ALUMINIZING TURBINE PARTS – PROCESSES AND COATINGS

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ABSTRACT

Hot section gas turbine parts need protection against oxidation and hot corrosion. The essential element is Al to build the protective Al_2O_3 . Al can be applied on the gas path surfaces by overlay techniques or by diffusion of Al into the base material – the "aluminizing". Aluminizing can be done by slurry, pack cementation, out of pack, or by "pure" CVD. Additional elements can be added to the aluminide.

The different techniques are discussed under the aspects of advantage/disadvantage, limits and possible coating structures.

INTRODUCTION

The majority of gas turbines in current service rely on the use of conventional nickel aluminide diffusion coatings to protect superalloy turbine components from both oxidation and hot corrosion. Commercial operators require blades to last as long as possible with 5000 to 10,000 hours being typical for aero engines, and 100,000 hours for industrial gas turbines. There is a variety of processing methods for producing turbine blade coatings [1-4] but each must satisfy a number of essential requirements. The process must be able to produce uniform, controlled thickness coatings on complex geometry parts which are metallurgically bonded to the substrate alloy. Although gas turbine technology is inherently expensive, the cost of coating cannot be ignored and must be considered against the unit blade cost especially when coating small or solid blades.

The coating technique mostly used in current operation is that of pack cementation [5-10]. This is generally considered a chemical vapor deposition process in which the element to be deposited is transferred to the surface of the components by Andrea Scrivani Turbocoating SpA Parma, Italy andreascrivani@turbocoating.it

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means of a volatile metal halide and then diffused into the base alloy. The production of aluminide coatings by this method is one of the most economical and well proven process routes.

From this pack cementation process the "out of pack" process has been developed by principally using the pack and a carrier gas which transports the Al-gases to the areas to be coated [11-14]. Other synonymous terms in the literature are "above the pack" or "out of contact".

More sophisticated is the "true" Chemical Vapor Deposition (CVD) where the reactive gases are created separately from the part: this allows a precise tailoring of the process parameters [15-20].

An alternative technique for producing aluminide coatings is the slurry process. The slurry containing the pure aluminum or low-melting aluminum alloys, for example Al-10Si, is sprayed onto the surface of the component, and then heat treated to form by diffusion of aluminum the aluminide diffusion coating [21-23]. (Slurries containing mixtures of aluminum alloys and halides are special forms of the pack cementation and are not discussed here)

ALUMINIZING TECHNIQUES Pack cementation

Pack cementation diffusion processed coatings may be considered as a CVD process carried out with the aid of a powder mixture (pack), in which the part to be coated (substrate) is immersed or suspended, containing a mixture of aluminum (or an aluminum alloy) as "donor", a halide "activator" (NH₄Cl, NH₄F or AlF₃) and an inert filler such as aluminum oxide.



Figure 1. Scheme of Pack Cementation, Out of Pack, CVD

These altogether are inserted in a cementation box. The cementation boxes are then heated to promote the diffusion process at temperatures ranging from 600 to 1100 °C for 2 to 24 hours. The halide activator decomposes, the halogen reacts with the aluminum or aluminum alloys to form aluminum halides. The aluminum halide vapor diffuses towards the surface of the substrate and disproportionates, releasing the Al halide to further react with the aluminum powder in the pack. The Al deposit on the surface of the part to be coated diffuses into the substrate to form a layer, the thickness of which is a function of time and temperature of the treatment.

The remaining powder has to be treated in most countries as special waste, it has then become an environmental problem. Masking can be done by hard masking, tapes, dry powder or if necessary by slurry.

The process is well established. Narrow diameters or complex shaped internal cooling channels are often restricted for engine parts by OEM specifications to be coated with the pack cementation as this might block cooling holes in service by remaining powder.

Out of pack

The out of pack aluminizing process uses a carrier gas to force the Al halides – formed in a pack which is separated from the part to be coated – at a temperature range of 800° C – 1100° C to the surfaces which will then be aluminized. Blades or vanes can be coated internally or externally.

The waste problem is analogous to the pack cementation if a powder mixture is used. Internal passages can be coated as it is a gas phase process.

CVD aluminizing

CVD produces the aluminum halides externally and a carrier gas Ar and/or H_2 transport these under reduced atmosphere to the surfaces of the parts – located in the retort - to be coated. Tooling and masking are more complex, the investment is relatively high but consumables are comparably cheap. All complex internal channels and external surfaces can be coated.

Slurry aluminizing

The slurry of Al (or AlSi) powder in an acidic phosphate mix is sprayed with a normal spray gun onto the surfaces to be coated. The slurry is then dried and finally baked in a furnace at temperatures of 870° C – 950° C to melt the Al powder – which is held in a ceramic phosphate matrix – and diffuse the Al into the base alloy. Areas not to be aluminized are easily masked: any maskant resistant to acidic phosphates can be used (tapes, stripes etc). The masking is removed before tempering the applied slurry. As a spray process this slurry process can be used for external surfaces only. The remaining polyphosphates – which do not diffuse with the Al – have to be removed carefully after the Al diffusion cycle. It has the lowest investment, but the diffusion leads to some environmental problems.

COATING MECHANISM General aspects

For the aluminizing of nickel superalloys the Al-Ni phase diagram is essential. Figure 2 shows the various Ni aluminides possible depending on the temperature range and the ratio of Al:Ni.



Figure 2. Al-Ni Phase diagram [24]

The important reactions dominating the formation of Ni_xAl_y are a) the diffusion rates of Al and the base alloy elements and b) in the gas phase reaction processes of pack cementation, out of pack and CVD the high temperature behavior of the Al-halides. The important Al-chlorides and –fluorides are at lower temperatures only stable in the 3-valent status. At higher temperatures (and/or lower pressures) the mono (sub)-chloride or -fluoride is the stable compound. This Al mono halide can react with nickel in nickel superalloys to the desired NiAl diffusion layers.

This is schematically expressed by the reactions a + b:

- a) $AlCl_3 + 2Al \rightarrow 3AlCl$
- b) $3AlCl + 2Ni \rightarrow 2NiAl + AlCl_3$

Although the principles are the same for the 3 cited processes the conditions for these reactions are very different. Thus processes may vary in coatings and coating thickness/composition ranges.

Pack cementation

Goward and Boone published in 1971 a paper [25] in which they established the mechanisms of the growth of aluminide coatings on nickel superalloys:

two diffusional growth mechanisms typify the pack cementation process of nickel superalloys. These depend on the aluminum activity in the pack the temperature and the diffusion coefficients of Al and Ni depending on the amount of Al in NiAl [26]. This gives rise to two coating structures.

- Low activity aluminide coatings, which grow by predominant outward diffusion of nickel presenting the archetypal two-zone structure. The outer zone is a phase pure NiAl layer saturated with alloying elements which diffuse outwardly from the substrate concurrently with the nickel.
- High activity aluminide coatings, which grow by inward diffusion of aluminum resulting in the formation of a Ni₂Al₃ layer. In that condition these coatings are typified by a single diffusion layer. As the coating is formed by predominantly inward aluminum diffusion, substrate structure and chemistry is reproduced in the coating. All the alloy elements are diluted in proportion to the amount of aluminum.

High activity coatings are subjected to a diffusion heat treatment to convert the initial Ni_2Al_3 layer into a more ductile and less oxidizable NiAl coating. During this transformation aluminum diffuses inwardly from the Ni_2Al_3 to meet and react with the nickel diffusing from the substrate. This gives rise to the single-phase NiAl middle zone of the archetypal three-zone structure of the inward-high activity type aluminide coating. The inner zone is created by the outward diffusion of the nickel from the substrate like the diffusion zone in the low activity coating.

Figures 3 and 4 present the microstructures of both: a low activity outward type coating and a high activity inward type coating, as coated and diffused on In 738.

Pack cementation can be carried out under argon inert gas atmosphere as the process formulations above don't indicate any need for hydrogen.



Figure 3. Low activity coating on In738 [25]



Figure 4. High activity coating on In738 [25]

Pack cementation reactions

The pack cementation with NH₄Cl is characterized by following reactions: while heating up the NH₄Cl decomposes at temperatures of 300°C to NH₃ (and further to N₂ and H₂) and HCl which will react with the Al source in the pack to AlCl₃. At temperatures > 600°C the AlCl₃ picks up additional Al to form the AlCl. On the Ni-alloy surface this AlCl disproportionates to Al and AlCl₃; the Al diffuses in the alloy to form the Ni aluminide while the remaining AlCl₃ picks up Al from the Al source again.



Figure 5. Reactions of the pack cementation aluminizing

The temperature range of this pack cementation is dependent on the temperature when the mono halides show significant partial pressure. Figure 7 shows the partial pressures in dependence on the temperature. As can be recognized the minimum temperature of a pack cementation is $\sim 600^{\circ}$ C.



Figure 6. Partial pressures of AIF and AlCl [7]

According to these reactions it is demonstrated that the classical pack cementation process is a **cyclic process**, i.e. this is a closed system and only a minimum activator is necessary. As this is evidently a closed system cyclic process other

consequences are:

- The reaction will start when the relevant temperatures are reached; there is no way of tailoring the process
- The temperature profile of any equipment is dependent on the load: full load with many parts has a higher heat capacity as if the retort is only loaded by the half. As a consequence of that the time/temperature profile is different. Running the same recipe will cause different results. The full load will take far longer to be heated up and especially to cool down; so the reaction time at higher temperature is prolonged, the coating thickness will be higher than that of a half loaded retort if the same time frame and powder mixture is used.
- A similar problem will arise if the temperature distribution within the retort is not homogeneous: parts located at the higher temperature spots will have higher coating thickness.

Coatings by pack cementation

The recognized 2 archetypal coating structures are generally claimed to be either a

- Low Temperature High Activity (LTHA) or a
- High Temperature Low Activity (HTLA)

coating structure.

Coating structures of aluminides by pack cementation depend very much on the activity of the Al source $(Al \rightarrow FeAl_3 \rightarrow Fe_2Al_5 \rightarrow FeAl_2 \rightarrow FeAl_3)$ and the base alloy elements:

- For the low temperature process the use of high activity Al donor is necessary and the resulting coating is of LTHA structure.
- For high temperatures the situation is slightly different: High Al content of the Al donor will result in a High Temperature High Activity (HTHA) structure first. Externally a NiAl_x is formed which can be transformed by a heat treatment to the desired NiAl.

The use of a high Al containing alloy with AlF_3 as activator for example, results at temperatures > 1000°C after 4 hours in an external layer of 56-60at% of Al independent of pure Ni, Ni20Cr, In738 or DSCM247LC used.

Different are the Ni contents of these layers: while with pure Ni and Ni20Cr the ratio Al:Ni is 56:44 (at%) the In738 or DSCM247LC alloys show an Al:Ni at% ratio of 60:30 (In738 [Fig.7]) and 54:35 (DSCM247LC).

All these formed diffusion layers are converted by a heat treatment for 2 hours @ 1120 °C to a NiAl diffusion layer with an at% ratio of Al:Ni as 38:62 (pure Ni), 33:59 (Ni20Cr) or 35:50 (In738 (Fig.8) & DSCM247LC).



Figure 7. In738 aluminide by pack cementation @ 1000°C



Figure 8. In738 aluminide after heat treatment @ 1120°C

This indicates the dominating effect of the Al donor: Al is transferred to the base alloy to a level which must stay beyond the Al-level of the donor. This is a cyclic process, i.e. the built NiAl_x diffusion layer can act as a donor as well. The consequence is that if the Al level of the donor will drop beyond the level of the NiAl_x layer then the coating cycle will change the direction. NiAl_x acts as the donor and the pack-donor will be coated by the NiAl_x.

In this case the final status depends on the pack volume close to the surface to be coated. A depleted Al donor region is developing in the pack mixture opposite the coated surface. This effect can be recognized after coating vanes internally. In the edges of trailing and leading edges the range of the pack depletion is reached during the process, the aluminizing stops. The result is a thinner coating in this area – compared to the other surfaces as demonstrated in Figure 9 after the internal aluminizing of a vane.



Figure 9. Internal aluminide thickness distribution in a vane by pack cementation

Out of pack aluminizing

Out of pack reactions

The reactions of the out of pack process are the same inside the pack as those discussed for pack cementation. The significant difference is now the open system: a carrier gas of Ar and/or H_2 transports the Al halide gases - formed in the pack - to the parts and out of the retort. The reaction flow is shown in Figure 10.



Side Reaction: AICI₃ / AICI + H₂ \rightarrow AI + HCI



The start of the reactions is the same as in pack cementation. But then there is a direction of the process: after having transported all activator out from the pack a reaction is no longer possible.

CVD aluminizing

The CVD aluminizing is based on the open reactor or flowing gas CVD principle, where the reactants (AlCl₃ and AlCl) are introduced in continuously and flow through the reactor.

The CVD aluminizing normally has an external generator for the AlCl₃ to flow in the reactor passing an internal generator with an additional Al source to generate the AlCl. This AlCl is carried by Ar and/or H_2 to the surfaces to be aluminized. The process is started when the AlCl₃ is generated by the start of an HCl flow. By the HCl control the Al halide formation can be started (and stopped) at any desired time and any temperature: the CVD coating process can be tailored precisely.

CVD reactions

The reactions of the CVD aluminizing are shown in Figure 11.



Side Reaction: AICI₃ / AICI + H₂ \rightarrow AI + HCI

Figure 11. Reactions of the CVD aluminizing

The external generator supplies the system with $AlCl_3$. In the internal generator this $AlCl_3$ picks up further Al to build the Al subchloride (Fig.12). This is an extraction reaction, the efficiency is dependent on the temperature and the geometric set up.



Figure 12. The subchloride process

The equilibrium reaction of $2Al(l) + AlCl_3(g) = 3AlCl(g)$ has been determined [27] to follow the equation:

$$\log K_{p} = P^{3}(AlCl) / P(AlCl_{3}) = -14,440/T + 9.87$$
$$\Delta G^{0}_{T} = 66,060 - 45.16T$$

The reaction of AlCl₃ with Al to AlCl starts at temperatures \sim 800°C with amounts that can be recognized (Fig.13). AlCl₂ is not recognized in the relevant temperature range [28].



Figure 13. Percentage of AlCl₃ converted to AlCl as a function of the temperature (Values calculated from [28])

After the reaction of AlCl with the Ni superalloy the remaining AlCl₃ is condensed in the external cooling trap.

From the viewpoint of thermodynamics the usually observed influence of the reduction of the Al chloride by hydrogen can be neglected due to the formation of NiAl at the surface (ΔG of the relevant reactions calculated with HSC chemistry see Figure 14).



Figure 14. Thermodynamics of Al deposition by Al chlorides

It was found, however, that the reaction is somewhat (<20%) accelerated by hydrogen. Analysis of the CVD process steps indicated that primarily the formation of Al subchloride is enhanced by the hydrogen while the NiAl is formed at a similar rate.

Coatings by CVD

The CVD coating structure depends on the AlCl amount in the carrier gas and the temperature. HTHA coatings are possible see Figure 15.



Figure 15. In738 aluminide by CVD

The flowing gas CVD principle causes a reduced aluminizing activity over the coating distance range - similar to the out of pack aluminizing.

Along the Al halide flow the AlCl amount is reduced in the flow along the distance range by loosing AlCl at the entrance because of the aluminizing reaction. When CVD coating a tube internally the aluminide thickness will be higher at the front of the tube than at the end as the AlCl concentration there is less. If parameters of the process are not set up properly the resulting thickness in a nickel superalloy tube can drop for example from 100 μ m at the entrance to 40 μ m at the end depending on the AlCl concentration formed in the internal generator and the range to be coated. (The same problem will arise with the out of pack process when coating a tube internally)

Additionally to the precise tailoring the CVD process has the ability to aluminize even smallest cooling channels in diameters which cannot be coated easily by pack cementation. The resulting CVD aluminides have high coating cleanliness. Further elements as Cr, Hf, Si etc. can be diffused with CVD by adding the relevant generators which makes the CVD system very flexible.

Aluminides by slurry application

Slurry reactions and coatings

The slurry reactions are mainly determined by the diffusivity of Al and especially AlSi.

The requested heat treatment to diffuse the Al (+Si) is normally \sim 870°C with Ni superalloys while for Co base alloys the temperature has to be higher.

The aluminide received is of LTHA structure but an additional heat treatment is recommended. Figure 15 shows a CERAL10 AlSi diffusion coating received by slurry application.



Figure 16. In738 CERAL10 AlSi-aluminide by slurry diffusion

PROCESS SELECTION

The selection of a process to aluminize turbine parts is dependent on a great variety of factors so a fixed recommendation cannot be given. The analysis for a process selection has to cover

- specification for thickness range and Al content
- part design and size
- amount of parts
- retort capacity (load size)
- areas to be coated (internal/external, ability to coat)
- areas to be masked
- masking material and labor for masking
- masking removal and cleaning
- tooling
- automation
- consumables (costs, safety, environment)
- environment & health and safety aspects
- investment costs

SUMMARY

The aluminizing of turbine parts for the protection against high temperature oxidation and hot corrosion can be done by several coating techniques. Although the principle reactions are the same the processes differ remarkably.

- The slurry process can be used for aluminizing external surfaces only. High activity coatings are received. Especially co-deposition of Al and Si can be done easily. The investment is low, the process is cheap, masking is easy and there is almost no waste.
- The pack cementation is simple and can be used for external surfaces and partially for internal surfaces. Limits are given by geometric data. Additional to the "classical" LTHA and HTLA aluminides a HTHA aluminide can be formed. Powder can be incorporated. Masking can be done by preventing the contact of the powder with the areas not to be coated by metal shield, tapes, dry powder or slurry masking. Process costs are mainly determined by the furnace costs as well as powder costs and labor. The remaining powder often has to be treated as a special waste.
- The out of pack process can be used for aluminizing surfaces externally and internally. The received activity depends on the pack, the aluminide thickness possible depends on the activator concentration, temperature and length to be coated. Process parameters cannot be varied during operation. Masking is complex. The remaining powder has often to be treated as a special waste.
- The CVD process is a flexible process. The process can be tailored precisely. Various Al activities are possible. The investment is – relatively – high, but the consumable costs (pure Al) are low. Masking is complex. There is no critical waste. Additional elements can be deposited at same time by adding further generators.

REFERENCES

- [1] S. Bose, 2007, *High Temperature Coatings*, Elsevier Science & Technology Books
- [2] Y. Tamarin, 2002, *Protective Coatings for Turbine Blades*, ASM International
- [3] H. Simon, M. Thoma, 1985, Angewandte Oberflächentechnik für metallische Werkstoffe, Hanser
- [4] G.W. Goward., L.L. Seigle, 1994, *Diffusion coatings for gas turbine engine hot section parts*, ASM Handbook, Surface Engineering, **5**, pp. 611-620
- [5] G.W. Goward, L. Cannon, J. Eng. Gas Turbines Power 1998, **110**, pp. 150-154
- [6] R. Pichoir, *Materials and coatings to resist high temperature corrosion*, 1978, pp. 271-291
- [7] Z. D. Xiang, J. S. Burnell-Gray, P. K. Datta, *J.Mat. Science*, 2001, **36**, pp. 5673-5682
- [8] R. Mevrel, C. Duret, R. Pichoir, *Mater. Sci. Technol*, 1986, 2, pp. 201-206
- [9] D.K. Das, V. Singh, S.V. Joshi, *Met. Mat. Trans. A*, 1998, **29**, pp. 2173-2187

[10] P.N. Walsh, *Proceedings of the Fourth International Conference on Chemical Vapor Deposition*, The Electrochemical Society, Princeton, NJ, 1983, pp. 147-168.

[11] G. Gauje, R. Morbioli, *High Temperature Protective Coatings*, The Metallurgical Society of AIME, Atlanta, GA, 1983, pp. 13-26

- [12] R. S. Parzuchowski, *Thin Solid Films*, 1977, **45**, pp. 349-355
- [13] H. Pillhöfer, M. Thoma, H. Walter, P. Adam, US Patent 1994, No. 5,308,399
- [14] Y. Matsuoka, Y. Matsanuga, K. Nakagawa, Y. Tuda, S. Taniguchi, *Mat. Trans.*, 2006, **47** (9), pp. 2341-2347
- [15] J. Kohlscheen, H.-R. Stock, Surf. Coat. Technol., 2007, 202, pp. 613-616
- [16] B.M. Warnes, D.C. Punola, Surf. Coat. Technol., 1997, 94-95, pp. 1-6
- [17] A. Kempster, Trans.I.M.F, 1988, 76 (6), pp. 88-93
- [18] A.B. Smith, S.M. Ng, Trans. I.M.F, 1996, 74 (2), pp.64-65
- [19] C. Duret, R. Pichoir, Coatings for High Temperature
- Applications, Applied Science, London, 1983, pp. 33-78

[20] A.B. Smith, A. Kempster, J. Smith, Surf. Coat. Technol., 1999, **120-121**, pp. 112-117

- [21] A.D. Joseph, US Patent 1963, No. 3,102,044
- [22] A. Allen, US Patent 1976, No. 3,248,251
- [23] M. Thoma, Proc. XI Surfair, Cannes, 1996

[24] T.B. Massalski, 1990, **1-3**, *Binary Alloy Phase Diagrams*, Materials Park, Ohio, ASM International

[25] G.W. Goward, D.H. Boone, *Oxidation of Metals*, 1971, **3** (5), pp. 475-495

[26] S. Shankar, L.L. Seigle., Met. Trans. A, 1978, 9, pp. 1468-1476

[27] T. Kikutschi, T. Kurosawa, T. Yagihashi, *Trans.J.Inst.Met.*, 1964, **5** (2), pp. 122-126

[28] D.B. Rao, V.V. Dadape, *J.Phys.Chem.*, 1966, **70**, pp. 1349-1353