Multi-Phase Cr-Based Alloys for Aggressive High Temperature Environments

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Introduction

The objective of this work is to develop and characterize a new family of Cr-based alloys for structural use in aggressive 900-1300°C corrosion environments. The potential advantages of Cr are high melting point, moderate density, and good high-temperature corrosion resistance in many environments [1]. However, these are currently negated by inadequate high-temperature strength, ambient-temperature brittleness, and susceptibility to environmental embrittlement at elevated-temperatures by rapid nitride subscale formation [1]. Over the course of this effort, two distinct approaches to overcoming these problems have been pursued: Cr_2Ta-reinforced Cr, and MgO-dispersed Cr. The Cr_2Ta-reinforced Cr alloys are based on the Cr-Cr_2Ta eutectic structure and contain a Cr solid solution matrix phase reinforced with lamellar Cr_2Ta Laves phase. They exhibit an attractive combination of high-temperature strength (tensile fracture strengths of 340-550 MPa at 1200°C), high-temperature ductility (15-40% tensile elongation above 1000°C), creep resistance (creep rupture life in excess of 1000 hours at 138 MPa loading at 1000°C in air), and oxidation resistance (comparable to that of commercial chromia-forming alloys in 1100°C, 1000 h cyclic oxidation screenings in air) [2]. However, no room-temperature ductility has been achieved and extensive microalloying and microstructural control efforts have led to only modest room-temperature fracture toughness of 12-14 MPa√m.

In contrast, the MgO-dispersed Cr alloys [3,4] exhibit tensile elongations of greater than 10% and fracture toughness in the 20-25 MPa√m range at room temperature. These alloys are based on Cr-(3-6)MgO wt.%. and are made by powder metallurgical processes, typically sintering or hot pressing and extrusion. They consist of a

Cr matrix phase with MgO and $MgCr_2O_4$ spinel (formed during powder consolidation) dispersions at the grain boundaries. Although ductile at room temperature, the yield strength of these alloys is only 200-240 MPa at room temperature, and efforts to improve strength have resulted in a concomitant reduction in ductility. Both classes of alloys exhibit excellent high-temperature corrosion resistance in many molten salt and slag environments, although they remain susceptible to nitride subscale formation. During this year, the development effort has focused on two key areas: (1) evaluation of the high-temperature corrosion behavior of baseline alloy compositions in coal combustion environments relevant to fossil energy power generation systems and 2) the effect of macroalloying additions of transition metals to further improve mechanical and corrosion resistance properties. Some success in improving toughness and environmental resistance was achieved with additions of transition metal(s). A patent application is forthcoming; for this report these additions are referred to as "X"

Discussion Of Current Activities

High-Temperature Corrosion Behavior

Coupons of a baseline Cr-Cr_2Ta alloy, Cr-9Ta-5Mo-2Si-0.15La-0.1Ti atomic percent (at.%), and a baseline MgO-dispersed Cr alloy, Cr-6MgO-0.75Ti weight percent (wt.%), were submitted to the Combustion and Environmental Research Facility at the National Energy Technology Laboratory for exposure under coal combustion conditions. (Cr-Cr_2Ta alloys are reported in at.% and Cr-MgO in wt.%). The tests were conducted using Prader Creek coal; the Cr-Cr_2Ta alloy coupons were exposed at temperature ranges of 1149-1204°C and 1260-1316°C for 350, 650, and 1000 h. The Cr-MgO alloy coupons were exposed at temperature ranges of 1038-1098°C and 1093-1149°C for 350 and 1000 h. After exposure, the coupons were analyzed by optical microscopy, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

Fig. 1 shows Cr-9Ta-5Mo-2Si-0.15La-0.1Ti after exposure for 1000 h at 1260-1316°C. A significant fraction of the coupon broke away as a result of the exposure (Fig. 1). Cross-section analysis revealed that a Cr_2O_3-based scale was formed, however extensive subscale nitridation of the Cr matrix phase (to form Cr_2N) and the Laves phase (to form mixed Cr-Ta-N/Cr_2N) also occurred. The failure of the coupon is attributed to the low fracture toughness of this alloy (~ 12 MPa-m$^{1/2}$ at room temperature) and embrittlement of the Cr matrix phase by the subscale nitridation. Previous work had shown that the Cr_2Ta Laves phase could selectively getter some incoming nitrogen, limiting nitridation of the adjacent Cr matrix phase. These results indicate that the gettering effect is overhwhelmed during long-term, high- temperature exposures.

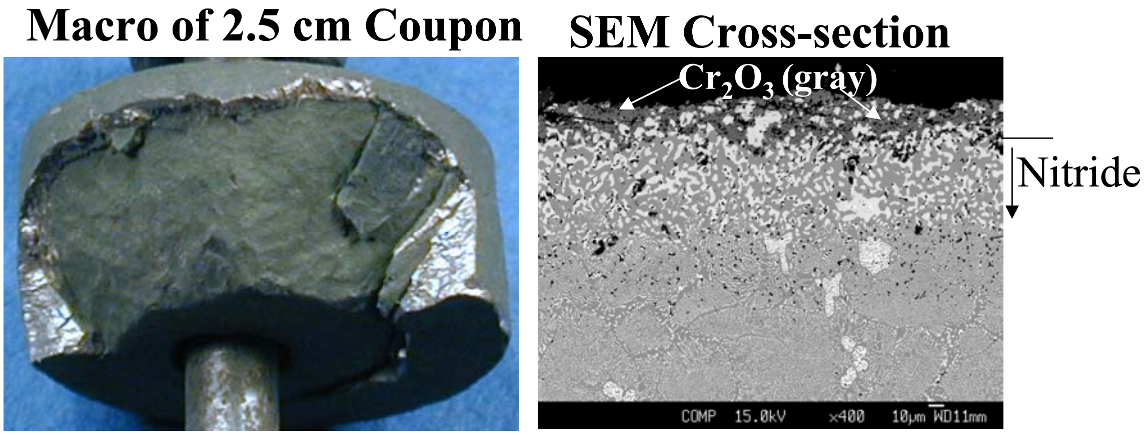
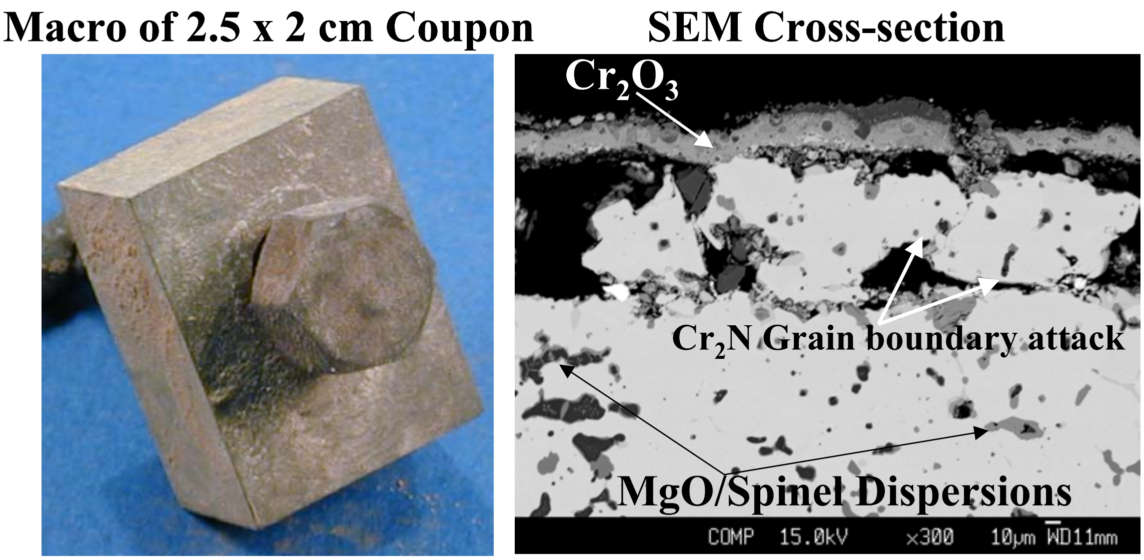


Fig. 1- Cr-9Ta-5Mo-2Si-0.15La-0.1Ti after 1000 h coal combustion test at 1260-1316°C.
Cr solid solution (dark), Cr_2Ta Laves (light).

Fig. 2 shows Cr-6MgO-0.75Ti after a 1000 h exposure at 1093-1149°C in the coal combustion environment. In contrast to the Cr-9Ta-5Mo-2Si-0.15La-0.1Ti alloy, the coupon remained intact and, further, showed good corrosion resistance over the course of the exposure. However, cross-section analysis revealed evidence of preferential subscale nitridation along the Cr matrix grain boundaries. Collectively, the coal combustion exposures suggest that the Cr-Cr_2Ta and Cr-MgO alloys exhibit good inherent resistance to ash deposit attack in oxidizing coal combustion environments; however, this resistance is negated by susceptibility to subscale nitrogen penetration.


Macro of 2.5 x 2 cm Coupon

SEM Cross-section

Fig. 2- Cr-6MgO-0.75Ti after the 1000 h coal combustion test at 1093-1149°C.

Macroalloying Effects

Macroalloying was initially investigated for the Cr_2Ta-reinforced Cr alloys in order to improve room- temperature fracture toughness. Additions of X were found to be particularly effective, with substitution of 25-35 at.% X for Cr yielding values greater than 15 MPa-$m^{1/2}$. When combined with a reduction in Ta level to maintain the eutectic structure (the X additions shifted the Cr-Cr_2Ta eutectic from about 9.5 at.% to the 5.5-7.5 at.% Ta range), room-temperature fracture toughness in the 20 MPa-$m^{1/2}$ range was achieved. A summary of room-temperature fracture toughness trends over the course of this program is shown in Fig. 3.

Somewhat unexpectedly, the addition of X was also found to significantly retard subscale nitridation on elevated-temperature exposure in air. Fig. 4 shows an SEM cross-section of Cr-35X-5.5Ta-4Mo-0.5Ti-0.3Si-0.1La at.% after eleven, 100 h cycles (1100 h total) at 1100°C in air. EPMA analysis of the zone underneath the Cr_2O_3 scale showed no evidence of nitride/nitrogen in the Cr matrix phase. Further, the Laves phase beneath the scale was selectively internally oxidized rather than internally nitrided, as is typical for Cr-Cr_2Ta alloys without X additions [6]. The apparent prevention of, or at least significant retardation of subscale nitridation is a key finding. Cr_2O_3 scales are generally permeable to nitrogen and subscale nitridation of Cr to form Cr_2N occurs at a faster rate than Cr_2O_3. The rapid formation of nitride subscales has been a major barrier to the use of Cr and Cr matrix alloys at elevated temperatures in nitrogen containing environments [e.g. 1]. It is not yet known whether the X additions act by making the Cr_2O_3 scale or the Cr(X) matrix phase impermeable (or at least much less permeable) to nitrogen, modifying the permeability of Cr(X) to oxygen, relative to nitrogen, or if they otherwise alter the relative reactivity of Cr_2O_3 vs Cr_2N formation by the alloy such that the nitride is not formed.

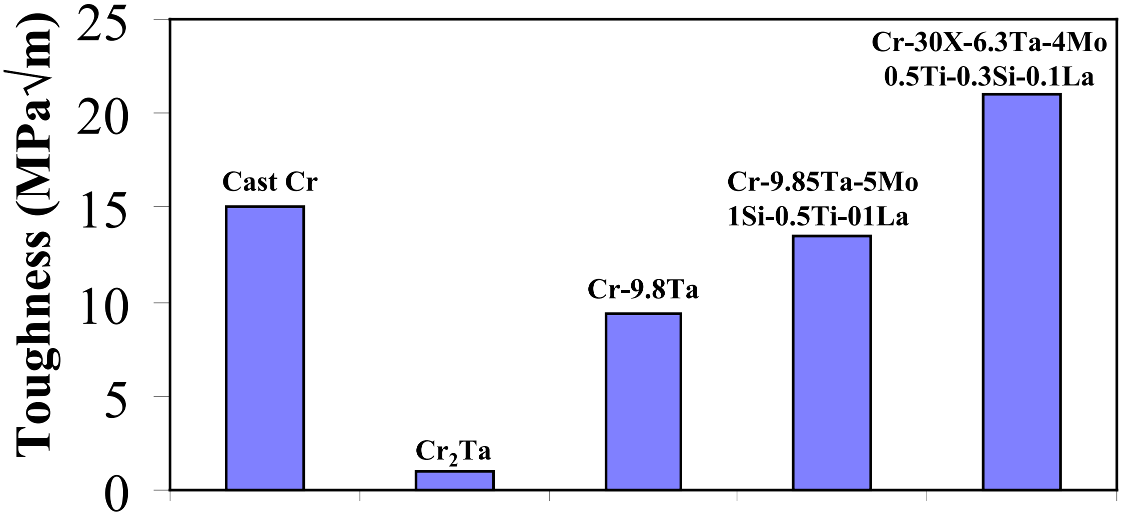


Fig. 3- Summary of room-temperature fracture toughness trends. The fracture toughness values were obtained using subsized chevron-notched three-point bend samples and should be considered semiquantitative (modulus of 300 GPa used for Cr and 250GPa for all other alloys, see reference 5 for further details of this technique).

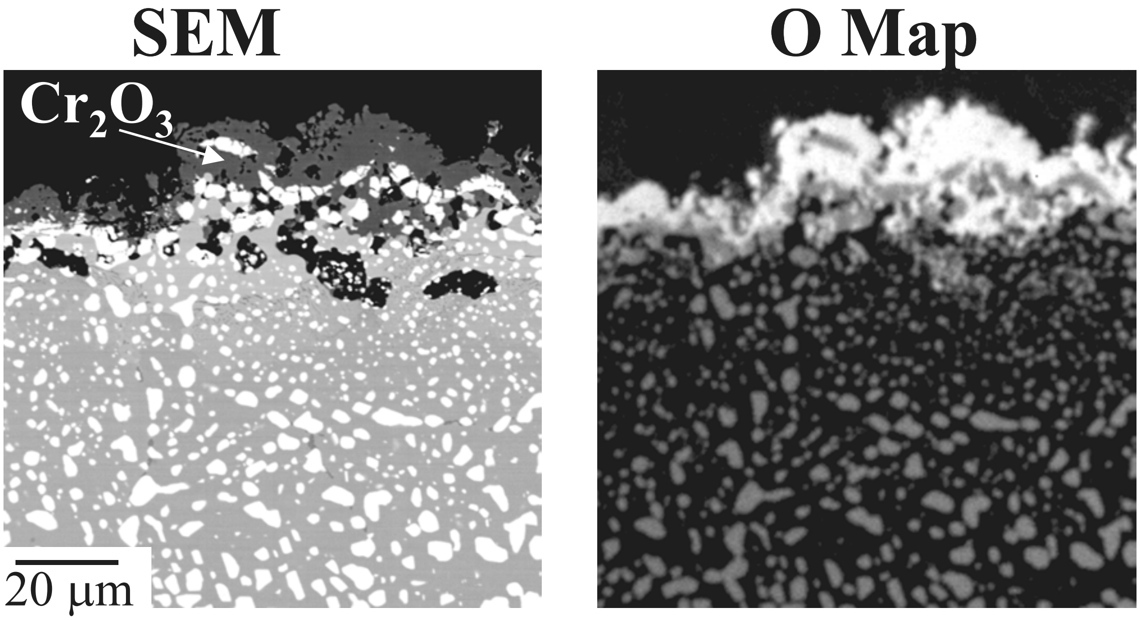


Fig. 4- Cross-section of Cr-35X-5.5Ta-4Mo-0.5Ti-0.3Si-0.1La at.% after eleven, 100 h cycles (1100 h total) at 1100°C in air. Cr solid solution (dark), Laves (light).

The levels of X additions needed to impart the improved toughness and limit/prevent subscale nitridation also depress the melting point of the alloy such that high-temperature strength is degraded. This is illustrated in Fig, 5, which shows yield strength at 1000°C as a function of X additions. Partial substitution of Co for X (5-10 at.% Co range) was investigated in an attempt to improve high-temperature strength. This approach was not effective, with a further decrease in strength at 1000°C, although tensile elongation at 1000°C was significantly increased (5% for Cr-30X-6.3Ta-4Mo-0.5Ti-0.3Si-0.1La vs 33% for Cr-20X-10Co-6.3Ta-4Mo-0.5Ti-0.3Si-0.1La). The best balance of room-temperature toughness and high-temperature strength was found for additions of 30 at.% X, with Cr-30X-6.3Ta-4Mo0.5Ti-0.3Si-0.1La exhibiting an attractive combination of over 20 MPa-m$^{1/2}$ toughness at room temperature and 350 MPa yield strength at 1000°C.

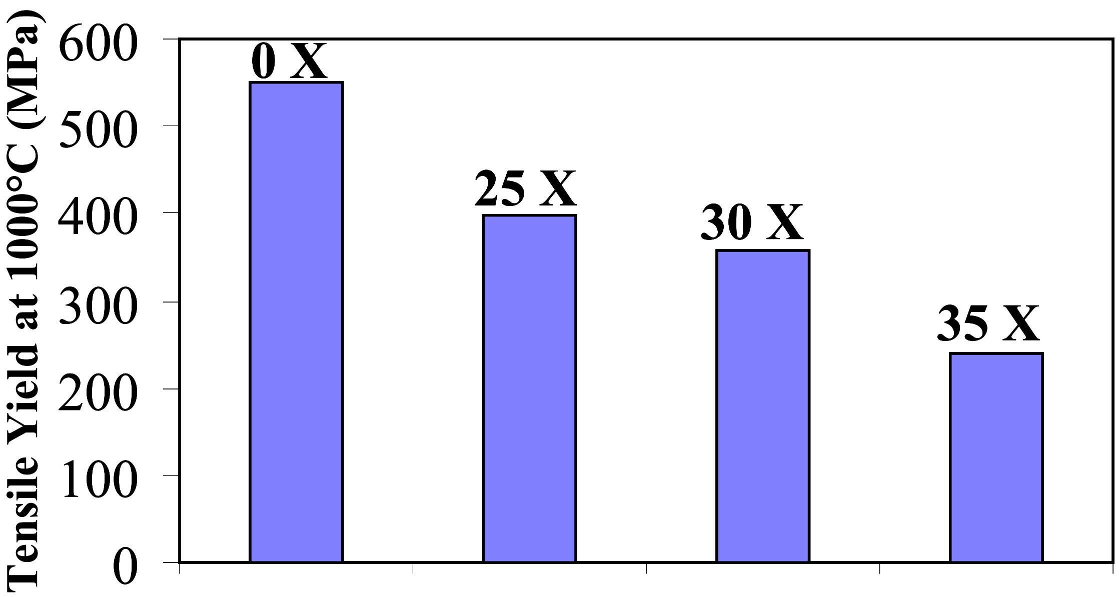


Fig. 5- Tensile yield strength at 1000°C for Cr-8Ta-5Mo-0.1La (0 X hypoeutectic alloy) and as a function of X content for Cr-X-Ta-4Mo-0.5Ti-0.3Si-0.1La at.% (Ta level adjusted to yield eutectic: 25X/6.8Ta; 30X/6.3Ta; 35X/5.7Ta). The data was obtained using sheet tensile samples ~0.6-0.7 mm thick with a gage length of 12.7 mm prepared to a 600 grit surface finish. The crosshead speed was 2.54mm/minute (initial strain rate of 3.3×10^{-3}/s). The samples were heated to 1000°C in air for testing in approximately 5 minutes.

Macroalloying with X was also investigated for the MgO-dispersed Cr alloys in an attempt to eliminate susceptibility to subscale nitridation. Short-term oxidation tests indicated a similar positive effect, with no subscale nitridation observed for Cr-44X wt.% with 6 wt.% MgO after a 120 h screening exposure at 1100°C in air (Fig. 6). (Cr-6MgO exhibited subscale Cr_2N formation under these conditions). The X additions also significantly increased room-temperature yield strength, from 200 MPa for Cr-6MgO to nearly 700 MPa for Cr-44X + 6 MgO, while preserving a small (1-2%) amount of tensile ductility at room temperature. However, the high strength was not well retained at elevated temperature, with a yield strength of only 90 MPa obtained at 900°C.

Future Plans

Collectively, this development program has succeeded in identifying approaches capable of mitigating the key limiting phenomena of Cr-based alloys (inadequate high-temperature strength, room-temperature brittleness, and embrittling nitride subscale formation). However, it does not appear possible to achieve them all in a single alloy. The alloys developed under this program will be spun off to an applied development effort for black liquor gasification in the paper and pulp industry, to take advantage of the excellent molten salt corrosion resistance of Cr. The understanding of the manipulation of multi-phase microstructures gained under this program will be transitioned to other alloy systems. Initial efforts will focus on intermetallic strengthened ferritic and austenitic alloys for improved elevated-temperature strength in applications such as superheater tubes.

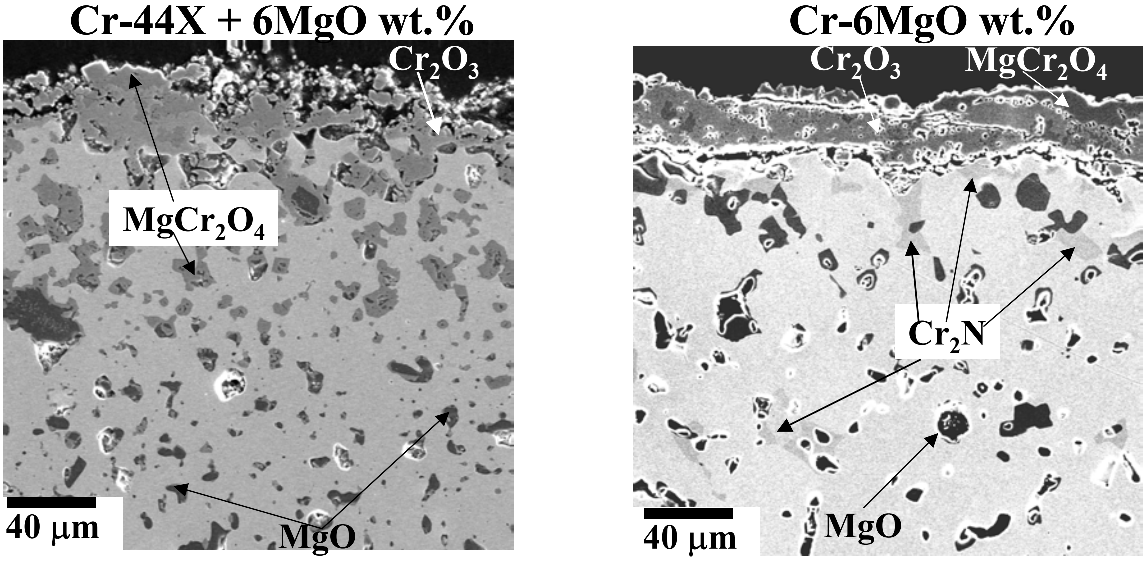


Fig. 6- SEM cross-sections after 120 h at 1100°C in air. No subscale nitridation was observed for the Cr-44X base alloy, although the Mg-based oxide dispersions were completely converted to $MgCr_2O_4$ underneath the scale (identification based solely on EPMA data).

References

1. W.D. Klopp, NASA TM X-1867, September 1969.
2. M.P. Brady, J.H. Zhu, C.T. Liu, P.F. Tortorelli, L.R. Walker, C.G. McKamey, J.L. Wright, C.A. Carmichael, D.J. Larson, M.K. Miller, and W.D. Porter, *Mate. High Temp.*, vol. 16, no. 4, pp. 189-193 (1999).
3. D.M. Scruggs, ‘Ductile Chromium Composition”, U.S. Patent 3, 175, 279 (Mar. 30, 1965).
4. M. P. Brady, I.M. Anderson, M.L. Weaver, H.M. Meyer, L.R. Walker, M.K. Miller, D.J. Larson, I.G. Wright ,V.K. Sikka, A. Rar, G.M. Pharr, J.R. Keiser, and C.A. Walls, *Mater. Sci. Eng. A* (in press 2003).
5. J.H. Schneibel, C.A. Carmichael, E.D. Specht, and R. Subramanian, *Intermetallics*, 5, p. 61 (1997).
6. M.P. Brady, J.H. Zhu, C.T. Liu, P.F. Tortorelli, and L.R. Walker, *Intermetallics*, 8, 9-11, pp. 1111-1118 (2000).

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