Memories of Georg Wahl

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After finishing my PhD thesis at University of Erlangen at the end of 1980, I started on the 1st of October at Brown Boveri research center in Heidelberg as a member of Georg Wahl's research group. This group was involved in CVD research on semiconductor layers as well as on abrasive layers for hard facing steels. A new research topic was high temperature corrosion of nickel base superalloys in helium containing traces of methane as well as water for high temperature gas cooled reactors, which were under development at the Research Center in Jülich, as well as other institutes and companies in Germany and Great Britain. One of the major problems associated with the impurities in helium was extended carburization of nickel base superalloys as IN 617 and Hastelloy X, resulting in precipitation of chromium rich carbides, especially at grain boundaries. Such internal carburization promotes embrittlement by significant reduction of alloy ductility. If high thermal or external stresses, as a consequence of high gas pressure and temperature changes, are applied it results in crack formation and propagation. Carburization experiments have been carried out in the temperature range from 600°C to 1000°C using high resolution microbalances to investigate carburization kinetic processes in controlled H_2/CH_4 gas mixtures with different carbon activities. For long-term application protective coatings are required, and an interesting system of siliconizing the alloy surface using CVD -techniques has been developed to increase the subsurface area of the alloy with silicon resulting in the formation of silicide precipitations in a Si-containing matrix. These coatings showed significant reduction of carbon uptake and carbon diffusivity which can be attributed to an increase of carbon activity within the subsurface alloy and a C-activity gradient /1/. This effect is best demonstrated by the famous Darken experiment coupling a Fe-C alloy with a Fe-C- Si alloy with identical C- content at the beginning. After high temperature exposure the carbon content in the binary alloy is increased and lowered in the Si containing alloy demonstrating the so-called up-hill diffusion effect as a consequence of the C-activity increase in the Si-containing alloy. The same effect is also responsible in nickel based alloys. The effect of Si on reduction of carbon uptake was more pronounced at lower temperatures and disappeared at around 1050°C. Similar investigations have been applied for CVD Ti-Si modified coatings and CVD aluminide coatings in carburizing environments /2,3/. Today Si-enriched coatings in combination with aluminide coatings are widely used to reduce carburization kinetics in methane crackers for hydrogen production in the chemical industry.

Calphad based simulation using Solgasmix PV, one of the first software programs to calculate equilibrium compositions in complex gas mixtures and alloy systems based on thermodynamic data to predict the resulting composition of precipitates and their component activities in complex alloys, ceramics and coatings, was an important research area and simulation tool of Georg Wahl's group and it has been successfully applied to many scientific applications in the area of CVD, high temperature corrosion and solid state reactions in high temperature alloys and ceramics.

A key research topic of high scientific value as well as industrial relevance in Georg Wahl´s group in the early 80s was the development of so-called MCrAlY – overlay coatings to protect hot gas path and turbine blades against oxidation and hot corrosion due to low melting sodium and potassium sulfates in oil and natural fired gas turbines, which became extremely important at that time. They were a prerequisite for increasing service temperatures of industrial gas turbines due to their higher hot corrosion resistance and ductility at high temperatures compared with aluminide coatings which are used in aero engines. Such coatings are still today essential, to increase gas inlet temperatures and efficiencies of industrial gas turbines as well as aero engines.

These coatings are based on Ni or Co and contain typically 20-30 % Cr, 5- 12 % Al, some minor additions of 1-3 % of elements like Si, Ta, and 0.2 to 1 % of rare elements based on Y, Hf or other rare elements to promote the formation of a slowly growing alumina scale. These coatings are applied by plasma spraying or EB-PVD technologies. These technologies have been developed in the 80s and are state of the art today to protect hot gas parts of aircraft engines and industrial gas turbines. Important research was performed in Georg Wahl´s group on both the development of new coating systems for gas turbines made by Brown Boveri and to develop the appropriate deposition technique using plasma spraying processes. /4/. The development of the coating chemistry was based on extended cyclic oxidation experiments of vacuum cast alloy samples with different composition to identify promising compositions with excellent oxidation resistance up to 1100°C und up to 10000 hours of operation /5/. High resolution electron microscopy and analytical SEM investigation had to be performed to understand the complex temperature dependent microstructure of the candidate coating systems and their degradation as a function of temperature, time and isothermal or cyclic oxidation conditions. The best 3 alloy compositions have been selected to produce powders by inert gas atomization in collaboration with H.C. Starck GMBH in the frame of a BMBF funded project to produce coatings on nickel base superalloys by vacuum plasma spraying and to determine their high temperature oxidation resistance, chemical compatibility with typical nickel base superalloys to be used in industrial gas turbines and their mechanical properties at high temperatures. The results confirmed the high oxidation resistance as measured on bulk alloy compositions and showed excellent chemical compatibility with IN 738 and IN 939, superalloys which were common for industrial gas turbines in the 80s ang 90s. The subsequent engine tests on front stage vanes and blades of large industrial gas turbines were very successful. Those coatings became the standard MCrAlY coatings on BBC gas turbines and later also at ABB after the merger of BBC with Asea AB, Sweden, and are still used in industrial gas turbines today.

Georg Wahl was an excellent scientist with a sound background in physics and materials science and with high capabilities to motivate and encourage young scientists and technicians. In his long-term special research area of CVD he was one of the leading scientists, combining novel high-level experimental techniques with simulation activities related to CFD /6/ and Calphad based simulation of composition and thermodynamic stability. This open and innovative environment of his group was very stimulating and extremely fruitful for my further scientific career in industry and afterwards in academia. Based on his excellent scientific research Georg Wahl was elected some years later as Director and Professor of the Institute for Surface Technology at TU Braunschweig to continue his research in the area of CVD and coating science.

/1/ G.Wahl, F.Schmaderer, W. Thiele, Thin Solid Films, 94 (1982), 257

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/5/ Lorenz Singheiser, Georg Wahl, Bernd Jahnke, US Patent 4909984

/6/ G. Wahl Thin Solid Films 40 (1977), 13