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# ULTRAHIGH TEMPERATURE INTERMETALLIC ALLOYS

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## ABSTRACT

A new family of Cr-Cr$_2$Ta intermetallic alloys based on Cr-(6-10)Ta (at.%) is under development for structural use in oxidizing environments in the 1000-1300°C (1832-2372°F) temperature range. Developmental objectives relate to high temperature strength and oxidation resistance and room temperature fracture toughness. The 1200°C (2192°F) strength goals have been met: yield and fracture strengths of 275 MPa (40 ksi) and 345 MPa (50 ksi), respectively, were achieved. Progress in attaining reasonable fracture toughness of Cr-Cr$_2$Ta alloys has been made; current alloys exhibit room-temperature values of about 10-12 $\text{MPa}\sqrt{\text{m}}$ (1.1 $\text{MPa}\sqrt{\text{m}}$ = 1 $\text{ksi}\sqrt{\text{in.}}$). Oxidation rates of these alloys at 950°C (1742°F) in air are in the range of those reported for chromia-forming alloys. At 1100°C (2012°F) in air, chromia volatility was significant but, nevertheless, no scale spallation and positive weight gains of 1-5 mg/cm$^2$ have been observed during 120-h, 6-cycle oxidation screening tests. These mechanical and oxidative properties represent substantial improvement over Cr-Cr$_2$Nb and Cr-Cr$_2$Zr alloys previously developed.

## INTRODUCTION

The objective of this work is to develop high-strength, oxidation- and corrosion-resistant intermetallic alloys for use as hot components in advanced fossil energy conversion and combustion systems that meet the 65% efficiency goal of the Vision 21 Concept. Successful development of these alloys is expected to allow improvement in thermal efficiency primarily through decreased cooling requirements in advanced gas turbines. Initially targeted applications include components such as vanes, seals, and nozzles. However, these materials may also find other uses as wear-resistant parts in coal handling systems (for example nozzles), drill bits for oil/gas wells, valve guides in diesel engines, and interconnects in solid oxide fuel cells.

Development efforts have focused on two-phase, in-situ composite alloys of the type Cr-Cr$_2$X, where Cr$_2$X is a Cr-based refractory Laves phase compound (Cr$_2$Nb, Cr$_2$Zr, or Cr$_2$Ta). Toughness and oxidation resistance are provided by a soft Cr$_{ss}$ (solid solution) matrix. The Cr$_2$X Laves phase acts as a reinforcement to the Cr$_{ss}$ matrix in order to provide high temperature strength. Recently, we identified a promising new class of alloys based on the Cr-Cr$_2$Ta system[1,2] (Fig. 1), with melting points in the 1600-1700°C (2912-3092°F) range[3]. Preliminary evaluation suggested that the Cr-Cr$_2$Ta based alloys possess superior mechanical properties and oxidation resistance to the Cr-Cr$_2$Nb and Cr-Cr$_2$Zr alloys previously developed in this program[3]. This report presents an overview of current Cr-Cr$_2$Ta alloy development objectives and performance.

## DISCUSSION OF CURRENT ACTIVITIES

Three properties are key to the initial development of the two phase Cr-Cr$_2$Ta based alloys: room temperature fracture toughness, high temperature strength, and high temperature oxidation resistance. The target mechanical properties are room temperature fracture toughness ≥ 15-20 $\text{MPa}\sqrt{\text{m}}$ (1.1 $\text{MPa}\sqrt{\text{m}}$ = 1 $\text{ksi}\sqrt{\text{in.}}$) and 345 MPa (50 ksi) tensile fracture strength at 1200°C (2192°F). Oxidation kinetics in the

range of commercial chromia ($Cr_2O_3$) forming alloys is the goal for temperatures up to about 900-1000°C (1652-1832°F). At higher temperatures, where chromia scale volatility is significant[4], the goal is noncatastrophic oxidation behavior of the bare substrate alloy such that use of a protective coating is a reasonable protection approach (ie. local coating failure would not result in immediate component loss).

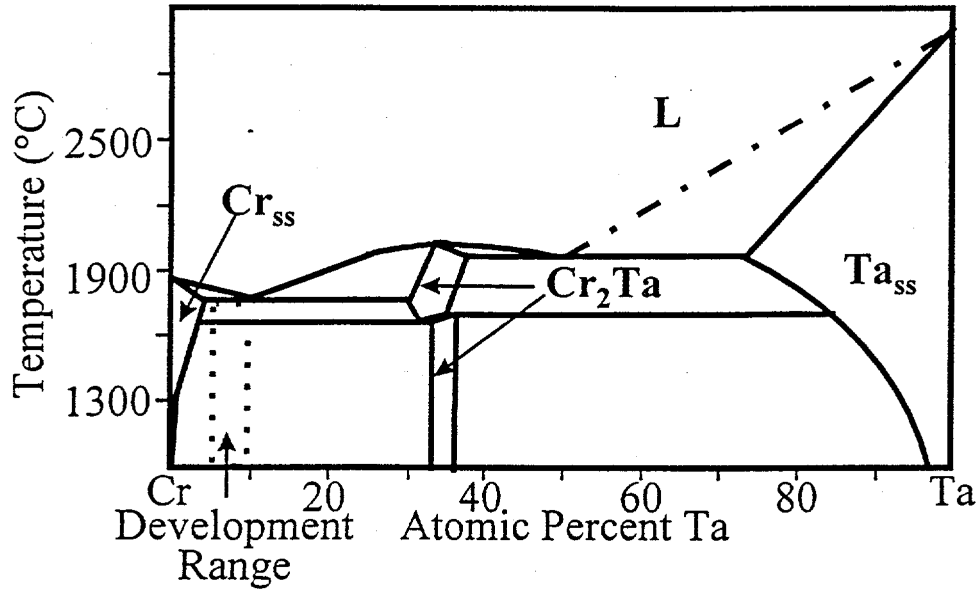

Fig. 1- Schematic binary Cr-Ta phase diagram[1,2].

## ALLOY PREPARATION AND PROCESSING

Alloys based on the Cr-$Cr_2Ta$ system weighing 400-500 g were prepared by arc melting and drop casting in a copper mold (2.5 cm diam x 7.6 cm long) preheated to 200°C (392°F). Small 40-60 g castings were also prepared by arc melting and drop casting in a chilled copper mold. High-purity chromium and other metal chips were used as charge materials. The alloys were easily cast and showed no evidence of cracking. After heat treatment, the larger 400-500 g alloy ingots were clad inside Mo billets and hot extruded at 1480°C (2696°F) and an extrusion ratio of 4:1. The hot-extruded material was then heat treated and used for tensile specimens. The small 40-60 g castings were used as-cast and/or after heat treatment to provide specimens for oxidation exposures and room temperature fracture toughness evaluation. The development range is based on Cr-(6-10)Ta atomic percent, at.% (Fig. 1). Detailed alloy compositions are not reported due to patent considerations, and are denoted in the report by the letter "X" followed by a number.

## ROOM TEMPERATURE FRACTURE TOUGHNESS

Chevron notched three-point bend samples approximately 3 mm x 4 mm x (20-25) mm were used to evaluate fracture toughness at room temperature. A modulus of 250 GPa (36 ksi) was estimated for the Cr-$Cr_2Ta$ based alloys. A modulus of 300 GPa (43 ksi) was used for the Cr-(0-0.1X10) alloys. Details of this technique are provided in ref. 5.

Current Cr-Cr$_2$Ta based alloys have a room temperature fracture toughness in the 10-12 MPa$\sqrt{m}$ range, with one alloy test sample exhibiting a toughness of 12.8 MPa$\sqrt{m}$ (Table 1). This represents significant progress beyond the 7-8 MPa$\sqrt{m}$ room temperature fracture toughness exhibited by the best Cr-Cr$_2$Nb based alloys previously developed under this initiative$^6$. However, it is still short of the goal levels of 15-20 MPa$\sqrt{m}$.

Room temperature fracture toughness values of several binary Cr-Ta and microalloyed Cr alloys are shown in Table 2. A comparison of Table 1 with Table 2 reveals that the alloy additions to the Cr-(8-10)Ta base have not significantly increased room temperature fracture toughness. The binary Cr-(8-10)Ta alloys exhibit room temperature fracture toughness values in the 9-10 MPa$\sqrt{m}$ range, only slightly below the 10-12 MPa$\sqrt{m}$ range achieved with further alloying. (It should be noted the alloying strategy adopted thus far has proven effective in improving high temperature strength and oxidation resistance).

Table 1- Room temperature fracture toughness of selected Cr-Cr$_2$Ta based alloys.

| Alloy No. | Composition (At.%) | Microstructure | Condition and Heat Treatment | Fracture Toughness (MPa$\sqrt{m}$) | |
|---|---|---|---|---|---|
| | | | | Best | Average (# of tests) |
| CN144 | Cr-8Ta-5X1-0.5X3-0.011X8 | Hypoeutectic | extruded,1200°C | **11.0** | **11.0 (1)** |
| | | | cast, 1000°C | 10.2 | 8.3 (2) |
| | | | cast, 1200°C | 8.3 | 7.9 (2) |
| CN145 | Cr-10Ta-5X1-0.5X3-0.011X8 | Hypereutectic | cast, 1000°C | 8.7 | 6.0 (2) |
| | | | cast, 1200°C | **12.8** | **11.1 (2)** |
| CN147 | Cr-9.5Ta-5X1-0.5X3-0.011X8 | Eutectic | cast, 1200°C | **11.7** | **10.7 (4)** |

Table 2- Room temperature fracture toughness of selected binary Cr-Ta and Cr alloys.

| Composition (At.%) | Microstructure | Condition and Heat Treatment | Fracture Toughness (MPa$\sqrt{m}$) | |
|---|---|---|---|---|
| | | | Best | Average (# of tests) |
| | | **Binary Cr-Ta** | | |
| Cr-8Ta | Hypoeutectic | cast, 1000°C | 10.4 | 9.8 (3) |
| Cr-11Ta | Hypereutectic | cast, 1000°C | 9.8 | 9.7(2) |
| Cr-9.8Ta | ≈ Eutectic | cast, 1000°C | 9.0 | 9.4 (2) |
| | | **Cr Matrix** | | |
| Pure Cr | Cr | cast, 1000°C | **16.1** | **15.2 (2)** |
| Cr-0.1X10 | | cast, 1000°C | **34** | **22.3 (3)** |

Alloying for further improvement in room temperature fracture toughness will focus on two key areas: the Cr$_{ss}$ phase and the Cr$_{ss}$/Laves phase interface. Pure Cr containing 200 O and 25 N weight parts per million, processed under similar conditions to the Cr-Cr$_2$Ta based alloys, exhibits a room temperature fracture toughness of 15-16 MPa$\sqrt{m}$ (Table 2). Microalloying additions to improve the toughness of Cr are currently under evaluation. For example, the addition of 0.1at.% of X10 was recently found to increase the room temperature fracture toughness to level of 34 MPa$\sqrt{m}$ in one test sample (Table 2).

Manipulation of the $Cr_{SS}$/Laves phase interface is the second route under consideration to further improve toughness. Understanding of processing/composition/microstructure relationships in the Cr-Ta system, including phase equilibria studies to determine the eutectic composition, has been achieved. Microstructures consisting of a fine dispersion of Laves particles in the $Cr_{SS}$ matrix or lamellar $Cr_{SS}$/Laves eutectic structures can now be produced (Fig. 2). Very preliminary results suggest that the lamellar eutectic structures (Fig. 2a) may exhibit greater room temperature fracture toughness than the fine dispersed structures (Fig. 2b). Future work will concentrate on confirming and optimizing this effect through adjustments of microstructural parameters such as lamellar spacing and lamellar colony grain size.

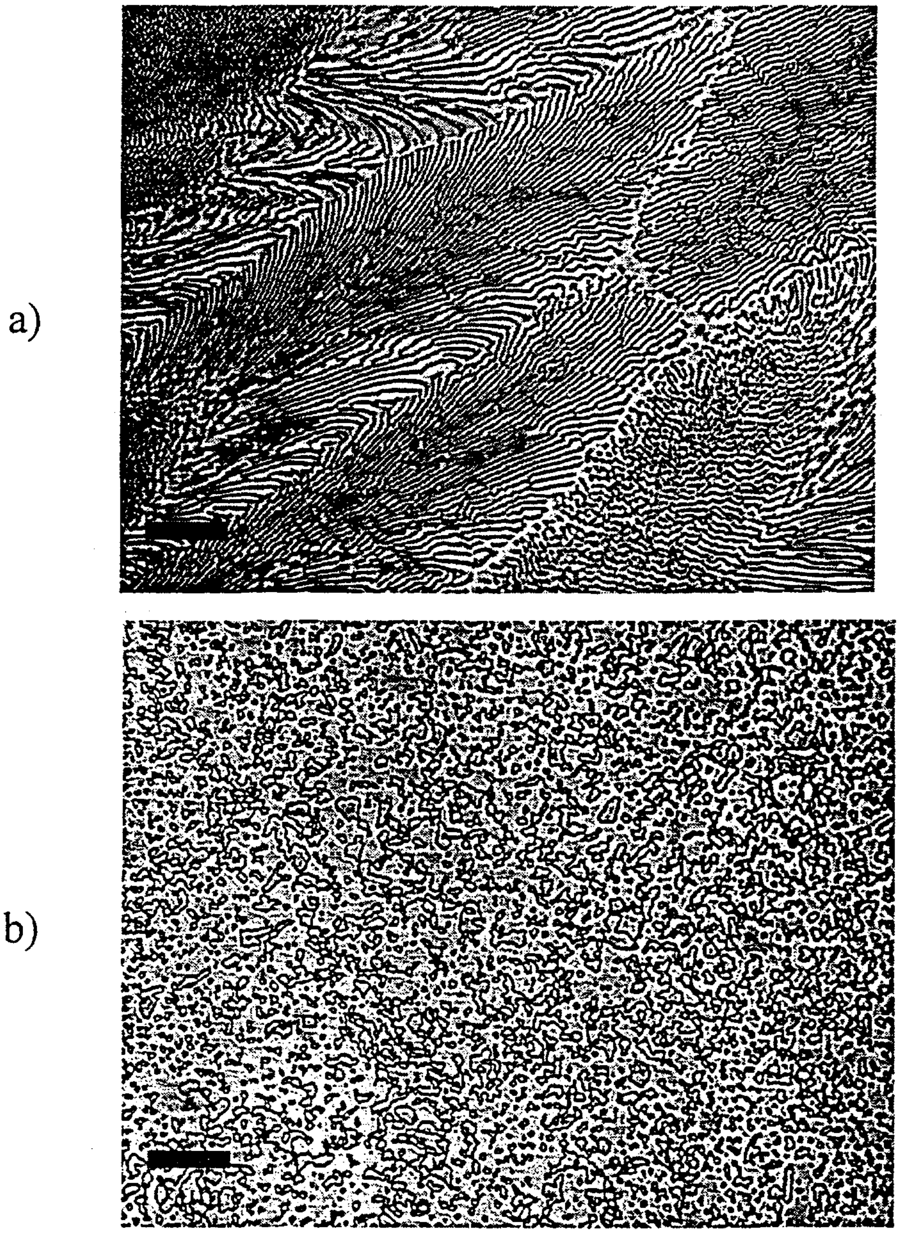

Fig. 2- Possible microstructures for Cr-$Cr_2Ta$ based alloys (light microscopy). a) lamellar eutectic b) $Cr_2Ta$ Laves particles dispersed in a $Cr_{ss}$ matrix.

## TENSILE PROPERTIES

Button-type tensile specimens with gage dimensions 0.31 cm diam x 0.97-1.3 cm long were cut from hot-extruded material by electro-discharge machining, followed by grinding and polishing with "0" Emery paper. The specimens were tensile tested at room temperature and 800°C (1472°F) in air, and at 1200°C (2192°F) in vacuum (crosshead speed of approximately 0.25 cm/minute). Tensile properties are summarized in Tables 3-5.

At room temperature, no macroscopic yielding prior to fracture was observed. However, tensile fracture strengths in excess of 700 MPa (100 ksi) were achieved (Table 3). At 800°C in air, tensile elongations on the order of 1% were observed in several alloys, with yield strengths of around 900 MPa (130 ksi) (Table 4). This suggests that the ductile to brittle transition temperature (DBTT) was just under 800°C (1472°F). At 1200°C (2192°F), elongations were generally in the 20-30% range, with several alloys exhibiting tensile fracture strengths in excess of 345 MPa (50 ksi) (Table 5). Thus, the Cr-$Cr_2Ta$ based alloys meet the high temperature strength goals of the program.

Table 3- Room temperature tensile properties.

| Alloy No. | Composition Cr-8Ta-0.5X3 Base (At.%) | Yield Strength ksi (MPa) | Fracture Strength ksi (MPa) | Elongation % |
|---|---|---|---|---|
| CN130 | 5X1 | >104 (717) | **104 (717)** | * |
| CN132 | 5X1-3X2-.05X6 | >71 (489) | 71 (489) | * |
| CN133 | 2.5X1-3X2 | >101 (696) | **101 (696)** | * |
| CN136 | 6.5X1-0.5X6 | >87 (600) | 87 (600) | * |
| CN137 | 6.5X1-0.05X6-0.022X8 | >92 (634) | 92 (634) | * |
| CN144 | 5X1-0.011X8 | >104 (717) | **104 (717)** | * |
| CN146 | 8X7-0.011X8 | >80 (552) | 80 (552) | * |

*Fracture Prior to Macroscopic Yielding

Table 4- 800°C (1472°C) tensile properties.

| Alloy No. | Composition Cr-8Ta-0.5X3 Base (At.%) | Yield Strength ksi (MPa) | Fracture Strength ksi (MPa) | Elongation % |
|---|---|---|---|---|
| CN130 | 5X1 | 120 (827) | 120 (827) | 0.8 |
| CN132 | 5X1-3X2-.05X6 | **134 (924)** | **137 (944)** | **1.2** |
| CN133 | 2.5X1-3X2 | >69 (476) | 69 (476) | * |
| CN136 | 6.5X1-0.5X6 | >118 (813) | **118 (813)** | * |
| CN137 | 6.5X1-0.05X6-0.022X8 | **128 (882)** | **131 (903)** | **0.9** |
| CN144 | 5X1-0.011X8 | **130 (896)** | **133 (917)** | **1.0** |
| CN146 | 8X7-0.011X8 | >116 (800) | 116 (800) | * |

*Fracture Prior to Macroscopic Yielding

Table 5- 1200°C (2192°F) tensile properties.

| Alloy No. | Composition Cr-8Ta-0.5X3 Base (At.%) | Yield Strength ksi (MPa) | Fracture Strength ksi (MPa) | Elongation % |
|---|---|---|---|---|
| CN130 | 5X1 | 37 (255) | 45 (310) | 16.6 |
| CN132 | 5X1-3X2-.05X6 | 42 (290) | 51 (352) | 18.5 |
| CN133 | 2.5X1-3X2 | 30 (207) | 36 (248) | 22.0 |
| CN136 | 6.5X1-0.5X6 | 46 (317) | 56 (386) | 14.3 |
| CN137 | 6.5X1-0.05X6-0.022X8 | 37 (255) | 45 (310) | 28.1 |
| CN144 | 5X1-0.011X8 | 37 (255) | 46 (317) | 39.0 |
| CN146 | 8X7-0.011X8 | 30 (206) | 36 (248) | 25.8 |

## HIGH TEMPERATURE OXIDATION

The development effort focused on optimization of chromia scale growth kinetics of Cr-$Cr_2Ta$ based alloys through microalloying, with an emphasis on reactive element (RE) additions. A series of alloys based on Cr-8Ta-5X1 with microalloying additions in the 0.05 to 1 at.% range was selected for evaluation. Disk shaped oxidation specimens of 8-13 mm in diameter and 1 mm thickness were sectioned from as-cast and/or heat treated material and polished to a 600 grit finish using SiC paper. Evaluation of oxidation was performed by thermogravimetric analysis (TGA) at 950°C (1742°F) in dry air for 168 h and short term cyclic oxidation screening at 1100°C (2012°F). Screening tests at 1100°C (2012°F) were performed in a tube furnace open to room air. The samples were placed in a covered alumina crucible and inserted/removed from the furnace at temperature after intervals of 1, 4, 10, 30, 48, and 120 h of cumulative exposure. Significant chromia volatility occurred as evidenced by green stains on the underside of the alumina crucible lid.

At 950°C (1742°F) in air, RE modified Cr-8Ta alloys exhibited a 2-7 fold decrease in the rate of oxidation relative to binary Cr-8Ta (Fig. 3). No isothermal scale cracking was observed for the modified alloys during a 168 h isothermal exposure and the scale remained adherent on cooling. This behavior is in contrast to binary Cr-8Ta, which exhibited a relatively low rate of oxidation but suffered from isothermal scale cracking and scale spallation on cooling to room temperature. The best RE modified Cr-8Ta based alloy oxidized at a rate within the range defined at the high end by Waspalloy, a commercial chromia-forming superalloy, and at the low end by MA754, a $Y_2O_3$ dispersed Ni-Cr alloy (1000°C data) which is among the most oxidation resistant chromia-forming alloys (Fig. 3). It should be noted that the oxidation kinetics of the RE modified Cr-8Ta based alloys were not parabolic, although the rate of oxidation did decrease with time.

Microalloying additions were also successful at reducing the rate of oxidation at 1100°C (2012°F). The alloys generally exhibited a 3-5 fold decrease in the rate of oxidation and exhibited no scale spallation during the short term 1100°C (2012°F) cyclic oxidation screening test. The most recent RE modified Cr-8Ta based alloy exhibited a 50 fold decrease in the rate of oxidation as compared with Cr-8Ta-5X1 (Fig. 4), although it should be noted that this result has not yet been repeated.

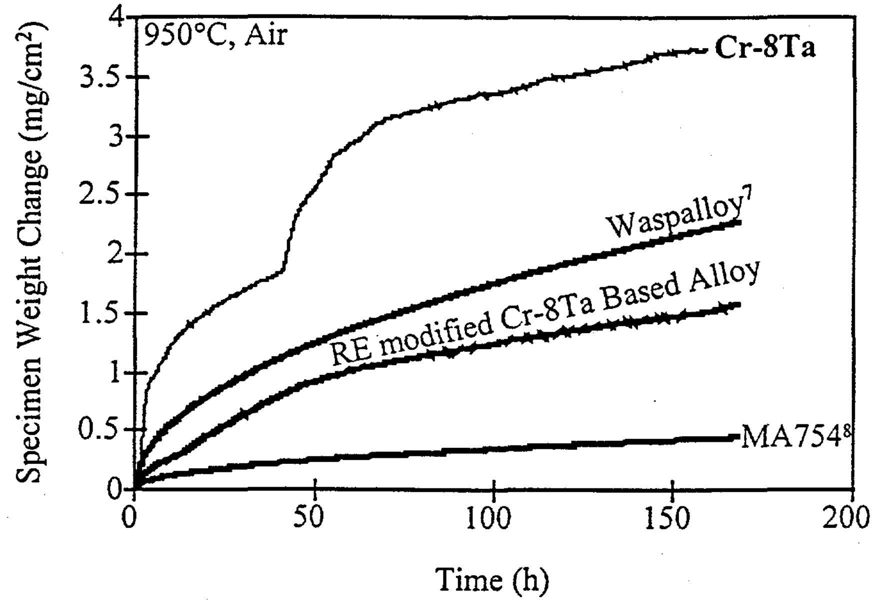

Fig. 3-TGA data at 950°C in dry air.

Overall, microalloying of the Cr-$Cr_2Ta$ based alloys was successful in reducing the rate of oxidation and in improving scale adherence, although further compositional optimization is needed. Short term (< 200 h) behavior was in the target goal range of chromia-forming oxidation kinetics below 900-1000°C (1652-1832°F) and noncatastrophic oxidation at 1100°C (2012°F). Although the behavior thus far is promising, longer term exposures (>1000 h) are needed (and planned) before an assessment can be made of the oxidation performance of the microalloyed Cr-$Cr_2Ta$ based alloys. Of particular concern is possible embrittlement from oxygen/nitrogen. Preliminary results suggest that the chromia scale formed on the Cr-$Cr_2Ta$ based alloys can provide some protection from this type of embrittlement, but only if the scale remains adherent.

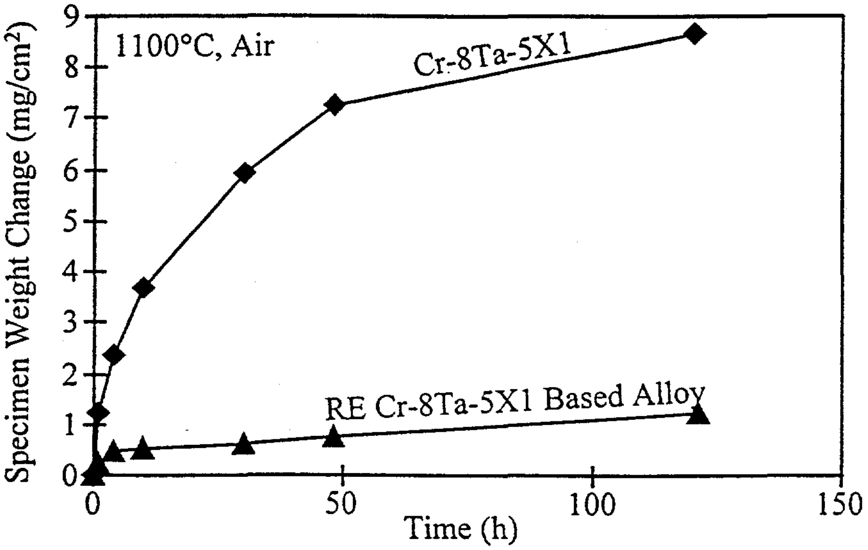

Fig. 4- Cyclic oxidation data at 1100°C in air.

## SUMMARY AND FUTURE WORK

The room temperature fracture toughness, high temperature strength, and oxidation resistance of a series of developmental Cr-$Cr_2Ta$ based alloys were evaluated. The developmental goal of 345 MPa (50 ksi) for tensile fracture strength at 1200°C (2192°F) was met. Significant improvement in room temperature fracture toughness over previously developed Cr-$Cr_2Nb$ based alloys was achieved, with the Cr-$Cr_2Ta$ based alloys exhibiting toughness in the 10-12 MPa$\sqrt{m}$ range as compared with 7-8 MPa$\sqrt{m}$ for Cr-$Cr_2Nb$. Although short of the goal of 15-20 MPa$\sqrt{m}$, further improvements are thought possible through microalloying of the $Cr_{ss}$ phase and manipulation of the $Cr_{ss}$/Laves phase interface. Microalloying with reactive elements successfully reduced the rate of chromia scale formation during short term 950°C (1742°F) and 1100°C (2012°F) exposures in air. Long-term oxidation studies and optimization of microalloying levels are planned.

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