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Examination of the high-temperature (850° C) oxidation of an Ni–Si–B powder

STEVEN A. BRADLEY, TERY L. BARR, KARL J. YOUTSEY
UOP Inc. Des Plaines, Illinois 60016, USA

An air-fired (850° C) alloy powder of Ni–Si–B has been prepared to test its suitability in silk screen conductor applications. The silicon and boron were included because, when alloyed with nickel, they greatly impede the oxidation of the latter, removing the necessity for inert gas firing. The physical aspects of this novel material have been examined by SEM, while its chemical nature was studied by ESCA. It was found that during airfiring the alloy powder forms a glass around the conductive metal particles impeding the oxidation of nickel. Preferential migration of boron and silicon to the surface of the powder is indicated. Speculations are presented for the conductive pathway for this material.

1. Introduction

The conducting metal pigments utilized in silk screen conductor applications, such as thick film hybrid circuits, are either noble metals or non-noble metals that are fired in an inert atmosphere. Nickel or copper powders oxidize too rapidly during the air-firing operation to be suitable as a conductive ink. One solution to this rapid oxidation problem is to add a reducing agent to the ink mixture, but this can produce spotty conduction zones. Another solution is to alloy the non-noble powder to reduce the oxidation rate.

The preferential oxidation of one component of an alloy to form a protective, external scale is an important technique in providing corrosion and oxidation protection to the base metal. Various studies have been conducted on the influence of alloying elements on the oxidation behaviour of nickel ([1] pp. 243–8, [2]). Alloys that develop Cr_2O_3, Al_2O_3 or SiO_2 scales can increase oxidation resistance [3–5] even at temperatures up to 1200° C. It is the purpose of this communication to demonstrate that the principles employed to develop high-temperature, oxidation-resistant alloys are also applicable to the development of a non-noble metal alloy substitute that will have suitable electrical conductivity after a 700 to 900° C ambient air firing. In the present case, an alloy powder was air-fired to 850° C with subsequent examination of the physical (SEM) and chemical (electron spectroscopy for chemical analysis – ESCA) aspects of the surface of the material. In addition, a combination of sputter etching and ESCA permitted an investigation of the subsurface of the material.

2. Experimental procedure

A conductive ink was made by mixing 85 to 99% metal powder with 1 to 15% vitreous frit (LP 90-4261 from Plessey Incorporated) and pine oil solvent. Frit composition was reported to be 35.5% SiO_2, 2.52% Al_2O_3, 55.25% PbO and 6.89% B_2O_3, with the resin being ethyl cellulose. The ink was silk screened onto a cleaned α-alumina chip. The firing schedule was as follows: heat to temperature at a rate of about $40\,^\circ\mathrm{C\,min^{-1}}$, hold at temperature for 10 min, and cool at a rate of about $50^\circ\,\mathrm{C\,min^{-1}}$ with forced air. In all instances firing was performed in an air atmosphere. All powders used were commercially obtained. Resistance was measured by a two-point probe technique utilizing a General Radio Bridge Type 1650A. Probes were 0.427 cm apart and the dimensions of the screened element were 3.175 cm × 0.635 cm.

The scanning electron microscopy was performed on a Cambridge Mark IIA instrument. All specimens were carbon evaporation coated prior to examination in the SEM.

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ESCA measurements were made using a Hewlett-Packard (H.P.) 5950A ESCA Spectrometer. It was necessary to use double stick adhesive tape to mount the conductive material in the spectrometer. The insulator qualities of the tape caused the ink to respond like a surface insulator to the photoelectron emission, necessitating the use of the H.P. 18623 A Electron Flood Gun to remove the resulting charge shift. Sputter etching was accomplished with a Physical Electronics Sputter Gun. Sputter etching materials in the physical form of these inks can be a haphazard operation; however, with care, qualitative and even semi-quantitative results may be realized. In the present case the sputtering was continued until a quasi-equilibrium seemed to occur. In view of this, the etching depths quoted in the text should be considered very rough estimates.

3. Results of the elevated temperature firing

Possible alloying candidates that might form protective coatings included Cr, Al, B and Si. Since the scale formed during firing must be adherent, relatively thin, and compatible with most vitreous frits, a non-noble metal alloy powder having the composition of nickel + 3.5% silicon and 1.5% boron was selected. Both Si and B will form glasses when oxidized at elevated temperatures.

When compacted, the alloy powder was not very conductive; but after oxidation at 840° C, the powder fused or sintered and became uniformly conductive. Since a conductive ink contains a vitreous frit to bind it to the ceramic substrate, the first mixture fired contained 15% of the glass frit. As this, the glass content was reduced, the resistivity declined as noted in Table I for nickel pastes heated in air at 840° C for 10 min. The resistivity was reduced by a factor of two when the glass content was decreased from 5% to 1%. There appeared to be no change in adhesion with variation in glass content, as the low-frit ink could not be easily removed from the substrate. Smaller particle size also decreased the resistivity. An alloy powder that passed through a 400 mesh screen had the lowest resistivity of 2.34×10^{-3} Ω cm. A silver paste fired under similar conditions had a resistivity that was less but within an order of magnitude of the non-noble metal alloy paste. Little difference in resistivity was observed for samples oxidized between 760 and 890° C (Table II). Higher temperatures seemed to form a thicker glass. Refiring the thick film increased the resistivity by a factor of one and a half. In contrast, a pure nickel paste after a single air firing under the same conditions as described in Section 2, had essentially infinite resistance. Thus, it was demonstrated that an Ni–Si–B alloy powder can be oxidized in an air atmosphere at 840° C and still have electrical conductivity comparable to that of a noble metal ink.

TABLE II Comparison of resistivity for Ni + 3.5% Si and 1.5 B alloy having 15% glass content fired for 10 min at various temperatures

Firing temperature (° C)	Resistivity (10^{-3} Ω cm)	Thickness (cm)
760	11.1	0.0102
790	11.1	0.0097
840	10.2	0.0086
890	12.8	0.0089

4. Analysis of the oxidized alloy powder

Microscopic analyses were conducted in order to obtain greater insight into the reason why this nickel alloy has such high conductivity. Metallographic examination showed the as-received powder to have a two-phase dendritic structure (Fig. 1a). Heating the alloy powder to 840° C for 2 h results in the formation of a single phase near

TABLE I Comparison of resistivity for various glass contents and materials fired at 840° C for 10 min

Material	Amount of Glass	Resistivity (Ω cm)	Thickness (cm)
Ni + 3.5% Si and 1.5% B	15%	10.2×10^{-3}	0.0086
Ni + 3.5% Si and 1.5% B	10%	10.7×10^{-3}	0.0099
Ni + 3.5% Si and 1.5% B	5%	8.98×10^{-3}	0.0097
Ni + 3.5% Si and 1.5% B	1%	4.25×10^{-3}	0.0102
Ni + 3.5% Si and 1.5% B (400 mesh powder)	15%	2.34×10^{-3}	0.0043
Ag	15%	0.437×10^{-3}	0.0046
Ni	15%	∞	0.0102
Ni + 30% Cu + 4% Si	15%	∞	0.0097

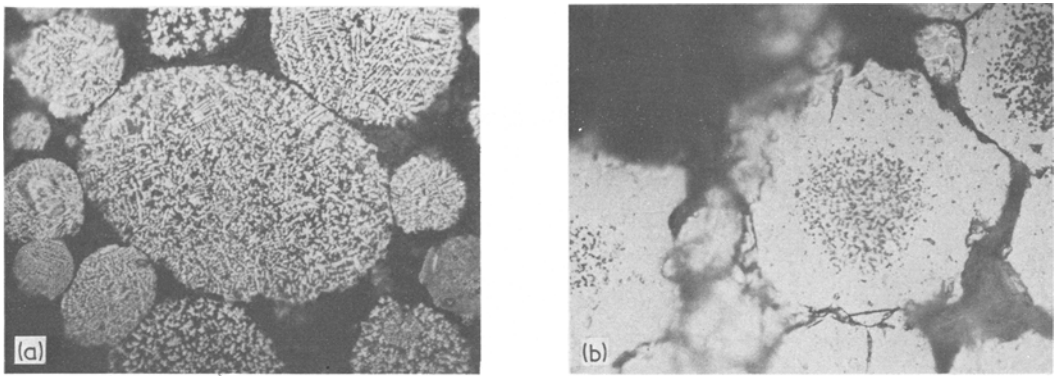


Figure 1 (a) As-received Ni + 3.5% Si and 1.5% B powder, × 600. Etchant–nitric and acetic acid 1:1. (b) Ni + 3.5% Si and 1.5% B powder fired at 840° C for 2 h, × 600. Etchant–nitric and acetic acid 1:1.

the surface; and a very thin coating surrounding the particles. These particles appear to be joined together by the fused glass produced during oxidation of the powder (Fig. 1b). The addition of the vitreous frit and binder to the alloy powder to form a paste, did not alter the macroscopic structure. The scanning electron micrograph of a thick film having 15% glass and fired at 840° C for 10 min (Fig. 2) shows how the glass covers the particles. Numerous short stringers extend from the glass. Similar photographs were taken of powders that had no vitreous frit.

An edge view of the fired ink demonstrates the excellent adhesion of the film to the alumina substrate (Fig. 3). The glass tends to wet and bind the powder to the surface although some porous areas are present. The glass fusion did not appear to be the only mechanism of particle–particle attachment. Some sintering has occurred as evidenced by the fracture appearing ductile in nature as depicted in Fig. 4 and this probably is the conduction path.

The conditions employed to oxidize the materials (840° C in air) should have proved sufficient to create a *thick* oxide layer of all constituents. In order to examine this point and also the chemistry of the constituents, ESCA spectra were generated of the outer surface of the oxidized material after cooling to room temperature. In addition, ESCA spectra were obtained from subsurface layers resulting after sputter etching to remove more than 50 Å of the material.

A general (0 to 1000 eV) scan of the outer, oxidized surface revealed a number of significant peaks including those for the three principal components (Ni, B and Si) and also O and C. Carbon proved to be the only significant impurity

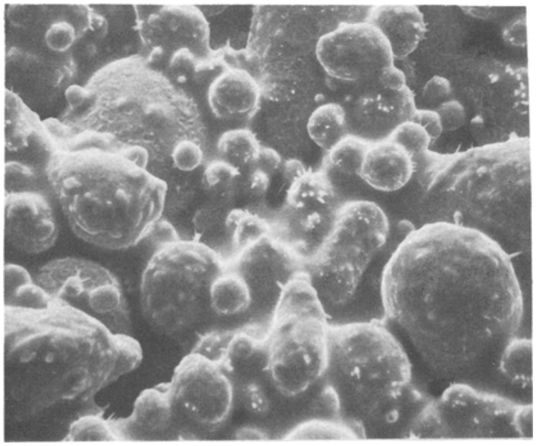


Figure 2 Ni + 3.5% Si and 1.5% B powder having 15% glass fired at 840° C for 10 min, × 450.

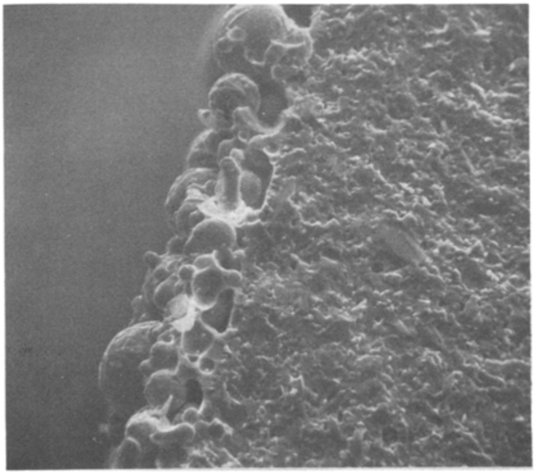


Figure 3 Edge view of Ni + 3.5% Si and 1.5% B having glass fired at 840° C for 10 min conductive coating on an alumina substrate, × 200.

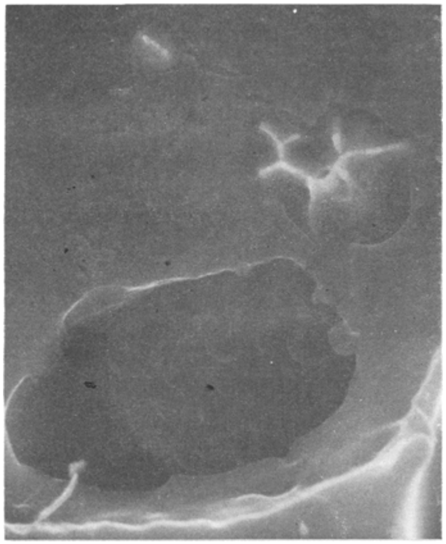


Figure 4 Fracture surface of Ni + 3.5% Si and 1.5% B having 15% glass fired at 840° C for 10 min, × 5000.

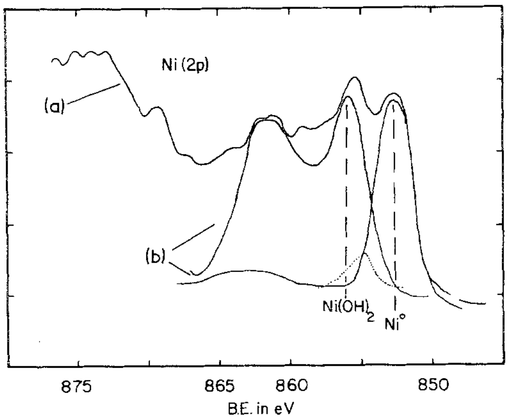
discovered by ESCA, and the amount indicated was not atypical for an ESCA analysis of this type of system. In any case, the effects to be discussed can be ascribed with reasonable certainty mainly to the presence and interaction of the Ni, B, Si and O.

A narrow scan of the Ni(2*p*) photoelectron peaks for the outer surface is displayed in Fig. 5a. This spectrum was obtained by computer enhancement of the original, and the poor resolution that remains after smoothing is not atypical for an Ni-containing system impregnated with large quantities of other species. The amount of Ni detected by the ESCA, however, is far less than expected for the Ni-rich system being examined. To improve the analysis the spectrum in Fig. 5a was deconvoluted (Fig. 5b). The deconvolution was accomplished by "force fitting" known spectra for Ni systems, e.g. $Ni(II)(OH)_2$ which from experience were expected to contribute to the system on hand [6–9]. As noted from the dotted lines, the most common nickel oxide, Ni(II)O, appears to make only a miniscule contribution to the manifold of Ni containing species in this thick film. This is not surprising, since the outer surface of the thick film has been exposed to air for some time, and it has been shown that upon exposure to air, all metals and their common oxides terminate their passivation in the highest possible oxidation state, and also become covered with significant layers of hydroxides (or aquo complexes) [10, 11]. In the case of Ni, this means that the principal oxidation products observed on the outer surface should be $Ni(III)_2O_3$ [7] and $Ni(OH)_2$ [6–9, 11]. (Note that the assignment of $Ni(III)_2O_3$ is uncertain.) Both of the latter species are known to have $Ni(2p_{3/2})$ binding energies near 855.5 eV with shakeup satellites at 861.0 eV [6–9], and within a few tenths of an eV, that is what is observed on the outer surface of the thick film.

The relatively large amount of Ni^0 detected in Fig. 5a is a significant and unusual result. It is quite common to find mixed Ni^0, Ni(II) and Ni(III) species in the preparation of thin oxidized films. As an example, consider Fig. 5c which is the result of the room-temperature passivation of an elemental nickel metal foil. In this case, the relatively low temperature produces a thin (~ 20 Å) film of oxidized metal [6–9, 11]. (Comparisons with individual spectra indicate that the oxidized species produced at the terminus are largely $Ni(III)_2O_3$ and $Ni(OH)_2$ as expected [11].) However, angular resolution studies reveals that most, if not all, of the Ni^0 detected in Fig. 5c is actually subsurface; i.e. elemental metal "seen" by the ESCA through an outer mantel composed almost entirely of the oxidized nickel [9]. Oxidation of nickel powder at 850° C, on the other hand, should produce a thick oxide film; Also, previous studies of the oxidation rate of impure nickel systems have found that they generally oxidize more rapidly than pure nickel ([1] pp. 90–2, [12]). Thus, the presence of significant amounts of surface Ni^0 is apparently an unusual feature, seemingly resulting from the presence of the Si and B. Ignoring the small binding energy shifts and obvious differences is spectral resolution, Fig. 5a and c are amazingly similar; except that the low-temperature oxidized thin film (Fig. 5c) has less Ni^0 than the high-temperature oxidized species (Fig. 5a). The small binding-energy shifts experienced by the components of the thick film may be a result of a matrix effect which should occur in alloy systems [13, 14].

TABLE III Relative quantitative analysis of Ni, B and Si based upon Ni(3*p*), B(1*s*) and Si(2*p*) peak heights – Normalized to outer surface Ni

	Before sputter	After ~ 50 Å sputter
Ni	1.0	1.7
Si	1.6	1.9
B	3.0	1.6



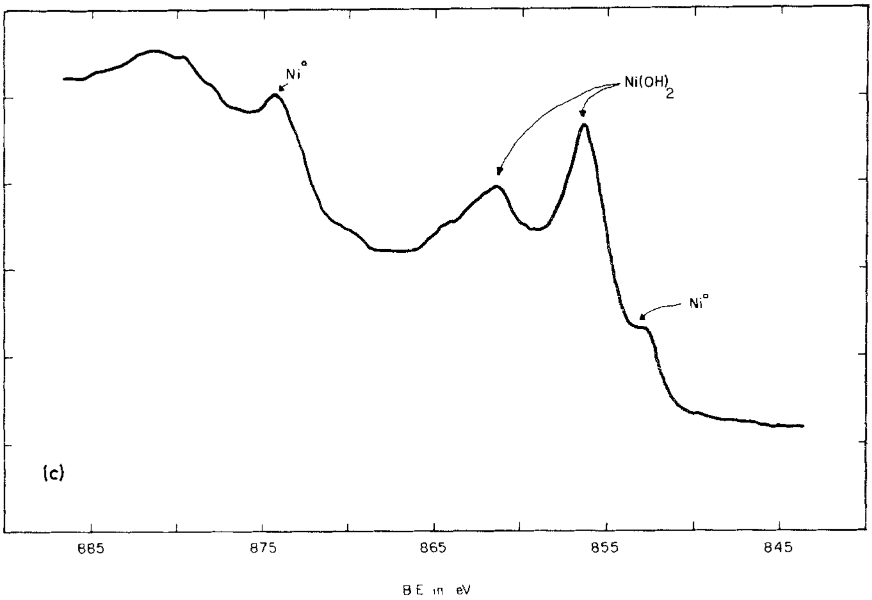


Figure 5 (a) Ni(2*p*) spectrum for outer surface of Ni–Si–B powder. (b) Deconvolution of Ni(2*p*) spectrum in (a). Major contributors appear to be $Ni(OH)_2$ and Ni°. Note that Ni(II)O produces small perhaps negligible contribution. (c) Ni(2*p*) spectrum for oxidized (passivated) surface of Ni foil.

Comparison of the O(1*s*) spectra for the thick (850° C air-fired Ni, B and Si) and thin (passivated Ni foil) systems (Fig. 6a and b) reveals some differences not apparent in the Ni(2*p*) spectra. The principal peak for both systems occurs at ~ 532 eV and is that due to the oxygen in OH^- and chemisorbed, dissociated O_2 [11, 15]. A peak at ~530 eV found only for the oxidized foil (thin film) (Fig. 6b), is a result of the bulk metal oxide formation, e.g. Ni(II)O [15, 16]. Apparently, the ESCA can detect Ni(II)O near the outer surface of the passivated foil, but not near the outer surface of the Si and B-doped thick film. Once again, the small binding-energy shift is probably a matrix effect [13, 14].

The ESCA spectra recorded for both the B and Si detected on the outer surface were unexpectedly well resolved, indicating substantial amounts of the two elements. The binding energies were typical of the "surface" oxides, SiO_2 and B_2O_3. Both of these species are also probably experiencing extensive hydration.

Sputter-etching the thick film powder to the approximate depth indicated above produced some interesting changes. First, a composite of the surface results for the three components, B, Si and Ni, indicates that the outer surface may in a relative sense be deficient in the latter species. Therefore, spectra were generated and their intensities compared both before and after sputtering to try to determine the relative extent of the "mixing" of the three constituents. Table III summarizes

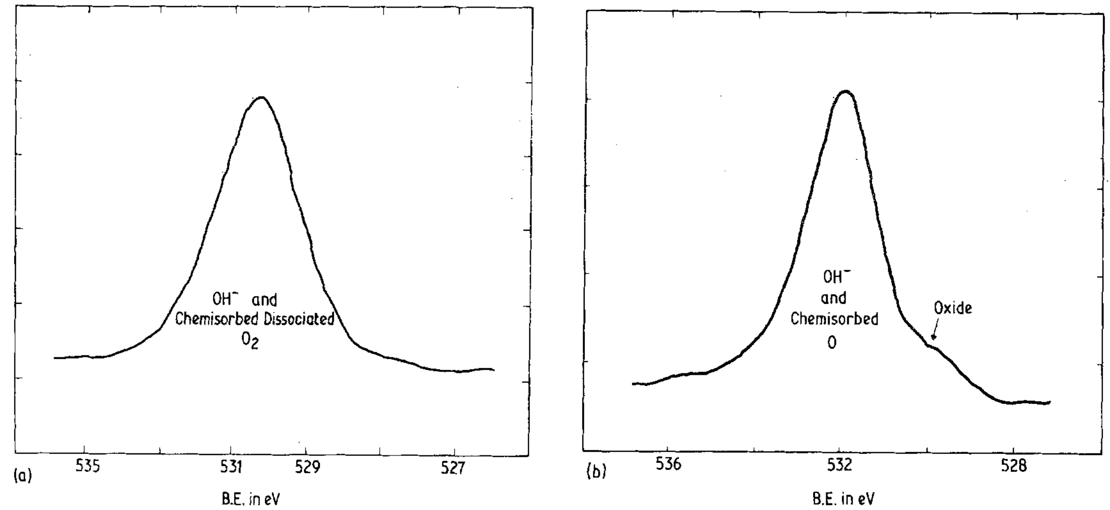


Figure 6 (a) O (1*s*) spectrum for Ni–Si–B powder before sputter etching. (b) O (1*s*) spectrum for passivated surface of Ni foil.

the most pertinent results of that determination. The individual values reported should not be employed out of context, since the data were determined from normalized peak heights rather than concentrations, and the ESCA peak selected for Ni was the relatively weak Ni (3*p*). However, the relative trend of these data do indicate the preferential migration of B and possibly Si to the outer surface of the thick film powder. Of particular significance are the post-sputtered results. The relative increase in amount of Si is not atypical for this type of physical process (sputtering), in which a material, among other things, is being cleaned of adsorbed species, such as CO_2. The significant increase in Ni and decrease in B, however, indicate that the former is primarily a "bulk" species, while the latter has been segregated to the outer surface.

Individual ESCA spectra indicate that after sputtering, the chemical forms of Si and B are still primarily their common oxides. The Ni spectrum (Fig. 7), on the other hand, demonstrates a nearly complete reduction of Ni to Ni^0. Some of this may result from the sputter reduction of nickel oxides to elemental nickel [17]; i.e. preferential sputtering of oxygen. Previous studies have shown that extended exposure of a single crystal of NiO to an intensive sputtering beam (~3 keV) will create a situation where only Ni^0 can be detected by ESCA [18]. However, the conditions used in this study are not considered severe enough to be

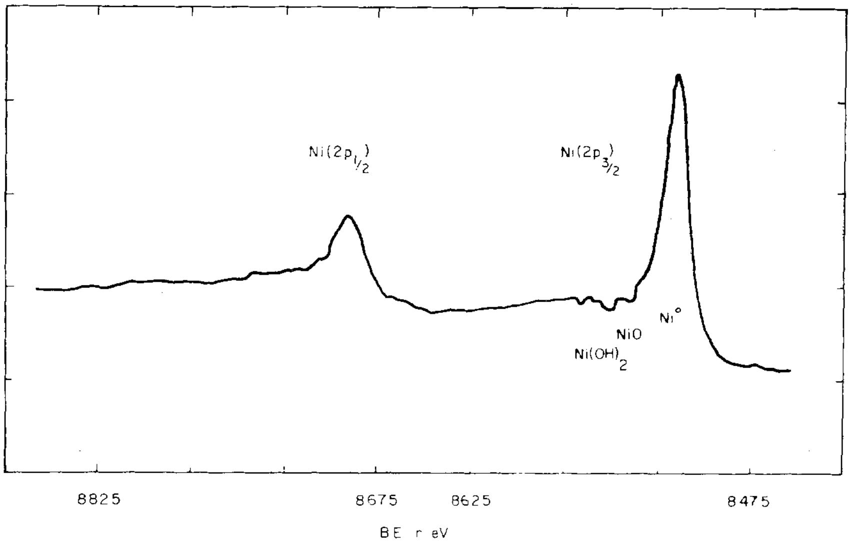


Figure 7 Ni (2*p*) spectrum for Ni–Si–B powder after ~ 50 Å sputter etch.

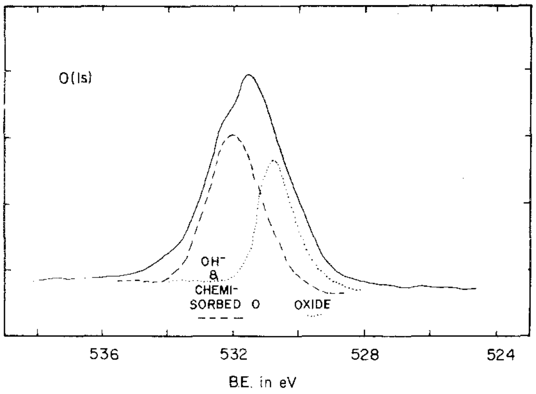


Figure 8 O(1*s*) spectrum for Ni–Si–B powder after ~ 50 Å sputter etch.

the exclusive cause of this result. A substantial amount of the Ni^0 revealed in Fig. 7, therefore, is thought to result from exposing the layer rather than creating it. The O(1s) spectrum following sputtering (Fig. 8) reveals an increased presence of matallic oxides (binding energy ~530.0 eV), relative to other oxygen-containing species. This is probably because of the conversion of hydroxides to oxides; e.g. $B(OH)_3 \rightarrow B_2O_3$.

From these analyses, the outer surface of the conductive ink appears to be primarily composed of $B(OH)_3$ and/or B_2O_3 with less $Si(OH)_4$ and/or SiO_2 and a relatively small amount of $Ni(OH)_2$ and/or $Ni(III)_2O_3$, as illustrated in Fig. 9. The inner surface tends to have as its main constituent SiO_2 with some Ni(II)O and Ni^0 and a marked reduction in B_2O_3. Further sputtering into the bulk reveals almost exclusively Ni^0. Thus, as a result of their greater affinity for oxygen, the B and Si seem to be preferentially oxidized during the firing operation. It would appear that the Si and B diffuse rapidly through the crystal lattice to the surface, where they are oxidized. The Ni just below the surface is largely not oxidized and provides the electrical conduction path in this Si- and B-depleted region. Conduction between particles may be through the partially sintered regions. The oxidized Si and B form a glass that slows around the particles assisting in fusing them together and also fusing the thick film to the substrate. The glass may further act as a barrier to reduce the diffusion of oxygen into the non-noble metal. The rapid preferential oxidation of Si and B with the resultant glass formation may be one reason that Inconel or stainless steel type 316 powders proved unsatisfactory as they had infinite resistance when heated to 780° C for 10 min.

5. Conclusions

(1) Based on the concept of preferential oxidation, a non-noble metal alloy, when fired in an oxidizing elevated temperature, has electrical conductivity similar to that for thick film noble metal conductive inks.

(2) The alloy powder forms its own glass upon heating that flows around the particles and fuses them together and to the substrate. The electrical conductivity might be further increased by adjusting the B and Si alloy content.

(3) ESCA can be utilized to study the preferential oxidation of complex systems and gain a greater understanding of the oxidation mechanisms. In this particular case, preferential migration to the surface (and subsequent oxidation) is indicated for B and Si. Surprisingly, the Ni in this system seems to largely avoid the thick oxide film, remaining in the bulk largely as Ni(O).

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B_2O_3 (main); SiO_2; Ni $(OH)_2$, Ni_2O_3 (?), Ni^0 (small); NiO (very small)			outer surface
B_2O_3; (less)	SiO_2; (main)	Ni + NiO (increasing)	inner surface
Ni			bulk

Figure 9 Model of distribution of oxides in surface of oxidized Ni + 3.5% Si and 1.5% B alloy powder.

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