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On Potential Application of Coated Ferritic Stainless Steel Grades K41X and K44X in SOFC/HTE Interconnects

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K41X is a ferritic stainless steel grade which was successfully developed in exhaust gas manifold where the temperature could reach 950°C. It contains about 18% wt of chromium and it is stabilized with both titanium and niobium to warranty a good weldability, formability and high temperature corrosion resistance. Moreover, an addition of niobium improves high temperature mechanical properties, in particular the creep resistance. K44X, an enhanced version of K41X with 19%-wt. of Cr plus niobium and molybdenum, was recently developed to be used up to 1000°C. It exhibits better high temperature properties and oxidation resistance. Thanks to their high temperature resistance and their cost competitiveness, these two grades were recently considered as potential candidates to be used as interconnects for Solid Oxide Fuel Cells (SOFC) and High Temperature Electrolysis (HTE), either bare or more certainly coated in order to increase the life duration of the SOFC or HTE systems. This paper will present the high temperature properties of K41X and K44X, in particular oxidation behavior in isothermal and cyclic conditions under operating atmosphere. The positive effect of the addition of a protective coating on these steel grades in terms of oxidation resistance will then be presented. Most of the studied coatings are Mn-Co spinels deposited by sol-gel, atmospheric plasma spray or electroplating, their aim being to limit the chromium evaporation and to fit the severe performance requirements. They lead to low and stable contact resistance, which is a requirement necessary for long-term SOFC/HTE operation: for example a contact resistance of 22 mΩ.cm^2 was obtained after 3500 h at 800°C in air with MnCoFe spinel coating. In this respect, K41X was recently chosen to be tested for the 3rd generation stacks of SOFC in the European project "REAL SOFC" or the prototypes in French ANR projects.

Introduction

SOFC and HTE cell development is facing different challenges to guaranty the sustainability of this means of energy production: improve performance and durability using low cost solution with large availability. Metallic interconnects (MIC), all canning and tubes may represent about 90% of the total weight of the stack. Ferritic stainless steels are very good candidates for interconnect due to their good high temperature corrosion resistance and their coefficient of thermal expansion (CTE) close to those of Yttrium doped stabilized zircon electrolyte (YSZ). Because of a manufacturing process including a mandatory protective coating on interconnect, more standard grades like K41X, are now tested for this application. K41X and K44X are ferritic stainless steel grades which have been developed for exhaust gas manifold application in order to reach operating temperature up to 950°C and 1000°C respectively.

SOFC and HTE conditions are in similar range of temperature 600-900°C but lifetime must reach few 10,000 h which is far from the time spent at high temperature by an exhaust line. Consecutively specific requirements must be fulfilled:

- Long term oxidation and in SOFC or HTE gas conditions
- Low electrical resistance of the formed oxide scale
- Compatibility with the protective coating which limits of the Cr-species evaporation from the oxide layer (poisoning effect at cathode-electrolyte interface).

Materials and Experimental Procedures

Materials

K41X and K44X are ferritic stainless steels from ArcelorMittal Stainless and follow standards EN1.4509/UNS441 and EN1.4521/UNS444 respectively. The two grades are 18-19% chromium content and are stabilized with titanium and/or niobium to fix carbon and nitrogen. This ferrite stabilization leads to good weldability, formability and an excellent corrosion resistance. Compared to the standard commercial 1.4521/444, the composition and the process of K44X have been optimized to enhance high temperature resistance. Chemical compositions are given in table I.

TABLE I: Typical Chemical Compositions (weight %)

Grades	C	Mn	Si	Mo	Cr	N	Other	Fe
K41X	0.02	0.5	0.6	0.1	17.8	0.02	0.2Ti +0.5 Nb	Bal.
K44X	0.02	0.3	0.6	1.8	19	0.02	0.6Nb	Bal.

Coatings

Despite their high temperature oxidation resistance, all candidate alloys for interconnects did not fulfill the requirements for the application and need a protective coating in order to inhibit the Cr-species evaporation phenomenon: migration of these species and its poisoning effect at cathode/electrolyte interface.

Main developed coatings are dense Cobalt-Manganese ceramic - manganese cobaltite spinel - deposed by atmospheric plasma spraying (APS), water-stabilized plasma spraying (WPS), via Sol-gel or screen-printing methods. Thickness of deposit varies but its order is few microns. A second philosophy is to depose metallic or oxide compound able to react with the growing oxide layer to form the protective coating during the first stage of the use. For example, EDF-EIFER is testing thin dense metallic coating by electroplating (1). Doping of the surface by rare earth element appears to be an interesting way of improvement (2). In this study, we tested the application of screen printed $MnCo_{1.9}Fe_{0.1}O_4$ ceramic coating on K41X

High Temperature Mechanical Properties and Oxidation Tests

High temperature tensile properties are determined following ASTM E21 standard. Creep resistance is evaluated using Sag-Test method giving a measure of the deflection of 200x20x1.5mm sample held horizontally at its ends, placed in a furnace at 950°C up to 100h. This test is well adapted to evaluate qualitatively if a material could support its proper weight load. Lower is the deflection better is the creep resistance.

High temperature corrosion is generally the first property characterized to evaluate an alloy for SOFC or THE application. Two types of tests have been performed:

- Continuous oxidation tests at 800°C – 3000 h under simulated SOFC anode gas - Ar-4%H_2-2%H_2O – and under air assumed to be close to cathode gas condition
- Cyclic oxidation tests under air at maximal temperature of 800 and 900°C -1000 h.

This last type of test allows evaluating the scaling resistance of the oxide layer, simulating start and stop situations. The cycle parameters are given in table II. Oxidation behavior is characterized by mass gain measure as function of time.

TABLE II: Cyclic Oxidation Parameters

	Cycle N°1	Cycle N°2
Tmax (°C)	800	900
Tmin (°C)	30	30
Heating (min)	20	20
Dwell-time (min)	225	225
Cooling (min)	45	45

Contact Resistance

Contact measurements were performed at 800°C in air on 25x25x1.5 mm coupon in stack condition i.e. with permanent current load of 0.3A/cm^2 and including a structured gas distributor layer as used in planar stacks. A contact layer (La,Sr)CoO_3 (LSC) was applied on the samples. For the coated sample, a $MnCo_{1.9}Fe_{0.1}O_4$ coating was applied on to the K41X using screen-printing method following by sintering at 800°C (3).

Microstructural Observations

Samples for cross sectional observation were prepared by mechanical polishing and the oxide layer was protected by a no-acid electroplating of copper before examination.

Scanning Electron Microscopy (SEM) observations have been conducted on MEB-FEG with EDS and WDS detector facilities.

High Temperature Behavior

Metallurgical Stability and Mechanical Properties

Composition of the two grades guaranties a stability of the structure and their properties for long time of exposure at high temperatures. The ferrite structure is kept at all temperature and the excess in niobium cancels the grain growth in the range RT-950°C for K41X, RT-1050°C for K44X. The only structural evolution is a precipitation of Fe-Nb intermetallic phases at grain boundary which increases the creep resistance (Fig.1). This precipitation happens in the first stage of use. Physical and thermal properties were determined and their evolutions with temperature were measured. In particular, the figure 2 shows CTE measured in range from 20 to 1000°C which confirms values close to those of the electrolyte YSZ, so between 10-12x10^{-6}.K^{-1}. Main differences with UNS430 or 439 ferritic grades are improved high temperature mechanical properties. Tensile strength values for K41X, K44X are presented on fig. 3 (left) in comparison with UNS439 in the range from 700 to 900°C. For creep resistance, comparison of Sag-test deflection of the K41X and K44X evidences the improvement brought by the K44X (fig. 3 right). These enhanced mechanical properties are due to the optimized level of niobium and molybdenum content (4).

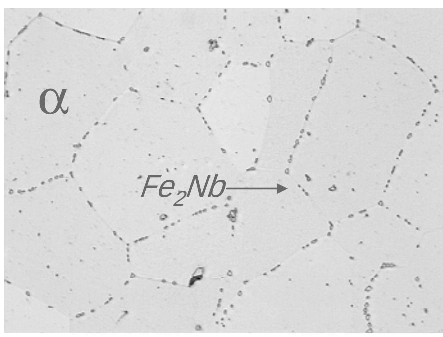

Figure 1.Optical micrograph of K41X after 950°C-100 h showing a grain size of about 30 µm and Laves Fe_2Nb intermetallic phase at grain boundary.

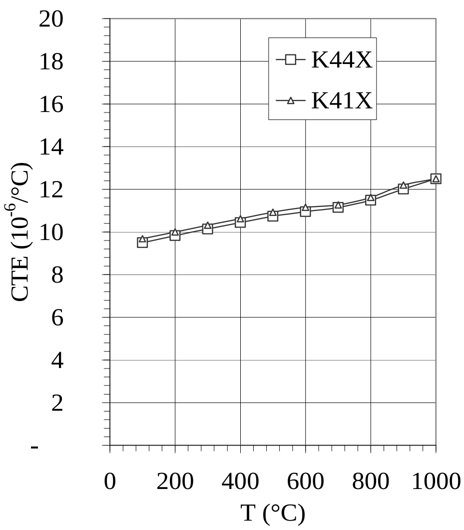

Figure 2. CTE as function of temperature for K41X and K44X steels.

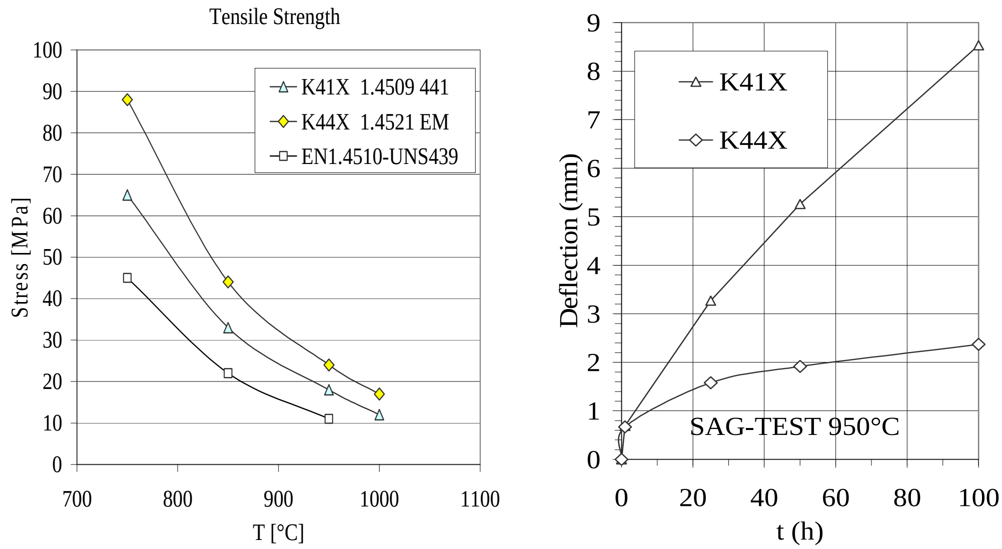

Figure 3. HT Mechanical properties of the K41X and K44X steels (left) HT tensile strength (right) Sag-test creep resistance.

Continuous and Cyclic Oxidation

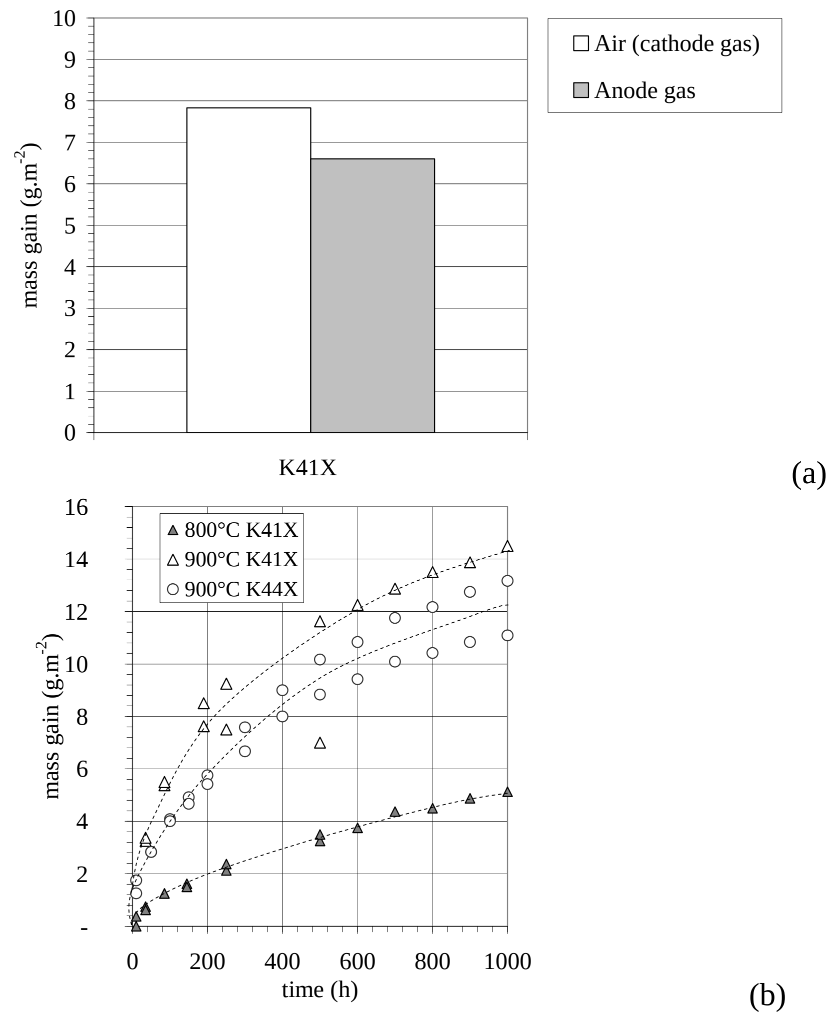

Figure 4. Oxidation results (a) continuous oxidation under SOFC simulated gas condition at 800°C – 3000 h (b) Cyclic oxidation under air at 800 and 900°C -1000 h.

Mass gain results obtained after a continuous oxidation at 800°C -3000 h under SOFC anode and cathode gas are showed on Figure 4a. Mass gain in the reductive anode gas is slightly lower than in oxidant cathode gas. These values are in the range of those determined on Crofer 22APU ferritic alloys (2) and so are in accordance with the requirements expected for the bare metal. Figure 4b presents the cyclic oxidation results: a classical parabolic oxidation kinetic law activated by temperature is obtained. For the longest test duration, a neglected spallation of the oxide may be observed. Kinetic determined at 900°C for the K44X is slightly slower than those of K41X but the main interest of K44X is its higher oxidation resistance for temperature around 1000°C showing no breakaway of the kinetic curve after 400 h.

Microstructural Observations and Composition of the Oxide Layer

Figure 5 shows the typical oxide layer microstructure and compositions observed on ferritic chromium grades, hereby the K41X after 1000 h at 900°C in cyclic conditions. These ferritic alloys use to form a duplex oxide layer of chromia at inner interface and spinel $(CrMn)_3O_4$ at outer interface with the air-atmosphere. In case of titanium stabilized

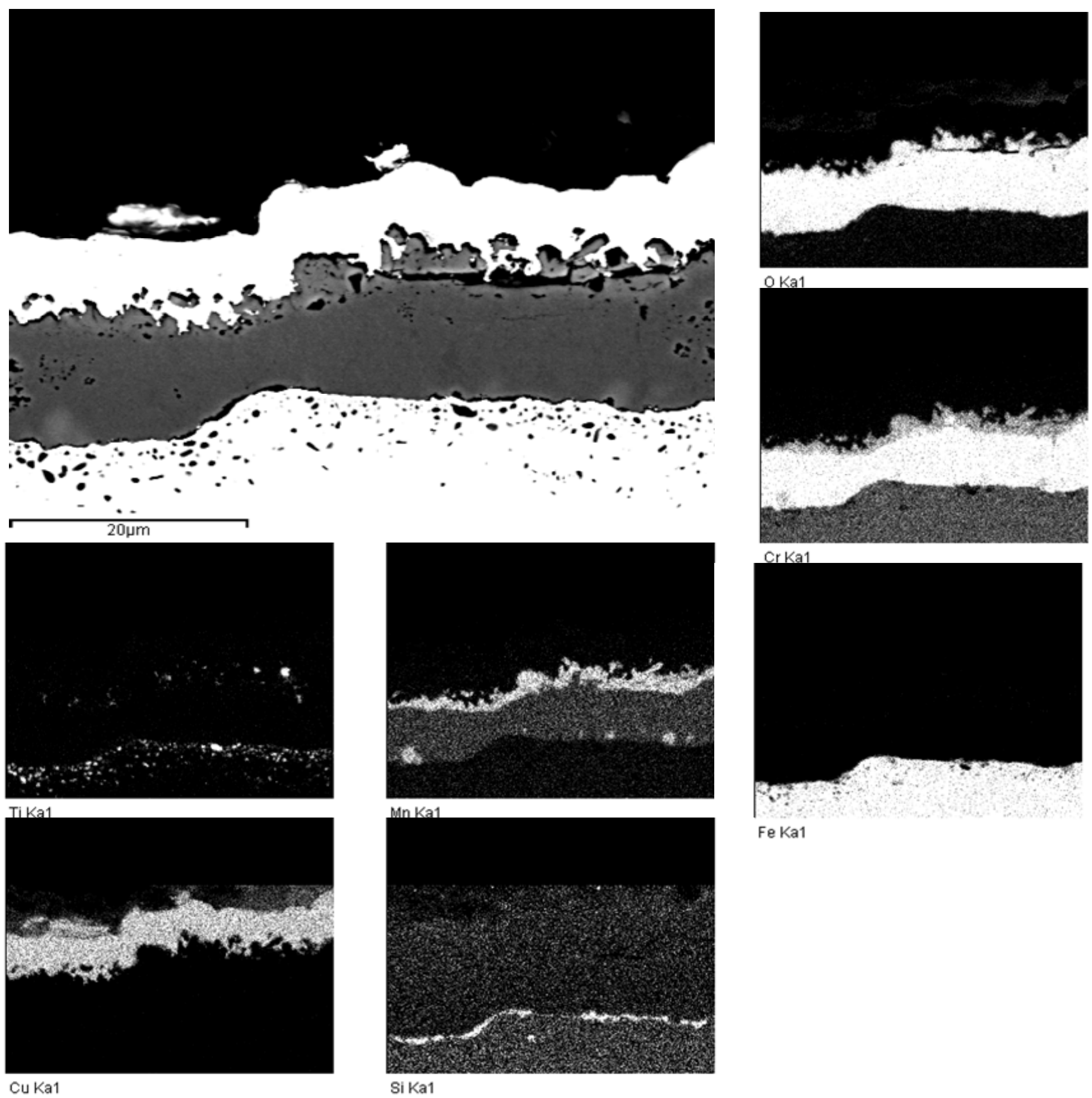

Figure 5. SEM cross-section and EDX mapping of K41X after 1000 h cyclic oxidation in air at 900°C.

grades like K41X, TiO_2 precipitates are observed in the base metal close to the interface. At the same location more or less discontinuous film of SiO_2 is formed. In the base metal, Fe-Nb precipitates can be observed, their role was explained previously.

Contact Resistance

Contact resistance measurements at 800°C as function of time are presented on figure 6. The contact resistance of bare K41X is stabilized at around 45 mΩ.cm^2 after 1000 h but due to the growth of the oxide layer it will no longer fulfill the requirement of a contact resistance below 50 mΩ.cm^2. On the other hand, the contact resistance was measured on K41X coated with $MnCo_{1.9}Fe_{0.1}O_4$ (Fig. 7), which represents the solution proposed to be applied for MIC. Contact resistance reached a stabilized value of about 22 mΩ.cm^2 after 3500 h at 800°C. This plateau value is known to depend strongly on temperature and was measured at 35 mΩ.cm^2 at 700°C and 85 mΩ.cm^2 at 600°C.

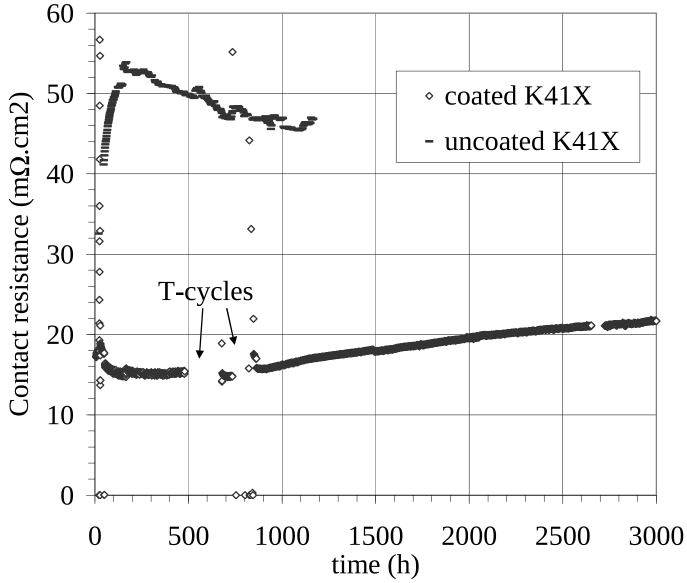

Figure 6. Contact resistances of coated and uncoated K41X alloys during oxidation in air at 800°C (T-cycles indicate stop-and-start cycles).

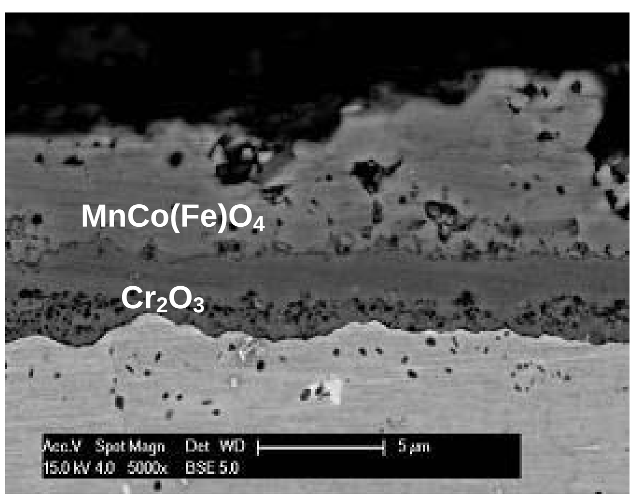

Figure 7. SEM cross-section of coated K41X after 3500h oxidation in air at 800°C.

Conclusion

Our study shows opportunities for more standard and cost effective ferritic stainless grades like K41X or K44X to be used in SOFC-HTE metallic interconnects application. All high temperature properties of these grades have been characterized, in particular oxidation resistance. In fact, all bare alloys did not fulfill the requirements for the application and need a protective coating in order to stop the Cr-poisoning. The K41X coated with Co-Mn spinel showed good result in terms of contact resistance at about a stable value of 22 $m\Omega.cm^2$ at 800°C lower than the requirement of 50 $m\Omega.cm^2$.

The new K44X will offer higher high temperature mechanical properties and could be used for more severe conditions in term of temperature.

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