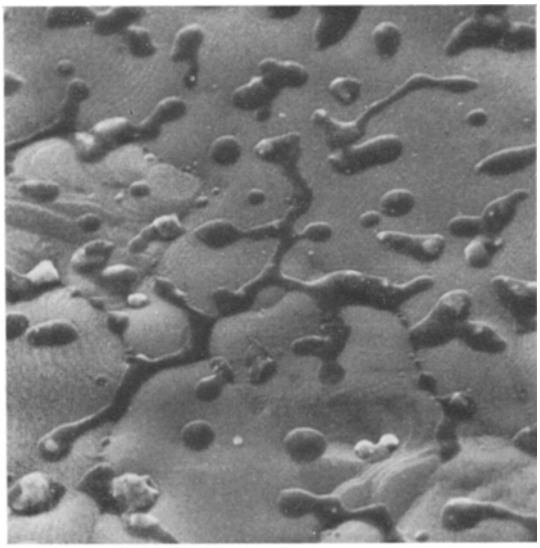

Figure 8 ½ h at 950°C (× 5000).

Figure 7 to 9 SEM of a commercial Ni/Fe annealed at different temperatures (½ h, nominally dry hydrogen).

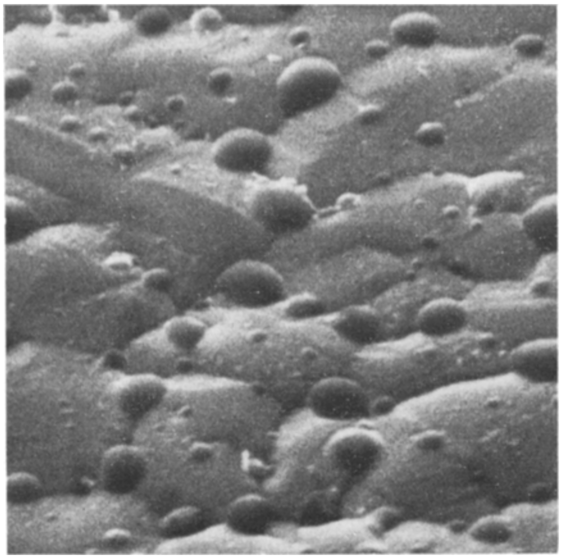

Figure 9 ½ h at 1150°C (× 5000).

the surface is not completely thermally etched and is still relatively rough, and also that a network of grain-boundary ridges has been set up. It is thought that these ridges are in fact a minor-phase since grain-boundary segregation of silicon was detected by electron microprobe analysis; this strongly suggests that one mechanism of formation of the minor-phases is indeed grain-boundary migration of impurity elements and subsequent reaction at the surface as postulated by Davies [1]. Figs. 7 and 8 should be compared with Fig. 9 which is a scanning electron micrograph taken at identical magnification of the same material (in wire form) annealed for ½ h at 1150°C in a similar atmosphere (nominally dry hydrogen). This micrograph clearly shows that the minor-phase has spheroidized completely to reveal grain boundary grooves (which, in Figs. 7 and 8, are masked to some extent by the minor-phase), and the surface can be seen to be made up of a thermally etched grain structure with a distribution (both at grain boundaries and within grains) of hemispherical particles of minor-phase.

3.2. Time

For given temperature and annealing conditions the effects of annealing time would suggest that the formation of minor-phase is diffusion controlled. For example at 950°C the form and distribution of the minor-phase on both grain boundaries and grain surfaces does not change with increasing time but for long annealing times much more massive segregation at grain boundaries and larger "hemispheres" on grain surfaces are observed. Some process of coalescence may also contribute to the coarsening of minor-phase mounds on grain surfaces.

3.3. Dew-point

Although this variable has not been controlled

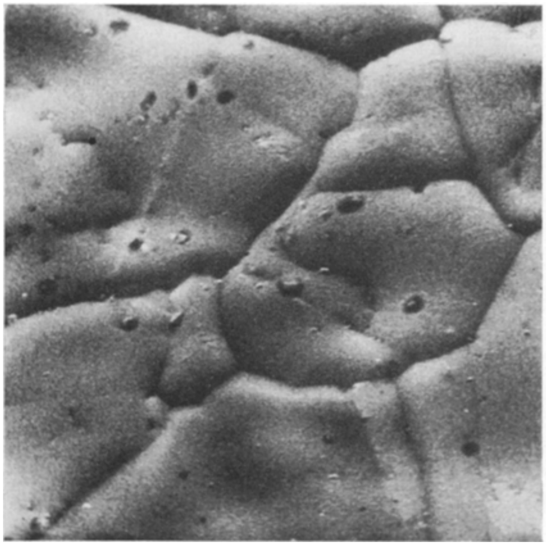

Figure 10 Annealed $\frac{1}{2}$ h at 950°C in nominally dry hydrogen. Very pure material (× 5000).

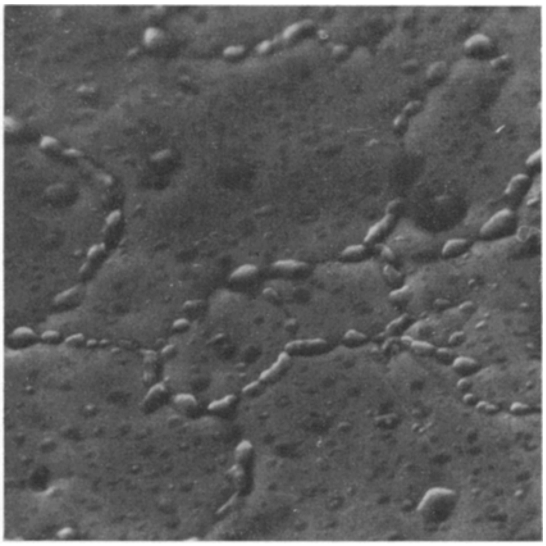

Figure 11 Annealed $\frac{1}{4}$ h at 1000°C in wet hydrogen. Impure material (× 5000).

Figures 10 and 11 Variability of Ni/Fe reed substrates examined by SEM.

very closely in the present work, Richards [2] has clearly demonstrated that the use of dry hydrogen atmospheres markedly inhibits the formation of the minor-phases.

3.4. Purity

The present work has shown that the impurity level of elements generally used as de-oxidants in the manufacture of nickel-iron (and particularly silicon) influences the quantity of minor-phase which segregates to the surface during annealing. It is thought that the phenomenon is caused by migration of impurity elements from the sub-surface regions. If this is so, the impurities in question would be those added in stoichiometric excess during de-oxidizing processes since it is difficult to imagine a mechanism by which impurity compounds such as manganese sulphide or siliceous slag inclusions can migrate through the nickel-iron, although it may be possible that some of these can be dragged to the surface by grain boundaries during grain growth. It is also possible that wire drawing lubricants and greases occluded in near-surface regions during wire drawing and forming could contribute to the segregation phenomenon.

The scanning electron micrographs of Figs. 10 and 11, at the same magnification, illustrate the great differences that can occur for the surface condition of nickel-iron reed substrates. Fig. 10 shows the surface of a particularly pure material annealed in nominally dry hydrogen for $\frac{1}{2}$ h at 950°C. Fig. 11 shows the surface of a less pure material annealed in wet hydrogen for $\frac{1}{4}$ h at 1000°C. The grain-boundary phase, so clearly visible in this latter micrograph, was found by electron microprobe analysis to be rich in silicon and manganese (with some aluminium and chromium, and smaller amounts of magnesium and calcium).

Some reed surfaces which had been heat-treated for 1 h at 1150°C in nominally dry hydrogen were coated with carbon and the replicas were etched off the substrates using dilute hydrochloric acid and examined in the transmission electron microscope. Extremely good replication was obtained and some of the "minor-phase" was successfully extracted. Selected area electron diffraction spot patterns were obtained from some, but not all, of the surface mounds. This would suggest that the phases are partially amorphous but can exhibit some degree of crystallinity. The overall impression gained was of a partially devitrified glass-like compound. The only recurrent *d*-spacings recorded were 4.47, 2.57 Å providing insufficient data for the positive identification of the crystallites. However, as the *d*-spacings of the Ni-Fe alloy are 2.066, 1.789, 1.265 Å the presence of Ni-Fe can be fairly definitely eliminated. Glancing angle electron diffraction on annealed reed surfaces also failed to provide definitive diffraction patterns. This is not surprising because R.H.E.E.D. patterns are notoriously sensitive to a number of factors (e.g. surface topography, environmental contamination) and therefore the negative result is not evidence that the minor-phases are amorphous. The surface mounds were easily extracted on carbon replicas using a hydrochloric acid etch and Fig. 12 is a transmission electron micrograph showing extracted minor-phase.

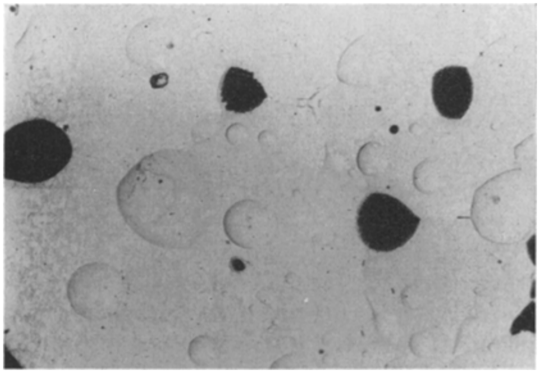

Figure 12 Transmission electron micrograph of extraction replica (× 1750).

Some of the minor-phases extracted on carbon replicas were sufficiently large to be examined by electron microprobe analysis. Analysis was carried out on a number of particles of minor-phase for the three main constituent elements, manganese, silicon and aluminium (no nickel or iron was detected). Unfortunately, the instrument is not sufficiently sensitive to oxygen for a meaningful semi-quantitative analysis of this sort. However, for the particles examined, the atomic ratio of the three main elements was fairly constant and was $Mn_3Si_8Al_3$.

4. Discussion

In the present investigation, electron microprobe analysis has shown that the small mounds observed on nickel-iron substrates after annealing in hydrogen atmospheres are rich in the impurity elements generally used as de-oxidants in refining processes. No nickel or iron can be detected within these mounds and they are not, therefore, merely surface blisters caused by gas evolution. It is, in any event, difficult to imagine how a gas produced at a grain boundary could result in the formation of such a symmetrical hemisphere of nickel-iron there. The grain boundary, which is elsewhere classically grooved, should still be visible somewhere on the "blister" owing to the establishment of an equilibrium configuration under the interaction of the grain-boundary energy and the surface energies of the two adjacent grains. Also, if water vapour, oxygen and hydrogen can diffuse into the grain boundaries to react with carbon, there would appear to be no reason to suppose that the CO, CO_2 and CH_4 gases produced cannot diffuse out equally as well. However, the question of whether any gas reaction is involved in the formation of the mounds of minor phase is still unresolved and would be difficult to establish experimentally.

It is possible that the mound formation is associated with gas evolution and that this evolution and a solid state diffusion operate concurrently. This possibility has been put forward by Richards [3]. Irradiation studies in other systems have shown that gas can migrate in solids via bubbles [4] ultimately escaping at the surface by bubble rupture or blistering [5, 6]. Mykura [7] has shown that impure nickel specimens containing 0.05% carbon and fired under vacuum at 1000°C develop grain-boundary ridges which, it is claimed, are caused by the formation of internal gas bubbles of CO and an associated diffusion of vacancies along grain boundaries, each vacancy adding one atom to the ridge. These ridges had the usual grain-boundary grooves superimposed on them and Richards [3] has also observed ridges of this type. However, the present work has shown no correlation between the quantity of minor-phase and the carbon content of the material (indicating that if a gas is involved then it is not CO, CO_2 or CH_4), no "burst" blisters have ever been observed and grain-boundary grooves have not been seen superimposed on grain-boundary ridges.

Electron microprobe analysis was also used to determine whether the mounds which appeared at grain boundaries were different from those observed on grain surfaces. Within the limits of resolution of the instrument no marked compositional differences have been revealed. However, Richards [3] has reported that whereas "in-grain" blistering reaches its ultimate size at water levels in the annealing atmosphere of a few hundred ppm, the grain-boundary blistering was observed to increase steadily with increase in water content of the hydrogen. This would suggest that there is some difference in the composition or mechanism of formation of mounds at grain boundaries compared with those on grain surfaces.

Grain-boundary diffusion coefficients are generally several orders of magnitude greater than those for volume diffusion and with decreasing temperature this difference is magnified because the activation energy for grain-boundary diffusion is generally much less than that for volume diffusion. On the basis of a diffusion-controlled formation mechanism this may well explain the differences observed between minor-phases formed at grain boundaries and those formed within grains. Evidence that the mound formation is diffusion controlled is present in Figs. 8 and 11. In these micrographs, the minor-phase at grain boundaries is not hemispherical whereas that on grain surfaces has a greater tendency to be so. A grain boundary represents a two dimensional high diffusivity path and it might be expected that impurities migrating to the surface of grain boundaries and reacting there with the annealing atmosphere would sit in the grain-boundary groove to form a ridge. For mounds formed within grains it might be expected that, initially, these would form very quickly (surface diffusion is generally several orders of magnitude faster than grain-boundary diffusion) but when the immediate surface or near surface supply of impurity elements had been used up, further growth would be slow because it would depend on relatively slow volume diffusion. In this case it would be expected that the minor-phase would tend to be spherical because within the plane of the grain surface there is relatively little directionality in the supply of the impurity elements. Therefore, in general, at lower temperatures it would be expected that the grain-boundary ridge distribution of minor phase would be the more prominent, whereas at higher temperatures (Figs. 2, 3, and 9), where grain boundary and volume diffusion rates are more nearly equal, a hemispherical mound distribution would predominate both at grain boundaries and within grains. Even in this latter instance, the mounds at grain boundaries may still be the larger since more impurities are available at grain boundaries than in the bulk of the material. The scanning electron microscopic evidence presented in the current investigation would support this hypothesis. The actual form of a particular mound of minor-phase would depend on the absolute values and temperature dependences of the surface and interfacial energies of the minor-phase and the nickel-iron.

The driving force for the proposed mechanism of mound formation would be the effective removal of solute impurities from the surface of the material by reaction with the atmosphere followed by the migration of impurities from within the bulk of the material into depleted regions to maintain an equilibrium concentration. Unfortunately, the minor-phases have not, as yet, been positively identified and, therefore, the nature of the reaction which takes place at the surface is unknown. Also several interesting effects (e.g. the "displacement" of surface mounds parallel to grain boundaries leaving them free of minor-phase, see Fig. 1) have been observed which still require satisfactory explanation. However, Richards [2] has shown that the quantity of minor-phase increases with increasing amounts of water vapour in the hydrogen. A possible explanation of this effect may be found if consideration is given to the equilibrium thermodynamic conditions necessary for the formation of oxides of the various impurity elements. This exercise is somewhat speculative because (a) there is no evidence that simple oxides are produced (in fact this is probably not the case), (b) equilibrium conditions may not prevail, and (c) the activities of the small amounts of impurity elements in solution will probably not be unity. Also, it is assumed that the elements migrate to the surface and react with the atmosphere much more quickly than either oxygen or water can diffuse into the material and react *in-situ* (i.e. internal oxidation). However, from Milner [8] (and including data for SiO_2), the pressures of water vapour in hydrogen at 1000°C necessary to oxidize the impurity elements are given in round figures in the Table below. Iron is included as a "base-line" and the elements are arranged in order of their oxidation potential (*see Table overleaf*).

From the Table, it is evident that the strongly oxidizing elements Ca, Mg, Al and Si will oxidize quite readily even in very dry hydrogen. Just 1 part of water vapour in 10^6 parts of hydrogen is required to oxidize silicon. To oxidize manganese, chromium and carbon, 10, 250 and 10000 parts of water vapour to 10^6 parts of hydrogen are needed. This may mean that in very dry hydrogen atmospheres (e.g. $<$ 10 ppm H_2O) these three elements will not take part in the reaction responsible for the formation

TABLE

Sample no.	Composition (wt %)		
	C	Si	Mn
1	0.003	< 0.01	0.66
2	0.007	0.01	0.64
3	0.019	0.05	0.54
4	0.005	0.06	0.50
5	0.002	0.10	0.48

H_2/H_2O	Element
$10^{13}/1$	Ca
$10^{12}/1$	Mg
$10^{10}/1$	Al
$10^{6}/1$	Si
$10^{5}/1$	Mn
$4 \times 10^{2}/1$	Cr
$10^{2}/1$	C
$1/1$	Fe

of the minor-phases. Furthermore, in the more normal dry hydrogen atmospheres used in large scale production processes (e.g. 10 to 100 ppm H_2O), manganese will take part in the reaction but chromium will not. There is some experimental evidence that this theoretical hypothesis may be valid; chromium has been found to be associated with the minor-phase following annealing in wet hydrogen (Fig. 11) but has not been found following annealing in nominally dry hydrogen. Thus, as the water content of the hydrogen atmosphere increases, more and more impurity elements become able to react with it, whereas for very dry hydrogen atmospheres, only those elements which form the most refractory oxides (e.g. Si, Al, Mg) can do so and, therefore, the quantity of minor-phase is restricted.

The situation is further complicated by the tendency of carbon to react with hydrogen to form methane. For steels annealed in dry hydrogen atmospheres no decarburization occurs below 700° C. At higher temperatures, if water vapour is present in the hydrogen, some of it will dissociate to give hydrogen and oxygen and the reaction

$$(C) + O \rightleftharpoons CO$$

will cause decarburization. However, even in quite dry hydrogen atmospheres carbon in steels will react with the hydrogen (above 700° C) to form methane.

$$(C) + 2H_2 \rightleftharpoons CH_4$$

This might indicate that if any gas is involved in the present phenomenon then it is more likely to be methane than CO or CO_2, as suggested by Richards.

Finally, although supposedly clean recrystallized alumina furnace tubes were used in all the laboratory experiments reported herein, the possibility of some contribution to the present phenomenon from the furnace walls etc. should not be discounted entirely, particularly where silicon compounds [9] are concerned.

5. Conclusions

As far as electroplating annealed nickel-iron substrates for electrical contact applications is concerned, the implications of this work are clear. For the very best results the substrate material should be as pure as possible and a dry (as dry as is economically practicable) hydrogen annealing atmosphere should be used.

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