

ON POTENTIAL APPLICATIONS OF FERRITIC STAINLESS STEEL GRADES IN HIGH TEMPERATURE ENVIRONMENT

APLICAÇÕES POTENCIAIS DE AÇOS INOXIDÁVEIS FERRÍTICOS EM AMBIENTES DE ALTA TEMPERATURA

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ABSTRACT

K41X (AISI 441, EN1.4509) is a commercial 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 mechanical properties and oxidation resistance. Thanks to their high temperature resistance and their cost competitiveness, these two grades were considered as best candidates to be used as high temperature Exhaust manifold, burner of heating systems, interconnects for Solid Oxide Fuel Cells (SOFC) and High Temperature Electrolysis developed for hydrogen production (HTE). The paper will recall the metallurgy of these stabilized ferritic grades and will present the high temperature properties of K41X and K44X, in particular oxidation behavior in isothermal and cyclic conditions under operating atmosphere, their high temperature (HT) tensile resistance and their improved creep and thermal fatigue resistances. A comparison with standard austenitic grade and refractory grades (AISI 304 EN1.4301, AISI 308S EN 1.4828) is done to enhance the advantages of each solution depending on in-use conditions.

Keywords: Ferritic stainless steel, refractory grades, high temperature properties, thermal cycle

RESUMO

K41X (AISI 441, EN1.4509) é um tipo de aço inoxidável ferrítico comercial, que foi desenvolvido com sucesso para a uso no coletor de escape de motores automotivos, onde a temperatura pode chegar a 950 ° C. Ele contém cerca de 18% em peso de cromo e é estabilizado com titânio e nióbio, ambos para uma garantia de boa soldabilidade, conformabilidade e resistência à corrosão à alta temperatura. Por outro lado, a adição de nióbio melhora as propriedades mecânicas em alta temperatura, em especial a resistência à fluência. K44X, uma versão melhorada do K41X com 19% em peso de Cr e ainda adições de nióbio e molibdênio, foi recentemente desenvolvido para ser usado até 1000 ° C. Ele exibe melhores propriedades mecânicas a alta temperatura e resistência à oxidação. Graças à sua elevada resistência a altas temperaturas e à sua competitividade de custos, estes dois tipos de aço inoxidável foram considerados como os melhores candidatos para a fabricação de coletores de escape, queimadores de sistemas de aquecimento, interligações de Células de Combustível de Óxido Sólido (do inglês, SOFC) e eletrólise a alta temperatura para produção de hidrogênio (do inglês, HTE). O artigo vai relembrar a metalurgia destes aços inoxidáveis ferríticos estabilizados e apresentará as propriedades a alta temperatura do K41X e do K44X e, em particular o comportamento em oxidação em condições isotérmicas e cíclicas, sob atmosfera de operação, a sua resistência a tração em altas temperaturas e suas melhores resistências à fluência e e à fadiga térmica. A comparação com o padrão de qualidade e com tipos austeníticos refratários (AISI 304 EN1.4301, AISI 308S PT 1.4828) é feita para comprovar as vantagens de cada solução, dependendo das condições de utilização.

Palavras-chave: aços inoxidáveis ferríticos, tipos refratário, propriedades a alta temperatura, ciclagem térmica

1. INTRODUCTION

Ferritic stainless steels, also known as the Chromium steels or 400-serie, are now widely known and used in many applications like automotive (exhaust system, decorative trim), white product appliance (washing machine, cooktop) and industry applications (hot water tank, heater, sugar plant). A recent International Stainless Steel Forum (ISSF) initiative was launched to remind stainless users how the ferritic solution could fulfill most of the requirements of many applications where the austenitic like AISI 304 EN 1.4301 and AISI 316L EN 1.4404 were well established (ISSF, 2007). Pushed by the more and more severe requirements in exhaust manifold applications in terms of temperature and hot corrosion conditions, the use of high temperature resistant ferritic grades (AISI 439 430Ti EN 1.4510, AISI 441 EN 1.4509) has increased. More recently we have developed a new ferritic grade K44X, that fits AISI 444 EN1.4521 standards, and exhibits improved HT properties compared to AISI 441 or the classic AISI444 grades. In many applications, components are in fact submitted to thermal cycle, at least because the system is started and stopped regularly. The thermal cycling affects significantly the resistance and the life of a part in such condition. In this aim and in addition to conventional isothermal tests we have developed specific tests like cyclic oxidation and thermal fatigue tests.

The paper will review the HT properties of stainless steels in both isothermal and thermal cycling condition and potential applications of the ferritic stainless steels.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Ferritic stainless steel

The considered grades are Ni-free and stabilized ferritic grades, consecutively they could offer a significant cost saving and exhibit a lower price volatility compared to an austenitic grade (Charles et al., 2008). Different strategies of stabilization exist and were early reviewed (Gordon, 1996). Stabilization by Ti and or Nb is the most common: it leads to a low-C and low-N solute solution ferrite and so warranty a good corrosion resistance of heat affected zone after welding by avoiding the $Cr_{23}C_6$ intergranular precipitation and consecutive depletion of chromium. An excess of niobium could lead to a significant improvement of the high temperature properties. Stabilized ferritic grades exhibits very good forming capability especially in deep-drawing because of soft ferrite (no solute C, N like in the common 430) and more due to their higher planar anisotropy compared to the austenitic. The addition of Mo enhances significantly the corrosion resistance (in particular pitting corrosion) and 444 grade could be considered equivalent to 316 austenitic grade. It must be point out that all of the considered stabilized ferritic grades discussed are located on Fe-Cr diagram between 12-20%Cr. In fact, it can be noticed the grades are staying with a same ferritic structure (α) up to fusion. So a grain growth may occur at the highest temperatures but it can be cancelled by an appropriate carbonitride or intermetallic precipitations.

The 409 (K09) - a the reference in the ferritic family – is a 12%Cr Ti stabilized ferritic grade that could offer a correct high temperature resistance up to 800°C. At higher temperatures first problem is the grain growth happening for long dwell times. In addition, 409 can be also limited by its corrosion resistance which is often insufficient in many of applications (corrosion by condensate, oxidation). Consequently, a minimum grade requirement is generally a 17%Cr ferritic grade (439) for such application. Mo-added ferritic grade are also interesting in some applications where an improved “cold” corrosion is needed (even hot part spend some time at room temperature and could be sensible to corrosion by condensate). Two corrosion grades K33X (containing 0.9%Mo) and K36X (436 grade containing 1.2%Mo) are available and their HT resistance are found close to 439 one. Consecutively the only Mo-containing grade presented in this paper would be the K44X, a 19%-Cr grade where Mo and Nb offer both improved corrosion resistance and high temperature

mechanical resistance. Table 1 presents all the ferritic grades characterized for HT applications to be compared to 304 and 308S austenitic grades.

Table 1: typical composition of studied grades

	ASTM	EN	C	Mn	Si	Mo	Cr	Ni	N	Other	Fe
K09X	409	1.4512	0.01	0.3	0.5		11.5		0.01	0.2Ti	
K39M	430Ti	1.4510	0.02	0.4	0.35		16.5		0.015	0.4Ti	
K41X	441	1.4509	0.02	0.5	0.6	0.1	17.8		0.015	0.2Ti +0.5 Nb	Bal.
K44X	~444	~1.4521	0.02	0.3	0.6	1.9	19		0.015	0.6Nb	Bal.
18-9ED	304	1.4301	0.04	1.2	0.5		18.2	8.1	0.055		Bal
R20-12	~308Si/309	1.4828	0.05	1.3	1.6		19.3	11.40	0.030		Bal

Tensile and creep tests

Tensile properties are evaluated using ASTM E-21 or EN 10002 standards on tensile machine equipped with a 1000°C furnace. Tensile strength and yield strength are main properties we considered, elongation data are recorded but did not really bring useable information. Due to the visco-plasticity of the metal at high temperature (effect of strain rate on stress level) the comparison of the data from different sources must be done carefully, in particular we must be sure that the tensile tests are done at same strain rate range.

Creep resistance is evaluated through a Sag-test which consists in maintaining in a furnace a flat sample held horizontally at its ends while monitoring the creep deformation driven by its proper weight. Typical temperature range is from 850°C to 1050°C with typical test duration of 100h. The deflection of the sample is measured as function of time but the results depend on geometry and thickness of the sample. Lower is the deflection, better is the creep resistance. This is a rough but simple method to evaluate the creep behavior of a grade compared to conventional creep to rupture or creep to deformation tests.

Fatigue at HT

Isothermal and thermo-mechanical fatigue tests, in particular high cycle fatigue, were carried out from RT up to 950°C in order to get Wohler curves. Low cycle fatigue and Manson-Coffin curves are also available. All tests were performed on hydraulic tensile/compression fatigue machine equipped with a 1000°C furnace.

Thermal fatigue test consists in submitting a thin plate of which the extremities are constrained to a thermal cycle to reproduce a typical thermal fatigue cycle through a restriction of the thermal expansion of the sample. A specific V-shaped specimen was developed to avoid any buckling of the geometry due to the compressive stress. Dwell times, minimal and maximal temperature of the cycle are controlled while monitoring the constraint force and the number of cycles. Due to the reduction of the mechanical properties of the metal with the increasing temperature, a plastic accommodation occurs during the first half cycle (first heating) leading to a state of minimum stresses at the highest temperature. Then, stabilized loops are rapidly observed and are characterized by a maximal tensile state of stress at the minimal temperature. Such cycles are designated as out-of-phase TMF cycles.

Oxidation test

Oxidation tests are carried out in cyclic condition on a 20 x 30mm sample under air at a maximal temperature between 650°C and 1050°C. Thermal cycle is composed of a 5min-heating up ramp, 20min-holding time and a 5min cooling. Test could reach a total holding time of 400h and 800 cycles. The test allows the evaluation of the oxidation kinetic, the mass gain as function of time, and the scaling resistance of the oxide layer.

3. MAIN RESULTS

Recall of physical properties

In terms of physical properties it must be recall that the coefficient of thermal expansion (CTE) of ferritic grade is significantly lower than austenitics with about $11-12 \cdot 10^{-6}/^{\circ}\text{C}$ for ferritic between RT and 950°C, compared to $18-20 \cdot 10^{-6}/^{\circ}\text{C}$ for austenitic grades (Fig.1). It leads to lower thermal strain and it is of great importance in many HT applications. In comparison with austenitic stainless steel, thermal conductivity of ferritic is higher, 25 vs. 15W/K.m, whereas the specific heat is lower, 460 vs. 500 J/K.kg.

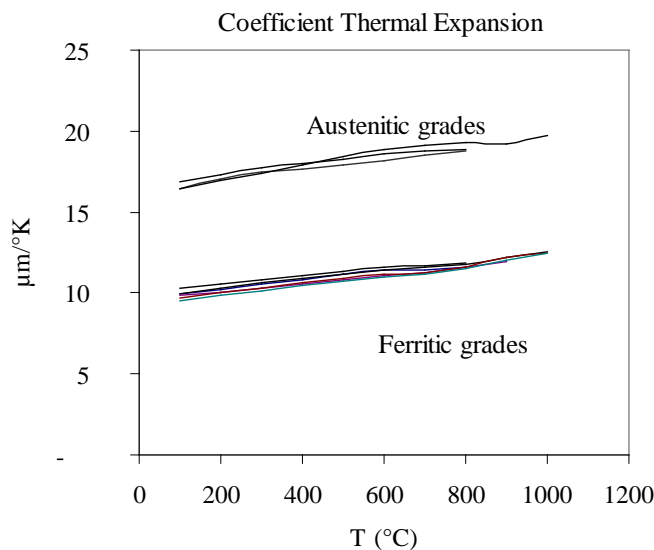


Figure 1: Thermal expansion coefficient of austenitic and ferritic grades

Mechanical Strength

High temperature tensile strength (TS) of a ferrite structure is intrinsically lower than austenitic one and there is no chance to reach the same level, if, in parallel we want to keep good forming ability. It is well known that an excess of niobium in solute solution and/or molybdenum addition could help to increase significantly the tensile strength at high temperature (Fugita, 2003) but not up to the level of austenitic refractory grade (Fig.2). Optimal additions of niobium and molybdenum in K44X lead to an increase of high temperature strength without detrimental effect on forming ability which remains close to that of 441 grade.

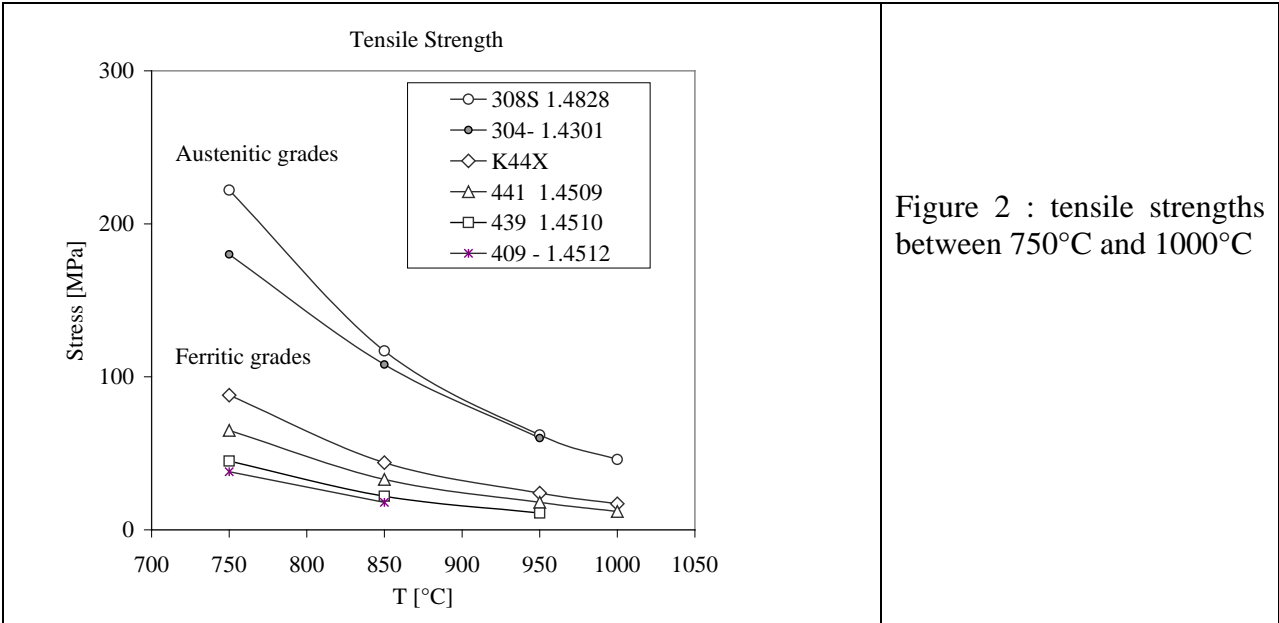


Figure 2 : tensile strengths between 750°C and 1000°C

Creep

On fig 3, the creep resistances at 850, 950°C and 1000°C after 100h are presented below and confirm a better behavior for 441 and K44X in comparison with other ferritic such as 409 and 439. For highest temperature, K44X shows also a better creep resistance than 308Si refractory grades. This creep resistance for both K41X and K44X is induced by an optimized precipitation of Fe-Nb intermetallic at grain boundary that reduces the creep slip. Especially Fe₂Nb₃ cubic intermetallic phase in K44X are significantly more stable than those of K41X such as Fe₂Nb hexagonal Laves-phase.

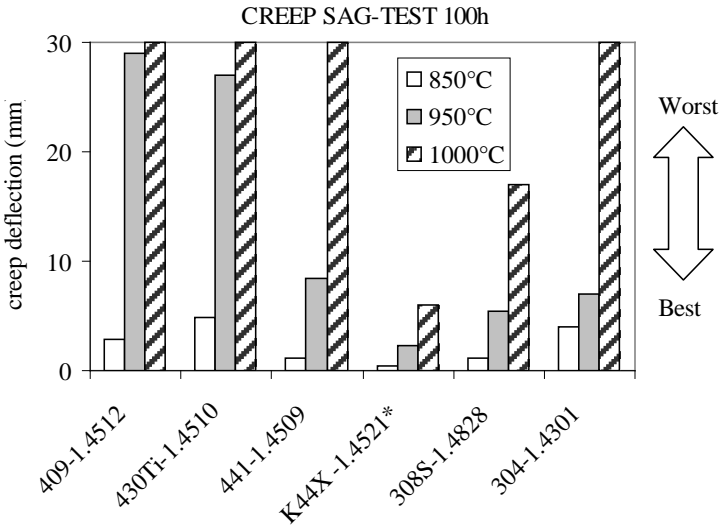
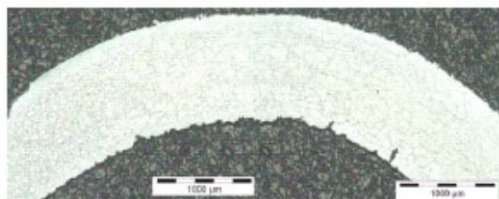


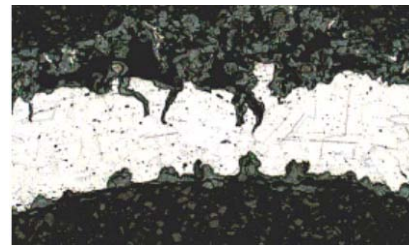
Figure 3: Sag-test creep resistances, deflection, at 850°C, 950°C and 1000°C after 100h of exposure.

Isothermal and thermal Fatigue

Regarding the isothermal fatigue, high cycle or low-cycle fatigue tests, the results can be related to the TS vs temperature curve.. At 850°C the endurance limits at $2 \cdot 10^6$ cycles of the K41X and K44X are respectively 40MPa and 65MPa for a stress ratio of -1, and confirms the improvement already observed for tensile and creep strength. Thermal fatigue tests - which couples both cyclic oxidation and fatigue damage processes - shows an advantage for ferritic stainless steels in these conditions. Origins of such advantage for ferritic like 441 were discussed earlier in papers (Santacreu et al., 2002, G.Chinouilh et al., 2007, Santacreu 2003). Figure 4 presents thermal fatigue lifetime for a 100°C-1000°C thermal cycle with an increase of the fatigue life of about 50% in case of K44X in comparison with 441. The 308S refractory grade exhibits a poor resistance because of a severe cyclic oxidation process coupled with creep mechanisms as shown on fig 4.



K44X at end of the thermal fatigue test



308Si at end of the thermal fatigue test

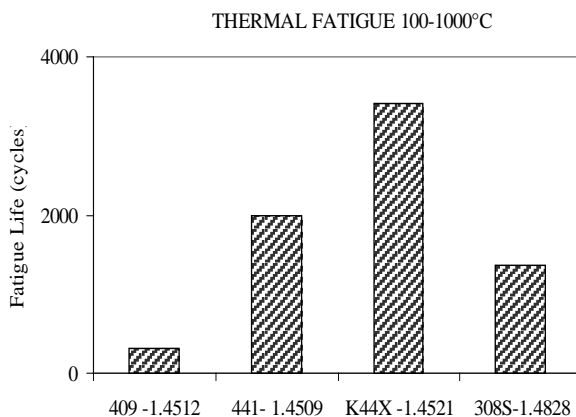


Figure 4: K44X, 409, 441 and 308 1.4828 after 100-1000°C thermal fatigue test.

Cyclic oxidation

Fig. 5a and 5b show the oxidation kinetic expressed by mass gain versus time for a maximal temperature of 950°C and 1000°C. Ferritic grades 441 and K44X have a parabolic kinetic when the refractory grade - here the 308Si - exhibits a linear kinetic with value of mass gain of about one order of magnitude higher compared to ferritic grades. This is mainly due to a more important scaling process of oxide layer in case of the austenitic, which can be explained by the mismatch between CTE of oxide and base metal. Furthermore a slower diffusion of Chromium in austenite could lead to a Cr-depletion at interface metal-oxide and accelerates the process. It is well illustrated by the adherence factor, ratio between remaining oxide and total oxide formed which is about 60% for ferritics and lower than 10% for 308S after 400h at 950°C.

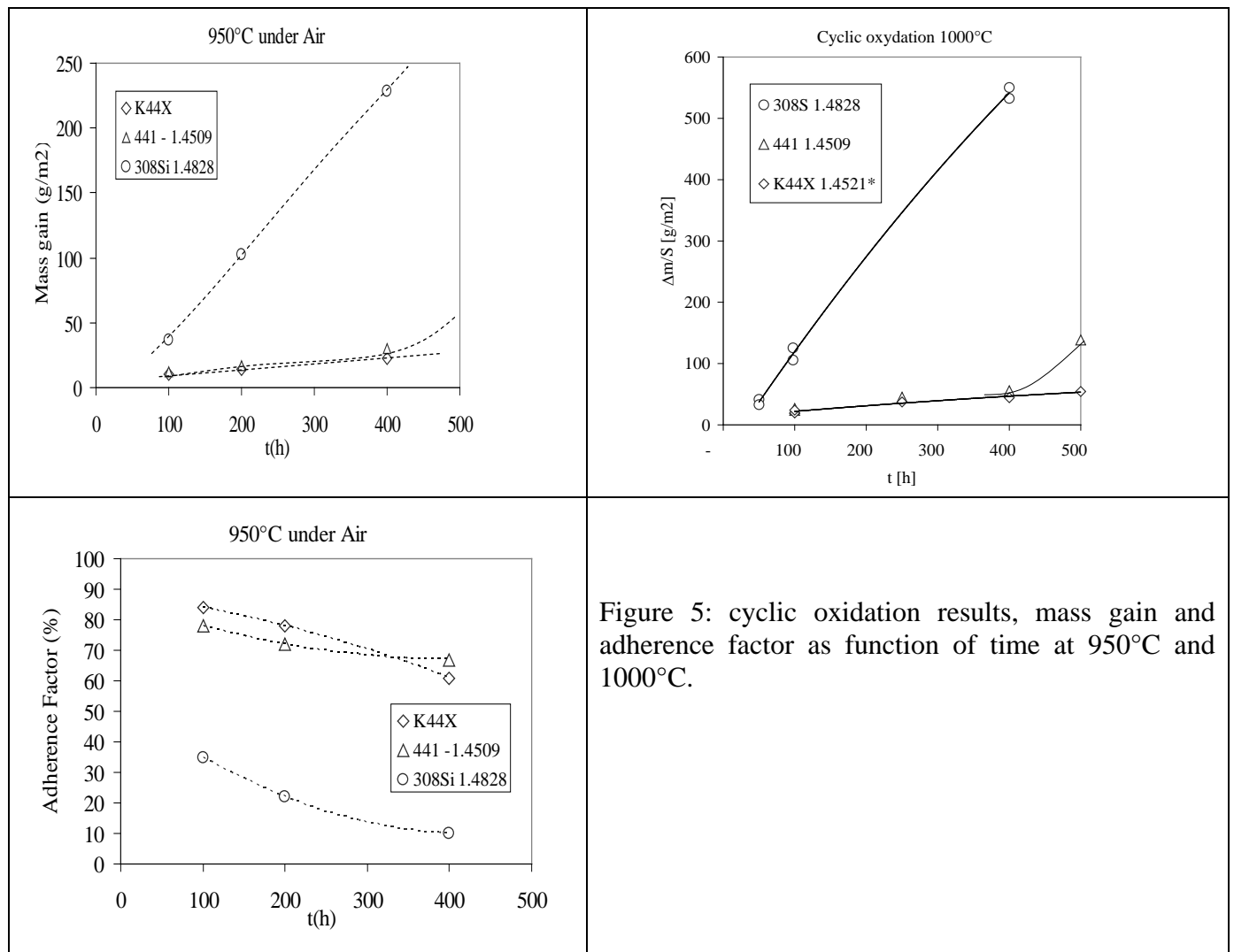


Figure 5: cyclic oxydation results, mass gain and adherence factor as function of time at 950°C and 1000°C.

4. MANUFACTURING FERRITIC PARTS

Ferritic grades are known to exhibit a moderate elongation compared to austenitic ones: the maximal elongation is generally around 35% for the softer ferritic grades like K09X (409). The hardening coefficient (n) and the anisotropy r-value are in fact more valuable parameters to characterize the formability of a grade. If the n-value of ferritic is still low, their r-mean value is higher than austenitic grades. This latter parameter is a key parameter to describe the deep-drawing capability because it is demonstrated that higher is the r-value, higher is the limiting drawing ratio. By means of an adapted stamping process, most of designs are accessible for ferritic grades. Laser, MIG, TIG or Electron beam welding of ferritic is also feasible without real difficulties. Large grain size of the fusion zone can be observed but do not lead to a loss of toughness when considering thicknesses below 5mm. In case of MIG/MAG, a low carbon filler metal such as 430LNb (1.4511), 308S or 316L must be used. Nevertheless ferritic filler metal (430LNb) must be preferred for high temperature and thermal cycling application to minimize the CTE mismatch between the base metal and weld seam. The high temperature behavior of ferritic weld seams is presented in details in (Renaudot, 2000, Faivre 2010).

5. CONCLUSIONS

If we are considering only static isothermal tests for material selection (eg. tensile strength), a wrong decision could be taken both on technical and cost-effectiveness points of view. In many cyclic HT application ferritic grades K41X and K44X behave better because of lower thermal stresses due the thermal expansion and also less damage of the oxide layer which inevitably formed during the life of the part. The case of self-supported parts like shells and tubes is a good example of potential competitiveness of ferritic grades.

For maximal temperature up to 950°C the K41X (AISI 441 EN 1.4509) grade could be sufficient and its use is developing in more and more applications like exhaust systems, calrod elements, heater, burners, and heat exchangers, but also for walls or conveyor belts of furnace. On the other hand, a demand for longer life guaranty and higher supported temperature is growing, which lead us to develop the K44X, a dedicated AISI 444 EN 1.4521 grade for improved HT resistance up to 1000°C. It offers a 30-50% increase in fatigue life in a wide range of temperatures and it could substitute 441 or 308S in the most severe conditions. Molybdenum content offers an added value in term of corrosion resistance to acidic condensates which could be a real issue in many high temperature applications like exhaust system but also in heater or chimney systems. Today K41X and K44X grades are investigated for the very severe conditions of interconnect (about 800°C for several 10000h) for Solid Oxide Fuel Cells (SOFC) and High Temperature Electrolysis for hydrogen production (HTE), as metal substrate.

References

- Charles J. et al., The ferritic stainless steel family : the appropriate answer to nickel volatility, 6th European Stainless Steel Conf. Science and Market Helsinki, Finland, June 10-13, 2008.
- Chinouilh G et al, Thermal Fatigue Design of Stainless Steel Exhaust Manifolds, SAE Technical paper 2007-001-0564, 2007.
- Faivre L et al., Thermal fatigue resistance of MIG/MAG and laser welded joints in stainless steel exhaust manifolds, 65th ABM conference, Rio, 2010.
- Fujita N et al, Changes of microstructure and HT properties during HT service of Nb added ferritic stainless steels, Mat. Sc. & Eng. A351, p272-281, 2003.
- Gordon W and A. van Bennekom, Review of stabilization of ferritic stainless steels, Mat. Sc. And Techn. Feb 1996 vol. 12.
- ISSF document “ the ferritic solution the essential guide to ferritic stainless steel, ISBN 2-930069, April 2007.
- Renaudot N et al. 430LNb a new ferritic wire for automotive exhaust applications, SAE Technical paper, 2000-01-314, 2000.
- Santacreu, P. O., Thermomechanical fatigue of stainless steels for automotive exhaust system, ABM conference, Rio, 2003.
- Simon, C., and Coleman “Thermomechanical Fatigue Behavior of Stainless Steel Grades for Automotive Exhaust Manifold Applications,” Thermomechanical Fatigue Behavior of Materials: 4th Volume, ASTM STP 1428, M. A. McGaw, S. Kalluri, J. Bressers, and S. D. Peteves, Eds., ASTM International, West Conshohocken, PA, 2002.

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