

## Interdiffusion between Ni-based superalloy and MCrAlY coating

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**Abstract.** Interdiffusion at the interface between a Co-36.5Ni-17.5Cr-8Al-0.5Y, MCrAlY coating and the underlying IN738 superalloy was studied in a large matrix of specimens isothermally heat treated for up to 12,000 hours at temperatures 875°C, 925°C or 950°C. Modelled results using the finite difference software DICTRA was compared with experimental average composition profiles measured across the interface using a new experimental approach.

**Introduction.** The most critical components in a gas turbine in terms of running costs and life time expenditure are hot section components such as blades and vanes. During service, exposure to the hot gas environment inside the turbine and to mechanical and chemical influences results in a degradation of the components. These hot section components are typically manufactured in nickel or cobalt base superalloys with high creep strength, and are also often equipped with protective coatings like the MCrAlY-type coating.

The life time of the MCrAlY-type coating depends on the availability of aluminium and chromium that form protective oxides at the outer surface. The formation of protective oxides is however not the only mechanism removing aluminium and chromium from the coating. At the interface between the coating and underlying superalloy, compositional differences can lead to significant loss of the active elements through interdiffusion. In the present work the interdiffusion between an IN738 superalloy and a Co-36.5Ni-17.5Cr-8Al-0.5Y, MCrAlY coating is modelled using the finite difference software DICTRA [1] and compared with experimental results obtained by a new method for composition profiling in the scanning electron microscope (SEM)

**Material.** Microstructural investigations were done for a matrix of isothermally heat treated MCrAlY/ IN738 specimens.

Average compositions of the MCrAlY coating and the IN738 superalloy are shown in tables 1 and 2. The MCrAlY coating was applied by low pressure plasma spraying after which, the specimens received a standard two step heat treatment:

- 1) 1120°C for 2 hours then air cooled with an average cooling rate of 35°C/min to 650°C.
- 2) 845°C for 24 hours then air cooled with an average cooling rate of 20°C/min to 650°C.

In the following the as-coated condition refers to specimens having received this initial heat treatment.

*Table 1: Average composition of MCrAlY coating.*

| MCrAlY | Ni   | Cr   | Al | Y   | Co  |
|--------|------|------|----|-----|-----|
| Mass%  | 36.5 | 17.5 | 8  | 0.5 | bal |

*Table 2: Average composition of superalloy IN738.*

| IN738 | Cr   | Co  | Al  | Ti  | W   | Ta   | Mo   | C    | Zr   | B    | Nb   | Ni  |
|-------|------|-----|-----|-----|-----|------|------|------|------|------|------|-----|
| Mass% | 16.0 | 8.5 | 3.4 | 3.4 | 2.6 | 1.75 | 1.75 | 0.11 | 0.04 | 0.01 | 0.85 | bal |

Specimens were then isothermally heat treated in air at 875°C for 500, 1,000, 2,000, 4,000 and 8,000 hours and at 925°C and 950°C for 250, 500, 2,000, 4,000, 8,000 and 12,000 hours.

Standard metallographic procedures were used to cut, mount and polish the specimens in cross-section. Specimens were ground and then diamond polished to 1  $\mu\text{m}$  finish. The metallographic specimens were then coated with approximately 50 nm evaporated carbon for observation in a JEOL 5900 scanning electron microscope (SEM) equipped with an INCA 400 energy dispersive x-ray spectroscopy (EDS) system from Oxford Instruments.

The interface between coating and superalloy was studied in cross-section both in polished and etched condition using backscatter contrast. Average composition profiles were measured using an approach that is described in detail in [2] and shortly outlined in the following.

**Microstructural investigations.** In previous work [3], it was found that diffusion of aluminium from the coating into the IN738 substrate resulted in the formation of a precipitate free layer in the interdiffusion zone and the formation of a  $\gamma'$ -rich layer on the superalloy side of the interface.

Fig. 1 shows the microstructure at the interface in a specimen isothermally heat treated at 925°C for 250 hours. The precipitate free zone is visible between the bulk coating and a zone with increased volume fraction of  $\gamma'$  on the superalloy side. The experimental work revealed that the following phases were present at the interface:  $\gamma$ ,  $\beta$ ,  $\gamma'$ ,  $MC$  and  $M_{23}C_6$ .

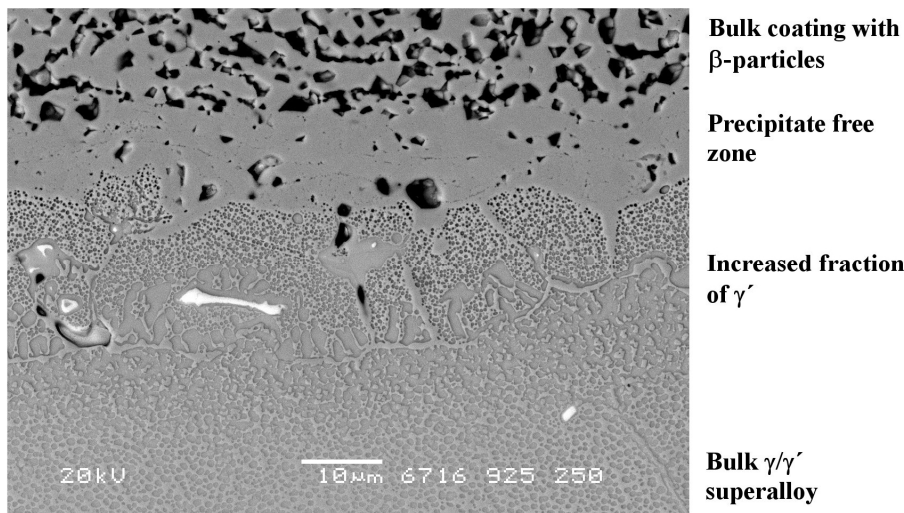


Fig. 1. Interface between coating and substrate for a specimen heat treated for 250 hours at 925°C. The precipitate free zone is visible.

**Experimental approach for obtaining average composition profiles.** In order to test the accuracy of the modelled results, detailed experimental data needs to be available for comparison. Obtaining composition profiles in the SEM is normally a time consuming task and can also be highly problematic in multiphase alloys. Therefore work was done to find a suitable approach for measuring average composition profiles across the interface between superalloy and applied coating. This is a difficult task because of the many precipitate phases present in both bulk superalloy and coatings. In the present work composition profiles across the interface were measured in the scanning electron microscope (SEM) using an approach that converts 2-D information from EDS x-ray maps into 1-D composition profiles.

The original x-ray dot maps provided only qualitative information about the distribution of single chemical elements in the form of a dot, if an element was present, and no dot if an element was not present. This qualitative information could not be translated into concentration profiles. Modern SEM EDS systems however provide the option of spectrum imaging where a single pixel contains a total measurement spectrum. The measured spectrum for a single pixel has very poor count statistics making it difficult to make a conversion from intensity to concentration because of the poor signal to noise ratio. However if pixels can be grouped in a sensible way the count

statistics and the signal to noise ratio can be improved immensely by obtaining average spectra from such groups of pixels. This has resulted in advanced auto-phase procedures [4] where each pixel is automatically assigned to a given phase from criteria based on the spectrums of the individual pixel.

The pixel selection criterion is much simpler for making profiles across straight interfaces such as the interface between a coating and substrate. We just have to select all pixels in lines parallel with the interface. Still this criterion is not implemented in commercial SEM software packages.

Since we have easy access to the actual x-ray map pictures that contain intensity information in the form of grey pixel values of single pixels (varying from 0 to 255), it was decided to simply calculate composition profiles based on the grey pixel intensity. In the SEM the superalloy/coating interface is aligned vertically when the x-ray maps are measured. The x-ray map pictures are then converted into spreadsheet data by converting the grey tone of each pixel into a number between 0 and 255, where 0 is black and 255 is white. In this way a large matrix of grey tone values is obtained. By summing up the values in strips of pixels parallel to the interface of interest and calculating the mean, a value for the average intensities across the interface(s) of interest can be obtained and plotted.

The intensity profiles can then be converted into composition profiles by applying a standard background correction and matrix correction scheme for atomic number correction, absorption correction and fluorescence correction for each average intensity value. The approach is superior to normal point by point measurements since the influences of inhomogenities and precipitate phases are suppressed and an average profile is obtained without using excessive SEM time. The approach is described in detail in [2]. The procedure is illustrated for the Cr x-ray map shown in *Fig. 2*.

For comparison with modelled results average composition profiles across the interface were obtained for all the isothermally heat treated specimens.

**Modelling.** Modelling was performed using the DICTRA software from Thermo-Calc AB. Thermodynamic data was obtained from the nickel-alloy database Ni-data v. 4 by Thermotech [5]. Kinetic mobilities were obtained from work by Boettinger et al. [6].

The standard DICTRA model developed by Engström et al. [7] is a so-called disperse phase model that only takes into consideration diffusion in the matrix phase while particles are handled as non-diffusion phases. The model therefore assumes that the  $\gamma$ -phase is a continuous phase and that diffusion only takes place in this phase. The other phases present are implemented as dispersed phases that act as point sinks or sources for solute atoms as the fraction of the phases grow or shrink in response to the simulated composition in specific node-points.

The impeding effect of the precipitate phases on the diffusion is then implemented by the use of a resistance parameter called the labyrinth factor that is a function of the volume-fraction of particles.

A common choice for the labyrinth factor is simplified versions of the bounds derived by Hashin and Shtrikman [8]. Hashin and Shtrikman used variational methods to derive upper and lower bounds for the effective magnetic permeability of macroscopically homogenous and isotropic multiphase materials. Such bounds are also applicable to diffusion and have been used by Engström et al. [9] and Gómez-Acebo et al. [10].

When  $D_\gamma \gg D_{particles}$  and  $f_\gamma > f_{particles}$  then the upper bound can be simplified to:

$$D_{eff}^{upper} = D_\gamma \left( \frac{2f_\gamma}{3 - f_\gamma} \right). \quad (1)$$

This expression was used by Gomez-Acebo et al. [10] in their calculations and is equivalent to the expression derived by Raleigh [11] for the influence of spherical particles.

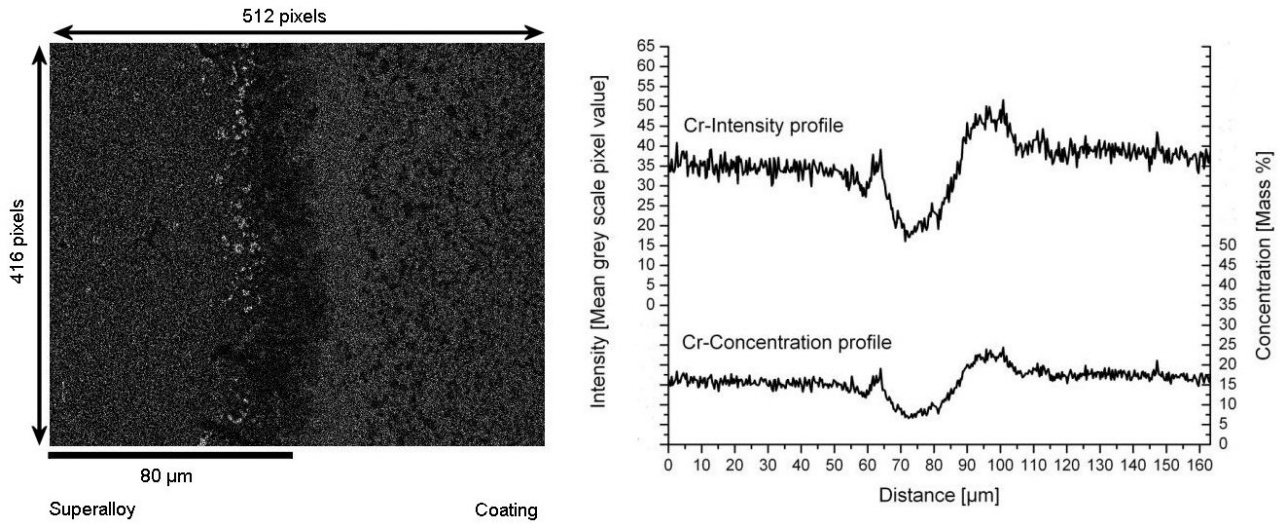


Fig. 2. Cr x-ray map for a specimen heat treated for 4000 hours at 875°C. The x-ray map has a resolution of 512x416 pixels., which results in 512 data points, each an average of 416 grey scale values, resulting in the Cr-intensity profile shown. Applying a standard background correction and matrix correction scheme, while taking all the chemical elements present into consideration, then allows us to calculate concentration profiles for all the elements. This approach gives us nice average concentration profiles (especially compared to traditional point by point measurements) that can be compared to the results of 1-D modelling and can be obtained using little SEM time.

In the present calculations the volume-fraction of  $\gamma'$  reaches a very high value at the interface between coating and superalloy because of diffusion of aluminium into the substrate. If the *Raleigh* expression is used, the labyrinth factor will then be almost zero, causing the diffusion to stop and the calculations to break down.

Therefore as a first approximation a labyrinth factor was used where it was assumed that when the volume fraction of  $\gamma$ -fcc approached zero, the diffusivity would be approximately an order of magnitude slower than in the pure  $\gamma$ -fcc ( $D_{particles} = 0.1D_{\gamma}$ ). Inserting this into the expressions derived by Hashin and Shtrikman, leads to the following expressions, where the term in brackets can be used as labyrinth factor in the calculations:

$$D_{eff}^{upper} = D_{\gamma} \left( 1 + \frac{3 - 3f_{\gamma}}{f_{\gamma} - \frac{10}{3}} \right). \quad (2)$$

$$D_{eff}^{lower} = D_{\gamma} \left( 0.1 + \frac{0.9f_{\gamma}}{4 - 3f_{\gamma}} \right). \quad (3)$$

In the present calculations the expression for the upper bound is used. It must however be emphasized that the used expression is an upper bound for a two-phase system where the diffusivity in the particle-phases is one tenth of the diffusivity in the matrix phase, it is not an upper bound for diffusion in the actual system. In order to employ the correct expressions for the system a model that could directly take the diffusion inside the precipitate phases into account would be needed.

**Initial conditions.** Initial concentration profiles were entered using an error function expression as shown below:

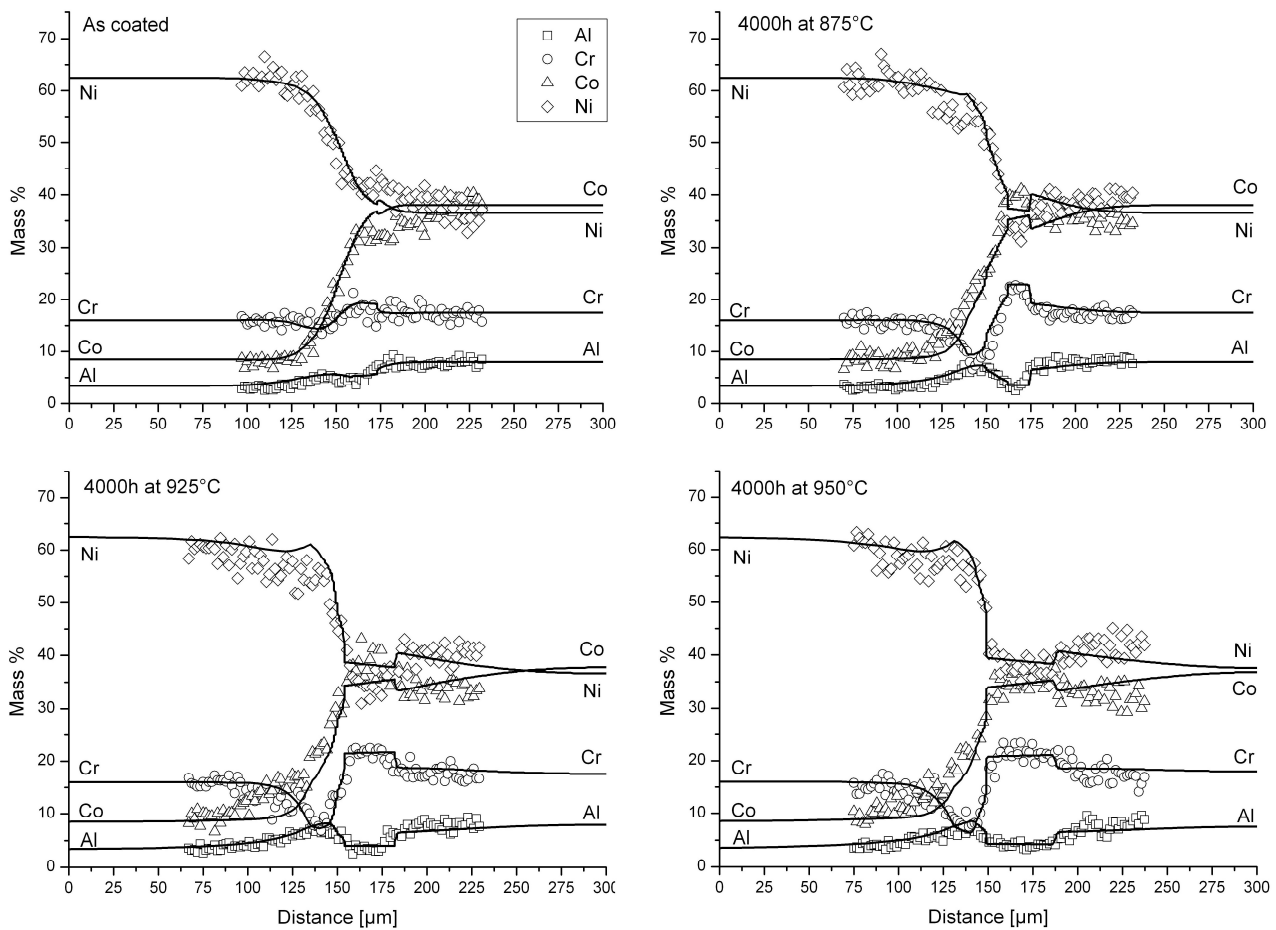
$$c_1 + \frac{c_2 - c_1}{2} \left[ 1 + \operatorname{erf} \left( \frac{x - x_i}{s} \right) \right]. \quad (4)$$

where  $c_1$  and  $c_2$  are the initial concentrations on different sides of the interface,  $x$  is the position on the x-axis,  $x_i$  is the position of the interface and  $s$  is a constant used to adjust the smoothness of the transition between the two concentrations in the vicinity of the interface.

The average specified compositions from *Table 1* and *Table 2* were entered as start values. The actual composition of the specimens may deviate somewhat from the average specified composition. The purpose of the present work is however to show that DICTRA can be used as a predictive tool for the behaviour of coated gas turbine components and for such components typically only the specified compositions are available.

Diffusion calculations were done considering the elements *Al, Ti, Cr, Co, Ni, Mo, Ta, W* and *C*. Phases considered in the calculation were  $\gamma$ -fcc,  $\gamma'$ ,  $\beta$ ,  $\sigma$ , bcc, MC and  $M_{23}C_6$ .

**Results of simulations.** *Fig. 3* shows a comparison between modelled and experimental results for specimens heat treated for 4000 hours at the three temperatures. Overall, there is a good consistency between the simulated and the experimental results.



*Fig. 3. Measured (symbols) and modelled (solid lines) composition profiles for the as-coated specimen and specimens heat treated at 875°C, 925°C or 950°C for 4,000 hours. Calculated initial interface was located at  $x=150\ \mu\text{m}$ .*

The modelled results are able to predict the formation of the precipitate free layer (see *Fig. 4 A*) between coating and substrate, formation of the zone enriched in  $\gamma'$ , and also the increased volume fraction of secondary carbides that can be seen as Cr-rich precipitates on the superalloy side of the interdiffusion zone in the Cr x-ray map shown in *Fig. 2*. Qualitatively the modelled results are therefore able to predict the interface behaviour in terms of correct trends in both composition profiles and phase-fraction diagrams.

The fit to the experimentally measured layer widths (see *Fig. 4 B*) is quite good, which is in fact a bit surprising since the result is obtained without any input of the true diffusion parameters for the  $\gamma'$ -phase that reaches a high volume fraction at the interface. The reason for the nice fit is probably that diffusion in the  $\gamma'$ -phase is very slow compared to  $\gamma$ -fcc and therefore it works as an effective block for diffusion both in the actual microstructure and in the simulations.

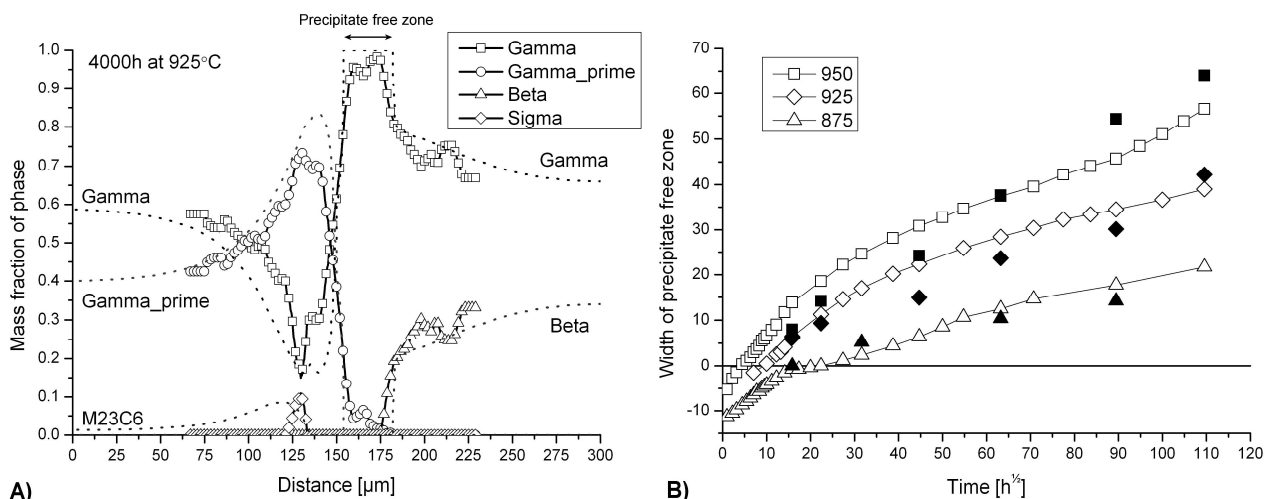


Fig. 4. A) Phase fraction diagram for specimen with 4000 hours at 925°C; solid lines with symbols are calculated from the measured composition profiles and dotted lines are modelled profiles. B) Modelled width of the precipitate free zone; solid symbols are experimental values measured in [3].

**Conclusion.** The complex interface behaviour between a MCrAlY coating and the underlying IN738 superalloy was quantified using a new experimental approach for obtaining average composition profiles and then modelled using the finite difference software DICTRA. Modelling was able to qualitatively describe phase transformations occurring at the interface and the width of the precipitate free zone formed between coating and superalloy were of the same size in the experiments and the simulations. A more sophisticated model able to take into account diffusion in the precipitate phases would be needed to precisely describe the interdiffusion.

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