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Intermetallics 7 (1999) 1011–1016

Intermetallics

Phase stability and mechanical behavior of $NbCr_2$-based Laves phases

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Received 5 January 1999; received in revised form 28 January 1999; accepted 29 January 1999

Abstract

The phase relations in pseudo-binary $Nb(Cr,X)_2$ systems, where X = Fe or Co, were determined experimentally to verify the e/a correlation with phase stability. The substitution of Fe or Co for Cr in $NbCr_2$ increases the average electron concentration of the alloy, thus leading to a systematic change of the crystal structures from C15 to C14 and C14 to C15. The experimental critical e/a values corresponding to the C15/C14/C15 phase transitions are consistent with those from the phase diagram survey: the C15 structure is stabilized at $e/a < 5.77$; the C14 structure is stable at $5.85 < e/a < 7.50$; the C15 structure is stabilized again at $e/a > 7.56$. As the Fe or Co content increases in the $Nb(Cr,X)_2$ phase, the volume of a 24-atom unit cell decreases linearly, while the Vickers hardness increases over the whole C15 and C14 ranges. The fracture toughness values are low for all the alloys; nevertheless, the fracture toughness of the C15 structure is greater than that of the C14 structure for the two pseudo-binary systems.
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Keywords: A. Laves phases; B. Fracture toughness; B. Phase diagram; E. Phase stability, prediction

1. Introduction

Laves phases, with a composition of AB_2, generally crystallize into one of the three topologically close-packed structures: cubic C15–$MgCu_2$ structure, hexagonal C14–$MgZn_2$ structure, and dihexagonal C36–$MgNi_2$ structure. Although Laves phases are generally stabilized by the size-factor principles, the stability of each crystalline structure is also influenced by the electron concentration factor (e/a). The classic work by Laves and Witte [1,2] demonstrated that, for several pseudo-binary alloy systems involving $MgCu_2$ and $MgZn_2$, the three polytypes exist in the order of C15, C36, and C14 with increasing valence electron concentration.

Currently, HfV_2-, $HfCr_2$- and $NbCr_2$-based two-phase alloys are being developed for high-temperature structural uses [3–8], due to their good retention of mechanical properties at elevated temperatures. However, the low fracture toughness of Laves phases is still the key limiting factor for structural applications of these materials. One attractive way to improve the deformability of complex Laves phases is to control their crystalline structure in such a way that stress-assisted phase transformation and/or mechanical twinning can be introduced during plastic deformation [9,10]. It is, thus, important to understand the factors governing the phase stability in transition-metal Laves alloys.

So far, little systematic work has been conducted regarding the phase stability and mechanical behavior of Laves phases. In our previous paper [11], a number of binary X–Cr and Nb–X and ternary Nb–Cr–X phase diagrams (where X is a transition-metal element, such as Ti, Ta, Mn, Fe, Co, Ni, or Cu) were surveyed and the electron concentration factor (e/a) was identified as the key parameter in controlling the C14/C15 phase stability in $NbCr_2$-based transition-metal Laves alloys. The e/a ratio is defined as the average number of electrons per atom outside the closed shells of the component atoms and thus the e/a ratio of a transition element is the number of electrons (s + d electrons) outside its inert gas shell. A brief summary of the main results is provided below and the readers are referred to Ref. [11] for more details.

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0966-9795/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0966-9795(99)00010-2

The stability ranges of the Laves phases in both binary and ternary systems were summarized and the e/a effect on the phase stability (C14/C15) in $NbCr_2$-based transition-metal Laves phases were demonstrated in Fig. 1. In the $NbCr_2$-based Laves phases, the e/a ratio for the C15/C14 phase boundaries were quite precise; the critical e/a values corresponding to the C15/C14/C15 phase transitions from the phase diagram information, as indicated in Fig. 1, are as follows: at e/a values lower than 5.76, the C15 structure was stabilized for both binary and ternary Laves alloys; by increasing e/a to 5.88, the C14 structure was stabilized; over the e/a range of 5.88–7.53, the C14 structure was more stable than the C15 structure; the C15 structure was stabilized again over the C14 structure when the e/a ratio increased further to 7.65 for the Nb–Cr–Co system. In the ternary Nb–Cr–Fe system, such a C14→C15 transition was not observed, since the highest e/a ratio was 6.69 in this system (Fig. 1). No $NbNi_2$ (with $e/a = 8.34$) and $NbCu_2$ (with $e/a = 9$) Laves phases existed in binary Nb-Ni and Nb-Cu systems (the e/a values for imaginary "$NbNi_2$" and "$NbCu_2$" were shown in Fig. 1), consistent with the observation by Bardos et al. [12] that at $e/a > 8$, a disordered structure was stabilized over the Laves phase in transition-metal systems. Also in agreement with Bardos et al. [12], the maximum e/a ratio for the Laves phases in the Nb–Cr–Ni system was around 8. However, no C14→C15 transition in the Nb–Cr–Ni system was reported at e/a ratios > 7.65. It should be noted that these observations regarding the e/a correlation with phase stability in transition-metal $NbCr_2$-based Laves phase systems are based purely on the phase diagram information.

In this paper, the phase stability in pseudo-binary $Nb(Cr,Fe)_2$ and $Nb(Cr,Co)_2$ systems were studied experimentally to verify the previously observed e/a correlation with phase stability. Since Fe and Co have 7 and 8 outshell electrons, respectively, the addition of Fe or Co to substitute for Cr ($e/a = 6$) in $NbCr_2$ is effective in increasing the average electron concentration. By a systematic replacement of Cr with Fe or Co, it is possible to observe a whole spectrum (e.g. C15→C14→C15) of changes in the crystal structure of the Laves phase, which will be correlated with the critical e/a values for the different Laves polytypes. The fracture toughness values of these Laves phases with different phase structures were then determined to see whether there is any correlation between the phase stability and fracture toughness of the material, i.e. whether it is possible to improve the deformability of Laves phase alloys via controlling its stability. The experimental data reported here include the phase structure, unit cell volume, hardness, and fracture toughness of the pseudo-binary $Nb(Cr,X)_2$ Laves phase systems as a function of X (Fe or Co) content in the alloys.

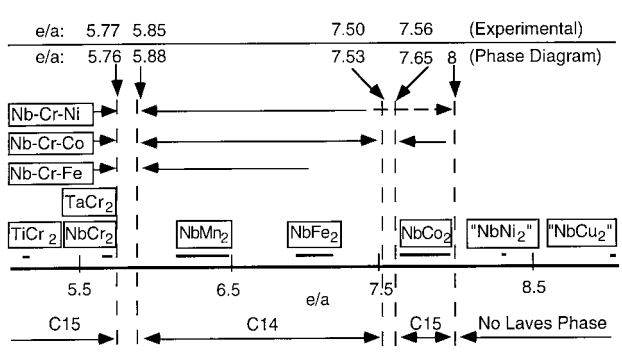

Fig. 1. Effect of average electron concentration (e/a) on phase stability in $NbCr_2$-based systems, with the critical e/a values for phase transitions both from phase diagram information [11] and experimental data.

2. Experimental procedures

A series of pseudo-binary $Nb(Cr,X)_2$ alloys, where X = Fe or Co, with the percentage of X varying from 0 to 66.7 at% were produced by replacing Cr with Fe or Co, while the content of Nb was kept at 33.3 at%. All the alloys of about 50 g were prepared by arc-melting techniques using high-purity starting materials. An excess amount (typically $\leqslant 0.1$ g) of Cr was added to compensate for the evaporation loss of Cr during melting. Arc-melting was carried out in a chamber which was evacuated with a mechanical pump and flushed with ultrahigh purity (UHP) argon gas four or five times, and finally backfilled with UHP argon gas. Several Zr pieces were melted prior to melting the alloy charge each time in order to getter the oxygen in the chamber. The arc-melting was done using a thoriated tungsten electrode on a water-cooled copper hearth. Each ingot was inverted and remelted at least seven times to ensure macroscopic compositional homogeneity. The alloys were homogenized in vacuum at 1300°C for 10 h, then furnace cooled. Finally, all the alloys were heat treated at 1000°C for 7 days, then water quenched to retain the equilibrium condition at 1000°C.

X-ray diffraction was made using a Scintag XD2000 diffractometer with Cu Kα ($\lambda = 0.15406$ nm) radiation for phase identifications and lattice parameter measurements. Powdered samples were used, and the lattice parameter was determined using 10–15 peaks. The microhardness was determined using a load of 500 g with a holding time of 15 s, and crack lengths were measured immediately after the indentation to eliminate the possibility of slow crack propagation following the removal of the indenter. The following equation was used to calculate the fracture toughness of the alloy [13,14]:

$$K_{IC} = A\left(\frac{E}{H}\right)^n \frac{P}{L^{3/2}} \tag{1}$$

where K_{IC} = fracture toughness (MPa$\sqrt{m}$), E = Young's modulus (GPa), which is assumed to be 218 GPa for all of the investigated alloys [15], H = Vickers hardness (GPa), P = load (N), and L = average length of the four radial cracks from the center of the indent to the crack tip. A and n are constants, which are taken as 0.016 and 0.5, respectively, for relatively brittle materials [14]. The fracture toughness values of the alloys with different phase structures were examined to determine the effect of phase stability on the fracture toughness behavior of the Laves phases.

3. Results and discussions

3.1. Experimental verification of the e/a correlation with phase stability

For the pseudo-binary $Nb(Cr,Fe)_2$ system, X-ray diffraction results showed that the Laves phase after the addition of up to 5 at% Fe maintained its original C15 structure, while the C14 structure was stabilized for alloys with the Fe content higher than 9 at%. The corresponding critical electron concentrations were calculated to be 5.77 and 5.85, respectively. For the alloys with Fe content between 5 and 9 at%, a two-phase mixture of C14 and C15 was observed with no intermediate structures such as C36 detected. Fig. 2 shows the diffraction patterns for $Nb(Cr,Fe)_2$ Laves phase alloys with 2 at% Fe (C15 structure), 7 at% Fe (two-phase C15/C14 structures), and 9 at% Fe (C14 structure).

For the pseudo-binary $Nb(Cr,Co)_2$ system, X-ray diffraction results showed that the Laves phase after the addition of up to 3.5 at% Co retained its C15 structure, while the C14 structure was stabilized for alloys with the Co content higher than 6 at%. The alloys retained the C14 structure, until the Co content was higher than 61.2 at%. At the Co content higher than 63.2 at%, the C15 structure was stabilized again. The alloys between C15 and C14 again exhibited a mixture of C14 and C15 phases, with no intermediate structures observed. The critical electron concentrations corresponding to the C15/C14/C15 phase transitions were calculated to be 5.77 for C15 on the Cr-rich side, 5.85 and 7.5 for the C14 structure, and 7.56 for the C15 on the Co-rich side. It should be noted that the critical e/a values for the C15/C14 transition are exactly the same at the low X content side for the two pseudo-binary systems of $Nb(Cr,Fe)_2$ and $Nb(Cr,Co)_2$.

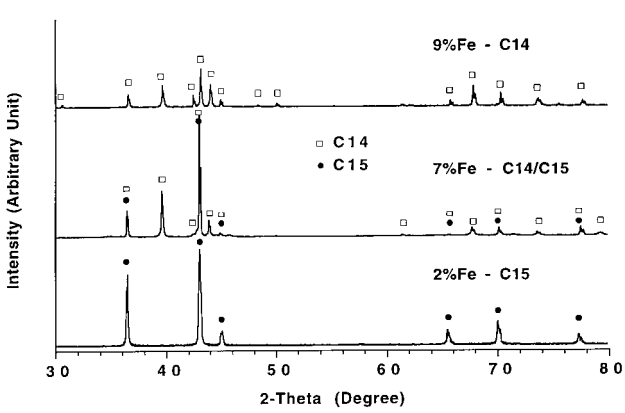

Fig. 2. X-ray diffraction patterns of $Nb(Cr,Fe)_2$ alloys with 2, 7 and 9 at% Fe, which have C15, C14/C15 and C14 structures, respectively.

It is clear that the electron concentration rule is obeyed in these two pseudo-binary systems. The phase transitions between C15 and C14 were determined by the average electron concentration in these alloys. The experimentally determined e/a values, corresponding to the phase transitions, are included in Fig. 1 for easy comparison with the previously obtained values from phase diagram information [11]. The experimental critical e/a ratios for the C15/C14/C15 transitions are very close to those from phase diagrams. These results were the first experimental determination of the critical e/a values for the different Laves phases in the pseudo-binary $Nb(Cr,X)_2$ systems.

Laves phases are generally considered size compounds, i.e. the size difference between A and B atoms is predominant in stabilizing the Laves phase. For example, it has been found that Laves phases can only be stabilized at certain atomic size ratios (R_A/R_B), where R_A and R_B are the metallic atom radii of A and B atoms, respectively [16,17]. The ideal R_A/R_B ratio for Laves phase formation is 1.225 and a R_A/R_B range of 1.05–1.67 is typically observed; outside this range, no Laves phase will be formed [17]. However, when the atomic size ratio is favorable for Laves phase formation, the specific structure that the Laves phase will have (C15, C14, or C36) is determined by the average electron concentration. In Laves and Witte's studies [1,2], ternary Mg-based systems were selected, and the valence electron concentration was found to control the occurrence of various Laves structures, with C15 stabilized at low e/a values, C14 stabilized at high e/a values, and C36 in between. The correlation is reasonably good; however, both non-transition and transition metals were involved in forming some Laves phases in their study, making it difficult to analyze the valence electron concentrations in the alloys. This difficulty results from the fact that for a transition element, the valence electron number is not a constant value, but varies in different systems. This behavior may contribute to the scattering in the critical e/a values corresponding to the phase transitions for the different ternary Mg-based systems. In contrast, this study indicates the phase boundaries are very precise and the critical e/a values for the C15/C14 transition are exactly the same for the pseudo-binary $Nb(Cr,Fe)_2$ and $Nb(Cr,Co)_2$ systems. This may be associated with the fact that all the components in the two pseudo-binary systems are transition metals.

The region between C15 and C14 should be a two-phase mixture of C14 and C15 from thermodynamic considerations. However, in reality, it is possible to obtain different intermediate structures, due to the metastable transformation of the one to the other and/or the low chemical free energies of some intermediate structures. In the pseudo-binary $Nb(Cr,X)_2$ systems studied here, no intermediate structures were observed between the C14 and C15 single-phase regions and only a two-phase mixture of C14 and C15 was detected. This observation is in agreement with the ternary Nb–Cr–Fe and Nb–Cr–Co phase diagrams [18]. However, this is in contrast with the situation in the pseudo-binary Mg-based system [1,2,19,20], where intermediate structures with different percentages of hexagonality, such as C36, were identified. Furthermore, a C36 phase was reported in a recent study of the Nb–Cr–Fe system [10]. The heats of formation of the C14, C36, and C15 polytypes of $NbCr_2$ Laves phase have been studied recently by first-principles calculations [21]. These structures are very close in bonding energies. Thus, it is possible that the stability of the C36 and other intermediate structures can be affected by a small change in annealing temperature, alloy composition, or impurity content in the Laves phases.

3.2. Unit cell volume, hardness, and fracture toughness

The crystal lattice parameters of the C15 and C14 Laves phases were measured for the pseudo-binary $Nb(Cr,X)_2$ alloys with various Fe or Co contents. The volumes for the unit cells of C14 and C15 structures were calculated using the experimental lattice parameters and are plotted in Fig. 3 as a function of Fe or Co content. The volumes of the unit cells of C14 and C15 structures were normalized as the volume of a cell with 24 atoms, for easy comparison between C15 and C14 structures. Since C15 has 24 atoms per unit cell, and C14 has 12 atoms per unit cell, the normalized unit-cell volume is twice its original volume for C14, while that of the C15 structure is equal to its original volume.

As the Fe or Co content increases, the volume per 24-atom cell decreases linearly, as shown in Fig. 3. This is not surprising, considering that the atomic sizes of Fe and Co are smaller than that of Cr. Since the atomic size of Fe is larger than that of Co, the Fe addition is expected to decrease the volume of the 24-atom cell less than the Co addition at the same alloying levels. The slopes of the two lines can be calculated to be −0.323 and −0.448 for $Nb(Cr,Fe)_2$ and $Nb(Cr,Co)_2$ Laves phases, respectively. This linear relation of 24-atom unit cell volume as a function of the ternary X addition indicates that the ternary element, Fe or Co, is exclusively substituting for the Cr atoms in the Laves phase, and Vegard's law is obeyed in these two pseudo-binary systems. The exclusive replacement of Cr by Fe or Co has also been confirmed by our density measurements, which clearly show that no vacancies are created in the Laves phases, and the measured density is in agreement with the calculated one by assuming that Fe or Co is replacing Cr in the $Nb(Cr,X)_2$ phase [22].

Note that the change in the crystal structure does not affect the slope of the line, indicating that the substitution of Cr by Fe or Co does not influence the bonding characteristics in the Laves phases. Furthermore, the volume difference between the C14 and C15 structures of the same composition should be small, since there is no abrupt change in volume during the C14/C15 phase transition.

The Vickers hardness values of the pseudo-binary $Nb(Cr,X)_2$ alloys with various Fe or Co contents are plotted in Figs. 4 and 5. The addition of Fe or Co to substitute for Cr increases the hardness of the Laves phase linearly. This can be attributed to the solid solution hardening effects of Fe or Co in $NbCr_2$. The slopes of the two lines in Figs. 4 and 5 were calculated to be 1.3 and 2.1 for $Nb(Cr,Fe)_2$ and $Nb(Cr,Co)_2$ systems, respectively. Thus, Co is a more potent hardener than

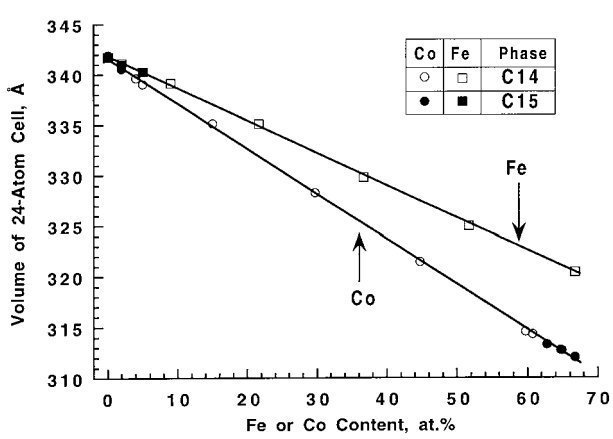

Fig. 3. Dependence of the volume of 24-atom cell of $Nb(Cr,X)_2$ Laves phase on the Fe or Co content.

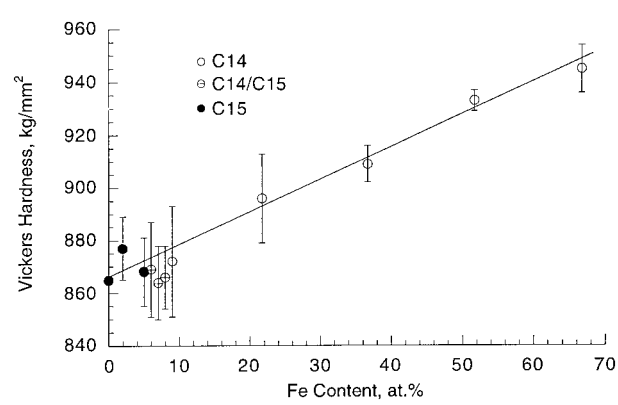

Fig. 4. The effect of Fe content on the Vickers hardness of $Nb(Cr,Fe)_2$ alloys.

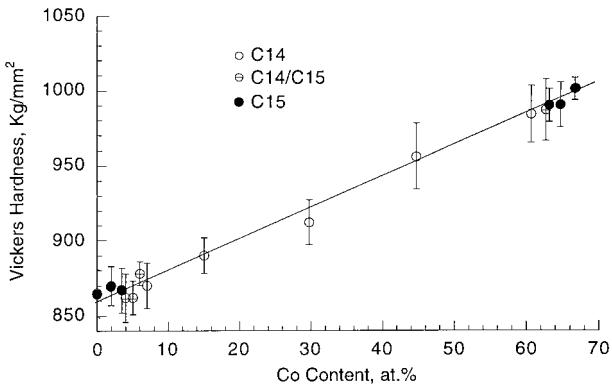

Fig. 5. The effect of Co content on the Vickers hardness of $Nb(Cr,Co)_2$ alloys.

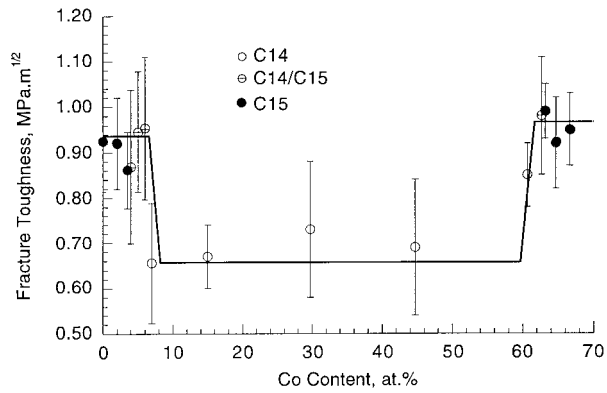

Fig. 7. Fracture toughness values of the Laves phases as a function of the Co content.

Fe in $NbCr_2$ alloys, which is consistent with the fact that the atomic size difference between Cr and Co is larger than that between Cr and Fe.

The fracture toughness values calculated using Eq. (1) as a function of Fe and Co contents are shown in Figs. 6 and 7, respectively. Basically, the fracture toughness of the monolithic Laves phase is very low, around 1 $MPa\sqrt{m}$, which is a consequence of the topologically close packing manner of the structure and the subsequent difficulty in activating dislocation sources in the material. However, the fracture toughness of the C15 structure is consistently higher than that of C14 structure for the ternary systems (Figs. 6 and 7), regardless of the X addition. This can be explained by the fact that the C15 structure is cubic, and thus, is more deformable than the hexagonal C14 structure. The toughness value near the phase boundary could be higher, in view of the fact that the associated structure is metastable with a lower stacking fault energy, thus making it easy for stress-assisted phase transformation and/or mechanical twinning to be triggered during deformation. However, such a trend was not observed in the present study. None of the alloys within the two-phase regions or near the phase boundaries exhibits any sign of increase in toughness. The toughness of the two-phase (C14 + C15) alloys is similar to that of the C15 phase. The toughness enhancement through stress-assisted phase transformation or mechanical twinning is not significant enough to be noted in the indentation test.

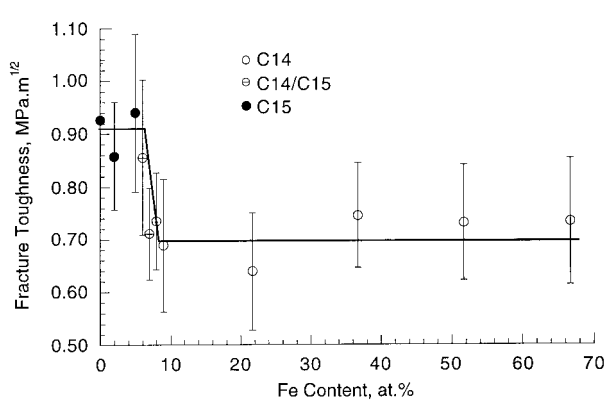

Fig. 6. Fracture toughness values of the Laves phases as a function of the Fe content.

Since enhancing the toughness through controlling the phase stability seems to be difficult in the present study, future research will concentrate on the investigation of point defects in the Laves phases, based on the consideration that certain Laves phases may have constitutional and/or thermal vacancies [23,24]. Toughening of the Laves phases may be facilitated through vacancy-assisted synchroshear deformation [25].

4. Conclusions

The e/a correlation with the phase stability was verified in the pseudo-binary $Nb(Cr,X)_2$ systems. The substitution of Fe or Co for Cr in $NbCr_2$ increased the average electron concentration of the alloy, thus leading to the change of the crystal structures from C15 to C14 and C14 to C15. The experimentally determined critical e/a values corresponding to the C15/C14/C15 phase transition were found to be consistent with those from the phase diagram information. At $e/a < 5.77$, the C15 structure was stabilized; at $5.85 < e/a < 7.50$, the C14 structure was stable; with e/a higher than 7.56, the C15 structure was stabilized again. No intermediate structure was detected for the $Nb(Cr,X)_2$ alloys.

As the Fe or Co content increased, the volume of the 24-atom cell decreased linearly for both C15 and C14 structures, while the Vickers hardness increased over the whole C15 and C14 ranges. The fracture toughness values were low for all the alloys; nevertheless, the fracture toughness of the C15 structure was greater than that of the C14 structure for the two pseudo-binary Laves phase systems.

Acknowledgements

This research was jointly sponsored by the Fossil Energy Advanced Research and Technology Development (AR & TD) Materials Program under subcontract 11X-SP173V to the University of Tennessee, and the Division of Materials Sciences, US Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. The authors are very grateful to Joe Wright, Elmer Lee, and Cecil Carmichael at the Oak Ridge National Laboratory (ORNL) for their technical assistance. Thanks are also due to C.G. McKamey and M.P. Brady for reviewing this paper.

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