New Stirrer Technology for the Glass Industry

LONG-TERM BENEFITS FROM THE 'DIFFUSION CHOKE'

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The function of stirring in glass making is to create uniform, homogeneous glass. Stirring equipment operates at high temperatures and under high mechanical stresses, so stirring devices have to be robust and often involve large amounts of platinum or platinum alloys. The stirrers, stirrer bars, blenders, homogenisers, screw plungers and plunging stirrers currently used are generally effective in operation, reliable and with predictable lifetimes. Thus there has been no incentive to improve the technology, and stirrer designs have changed little in the last twenty or thirty years. However, the current economic climate in the glass industry demands lower costs, improved operational efficiency, and reduced platinum inventories – glass making uses large quantities of platinum, with stirring devices taking a large part of it. To help reduce these amounts work has been undertaken on stirrer technology. and recent developments have resulted in lower platinum requirements (in some cases by over 90 per cent) without jeopardising stirring effectiveness or stirrer longevity. Different types of glass stirrers are examined here and a new concept in stirrer design, a 'diffusion choke', is described.

Good quality glass has to be homogeneous. To achieve this, glass melting furnaces have been developed to give a high degree of mixing and capability to deliver uniform glass into the forehearth. However, the necessity to continuously condition (heat, cool, or de-gas, etc.) the glass flowing towards the working end can negate some of this design and can cause thermal and compositional inhomogeneities in the flowing glass. This could compromise the quality of the finished product. To produce homogeneous glass it is therefore necessary to stir the glass in the forehearth, and this is widely employed. However, the introduction of stirrers has repercussions; the function of stirring is of value, but the physical presence of the stirrer is a drawback.

The choice of material for the stirrer helps to determine the optimum benefit, as the cost, effectiveness and durability need to be balanced. Each of these aspects depends on the final application of the glass and the nature of the molten glass, specifically, its viscosity, temperature, corrosivity, quality and value. Stirrers with their glass contact surfaces made in platinum or platinum alloys provide the best solution to this issue, but for many installation sites, such as container glass forehearths, where the

value of the product has traditionally been low, the cost of fabricated platinum stirrers has historically been too high.

The introduction in 1994 of ACT™ platinum-coated ceramics changed this (1, 2). ACT™ technology provided great improvements in the resistance of ceramics to molten glass at relatively moderate cost by providing enhanced durability and longevity compared with prior used unprotected ceramic (3).

For glasses of very high value, specifically optical glasses where quality and clarity are paramount, stirrers fabricated from platinum alloys have always been used, although they have limited durability in high viscosity glass, especially when the glass is used for large components.

Stirrer cores made from molybdenum have been found (at least 15 years ago) to provide the strength that is required by platinum for parts used in high value glass making, such as in gobbing and high energy stirrers. Separation of the platinum and the molybdenum by an oxide diffusion barrier and evacuation of the resulting space are necessary to avoid the cores from volatilising at temperatures above ~ 400°C.

Other materials evaluated over the years for

Fig. 1 Three stirrers that were used together at the same time for the same time (approximately six months) in a colouring forehearth. The glass immersion line can be seen.

The stirrers were identical except the one on the left has an ACT™ platinum coating.

The stirrers rotate in the glass. They are ~ 1 m in length and made from an alumino-silicate ceramic

stirrer cores and similar applications in the glass industry have included platinum alloy coated, high strength oxide dispersion strengthened (ODS) superalloys, but without significant success. However, the recent development of 'diffusion choke' technology has overturned these failures and enabled the use of these superalloys. This paper looks at the background to the 'diffusion choke' development and the improvements that are now possible.

Recent Stirrer History
ACT™ Platinum Coated Stirrers

ACT™ platinum coating technology has been used in molten glass furnaces for more than ten years (1, 2). Some of the earliest applications were coated ceramic stirrers for application in the severest conditions, such as in opal and borosilicate glass and colouring forehearths (where colour is added to glass). The objective was to prevent the ceramic from being eroded and to allow continuous efficient stirring. The effectiveness of the ACT™ technology can be seen by the uncorroded stirrer on the left in Figure 1; all three stirrers had experienced six months of continuous service. ACT™ technology is now being used to re-define the nature of stirrers and to give more advantages over conventional fabrications, see, for example Figure 2.

In a recent application, co-planar ceramic stirrers with ACT™ platinum alloy coatings, see Figure 3, replaced helical stirrers fully fabricated from platinum alloy sheet. The improved performance they achieved in stirring molten TV panel glass has dramatically assisted in this economically difficult area. In one case, ACT™-coated ceramic

Fig. 2 A conventional fabricated helical screw glass stirrer made of 10%Rh-Pt. This stirrer typically has a life of about 5 years. Such stirrers are used for all glass making that is inherently expensive due to the large amount of precious metal required. Welded joins on this stirrer are visible

In a forehearth there may be from 2 to 16 such stirrers operating in banks of up to 4. They are mechanically operated in optimum stirring 'patterns', with the other end of the stirrer being fixed to a geared drive
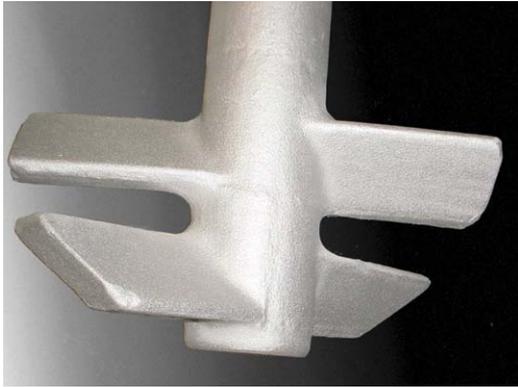
Fig. 3 An ACT™ coated co-planar stirrer as used for homogenising and disturbing laminar flows of glass.

These vanes will be fully immersed in the glass, with the glass surface being a few centimetres above the upper vane. The vanes operate in simple rotation but each pair of stirrers will be contra-rotated

stirrers replaced traditional fabricated platinum ones, and thus reduced the platinum that was being used from a total of 84 kg to only 8 kg. This reduction was partially accomplished by the superior design of the stirrer so that fewer were needed (from 10 to 4), and by the reduced thickness of the coating as compared to the prior fabricated stirrer. The design of an ACT™ coated stirrer is dictated by the ceramic and the requirements of the application. Many different configurations have been defined and utilised.

Platinum-Clad Base Metal Stirrers

For many years molybdenum has been used as the material of choice for structural applications within the glass furnace as it performs well in molten glass. However, although it is used extensively as electrodes in electrically heated furnaces, if free oxygen impinges on its hot surface, it burns rapidly. This is a major limitation. To be effective the molybdenum must be protected if it is to function at any temperature > ~ 400°C. Therefore in its major application of resistance-heating electrodes, it must be water-cooled to ensure that the zone not protected by immersion in molten glass is kept below this critical temperature.

Platinum does not have this limitation and can be successfully used in such applications without water-cooling. It is assumed that using platinum would make an electrode too expensive, but this is not always the case and the introduction of ACT™ platinum coating technology has allowed electrode designs to be generated that have all the advantages of platinum without the disadvantages of

molybdenum. Indeed, in some applications where a solid electrode is required, iridium, which has unmatched stability in glasses that are especially aggressive when molten, and high environmental resistance, is now being considered as a viable alternative to molybdenum.

In glass stirrer technology it is desirable to make use of the strength of molybdenum for applications where the shear strength requirements are very high and where unexpected failure would be expensive. Protecting the molybdenum is critical in achieving this. Platinum cladding has conventionally been utilised in a simple symbiosis: a platinum alloy cladding protects the strength-donating molybdenum. As in many symbiotic relationships there is a parasitic component, and the two materials can, under some circumstances, interact and form potentially detrimental intermetallic phases (4). The effect of this can be seen in Figure 4 which shows the weight losses observed for a series of molybdenum samples protected by platinum coatings of high thickness. The simple platinum layer can protect the substrate until interdiffusion and interaction promote failure of the platinum layer. Once this happens rapid oxidation of the molybdenum occurs with dramatic loss of weight.

The addition of a ceramic barrier layer to keep the two metals apart was a natural progression. A ceramic barrier can control interdiffusion and oxygen removal from the inner space (the volume between the cladding and the molybdenum substrate) (5). This situation must be maintained for the duration of the service life of the component.

These stirrer designs have been used to great
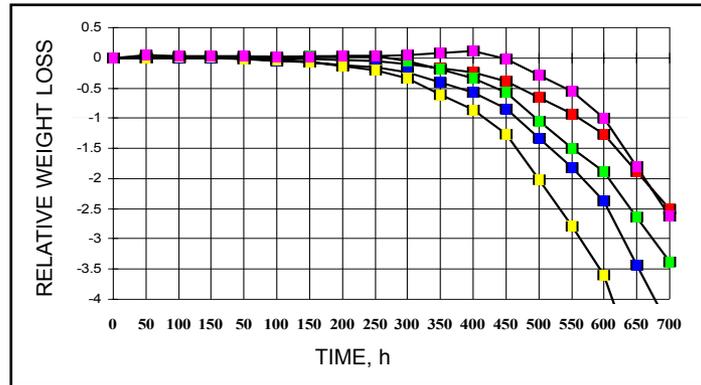
success for several decades, and with care can have lives of more than five years. However, when the cladding fails either by mechanical damage, physical change or chemical attack, the introduction of oxygen onto the molybdenum can cause a dramatic and rapid failure. This failure can be anticipated and avoided, but if it is unexpected the damage to the forehearth and the resulting down-time can be extreme.

Alternative core materials have been tested, and superalloys are most likely to be suited to this arduous task. These materials were developed specifically for the gas turbine industry and were designed to have excellent strength, and very good oxidation resistance up to temperatures of ~ 1100°C. Oxide dispersion strengthened (ODS) alloys can, of course, be used to provide strength at temperatures up to 1300°C. Some of these ODS alloys have considerable resistance to the harsh environment above molten glass and also when submerged in glass, but they tend to erode relatively rapidly at the glass line. This causes both

structural weakening and potential glass colouration problems. It would seem feasible to use a platinum cladding to negate this weakness, but work done a few years ago (6) showed that the tendency of the nickel in the ODS alloy and platinum to interdiffuse was too great for long term success.

Figure 5 shows an example of a stirrer made from an ODS alloy of this type. It was ACT™ platinum coated and then laboratory tested in molten TV glass for 300 hours at 1150°C. Approximately the top quarter of this component had platinum deposited directly onto the base metal substrate. Through-diffusion resulted in the development of surface oxide on top of the platinum. The lower three quarters of the sample had a ceramic interlayer which effectively blocked the diffusion, although there was slight colouration of the glass still attached to the sample surface. This indicates that iron, nickel or chromium migrated from the core alloy. Thus, while ACT™ coating technology offers improvement, a further technological advance is required to allow the effective

Fig. 6 *The typical structure of a knitted 'diffusion choke' gauze or mesh made from 10%Rh-Pt alloy. Here it is wrapped around the core of a stirrer*

use of the ODS materials.

Innovative technology has now been developed and patented (7), and the design and performance of a stirrer made using it is described below.

The 'Diffusion Choke'

The process of melting glass and forming it into high quality shapes requires stirrers that can operate reliably for long periods in the temperature range 1000 to 1300°C. Technical solutions do exist, but all have limitations either in performance or cost. These include the inherent limitations in design embodied in ACT™-coated ceramic stirrers, or the cost and inherent potential for catastrophic failure of the extremely strong platinum-clad molybdenum stirrers. The 'diffusion choke' was designed as an alternative to the latter. Elimination of the risk of catastrophic failure can allow for some potential reduction in the usual platinum cladding thickness, and hence some modest cost reduction.

The technology was tested by a stirrer with a PM 2000 stirrer shaft and a 20%Rh-Pt sheet metal fabrication or cladding. A mesh or gauze of finely knitted 10%Rh-Pt alloy, the 'diffusion choke', was placed between the two materials, see Figure 6. Advantages of 'diffusion choke' technology are:

• The 'diffusion choke' is designed to separate cladding from the substrate, and thus reduce the diffusion that arises from contact at high temperature causing the problems seen in Figure 5.

• The 'diffusion choke' is designed to maintain an airway to the outside and ensure that adequate amounts of oxygen reach the surface of the core. This enables the inherent oxidation properties of the ODS alloy to develop and remain throughout
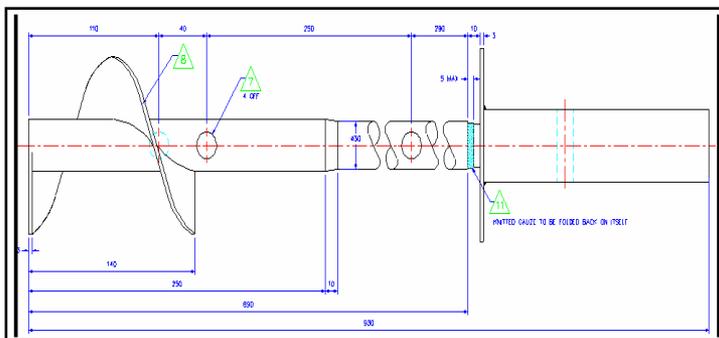

Fig. 7 *Schematic diagram of a typical helical bladded stirrer. The position of a 'diffusion choke' in the form of knitted gauze is indicated in blue. This would then cover the stirrer core before being coated with platinum*

Fig. 8 Preliminary sectioning of a stirrer core of PM 2000 with a 20%Rh-Pt sheet metal cladding between which was a gauze of finely knitted 10%Rh-Pt alloy. This stirrer was used in a hostile environment for 20 months.

The numbers represent positions where analyses were performed.

The stirrer has been divided into four sections:

Section A is the top section linked up to the drive motor;
Section B fits into Section A;
Section C fits into Section B and to Section D;
Section D is the stirrer blade end
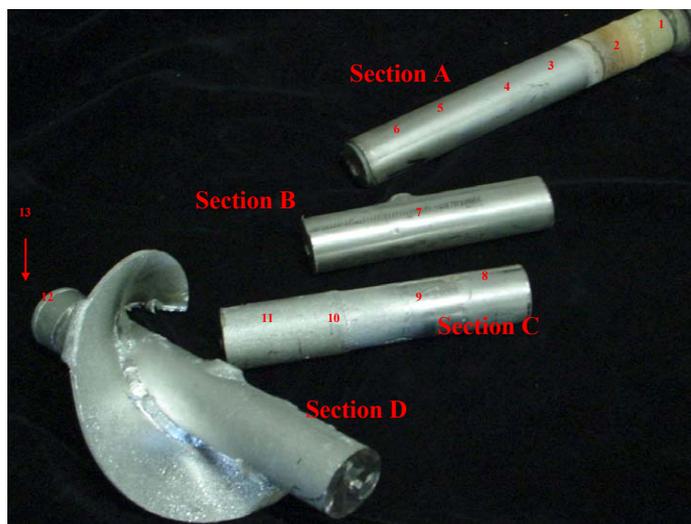
prolonged operation at elevated temperatures.

• The 'diffusion choke' restricts oxygen flow to the alloy surface, and ensures that excessive oxide thickness cannot develop. Under certain conditions this might otherwise give rise to an aggressive form of rapid oxidation.

• An interesting further advantage results from the platinum of the 'diffusion choke' being in contact with the core alloy, which has a known effect of increasing oxide stability (8).

A typical stirrer design is shown in Figure 7. This was tested in glass for TVs. The initial test period was extended from 6 to 20 months, and though still performing well, the stirrer was removed for investigation. Initial visual examination indicated no surface degradation at any point along its length. Figure 8 shows sections of the stirrer prior to further dismantling. The discolouration at the upper end of the shaft in Section A was crusty and mineralised, indicative of deposition from the furnace vapours. At the glass line the platinum alloy was slightly brighter possibly indicating some minor surface interaction. A microfocus XRF unit examined the composition

Table I

Microfocus X-Ray Fluorescence Analysis of the Stirrer Surface

Sample	Pt, %	Rh, %	Fe, %	Cr, %	K, %	Ca, %	Sb, %	As, %	Bi, %	Ba, %
1	27.4	19.7		0.7	44.1		7.5	0.6		
2	14.5	27.7	0.2		5.2	21.3	31.0			0.1
3	77.2	17.6	1.1		3.4				0.7	
4	77.9	18.8			2.5				0.7	
5	79.7	19.3			1.0					
6	80.2	19.2			0.6					
7	80.4	19.6								
8	80.1	19.5								0.3
9	80.1	19.9								
10	80.3	19.7								
11	80.4	19.6								
12	80.9	19.1								
13	80.7	19.3								

Table II
XRF Results for the Inner Rh-Pt Tube Surface

Sample	Pt, %	Rh, %	Fe, %	Cr, %
1i	79.8	20.2		
2i	79.1	20.9		
3i	83.7	16.3		
4i	83.4	16.6		
5i	83.4	16.6		
6i	82.5	17.5		
8i	82.7	17.3		
9i	82.6	17.4		
10i	82.4	17.6		
11i	82.9	16.9		0.2

of the external surfaces, see Table I.

Analysis of the upper region of the stirrer, positions 1 to 6 showed that the yellowish encrustation

Table IIIa
Analysis of the Outer Surface of the Diffusion Choke Gauze

Sample	Pt, %	Rh, %	Fe, %	Cr, %	Y, %	Ti, %
1g	88.3	11.7				
6g	87.8	12.2				
8g	86.1	13.9				
11g	85.8	14.1		0.1		

Table IIIb
Analysis of the Inside Surface of the Diffusion Choke Gauze

Sample	Pt, %	Rh, %	Fe, %	Cr, %	Y, %	Ti, %
1gi	89.6	10.4				
6gi	87.7	11.2	0.3	0.1		0.7
8gi	85.7	13.7	0.2	0.4		
11gi	85.9	13.0	0.2	0.5		0.3

Table IV
Microfocus XRF Analysis of the Substrate Core Surface

Sample	Pt, %	Rh, %	Fe, %	Cr, %	Y, %	Ti, %
14	1.0	0.1	79.1	17.8	0.8	1.1
15	5.8	0.5	73.6	18.2	0.8	1.1
16a (light)	6.1	0.5	72.9	18.5	0.7	1.2
16b (dark)	2.5	0.3	75.1	18.5	0.7	2.9
17	22.6	1.7	56.3	17.7	0.7	1.0
18	7.4	0.7	72.7	17.1	1.1	0.9

was derived from the molten glass probably via condensation from the gas phase. This is, of course, normal and expected. The rhodium contents of the alloy are exactly as the original alloy specification, within the error expected for the analytical equipment. On the lower portion of the stirrer there were no 'foreign' elements detected on the alloy surface except for a trace of barium, a glass component, in the region of the glass line. This lack of any surface impurities after immersion in molten glass indicates that the component had been quite well cleaned before being returned for investigation, and thus the lack of evidence of through-diffusion from the substrate was still unproven. Further disassembly of the stirrer was therefore needed.

The cladding on Section A slid easily from the base metal shaft. The 'diffusion choke' was retained within the 20%Rh-Pt tube, but further examination showed this was by very slight adhesion and minimal tension was required to remove the gauze. The same situation was found for the whole length of shaft (except, of course, where the fixing screws had been securely positioned to transfer torque on the shaft to the cladding and hence to the stirrer blades themselves). Along most of the length of the shaft the gauze remained shiny and metallic, but in one region there was some greyness and at the very top some gauze was yellow/brown.

Analyses of the inside of the tube and of gauze samples at points corresponding to the external analyses are given in Tables II and III, respectively.

Analysis of the inner surfaces of the 20%Rh-Pt protective tubing showed that no elements were present that would not have been present in the original alloy, with the possible exception of one sample below the glass line. Interestingly, the rhodium level in the inside surface of the tube showed an approximate 3% reduction from the original bulk alloy composition, as did

the average outer surface composition. Analysis of the 'diffusion choke' showed where the rhodium had gone. This showed a corresponding increase in rhodium content indicating that either a diffusion process or a vapour phase transfer process had been operating. In addition to an increased average rhodium content the 'diffusion choke' gave measurable levels of iron, chromium and titanium on the side in contact with the base metal substrate, but almost none on the side in contact with the Rh-Pt tube. The surface of the choke in contact with the core was slightly discoloured, and appeared to have physical contamination rather than a chemically-bonded contamination.

PM 2000, the core of the stirrer, is an iron-based ODS alloy with major additions of chromium and aluminium plus various other minor ones. The key to its high strength at elevated temperature is the presence of yttria which, as a dispersed stable oxide, provides grain boundary strengthening. Table IV shows the results for microfocus XRF of the surface of the core PM 2000 alloy after service. The absence of values for aluminium is linked to the analytical technique, rather than being a mechanistic issue. Alternate analytical techniques can be used to confirm that aluminium has been retained.

The presence of the occasional high values for platinum on the surface of the base metal core was due to very small adhered flecks of platinum. The nature of this tiny platinum-rich particulate has not been determined, so it is impossible to say whether they have been transported by a vapour phase mechanism or are simple physical artifacts. Visual observation, however, clearly indicated that a thin, protective surface oxide had been formed. This would be expected to change only slowly allowing protection to the substrate for a very long time.

Conclusions

The 'diffusion choke' maintained an effective barrier to degradation of the stirrer for 20 months' service. Indeed, the analyses suggests that the component would have maintained integrity for a much longer time perhaps comparable to the maximum life of clad molybdenum of 5 to 10 years.

The in-service trial and subsequent destructive analysis of the 20%Rh-Pt clad, ODS iron-based alloy stirrer reported here demonstrates that there is new technology to overcome many of the problems associated with traditional clad-molybdenum stirrers. The technology offers a breakthrough in stirrer design and thus additional help to the glassmaker when using stirrers for improving glass quality. In this trial the stirrer design was simple, with reliance on traditional fabrication skills in its construction. 'Diffusion choke' technology has potential for use in a wider range of stirrer types, and perhaps additional applications, where high strength, durability and longevity, without risk of catastrophic failure, are paramount.

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