Discussion

Comments on "Aluminization of nickel-formation of intermetallic phases and Ni_2Al_3 coatings"

In the paper by Thevand *et al.* [1], the effects of pack coating in alumina retorts, of dimensions 38 mm diameter and 30 mm height, with 10 mm × 10 mm × 2 mm thick Ni specimens, were reported. The pack amount used was very low and was comparable to the specimen dimensions. This condition implies that the aluminium deposition from the pack will occur only for a short initial period and, hence, any conclusion drawn from this study is not applicable to typical pack aluminide coating processes where each sample will have enough quantity of pack surrounding it. This problem of limited pack quantity shows up as reduced coating thickness when the number of samples was increased from 1 to 4, as indicated in Table III of [1]. In addition, the authors have used a pure Al pack with very high metallic content (40 wt%) which increases the chance of direct contact between the samples and the molten Al droplets in the pack. This should have also posed the problem of the pack getting very hard due to sintering at the end of the coating runs.

Pack cementation process can be conceived of by the following two stages:

(a) interaction of the surrounding medium with the surface of the specimen (Ni); and

(b) diffusional redistribution of the coating element (Al) within the specimen.

To determine the rate of the process, the kinetics of the chemical reactions in the vapour phase and the diffusional parameters in the vapour and solid phases must be known. Under different conditions, the limiting factor may either be the chemical reaction, or the mobility of atoms in the vapour or solid phase. Relationship between the surface composition of the specimen being coated to the pack composition is a good criterion for establishing the rate-controlling factors during pack aluminizing. If the surface activity quickly approaches that of the pack and remains constant with time, then diffusion in the solid is controlling the rate of coating formation. Otherwise, vapour transport in the pack or surface reaction has significant influence on the kinetics. The present authors have not carried out any analysis of the surface composition and, hence, the effect of cement composition on the type of coating phase formed remains unexplained. Especially puzzling is the formation of all the three Ni_2Al_3, NiAl and Ni_3Al coating phases, as shown in Fig. 2c of [1], in a pack containing 34.65 wt% Al and 14.50 wt% Cr (corresponding to about 82 at% Al and 18 at% Cr) in 120 h at 760° C. As there was no deposition of Cr, its role is only to lower the activity of Al in the pack, very similar to the other alloy packs containing Ni. In this pack, due to high Al activity, most of the coating should have been the Ni_2Al_3 phase, as its diffusion coefficient, D, is at least an order of magnitude higher than even the D value of Al-rich NiAl [2, 3]. However, the above observation implies that Ni_2Al_3 phase was initially formed and subsequently there was no further Al deposition from the pack. Now the system constitutes a Ni_2Al_3–Ni diffusion couple with the growth of NiAl and Ni_3Al intermediate phases. The authors have proposed, without evidence, that the rate of Al supply through the gas phase was lower than the diffusion rate into the substrate. If this were the case, there would have been transfer of Al from the substrate to the pack resulting in a lowering of the surface composition with time. Study of the coating kinetics at short times would help in determining the mechanism of such coating formation.

The reasoning given by the authors that Al should be the major diffusing species in both the Al-rich NiAl and Ni_2Al_3 on the basis of structure is quite reasonable. This view was put forward by Goward *et al.* [4] to explain the observed microstructure of aluminide coating on complex Ni-base superalloys. From our study of diffusion in the Al–Ni system, we have proved this to be the case [2, 5]. Much of the confusion on this aspect has arisen due to the incorrect interpretation of the marker experiments by Janssen and Rieck [6]. From the marker location, the ratio of intrinsic diffusivities of the two elements can only be determined from that composition defined by the marker plane in the phase in which the markers are located. This fact has been ignored in the

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above study. It is interesting to point out that the problem of predicting where the markers will lie *ab initio*, in the case of a multi-phase diffusion problem, is yet to be solved.

The authors have also not given any explanation for the lowering of the rate of deposition with increasing amount of activator (Table III of [1]). This has also been observed by Seigle *et al.* [7]. In the case of fluoride-activated packs, there is condensation of AlF_3 on the specimen surface. This has been confirmed experimentally. This condensation on the surface possibly impedes further transport of Al to the specimen surface.

With regard to the influence of temperature, we have developed a theory of pack aluminizing [8], combining both the gaseous and solid-state diffusion rates. This theory predicts that in the pure Al pack, at low temperatures (~ 800° C), the coating phase that is expected is Ni_2Al_3, and at higher temperatures, it would be liquid + $NiAl_3$. This difference comes about due to the change in the rates of Al deposition and diffusion in the solid. It is difficult to conceive of any basis for the increase in aluminium activity with temperature, as stated by the authors. Even though this theory in its present form qualitatively explains some of the observations, it still needs further refinement. For instance, even though the aluminium-depleted zone has been observed experimentally, it has been assumed that this depleted zone thickness increases parabolically with time, which has not been borne out by experiments. It is to be noted that the formation of this depleted zone adjacent to Ni samples, in pure Al pack is reasonable. Initially, Al is transferred to the sample, as it involves less gaseous transport distance. As Al is consumed, the particle size decreases and, consequently, the vapour pressure increases. Al adjacent to the samples is fully consumed and further Al deposition occurs from the areas adjacent to the depleted zone. However, an analysis of the growth of this depleted zone is quite complex and requires further detailed investigation.

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Reply to 'Comments on "Aluminization of nickel-formation of intermetallic phases and Ni_2Al_3 coatings"'

The purpose of the original publication [1] was to present a more complete view of the morphology and the structure of the coatings formed by pack aluminization of pure nickel, without dealing with the growth kinetics whose study has been detailed elsewhere [2]. In particular, the optimum conditions for the formation of Ni_2Al_3 coatings were determined. Using a pack with high pure-Al content the cementation was carried out in such conditions that an excess of supply of aluminium is present during the time of the runs investigated in this study (20 h). This high Al content provides the answer to the question of limitation of pack quantity posed by the letter [3] commenting on our paper [1]. The dimensions of our pack box are quite comparable to those of the pack box described by Seigle *et al.* [4], which was used by Sivakumar [5]. They used a cylindrical iron retort, 34 mm in diameter and 120 mm in height, but two or three specimens, 10 mm long, cut from a nickel rod 9 mm in diameter, were stacked at equal intervals in the centre of the pack which contained only 10 wt% or less aluminium. Hence, the pack amount used in our investigations was higher than in theirs, since the standard state of these investigations consisted of the cementation of one sample per

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retort. The growth kinetics of the coatings [2] proves that the aluminium deposition occurs during the whole duration of the coating. The kinetics follows a parabolic law, which implies that the rate-controlling process is the solid-state diffusion, and that the gas-phase supply of aluminium to be deposited is ensured. A retardation of the growth rate, that is, a lack of aluminium supply due to depletion of the pack, appears only for coating weights of about 132.50 mg, e.g., after cementation for 40 h at 850° C. Only once, in a case of a pack containing 4 samples, could an impoverishment of the cement after a cementation run of 20 h at 760° C be hypothesized, because of a slight decrease in coating thickness. Nevertheless, the pack surrounding these samples does not show a visible depleted zone. Such a depleted zone has been observed only around one sample subjected to cementation for 64 h.

Therefore, the conclusions drawn from the study of the formation and the morphology of Ni_2Al_3 coatings can be applied to a typical pack aluminide process. A careful mechanical homogenization of the cement prepared by a two-step annealing, as described, avoided sintering of the pack. The pack remained practically as powdery and fluid after the coating runs as it was before the coating runs. Molten Al-droplets, due to flocking together of the aluminium particles in the cement, were found only in packs that had been used in high-temperature cementations (850° C and above).

The pack cementation process for aluminide coating can be described by the following equations:

$$3\,CrF_{2(s)} + 2\,Al_{(l)} = 2\,AlF_{3(g)} + 3\,Cr_{(s)}, \quad (1)$$

$$2\,AlF_{3(g)} + Al_{(l)} = 3\,AlF_{2(g)}, \quad (2)$$

$$AlF_{2(g)} + Al_{(l)} = 2\,AlF_{(g)}, \quad (3)$$

$$3\,AlF_{(g)} + Ni_{(substrate)} = 2Al_{(diffusing\ into\ Ni)} + AlF_3 \quad (4)$$

and

$$3\,AlF_{2(g)} + Ni_{(substrate)} = Al_{(diffusing\ into\ Ni)} + 2\,AlF_3. \quad (5)$$

The coating formation process can be controlled either by solid-state diffusion of Al in Ni, or by the supply of Al to the surface to be coated. The working composition of gaseous mixture was calculated by Arzamasov and Prokoshkin [6] who concluded that the predominant aluminium-bearing species was the dihalide. The activity of the aluminizing pack will therefore depend on the amount of dihalide in the working gaseous mixture.

The nature, i.e., the composition, of the coating phases was verified by X-ray diffraction and microprobe analyses and, in the case of the eutectic surface structure, by X-ray micro-analysis in scanning electron microscopy. This allowed us to classify the coatings, following the traditional classification given by Goward and Boone [7] for aluminide coatings on complex Ni-base alloys, in "high activity" pack coatings for the Ni_2Al_3 coatings and in "low-activity" pack coatings for the NiAl coatings. The growth of the Ni_2Al_3 coatings follows a parabolic law from the beginning, and without alteration with time [2], which indicates that diffusion in the solid controls the rate of this coating formation. The decrease of the Al activity in the pack by alloying Al with Ni involves the formation of a coating with lower Al composition, in this case NiAl. A study of the structure and growth of NiAl-type coatings, more particularly with regard to the relationship of the composition of the coating to pack activity, has been published elsewhere [8].

The coating formed in the "chromaluminizing" pack may be described as an intermediate case of the expanded classification of aluminide packs proposed by Levine and Caves [9]. Thus, we can express in other terms the proposed growth mechanism of this multi-phase coating. The decrease in pack activity due to the alloying of Al with Cr implies that the ability of the pack to supply Al is in balance with the ability of the substrate to supply Ni. This results in the formation of the Ni-rich NiAl and Ni_3Al phases under the initially-formed Ni_2Al_3 coating. The study of the growth kinetics of this coating [10] shows that the various phases follow a parabolic law, which implies that the rate is also controlled by solid-state diffusion.

The theory developed by Sivakumar and Seigle [5], combining solid-state diffusion and gaseous diffusion through an aluminium-depleted zone in the pack, cannot be applied to the high-Al content pack we used in our investigation. Indeed, we can assume that the supply of Al to the surface is not limited, within the duration of our experiments, and that an excess of the aluminium-bearing phase ensures a constant value of Al activity at the surface of the coating, even if the coating composition is less than the nominal pack composition. This is in accordance with the solid-state diffusion process controlling the parabolic growth kinetics. Now this pack activity is related to the concentration of the sub-halide carrier of the Al in the chemical transport reaction. Arzamasov and Prokoskhin [6] have demonstrated that the concentration of both the predominant dihalide and the monohalide involved in the above chemical reaction increase in the temperature range up to 1400° C. On this basis we had proposed that above 950° C the surface activity of Al on the coating shifted to the liquid part of the Al–Ni phase diagram. This involves the formation on the surface of the coating of a liquid phase which precipitates as the hypereutectic structure on cooling. Our observation of the occurrence of this $NiAl_3$/eutectic layer as part of the coating may be ascribed to the unusually high Al content in the pack in comparison with the pack composition of other aluminization studies [5, 9]. In the theory of Sivakumar [3] it is difficult to conceive that the decrease in vapour pressure is a consequence of the particle-size decrease. A study is in progress to determine by laser Raman spectroscopy the nature and the concentrations of the species involved in the chemical transport reaction of pack aluminization. This should enable the determination of the relationship between the composition of the working gas-phase to the composition of the formed coating, and explain the role of the activator concentration in lowering the deposition rate with increasing amount of activator in the pack.

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