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Wettability of transition metal boride eutectic alloys to graphite

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The wetting of nickel, platinum and palladium boride eutectics ($Ni_{55}B_{45}$, $Ni_{62}B_{38}$, $Pd_{72}B_{28}$, and $Pt_{72}B_{28}$) to polycrystalline graphite has been studied by sessile drop and surface analytical techniques. The wettability is critically influenced by surface segregation of low-level bulk impurities in the alloys. At the melting temperature, the impurities segregate to the surface of the liquid alloy and inhibit wetting. A poorly-wetted droplet with a large contact angle results. Good wetting results by introducing materials into the contact system which possess high chemical reactivity to the major segregant species, either as a surface coating or by incorporation into the alloy during manufacture. The materials act to suppress segregation by tying up the alloy impurities through compound formation. The results indicate that the use of surface-sensitive techniques in the study of wetting is essential.

1. Introduction

The wetting of solid surfaces by liquid metals occurs in many technological processes and constitutes an integral part of the structure of materials. Processes of liquid-phase sintering, impregnation of porous materials by liquid binders, detergency, adhesion, wear, catalysis, and crystalline growth from the melt are determined largely by the ability of a liquid to spread evenly over a solid. Elucidation of the interaction mechanisms at the interfacial boundary between solid and liquid is therefore of great importance.

A currently emerging technology whose properties and operational parameters depend crucially on the characteristics of the liquid–solid interface is the production of high brightness, focused ion beams [1–4]. Liquid metal ion sources (LMIS) are based upon a low volatility metal film which flows to the apex of a solid needle support structure (Fig. 1). Application of a sufficient electric field deforms the liquid film into a conical protrusion and results in ion emission by field evaporation [5–8]. Interest in LMIS has been rapidly increasing due to their potential application in microcircuit fabrication, analytical microprobe instruments, maskless ion implantation, ion milling, semiconductor mask repair, and reactive ion etching [9–11].

A variety of technologically important ions may be generated by the use of eutectic alloy films containing the appropriate element. Metallic alloys are necessary to lower the vapour pressure and/or the melting point of the source material. For maskless implantation of semiconductor material, for example, sources which generate ions of boron, arsenic and phosphorus are required. Until recently, it has proven difficult to produce LMIS based upon these species because boron possesses a high melting point and strongly attacks most refractory metal supports, while arsenic and phosphorus have high vapour pressures. Further, little is known about the critical properties of the liquid metal and substrate which are required for successful source operation.

In the present work, we report experiments which concern the wetting of graphite by eutectic alloys of the platinum–boron, nickel–boron and palladium–boron systems. The results indicate that a crucial role is played by surface segregation in the wetting process, and that use of surface analytical techniques is necessary to fully understand the nature of wetting and interfacial phenomena. There presently exist only a handful of published reports on the application of surface analytical techniques to the liquid–gas interface; this is especially true for Auger electron spectroscopy (AES). Hardy and Fine [12], for example, in a 1982 paper remark that they were aware of only two previous applications of AES to the study of liquid surfaces [13, 14]. In the light of the limited studies of the liquid–gas interface, this report presents some of the first conclusions from studies of surface behaviour in liquid metal contact systems.

2. Materials and experimental technique

Wetting studies were carried out in an Ultek TNB-X 250 l/s ultra-high vacuum chamber containing a Physical Electronics CMA Model 10-155 fixed-beam Auger electron spectrometer (Fig. 2). This system has a base pressure of 1×10^{-10} torr, which was maintained throughout a series of preliminary studies of the alloy surfaces. Later work showed higher system pressures to have little effect on the contact properties,

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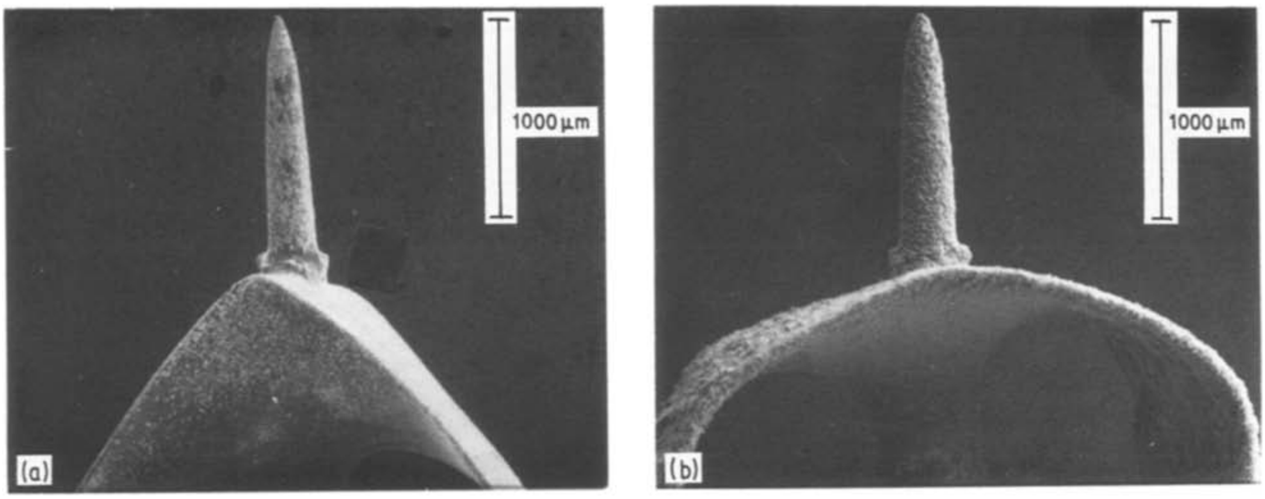


Figure 1 A typical liquid metal ion source. (a) Source structure with loaded alloy. (b) Source structure after alloy exhaustion.

and this requirement was relaxed. Nevertheless, no experiment was performed at pressures greater than 1×10^{-7} torr background. The experimental system was also equipped with a quadrupole mass spectrometer in order to measure alloy volatility and a field emission retarding potential (FERP) gun [15] to permit work function studies of the alloys.

In a typical wetting experiment, the substrate and support mechanism were mounted in a vertical orientation within the vacuum chamber, and a small fragment of solid alloy was placed in contact with the top surface of the substrate. Contact was maintained by gravity and no adhesive was used. The system was subsequently evacuated to below 1×10^{-7} torr. Wetting was initiated by resistively heating the substrate with a d.c. power supply until the alloy melted and wetting was observed. If wetting occurred with a large contact angle, Auger analysis of the liquid alloy surface was immediately possible. If wetting occurred with a small contact angle, it was necessary to vent the chamber and remount the wetted sample to access the Auger beam.

Alloy temperatures were measured by means of a single-wavelength optical pyrometer by comparison with the substrate brightness, whose emissivity characteristics were well known [16]. Eutectic melting temperatures were determined by direct observation during heating. An overall morphological change in the solid alloy fragment, accompanied by a sudden change in reflectivity of the alloy surface, could be easily detected in both optical and scanning electron microscopes. The melting temperature of off-eutectic compositions was more difficult to determine, as the sequence of melting events prohibited a sharp contrast from solid to liquid. Small amounts of low-level impurities in the alloys appeared to have little effect on the measured melting points, and we estimate our temperatures to be accurate to $\pm 20°$. The alloy surfaces were effectively cleaned of adsorbed gases by annealing and no sputtering was necessary. The Auger surface compositions reported are calculated on the basis of sensitivity factors given by Palmberg *et al.* [17].

The alloys studied were eutectic or near-eutectic compositions of Ni–B, Pd–B and Pt–B ($Ni_{55}B_{45}$, $Ni_{62}B_{38}$, $Pd_{72}B_{28}$ and $Pt_{72}B_{28}$) manufactured by the arc-melting technique. The phase diagrams of these systems are provided in Fig. 3. It is observed that each of these systems have broad, low-melting stoichiometries over which the alloy remains liquid. Details of

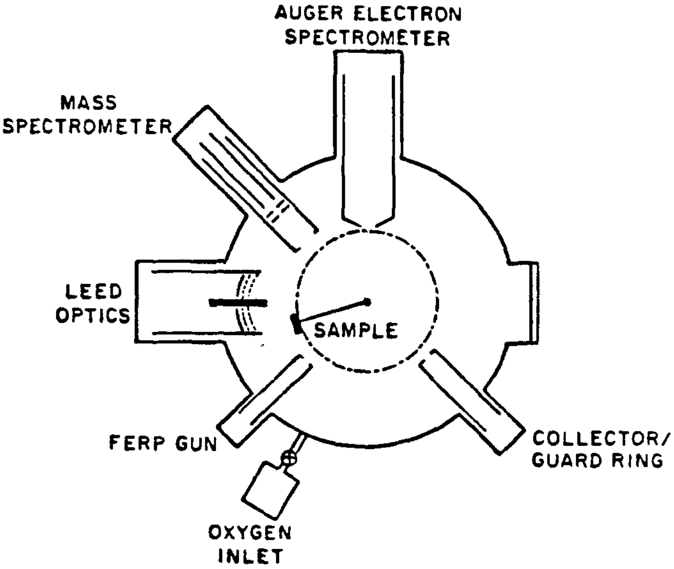


Figure 2 Schematic diagram of the ultra-high vacuum surface analysis system used in wetting studies of the liquid metal alloys.

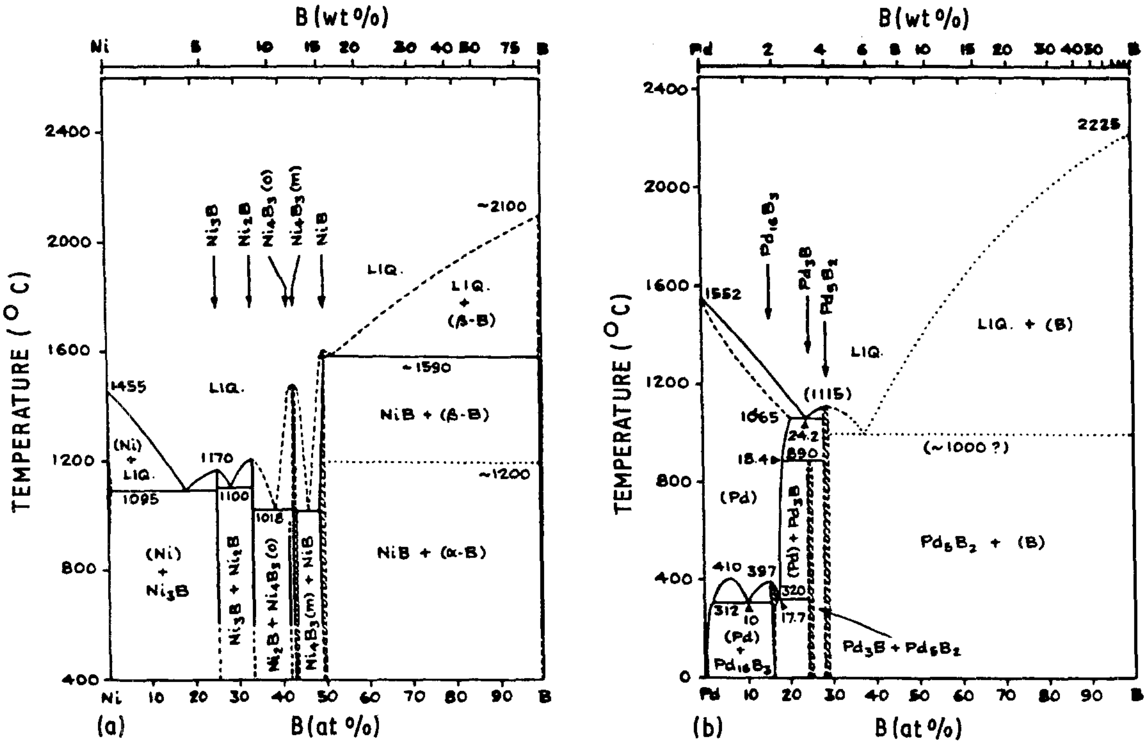
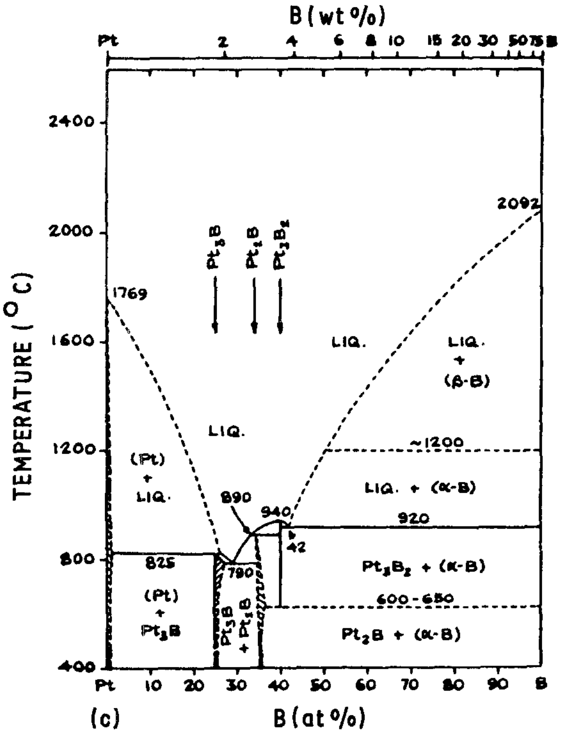


Figure 3 Binary phase diagrams of (a) Ni–B, (b) Pd–B and (c) Pt–B systems. (Data from Moffatt [18], used by permission.)



the arc-melting synthesis follow. Stoichiometric amounts of boron powder and Pt/Ni/Pd metal were weighed and mixed mechanically. The mixture was placed in a graphite crucible with a molybdenum lid and enclosed in a second graphite crucible. The entire unit was then placed in a sintering furnace that was backfilled with 635 torr of He and the alloy was sintered for 1.0 h at a temperature of 1000° C. The furnace heating elements were also graphite and a quartz evaporation shield to detect evaporation losses during sintering was added to the furnace. No losses were observed. The sintered specimen was next introduced into the arc melter which was previously purged with pure argon gas, a 1 : 1 Ar–He mixture, and pure helium. The arc melter was then backfilled with a 1 : 1 mixture of Ar–He to a pressure of 508 torr, and the tungsten stinger was applied to the sintered mixture and worked through the alloy for complete mixing. Table I summarizes the emission spectroscopic characterization of a typical Ni–B alloy. The major impurities were carbon, nitrogen and oxygen with traces of other contaminants commonly observed in previous uses of the arc-melting apparatus. The emission spectra of the Pt–B and Pd–B binaries were not measured, but the alloys were fabricated in a similar fashion and presumably contain the same relative impurity levels.

The wetting substrate was polycrystalline graphite sheet available commercially from Union 76 Corporation (Decatur, Texas, USA) and sold under the name Poco (DFP-3) graphite [19]. Graphite was selected as an appropriate wetting substrate for liquid metals of boron due to its favourable free energy of reaction with boron and ease of fabrication into sharp emitters which are necessary for use as liquid metal ion sources.

TABLE I Emission spectroscopic analysis of the $Ni_{55}B_{45}$ alloy

Element	Relative abundance (wt %)*
Ni	90.5
B	> 10.0
C	0.019
N	0.003
O	0.0011
W	0.1 to 1.0
Mo	0.01 to 0.1
Fe	0.01 to 0.1
Ti	0.01 to 0.1
Cu	0.001 to 0.01
Mg	0.001 to 0.01
Al	0.001 to 0.01
Si	0.001 to 0.01

*Analysis provided by Oregon Titanium, Albany, Oregon 97321.

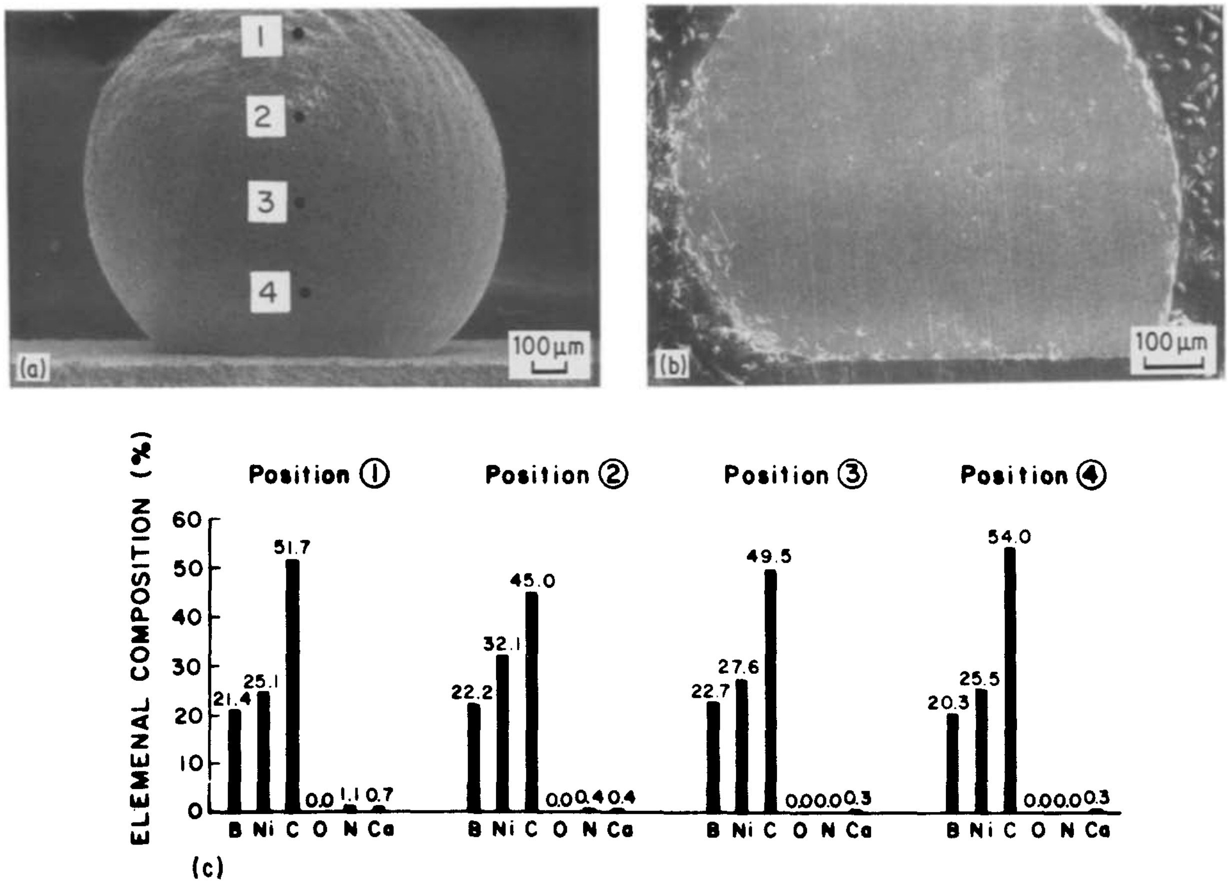


Figure 4 Wetting of $Ni_{55}B_{45}$ on graphite. (a) View of the contact angle after quenching from the molten state. (b) A cross-sectional slice through the droplet. (c) Auger surface elemental compositions of four positions on the molten droplet at 1350 K (m.p. = 1490 K). High surface concentrations of carbon are observed.

The sheet was supplied with a thickness of 100 μm, and subsequently cut into small ribbons which were easily mountable in the vacuum chamber. Surface studies of the graphite surface showed it to be extremely inert. Only carbon was detectable in the Auger spectra of the graphite after introduction into the vacuum chamber, and it was possible to clean the surface by mere pumping in ultra-high vacuum at room temperature. No sputtering or thermal annealing of the substrate was necessary.

The degree of wettability was measured by direct observation of the contact angle formed between the melt and the solid substrate. After detailed Auger analysis of the molten surface, the alloy was rapidly quenched and examined edge-on by a scanning electron microscope. In several cases, the solidified alloys were sectioned and reaction products were examined by high resolution scanning Auger spectroscopy.

3. Results

3.1. Wetting of transition metal borides to graphite

Transition metal borides of platinum, palladium and nickel are excellent candidates for use as liquid metal ion sources of boron. They have relatively low melting points (~ 1000° C) over a fairly wide range of stoichiometries near 50 at % B and are expected to wet graphite. For the case of Ni–B, this expectation is based upon reported evidence [20] that elemental nickel wets graphite with a contact angle of 45° and that boron is often used as an additive to promote wetting on graphite. Pure copper, for example, has been reported to exhibit a contact angle of 140° on graphite, but (Cu + 5% B) has a contact angle of 36° [21]. There is precedence then, to expect that eutectic borides of nickel, platinum and palladium will wet graphite. That experimental observations of wetting behaviour prove otherwise will be explained below.

We focus on the wetting behaviour of the Ni–B system since the Pt–B and Pd–B systems displayed similar wettability on graphite. A sample of nickel boride was applied to a flat ribbon of graphite and heated to melting. Wetting proved to be unsuccessful. The melted alloy formed a poorly-wetted droplet with a contact angle greater than 90°. Auger analysis of the molten droplet surface at temperatures near the measured alloy melting point (1290 K) revealed substantial concentrations of carbon (and often nitrogen). A representative case is shown in Fig. 4. It was frequently possible to elicit wetting by fracture of the alloy droplet by sudden increases in temperature. Fracture of the droplet surface resulted in ejection of alloy material from the droplet interior which moved out over the graphite surface with a contact angle of near-zero (Fig. 5). Auger analysis showed that the molten wetting front consisted solely of alloy components with no trace of carbon (or nitrogen), while the residual droplet shell continued to exhibit large concentrations of carbon and nitrogen. Eutectics of Pt–B and Pd–B behaved similarly during wetting to graphite. In the case of $Pt_{72}B_{28}$, the wetting was usually so poor that the molten droplet rolled off the

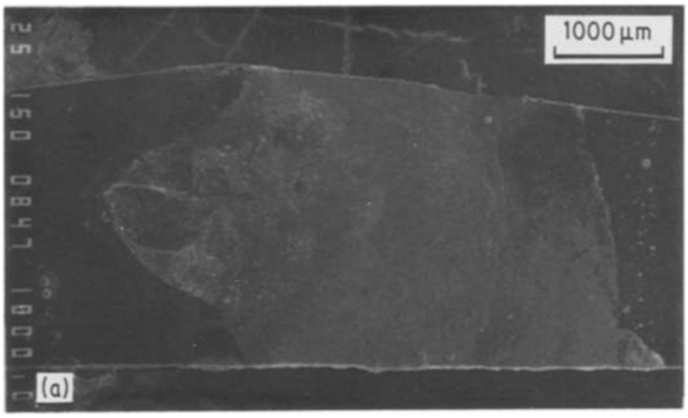
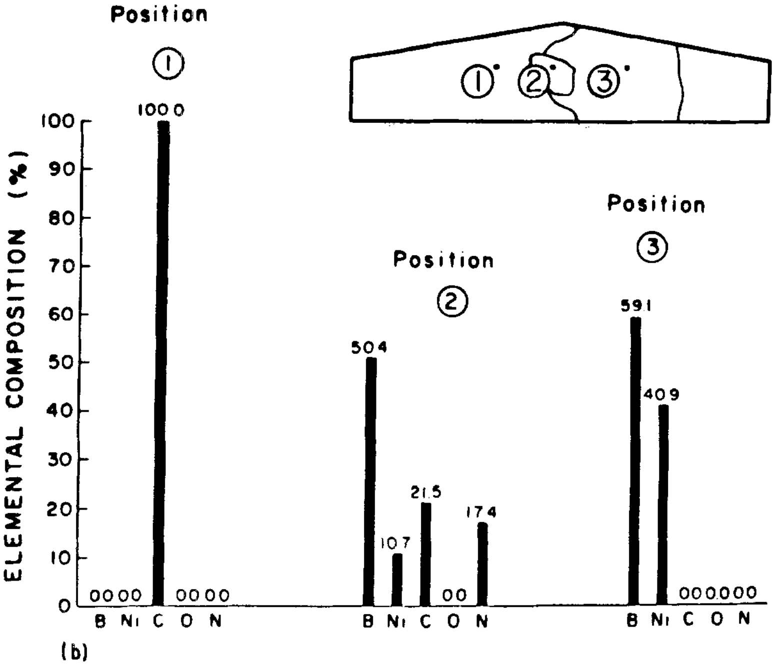


Figure 5 The wetting behaviour of $Ni_{55}B_{45}$ after fracture of the surface shell. (a) After the surface shell is fractured, an efflux of alloy material is emitted to the right of the droplet which wets the graphite with a contact angle of near-zero. (b) Auger surface elemental compositions of the graphite substrate, the fractured droplet shell, and the alloy material which has originated from the droplet interior.



substrate and into the vacuum chamber. Large concentrations of carbon and nitrogen were again observed at the poorly-wetted molten alloy surfaces. In summary, pure Ni/Pt/Pd boride eutectics wet and spread over graphite with a contact angle of near-zero, but Ni/Pt/Pd boride eutectics containing high surface concentrations of carbon and/or nitrogen wet graphite reluctantly or not at all.

3.2. The origin of the surface carbon and nitrogen

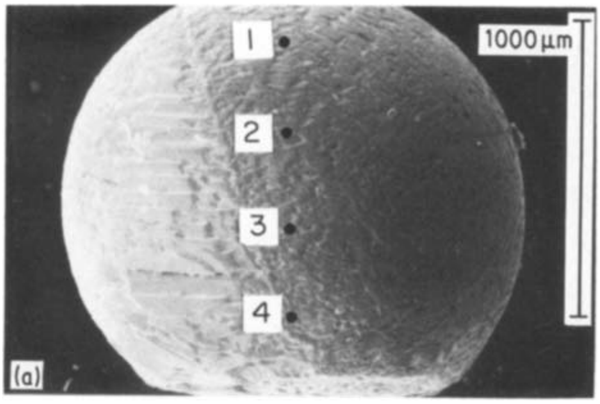
In order to isolate the source of the carbon and nitrogen found in the molten alloy surfaces, wetting to non-carbon substrates was investigated. This procedure eliminated dissolution of the substrate as the source of carbon.

Wetting of an Ni–B eutectic composition to aluminium oxide is shown in Fig. 6. The choice of Al_2O_3 was based upon evidence from Lugscheider *et al.* [22] which suggested that nickel boride alloys used as brazing materials were observed to wet an Al_2O_3 layer. As Fig. 6 shows, the wetting was poor, and a contact angle of about 130° was formed. More significantly, large concentrations of carbon and nitrogen were observed at the poorly-wetted molten surface. This material could only originate from the alloy itself in the form of low-level surface-segregated impurities. This is because the experiment was performed under conditions of ultra-high vacuum and the alloy was completely isolated from outside sources of these elements. Similar behaviour was found in wetting to other non-carbon substrates. In particular, when $Pt_{72}B_{28}$ was wetted to rhenium, although the wetting was excellent, the molten surface was found to possess large concentrations of carbon and nitrogen (Fig. 7).

3.3. Evidence for surface segregation of low-level impurities in the liquid alloys

The wettability of solids by liquid metal alloys has been shown to depend critically on the existence of surface segregation of low-level impurities inherent to the alloys. Segregation of these impurities to the molten surface has been observed in every alloy system we have studied, and we suspect that the phenomenon occurs in a much wider range of material systems than those investigated here. Further, the existence of surface segregation casts doubt on several previous studies of wetting, as the existence of parts per hundred thousand (p.p.m.) impurities in the wetting materials can radically affect the contact angle. The evidence for surface segregation is summarized below.

1. Direct experimental observations of large relative concentrations of low-level impurities at molten



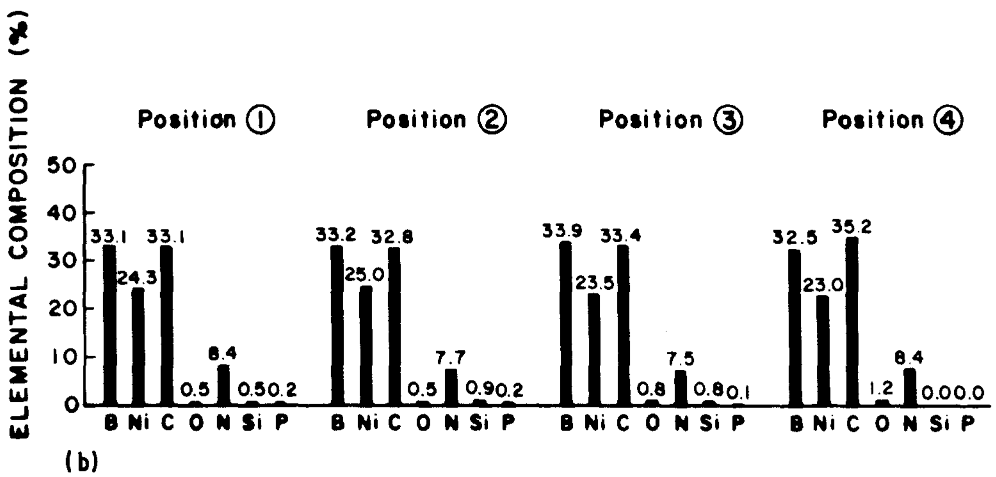


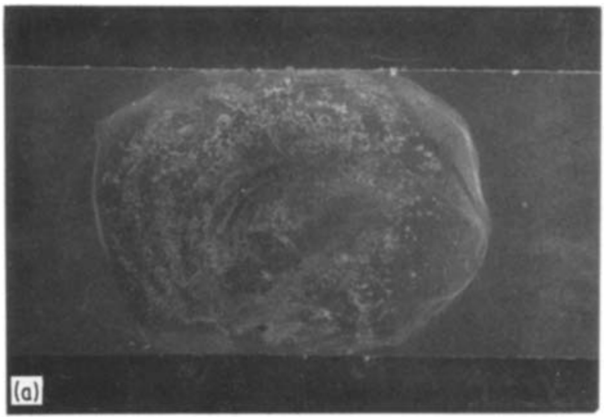
Figure 6 (a) Wetting of $Ni_{55}B_{45}$ on Al_2O_3. (b) Auger surface elemental compositions of the molten surface at 1355 K show large concentrations of carbon and nitrogen. The view is after quenching.

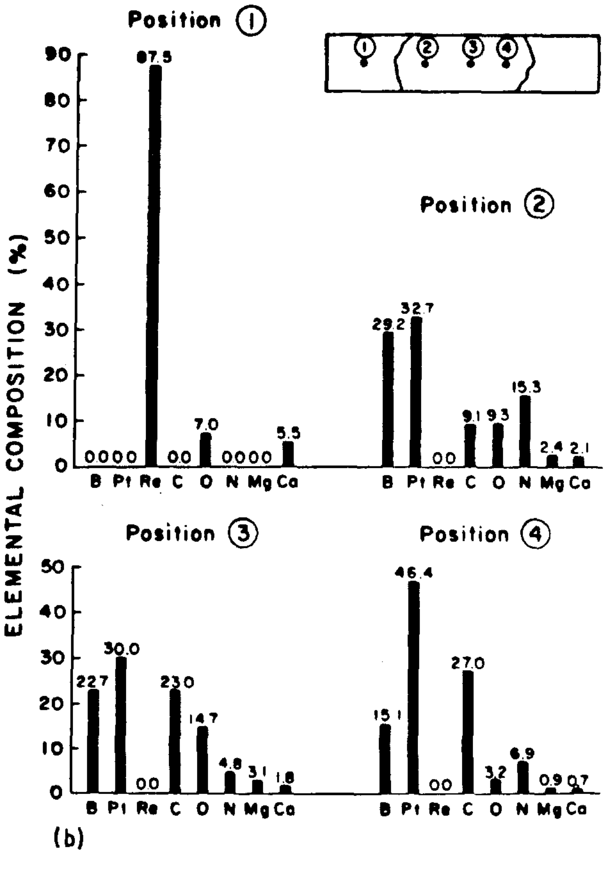
alloy surfaces, sometimes as high as 50 to 60 at %. When wetting to non-metallic solids such as graphite, the segregated materials act to inhibit wetting. On refractory metals such as tungsten and rhenium, wetting occurs with small contact angles despite the presence of the surface impurities. This is because of the strong chemical reaction of most refractory metals with boron and carbon, which are known to readily diffuse into the metal substrate to form metal borides and carbides [23].

2. Theoretical calculations of surface enrichment. In particular, Table I shows that a typical level of carbon impurity in the boride alloys was 0.019 wt %. If we assume that the entire weight percentage of carbon segregates to the surface of a spherical droplet of $Ni_{50}B_{50}$ whose dimensions are comparable to the droplet size in a typical wetting experiment (0.5 mm radius), the thickness L of the carbon layer formed about the droplet is calculated to be

$$L = 3.17 \times 10^{-6} \times D(\mathrm{NiB})/D(\mathrm{C})\,\mathrm{cm} = 114\,\mathrm{nm}$$

Figure 7 Wetting of $Pt_{72}B_{28}$ on rhenium. (a) View of the wetting after quenching. (b) Auger surface elemental compositions atop the rhenium substrate and the liquid surface at the alloy melting temperature (m.p. = 1065 K). The alloy is able to wet rhenium despite the presence of large concentrations of carbon, nitrogen and oxygen.





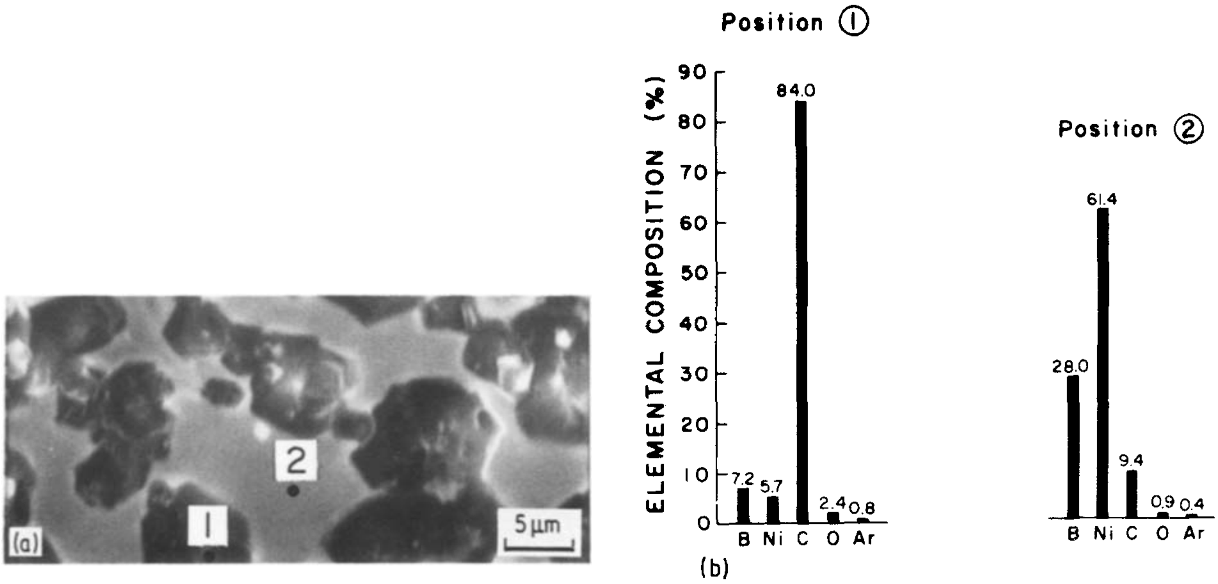


Figure 8 (a) The surface microstructure of a typical poorly-wetted droplet of $Ni_{55}B_{45}$ on graphite. The view shown is a higher magnification of the surface structure seen in Fig. 4 after 10 nm Ar^+ sputter cleaning. The hexagonal structures are precipitated graphite. (b) Auger surface elemental composition of two positions in (a).

where D(NiB) and D(C) are the densities of the nickel boride alloy and graphite, respectively. We have assumed the density of graphite to be 2.0 g cm^{-3} and have calculated the density of NiB (7.2 g cm^{-3}) from values given in the literature [24, 25]. This demonstrates that it is possible for the high concentrations of carbon observed at the molten surfaces to originate from surface-segregated material. Since the alloy fragments used in the wetting experiments were fractured from the interior of the melt, the impurities are characteristic of bulk material.

3. Metallographic examinations show differences between the near-surface and interior microstructure of poorly-wetted droplets. A typical case is given in Fig. 4a above, which shows a scanning electron micrograph of a quenched nickel boride eutectic above graphite. Prior to quenching, Auger analysis of the molten droplet showed that the surface was composed of large atomic percentages of carbon and nitrogen, shown in the accompanying bar charts (Fig. 4c). After quenching, the droplet surface is covered with crystallized hexagonal graphite (Fig. 8). Similar examinations of cross-sectional slices through poorly-wetted droplets showed no evidence of second-phase graphite in the droplet interior.

4. The composition of alloy material in the interior of poorly-wetted droplets. As shown above, it is possible to fracture the high surface tension "shell" surrounding unwetted alloy droplets by thermal treatment. The resulting efflux of alloy material consists of pure alloy components that exhibits excellent wetting of the graphite substrate (Fig. 5). It is also possible to fracture the shell-like feature by mechanical puncture by a second, tapered edge of graphite. When penetrated, the adhesion is so large between the tapered graphite and the alloy in the droplet interior that the droplet may be pulled away from the original poorly-wetted graphite. That impurities are found on the surface of the droplet but not in the droplet interior is further evidence for surface segregation which occurs on melting.

3.4. The influence of surface coatings and boron additives on wetting

It has been shown that wetting is governed by surface segregation of low-level bulk impurities which arise from within the alloy. The segregated impurities form a barrier which inhibits reaction between alloy and substrate and results in poor contact angles. There are three possible solutions to this problem. The first solution is to eliminate the bulk alloy impurities by employing ultra-pure starting materials and strict control of the arc-melting process. This is not easy to accomplish in a cost-effective way. The impurity level necessary to prevent build-up of a few monolayers of segregated material is in the range of a few p.p.m. and would require extraordinary processing conditions. The second solution is to devise a method to skim away the alloy impurities after the impurities have segregated. We have shown that once the bulk impurities have surface-segregated, the interior of the poorly-wetted alloy droplets consists of pure alloy materials. In this way, segregation works to advantage as a method for producing ultra-pure alloys. The third solution is to introduce materials into the contact system which possess high chemical affinity for the segregating impurities. The materials can be introduced either as a surface coating or by incorporation into the alloy during the arc-melting process, and act to suppress segregation by tying up the alloy impurities during compound formation. Due to the favourable Gibbs free energies of formation of SiC and B_4C, boron and silicon are expected to combine with the segregated carbon and promote wetting. We describe here the use of surface coatings and the incorporation of excess boron to improve wetting. The wetting of boron-rich non-eutectic compositions and detailed thermodynamic analyses will be provided in subsequent publications [26].

The improvement in wetting when a boron surface coating is used is shown in Fig. 9. A sample of nickel boride alloy was wet to a graphite substrate whose front surface was coated with a slurry of 325 mesh red

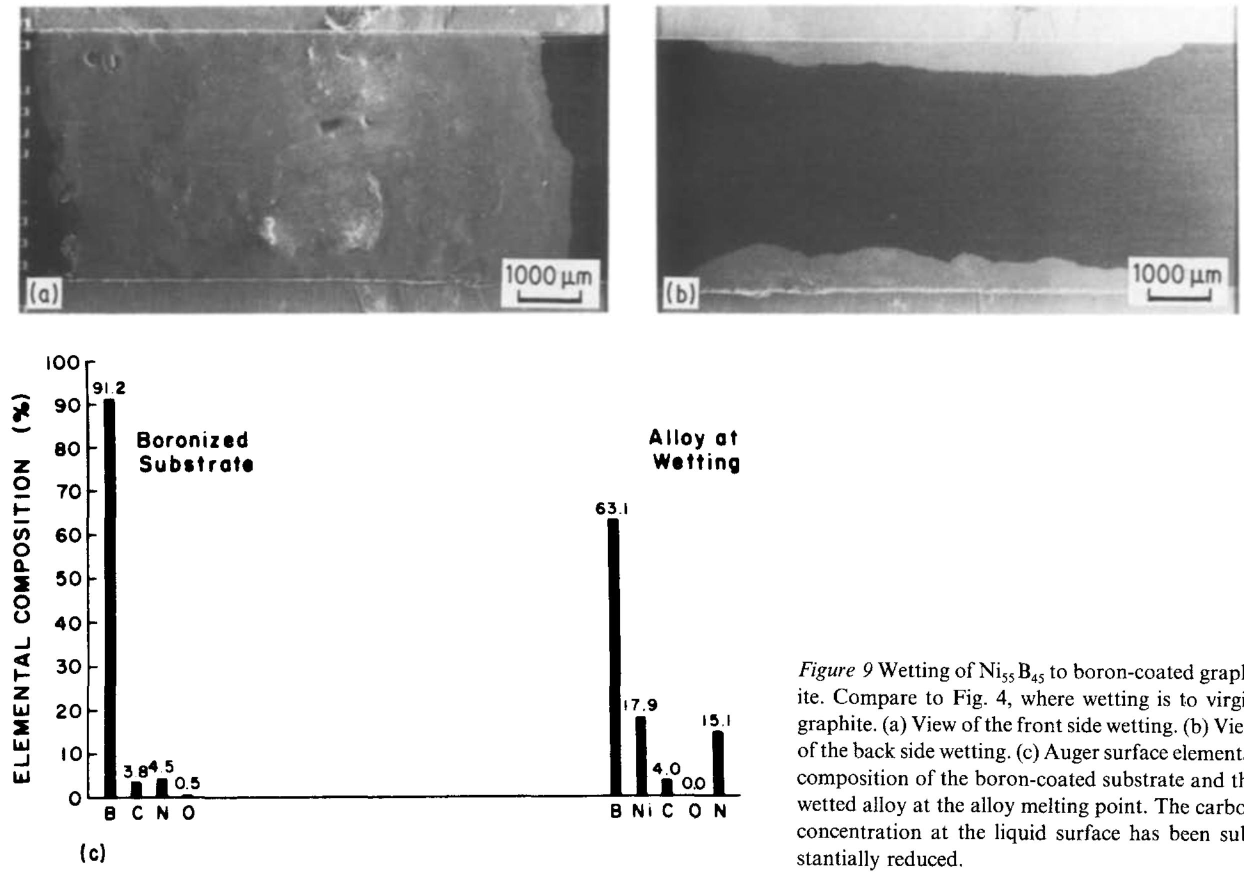


Figure 9 Wetting of $Ni_{55}B_{45}$ to boron-coated graphite. Compare to Fig. 4, where wetting is to virgin graphite. (a) View of the front side wetting. (b) View of the back side wetting. (c) Auger surface elemental composition of the boron-coated substrate and the wetted alloy at the alloy melting point. The carbon concentration at the liquid surface has been substantially reduced.

boron powder. The boron layer was applied as a slurry with acetone using a small paintbrush, and the contact system was mounted into the vacuum chamber in the usual fashion. Auger analysis of the boron powder showed that it was relatively pure (impurities: $N < 5$ at %). As seen in Fig. 9, the wetting was excellent, and flow was observed to occur beyond the boron underlayer and on to the non-boron-coated backside of the ribbon. Auger analysis of the molten alloy surface showed greatly reduced levels of surface carbon when compared to the situation on virgin graphite (Fig. 4). It was also observed that the liquid surface was enriched with boron and had a much different stoichiometry than the bulk. This was not due to the addition of the boron coating, but rather to the existence of surface segregation in the purified alloy, which arises because (non-metallic) boron possesses a lower surface tension than (metallic) nickel. The effect was observed in several alloys during our studies. Surface segregation of low surface tension components is expected in multicomponent alloy systems, and is particularly prevalent in liquid alloys where diffusion is rapid and no internal sinks (such as grain boundaries) are present to reduce the relative concentration of surface-segregated species. Eutectics of Pd–B and Pt–B also exhibited improved wetting when the graphite was boron-coated.

Surface coatings of silicon affected wetting similarly. Fig. 10 shows the wetting of a palladium boride alloy to a polycrystalline graphite LMIS containing an underlayer of silicon. The silicon was applied to the emitter in powdered form in a slurry with propanol and then heated until the silicon melted. Subsequent wetting of these two materials was superb, and the silicon wet and spread over the graphite with a contact angle of zero. The interfacial compound which formed was SiC, which was verified by comparison to Auger chemical shifts for a standard of SiC after flashing away the free silicon [27]. The wetted substrate was therefore a layer of SiC covered by a thick layer of free silicon. A layer of free silicon resulted in the best wetting. To the heavy silicon layer was added the Pd–B eutectic in powdered form with propanol, which was then electron bombarded in a vacuum of $\sim 10^{-6}$ torr until the alloy melted. As seen in Fig. 10, the wetting of $Pd_{72}B_{28}$ to the silicon-coated graphite was excellent, and the alloy was observed to wet and spread past the boundary of underlying silicon and on to the virgin graphite.

The improvement in wetting when extra boron is mechanically added to the alloy is shown in Fig. 11. In this experiment, a specimen of powdered $Ni_{55}B_{45}$ alloy was mechanically mixed in a mortar and pestle with 3% (by weight) red boron powder. The resulting mixture was then applied to a virgin graphite substrate and mounted into the ultra-high vacuum chamber. Wettability was inferior to the case of wetting of $Ni_{55}B_{45}$ of boron-coated graphite (Fig. 9), but superior to the case of wetting $Ni_{55}B_{45}$ to virgin graphite (Fig. 4). This shows that an additional decrease in contact angle is possible when materials reactive to the segregated carbon are introduced in even the crudest manner.

4. Discussion and summary

Surface segregation of low-level, low surface tension impurities is the primary cause for wetting failure in contact systems of transition metal alloys of nickel, platinum and palladium with graphite. The major impurities have been found to be carbon and nitrogen

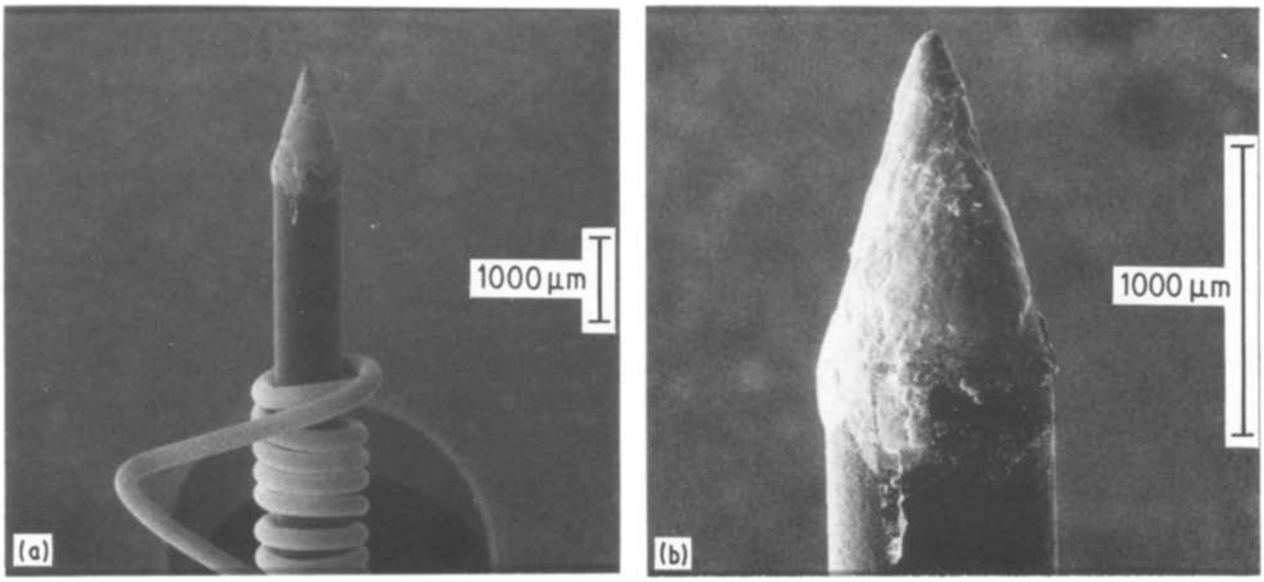


Figure 10 (a, b) Wetting of $Pd_{72}B_{28}$ to a silicon-coated graphite emitter structure. The wetting is excellent. The melting point of this alloy was determined to be 1310 K.

in the form of free carbon, B_4C and BN. We say that nitrogen in the form of BN segregates because it is unlikely that nitrogen exists in the alloys in elemental form. Further, BN has been directly identified in the alloy surfaces by evaluation of Auger chemical shifts. B_4C has similarly been identified. At melting, the resulting surface layer of carbon, BN and B_4C act to inhibit interaction between the alloy and substrate and an unfavourable combination of surface tensions results. Boron nitride and boron carbide possess favourable Gibbs free energies of formation and probably form during the arc-melting process and at temperatures near the melting point of the boron-containing eutectic alloys.

Surface coatings of boron and silicon facilitate wetting by tying up the carbon and nitrogen impurities that would otherwise surface-segregate through formation of interfacial boron carbide and silicon carbide. Effectively, the surface coatings act as a getter for segregated material. The concurrent surface reaction is precisely what is necessary for wetting. Surface coatings of materials which possess favourable Gibbs free energies of reaction with the segregant species are successful because the C–C non-reaction is replaced by a C–B or C–Si reaction. When the alloy is purified in this fashion, it can then wet virgin material because of the elimination of segregated material. This explains why the liquid alloy initially requires a surface coating

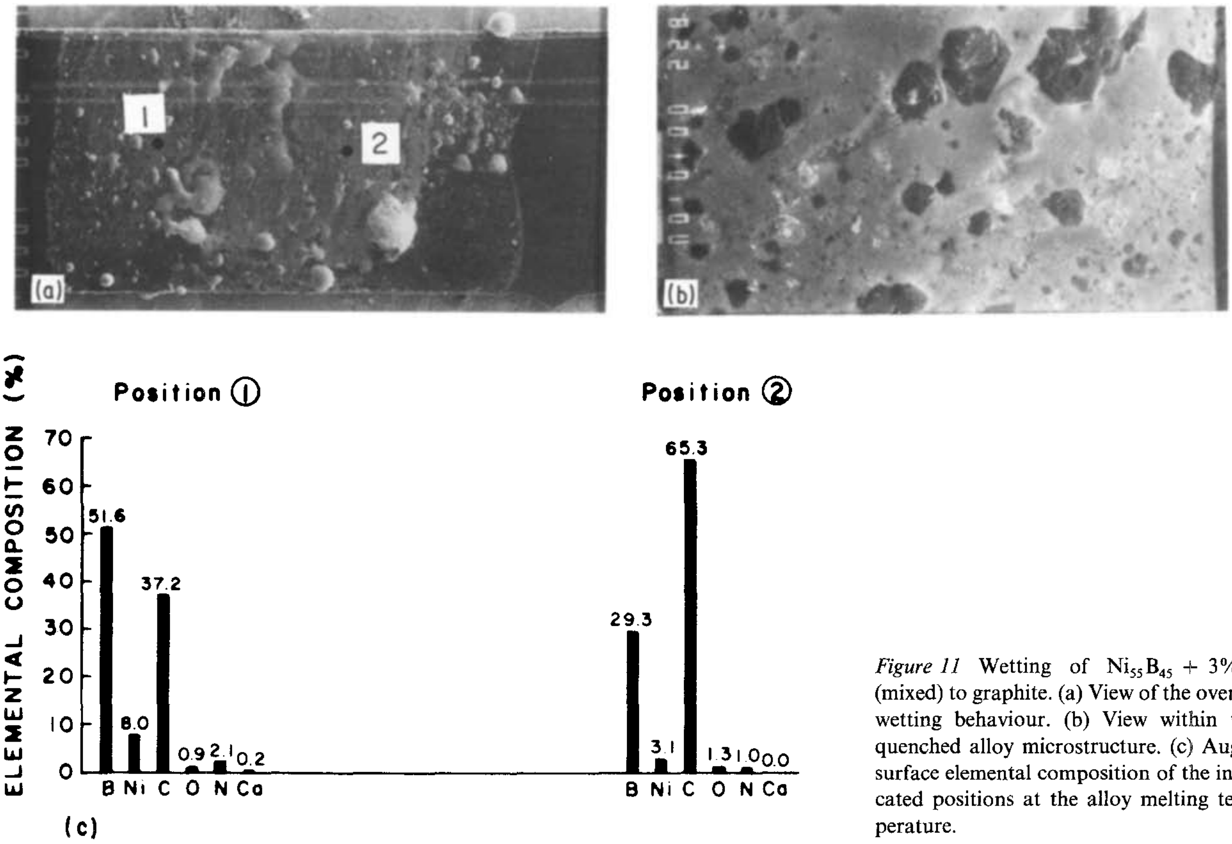


Figure 11 Wetting of $Ni_{55}B_{45}$ + 3% B (mixed) to graphite. (a) View of the overall wetting behaviour. (b) View within the quenched alloy microstructure. (c) Auger surface elemental composition of the indicated positions at the alloy melting temperature.

for wetting, but subsequently wets and spreads over virgin graphite. Boron which is mechanically added to the alloy affects wetting similarly. The added boron facilitates formation of boron carbide in the alloy and lowers the activity of carbon in the surface shell which forms at melting.

The greatest impact of surface coatings on wetting results when the coating is a thick (i.e. $> 5\,\mu m$) layer of free boron or silicon. Surfaces where these coatings are thermally desorbed (by overheating), or surfaces that consist of carbides of boron and silicon, are poorly wetted. This may be explained by consideration of the relative magnitudes of cohesion and adhesion in the contact system. Naidich [28] has shown that best wetting is attained when the adhesion between substrate and the alloy (as measured by the Gibbs free energy function) is large compared to the cohesion of either material. With all else equal, wetting is best for substrates of low relative thermodynamic stability. Since the Gibbs free energy for carbide formation is lower (i.e. more negative) than that for elements, wetting to substrates of free silicon and boron is energetically favoured. Stated otherwise, free silicon and boron are necessary to tie up segregated carbon in the system, and this action is facilitated if these elements are not already tied up as carbides.

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