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MULTI-PHASE Cr-BASED ALLOYS FOR AGGRESSIVE HIGH TEMPERATURE ENVIRONMENTS

M.P. Brady, C.T. Liu, I.M. Anderson, P.F. Tortorelli, *J.H. Zhu, I.G. Wright, V.K. Sikka, C.A. Walls, L.R. Walker, S.B. Waters, J.L. Wright, and C.A. Carmichael
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6115

*Tennessee Technological University
Cookeville, TN 38505-0001

ABSTRACT

Attractive high-temperature mechanical properties and oxidation/hot corrosion resistance have been achieved in a new family of Cr₂Ta-reinforced Cr alloys. However, inadequate room-temperature toughness remains a key challenge, with the best Cr-Cr₂Ta alloys exhibiting only modest toughness in the range of 12-14 MPa m^{1/2}. The addition of MgO has been shown to significantly improve the room-temperature mechanical properties of unalloyed Cr and was investigated as a means for improving the room-temperature mechanical properties of the Cr-Cr₂Ta alloys. Microstructural analysis of a series of Cr and Cr-6MgO base alloys was used to investigate the proposed ductilization mechanism of nitrogen gettering by a MgCr₂O₄ spinel phase, which forms during consolidation of Cr and MgO powders. Nitride and related impurity precipitates have been linked to reduced ductility in Cr at room-temperature. Surprisingly, nitride (and carbide) impurity precipitates were found in hot-pressed Cr-6 MgO base alloys despite room-temperature tensile ductility of 5%. These precipitates were found adjacent to MgO/MgCr₂O₄ particles and were somewhat more blunt than those observed in unalloyed Cr. The addition of TiO₂ to unalloyed Cr resulted in similar morphological changes to the nitride and carbide impurity precipitates; however, the TiO₂ dispersed alloy was brittle at room-temperature. Why MgO dispersions are effective in ductilizing Cr, but others such as TiO₂ are not, is not clear and is the subject of ongoing study. Efforts to introduce the effect in Cr-Cr₂Ta-MgO alloys were not successful, and it was concluded that significant modification of the Cr matrix phase in the Cr-Cr₂Ta alloys by macroalloying is necessary to improve room-temperature mechanical properties. Preliminary attempts at macroalloying with Fe were quite successful and resulted in an increase in room-temperature toughness to 18-20 MPa m^{1/2} in Cr-Cr₂Ta + Fe alloys.

INTRODUCTION

A new family of structural Cr alloys based on Cr-(6-10)Ta (at.%) is under development for high-temperature use (900-1300°C) in the oxidizing and aggressive hot corrosion environments encountered in advanced fossil energy conversion and combustion systems [1-4]. The microstructures of these alloys consist of a Cr solid solution matrix reinforced with the intermetallic Cr₂Ta Laves phase for high-temperature strength. The compositions of interest are in the range of: Cr-(6-10)Ta-(3-6)Mo-(0.5-3)Si-(0.2-1.0)Ti-(0.05-0.2)La/Ce at.%. The Mo is added for solid solution strengthening, Si (primarily) for oxidation resistance, Ti for interstitial gettering, and La or Ce for oxidation resistance and interstitial gettering.

Substantial progress has been made in developing attractive high-temperature properties. Microalloying with Si and La has yielded alloys with oxidation resistance in the range reported for commercial Cr₂O₃-forming alloys (900-1100°C, air, 1000 h duration) [1]. Immersion screenings in molten alkali salts and coal slags have also indicated promising behavior [2]. The alloys exhibit tensile fracture strengths in excess of 700 MPa at 1000°C and in excess of 400 MPa at 1200°C [1]. Cast Cr-8Ta-5Mo-0.5Ti-0.01Ce at.% was creep tested up to 1438 hours at 1000°C in humid room air under a load of 138 MPa, at which point the test was stopped due to failure of the grip rods [1]. However, room temperature fracture toughness remains the key challenge for development. Current compositions exhibit a brittle to ductile transition temperature in the range of 800-1000°C [1,2]. At room temperature, tensile fracture strengths are in excess of 700 MPa, but no plastic tensile elongation is observed and fracture toughness of the best alloys is in the range of only 12-14 MPa m^{1/2} [2].

Two approaches for improved fracture toughness at room temperature were investigated: 1) ductilization of unalloyed Cr by the addition of MgO [2, 5] and 2) macroalloying to improve the fracture toughness of the Cr matrix phase in Cr-Cr₂Ta alloys. This paper presents the results of microstructural analysis of Cr and Cr-MgO alloys aimed at gaining an understanding of the mechanism by which MgO additions ductilize unalloyed Cr. Promising preliminary results showing significant improvement in room-temperature fracture toughness by macroalloying of Cr₂Ta-reinforced Cr alloys with Fe are also presented.

MEASUREMENT OF ROOM-TEMPERATURE MECHANICAL PROPERTIES

Room temperature tensile properties were evaluated using dogbone 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/minute was used (strain rate of 3.33×10^{-3} /s). Subsize chevron-notched three-point bend samples approximately 3 × 4 × 25 mm were used to evaluate fracture toughness at room temperature. 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 for Cr-Cr₂Ta based alloys and 300 GPa for Cr-based alloys. Fracture toughness values obtained by this technique should be considered semiquantitative; details are provided in reference 6.

DUCTILIZATION OF UNALLOYED Cr BY MgO

A major contributor to the ambient brittleness of Cr is the presence of impurity nitrogen [e.g. 7-9]. Work by Scruggs and co-workers demonstrated that plastic tensile elongations up to 20% could be achieved at room temperature in Cr via the addition of MgO [10-12]. The baseline composition of these alloys was Cr-(3-6)MgO-0.5Ti wt.%. During powder processing, some of the MgO particles convert to a MgCr₂O₄ spinel, which was hypothesized to getter nitrogen (and other impurities) from the Cr, rendering it ductile [10-12]. A sintered and extruded ingot of Cr-6MgO-0.5Ti wt.% provided by Scruggs was found to exhibit an average plastic tensile elongation of 8.2% (3 samples) with a 600 grit surface finish and a strain rate of 3.33×10^{-3} /s, despite a nitrogen impurity level of 0.03 wt.% [2]. For unalloyed Cr (without MgO additions) to exhibit appreciable room-temperature ductility at these strain rates, high purity (< 0.001-0.005 wt.% nitrogen), cold work (usually but not always), and electropolished surfaces (to eliminate local notches) are needed [7-9].

A series of Cr, Cr-0.5Ti, Cr-6MgO, and Cr-6MgO-(0-1)Ti wt.% alloys was made in order to investigate the ductilizing effect of MgO on unalloyed Cr and assess the potential of this approach to improve the room-temperature mechanical properties of the Cr₂Ta reinforced Cr alloys. Control alloys of Cr-6Y₂O₃,

La₂O₃, or TiO₂ wt.% were also studied. The alloys were produced by oblique blending commercial purity 1-5 micron size powders for 24 h using zirconia balls and hot-pressing under vacuum in a graphite die at 1590°C for 2 h at a load of approximately 20 MPa (the Cr-0.5Ti alloy was made by hot isostatic pressing in a Nb can at 1600°C for 1.5 h). Selected alloys were further processed by sealing the hot-pressings in a steel can and extruding at 1300°C with a 9:1 reduction ratio. Both hot-pressing and hot-pressing/extrusion yielded fully dense material. The hardness of the hot-pressed, and hot-pressed and extruded, Cr-6MgO-(0-1)Ti wt.% alloys was in the range of 150-180 VHN, similar to the original Scruggs Cr-6MgO-0.5Ti alloy and consistent with a recrystallized structure. Chemical analysis of the Cr, Cr-Ti, Cr-MgO, and Cr-MgO-Ti alloys indicated that the nominal compositions were achieved, with nitrogen and carbon impurity levels in the range of 0.03-0.06 wt.%.

The unalloyed Cr, Cr-0.5Ti, and Cr-6Y₂O₃, La₂O₃, or TiO₂ control alloys all exhibited brittle behavior at room-temperature, with plastic tensile elongation less than ~2%. However, plastic tensile elongation in the ~3-5% range was observed for hot-pressed Cr-6MgO-(0-1) Ti alloys. It should be noted that the grain size of the Cr and Cr-0.5Ti alloys was on the order of 0.5 millimeter while the grain size of the hot-pressed alloys with oxide dispersions (e.g. MgO) was on the order of 50 microns. Subsequent extrusion more than doubled the plastic tensile elongation at room temperature, with ~10-12% elongation observed for hot-pressed and extruded Cr-6MgO-0.75Ti wt.%.

The scanning electron microscopy (SEM) technique of low-voltage EDS spectrum imaging (LV-EDS) was used to examine alloy microstructures for the presence of nitride and other impurity phases [13]. This technique provides an attractive alternative to electron probe microanalysis (EPMA) for mapping of different phases through their characteristic X-ray spectra, although it is not as good for quantitative analysis. A low operating voltage is used relative to the EPMA, which results in an order of magnitude better spatial resolution (~150 nm for 4 kV); however, many of the X-ray lines most suitable for quantification (e.g., Cr-K) are not excited at these voltages. The much poorer spectral resolution of EDS relative to WDS also compromises quantitative compositional analysis. However, because a full spectrum, rather than the intensities of a few selected X-ray lines, are acquired at each pixel in the image, low-voltage EDS spectrum imaging provides a true phase, rather than elemental, mapping technique. In-house ORNL multivariate statistical analysis software is used to identify all spectrally-distinct phases in the image, and also robustly distinguishes phases having spectral overlaps (e.g., O-K and Cr-L) [14, 15].

Acicular Cr-nitrides and Cr-carbides were detected at the grain boundary regions in unalloyed Cr (Fig. 1). Such impurity phase formation significantly contributes to the poor room-temperature ductility of Cr. The microstructure of hot-pressed Cr-6MgO is shown in Fig. 2. The alloy grain boundaries were decorated by MgO and Mg-Cr-O phases. The composition of the ternary oxide phase was determined by electron probe microanalysis (EPMA) to be 12Mg-52Cr-36O (wt.%), consistent with the MgCr₂O₄ spinel phase. Within the sensitivity limits of EPMA, nitrogen was not detected in the spinel phase. A similar microstructure was observed for hot-pressed Cr-6MgO-0.5Ti and Cr-6MgO-1Ti, except that Ti was present in the spinel phase (Ti segregation to the spinel phase was also observed in the Scruggs Cr-6MgO-0.5Ti alloy).

An LV-EDS spectrum image phase map for Cr-6MgO is shown in Fig. 3. In addition to the Cr matrix, MgO and MgCr₂O₄ phases, chromium nitride and sulfide phases were also identified. The nitrides were typically located adjacent to the MgO and MgCr₂O₄ oxide dispersions. Qualitatively, the nitrides appeared more blocky (Fig. 3) than the acicular nitrides typically observed in unalloyed Cr (Fig. 1). Similar nitrides were also observed in hot-pressed Cr-6MgO-1Ti. Given that up to 5% plastic tensile elongation at room-temperature was exhibited in these hot-pressed Cr-MgO alloys, the observation of Cr nitrides was very

surprising. This result suggests that the ductilization of Cr by MgO is more complicated than the spinel nitrogen gettering mechanism proposed by Scruggs [10-12].

The addition of other oxide dispersions (6 wt.% Y_2O_3 , La_2O_3 , or TiO_2) did not result in room-temperature tensile ductility as did MgO. Fig. 4 shows an LV-EDS spectrum image phase map for Cr-6TiO₂ wt.%. As with the Cr-MgO alloys, impurity nitride phases were observed to precipitate in a somewhat blunt

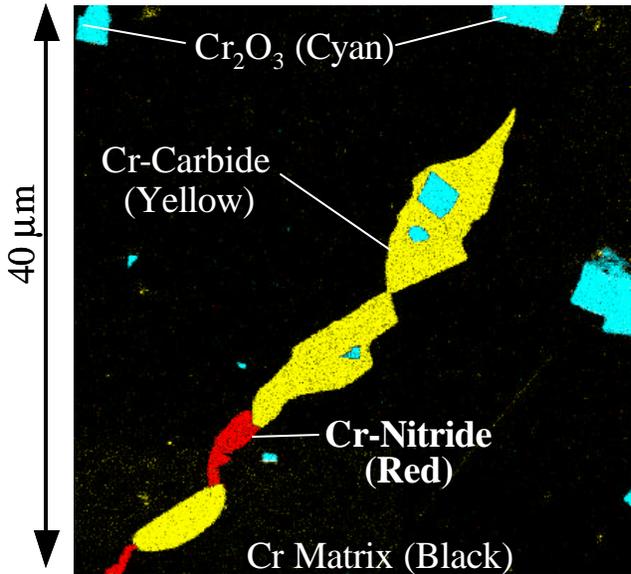


Fig. 1- Low voltage EDS spectrum image phase map of hot-pressed, unalloyed Cr.

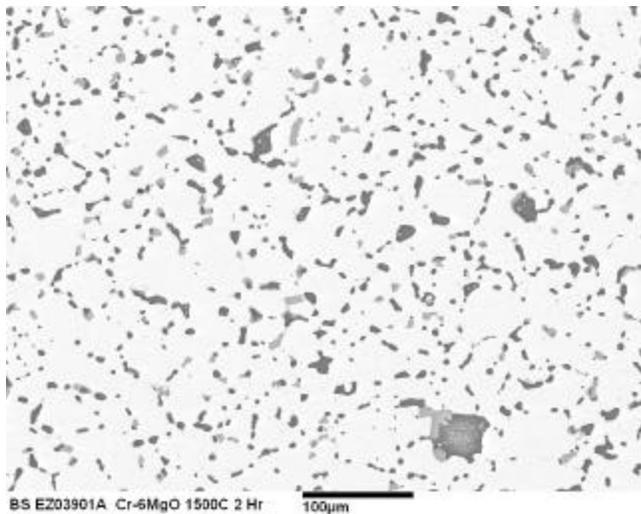


Fig. 2- SEM secondary image micrograph of hot-pressed Cr-6MgO wt.%. The light gray phase is the $MgCr_2O_4$ spinel and the dark gray phase is MgO.

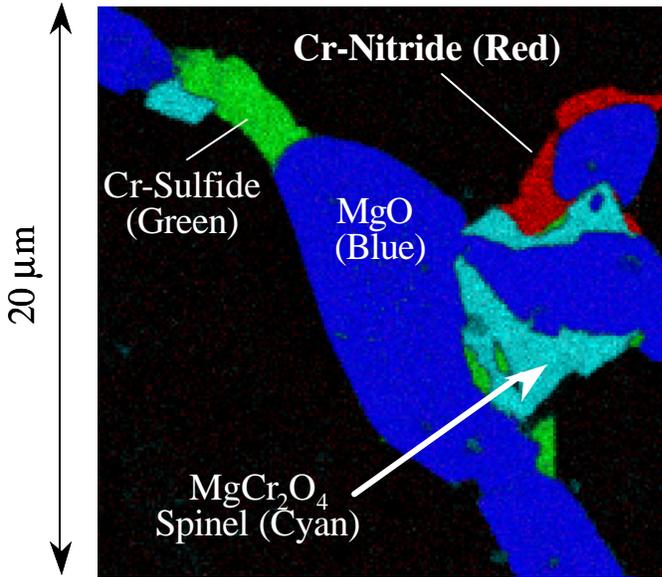


Fig. 3- Low voltage EDS spectrum image phase map of hot-pressed Cr-6MgO wt.% from Fig. 2.

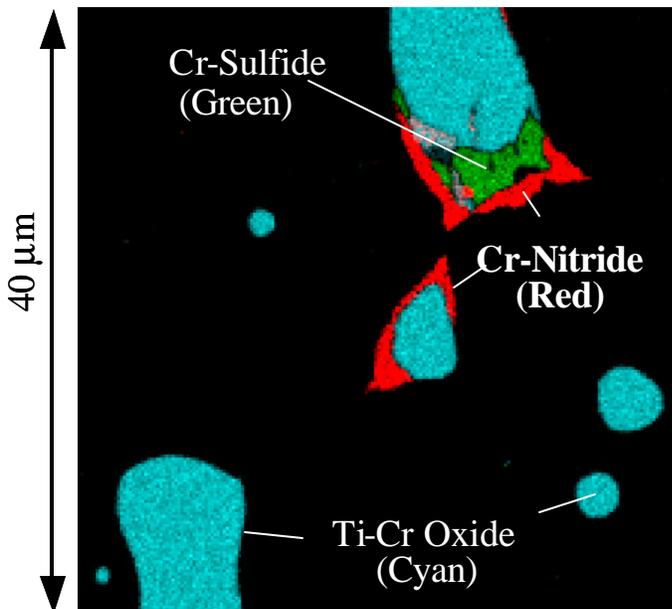


Fig. 4- Low voltage EDS spectrum image phase map of hot-pressed Cr-6TiO₂ wt.%.

morphology adjacent to the oxide dispersions. Why MgO dispersions are effective in ductilizing Cr, but others such as TiO₂ are not, is not clear and is the subject of ongoing study.

In the present work, subsequent extrusion of hot-pressed material more than doubled the observed plastic tensile elongation at room-temperature to greater than 810%. Analysis of the sintered and extruded Scruggs Cr-6MgO-0.5Ti alloy and a hot-pressed and extruded Cr-6MgO-0.75Ti alloy of the present study by EPMA and LV-EDS spectrum image phase mapping did not reveal the presence of nitrides despite similar levels of nitrogen impurities to the hot-pressed material shown in Figs. 1-4 (0.02-0.04 wt.%), in which nitrides were easily detected. To investigate whether the increased ductility with extrusion resulted from complete removal of the nitride precipitates (observed in hot-pressed material) by MgCr₂O₄ spinel phase gettering, the Scruggs Cr-6MgO-0.5Ti extrusion was analyzed by electron energy-loss spectroscopy (EELS) in the transmission electron microscope (TEM). The EELS analysis did not reveal the presence of nitrogen in either the MgCr₂O₄ spinel phase particles, the MgO particles, or the Cr matrix. This result strongly suggests that nitrogen gettering by the spinel phase as originally postulated by Scruggs [10-12] may not occur.

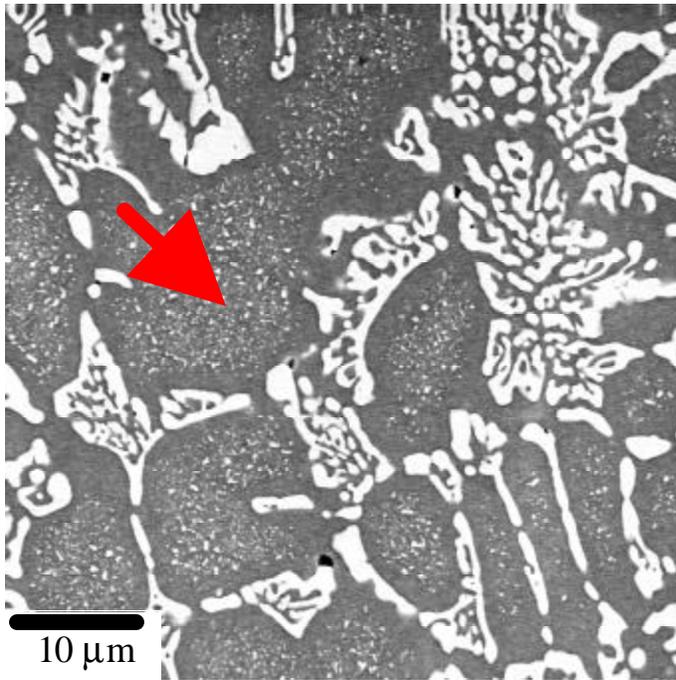
The inability to detect any nitrogen or nitride anywhere in the extruded Cr-MgO alloys by SEM, EPMA, and EELS (despite confirmation by bulk chemical analysis that nitrogen was indeed present) is not understood. It is speculated that the extrusion process breaks up the nitride precipitate particles formed during the initial hot-pressing or sintering step such that they are not retained during sample preparation for SEM and TEM analysis, i.e. the inability to identify nitrides in the extruded material may be an artifact of the sample preparation. The increased ductility due to extrusion is attributed to the aligned columnar grain structure introduced by the extrusion (the tensile axis was aligned with the extrusion direction) and refinement in the size of MgO/MgCr₂O₄ particle agglomerations.

Attempts to introduce the ductilizing effect of MgO into the high-strength Cr₂Ta reinforced Cr alloys were not successful. Therefore, it is concluded that significant modification of the Cr matrix phase by macroalloying is needed to achieve the toughness goals of this project.

MACROALLOYING EFFECTS FOR Cr-Cr₂Ta ALLOYS

Fig. 5a shows the resultant microstructure of an initial attempt at macroalloying a Cr-Cr₂Ta base alloy with Fe. Due to patent considerations, detailed compositions are not reported here. Despite the presence of a high concentration of fine Laves phase precipitates in the primary Cr regions, a fracture toughness in the range of 14-15 MPa m^{1/2} was achieved. EPMA analysis indicated that the Fe partitions in both the Cr-rich matrix (dark contrast) and the Cr₂Ta-type Laves phase (bright contrast) in Fig. 5. Adjustment of Fe/Ta levels produced a nearly 100% eutectic structure (Fig 5b). This resulted in room-temperature fracture toughness in the range of 18-20 MPa m^{1/2}, which is significantly higher than any other Cr₂Ta reinforced Cr base alloy evaluated in this effort and meets the fracture toughness goals of this program.

Detailed study and confirmation of these results, as well as full characterization of high-temperature physical, chemical, and mechanical properties, are planned.



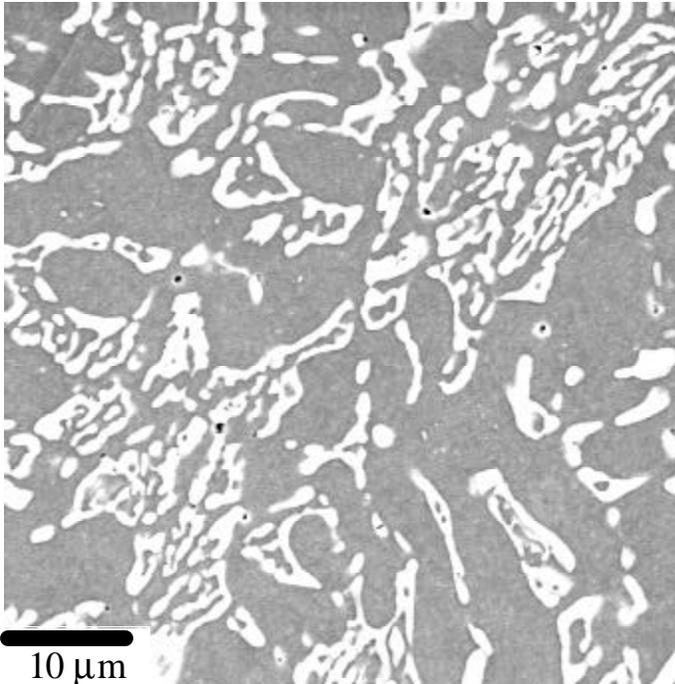


Fig. 5-SEM images of Fe modified Cr-Cr₂Ta base alloys. The light phase is the Cr₂Ta Laves phase and the dark phase is the Cr phase. A) top: hypoeutectic alloy exhibiting 14-15 MPam^{1/2} fracture toughness at room-temperature (primary Cr regions marked by arrow B) bottom: eutectic alloy exhibiting 18-20 MPam^{1/2} fracture toughness at room-temperature.

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