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SHEATHED THERMOCOUPLES FOR CONTINUOUS MOLTEN STEEL TEMPERATURE MEASUREMENT DURING THE LADLE TREATMENT PROCESS

Final Report

By
R. Michael Phillippi

September 1989

Work Performed Under Contract No. AC07-76ID01570

For
EG&G Idaho, Inc.
Idaho Falls, Idaho

By
Vesuvius Crucible Co.
Pittsburgh, Pennsylvania

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ABSTRACT

The evolution of a thermocouple protection sheath for use in liquid steel during the ladle treatment process is described. Five different designs constructed of boron nitride, alumina-graphite, and magnesia-graphite were evaluated. Results show that excellent slag wear characteristics are possible using magnesia-graphite but improvements in thermal shock resistance and response time are required. Temperature profiles during argon stirring, addition of chill scrap, and natural cooling are presented.

ACKNOWLEDGEMENT

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	v
1. INTRODUCTION	1
2. SYSTEM COMPONENTS, INSTALLATION, AND OPERATION	2
3. SHEATHED THERMOCOUPLE DESIGN AND PERFORMANCE	5
3.1 Boron Nitride Protection Sheaths	5
3.2 Alumina-Graphite Protection Sheaths	7
3.3 Magnesia-Graphite Protection Sheaths	14
4. IMPACT OF CONTINUOUS LADLE TEMPERATURE	22
5. CONCLUSIONS	22
6. FUTURE WORK	24
REFERENCES	25

LIST OF FIGURES

		Page
Figure 1.	Schematic diagram of thermocouple installation at Bethlehem Steel Corporation's Sparrows Point Plant.	3
Figure 2(a).	Ladle treatment platform and access port used for thermocouple testing.	4
Figure 2(b).	270,000 kg ladle used at BSC's Sparrows Point Plant showing typical slag cover.	4
Figure 3.	Segmented BN sheath showing fixturing holder and ceramic protection sleeve housing the thermocouple.	6
Figure 4.	Segmented BN sheath showing actual dimensions.	6
Figure 5.	Composite BN and A-G thermocouple sheath.	8
Figure 6.	Molten steel temperature data for the segmented and hybrid BN thermocouple probes.	8
Figure 7(a).	Segmented BN sheath showing slag wear after 6 minutes of immersion time.	9
Figure 7(b).	Segmented BN sheath showing non-wetting characteristics. Slag was easily peeled away.	9
Figure 8(a).	Hybrid BN sheath after 12 minutes of immersion time.	10
Figure 8(b).	Hybrid BN sheath showing comparative wear with A-G.	10
Figure 9.	Construction of A-G thermocouple sheath.	11
Figure 10.	Molten steel temperature data for A-G thermocouple probe.	12
Figure 11(a).	A-G thermocouple sheath and immersion lance used for insertion.	12
Figure 11(b).	Failed A-G sheath after 29 minutes of immersion time.	13
Figure 11(c).	Close-up of A-G sheath showing uniform slag wear to the separation point.	13

Figure 12.	Construction of M-G thermocouple sheath.	14
Figure 13(a).	Molten steel temperature data for first M-G sheath tested.	16
Figure 13(b).	Molten steel temperature data for second M-G unit tested. Note failure from chill scrap addition.	16
Figure 14(a).	M-G sheath with attached slag thought to be responsible for extended response time on subsequent immersion.	17
Figure 14(b).	M-G sheath after 30 minutes of immersion time. Approximately half the wall thickness had eroded away.	17
Figure 15.	Construction of second generation M-G sheath.	18
Figure 16.	Molten steel temperature data from second generation M-G thermocouple probe. Failure was believed to be caused by thermal shock.	18
Figure 17.	Molten steel temperature data from second generation M-G thermocouple probe showing the effect of chill scrap addition and argon stirring.	19
Figure 18(a).	M-G sheath suspended over access port in preparation for test.	20
Figure 18(b).	M-G sheath after immersion showing attached slag.	20
Figure 19.	Failed M-G sheath after 59 minutes of immersion time. No slag line erosion was visible.	21

1. INTRODUCTION

Energy consumption in the industrial sector of the U.S. economy alone accounts for approximately 39% of the total U.S. energy consumed (1). As a result of this prodigious consumption figure, the Department of Energy (DOE) Office of Industrial Programs sponsors research and development to reduce energy use by increasing the end-use energy efficiency and productivity of industrial operations.

Continuous temperature measurement in liquid steel has been identified by DOE as a method to improve both energy conservation and control of metallurgical processes (1). To this end, DOE has sponsored several sensor development programs, including the research and development of a boron nitride (BN) sheath to protect thermocouples while immersed in liquid steel (2). Unlike the widely accepted disposable technique of temperature measurement, this preliminary work indicated that BN sheaths were capable of five hour lifetimes in continuous caster tundish applications. Since this initial work in 1985, the private sector has been successful in commercializing a temperature measurement system for tundish applications using an alumina-graphite composite sheath (3). However, before this writing there was no serious attempt by either DOE or the private sector to develop a thermocouple sheath for ladle treatment operations.

The ability to continuously monitor temperature during the ladle treatment process offers a very appealing impact on energy conservation. DOE estimates that direct energy cost savings would exceed $0.25/ton if continuous measurements were made in ladle metallurgy operations and continuous caster tundishes (1). Based on 1986 production figures, this amounts to a savings of $24 million/ year (less installation and operation costs) to the U.S. economy (1). Additional savings related to improved product quality could be far in excess of this amount. Indirect benefits include the ability to measure high temperature phase changes, chemical reactions, and other phenomena related to a broad spectrum of scientific inquiry (1).

Under the cost-shared effort between DOE and Vesuvius Crucible Company described herein, specific program objectives were to develop a system capable of continuous temperature measurement during actual ladle treatment and to compare the technical and economic suitability of BN sheaths developed during an earlier DOE research program with competing materials.

In subsequent sections of this report, the design and performance of 10 sheathed thermocouple assemblies is described. These assemblies were constructed of three different materials; boron nitride, alumina-graphite, and magnesia-graphite. Using these three materials, five different design configurations were tested with varying degrees of success. Based on the temperature profiles obtained, the effects of natural cooling, argon stirring, and chill scrap addition on temperature are also examined. Most significantly, the accumulated data, although preliminary, suggests that if commercially available, continuous temperature measurement during ladle treatment would allow reduction in the amount of required basic oxygen furnace (BOF) superheat.

Section 2 describes the required system components, installation, and operation. The design and performance of thermocouple assemblies tested appear in Section 3. A short discussion of the potential impact of continuous temperature measurement is presented in Section 4 with conclusions and recommendations for future work appearing in Sections 5 and 6 respectively.

2. SYSTEM COMPONENTS, INSTALLATION, AND OPERATION

The temperature measurement system tested consists of three components; the sheathed thermocouple assembly described in the subsequent section, a reusable immersion lance, and high resolution readout/recording instrumentation. A schematic diagram of the physical installation at Bethlehem Steel Corporation's (BSC) Sparrows Point plant where all testing was performed is shown in Figure 1.

Special care was required in the design of the immersion lance. To avoid introducing measurement error, the transition junction from Type B (Pt-6%Rh/Pt-30%Rh) thermocouple wire to compensated extension lead must not exceed 120 $^{\circ}$C. To avoid this problem, a transition junction was formed from extension lead to Type B thermocouple wire 3m from the top of the lance. The leads were contained within the argon cooled lance to shield them from heat radiation and splatter. Further, it was necessary to provide a method to ensure a true platinum-to-platinum connection at the thermocouple probe without introducing additional (parasitic) thermocouples in the circuit. Because of the weight (35 to 40 kg) of the lance and thermocouple probe, particularly with attached slag, it was necessary to position the assembly with an overhead crane.

Ladle temperatures were monitored using a digital display and an analog (strip chart) recorder that allowed adjustable span and offset. To obtain high resolution recordings the analog recorder was adjusted to indicate 1550 to 1650 $^{\circ}$C at zero and full scale respectively.

Figure 2(a) shows the ladle treatment platform and the access port (approximately 45 x 30 cm) used during testing. In normal operation, this port is used for automatic disposable temperature measurements and metal sampling.

Figure 2(b) shows the 270,000 kg (300 ton) ladles used at BSC's Sparrows Point plant. Note the slag cover (approximately 20 cm) which varied in thickness during testing.

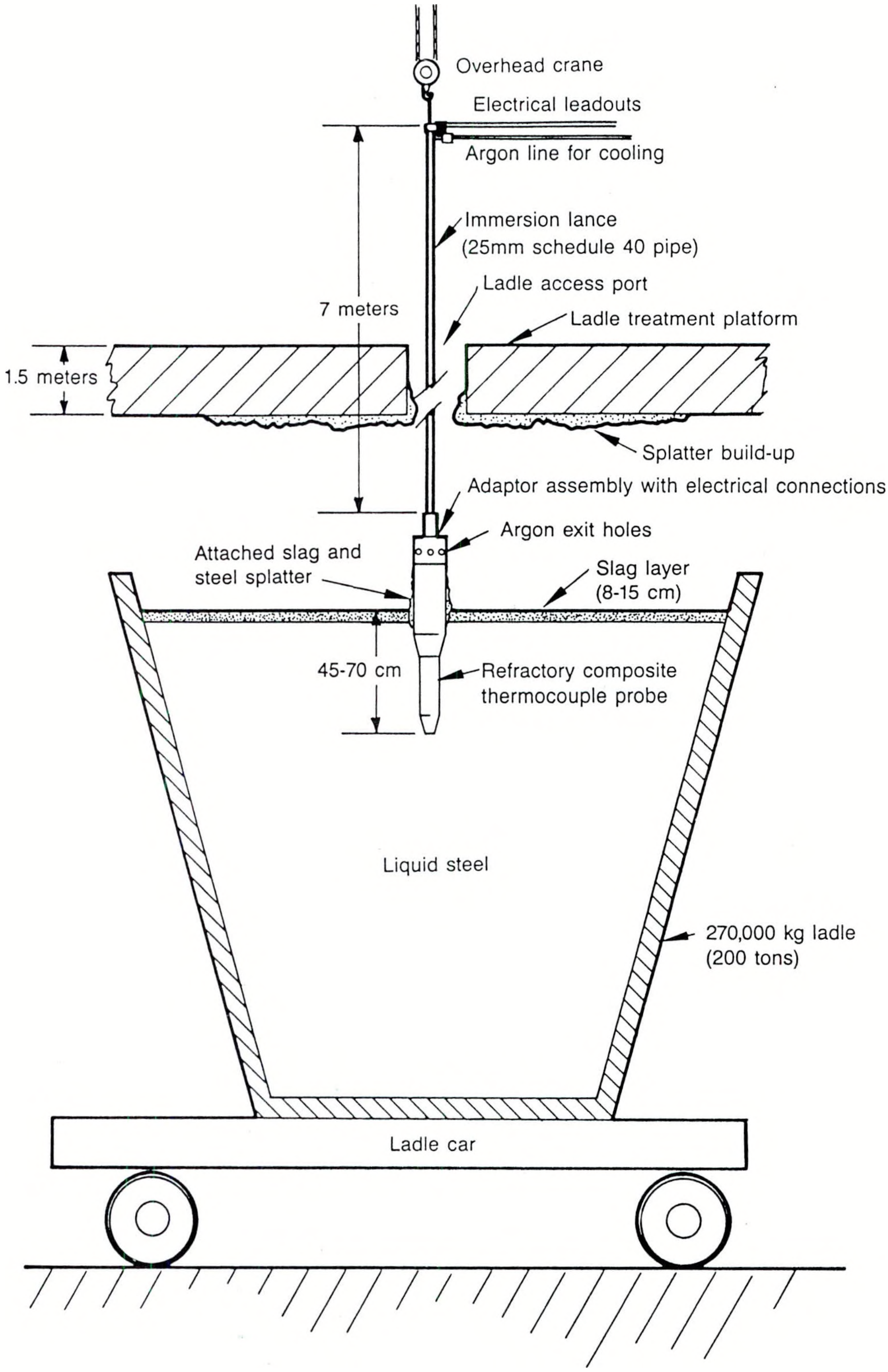

Figure 1. Schematic diagram of thermocouple installation at Bethlehem Steel Corporation's Sparrows Point Plant.

Figure 2(a). Ladle treatment platform and access port used for thermocouple testing.

Figure 2(b). 270,000 kg ladle used at BSC`s Sparrcws Point Plant showing typical slag cover.

3. SHEATHED THERMOCOUPLE DESIGN AND PERFORMANCE

Development of a thermocouple sheath suitable for continuous liquid steel temperature measurement has historically been a significant problem. While the technical requirements for continuous measurement in tundishes have recently been met, a simple extension of this technology proved inadequate for ladle treatment applications. Extremely aggressive slags, thermal shock, violent turbulence from chill scrap additions, argon stirring, splashing and skulling, and mechanical fixturing difficulties partially describe the technical obstacles encountered.

An iterative design approach consisting of a series of five different designs is described in this section. Two designs constructed of BN were tested and, as per DOE program requirements, acted as a performance gauge for results obtained using alumina-graphite and magnesia-graphite sheaths. Results from each series of tests were used as a guide for the subsequent test. In this manner it was possible to make significant progress toward a workable system. However, several key technical problems remain unsolved.

3.1 Boron Nitride Protection Sheaths

The major objective of this program was to test previously developed BN sheaths in ladle applications and to compare the suitability of BN sheaths with competing materials. Two distinct designs using BN sheaths were tested. The first design is shown in Figures 3 and 4. It was necessary to segment BN sections together because the hot isostatic pressing operation used for manufacture was limited to lengths of 30 cm. In all tests, the boron nitride was of high-purity BN-DUR (2), and two units were tested of the design shown in Figure 4. Thread tolerance was critical at the lower junction to prevent steel penetration. As an additional precaution, boron nitride paint was used to seal the threads. Again an alumina-encapsulated Type B thermocouple was inserted into the bore of the BN sheath and alumina powder introduced into the annulus to a depth of approximately 8 cm.

During the first BN test a frozen crust existed on the steel surface. A hole was broken through the crust using a pipe and the BN probe was immersed. A slight misalignment was present between the hole and probe; thus when the freshly broken hole began to re-freeze, the unit severed at the holder. There was not sufficient time for equilibration to occur and recovery of the unit was not possible.

In order to prevent a similar occurrence, the second BN probe was immersed after argon stirring which broke up the slag. The unit was first lowered over the ladle and allowed to achieve a temperature of 600°C. Upon insertion, full

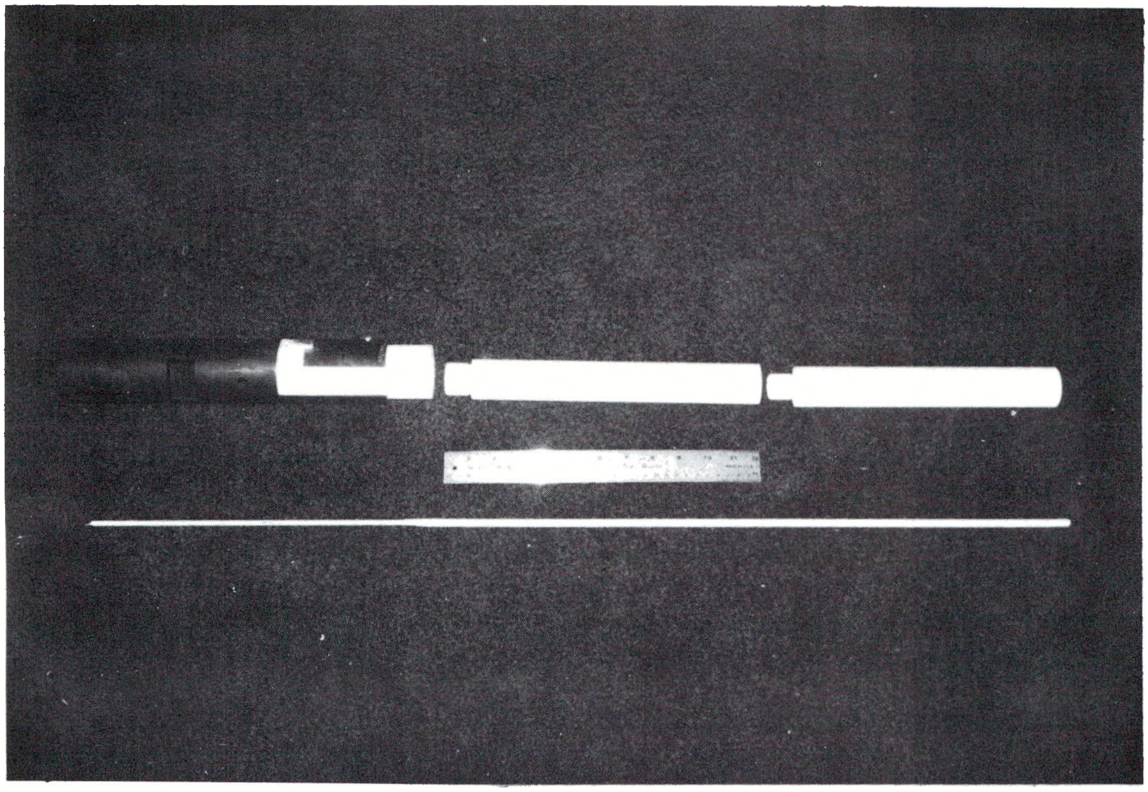

Figure 3. Segmented BN sheath showing fixturing holder and ceramic protection sleeve housing the thermocouple.

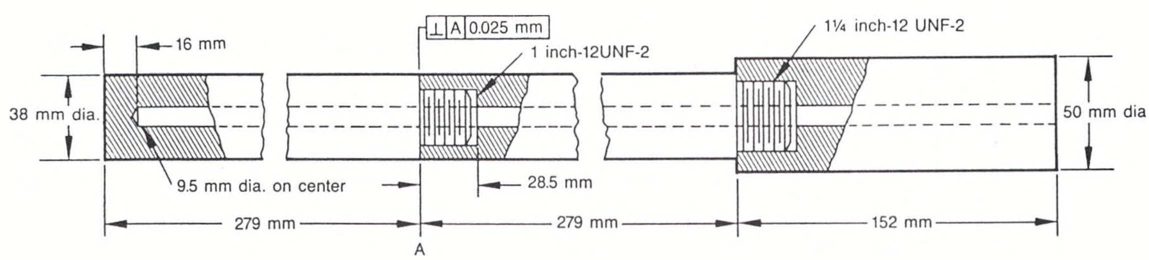

Figure 4. Segmented BN sheath showing actual dimensions.

equilibration required just under 6 minutes (Figure 6). A disposable temperature measurement was taken and the two systems were found to agree within 2^{o}C. Failure occurred almost simultaneously with temperature equilibration from severe slag line erosion [Figure 7(a)]. Figure 7(b) shows the unique non-wetting nature of BN; the attached slag was easily peeled away.

Based on the severe slag line erosion it was collectively decided with DOE to construct a hybrid BN sheath for further testing. The basic intent was to evaluate BN wear characteristics at locations not in contact with slag (i.e. the fully submerged portion). This design is shown in Figure 5. In this design, an alumina-graphite (A-G) tube was fitted with a BN closed-end sleeve, cemented, and pinned in place with an alumina rod. Again alumina powder (not shown) was placed in the annulus to a depth of approximately 8 cm.

The hybrid BN unit was immersed to a depth of 36 cm with no preheating and slightly over 6 minutes was required for temperature equilibration (Figure 6). At this point it was removed for inspection and reimmersed. At a total immersion time of 12 minutes the unit was removed for analysis. In the area immediately adjacent to the A-G sleeve an unusual double hour-glass wear pattern was observed [Figure 8(a)]. The bottom 10 cm of BN appeared to be unaffected by wear. A longitudinal crack running the entire exposed length of BN was, however, observed. From Figure 8(b) a relative comparison of wear between the BN and A-G may be made. Some necking of the A-G sleeve is apparent but not nearly as significant as the BN wear.

3.2 Alumina-Graphite Protection Sheaths

Based on the success of alumina-graphite (A-G) protection sheaths in tundish applications, this material became an obvious candidate for ladle treatment. Specifically, this composite material consists primarily of isostatically pressed alumina and graphite. The monolithic body is glazed to prevent oxidation of the graphite. As a generic industrial material, A-G is used routinely for ladle shrouds and tundish tubes and is available from a number of sources.

Construction of the A-G thermocouple probe is shown in Figure 9. The Type B thermocouple was contained in a high purity (99.8%) alumina double-bore insulator, that in turn was contained in a high-purity alumina closed-end sleeve to guard against contamination. It should be noted that this method of thermocouple construction was used in all assemblies tested. The clad thermocouple was then inserted into the A-G protection sheath and secured by tamping dead-burned (fully reacted) alumina powder (-325 mesh) into the annulus.

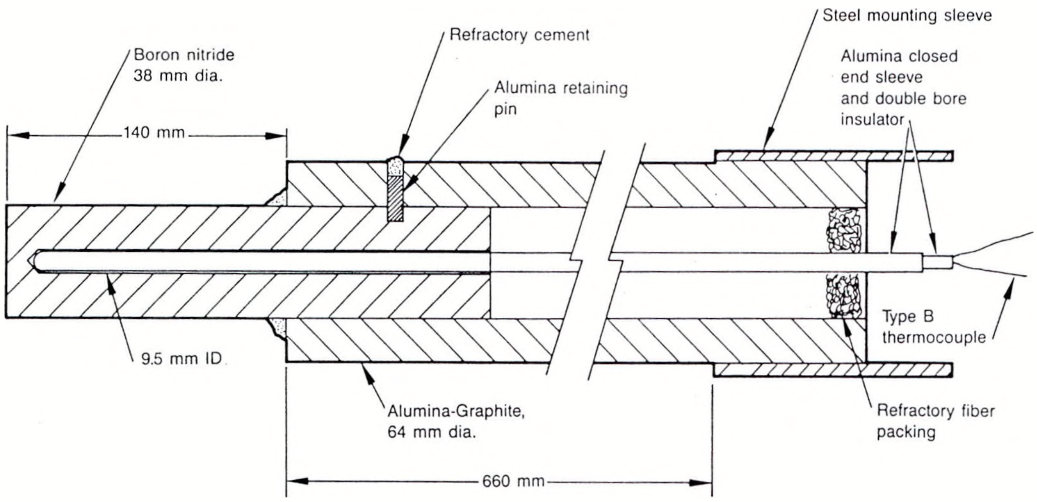

Figure 5. Composite BN and A-G thermocouple sheath.

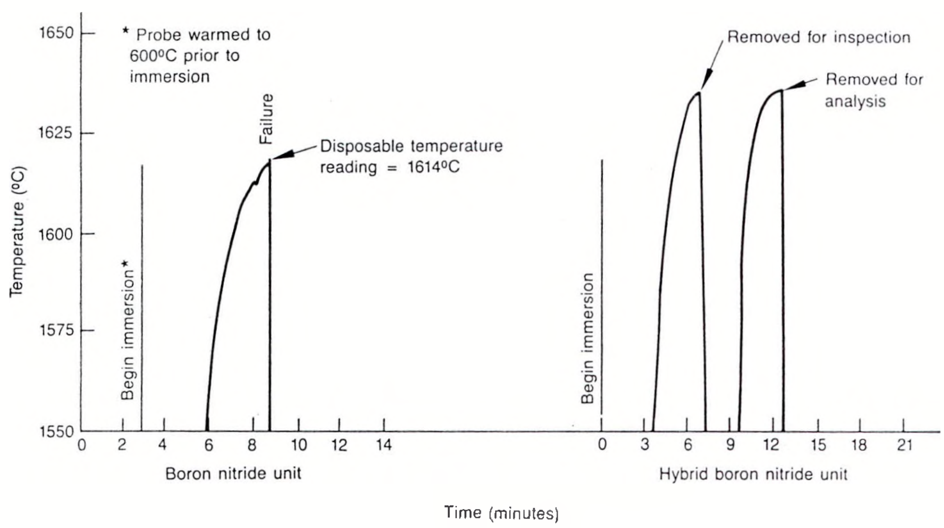

Figure 6. Molten steel temperature data for the segmented and hybrid BN thermocouple probes.

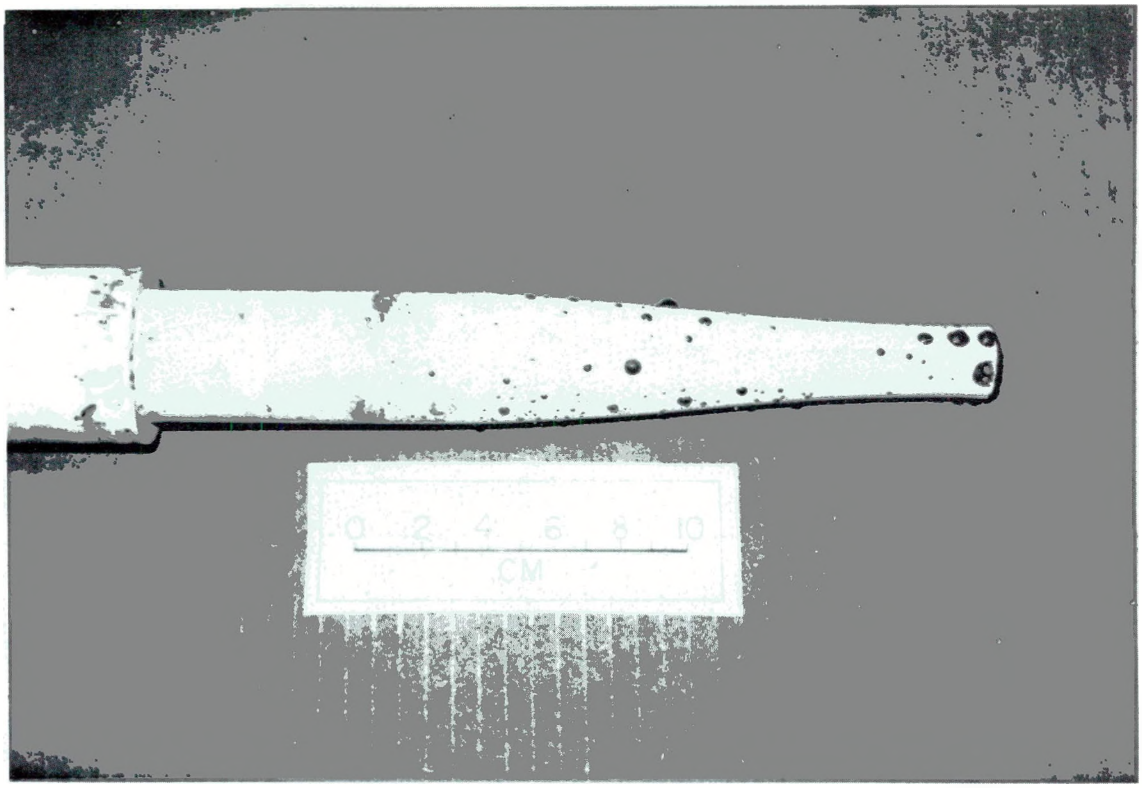

Figure 7(a). Segmented BN sheath showing slag wear after 6 minutes of immersion time.

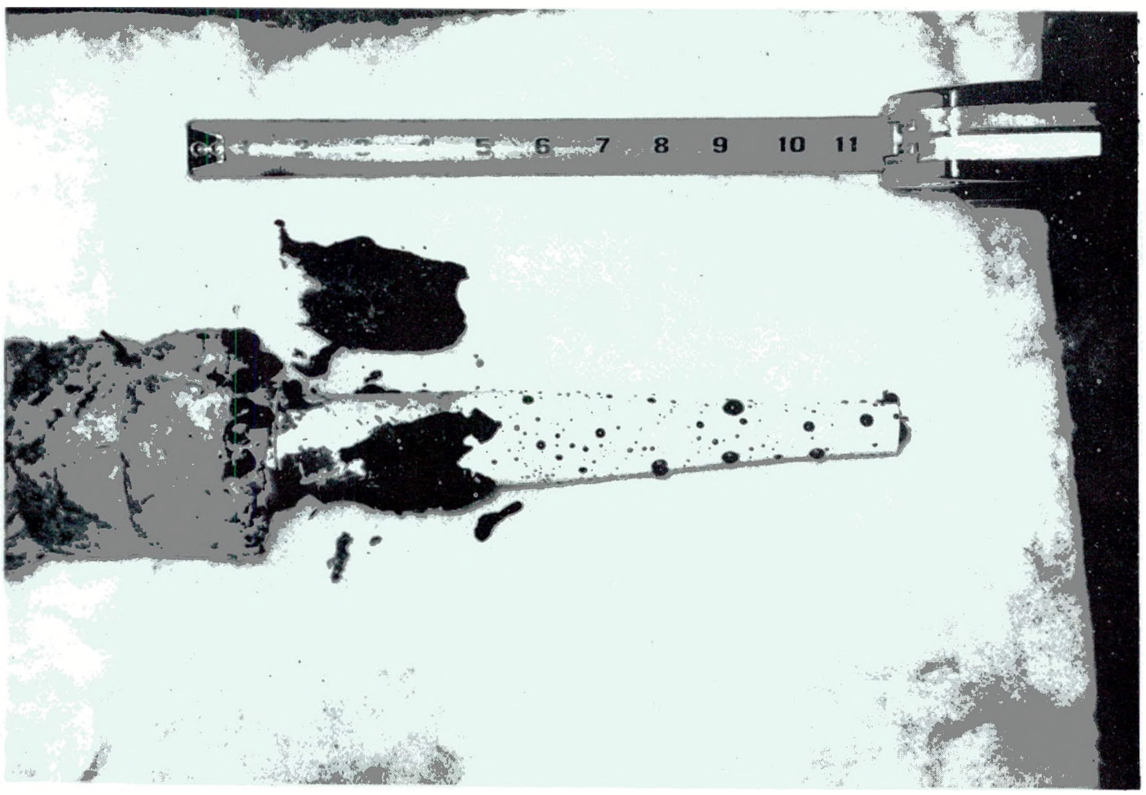

Figure 7(b). Segmented BN sheath showing non-wetting characteristics. Slag was easily peeled away.

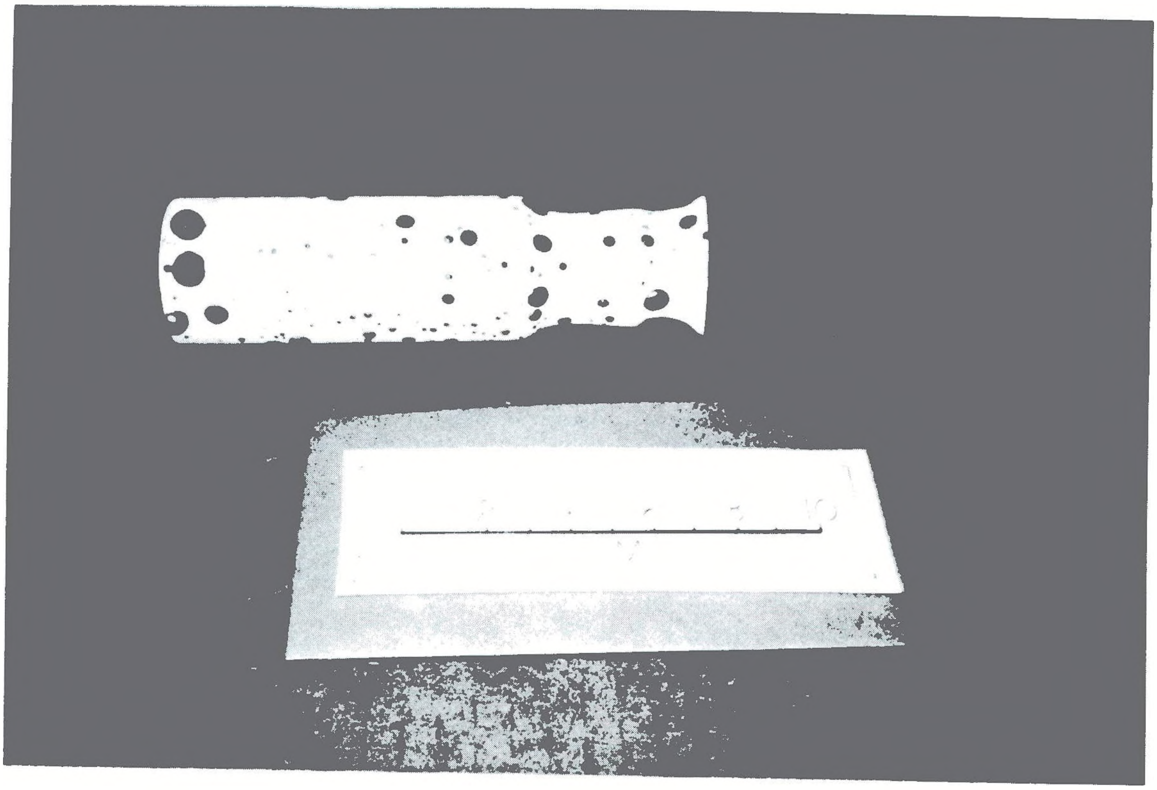

Figure 8(a). Hybrid BN sheath after 12 minutes of immersion time.

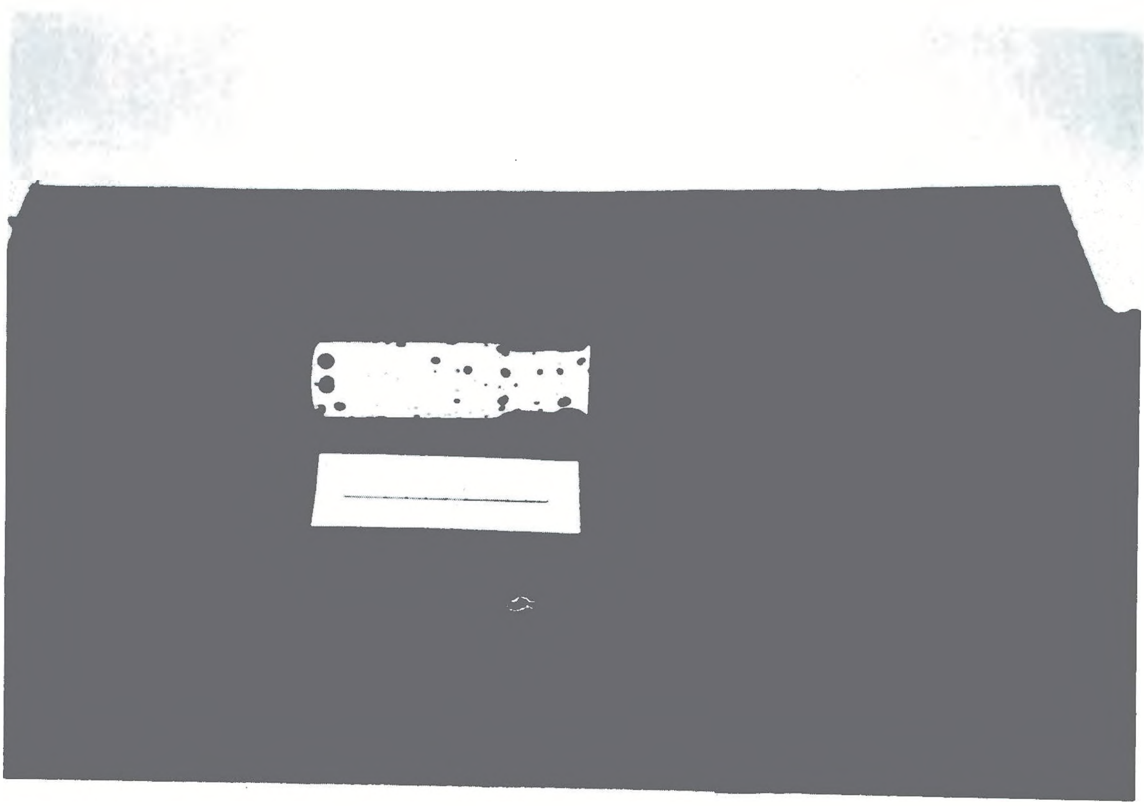

Figure 8(b). Hybrid BN sheath showing comparative wear with A-G.

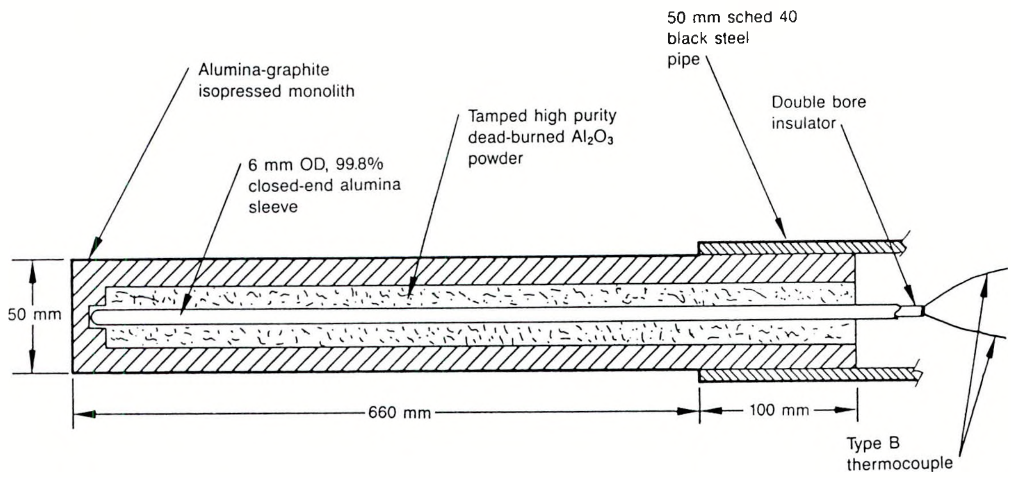

Figure 9. Construction of A-G thermocouple sheath.

During in-plant testing, the protection sheath assembly was joined to the immersion lance and immersed into the ladle with no preheat. After approximately 2 minutes, an apparent internal explosion occurred within the sheath which sheared the platinum thermocouple leads. Two possible explanations exist. First, the alumina powder could have absorbed moisture after assembly resulting in a steam explosion. As received, however, the powder moisture level was verified to be between 0.1 and 0.2 wt %, which is within acceptable limits. The second possibility is that voids existed within the powder resulting in a simple trapped gas explosion.

Subsequently, a second A-G unit was tested. Although most of the alumina powder was removed, approximately 8 cm was left in the bottom to increase thermal response. The unit was further baked at 120 ^{O}C for 24 hours and warmed to 500 C over the ladle before immersion. No problems were encountered upon immersion and temperature recordings were obtained. From Figure 10 it can be seen that the unit exhibited an unacceptably long thermal equilibration time (10 to 12 minutes). However, ability to withstand multiple immersions was demonstrated. Failure occurred from severe slag erosion at a total immersion time of 29 minutes. Before and after photographs of the A-G unit are shown in Figures 11(a) and 11(b). Based on the length of the wear zone shown in Figure 11(c) the slag layer was at least 15 cm thick.

The failed unit and a slag sample were examined both by scanning electron microscopy (SEM) and x-ray diffractometry. The chemical content of the slag sample was consistent with the typical analysis obtained from BSC's metallurgy department for low carbon steel which is shown in Table 1.

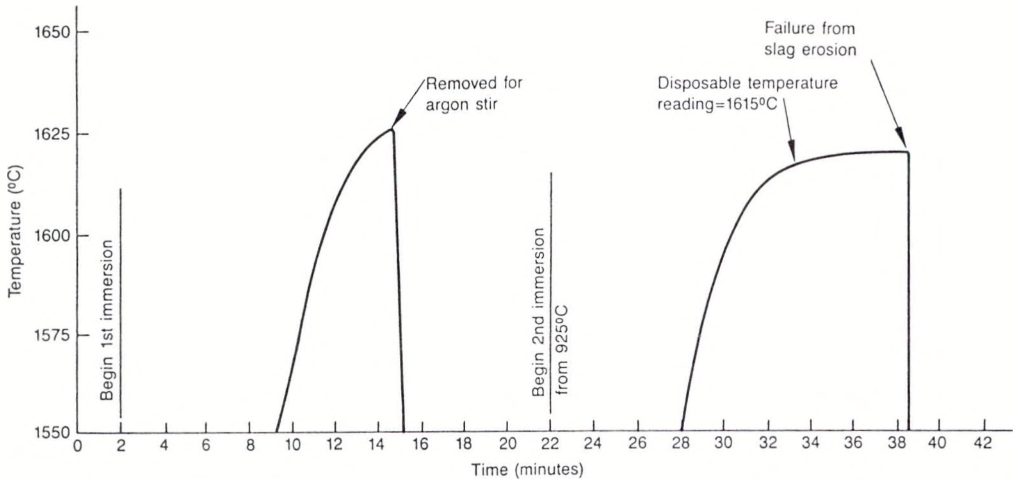

Figure 10. Molten steel temperature data for A-G thermocouple probe.

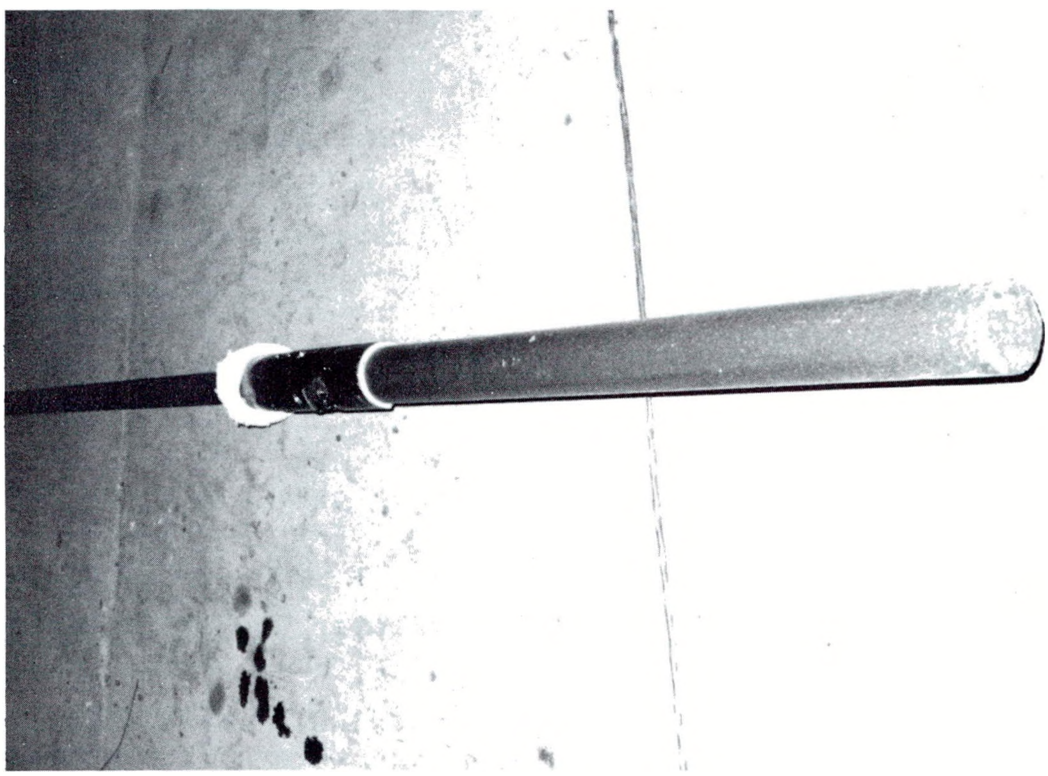

Figure 11(a). A-G thermocouple sheath and immersion lance used for insertion.

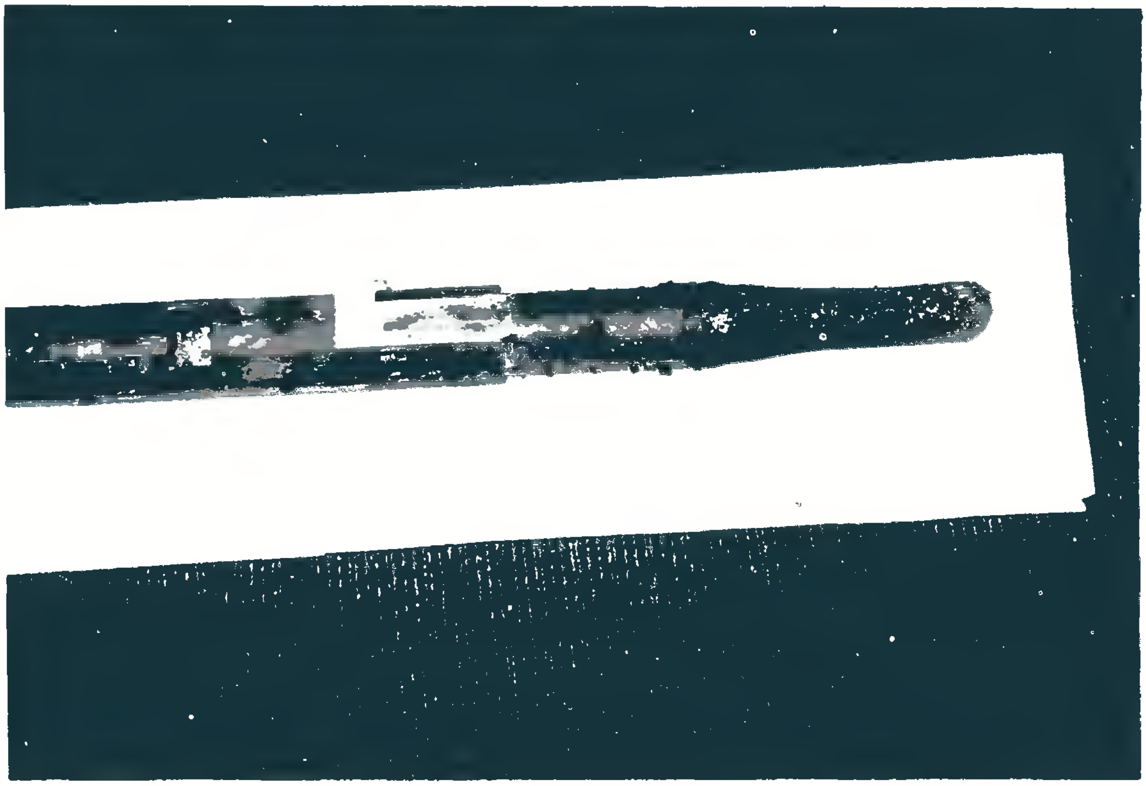

Figure 11(b). Failed A-G sheath after 29 minutes of immersion time.

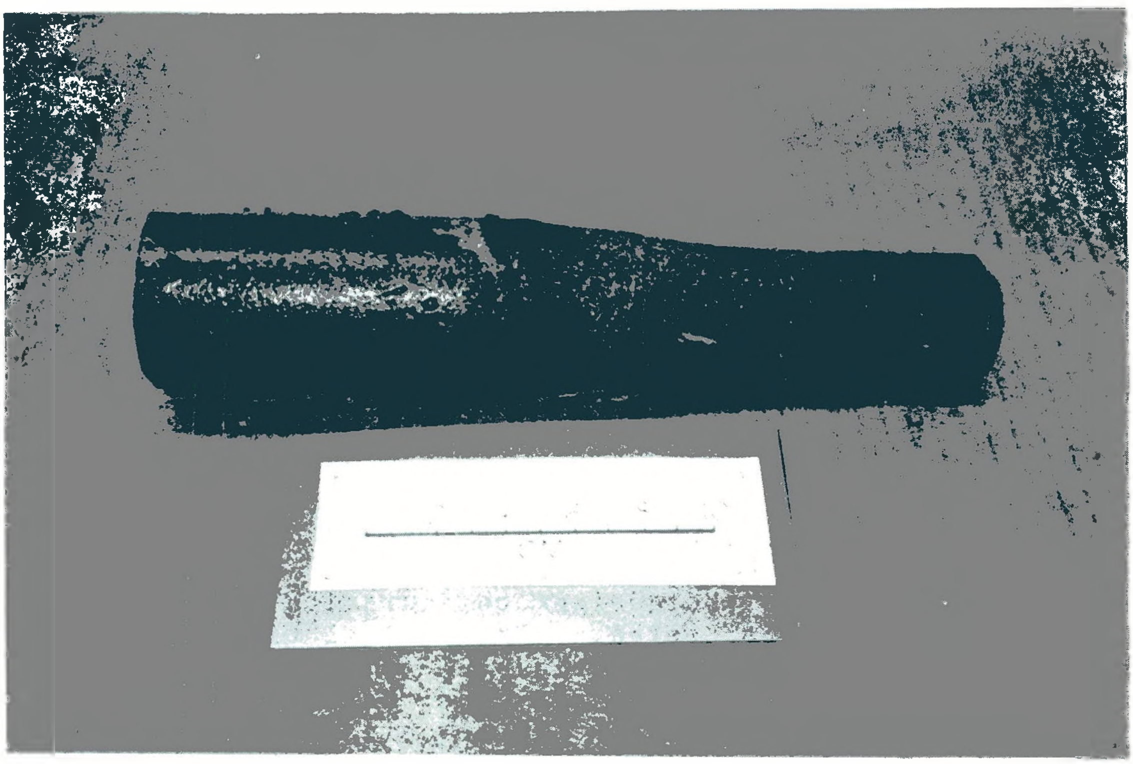

Figure 11(c). Close-up of A-G sheath showing uniform slag wear to the separation point.

Compound wt %

CaO	-	30 to 40
SiO_2	-	6 to 10
Al_2O_3	-	9 to 22
FeO	-	7 to 15
MgO	-	8 to 10
MnO	-	4 to 7

Table 1. Typical Ladle Slag Analysis for Low Carbon Steel

The large amount of CaO present results in a very basic slag, that when coupled with the large amount of FeO, yields an extremely corrosive environment. Based on the above slag analysis it was decided that a magnesia-graphite (M-G) material would be more suitable for a basic slag. Results using M-G are described in subsequent sections.

3.3 Magnesia-Graphite Protection Sheaths

In order to lower the chemical reaction potential between the protection sheath and the very basic ladle slag, five units were constructed of a magnesia-graphite (M-G) isopressed composite. Using an iterative approach, three sheaths were initially tested and these served to guide the redesign and testing of the remaining two.

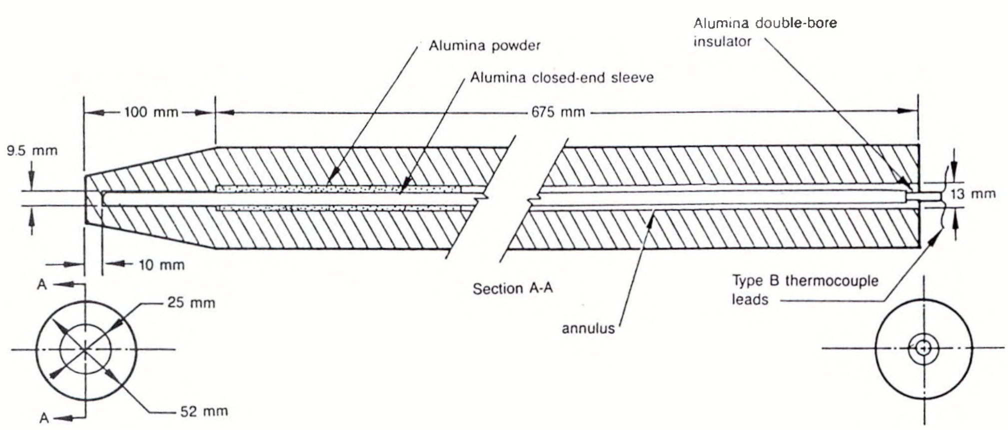

Figure 12. Construction of M-G thermocouple sheath.

Figure 12 shows the design configuration for the first three M-G sheaths tested. The conical tip, which is a departure from earlier designs, was added to enhance the thermal response. Additionally the thermal conductivity for for the M-G material is 10% higher compared to that for A-G. These two factors are responsible for a significant improvement in thermal response. The first M-G unit tested was immersed with no preheating and 4 minutes were required to achieve temperature equilibration [Figure 13(a)]. To circumvent premature breakage the unit was withdrawn before the argon stir. The same unit was immersed a second time after cooling with no preheating [Figure 13(a)]. Failure occurred from mechanical breakage at approximately 8 minutes into the second immersion. Note the greatly extended time required for temperature equilibration (8 minutes) as compared to the initial immersion time (4 minutes). Although it is not known for certain, it is presumed this is due to the insulation of the slag layer that was attached to the probe on withdrawal [Figure 14(a)] and had not yet melted on subsequent immersion. The exact reason for the mechanical failure is also not known. M-G material is more thermal shock sensitive than the A-G material and lack of preheating would suggest a high probability of thermal shock failure.

The second M-G unit was also directly immersed with no preheating and exhibited a time to temperature equilibration of approximately 4 minutes [Figure 13(b)]. Agreement with a disposable temperature measurement was within 2 $^{\circ}$C. After 14 minutes of immersion time the unit was withdrawn and showed little physical erosion. The same unit was again immersed, after cooling to ambient temperature, without preheating and remained in the ladle during the addition of chill scrap and argon stirring. Within 30 seconds from the beginning of chill scrap addition, the sheath separated and the thermocouple failed. Despite the severe mechanical violence, the failure could have been initially induced from thermal shock microcracking.

A third M-G sheath was tested, but no temperature data was obtained because of an on-site failure of the recording instrument. This unit, again without preheating was immersed into a quiescent ladle, quickly became frozen in slag, and remained in this condition for exactly 30 minutes. During the next argon stir it was possible to extract and recover the unit. Approximately half the wall thickness had eroded away at the slag line [Figure 14(b)], from which a total life of 1 hour was estimated.

Based on results from the first three M-G sheaths tested (Figure 12) it was apparent that even though significant improvements in response time were observed, progress with respect to thermal shock resistance and slag wear was insufficient. To afford additional protection at the slag line without adversely affecting thermal response, two tapered heavy-wall M-G units were fabricated (Figure 15). During test these units were first preheated over the ladle to approximately 500 $^{\circ}$C. To further minimize thermal shock the sheath was first immersed to a depth of 30 cm and was allowed to remain at this depth for 30 seconds, after which the immersion depth was increased to 70 cm. In so doing, the heavy-walled section was preheated by stem conduction from the thin-walled section. The first unit tested nearly achieved equilibration before the temperature reading was

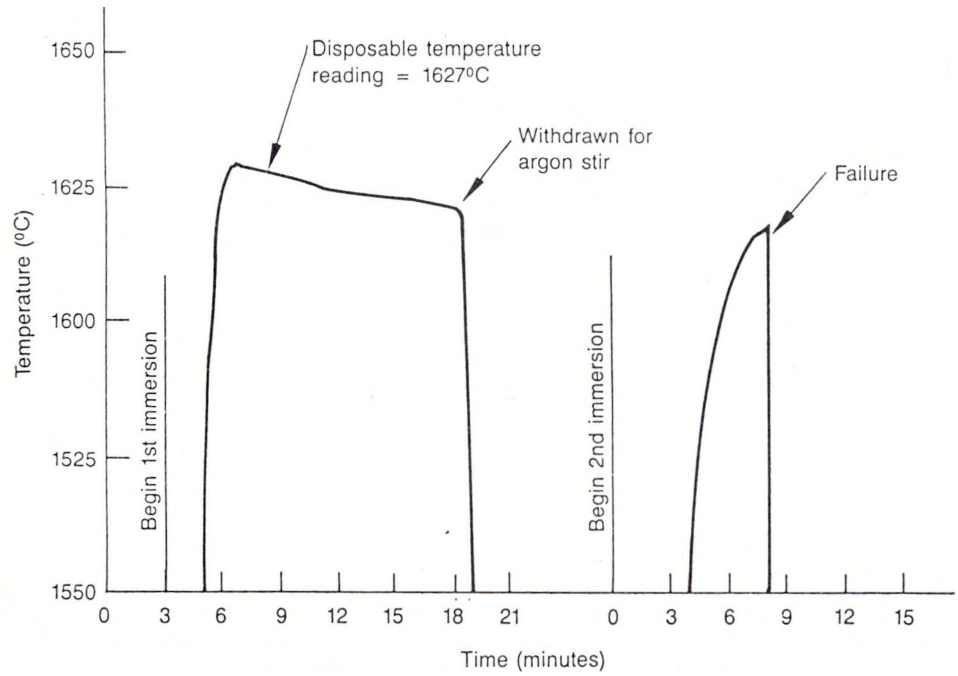

Figure 13(a). Molten steel temperature data for first M-G sheath tested.

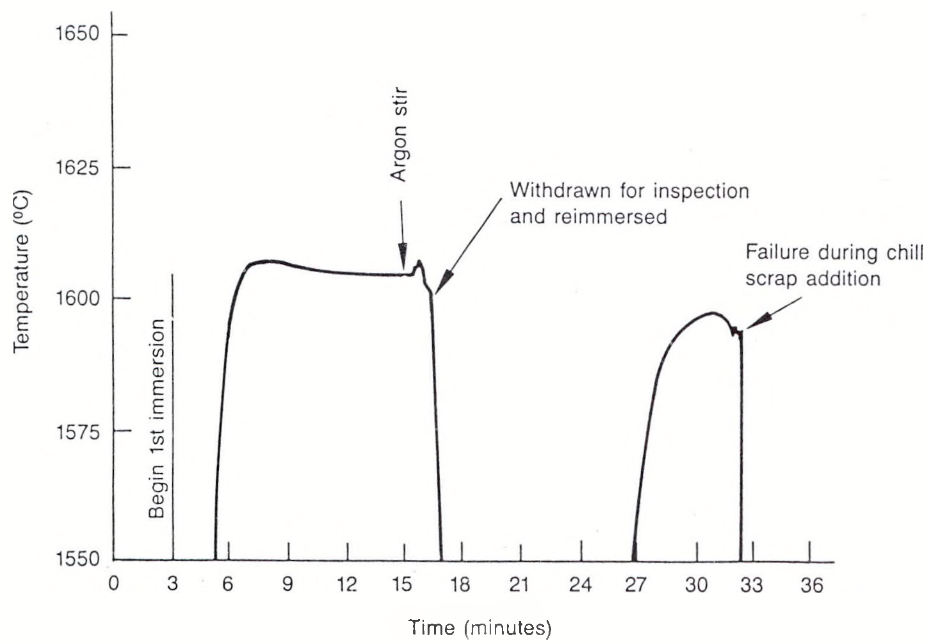

Figure 13(b). Molten steel temperature data for second M-G unit tested. Note failure from chill scrap addition.

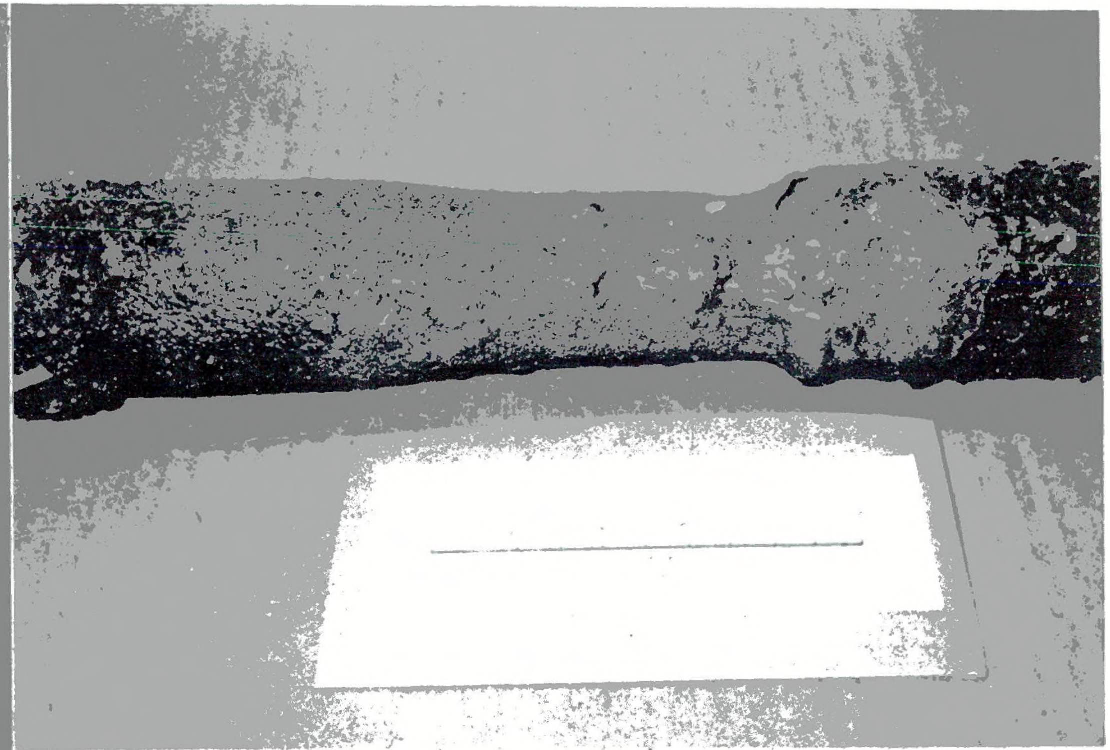

Figure 14(a). (left) M-G sheath with attached slag thought to be responsible for extended response time on subsequent immersion.

Figure 14(b). (above) M-G sheath after 30 minutes of immersion time. Approximately half the wall thickness had eroded away.

lost, at which time it was withdrawn for inspection. It appeared to be in tact and was reimmersed. It then began to indicate temperatures as shown in Figure 16. The indicated temperatures, however, were 14 °C lower than that indicated by a disposable thermocouple. At a total immersion time of 20 minutes, the sheath separated in the heavy-walled region during withdrawal. The fracture surface exhibited a wedge shaped appearance with no slag erosion; this was believed to result from thermal shock.

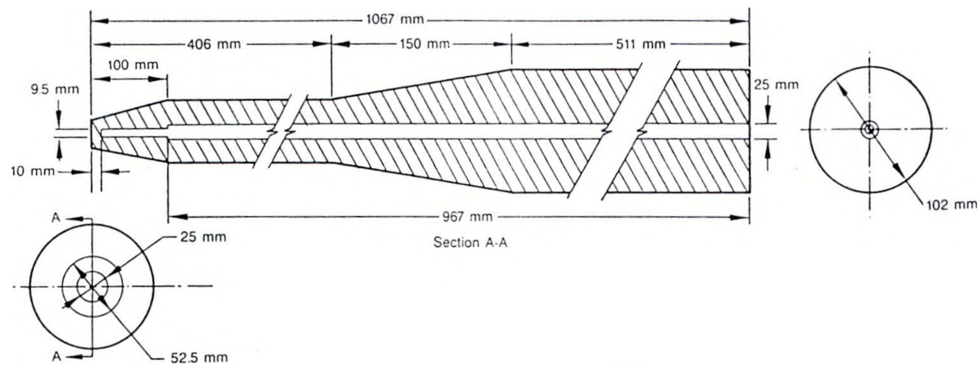

Figure 15. Construction of second generation M-G sheath.

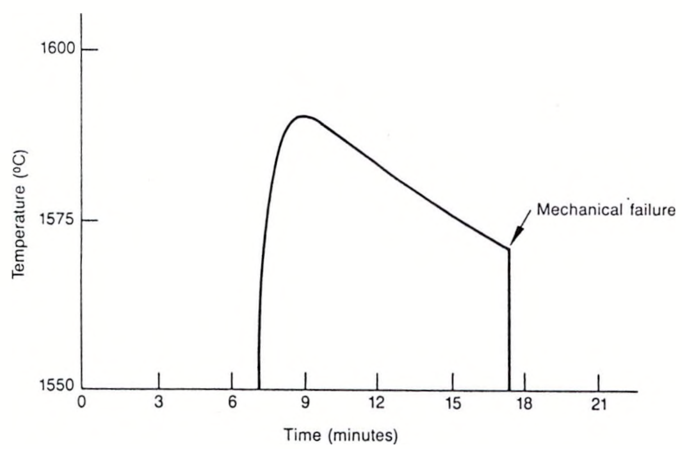

Figure 16. Molten steel temperature data from second generation M-G thermocouple probe. Failure was believed to be caused by thermal shock.

The second heavy-walled unit was similarly immersed. After temperature equilibration the indicated temperature was again 14 °C low compared with the disposable thermocouple measurement, and the temperature indications became intermittent (Figure 17). After withdrawal and inspection, which revealed no apparent damage, the probe was reimmersed. At approximately 10 minutes of total immersion time the temperature reading became stable. The temperature profile during the addition of chill scrap was recorded twice, and the metal cooling rate during argon stirring was also recorded (Figure 17). The probe was withdrawn after the first treatment cycle and immersed into the next ladle while still red hot. Because no chill scrap was added and the ladle was not argon stirred until 30 minutes later, a thick slag cover developed freezing the probe in place. Approximately 40 minutes of temperature data was recorded during the second treatment (Figure 17). The sheath exhibited no visible slag erosion after a total immersion time of 59 minutes [Figures 18(a) and 18(b)]. The probe was immersed into the third heat after cooling to approximatly 400 °C without any attempt at gradual entry. Temperature equilibration was never achieved and the unit separated in the heavy-walled section during withdrawal (Figure 19). Again a wedge shaped fracture surface was observed. Note the heavy buildup of attached slag.

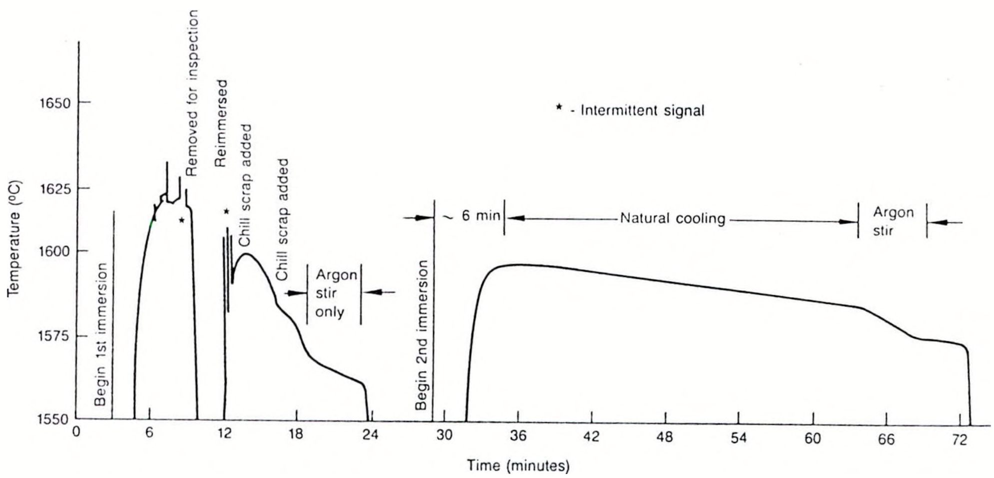

Figure 17. Molten steel temperature data from second generation M-G thermocouple probe showing the effects of chill scrap addition and argon stirring.

Analysis of the two failed sheaths suggest that failure occurred from thermal shock in both cases because of the relatively thick walled (38 mm) upper section. The increased wall thickness, however, is also believed to be responsible for virtually eliminating slag erosion. It was observed during testing [Figures 18(b) and 19] that a skull forms on the circumference of the probe at the slag line presumably caused by the greatly enhanced stem conduction of the 100 mm diameter section. It is further believed that the frozen slag acts to insulate the slag line from much of the erosion observed on previously tested, smaller diameter units.

It is not known for certain why a discrepancy in temperature

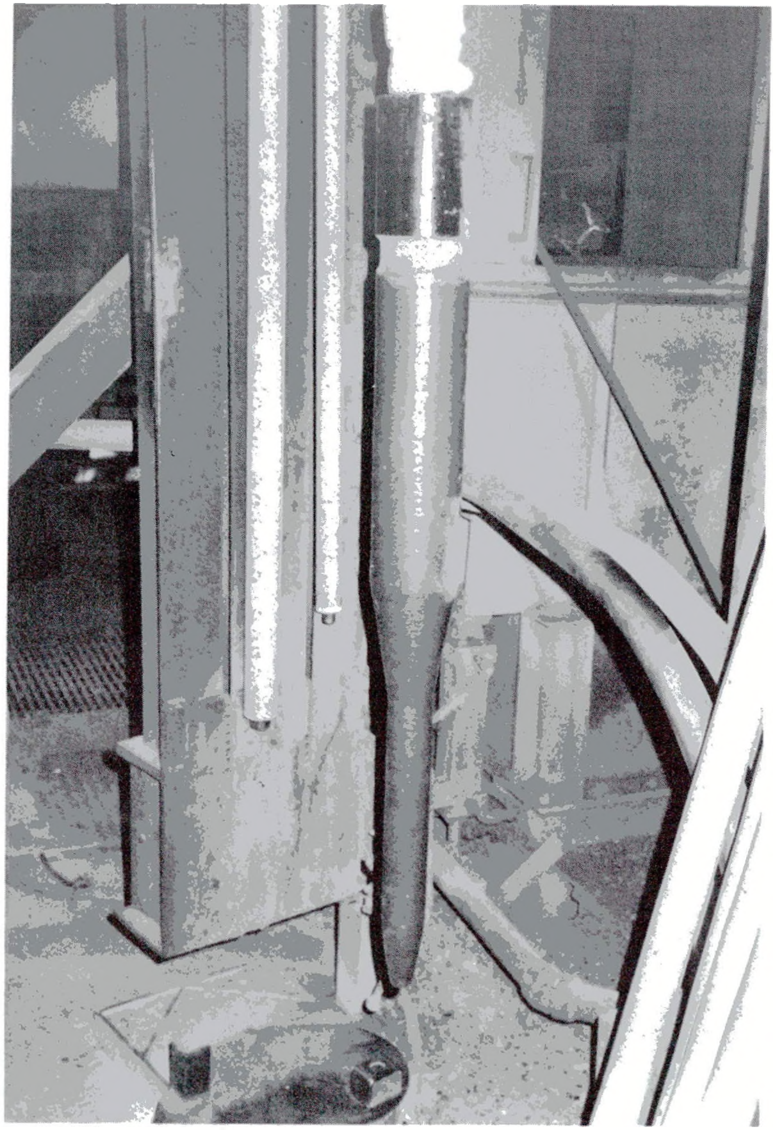

Figure 18(a). M-G sheath suspended over access port in preparation for test.

Figure 18(b). M-G sheath after immersion showing attached slag.

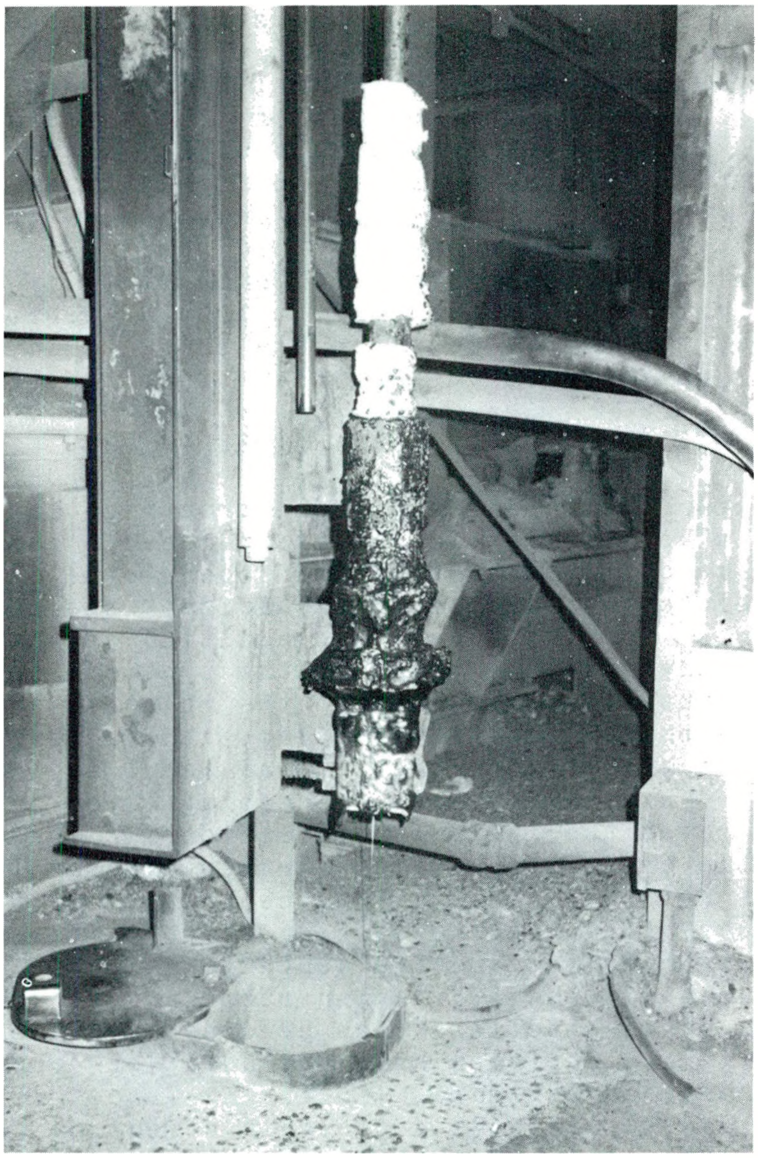

Figure 19. Failed M-G sheath after 59 minutes of immersion time. No slag line erosion was visible.

indications existed. Tests performed earlier with smaller diameter units had shown good agreement, and two possible explanations are suggested. First, it could be that the probe tip is not truly isothermal because of the greatly increased thermal stem conduction of the larger diameter section. Second, it was not possible (in contrast to the smaller units tested earlier) to form a true platinum-to-platinum connection between the probe and the immersion lance. A terminal pad was used that added parasitic thermocouples in the circuit. Generally, if the terminal pad is reasonably isothermal, little error would be introduced; however, considerable error could be expected because of the extreme radiant heat from the ladle.

4. IMPACT OF CONTINUOUS LADLE TEMPERATURE

Temperature measurement during ladle treatment has long been recognized as a key element in the assurance of steel quality. Many factors beyond the control of operators can, however, influence steel temperature which emphasizes the need for real-time measurement. For instance, the addition of chill scrap is not precise in many cases. Further the type of scrap added can have a significant effect because of the relative specific heats and associated chemical activity. Also, the development of the slag layer seriously effects the natural cooling rate and the amount of slag varies with time. The slag layer breaks up when the ladle car moves the ladle into position for treatment, but subsequent to the treatment, which further exposes liquid steel, the slag layer reforms, insulating the heat from radiant heat loss. The effect of the nature of slag on steel temperature, the rate at which it reforms and the depth to which it will develop are left to human judgement. Argon stirring (common practice during treatment) is also less than precise. Estimated numbers for the cooling rate during a stir are used by operators, but again this is only an estimate. Stirring lance configuration, flow rate, and size can have a dramatic affect on cooling rate. A more subtle, but nonetheless important effect is the previous thermal history of the ladle. A ladle which is "on-the-run" versus a ladle which has come off the dryer exhibit very different cooling rates during treatment. Again an operator must take all these factors into consideration when estimating the cooling rate during treatment. Continuous measurement of temperature would alleviate the guess work currently required during this critical operation.

Most significantly, with all considerations assessed, continuous measurement would afford a reduction in BOF superheat. Reductions in consumed energy alone would be dramatic, not to mention the additional refractory life of BOF and ladle linings.

5. CONCLUSIONS

Under this cost-shared effort, five different thermocouple sheath designs were tested during actual ladle treatment operations. A total of 10 sheaths constructed of three different materials (BN, A-G, and M-G) were consumed. Thermal shock, response time, and slag wear results varied widely.

Two designs of BN sheaths were tested (Figures 7 and 8). The unit shown in Figure 7 exhibited a time to equilibration of approximately 6 minutes and the poorest slag wear characteristics of all sheaths tested, with failure from slag line erosion occurring at 6 minutes. Evaluation of thermal shock properties resulting from repeated immersions was not possible because of premature failure. The cost of BN is somewhat prohibitive as well, being in excess of $2000 for the unit shown in Figure 7. To reduce cost and improve slag wear properties, a hybrid design (Figure 8) was constructed and tested. This unit showed improved wear characteristics, and based on the erosion present at 12 minutes of immersion time a 20 minute lifetime was projected. Total cost of BN required for this unit was approximately $700.

A-G isostatically pressed composite sheaths (Figure 3) were also tested exhibiting slightly improved slag wear characteristics compared with the hybrid BN design. Failure occurred at the slag line after a total immersion time of 29 minutes. An unacceptably long temperature equilibration time (10 to 12 minutes) was observed. However, this unit was able to withstand multiple immersions.

The best overall success was achieved using a M-G composite material. Two different designs were tested (Figures 12 and 15). Common to both designs, a conical tip was added to enhance thermal response. The smaller of the two designs (Figure 12) exhibited a temperature equilibration time of less than 4 minutes and a total estimated lifetime of 60 minutes. It was noted that, presumably because of the attached slag, temperature equilibration time was greatly extended (approximately 8 minutes) on a subsequent immersion.

To extend service life, heavy-walled M-G units were constructed and tested (Figure 15). Because of the additional wall thickness, these units were gradually immersed to reduce thermal shock. A dramatic improvement in slag wear was observed with this design. After 59 minutes the unit exhibited no visible slag wear, although a frozen skull had formed on the probe at the slag line because of the much higher thermal stem conduction. It is this frozen skull formation that is believed to protect the slag line zone from the erosion previously observed. Temperature equilibration time was extended to 6 minutes using the heavy-walled units, but these units appeared to be more thermal shock sensitive than units previously tested.

In summary, an M-G thermocouple sheath has evolved that is capable of withstanding an entire ladle treatment cycle at much lower cost. Estimated cost to the end-item user of the sheath (thermocouple not included) would be in the $150 range. Further, it was shown that dramatic improvements in slag wear properties were obtained through appropriate design and that multiple immersions are possible with judicious preheat.

6. FUTURE WORK

Future effort should focus on improving thermal shock resistance and response time. An obvious initial approach would be to modify the relative ratios of magnesia and graphite because a higher ratio of graphite to magnesia would improve both thermal shock sensitivity and response. The drawback is that resistance to slag line erosion would be compromised. However, if a sufficient wall thickness were maintained (i.e. sufficient wall thickness to maintain a protective frozen skull at the slag line), the resistance to erosion could be acceptable. Further, efforts should also focus on the reduction of wall thickness to improve thermal shock resistance while maintaining satisfactory slag wear properties. This approach presents a trade-off situation with mechanical strength and would probably require extensive field evaluation.

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SHEATHED THERMOCOUPLES FOR CONTINOUS MOLTEN STEEL TEMPERATURE MEASUREMENT DURING THE LADLE TREATMENT PROCESS

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