CONCEPTS FOR SMART PROTECTIVE HIGH-TEMPERATURE COATINGS

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ABSTRACT

The high-temperature oxidation and oxidation-sulfidation of TiAlCr compositions were qualitatively evaluated as part of efforts to develop schemes for using multiphase alloy coatings for corrosion protection under aggressive high-temperature environments. Preliminary results showed that certain TiAlCr alloys offer good sulfidation resistance when compositions and microstructures yield protective alumina at low oxygen partial pressures associated with gasification processes.

INTRODUCTION

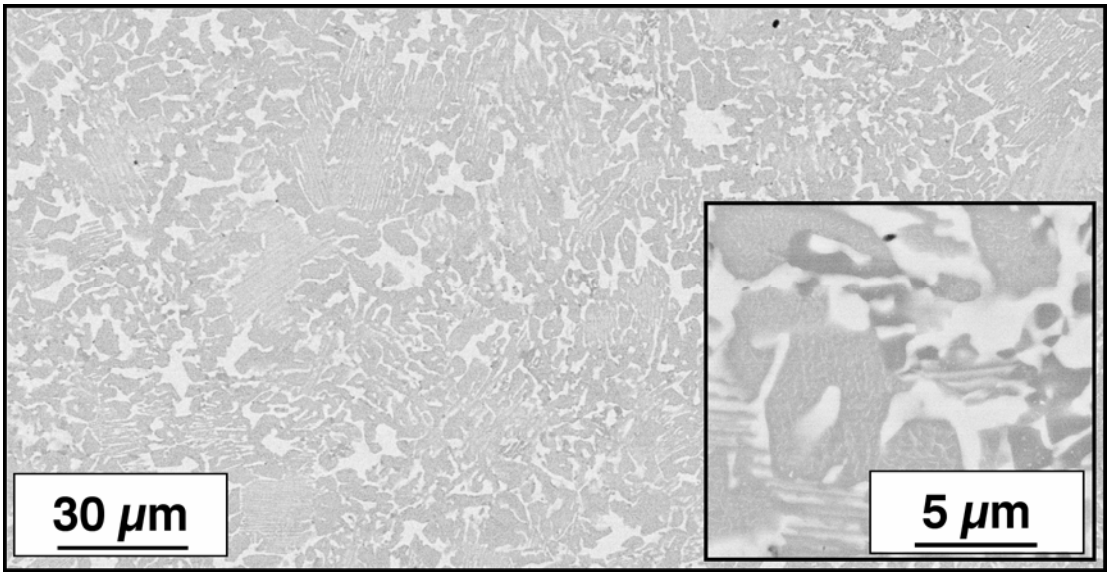
The need for high-temperature environmental resistance is a critical material barrier to the operation of fossil systems with the improved energy efficiency and emissions goals of the U.S. Department of Energy's Office of Fossil Energy. High-temperature materials degradation due to reactive species in fossil fuel environments often limits performance such that efficiency, emission, and/or economic targets or requirements are not realized. Therefore, historically, the development of materials for fossil-fuel combustion and conversion systems has been closely linked to corrosion studies of alloys and ceramics in appropriate environments. This work is somewhat different; it focuses on the feasibility of new routes to controlling the critical chemical and mechanical phenomena that collectively form the basis for environmental protection by exploring compositional and microstructural manipulations and cooperative phenomena that have not necessarily been examined in any detail for relevant fossil systems. This approach can hopefully lead to concepts for "smart" coatings or materials that have the ability to sense and respond appropriately to a particular set or series of environmental conditions in order to provide high-temperature corrosion protection.

The strategies being explored in this work involve cooperative or in-place oxidation or sulfidation reactions of multiphase alloys.[1,2] The first material system evaluated involved the Mo-Si-B system, as there was some evidence that such materials have enhanced resistance in oxidizing-sulfidizing and sulfidizing environments and in air/oxygen at very high temperatures.[3] This work showed that Mo-rich, B-containing silicides can have good high-temperature sulfidation resistance.[4,5] More recently, as described below, the oxidation and sulfidation of TiAlCr and TiAlCr-X compositions (X = Nb, Ta, or both) have been investigated.

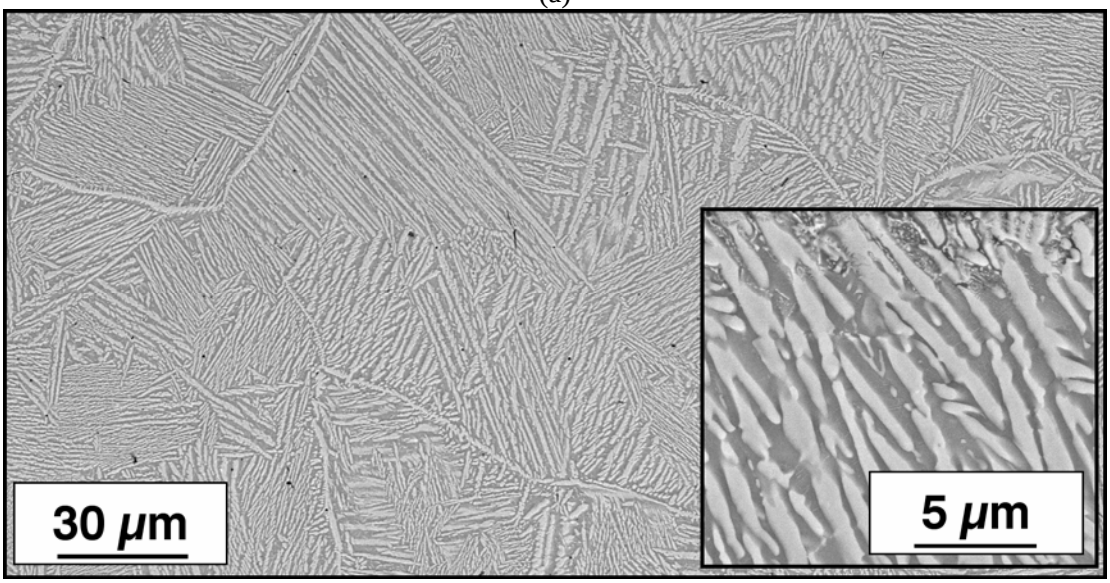
The oxidation behavior of ternary, multi-phase γ-TiAl + $Ti(Al,Cr)_2$ Laves Phase alloys has been extensively studied.[6-8] The presence of Cr promotes the exclusive formation of alumina by modifying subsurface depletion and stabilizing and sustaining the $Ti(Cr,Al)_2$ Laves phase at the alloy/scale interface rather than deleterious, less oxidation-resistant phases such as α_2-Ti_3Al. Accordingly, the present work sought to conduct a preliminary assessment of similar compositions of TiAlCr in terms of their behavior under sulfidizing conditions as good resistance would be anticipated if alumina layers can still form. The addition of X = Nb,Ta was made in an attempt to enhance their resistance to sulfidation, as Nb and Ta sulfides should be slow growing.[9] There is also some limited prior evidence that titanium aluminides have good sulfidation resistance (under less aggressive conditions than the present work).[10] Because of this, and the ability to form protective alumina over a range of oxygen partial pressures, the TiAlCr system could have potential as a basis for smart coatings that perform well in multiple or varying high-temperature environments. Furthermore, application of such compositions as (thermal spray) coatings has already been demonstrated.[11]

RESULTS AND DISCUSSION

Four TiAlCr-based alloys in the as-cast condition were included in this study: Ti-51Al-12Cr, Ti-45Al-15Cr-15Ta, Ti-45Al-15Cr-15Nb, and Ti-48Al-13Cr-10Nb-5Ta (at.%, nominal). All have multi-phase microstructures; examples are shown in Fig. 1. Coupons were ground and then screened for oxidation and sulfidation resistance using 800ºC exposures in air for 100 h and in H_2S-H_2-H_2O-Ar for 50 h, respectively. The composition of the H_2S-H_2-H_2O-Ar gas was set to yield partial pressures of 10^{-6} atm of S_2 and 10^{-22} atm of O_2. This environment represents severe coal gasification conditions, but has been used previously to evaluate the corrosion of the most sulfidation-resistant alloys.[12,13] Under this exposure condition, the Ti-51Al-12Cr composition falls within the calculated stability of Al_2O_3 based on equilibrium thermodynamics. This is the desired protective product, but the relative sulfidizing and oxidizing potential of the reference environment lie close to the phase boundary of Cr and Ti sulfides. It



(a)



(b)

Fig. 1. Microstructures of (a) Ti-51Al-12Cr; (b) Ti-48Al-13Cr-10Nb-5Ta (at.%)

is therefore important to conduct experimental screening as described to determine whether kinetic considerations can result in the formation of fast growing sulfides.[12,14]

Air exposure of the Ti-51Al-12Cr alloy yielded a very small mass gain after 100 h. Consistent with this, an Al-rich surface oxide (presumably containing appreciable mounts of Al_2O_3) was observed on a polished cross section after exposure– see Fig. 2. More importantly for present purposes, an Al-rich oxide layer formed when the same alloy was exposed to the sulfidizing H_2S-H_2-H_2O-Ar gas (Fig. 3) and,

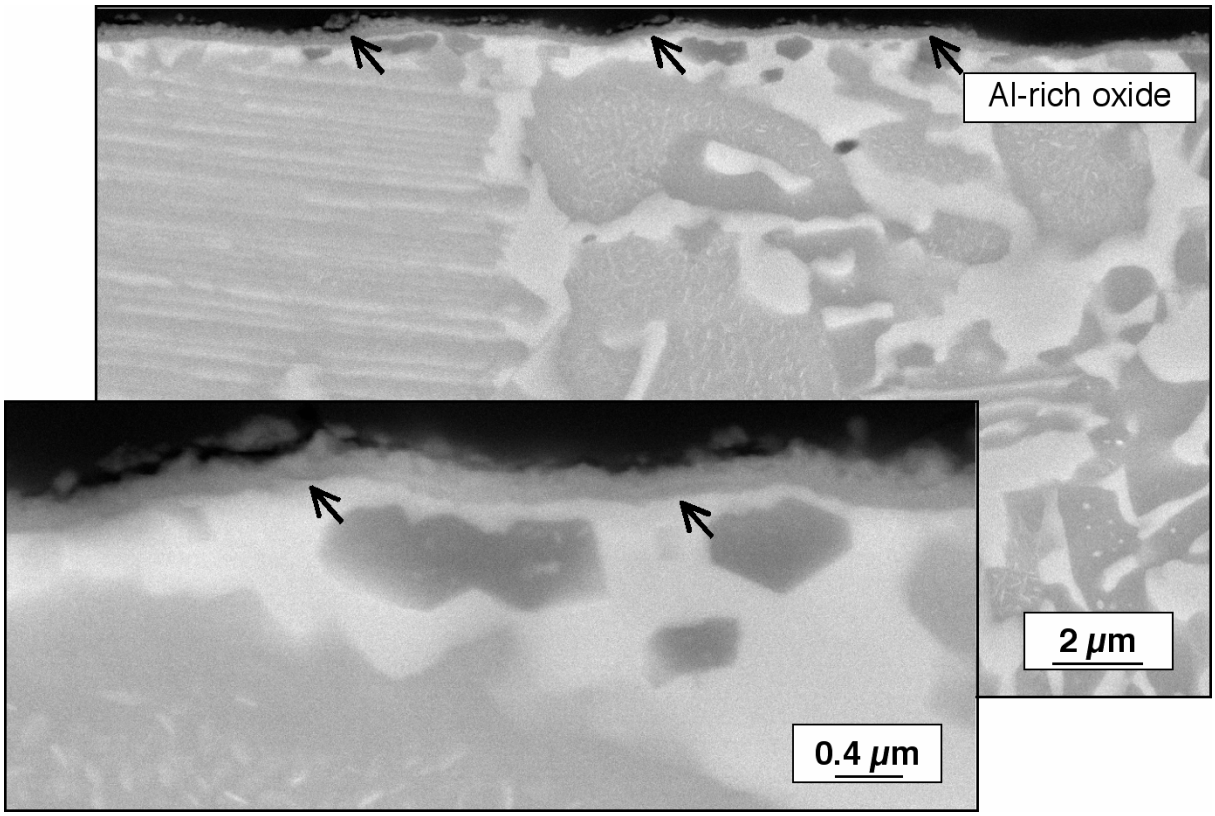


Fig. 2. Ti-51Al-12Cr exposed to dry air at 800°C for 100h. Arrows denote thin aluminum-rich oxide that formed upon exposure

as with the air exposure, a relatively small mass gain was measured. As shown in Fig. 4, this mass gain was substantially lower than an Fe-20Cr-10Al, which formed a significant amount of Cr sulfides under these exposure conditions, but still had a modest mass gain compared to a model type 310 stainless steel.[14] Assuming the Al-rich oxide layer shown in Fig. 3 is predominately Al_2O_3, its formation on the TiAlCr is consistent with the thermodynamic prediction. Thus, the base Ti-Al-Cr alloy system seems to hold some promise in terms of high-temperature sulfidation resistance. Though not apparent under the contrast conditions used for the image in Fig. 3, some sulfide whiskers formed above the Al-rich layer, as shown in plan view in Fig. 5. These sulfides appeared to be like those found on Fe_3Al-Cr exposed under similar conditions.[14] However, as shown by the gravimetric results (Fig. 4), the extent of sulfidation did not appreciably add to the measured mass gain (degrade the corrosion resistance).

Based on mass gains, the addition of 15%Ta or 10%Nb + 5%Ta to the base Ti-Al-Cr did not appear to significantly affect either the oxidation or sulfidation resistance, while the 15%Nb addition had a definite deleterious effect under both conditions. In particular, the average mass gain in the sulfidizing environment was about 3 times greater those measured for the other alloys (Fig. 6). While the reasons for such require more study, it is clear that the greater sulfidation of the Ti-Al-Cr-Nb alloy correlated with the

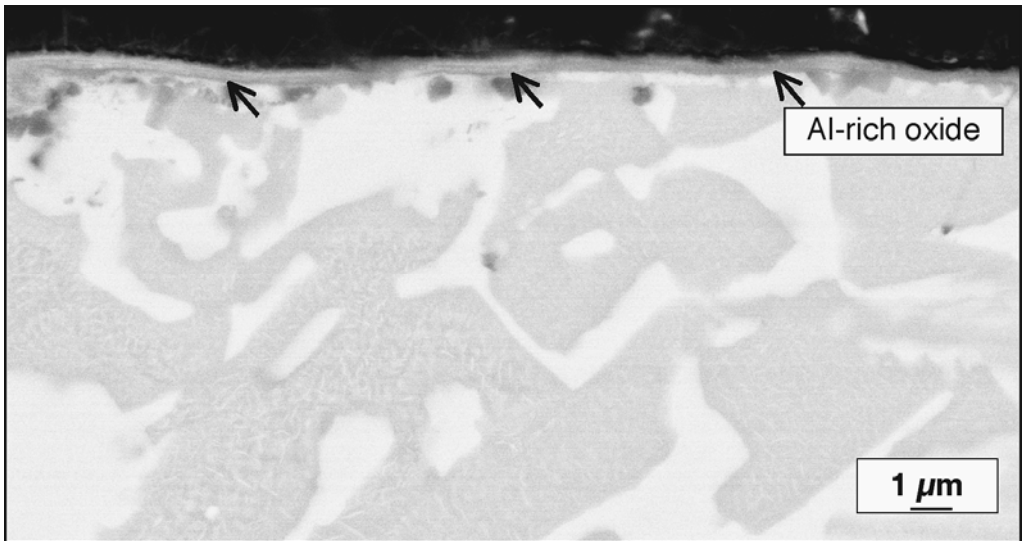


Fig.3. Ti-51Al-12Cr exposed to the H_2S-H_2-H_2O gas at 800°C for 50 h.

inability to develop a continuous protective Al-rich oxide layer. Rather, a mixed (Al, Nb) oxide layer and Nb-, Cr-, and Ti-rich sulfides formed after 50 h of exposure to the H_2S-H_2-H_2O-Ar gas (Fig. 7). The total volume of reaction products was obviously sufficient to account for the higher average mass gain indicated in Fig. 6. (The respective sulfides were distinguished by their different morphologies, as shown in Fig. 8.) Because the Ti-Al-Cr-15%Nb alloy also showed a significantly greater mass gain after the 100 h exposure in air, it appeared this particular composition/microstructure did not promote a fundamentally protective Al_2O_3 scale even in the absence of sulfur in the environment and that the addition of Nb at this concentration does not improve sulfidation resistance for as-cast structures.

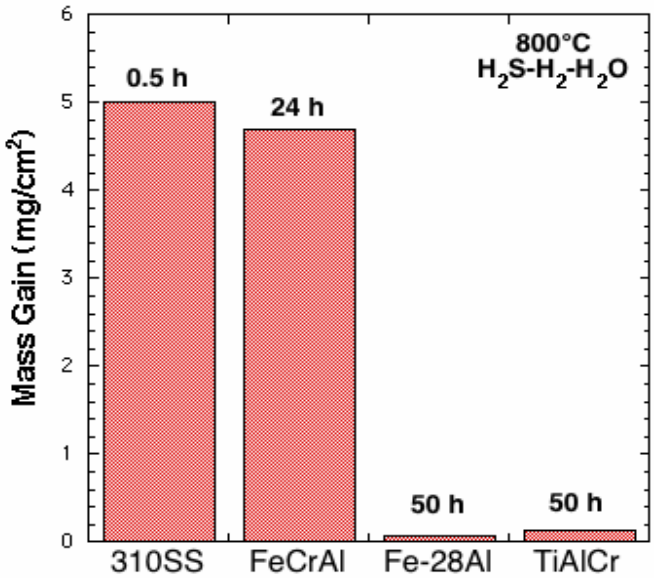


Fig. 4. Mass gains after indicated time periods for exposures to the H_2S-H_2-H_2O gas at 800°C

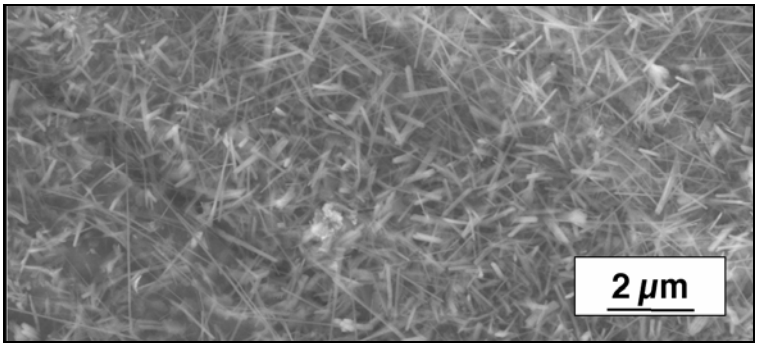


Fig 5. Surface of Ti-51Al-12Cr exposed to the H_2S-H_2-H_2O gas at 800°C for 50 h.

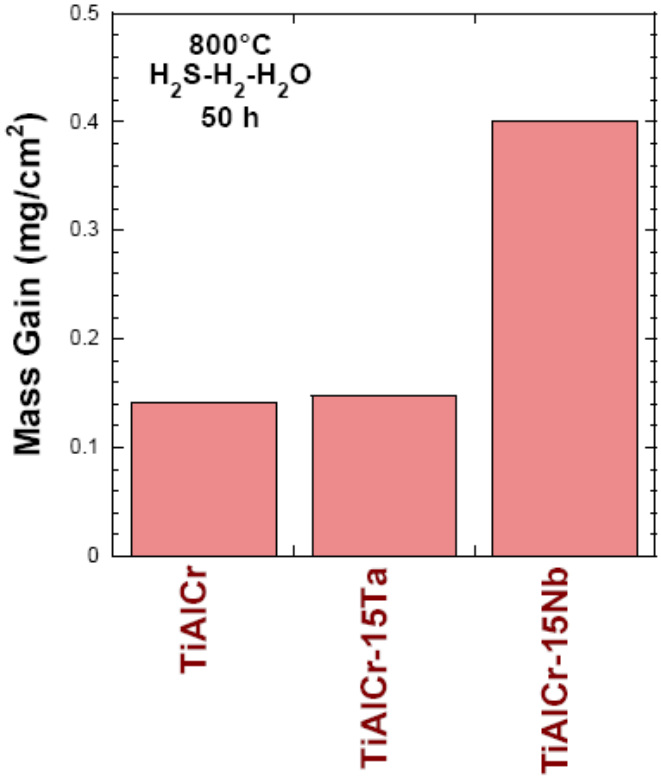


Fig. 6. Mass gains after 50-h exposures to the H_2S-H_2-H_2O gas at 800°C

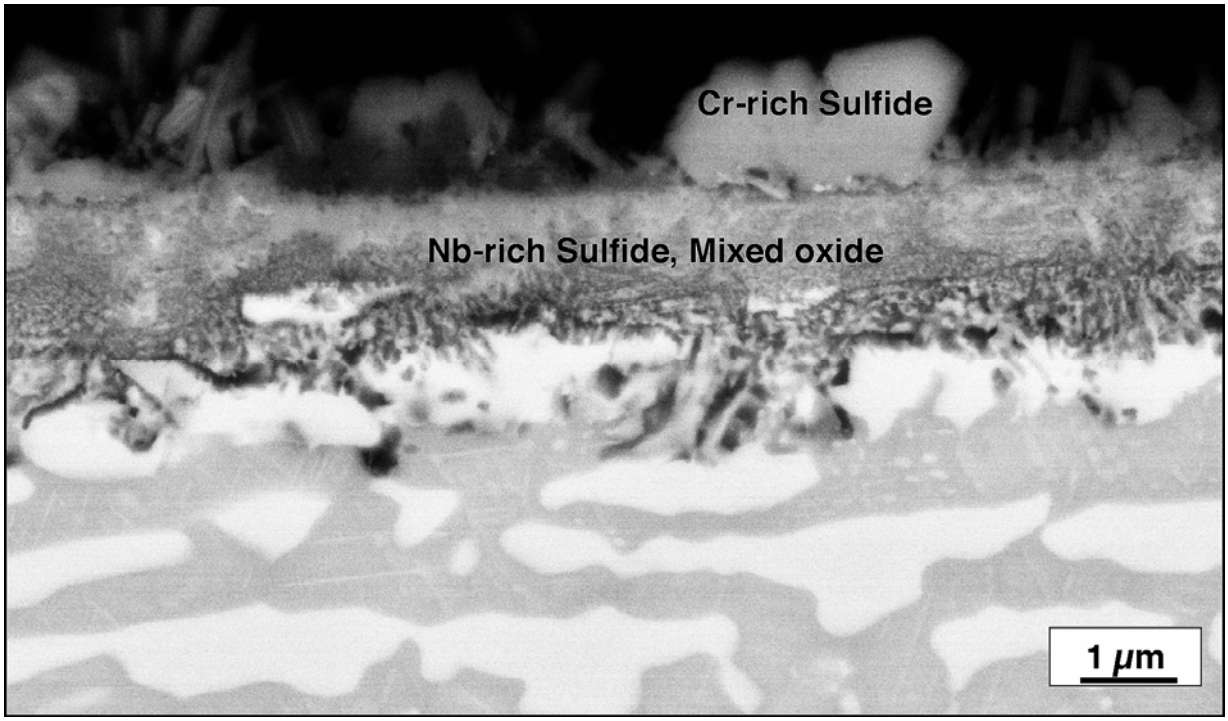


Fig. 7. Ti-48Al-15Cr-15Nb exposed to H_2S-H_2-H_2O gas at 800°C for 50 h.

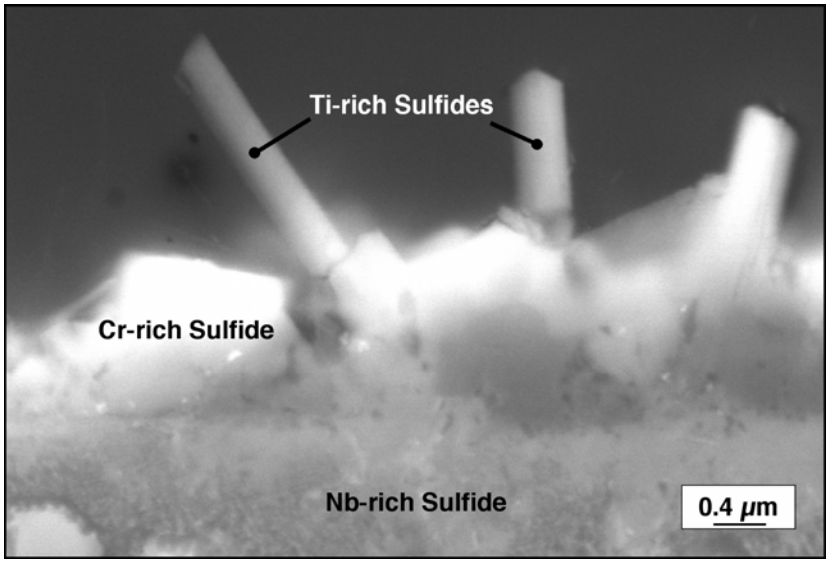


Fig. 8. Ti-48Al-15Cr-15Nb exposed to H_2S-H_2-H_2O gas at 800°C for 50 h

Future work will include longer exposures of selected TiAlCr alloys to H_2S-H_2-H_2O-Ar to gauge sulfidation resistance more rigorously and to measure corrosion rates under isothermal and thermal cycling conditions. The knowledge gained from such will be used to help explore phase-size and composition manipulations in the Ti-Al-Cr system in order to evaluate the possibilities of developing these compositions as protective coatings.

SUMMARY

Smart protective coatings may provide one of the breakthrough areas to overcome materials barriers imposed by the requirements of advanced fossil energy systems. To this end, the high-temperature oxidation-sulfidation of TiAlCr-(Nb,Ta) compositions was qualitatively evaluated as part of efforts to develop schemes for using alloy coatings for corrosion protection under aggressive high-temperature environments. Preliminary results showed that the TiAlCr ternary composition showed very good sulfidation resistance after isothermal exposure to H_2S-H_2-H_2O-Ar at 800ºC because a protective Al-rich oxide layer formed at the low oxygen partial pressure associated with this simulated syngas. An alloy based on TiAlCr-Nb showed substantially greater sulfidation under the same exposure conditions as a continuous alumina layer did not form.

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REFERENCES

1. F. Gesmundo and B. Gleeson, *Oxid. Met.* 44 (1995) 211-37.

2. M. P. Brady, B. Gleeson and I. G. Wright, *JOM* 52 (2000) 16-21.

3. M. P. Brady, B. A. Pint, P. F. Tortorelli, I. G. Wright and R. J. Hanrahan Jr., pp. Chapter 6 in Corrosion and Environmental Degradation of Materials, M. Schütze (eds.), Wiley-VCH, Weinheim, Germany, 1999.

4. P.F. Tortorelli, J.H. Schneibel, K.L. More, and B.A. Pint, *Mater. Sci. Forum* 461-464 (2004) 1063-70.

5. P.F. Tortorelli, M.P. Brady, and I.G. Wright, *Proc 18th Annual Conf. Fossil Energy Materials.*, R.R. Judkins and L.S. Mack (compilers), U.S. Department of Energy, 2004; http://www.ms.ornl.gov/FEM/pdf/Proceedings18Fossil04.pdf

6. M.P. Brady, J.L. Smialek, J.W. Smith, and D.L. Humphrey, *Acta Mater*. 45 (1997) 2357-69.

7. M.P. Brady, J.L. Smialek, D.L. Humphrey, and J.W. Smith, *Acta Mater*. 45 (1997) 2371-82.

8. N.S. Jacobson, M.P. Brady, and G.M. Mehrotra, "Thermodynamics of Selected Ti-Al and Ti-Al-Cr Alloys", *Oxid. Met.* 52 (1999) 537-56.

9. S. Mrowec, *Oxid. Met.* 44 (1995) 177-209.

10. J.J. Soler, J.F. Norton, M. Noth, and M. Schütze, *Mater. and Corros.* 50 (1999) 394-404.

11. M.P. Brady, W.J. Brindley, J.L. Smialek, and I.E. Locci, "Oxidation and Protection of γ-Based Titanium Aluminides", JOM, Vol. 8, Num. 11, pp. 46-50 (1996).

12. J.H. DeVan and P.F. Tortorelli, *Mater. at High Temp.* 11 (1993) 30-35.

13. K. Natesan and P.F. Tortorelli, pp. 265-80 in Nickel and Iron Aluminides: Processing, Properties, and Applications, S. C. Deevi, V. K. Sikka, P. J. Maziasz and R. W. Cahn (eds.), ASM International, Materials Park, OH, 1997.

14. J. H. DeVan, pp. 107-15 in Oxidation of Intermetallics, T. Grobstein and J. Doychak (eds.), TMS, Warrendale, PA, 1989.