ASSESSMENT OF THE COMPOSITIONAL INFLUENCES ON THE TOUGHNESS OF TiCr₂-BASE LAVES PHASE ALLOYS

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ABSTRACT

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Systematic studies of alloys based on TiCr₂ have been performed in order to improve the toughness of Laves phase intermetallics. The extent to which alloy compositions and annealing treatments influence the toughness was quantified by Vickers indentation. The single-phase Laves behavior was first established by studying stoichiometric and nonstoichiometric TiCr₂. Next, alloying effects were investigated with ternary Laves phases based on TiCr₂. Different microstructures of two-phase alloys consisting of (Ti,Cr)-bcc+TiCr₂ were also examined. Various toughening theories based on vacancies, site-substitutions, crystal structure ($C14$, $C36$, or $C15$) stabilization, and the presence of a second phase were evaluated. The most effective factors improving the toughness of TiCr₂ were determined, and toughening mechanisms are suggested.

INTRODUCTION

While several studies have addressed the problem of brittleness in Laves phases, basic understanding of which factors affect the toughness and to what extent toughness can be improved, has not been well documented for this particular class of intermetallics. The first reports of deformation in a Laves phases were HfV₂-base compounds in a two-phase alloy that could be rolled at room temperature without cracking [1]. Livingston and Hall [2] proceeded to show by TEM that HfV₂ Laves phases displayed increased twinning with additions of Nb and Ti. They suggested that alloying to substitute on both sublattices of the intermetallic and/or that lowering the stacking fault energies could improve the toughness of Laves phases. Alloying elements [3] or vacancies [4] may affect the synchroshear deformation process, and thus potentially improve the mechanical properties. Much work has also been done on two-phase Laves systems [5,6] to evaluate their potential as structural materials.

This study attempted to understand and quantify changes in the fracture toughness due to different factors in a single Laves system. Several different alloys based on the TiCr₂ Laves phase were examined. The role of defects and stoichiometry are addressed in the first section concerning the single-phase Laves alloys. Alloying element site occupancy and crystal structure stabilization are then investigated in ternary TiCr₂-base Laves phases. Finally, two-phase systems of TiCr₂ in a Ti-rich and a Cr-rich bcc solid solution are studied. Comparisons are made in order to help direct future development of Laves phase alloys.

EXPERIMENTAL PROCEDURES

The alloys were arc-cast and subjected to various homogenization and annealing treatments. Anneals at and above 1200°C were performed in a vacuum furnace and oil-quenched. Nominal compositions and phases of the alloy samples can be found in Table I.

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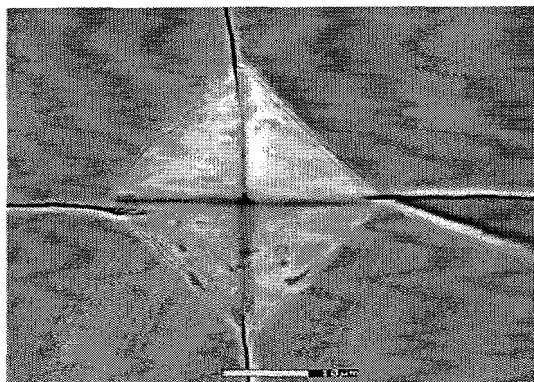document.

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Figure 1. SEM micrograph of radial cracks from the indentation impression corners of a $(Ti,Nb)Cr_2$ ternary Laves alloy.

Standard metallographic procedures were used, and compositions were determined by electron microprobe analysis (EMPA). Phases and lattice constants were determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Vickers indentations were made at room temperature and then measured with an environmental scanning electron microscope (ESEM). Figure 1 is an SEM micrograph depicting typical radial cracks originating from the indentation impression corners. Toughness values were computed from average crack lengths, following equations by Antis, et al. [7]. Room-temperature compression tests of the two-phase alloys were performed with a crosshead speed of 0.0025 cm/min.

Table I. Nominal Compositions (at%) and Phases of Alloy Samples.

Nominal Alloy Composition	Annealing Treatments	Phases
Single-Phase Binary Alloys		
Ti-62 Cr	1300°C, 1200°C, 1000°C	$C14+\beta$, $C36+\beta$, $C15+\beta$
Ti-64 Cr	1300°C, 1200°C, 1000°C	$C14$, $C36$, $C15$
Ti-66 Cr	1300°C, 1200°C, 1000°C	$C14$, $C36$, $C15/(C36)$
Ti-67 Cr	1300°C, 1200°C, 1000°C	$C14$, $C36$, $(C36)$
Ti-68 Cr	1300°C, 1200°C, 1000°C	$C14+\beta$, $C36+\beta$, $(C36)+\beta$
Ti-69 Cr	1300°C, 1200°C, 1000°C	$C14+\beta$, $C36+\beta$, $(C36)+\beta$
Ternary Alloys		
33 Ti-10 Fe-57 Cr	1300°C	$C14$
33 Ti-20 Fe-47 Cr	1300°C	$C14$
33 Ti-30 Fe-37 Cr	1300°C	$C14$
28 Ti-05 Nb-67 Cr	1300°C, 1200°C	$C15/C36$, $C15$
23 Ti-10 Nb-67 Cr	1300°C, 1200°C	$C15$, $C15$
18 Ti-15 Nb-67 Cr	1300°C, 1200°C	$C15$, $C15$
31.8 Ti-4.5 V-63.7 Cr	1300°, 1200°C, 1000°C	$C14+\beta$, $C15/C36+\beta$, $C15+\beta$
32 Ti-7 V-61 Cr	1300°, 1200°C, 1000°C	$C15$, $C15/C36+\beta$, $C15$
30.8 Ti-7.5 V-61.7 Cr	1300°, 1200°C	β, $C15/C36+\beta$
29 Ti-7 V-64 Cr	1300°, 1200°C	β, $C15/C36+\beta$
34 Ti-4 Mo-62 Cr	1300°, 1200°C, 1000°C	$C14+\beta$, $C15/C36+\beta$, $C15$
32 Ti-4 Mo-64 Cr	1300°, 1200°C, 1000°C	$C14+\beta$, $C15/C36$, $C15$
30 Ti-4 Mo-66 Cr	1300°, 1200°C, 1000°C	$C14+\beta$, $C15/C36+\beta$, $C15$
Two-Phase Binary Alloys		
Ti-30 Cr	800–1000°C	$C15+\beta$(Ti-rich)
Ti-40 Cr	800–1000°C	$C15+\beta$(Ti-rich)
Ti-85 Cr	1200°C, 1000°C	$C14/C36+\beta$(Cr-rich), $C15+\beta$
Ti-87.5 Cr	1200°C, 1000°C	$C14/C36+\beta$(Cr-rich), $C15+\beta$

RESULTS AND DISCUSSION

Single-phase TiCr$_2$

Nominal alloy compositions from Ti-62at% Cr to Ti-69at% Cr were selected to represent the single-phase TiCr$_2$ alloys, and were annealed to isolate particular crystal structures. A range of approximately 2.5 at% solubility was found, and three of the six alloys fell within the single-phase field to represent the stoichiometric and nonstoichiometric Laves phase (see Table I). Earlier work on these alloys suggested that the defect mechanism of the Ti-rich, nonstoichiometric TiCr$_2$ Laves phases may be a combination of vacancies and anti-site substitutions [8]. These alloys were then indented to study the effect of stoichiometry and crystal structure.

Figure 2 displays the compositional dependence of the fracture toughness of the C36 alloys at a load of 500 g. The C14 alloys did not show any apparent trend with respect to composition, and generally had slightly worse toughness values for the completely single-phase samples. The C15 crystal structure was not fully attained in all the alloy samples for comparisons, but the toughness of the two C15 samples available appeared to be higher (about 25%) than in the hexagonal phases of the same composition.

The consistent and repeatable trend of the C36 alloys revealed that a minimum in toughness occurs at the stoichiometric composition of TiCr$_2$. Going off-stoichiometry imparts some resistance to cracking and offers the prospect of gaining some toughness when designing new alloy compositions. The possible vacancies in the nonstoichiometric compositions may aid the complicated atomic motions involved in the synchroshear deformation mechanism. Hazzledine [4] has proposed that a Shockley dislocation core can be split over two closely-spaced planes, where the atoms must change positions for synchroshear to occur in Laves phases. The vacancies facilitate this process without much dilatation of the crystal. Although no direct evidence of vacancies assisting the movement of dislocations has been reported, results from this study support such a theory.

Larger improvements in the fracture toughness were found in the alloys containing small amounts of a second phase, the bcc-beta phase. This phase was uniformly dispersed throughout the alloys and proved to be effective in reducing the crack lengths compared to the single-phase Laves samples. Crack interaction by the second phase and debonding of the bcc/TiCr$_2$ interface expends some of the crack energy, which leads to the greater toughness values. These findings hint that a two-phase system with large volume fractions of a second, more ductile phase will greatly improve the toughness, as will be discussed later.
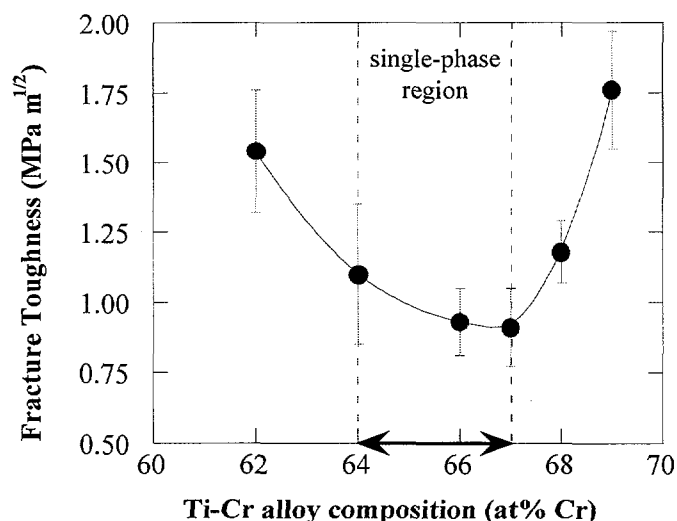

Figure 2. The compositional dependence of indentation fracture toughness for the C36 TiCr$_2$ alloys. The lowest toughness value occurs at the stoichiometric composition. Small amounts of a second phase improves the toughness.

A systematic study of the effect of alloying element site occupancy was made with the TiCr$_2$-base ternary alloys. These compositions were selected for the alloying element to substitute on specific sublattices of the AB$_2$ Laves phase. The Fe atoms substituted for the Cr atoms on the B-sublattice to form Ti(Fe,Cr)$_2$ Laves phases, while the Nb atoms substituted on the A-sublattice to form (Ti,Nb)Cr$_2$. V was found to reside primarily on the Cr-sublattice, and Mo could occupy both A and B sublattice sites (depending on the nominal alloy composition). Microprobe analysis and lattice constant measurements aided these determinations [9]. Alloying additions can also affect the electron concentration and thus, the stacking fault energies and crystal structures [10]. The different alloying elements did stabilize certain crystal structures, as listed in Table I.

The indentation results were analyzed as a function of alloying element, concentration of the alloying element, alloying element sublattice site occupancy, crystal structure, and microstructure. Fracture toughness values of the single-phase ternary alloys are plotted in Figure 3. Overall, the alloyed TiCr$_2$ samples do not show dramatic improvements in toughness, but some interesting trends do appear. The C14 Ti(Fe,Cr)$_2$ alloys actually demonstrated worse cracking (not all data points plotted), while the C15 (Ti,Nb)Cr$_2$ alloys had similar values as TiCr$_2$, which then decreased with Nb-content. The Mo alloys had slightly higher toughness values, and the V alloys showed roughly 25% improvements over the binary TiCr$_2$ Laves phase. These improvements in toughness occurred with relatively small concentrations of the alloying element, and may suggest that greater solubility may produce greater effects. Other Laves systems and processing techniques may extent the solubility limits for better toughening opportunities [11].

Alloying elements may extend the Laves phase field, or may induce the formation of a second phase. Some of the ternary alloys contained small amounts of the beta phase, and showed higher toughness values, as in the binary TiCr$_2$ alloys with small amounts of beta. In addition, the ternary alloys demonstrated that the alloying effects on crystal structure should be considered. For instance, the cubic C15 structure generally exhibited better toughness values
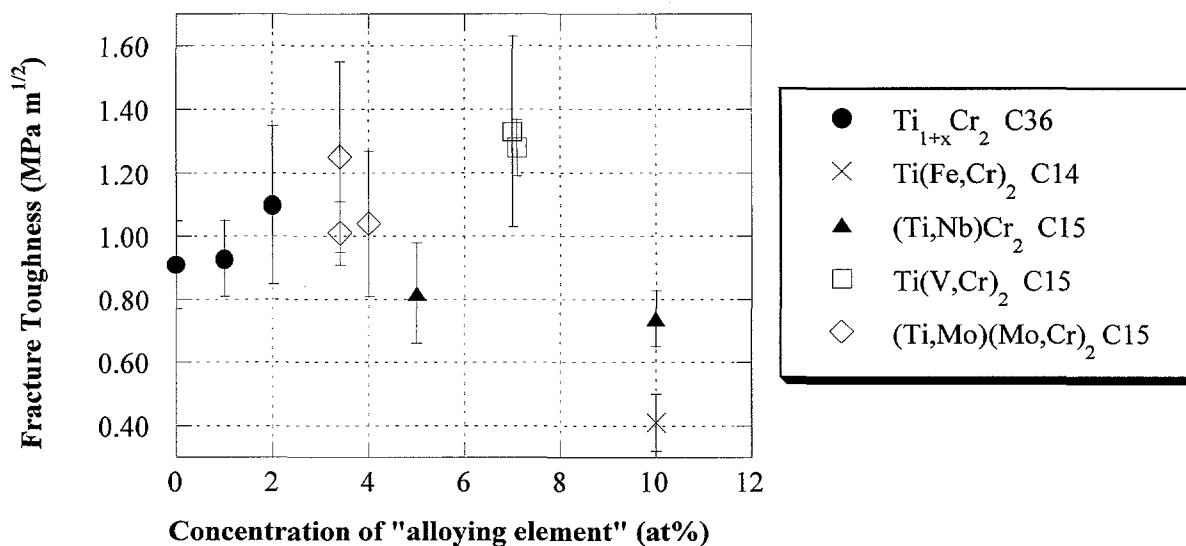

Figure 3. Fracture toughness of the (single-phase) TiCr$_2$-base ternary Laves phases.

than the hexagonal $C14$ and $C36$ structures. The cubic system offers more slip systems for deformation, and thus alloying elements could be selected to stabilize the $C15$ structure. Such a technique has been employed for other intermetallics [12]. These approaches to alloying offer several strategies to improve the toughness of Laves phases.

Two-phase Ti-Cr alloys with TiCr$_2$

The two-phase alloys discussed in this section have considerably larger volume fractions than those mentioned earlier, and in most cases, the bcc Ti-Cr solid solution is the matrix while the TiCr$_2$ Laves phase is the reinforcement. The annealed Ti-rich and Cr-rich two-phase Ti-Cr alloys have quite different microstructures, as can be seen in Figure 4. In the Ti-rich alloys, the TiCr$_2$ Laves phase precipitates from the beta solid solution as discrete particles, while the Cr-rich alloys, resemble eutectoid microstructures. The Laves phase in the Cr-rich alloys actually has a interconnected structure, as seen by TEM. These differences in microstructure have direct consequences on their respective mechanical properties.

The discrete TiCr$_2$ particles have been found to deform under room-temperature compression [13], and demonstrate that under the appropriate conditions, the Laves phase can experience some room-temperature plastic deformation before fracture. On the other hand, the Cr-rich alloys fractured almost immediately under compression, most likely due to the network of the Laves phase. However, the Cr-rich alloys showed high hardness values and improved fracture toughness values.

At the usual load of 500 g, no cracks were formed and an indentation load of 15 kg had to be used in order to initiate cracks for toughness measurements of the Cr-rich, two-phase alloys. The fracture toughness values were roughly five to seven times greater than that of the single-phase TiCr$_2$ alloys. Crack blunting, deflection, and bridging were identified by SEM. The dual phase microstructure disrupted the propagation of the cracks, and decohesion of the bcc/Laves phase interface occurred. The Ti-rich alloys did not experience cracking with the indentation load of 15 kg, although the larger sized TiCr$_2$ particles did show some cracks. Even better mechanical properties are expected with optimized microstructures, such as a uniform dispersion of fine Laves phases in a ductile matrix. Other studies [14,15] have shown the Laves phase to be a potent strengthener in a two-phase system.

SUMMARY AND CONCLUSIONS

Within the single-phase TiCr$_2$ Laves field, the stoichiometric composition displayed the lowest fracture toughness values. Constitutional defects found in the nonstoichiometric compositions may be assisting the synchroshear deformation mechanism. The Fe and Nb additions to TiCr$_2$ did not show improvements in the toughness, but the limited solubility of Mo and V resulted in slightly higher toughness values. The ternary alloys also suggested that the toughness may be improved if the alloying element stabilizes the $C15$ crystal structure. The largest improvements in toughness were seen with the two-phase alloys. Incorporation of a more ductile phase enables crack bridging, crack deflection, and interface debonding to occur. Development of the Laves phases may best be approached by a combination of selecting the appropriate Laves phase composition and optimizing the microstructure of two-phase systems.
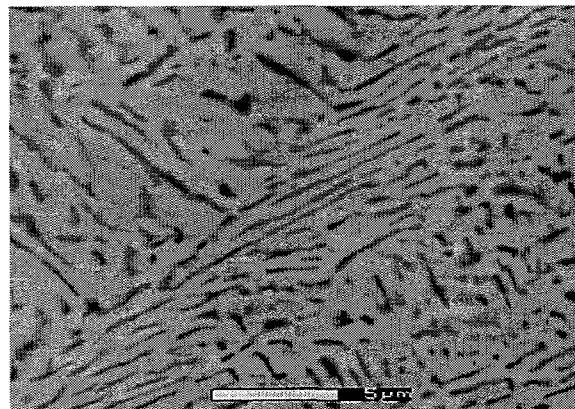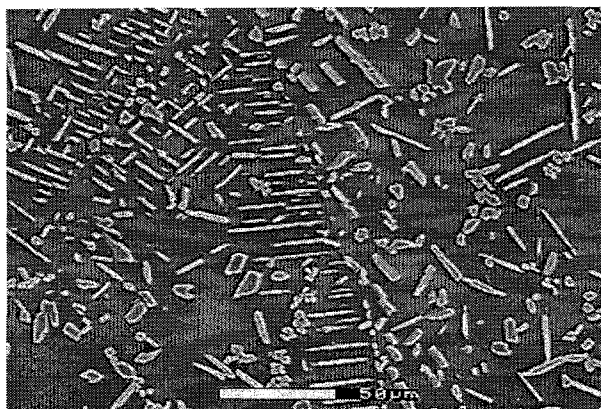
Figure 4. (a) SEM of the Ti-30 Cr two-phase alloy. The $TiCr_2$ Laves phase precipitates out as lath-shaped structures. (b) SEM of the Ti-80 Cr two-phase alloy, where the darker phase is the $TiCr_2$. Note the difference in microstructural size scale and morphology.

ACKNOWLEDGEMENTS

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