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IMPROVEMENT IN HYDROGEN MEASUREMENT TECHNIQUE FOR MOLTEN ALUMINUM

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Abstract

The hydrogen content of molten aluminum can be assessed through in-line measurements using equipment such as AlSCAN, Telegas, or Notorp and through laboratory methods such as LECO Nitrogen Carrier Fusion or Hot Vacuum Subfusion Extraction (HVE). It is generally recognized that differing hydrogen results can be obtained by different methods. The AlSCAN method has been observed to have a bias relative to other methods that produces higher hydrogen measurements. The extent of this bias appears to depend on ambient humidity and temperature. An explanation for the bias has been discovered and an equipment modification to eliminate it has been developed and extensively tested through comparisons with Notorp and LECO.

Introduction

The ability to accurately measure low levels of dissolved hydrogen is critical in the casting of ingots for aerospace applications. Excess hydrogen in the molten metal can generate porosity in the ingot which is not removed in subsequent processing steps. Hydrogen specifications are typically in the range of 0.1 to 0.2 ppm, so the measurement method must be capable of providing reliable values at quite low concentrations. If the measurement method is to be used to determine if the ingots are acceptable for further processing, an on-line method that provides immediate results is preferred. While hot vacuum subfusion extraction (HVE) has generally been considered the most accurate technique, the specialized equipment it requires makes it impractical for production use [1].

Within Alcoa, hydrogen measurements are typically done by either the nitrogen carrier fusion or closed-loop recirculation techniques. In nitrogen carrier fusion, a solid metal sample is subjected to a standardized power/time cycle to independently vaporize surface hydrogen and dissolved hydrogen into a stream of argon [2]. The hydrogen content of the gas is measured by thermal conductivity. This off-line method will be referred to in this paper as LECO, the manufacturer of the instrument used for the analysis. Closed-loop recirculation techniques include the Telegas and AlSCAN instruments [3, 4]. These instruments circulate a small volume of nitrogen carrier gas through a ceramic probe immersed in the metal. The hydrogen content of the carrier gas, measured by thermal conductivity, eventually reaches equilibrium with the hydrogen in the metal. To assure equilibrium, the carrier gas circulates for 5 minutes or more. The analyzer then calculates the hydrogen content of the metal, corrected for both metal temperature and alloy composition, according to Sievert's Law. A third type of instrument, Notorp, developed by TYK Corporation, was used in this work. Notorp uses a high temperature proton conductor as a solid electrolyte to generate a hydrogen concentration cell in the sensor. A standardized gas containing about 1% hydrogen provides a reference state and the hydrogen content of the metal is calculated from the emf of the electrochemical cell.

Several previous studies have compared the performance of the HVE, LECO, Telegas, and AlSCAN techniques [5, 6]. These studies indicate that AlSCAN measurements give slightly higher hydrogen concentrations than the other methods. Although the LECO technique is subject to inaccuracies from sampling technique and equipment maintenance, it can produce hydrogen measurements consistent with HVE and Telegas results.

The Alcoa Davenport ingot plant relied on Telegas measurements to assess hydrogen content until Alcoa stopped supporting those instruments in the mid-1990's. Extensive testing was carried out at that time to compare AlSCAN and Telegas measurements. A consistent bias was demonstrated where AlSCAN read higher than Telegas, requiring an adjustment to Davenport's internal specifications. The extent of the bias appeared to change with the ambient dew point leading to two internal limits, depending on the season. Although this was an undesirable situation, extensive testing was unsuccessful in determining the source of the bias.

Background

In an effort to improve the availability of the AlSCAN units, a decision was made to see if some routine repairs could be performed in-house instead of returning the units to the manufacturer. The internal pumps of the AlSCAN units had been known to occasionally fail and were identified as being a relatively easy component to replace. A supplier of pumps for medical devices was found where pumps could be readily ordered and received in a short period of time. It was discovered that the pump supplier offered various elastomers for the pump components, including silicone, neoprene, Viton, EPDM and natural rubber. It was known that a silicone membrane was specified for the AlSCAN pump and an investigation into other elastomers was made to determine if there was a more suitable material for measuring hydrogen that would result in a longer pump life.

Research into the attributes of elastomer materials led to the Cole-Parmer® General Catalog [7]. The primary concern in selecting an alternative elastomer was in identifying one that had good to excellent chemical resistance to products that may be drawn into the AlSCAN unit when it measures the hydrogen content of molten metal. Maintaining the integrity of the pump elastomer components was critical in determining the elastomer material, as an improper selection could result in an unknown failure that would allow ambient air to be entrained into the analysis gas flow, resulting in erroneous measurements. The gas analysis products thought to potentially have an impact on the chemical resistance were identified as aluminum chloride, aluminum fluoride, hydrochloric acid, low concentrations of hydrofluoric acid and hydrogen gas. Comparison of the general performance characteristics across the possible elastomer materials revealed that Viton had the best resistance to chemical attack, as shown in Table 1.

Table I. Chemical Resistance Ratings [7]

Chemical	EPDM	Natural Rubber	Neoprene	Silicone	Viton
Aluminum Chloride	A	A	A	B	A
Aluminum Fluoride	A	B	A	B	A
Hydrochloric Acid	A	A	C	D	A
Hydrofluoric Acid (20%)	D	B	B	D	A
Hydrogen Gas	A	B	A	C	A

A – No Effect, B – Minor Effect, C – Moderate Effect, D – Severe Effect

Three Viton elastomer pumps were ordered and one was installed into an AlSCAN unit. Leak checks, pressure checks, flow checks and calibration checks were performed using the procedure described in the AlSCAN Maintenance and Operation Manual [8]. The critical components that were replaced with Viton material were the pump diaphragm, seals and gaskets. Figure 1 shows the components for the original pump and the Viton pump.

The initial hydrogen analysis using this AlSCAN unit was made on a production drop of ingots with a standard AlSCAN unit running beside it to verify that the Viton pump change did not affect the measurement results. A difference in measurement results between the two AlSCAN units was observed with the unit containing the Viton pump having lower hydrogen content. Several changes were made to different AlSCAN units with both standard pumps and Viton pumps to try to understand what contributed to the measurement differences. In addition, increased maintenance checks for leaks, pressure, and flow were performed weekly, and whenever pumps were changed out, to ensure that the AlSCAN would operate properly. Hydrogen measurements were also obtained using Notorp instruments; both Notorp and LECO® hydrogen analyses produced results that were consistent with the Viton pump AlSCAN. It was not initially recognized that the differences observed in the measurement results were a significant discovery related to the elastomer material used in the pump itself. When repeated production measurements from the side-by-side AlSCAN units equipped with Viton and standard pumps produced consistently different results, it was realized that a more controlled evaluation was necessary.

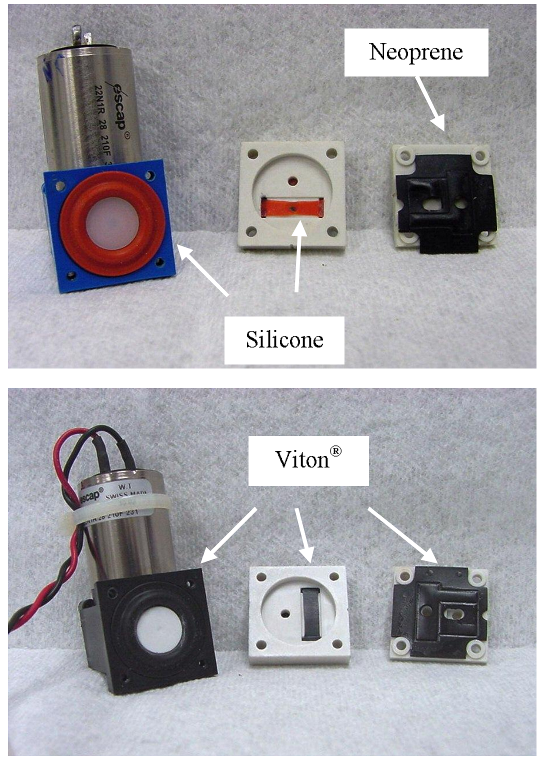

Figure 1. AlSCAN pump elastomer components: standard pump and Viton® pump.

Technical Results and Discussion

Several trials were designed and carried out to determine if the Viton pumps were responsible for the measurement differences or if other factors may have contributed. The trials consisted of obtaining hydrogen readings on a number of production drops with different aluminum alloys, differing ambient dew point conditions and atmospherically controlled chambers for the AlSCANs. AlSCAN readings were taken every minute for ten minutes prior to the start of the next AlSCAN cycle. The tenth reading in each cycle is considered to be the hydrogen content for that particular cycle. As the hydrogen measurements are taken with the AlSCAN, each cycle tends to have a lower hydrogen reading; this was thought to have been the result of moisture in the measurement loop being eventually driven off. In addition, the slope of the curve through the ten minute cycle typically remains steep throughout all the measurement cycles for any given production drop.

All of the trials were run on production drops of rectangular sheet ingots and across a number of different alloys including 2xxx, 5xxx, and 7xxx alloy series. The AlSCAN and Notorp units were positioned downstream of a multi-stage degasser. Measurements were taken from the metal stream in the casting station's distribution trough.

One evaluation was performed on a 7xxx alloy being cast using two AlSCAN units running side-by-side. The ambient dew point during the cast was recorded as 30°F. One AlSCAN unit was equipped with a Viton pump and the other with the standard pump. Two Notorp units were also positioned next to the

AlSCAN units to measure the hydrogen content. The results of the hydrogen readings are shown in Figure 2.

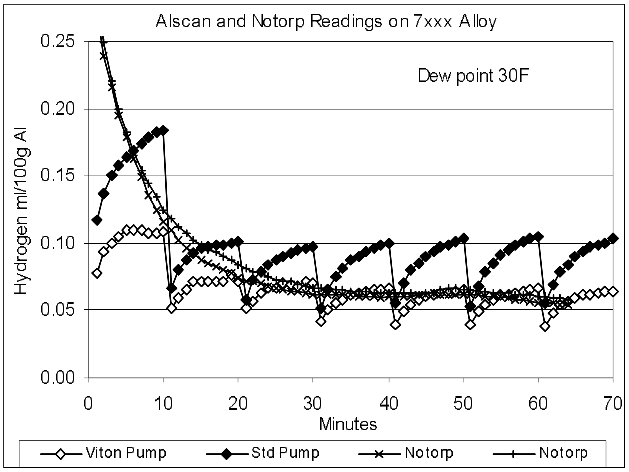

Figure 2. Low dew point AlSCAN and Notorp hydrogen results on 7xxx alloy using Viton® pump AlSCAN, standard pump AlSCAN and Notorp®.

The hydrogen measurements show that the two Notorp units and the Viton pump AlSCAN had lower hydrogen readings after the first measurement cycle. As the cycles progressed, the readings from the Viton pump AlSCAN flattened out through each ten-minute cycle and progressively measured slightly lower hydrogen content, consistent with the continuous Notorp results. The AlSCAN with the standard pump measured higher hydrogen content with a steeper slope within each cycle. At lower ambient dew points, the difference between the AlSCAN units with the different pumps can be clearly observed.

At higher ambient dew points, the difference between the AlSCAN equipped with the Viton pump and the standard AlSCAN becomes even more pronounced. Two AlSCAN units with Viton pumps were placed side-by-side with a standard pump AlSCAN and a Notorp unit. The results from this 7xxx alloy being cast with an ambient dew point of 59°F are shown in Figure 3. The metal flow rates between this trial and the one shown in Figure 2 were comparable.

The results show that the AlSCAN measurements with the standard pump are substantially higher throughout all the measurement cycles compared to that of the AlSCAN with the Viton pump, as well as the Notorp unit. The two Viton pump AlSCAN units tracked closely with Notorp results over the course of the drop. The measurement slope within each cycle for the Viton pump AlSCAN is much flatter and more similar to that from the low dew point trial. However, the standard AlSCAN measurement slope is more pronounced at the higher dew point when compared to the same unit at a lower dew point.

The results illustrated by these two trials, along with supporting results from similar trials not reported here, indicate that the measurements from the Viton pump AlSCAN are relatively insensitive to changes in dew point compared to the standard pump AlSCAN. The evidence from these trials indicates that during high dew point conditions, the standard pump AlSCAN over-states the actual hydrogen content.

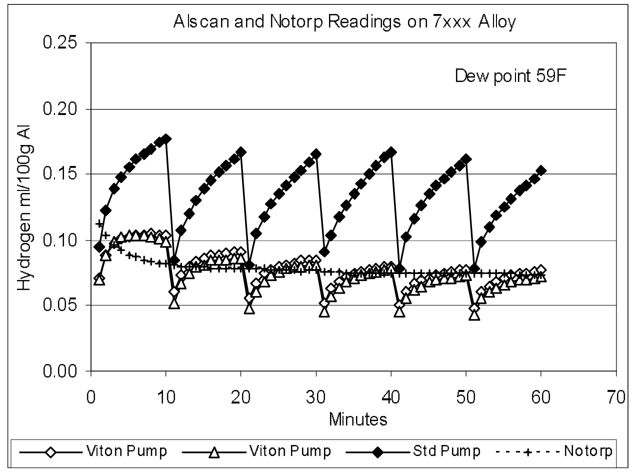

Figure 3. High dew point AlSCAN and Notorp hydrogen results on 7xxx alloy using Viton pump AlSCAN, standard pump AlSCAN and Notorp.

To further help understand the relationship between dew point and the elastomer material used in the AlSCAN pump, a chamber was constructed to house the AlSCAN units. Dry air was used to control the atmosphere in the chamber to a dew point of less than 5°F. A Viton pump AlSCAN and a standard pump AlSCAN were placed in this chamber. Figure 4 shows the chamber used to house the two AlSCANs.

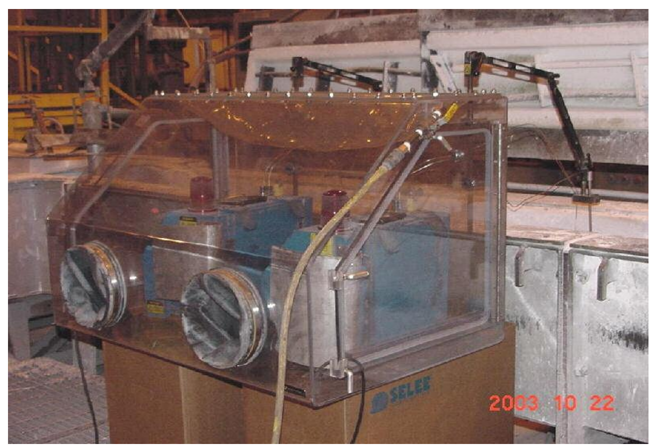

Figure 4. Dry air chamber housing AlSCAN units.

The chamber was constructed from ordinary materials available in the cast house and consisted of a clear plastic box fitted with an air line for dry air and two mounts for the AlSCAN probe arms. Inlets holes were drilled for the probe tubing and thermocouple wires. A high performance digital thermo-hygrometer was placed inside the box to measure dew point.

Outside of the controlled-atmosphere chamber, another Viton pump AlSCAN was run side-by-side with two Notorp units. The trial was performed on a 7xxx alloy series production cast of ingot with an ambient dew point of 63°F. Results from the five hydrogen measurement units are displayed in Figure 5 and some minor variability between devices can be seen. It is clear from the graphical data that during the first part of the test all of the AlSCAN units, including the standard pump AlSCAN inside the dry air chamber, are behaving in a similar manner. A flatter measurement slope for hydrogen is evident within each measurement cycle. This is typical to that seen with the Viton pump AlSCAN units in Figures 2 and 3. After recording measurements for 41 minutes, the dry air to the chamber was turned off and the doors were opened to allow the humid, 63°F dew point air to fill the chamber. An immediate change was noted with the standard pump AlSCAN housed in the dry air chamber. The slope of hydrogen results within the measurement cycle became steeper for the standard pump AlSCAN and it showed a significant increase in its value for the hydrogen content of the melt.

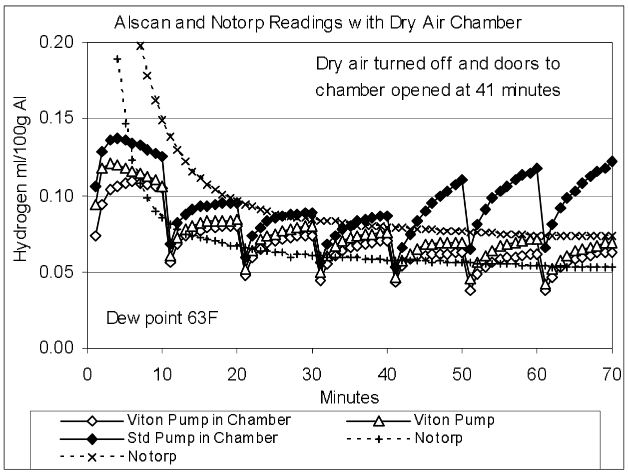

Figure 5. Dry air chamber AlSCAN and Notorp® hydrogen results on 7xxx alloy using Viton® pump AlSCAN, standard pump AlSCAN and Notorp®.

Another trial, illustrated in Figure 6, was run with a Viton pump AlSCAN and a standard AlSCAN in the dry air chamber. The chamber was left open at the start of a 7xxx alloy series production cast of ingots. The ambient air, with a dew point of 70°F, was allowed to flow into the chamber prior to the start of casting. Significantly higher hydrogen readings were measured with the standard AlSCAN unit while the Viton pump AlSCAN and Notorp showed close agreement. After 30 minutes, the chamber doors were closed and the dry air was turned on. No changes were observed in the hydrogen readings for the Viton pump AlSCAN and Notorp, but the standard AlSCAN started to read values comparable to the other units in the trial. Within 20 minutes after the chamber was sealed, both AlSCAN units gave similar results. At that time, 50 minutes into the production drop, the dry air was turned off and the box was opened again to the humid, ambient conditions. The standard AlSCAN immediately began giving higher hydrogen readings when the dry air atmosphere was removed.

The dry air chamber results are the strongest evidence supporting the hypothesis that the Viton pump is unaffected by ambient dew point influences in the AlSCAN measurement of hydrogen content of molten metal. The results show that the Viton pump produces a much flatter measurement slope for hydrogen within a measurement cycle compared to the standard pump. When the standard pump is placed in the dry air chamber, it too produces the same flatter slope of hydrogen readings within a cycle. The Viton pump shows no significant differences between a unit housed in the dry air chamber and a similar unit outside the dry air chamber when measuring the same molten metal stream. The final, end of cycle hydrogen results are similar between the Viton pump AlSCAN, Notorp unit and the standard pump AlSCAN housed in the dry air chamber, regardless of the ambient dew point conditions.

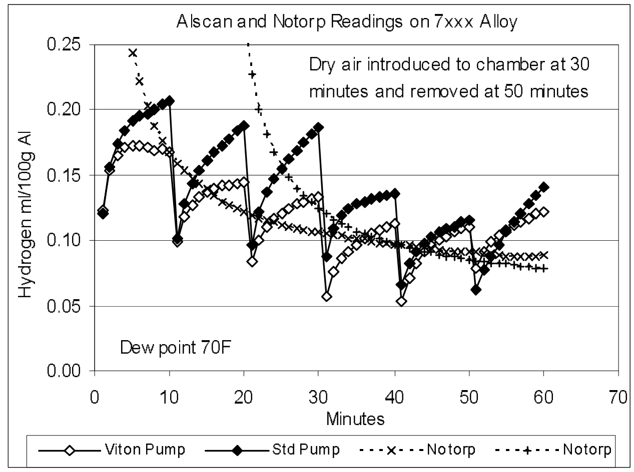

Figure 6. Dry air chamber AlSCAN and Notorp hydrogen results on 7xxx alloy using Viton pump AlSCAN, standard pump AlSCAN and Notorp.

The Viton pump trials have also provided additional information on the ability to detect changes in melt hydrogen content. Notorp is excellent in detecting rapid hydrogen changes and the Viton pump can also detect increases in hydrogen content, although it is not as sensitive to these changes as Notorp. Figure 7 shows increases in readings as the metal level rapidly rises in the casting trough, generating a high transient metal flow rate and reducing the residence time in the degassing unit. The spikes in hydrogen readings observed with Notorp correlate to the metal level increase in the distribution trough. There is a slight increase in the results from the Viton pump AlSCAN but it is not detectable with the standard pump AlSCAN operating outside of a dry air chamber.

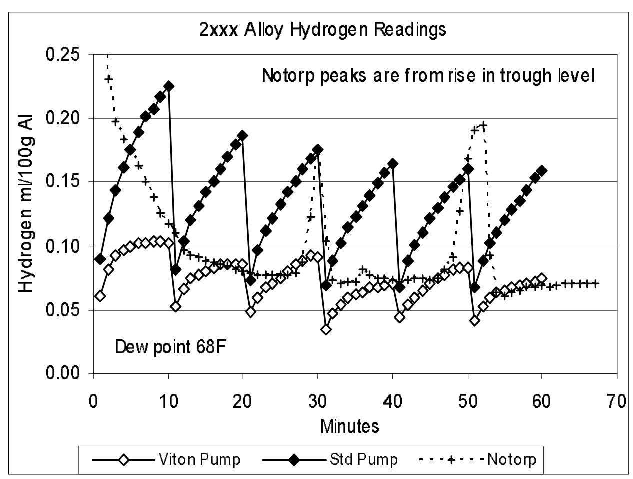

Figure 7. Viton pump AlSCAN sensitivity to hydrogen changes.

It is not fully understood why the Viton pump solves the bias in the AlSCAN measurements. It is clear from the numerous trials, and also not surprising, that as the humidity increases, so does the hydrogen content of the melt. The AlSCAN results taken during periods of high humidity, such as during summertime periods, produced hydrogen readings that were grossly overstated when compared to the expected calculations from in-line degassing models. Prior to this work, the difference could not be explained. The dry air chamber tests results show that high dew points artificially inflate the hydrogen content of the melt when using a standard pump AlSCAN under ambient conditions. However, low dew points from the dry air chamber tests did not understate the hydrogen results from the standard pump AlSCAN, but instead correlated well with the Viton pump AlSCAN and Notorp results. One possible explanation for the overstatement of standard AlSCAN hydrogen results during high dew point conditions and not during low dew point conditions is that moisture may act on the silicone and neoprene components in a way that results in losing the seal, entraining ambient air into the pump analysis loop.

Summary and Conclusions

Efforts to increase the AlSCAN equipment availability, through in-house maintenance of the units, lead to an unexpected and beneficial discovery. The selection of a different elastomer material, Viton, for the AlSCAN pump enabled the seasonal bias in hydrogen content to be explained. Extensive testing of over 100 production drops on 14 alloys has proven that the Viton pump material is unaffected by seasonal changes in dew point while the standard pump significantly inflates the actual hydrogen content during high dew point periods.

The consistency among hydrogen results from the Viton pump AlSCAN, the dry air chamber standard AlSCAN, and the Notorp indicate that Viton is the preferred material for the AlSCAN pump assembly. Consistency in measurement is critical in assessing degassing equipment performance and in establishing critical product limits. There is no longer a need to develop seasonal biases for summer and winter production.

As a result of this work, Alcoa was awarded U.S. patent 7,086,274 on August 8, 2006 covering the method and apparatus for measuring gas concentrations levels in liquids.

References

1. C.E. Ransley and D.E.J. Talbot, "The Routine Determination of the Hydrogen Content of Aluminum and Aluminum Alloys by the Hot Extraction Method," *Journal of Institute of Metals*, 84 (1955-56), p. 445-452.

2. F. Degreve and C. Jardin, "New Methods for the Determination of Hydrogen Content of Aluminum and its Alloys: Part II. Rapid Determination by the Nitrogen Carrier Fusion Method," *Metallurgical Transactions B*, 6B (1975), p. 545.

3. C.E. Ransley, D.E.J. Talbot, and H.C. Barlow, "An Instrument for Measuring the Gas Content of Aluminium Alloys during Melting and Casting," *Journal of Institute of Metals*, 86 (1958), 212-219.

4. J.-P. Martin, F. Tremblay, and G. Dube, "AlSCAN: A New and Simple Technique for In-line Analysis of Hydrogen in Aluminium Alloys," *Light Metals* (1989), 903-912.

5. L.D. Ray, "A Comparative Assessment of Quantitative Hydrogen Analyzers Commonly Used in the Aluminum Industry," *Light Metals* (1992), 1031-1047.

6. C. Dupuis, Z. Wang, J.-P. Martin, and C. Allard, "An Analysis of Factors Affecting the Response of Hydrogen Determination Techniques for Aluminum Alloys," *Light Metals* (1992) 1055-1067.

7. *Cole-Parmer General Catalog*, Chemical Resistance Charts, Cole-Parmer Instrument Company (2004) pp. R10-R19.

8. *AlSCAN Version 2.2 User's Manual*, Chapter 9, Bomem Inc., Quebec (1991) pp. 35-46.