

Summer 6-26-2014

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M. Vilasi
Université de Lorraine

S. Matheieu
Université de Lorraine

S. Knittel
IJL-UMR

L. Portebois
IJL-UMR

T. Katrina
IJL-UMR

See next page for additional authors

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Recommended Citation

M. Vilasi, S. Matheieu, S. Knittel, L. Portebois, T. Katrina, C. Rapin, C. Petitjean, P. J. Panteix, and S. Drawin, "Manufacture of silicide coatings for the protection of niobium alloys against high temperature oxidation" in "Thermal Barrier Coatings IV", U. Schulz, German Aerospace Center; M. Maloney, Pratt & Whitney; R. Darolia, GE Aviation (retired) Eds, ECI Symposium Series, (2015).
http://dc.engconfintl.org/thermal_barrier_iv/39

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Authors

M. Vilasi, S. Matheieu, S. Knittel, L. Portebois, T. Katrina, C. Rapin, C. Petitjean, P.J. Panteix, and S. Drawin

MANUFACTURE OF SILICIDE COATINGS FOR THE PROTECTION OF NIOBIUM ALLOYS AGAINST HIGH TEMPERATURE OXIDATION

M. Vilasi, Université de Lorraine, France

S. Mathieu, Université de Lorraine, France

S. Knittel¹, L. Portebois¹, T. Katrina¹, C. Rapin¹, C. Petitjean¹, P.-J. Panteix¹, S. Drawin²

¹IJL-UMR 7198, dept. CP2S, B.P 70239 – 54506 Vandoeuvre-lès-Nancy

²ONERA/DMSM, BP72, 29 av. De la Division Leclerc, 92322 Châtillon Cedex

Key Words: Nb-Based alloys, silicide coatings, packcementation, CMAS corrosion

At the moment, silicide coatings provide the best protection against high temperature oxidation for niobium alloys. These are envisaged for replacing nickel base alloys currently used in the hot section of turbo-engines. Silicides confer higher protectiveness to Nb base system when compared to the environmental resistance presented by Nb alloys coated with aluminides. One major advantage of silicides is probably the great number of possibilities for modifying their composition as well as their crystallographic structure. Thus, many elemental substitutions were performed over the past 20 years in order to optimize their performances in terms of oxidation resistance. The works performed at the University of Nancy focused currently on the M3M'3CrSi6 phase which has Nb3Fe3CrSi6 as prototype [i]. Initially, the coatings were developed for the protection of niobium alloys, strengthened by solid solution and in which the niobium content was rather high, in the range of 95 weight %. The first stage of the works was devoted to thermodynamic studies leading to the determination of phase equilibria in the Nb-Fe-Cr-Si system. Then, the obtained results were used to determine the compositions of masteralloys and the conditions of the pack-cementation processes (temperature, gas atmosphere and time) for depositing the Nb3Fe3CrSi6 phase as superficial layer, in avoiding the growth of brittle silicides as well as silicide sensitive to pest phenomenon.

Further, the works were turned towards the optimization of protective coatings for metal and silicide in situ composites (MASC). The composition of MASC alloys is rather complex as it comprises up to seven elements with a niobium content in the range of 60 weight%. The works for optimizing the coating led to consider the various substitutions permitted by the M3M'3CrSi6 intermetallic structure. These substitutions permit i) the minimization of the mismatch of coefficient of thermal expansion existing both between constitutive phases of the coating and between coating and alloy (Ti was substituted for Nb), ii) to lower the content of very oxidizable elements which oxides are not protective (Ni and/or Co, Ni and/or Fe was substituted for pure Fe) and iii) to maximize the content of elements efficient in oxidation protection (Cr, B).

The high temperature oxidation tests conducted on the range 800 and 1300°C in air with or without water vapor led to the formation of protective oxides mainly constituted of chromia and silica. These latter form the thermally grown oxide (TGO) enabling the adhesion of a thermal barriers based on Gd2Zr2O7 and deposited by DLR. In a potential application, this oxide layer should act also as the last shield resisting to corrosion by CMAS in case of deep infiltration.

The present communication aims at highlighting i) the approaches used to optimize protective coatings, ii) the oxidation rate of both pure silicides and coatings, iii) the nature and the microstructure of protective oxides and iv) finally the chemical behavior of chromia in the presence of simplified molten silicate glasses characterized by different basicity and oxygen fugacity. This last action is intended to simulate the corrosion degradation potentially encountered by the silicide coatings (or bond coat) in the particular case of deep infiltration of liquid CMAS.

[i] M. Vilasi, G. Venturini, J. Steinmetz, B. Malaman, Crystal structure of triniobium triiron chromium hexasilicide Nb₃Fe₃Cr₃Si₆: an intergrowth of Zr₄Co₄Ge₇ and Nb₂Cr₄Si₅ blocks, J. Alloy. Comp., Vol.194, p.127, (1993).