

# Aluminum Soldering Performance Testing of H13 Steel as Boron Coated by the Cathodic Arc Technique

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## ABSTRACT

A unique, cathodic (or vacuum) arc-based technique for boron (B) and boron-rich plasma generation has been developed for use as a coatings technology and other applications. Boron would make an excellent coating for dies for Al-alloy casting because it has a repulsive chemical interaction with aluminum but a highly attractive interaction for steel. Other properties such as hardness, abrasion resistance, corrosion resistance and refractive qualities also appear favorable. In this case, owing to the attractive chemical forces, the coating was partially in-diffused into the H13 steel coupons. The high ion energies inherent in cathodic arc deposition may have also contributed to this effect. An automated test cycle consisting of immersion of coated coupons in pure molten Al at ~700°C, followed by removal and quenching was used. Failure was indicated by soldering to the extent that removal from the melt through a wiping aperture of 1/16 inch larger in diameter than the coupon could not be accomplished. The control sample was completely wetted after the first cycle. It was possible to obtain 50 cycles on the B-coated sample, with about half the sample area being soldered and about half remaining unwetted. Soldering, where it occurred, was attributed to weak areas in this particular coating. It is concluded that boron shows promise as a life-extension coating for aluminum casting steel dies.

## INTRODUCTION

Liquid aluminum is extremely reactive and easily alloys with alloy constituents of H13 die steels. Researchers have investigated various protective coatings and coating methodologies to prevent the erosion-corrosion in die casting dies. Most of the research and development efforts have concentrated on developing and evaluating thin coatings typically applied by physical vapor deposition techniques (PVD), chemical vapor deposition (CVD), and nitriding techniques. Coatings typically deposited by these techniques include CrN, CrC, B<sub>4</sub>C, VC, CrN<sub>2</sub>, and Ion Nitriding. The materials have been chosen due to their resistance to soldering in the presence of liquid aluminum. The primary failure mechanism of these coatings is spalling due to differences in the coefficient of thermal expansion (CTE) between the coating and the substrate. The CTE of H13 steel is approximately  $12 \times 10^{-6}/K$ , while the CTE of CrN is  $0.7 - 3.1 \times 10^{-6}$ , that of VC is  $6.5 \times 10^{-6}$ , B<sub>4</sub>C is  $4.5$

$\times 10^{-6}$ , TiN is  $8 \times 10^{-6}$ , and Cr<sub>2</sub>C<sub>3</sub> is  $10.3 \times 10^{-6}$ . With typical temperature cycles in excess of 500°C, the expansion and contraction of the steel make the survivability of these ceramic type coatings difficult to impossible. Therefore, even if a material is solder resistant, the ability to coat it on a die surface and keep it on a die surface is a technical challenge.

Residual stress control and the prevention of fatigue cracks due to thermal cycling of these dies are two additional and important objectives in coating development. Some coatings offer some resistance to soldering but the results are often qualitative and strongly depend on the die, die location, melt temperature, and many other variables. Various types of PVD, CVD, and nitriding approaches have been attempted [1-7]. Multiple layer approaches to help accommodate stresses and diffusion barriers are also being considered [4]. However, these approaches are often very expensive. Other recent investigators [8] are utilizing cermet coatings which offer the potential solder resistance of the low CTE ceramic materials and the stress accommodating properties of metals. The key in depositing these coatings is the ability to fuse the cermet to the steel without dissolving the steel and not allowing iron to be present at the coating surface. Testing of these coatings by the industry has had mixed reviews due to the complex environment experienced in the die casting industry.

This paper describes the recent results and promising die solder resistance of a H13 steel pin coated with boron utilizing a cathodic arc plasma generation process.

## COATING TECHNOLOGY

### Coating Process

HY-Tech Research Corporation has developed and patented a unique coating technology which allows the deposition of boron in an economically viable way. Typically, boron is extremely difficult to work with and deposit onto a substrate. It does not sputter well and it cannot be electroplated. Typically, gaseous compounds for use in CVD are toxic and/or explosive. However, HY-Tech's method produces a supersonic plume of boron plasma (fully ionized gas) out of solid feedstock. The latter, made of consolidated boron powders, is the cathode in a type of electrical discharge referred to as a vacuum (or cathodic) arc [9, 10]. Figure 1 shows a typical

cathodic arc setup. This technology has lately become a very common type of PVD because of its superior rate of deposition over magnetron sputtering. However, its application is limited to metal cathodes for the production of metal nitride coatings or graphite cathodes for the deposition of amorphous carbon coatings.

One of the key elements of successful development of a cathodic arc with a non-metal boron cathode has been in the sintering technology for the consolidation of boron cathodes from powder. Since the vacuum arc is a very intense electrical discharge, it produces immense stresses on the cathode, where the footprint of the discharge is anchored. Similar to metal-cathode vacuum arcs, the footprint is usually in the form of one or more non-stationary spots of about  $10\mu\text{m}$  in diameter. These spots carry current densities as high as  $100,000,000$  amperes per square centimeter. They are extremely bright. This is where solid is directly converted to the plasma state. The specially processed boron cathodes are able to withstand the stresses induced on them by this process. Even these robust cathodes must be heated to over  $800^\circ\text{C}$  to make the boron cathode conductive [11]. Compared to previous attempts at a dc arc with a B cathode [11], these special cathodes allow for uniform erosion without transition to a diffuse (non-spot) mode.

In this new technique, the arc is struck from an anode to the pure boron cathode, producing a dense plasma plume of boron ions with 100% ionization, and a rather high energy. Polarization of the target can increase the energy as the ions approach the target. Because of the density of the plasma, the resulting thin plasma sheath, and the polarization, the ability to treat intricate shapes helps make this a unique and useful coating technique. Although the cathodic arc is not unique to boron, the boron and boron carbide cathodes are unique. Other coating materials of interest for dies, such as chrome nitride, are also best generated by cathodic arc. In fact, good results have been reported by a number of researchers using metal cathodic arc in a nitrogen background to reactively deposit CrN and TiN, sometimes doped with other materials [2, 6].

## COATING EQUIPMENT

Since the plume produced is fully ionized, it can be guided with the aid of a magnetic solenoid. Proper control of the electrical biasing of the substrate can not only help with the adhesion of the coating, but also can allow for conformal coating of non-planar substrates (as illustrated in Figure 1).

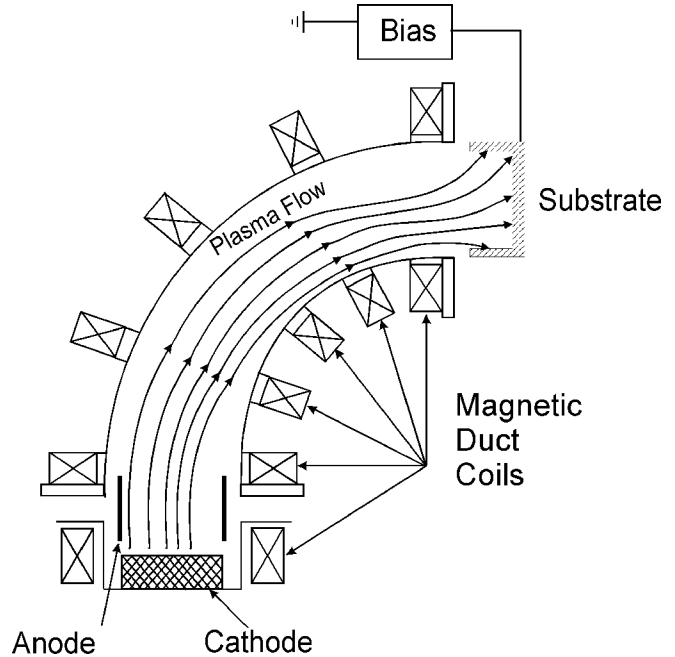


Figure 1: Illustration of typical cathodic (vacuum) arc deposition with a  $90^\circ$  bend magnetic duct to filter out solid or liquid particle debris from the solid cathode, which is also the source of the material converted into fully-ionized plasma guided by the duct.

Typically a curved solenoid is used to take the substrate out of the line-of-sight of the source. This prevents any debris that can also come from the cathode (small fragments or molten material) from depositing onto the substrate. This debris, usually referred to in the literature as macro-particles, is the main drawback of the vacuum arc as a thin film deposition process. However, the deposition rates obtained with this technique far exceed those of other plasma-discharge deposition methods; even after substantial plume attenuation in a filter (simple curved solenoids transmit only about 10% per turn). The setup at HY-Tech used for the studies reported here did not have an optimized filter and the coatings incorporated a significant number of macro particles in most regions of cylindrical samples coated. However, there were some particle free regions and this provided an opportunity to study the effect of the macro particles on soldering by molten Al.

Two important advantages for the vacuum arc deposition process for this application stem from the fully ionized nature

of the plasma stream: (1) the effective use of substrate biasing to guide the ions to surfaces that may be at various angles with respect to the stream—an important benefit for die-casting dies whose shapes tend to have complex (non-planar) surfaces (often including crevices hard to reach with line-of-site deposition techniques); (2) the potential for control of the energies with which the ions impinge onto the surface, allowing variations of the degree and nature of atomistic mixing that will occur at the coating-substrate interface. This mixing is expected to determine the adhesion of the coating, an important property. In the case of boron, the primary effect of the energetic ions has appeared to be enhanced diffusion into the steel substrate, as discussed in this paper.

### Coating Material Selection

Thermodynamic calculations suggested that boron would be an excellent candidate for a non-wetting coating that would also bond well to an iron-based substrate (e.g., H13 steel). A short explanation behind this hypothesis is described in the Results and Discussion Section below. Figure 2 shows the results of a Rutherford backscattering (RBS) analysis of an area for which the entire boron deposition had in-diffused over a depth of 0.5 microns.

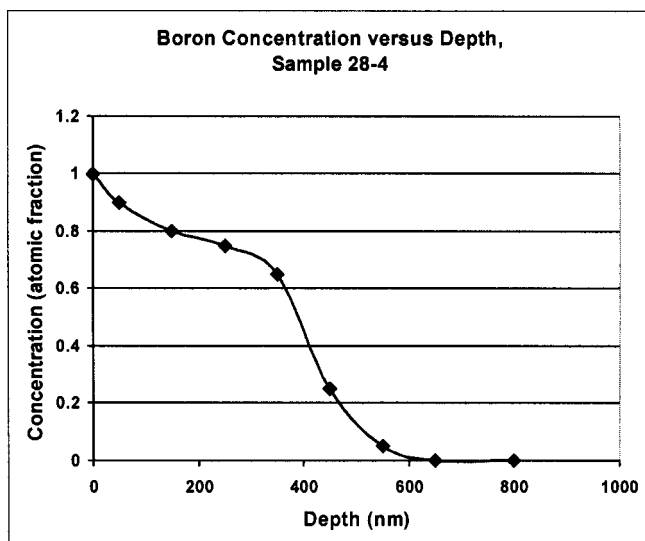


Figure 2: Boron concentration versus depth for sample 28-4 derived for the RBS data. Almost all the boron has reacted/diffused inward to yield a reaction layer ~0.5 microns thick.

Thus, there was not actually a coating, but a surface alloy. Such results were not consistent from one area to the next. Differences probably depend on temperatures reached during

coating. This result confirms the expected tendency for strong bonding, as was predicted from the thermodynamics calculations.

## EXPERIMENTAL TESTING

### Sample Preparation

The H13 substrate samples were 1/2 inch diameter x 1 inch long cylinders coated using the HYBron™ process of HY-Tech Research Corporation. This process is based on the cathodic arc technique. This technique evaporates boron from a solid cathode and converts the vapor into a supersonic, fully ionized boron plasma. The resulting coating is primarily pure boron, a naturally hard amorphous material. A small oxygen concentration improves the coating properties, e.g. improved adhesion and a low modulus of elasticity [12]. The samples were mounted with the cylindrical axis perpendicular to the plasma plume. Some rotation of the sample about its axis of symmetry was used to attempt uniform deposition. This was not achieved because of insufficient control of the deposition rate in the present system. The free end of the cylindrical substrate, which was at 90° with respect to plasma plume, was coated as well. This region of the coating was entirely free of macro particle contamination.

### Bench Testing

Using a bench-scale soldering test apparatus (referred to as the dipper) (Figure 3) designed and built at Oak Ridge National Laboratory (ORNL), dip tests were conducted in molten aluminum to evaluate the soldering and thermal fatigue resistance of H13 die casting pins that were coated with boron utilizing the cathodic arc technique. Using this coating for automotive die applications seemed ideal based on previous thermodynamic calculations that indicated a positive, i.e. repulsive heat of formation, interaction between B-Al (Figure 4). The test was designed for testing the compatibility of coatings for H13 steel die-casting components, e.g. die pins. In order to simulate the die casting operational process steps, three stations were incorporated into the dipper testing apparatus: a die lubrication station, an air blast station, and the furnace containing molten aluminum. Programmable computer controls enable the control of each process step, the dipping times in the die lubricant in the air spray, and in the molten aluminum. The temperatures are set based on the selected liquid metal aluminum alloy. Prior to starting the trial cycles, the sample is first brought to the required molten alloy temperature, and then dipping trials are initiated. A testing cycle consists of first dipping the pin into the die lubricant, followed by an air blast, then a dip into the (~650°C - 700°C) molten aluminum alloy, followed by quenching in the cooled liquid lubrication.

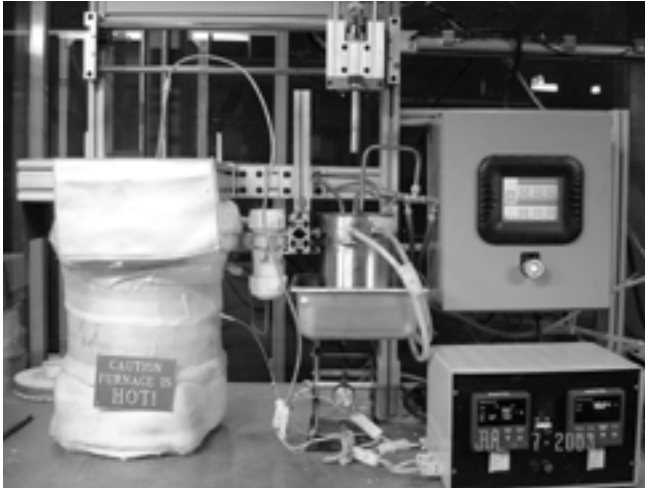


Figure 3: Schematic illustration of automated dipper test apparatus set-up.

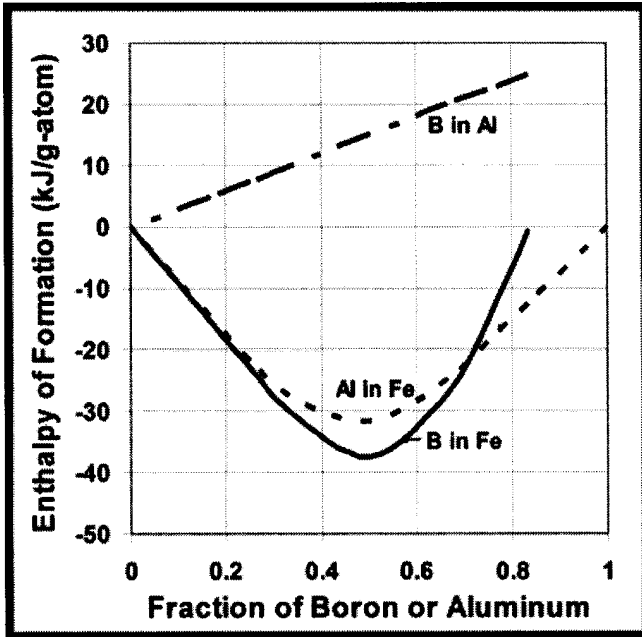


Figure 4: Illustration of thermodynamics of relevant alloy systems.

## EXPERIMENTAL RESULTS

Preliminary baseline soldering trials and analyses had previously been completed on uncoated H13 pins, with results demonstrating that soldering occurred on uncoated H13 pins after only eight dipper cycles. After only eight dipper cycles, the uncoated H13 pin exhibited soldering along its surface, and on the bottom of the pin. However, experimental dipper tests conducted on the B coated pins, under the same experimental dipper test conditions, confirmed that the molten aluminum did not wet the B coating, as predicted by the thermodynamic calculations. The B-coated pin exhibited no

soldering where the B coating was free of macro particles. In particular, no macro particles formed on the end of the pin during the cathodic arc process. Figure 5 shows the appearance of the end of a boron-coated steel pin sample after 50 dipper cycles demonstrating the resistance of the boron coating to wetting by the molten aluminum, as predicted by thermodynamic data.

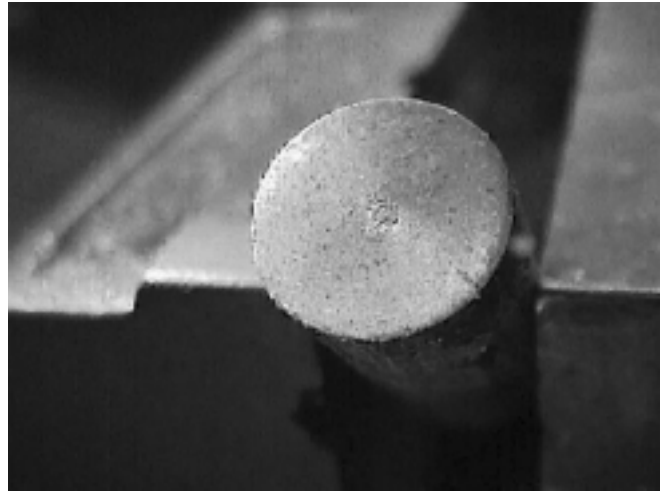


Figure 5: Macro-particle-free end of a boron coated steel pin exhibiting no apparent soldering after 50 dipper cycles in molten aluminum. Typical cylindrical pin dimensions are 2" long x 0.75" in diameter.

Subsequent Rutherford Backscattering Spectroscopy (RBS) of the sample analyzed demonstrated the most dramatic effect. This test sample had more boron than the coated samples, and virtually all of it had diffused into a reaction layer ~ 0.5 microns thick. The original data, together with a fit by simulation, used six layers in the composition grade. Figure 2 is a transposition of this data to boron concentration versus depth. These data are for the cylinder wall. This reaction effect is assumed to be kinetically facilitated by heating during deposition, although the tendency to react is intrinsic (see below).

This reaction result illustrates part of the original theory hypothesized, i.e. that the boron will have a strong tendency to bond to the steel substrate. The thickness of this reaction layer suggests that the interstitial B diffuses readily, but since the solid solubility is low, the diffusion mechanism may also involve some successive bonding, perhaps as a compound, then release of the B, further diffusion and, re-precipitation. The phase diagram for the Fe-B system exhibits a eutectic at 1174°C. Boron does not lower the austenite transition temperature. Experimental results demonstrated that the boron was highly adhesive during testing in the molten aluminum. This reaction bonding tendency appears to eliminate the need for a separate bonding layer, contrary to compounds like CrN

or TiAlN [1]. Although one could argue that much of the chemical potential is used in forming the compounds, and so little reactivity would be left over for bonding to the substrate, this appears not to be true for B. This argument appears to be true for an element that is protected against a rapid reaction (oxidation) on the outside by a passive oxide, e.g. Ti and Al. Also, although boron is attractively bonded to steel, it has a repulsive chemical interaction with Al. Figure 3 illustrates the thermodynamic calculations for the heats of formation of three pertinent alloy systems over a composition range. The exothermic reaction with Fe-based systems is predicted for B and Al, thus supporting the bonding of B to steel and the wetting of Al. In addition, the heat of formation in the B-Al system is positive, indicating little tendency to react. Moreover, the terminal heats of solution were very favorable for no wetting of B by Al. The value for B in Al was 30 kJ/g-atom, indicating a possibility for slight solubility of B in Al at high temperature. The eutectic composition is at 0.055 at. % B at 660°C. At the opposite composition extreme, there is no possibility for reactivity of Al in solid B. Thus, it was anticipated that the B coating would be highly adherent to steel, but would also be resistant to wetting by Al.

## DISCUSSION

The fact that the sample was non-uniform over the area in soldering performance is probably explained by the macro particles. Many of these particles bounce off of a hard material such as H13 steel, but some stick for a while and then fall off during handling, etc. If a particle is sticking during coating it screens the area and when it falls off it leaves an unprotected area. A similar result was observed with 52100 steel. Failures start in the pores left by macro particles. In the present case, the first sign of failure was a mechanical clinging, e.g. a “Velcro”-like effect due to apparent roughness of the surface for the areas that (hypothetically) contained pores. Upon solidification the aluminum fell off as a solid, leaving the coated surface as-new. Apparently, wetting finally occurred for these areas.

This same idea may explain why the end of the sample never became wetted. As was described above, during coating, the cylinder wall was more or less perpendicular to the plume propagation direction. Because of polarization and sheath effects, the end could still be exposed to plasma, but the macro particles passed the end at grazing angles and would have tended to have been reflected from this hard substrate. Thus the end may not have had pores. The remedy in all cases under these ideas is an adequate filter. The coating on the end was highly in-diffused after the test. Although the number of cycles was small, heat checking (cracking) was also not observed.

In that regard, there is room for speculation on known atomic mechanisms in all aspects of performance. The in-diffusion of boron has been mentioned. Adhesion would definitely not be an issue. The fact that the in-diffusion was much greater after the tests than before confirms the high mobility of the boron at the test temperature. Such a mobile agent in the lattice in the near-surface region could move to ameliorate stresses in accordance with text book metallurgical mechanisms, such as the Snoek effect or the Cottrell-Bilby mechanism, wherein regions of high compressive stress are vacated by the mobile solute and precipitation occurs in regions of tension.

Finally, it might be noted that the interaction of the melt may be mainly with the boron oxide at the interface, rather than the elemental boron. Boron has a strong passivating oxide which is reducible by elemental aluminum. If some oxide is somehow removed by a combination of chemical and wear effects due to impact of the molten Al, and if no boron is available for new oxidation except that which has diffused in, a new oxide will form from the most accessible boron near the surface. This denuded zone will create a Fick's law or entropic chemical force, which will tend to make some of the boron come back out to fill it. Thus the in-diffused boron could become a reservoir for reformation of surface oxide.

## CONCLUSIONS

1. Experimental results have confirmed the primary goal and hypothesis of this work, i.e. based on thermodynamic-based predictions, cathodic arc vacuum deposited boron coatings would resist wetting by aluminum.
2. The cathodic vacuum deposited boron coating strongly adheres to the substrate, while simultaneously resisting wetting by aluminum as predicted/hypothesized from thermodynamic calculations.
3. Despite the developmental state of this processing technology, all surface areas where the boron was deposited uniformly (i.e. without boron particle inclusions) demonstrated that the aluminum did not wet the H13 pin.
4. No cracking occurred in the coating or the substrate during or after the soldering/dipper bench tests.
5. Macro-particle management is the biggest challenge for the implementation of this technology, but preliminary conceptual equipment designs indicate that this is a solvable issue.
6. Boron shows promise as a life extension coating for die casting applications.
7. Further research and development would catapult this process technology into an industrially robust coating solution for the prevention of soldering and thermal fatigue of aluminum casting dies.

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