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 strengthened with intermetallic second phases for structural use in aggressive corrosion environments at 900 to 1300°C. The potential advantages of Cr are high melting point, moderate density, and good high-temperature corrosion resistance in many environments. However, these are negated by inadequate high-temperature strength, ambient-temperature brittleness, and susceptibility to environmental embrittlement at elevated-temperatures by nitrogen penetration. The developmental alloys consist of a Cr solid solution matrix reinforced with the intermetallic Cr_2Ta Laves phase as a dispersed second-phase particle or of lamellar Cr solid solution-Cr_2Ta eutectic structures [1-4]. Substantial progress has been made in developing attractive high-temperature tensile strength, creep resistance, and oxidation/hot corrosion resistance through control of alloy composition and microstructural features [1,3]. For most potential components/applications, it is desirable to have a minimum room-temperature fracture toughness of at least 15-20 $MPa\sqrt{m}$. However, efforts to improve room-temperature toughness by microalloying the Cr matrix phase and microstructural control have not yet been successful, with the best alloys exhibiting only modest ambient-temperature fracture toughness of 12-14 $MPa\sqrt{m}$.

Two approaches for improved fracture toughness at room temperature have been investigated: 1) ductilization of unalloyed Cr by the addition of MgO [5-7] and 2) macroalloying to improve the fracture toughness of the Cr matrix phase in Cr-Cr_2Ta alloys [8]. Tensile elongations in excess of 10% were achieved with extruded MgO-dispersed Cr alloys at room temperature. However, these alloys exhibit relatively low yield strengths (30 ksi range) and efforts to increase strength by Cr_2Ta

precipitates without sacrificing the gains made in room-temperature ductility have not been successful. The MgO-dispersed Cr alloys were also found to exhibit excellent corrosion resistance in alkali molten salts, which makes them of great interest for applications in high-temperature black liquor gasifiers and Kraft recovery boilers [9], for which high strength is not a key issue for many components. Development efforts devoted to Cr-MgO alloys were successfully spun off during FY 2002 into a new project under the Office of Industrial Technologies Forest Products Program specifically targeted to these applications.

Recent efforts devoted to macroalloying additions have succeeded in significantly improving the room-temperature fracture toughness of the Cr-Cr_2Ta family of alloys by the addition of significant amounts of transition metal(s), referred to as X due to patent considerations [8]. During this year, the development effort has been focused on the effect of X additions on the microstructure and properties of Cr-Cr_2Ta alloys.

DISCUSSION OF CURRENT ACTIVITIES

Experimental

Subsized chevron-notched three-point bend samples approximately 3 × 4 × 25 mm were used to evaluate fracture toughness at room temperature. Fracture toughness values obtained by this technique should be considered semiquantitative; details are provided in reference 10. The samples were prepared to a 600 grit surface finish and then notched using a low speed diamond saw. The crosshead speed was 0.6 mm/min. A modulus of 250 GPa was estimated. Tensile properties were evaluated at 1000°C in air (5 minute heat up) using sheet tensile samples approximately 0.6-0.7 mm thick with a gage length of 12.7 mm. The samples were prepared to a surface finish of 600 grit and a crosshead speed of 2.54 mm/min. was used (strain rate of 3.33×10^{-3}/s). Isothermal oxidation behavior was evaluated at 1100°C in air by thermogravimetric analysis (TGA) using 12 mm x 12 mm x 1 mm coupons prepped to a 600 grit finish. Cyclic oxidation was evaluated at 1100°C in air for eleven, 100 h cycles (1100 h total exposure).

Microstructure

Analysis of a series of Cr-Ta-X base alloys by electron probe microanalysis (EPMA) indicated that additions of X preferentially partition to the Cr_2Ta Laves phase (1.4 to 1 where 1 represents the overall bulk X content in the alloy) resulting in X depletion in the Cr matrix phase (0.85 to 1). The eutectic composition was, however, strongly affected. The eutectic composition of the Cr-Cr_2Ta base alloys without the X element contains 9.8 at.% Ta, but is shifted to lower concentrations of Ta (several at.%) with increasing levels of X additions. A typical eutectic structure is shown in Fig. 1.

Mechanical Properties

The shift in eutectic composition had a profound effect on the mechanical properties of these multi-phase alloys at room and elevated temperatures, with the best toughness values, in the range of 18.5 to 21 $MPa.m^{1/2}$, obtained with eutectic structures. The eutectic compositions with lower levels of Ta (higher levels of X) were generally tougher, yielding a fracture toughness >20 $MPa.m^{1/2}$ at room temperature (Table 1). However, the shift to the lower Ta eutectic compositions also weakened the alloy at high temperatures (Table 2). For instance, the reduction of Ta in the eutectic composition from 6.8 to 5.7 at.% Ta resulted in a decrease of the tensile yield strength from 400 to 240 MPa at 1000°C. The room-temperature fracture toughness values obtained by X additions, with appropriate levels of Ta to yield the eutectic structure, meet the targeted goals of this program and are considered sufficient for handling and installation of components in low-impact applications. Current efforts are devoted to enhancement of the high-temperature strength by minor alloying additions.

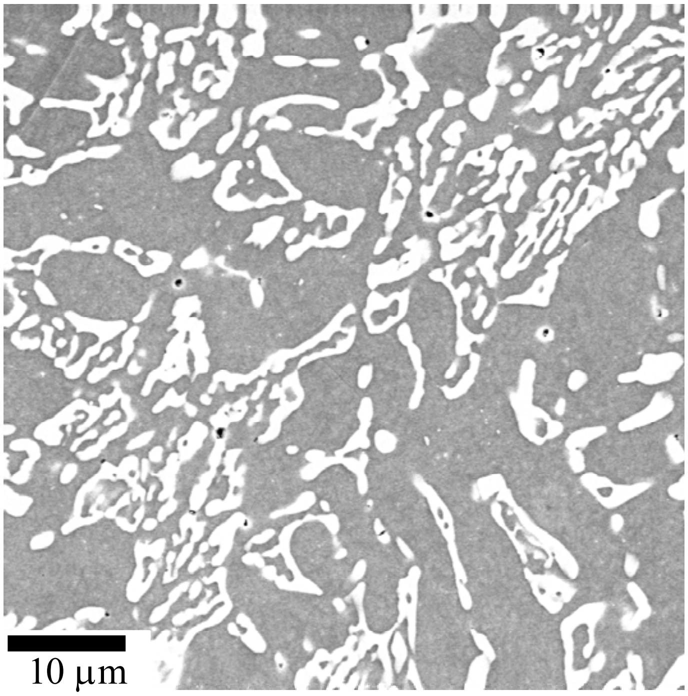


Fig. 1- Scanning electron microscopy (SEM) image showing the typical eutectic structure in a X-modified Cr-Cr_2Ta base alloy. The light phase is based on the Cr_2Ta Laves phase and the dark matrix is the Cr solid solution phase.

Table 1- Room-temperature fracture toughness (* near eutectic composition).

Alloy Designation	X (at.%) A<B<C	Ta (at.%)	Room-Temperature Fracture Toughness (MPa $m^{1/2}$)
CN 175	Level A	5.0	12.9
CN 176	Level A	5.5	14.7
CN 177	Level A	6.0	14.4
CN 183	Level A	6.6	17.8
CN 185	Level A	6.8*	18.5
CN 182	Level A	7.0	17.5
CN 188	Level B	6.3*	21.0
CN 178	Level C	5.0	18.5
CN 179	Level C	5.5	20.0
CN 181	Level C	5.7*	20.3
CN 180	Level C	6.0	18.6

Table 2- Tensile properties at 1000°C (Ta level adjusted to yield eutectic structure).

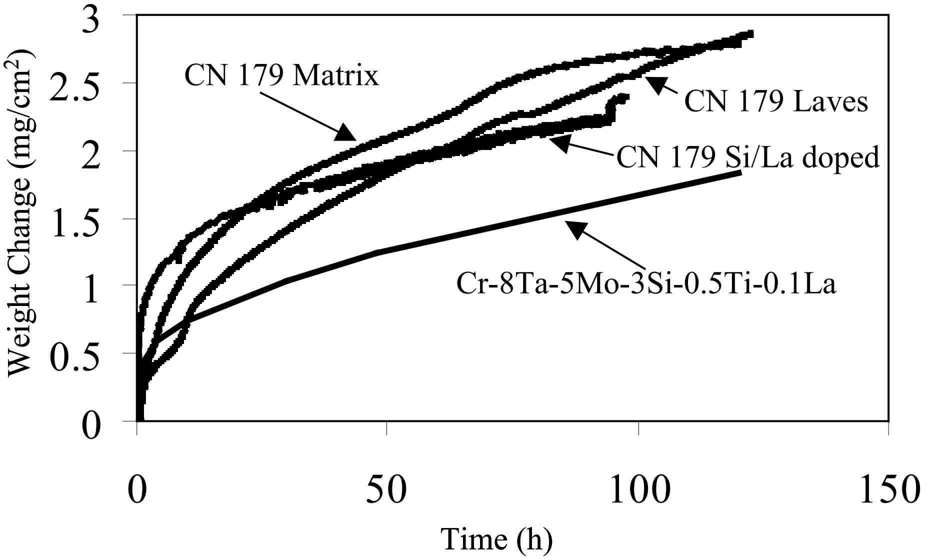
Alloy Designation	X (at.%), Ta (at.%) A<B<C	Tensile Yield Strength [ksi (MPa)[	Ultimate Tensile Strength [ksi (MPa)]	Elongation (%)
CN 185	Level A, 6.8	57.7 (398)	69.3 (477)	2.8
CN 188	Level B, 6.3	51.8 (357)	56.7 (391)	4.4
CN 181	Level C, 5.7	34.8 (240)	41.2 (284)	18.2

High-Temperature Oxidation and Corrosion Behavior

The first generation of Cr-Cr_2Ta base alloys showed good resistance to air oxidation in the 900-1100°C temperature range, comparable to the better commercially available Cr_2O_3-forming alloys. Further, these alloys have exhibited some promising resistance in molten alkali salts (950-1000°C), coal ash deposits (950°C), and coal slag (up to 1300°C) [2,9]. Preliminary evaluation and characterization suggests that alloying of Cr-Cr_2Ta alloys with X additions does not significantly degrade air oxidation resistance and that the mechanism of oxidation is similar to the previously developed alloys.

Thermogravimetric data at 1100°C in air for a series of alloys based on a baseline Cr-Ta-X alloy, CN 179 (described in Table 1, also contains additions of 3Si and 0.2La at.%), showed similar (slightly higher) kinetics as compared to Cr-8Ta-5Mo-3Si-0.1La at.%, an optimized Cr-Cr_2Ta alloy (Fig. 2). Alloy compositions corresponding to the Cr matrix phase composition (CN 179 Matrix) and Laves phase dispersion (CN 179 Laves) also exhibited similar oxidation kinetics (Fig. 2). An alloy CN 179 coupon (with less than optimum levels of Si and La additions) was also subjected to eleven, 100 h cycles at 1100°C in air (1100 cumulative hours at 1100°C). Although some spallation was evident, total coupon weight change was only on the order of 10 mg/cm^2, indicative of a reasonable degree of oxidation resistance. Preliminary evaluation of the oxidized CN 179 and related alloy coupons suggested that X additions significantly reduced the extent of embrittling Cr_2N subscale formation in the Cr matrix phase. A high level of X additions was, however, found to significantly degrade molten alkali salt resistance (100 h immersion screening in molten smelt at 950-1000°C [2,9]), presumably due to the resultant lower levels of Cr and/or Ta in the alloy. Further characterization and study of these effects are planned in order to optimize oxidation resistance, hot corrosion resistance, and mechanical properties.

Fig. 2- TGA data at 1100°C in air.



Interestingly, initial attempts to further improve oxidation resistance of the Cr-Ta-X alloys by Al additions resulted in the formation of a continuous Al_2O_3 scale at 1100°C in air, rather than the Cr_2O_3 base scale typically formed on these alloys (Fig. 3). Alumina scales exhibit lower oxidation kinetics than Cr_2O_3 scales and are much less prone to volatility related losses at elevated temperatures, particularly in water vapor containing environments. Both of these factors would effectively extend the upper temperature air oxidation limit of this family of alloys and/or reduce/eliminate the need for a protective coating. Full characterization of the microstructure of this alloy and an initial assessment of mechanical properties are planned.

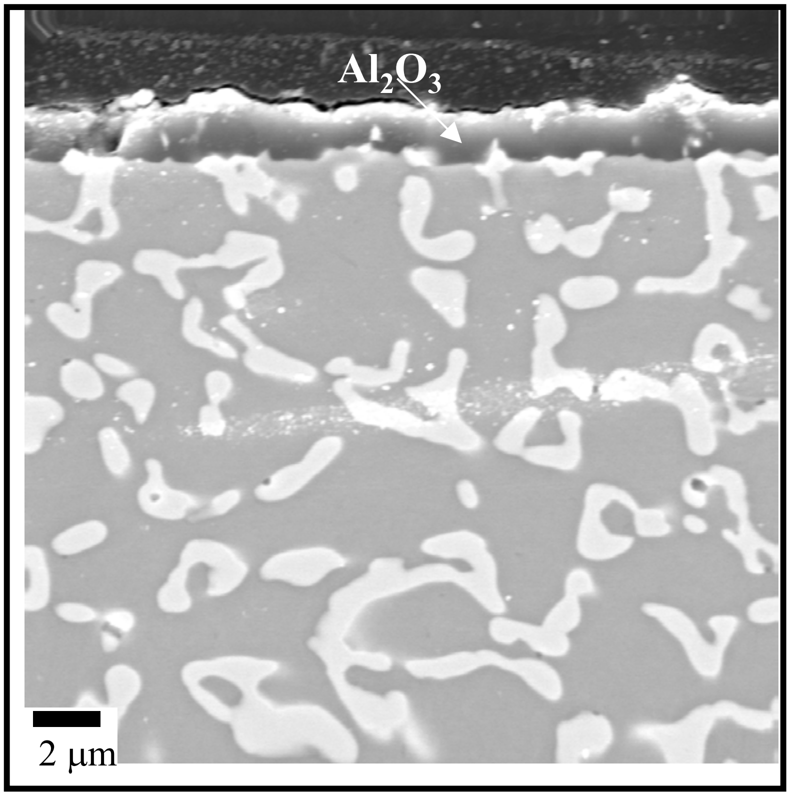


Fig. 3- SEM cross-section micrograph of an Al-modified Cr-Ta-X base alloy after 24 h oxidation at 1100°C in air. The dark phase is the Cr solid solution matrix phase and the light phase is based on the Cr_2Ta Laves phase.

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