Anodizing of Castings

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Abstract:
The quality of Type III anodic coatings formed on casting AlSi7Mg (AA 356.0), sand cast under twenty-one different conditions, varies significantly from casting to casting. The anodic coatings are formed by pulse anodized using the Yokoyama pulse technique and the formation of alumna is mainly made in sulfuric acid as in conventional hard anodizing.

Depending on specifications (technical performance or coast reductive circumstances), significant improvements can be achieved by combining knowledge within the casting industry with knowledge from the hard anodizing industry.

The results of this research project clearly illustrates that the differences in the outcome of hard anodizing castings from job shop to job shop could also be a result of variation in the quality of castings from one casting operation to another. Hence a casting is not necessarily a casting. The technical performance and quality of the oxide film may vary significantly even though the alloying constituents are identical.

Introduction

It is well known that different aluminum alloys have to be anodized differently. Also alumna properties change from one anodizing job shop operation to another because the process conditions of the surface treatment are not identical. At the same time, one specific cast alloy anodized identically might have different properties because the quality of the alloy varies. The conditions of the aluminum surface are highly dependent on the casting conditions such as modification of the melt, addition of grain refiners, hydrogen content, feeding temperature, the mold type, etc.

The purpose of this study is to combine the knowledge within the casting industry and surface treatment of aluminum, thereby produce sand cast aluminum with an optimum surface for production of high quality oxide coatings. This paper summarizes some results obtained when seven different casting conditions along with modification of the mold are pulse anodized in sulfuric acid and in a proprietary anodizing electrolyte called U-Acid (“U”=”Unknown”). The objective is not too explain why the technical qualities of the oxide coating varies by merely to identify the range of variation of the hard coats and the best casting conditions for anodizing.

Pulse Anodizing

The pulse anodizing technique in the Yokoyama process (Y-process) uses square formed pulses of 5 - 100 seconds duration (1). The main objective is to disperse the heat generated and to control the morphology of the oxide produced during galvanostatic or potentiostatic anodizing. The alumna formed consists of a multi-layered structure, where thin layers of small-sized unit cells separate thick layers of large-sized unit cells. The heat generated during a pulse period at high current is dispersed in the following period where the current is low. This makes it possible to form thick and dense oxide layers without the occurrence of burning.

The advantage of using pulse anodizing versus conventional direct current (D.C.) anodizing is the strongly increased number of independent parameters controlling the anodizing process. The final result of the surface treatment depends on the applied pulse pattern, the electrolyte, and the aluminum substrate. The optimum conditions have to be determined through experiments, although some general guidelines do exist.

Experiments have shown that it is possible with the Y-process to form a thick and compact alumna that is superior to oxide coatings formed during conventional D.C. anodizing at low temperatures (2,3). Furthermore, is has also been shown that coatings produced in U-acid are superior to aluminum pulse anodized in sulfuric acid (4).

Casting of aluminum

A liquid metal is a highly reactive metal. It will react with both the gases above it and the solid material, which contains it. The driving force for these parameters are the striving of the melt to come into equilibrium with its surroundings. Its success in achieving equilibrium is limited by the rate at which reactions take place and the time available. When the liquid metal enters the mold, it reacts violently resulting in changes to the shape of the mold. Therefore, much work has been carried out in effort to increase its rigidity. Greensand has been the most used casting process during history and addition of clay (Bentonite) is one method of enabling a denser and harder mold to be made. The action of the clay is complex: not only is it important as the main component of the binder, but it also shrinks appreciably on drying, helping to counter the expansion of the sand during heating. Mold surface failures because of thermal expansion can be reduced or eliminated if the sand is added Chromite or zircon.

The most important reaction at the metal surface is the reaction of the metal with water vapor, which results in a surface oxide and hydrogen evolution. Hydrogen from a surface reaction can diffuse sufficiently far in time available during the solidification of a casting and thereby contribute to the formation and growth of subsurface porosity.

When the conversion from liquid to solid occurs, it is first by a process of nucleation and then by growth. Nucleation is the process of the aggregation of clusters of atoms, which represents the first appearance of the new phase. Growth is self-evidently, getting bigger. The nucleation process can be influenced by a number of metals. Grain refinements are achieved by addition of Sodium (Na) and Strontium (Sr).

Experimental

The alloy used in this survey is AlSi7Mg0.3 made by Elkem Aluminium from a series called Sibloy. A chemical analysis of the alloy is shown in Table 1. The casting temperature is 700°C (1292°F) and all castings are bars with a diameter of 36 mm. The conditions investigated are as follows:

1. Chill casting with a very high cooling rate (47 seconds calculated on the dendrite spacing). The productivity of this method is low (8 to 10 casting per hour) and the expenses high. The needs for an insulating pasta and a controlled cooling rate are two more drawbacks.

2. Quarts sand added Chromite, where the mold is bound chemically by Sodium Silicate. The addition of Chromite reduces the thermal expansion of the mold, reducing the risk of surface failure of the casting. The cooling rate is fairly low and the expenses fairly high because of Chromite.

3. Magnetite is a mixture of silica sand and iron ore. The cooling rate is fairly low: 104 seconds. The operating costs are low and the productivity is very high (360 castings per hour).

4. Quarts sand bound chemically by sodium silicate (Quarts) has a very low cooling rate: 175 seconds. The productivity is high (360 castings per hour) and the production costs very low. The risk of surface failure is present because of thermal expansion of the mold.

5.Quarts sand bound with clay (Quarts/Bentonite) has a fairly high cooling rate because of the water content: 85 seconds. The productivity is high (as quarts) and the production costs are low.

6. Quarts sand and iron ore bound with clay (Magnetite/Bentonite) has a cooling rate which is comparable to chill casting: 55 seconds. The productivity is high (as quarts) and the production costs are low.

7. Quarts sand added Zirconium has a fairly high cooling rate: 80 seconds.

Elements	Al	Si	Fe	Mg	B
W/w %	92.48	7.16	0.09	0.25	0,02

Table 1. *AlSi7Mg: Composition analysis of the castings used in the experiments.*

Also investigated are unmodified melts and melts added grain refiners Sodium (Na) or Strontium (Sr), which increase the total number of casting conditions investigated to twenty-one (21).

All the sides of the cast bars are mechanically machined (Ra≈1µm), leaving only the top and bottom areas in "as cast" conditions. The surface roughness (Ra) is measured on the mechanically machined surface before and after anodizing (n=5).

Each bar is numbered randomly in order to minimize subjectivity. Pulse anodizing is made in 15 w/w % sulfuric acid at 14°C. The process time is 50 minutes. The pulse conditions are 4 A/dm² for 60 seconds followed by 1 A/dm² for 20 seconds. The pretreatment consists of degreasing and bright dip in 50 v/v % nitric acid. Pulse anodizing in the proprietary U-acid electrolyte is produced with a pulse pattern under process conditions, which maximizes microhardness of the anodic coating.

The thickness of the oxide coating is measured microscopically on a cross section (n=10). The homogeneity of the coating thickness is represented by the Standard Deviation (St. Dev.) of the measurements. The microhardness is measured as Vickers Hardness with a load of 25 g (n=8) on a cross section.

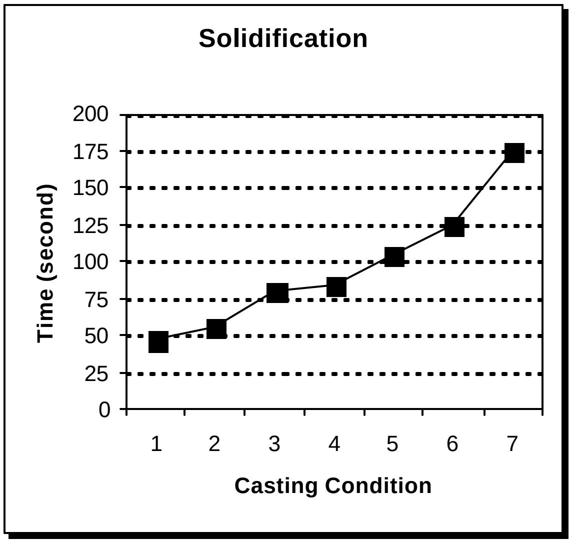

Figure 1. *The cooling rate of the castings investigated measured as dendrites spacing.*

Results

The solidification profile measured as solidification time, in the seven castings investigated is presented in Figure 1. The solidification time is calculated using the spacing of the dendrites, which is correlated with the conditions during solidification. Investigated are cooling rate from 50 seconds to 175 seconds.

The anodic formation rate is highly related to the anodizing potentials of the surface. It is well known that cast surfaces anodizes at a slower rate that machined surfaces. It is nicely illustrated in Figure 2, where the coating thickness is significantly higher on the machined surfaces. And in addition within each surface category ("machined" versus "as cast"), a large variation is also noticed.

On the machined surface the maximum thickness after 50 minutes of pulse anodizing at elevated temperature is approximately 90µm. This corresponds to a formation rate of 1.8 µm/minute, which is close to a doubling of the formation rate in conventional Type III anodizing. The lowest thickness measured is close to 55µm, which is close to a formation rate experienced in conventional hard coat anodizing. However the difference is a result of the conditions of the castings, not the anodizing conditions.

An uniform coating thickness over a part, which contains "machined" and "As Cast" surfaces, is important for the corrosion

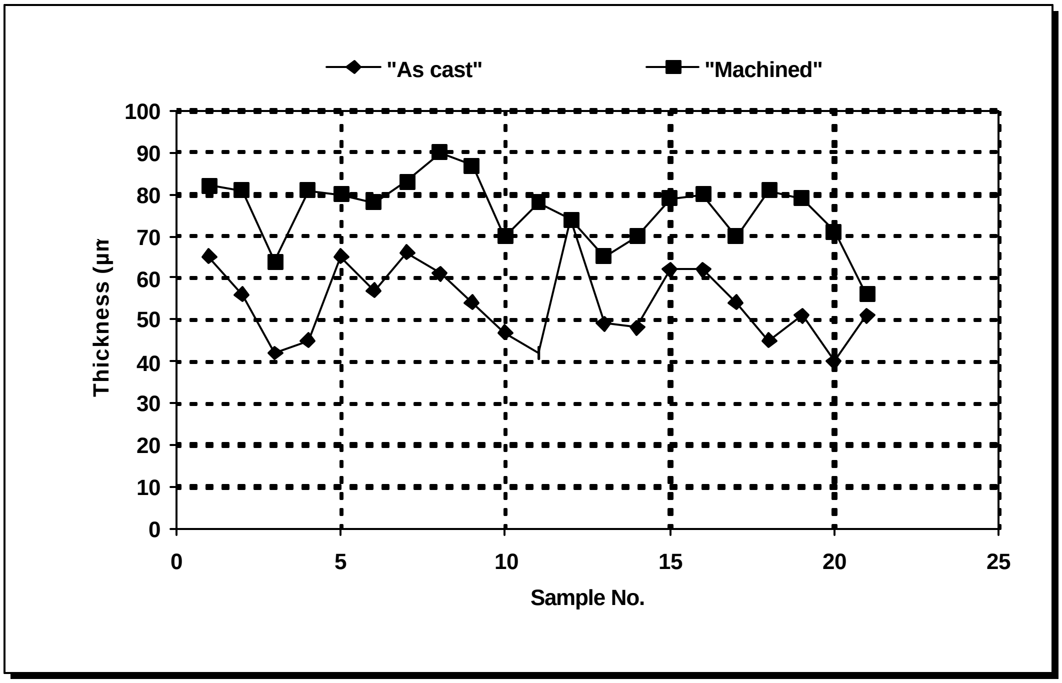

__Figure 2.__ The anodic coating thickness on the castings investigated. The thickness is measured cross sectional and represents the average of 10 random readings.

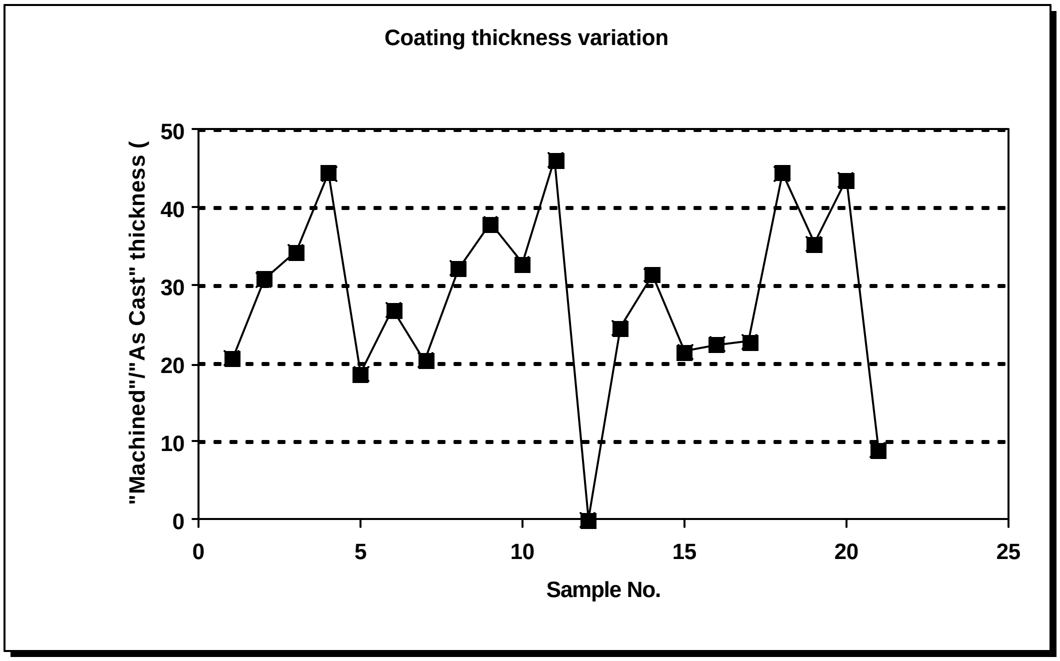

__Figure 3.__ The difference (%) in coating thickness between "machined" and "as cast" surfaces versus the casting conditions investigated.

protection. Depending on the conditions during solidification of the molds, some conditions reduce the difference in thickness between machined and as cast surfaces significantly (sample#12 and #21 in Figure 3). However some casting conditions results in a difference close to 50%.

Another important factor influencing not only corrosion performance, but also wear performance is the variation in coating thickness within a casting. Figure 4 illustrates the relation between the thickness homogeneity calculated as 95% C.L. on the Standard Deviation of the cross sectional measured thickness (n=10 per sample) for casting produced without grain refiners. The trend line of the data does not indicate any correlation between solidification rate and thickness uniformity. The situation is different if the molds are added the grain refiner Strontium (Sr). The higher the cooling rate is, the smaller is the thickness variation (Figure 5).

During conventional direct current Type III anodizing, surface roughness prior to processing is known to increase significantly after oxide formation. The increase can be as high as 400-500% for castings.

Figure 6 illustrated the increase in surface roughness (R_a) for the casting conditions investigated with addition of the grain refiner Strontium (Sr). Obviously the data show that a fast cooling is appropriate if the increase in surface roughness must be low. However, the data also shows that when the cooling times is 80 seconds and higher, the solidification process do not influence the change in surface roughness. Worst-case scenario is cooling rates at around 75 seconds.

Microhardness is another property important for characterizing the technical quality of an aluminum oxide coating. It is generally accepted that during conventional anodizing microhardness decreases as thickness increases. In pulse anodizing microhardness is independent on processing time, hence thickness (4).

The data shows the relation between microhardness and thickness known from

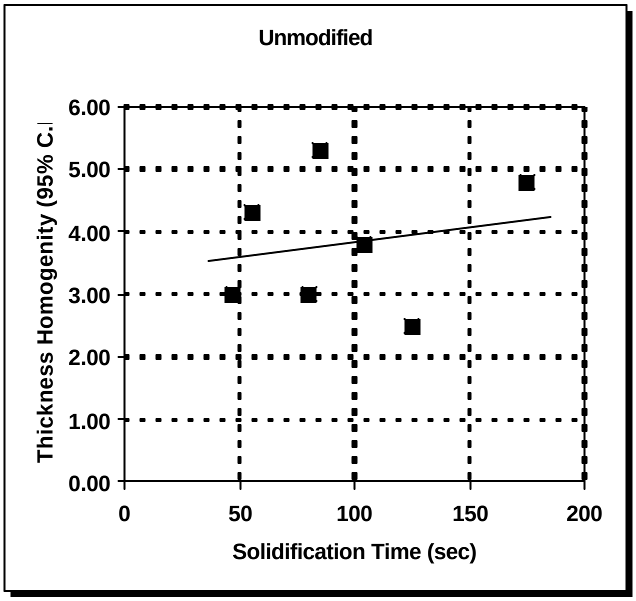

Figure 4. *The uniformity of the anodic coating calculated as 95% C.L. of the standard deviation from the cross sectional thickness measurements for casting without addition of grain refiners versus cooling rate*

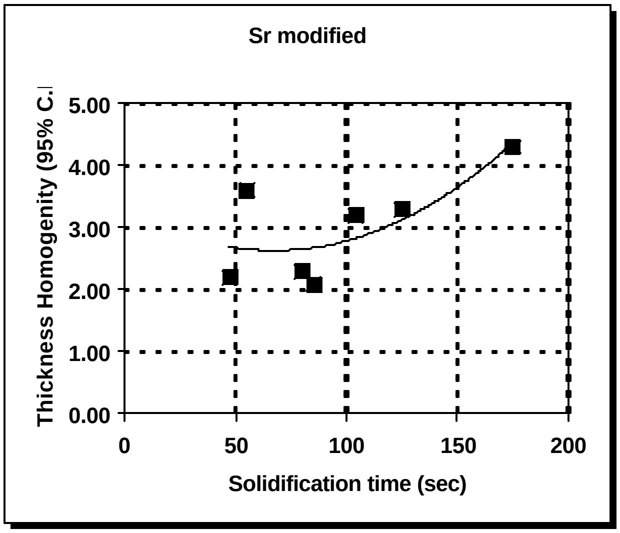

Figure 5. *The uniformity of the anodic coating calculated as 95% C.L. of the standard deviation from the cross sectional thickness measurements for casting added Strontium (Sr) as grain refiner versus cooling rate*

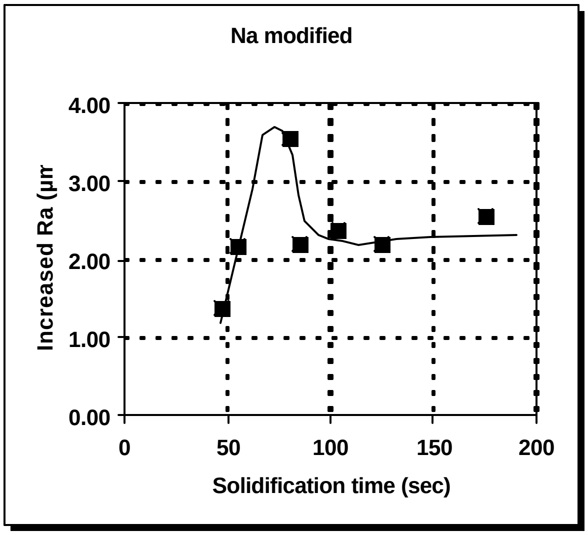

Figure 6. *Increase in surface roughness (Ra) versus cooling rates for castings added Sodium (Na) as a grain refiner.*

conventional anodizing is also present when anodized using the pulse technology if the casting is added Strontium (Sr) as a grain refiner (Figure 7). The correlation between microhardness and coating thickness is not present if the castings are made without grain refiners (Figure 8).

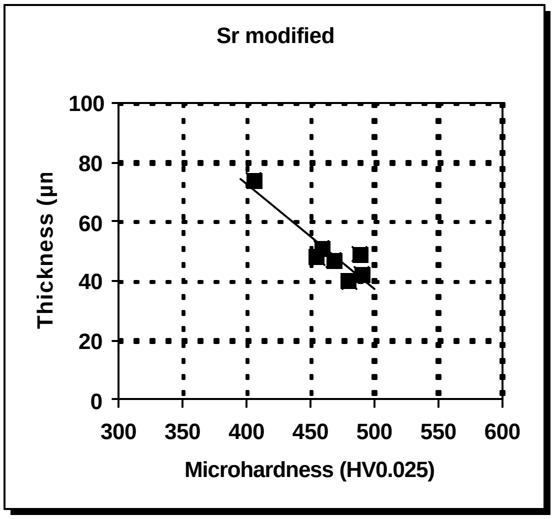

Figure 7*. Microhardness versus coating thickness for castings added Strontium (Sr) as a grain refiner*

Obviously, the correlation between casting quality and the microhardness of the anodic coating formed during anodizing is complex of nature.

Microhardness could be related to the conditions during solidification. At least it is an option. However the data from this research project do not support any correlating between the casting conditions and the microhardness when anodizing is made in sulfuric acid (Figure 9).

Obviously the microhardness seems to be more dependent on the anodizing conditions and not so much on the cooling conditions during solidification of the castings. However, the relation between coating thickness and microhardness is to some degree related to the grain size, which illustrated by the results in Figure 7 and 8.

If the microhardness is mainly related to the anodizing conditions a change in anodizing chemistry should result in changes microhardness.

Pulse anodizing in U-acid do show that the conditions during casting (here measured as the cooling time) is independent on the microhardness (Figure 10). It also shows that the chemistry of the

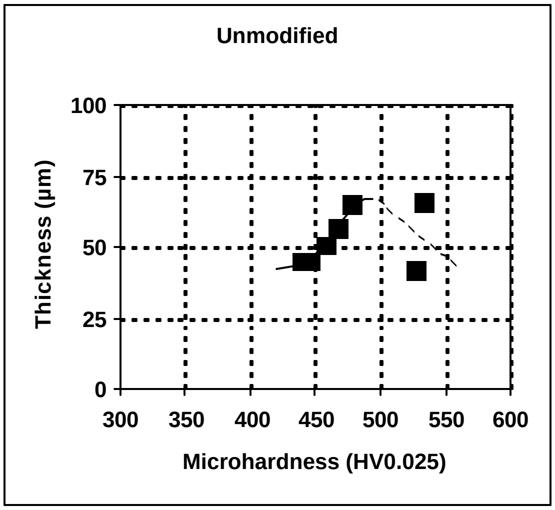

Figure 8*. Microhardness versus coating thickness for castings without a grain refiner.*

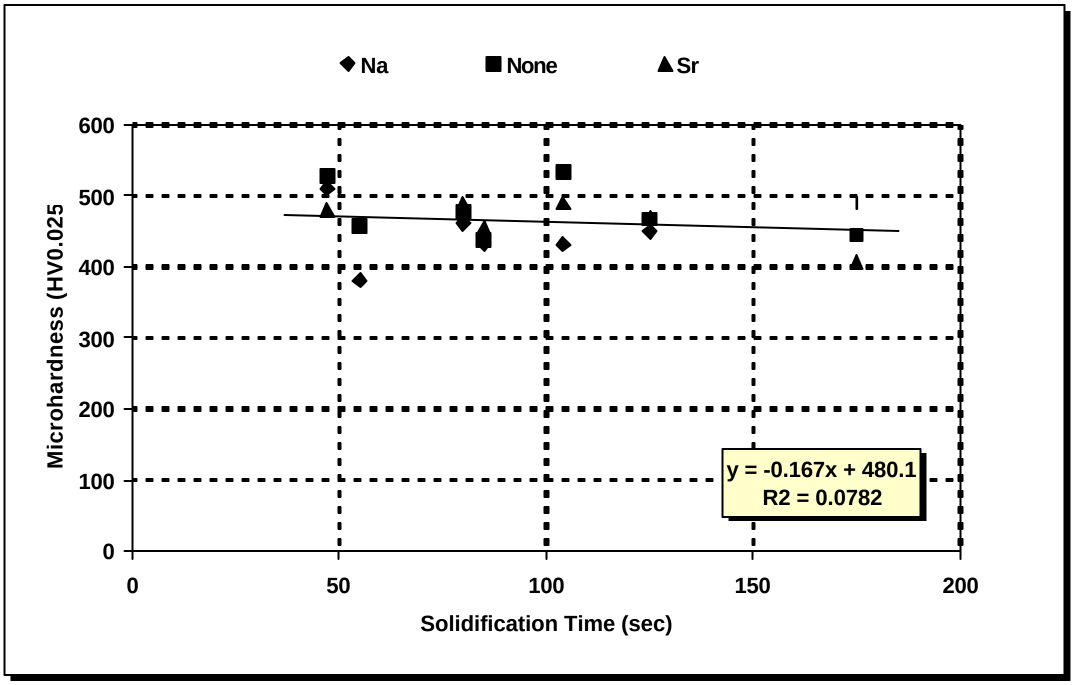

Figure 9. *Microhardness and cooling time for the casting investigated.*

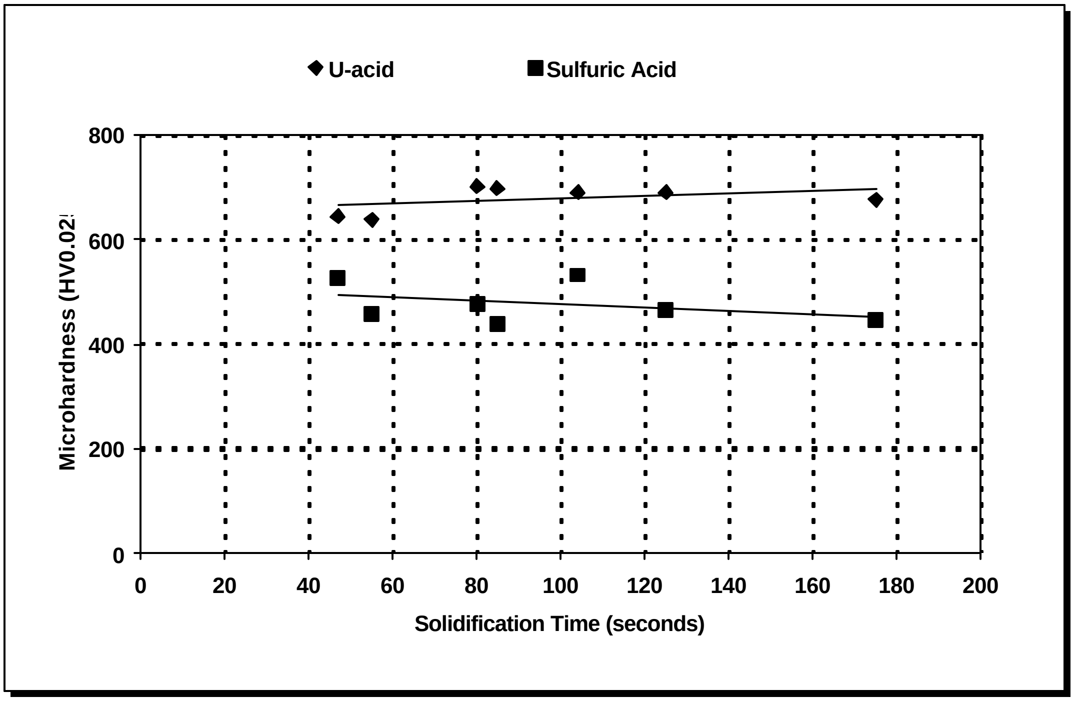

Figure 10. *Microhardness of anodic coatings from anodizing in Sulfuric Acid and U-Acid for castings without addition of grain refiners*

electrolyte is an important factor controlling the technical quality of the anodic coatings.

The microhardness values achievable in U-acid are approximately 200 $HV_{0.025}$ higher than when anodizing in Sulfuric Acid electrolytes.

Conclusion.

In relation to job shop operations, the experiments have shown that if an oxide coating fails a quality test and all anodizing parameters are within tolerance, it is likely that the failure is related to the quality of the casting process. These results could be from either a change in the casting conditions or because the customer has changed to another supplier of castings.

The experiments also show that if high quality of the oxide coatings is a priority, it is important that the surface finisher become involved early in the development of a product. The advantages are increased overall quality by being involved in the recommendations of the casting conditions or help identifying the optimum conditions for the casting process ensuring maximum anodic coating performance.

Acknowledgments.

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