Microstructure Characterization and Fracture Toughness of Laves Phase-Based Cr–Nb–Ti Alloys

Yun-Long Xue · Shuang-Ming Li · Hong Zhong · Lai-Ping Li · Heng-Zhi Fu

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Abstract Three Laves phase-based alloys with nominal compositions of $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$, in at%) have been prepared through vacuum non-consumable arc melting. The results show that the microstructures of $\text{Cr}_2\text{Nb}-(20, 30)$ Ti alloys are composed of the primary Laves phase $\text{C15}-\text{Cr}_2(\text{Nb}, \text{Ti})$ and bcc solid solution phase, while the microstructure of $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy is developed with the eutectic phases $\text{C15}-\text{Cr}_2(\text{Nb}, \text{Ti})/\text{bcc}$ solid solution. The measured fracture toughness of ternary Laves phase $\text{C15}-\text{Cr}_2(\text{Nb}, \text{Ti})$ is about $3.0 \text{ MPa m}^{1/2}$, much larger than $1.4 \text{ MPa m}^{1/2}$ for binary Laves phase Cr_2Nb . Meanwhile, the fracture toughness of $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys increases with increasing Ti content and reaches $10.6 \text{ MPa m}^{1/2}$ in $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy. The eutectic microstructure and addition of Ti in Cr_2Nb are found to be effective in toughening Laves phase-based alloys.

KEY WORDS: Laves phase-based alloys; Microstructure characterization; Fracture toughness; Crack propagation; Fracture

1 Introduction

Laves phase Cr_2Nb , a high-temperature material, has attracted more attention due to its high melting point ($1,770^\circ\text{C}$), relatively low density (7.7 g/cm^3), excellent high-temperature strength, reasonable oxidation resistance, and appreciable creep resistance [1–5]. However, low fracture toughness ($\sim 1.4 \text{ MPa m}^{1/2}$) limits its engineering applications [6, 7].

To overcome the brittleness of Laves phase Cr_2Nb , one promising approach is the introduction of alloying

elements. It was indicated that the additions of V and Mo in Cr_2Nb can enhance the dislocation movement without introducing significant hardening [8]. The effect of W on the fracture toughness of Cr_2Nb depends on its sites preference [9]. When W occupies Nb sites, the fracture toughness of Cr_2Nb can be improved, and when it occupies Cr sites, the situation is just opposite. Furthermore, the elements Si and Al are both beneficial to the fracture toughness of Cr_2Nb , and the element Ti is suggested to be more effective in toughening Cr_2Nb [10, 11].

Another attractive way to overcome the brittleness of Laves phase Cr_2Nb is the incorporation of toughness phase [12–15]. The dual-phase alloys achieved by eutectic reaction have exhibited remarkable improvement in toughness ($\sim 7 \text{ MPa m}^{1/2}$) [16], and they are still brittle for structural engineering materials ($\geq 15 \text{ MPa m}^{1/2}$) [17]. The “ductile-phase toughening” is not functioning as envisioned. When introducing the third-element Ti into Laves phase Cr_2Nb and simultaneously forming a composite, the fracture toughness of composite can attain $20.1 \text{ MPa m}^{1/2}$ [18]. However, the volume fraction of Laves phase in this

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Y.-L. Xue · S.-M. Li (✉) · H. Zhong · H.-Z. Fu
State Key Laboratory of Solidification Processing, Northwestern
Polytechnical University, Xi'an 710072, China
e-mail: lsm@nwpu.edu.cn

L.-P. Li
Northwest Institute for Non-Ferrous Metal Research,
Xi'an 710016, China

composite is low ($\sim 27\%$), inevitably decreasing the high-temperature properties of the alloy (e.g., high-temperature strength and creep resistance).

In an attempt to balance the volume fraction of Laves phase and mechanical properties of composite $\text{Cr}_2\text{Nb-Ti}$, three alloys with nominal compositions of $\text{Cr}_2\text{Nb-}x\text{Ti}$ ($x = 20, 30, 40$) (all compositions in this paper are given in at% unless otherwise stated) have been prepared. Based on the phase diagram of Cr-Nb-Ti [19], the volume fractions of Laves phase in three alloys have been calculated to be 68%, 53%, and 34%, respectively. The effect of Ti on solidified microstructures and fracture toughness of these three alloys have been investigated. The fracture mechanism and crack propagation are discussed in detail to illustrate the deformation behavior of the alloys.

2 Experimental

$\text{Cr}_2\text{Nb-}x\text{Ti}$ ($x = 20, 30, 40$) alloys were produced using high-purity metals (99.9 wt% Cr, 99.99 wt% Nb, 99.95 wt% Ti) through vacuum non-consumable arc melting. Every ingot was remelted for five times to ensure chemical homogeneity. The samples were cut from the arc-melted ingots by electro-discharge machining (EDM). Subsequently, these samples were ground, polished, and etched with a solution of 50 mL H_2O , 25 mL HF, 25 mL H_2SO_4 , and 4 mL HNO_3 for approximately 4 s.

Microstructural analysis was performed on a scanning electron microscope (SEM, JSM-6390A) equipped with an energy-dispersive X-ray spectroscopy system (EDS, INCAPentaEFTx3) and a transmission electron microscope (TEM, Tecnai G^2 F30). Single-edge notched bending samples (SENBs) with dimensions of 2.5 mm $\times$ 5 mm $\times$ 30 mm were used for fracture toughness measurement at room temperature. The single notch with about 2.5 mm length was introduced by EDM. Three-point bending tests were taken on Instron-3382 universal test machine with a crosshead speed of 0.1 mm/min.

The fracture toughness was also evaluated by indentation method. The tests were conducted with a load of 300 N and duration time of 15 s for the alloys and a load of 5 N and duration time of 10 s for single Laves phase. The fracture toughness can be calculated as [20]:

$$K_{\text{IC}} = A(E/H_V)^{1/2} (P/C^{3/2}), \quad (1)$$

where A is a constant 0.016, E is the Yong's modulus, H_V is the Vickers hardness, P is the indentation load, and C is the average radial cracks. The Vickers hardness can be written as [20]:

$$H_V = 1.854 \frac{P}{d^2}, \quad (2)$$

where d is the mean diagonal length of the indentation.

3 Results and Discussion

3.1 Microstructure Characterization

Figure 1 illustrates the XRD patterns of samples taken from the bottom and top of arc-melted ingots. For convenience, the samples taken from the bottom and top of the ingots are labeled as Bx and Tx ($x = 20, 30, 40$), respectively. It can be seen that all samples are composed of Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ and bcc solid solution phase. The microstructures of $\text{Cr}_2\text{Nb-20Ti}$ alloy are shown in Fig. 2a, b. EDS analysis results in Table 1 indicate that the lath-like phase is Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$, and the white one is Nb-rich bcc solid solution phase. The $\text{C15-Cr}_2(\text{Nb,Ti})$ laths in the sample B20 show a uniform distribution, and the $\text{C15-Cr}_2(\text{Nb,Ti})$ laths in the sample T20 become coarsened due to the slow cooling rate on the top of ingot.

The Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ in the sample B30 (Fig. 2c) exhibits a polygon morphology, and it is surrounded by Ti-rich bcc solid solution phase. In the sample T30 (Fig. 2d), the blocky Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ is surrounded by both Ti-rich bcc and Nb-rich bcc phases. This indicates that the solute concentration in between the $\text{C15-Cr}_2(\text{Nb,Ti})$ may vary with the position of the ingot, forming bcc phases with different compositions, especially at the slow cooling rate on the top of ingot.

The eutectic microstructure of $\text{Cr}_2\text{Nb-40Ti}$ alloy is observed with Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ and bcc solid solution phase, showing smaller lamellar space in the sample B40 (Fig. 2e) and larger lamellar space in the

Fig. 1 XRD patterns of Laves phase-based $\text{Cr}_2\text{Nb-}x\text{Ti}$ ($x = 20, 30, 40$) alloys

Fig. 2 SEM micrographs of Laves phase-based $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys: **a** sample B20; **b** sample T20; **c** sample B30; **d** sample T30; **e** sample B40; **f** sample T40

Table 1 EDS results and volume fractions of Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ in $\text{Cr}_2\text{Nb-Ti}$ ($x = 20, 30, 40$) alloys

Sample	Composition (at%)			Phase	Fraction of $\text{Cr}_2(\text{Nb,Ti})$ (vol%)	
	Ti	Cr	Nb		Theo.	Exp.
B20	10.7–11.4	54.3–56.8	31.5–33.4	$\text{C15-Cr}_2(\text{Nb,Ti})$	68	89
	32.2–33.7	22.7–23.6	42.9–44.4	Nb-rich bcc		
T20	8.9–9.4	55.3–58.4	31.8–33.2	$\text{C15-Cr}_2(\text{Nb,Ti})$	53	81
	32.1–33.9	19.4–20.5	44.8–46.5	Nb-rich bcc		
B30	16.5–17.6	54.3–56.8	24.8–25.9	$\text{C15-Cr}_2(\text{Nb,Ti})$	53	69
	39.4–41.9	28.4–29.5	28.6–29.7	Ti-rich bcc		
T30	15.7–16.4	55.8–57.6	25.5–26.7	$\text{C15-Cr}_2(\text{Nb,Ti})$	34	64
	27.1–28.7	24.3–25.7	42.3–45.9	Nb-rich bcc		
	70.4–76.3	15.4–16.7	8.9–9.7	Ti-rich bcc		
B40	21.2–22.9	53.9–56.8	19.7–20.8	$\text{C15-Cr}_2(\text{Nb,Ti})$	34	56
	54.8–58.3	9.8–11.2	29.7–31.7	Ti-rich bcc		
T40	19.2–21.8	54.3–57.9	18.9–20.5	$\text{C15-Cr}_2(\text{Nb,Ti})$	34	54
	56.6–58.8	10.4–10.9	30.2–32.4	Ti-rich bcc		

sample T40 (Fig. 2f). The volume fractions of Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ in eutectic were measured and are shown in Table 1. It indicates that the arc-melted Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ has much solution element Ti due to the non-equilibrium effect in rapid solidification process. Note that Ti preferentially occupies Nb sites, and then, the excess Nb occupies Cr sites in Cr_2Nb , leading to substantial anti-site defects, which can enlarge the volume fraction of Laves phase [21–23]. As a result, the volume fractions of

Laves phase $\text{C15-Cr}_2(\text{Nb,Ti})$ in arc-melted ingots are larger than the values calculated by the phase diagram [19]. Meanwhile, bigger cooling rate in the samples Bx ($x = 20, 30, 40$) brings about larger amounts of $\text{C15-Cr}_2(\text{Nb,Ti})$ phase.

In addition, the eutectic of $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy is very small and exhibits a lamellar morphology, as shown in Fig. 3a. TEM observation was employed on the selected areas A and B. The diffraction patterns at these areas are

Fig. 3 TEM results of the eutectic in arc-melted Cr_2Nb –40Ti alloy: **a** bright-field image of the eutectic; **b** SAD pattern of the bcc solid solution at position A; **c** SAD pattern of the C15– $\text{Cr}_2(\text{Nb,Ti})$ at position B

Fig. 4 Fracture toughness of Laves phase-based Cr_2Nb – $x\text{Ti}$ ($x = 20, 30, 40$) alloys inserted with the typical indentation produced on single Laves phase $\text{Cr}_2(\text{Nb,Ti})$

shown in Fig. 3b, c. The results indicate that the areas A and B are the bcc solid solution phase and Laves phase C15– $\text{Cr}_2(\text{Nb,Ti})$, respectively, agreeing well with the result of Fig. 1.

3.2 Fracture Toughness, Crack Propagation, and Fracture Surface

By employing the indentation method, the fracture toughness of single Laves phase C15– $\text{Cr}_2(\text{Nb,Ti})$ is determined, and the typical indentation is presented in the lower part of Fig. 4. The measured fracture toughness of C15– $\text{Cr}_2(\text{Nb,Ti})$ is about $3.0 \text{ MPa m}^{1/2}$, larger than $1.4 \text{ MPa m}^{1/2}$ for binary Laves phase Cr_2Nb [11, 22, 24]. It indicates that the addition of Ti is effective in toughening binary Laves phase Cr_2Nb .

For Cr_2Nb – $x\text{Ti}$ ($x = 20, 30, 40$) alloys, the values of fracture toughness measured by three-point bending test and indentation method are in the same level and are shown in Fig. 4. It is found that the fracture toughness of the alloys increases with increasing Ti content and reaches $10.6 \text{ MPa m}^{1/2}$ in Cr_2Nb –40Ti alloy. Also, the fracture toughness of the alloys varies with the sample position. For Cr_2Nb – $x\text{Ti}$ ($x = 20, 30, 40$) alloys, the values of fracture toughness of samples T are about 81.91, 46.42, and 18.04% larger than those of samples B, respectively. The change in fracture toughness of the alloys can be attributed to the different volume fractions of Laves phase C15– $\text{Cr}_2(\text{Nb,Ti})$.

As shown in Table 1, with the increase in Ti content, the volume fraction of Laves phase C15– $\text{Cr}_2(\text{Nb,Ti})$ decreases, resulting in the increased fracture toughness of Cr_2Nb – $x\text{Ti}$ ($x = 20, 30, 40$) alloys. For the same reason, the volume fractions of Laves phase in samples T are lower than those in samples B, leading to better fracture toughness measured on the top of ingots.

The microstructure morphologies also play a key role in determining the fracture toughness of the alloys. As demonstrated in Fig. 5, the crack propagates continuously in the sample B20 (Fig. 5a), while the occurrence of crack deflection and bridging is obvious in the sample T20 (Fig. 5b), indicating better fracture resistance of the top ingot in Cr_2Nb –20Ti alloy. This observation matches well with the result of Fig. 4.

For Cr_2Nb –30Ti alloy, as shown in Fig. 5c, d, the crack deflection and bridging take place both in samples B30 and T30. It is noted that there exists the branch cracks propagating in a zigzag route (Fig. 5d), implying better fracture toughness of the sample T30.

Similarly, the crack of Cr_2Nb –40Ti alloy propagates straightly in the trough-thickness direction, and there is no any trace of crack deflection and bridging in the sample B40 (Fig. 5e). However, the crack deflection and bridging

Fig. 5 Crack propagations in Laves phase-based $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys: **a** sample B20; **b** sample T20; **c** sample B30; **d** sample T30; **e** sample B40; **f** sample T40

Fig. 6 Low-magnification fracture surfaces of Laves phase-based $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys: **a** sample B20; **b** sample T20; **c** sample B30; **d** sample T30; **e** sample B40; **f** sample T40

observed in the sample T40 (Fig. 5f) occur. As the crack deflection and bridging are effective in toughening brittle materials [25–27], the fracture toughness of the sample T40 would be better.

Figure 6 shows the low-magnification fracture surfaces of three arc-melted alloys, demonstrating that all samples

fracture in a brittle manner with some difference in detail. As shown in Fig. 6a, b, there are some tiny cracks in the sample T20 comparing with the sample B20. For $\text{Cr}_2\text{Nb}-30\text{Ti}$ alloy, the fracture surface of sample B30 (Fig. 6c) is much smoother than that of sample T30 (Fig. 6d). The fracture surface of the sample T40 in $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy

Fig. 7 High-magnification fracture surfaces of Laves phase-based $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys: **a** sample T20; **b** sample T30; **c** sample T40

exhibits some visible steps in contrast to that of the sample B40, as indicated in Fig. 6e, f.

According to the previously reported results [15, 16, 28–30], the brittle fracture prevails in Laves phase alloys, agreeing well with the observation of this study. The difference between the previous results and this work lies at the detailed information seen from the high-magnification fracture surfaces of Fig. 7. It indicates that the cracks arise from the toughness phases undergoing some deformation (Fig. 7a, b). The toughness phase, bcc solid solution, is showed to be effective in toughening Laves phase-based alloys, as the crack deflection and bridging are observed frequently, especially in the samples from the top part of ingots. Moreover, the improved fracture toughness is also related to the intrinsic property of Laves phase, since the ternary Laves phase $\text{Cr}_2(\text{Nb,Ti})$ is much more ductile than binary Laves phase Cr_2Nb . As a result, the high-magnification fracture surface of Fig. 7c appears some small planes and visible ridges in $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy, meaning these two factors are all beneficial to the improvement of fracture toughness of the alloy.

It is noted that, for arc-melted $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy, although the volume fraction of Laves phase exceeds 50%, the alloy fracture toughness reaches $10.6 \text{ MPa m}^{1/2}$. This value is much larger than that of single Laves phase Cr_2Nb and gradually close to the requirement of engineering applications.

4 Conclusions

1. The arc-melted microstructures of $\text{Cr}_2\text{Nb}-(20, 30) \text{ Ti}$ alloys are composed of the primary Laves phase $\text{C15}-\text{Cr}_2(\text{Nb,Ti})$ and bcc solid solution phase. The microstructure of $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy is developed with the eutectic phases $\text{C15}-\text{Cr}_2(\text{Nb,Ti})/\text{bcc}$ solid solution.
2. The fracture toughness of $\text{Cr}_2\text{Nb}-x\text{Ti}$ ($x = 20, 30, 40$) alloys increases with increasing Ti content and reaches

$10.6 \text{ MPa m}^{1/2}$ in $\text{Cr}_2\text{Nb}-40\text{Ti}$ alloy. The eutectic microstructure are found to be effective in toughening Laves phase-based alloys.

3. The measured fracture toughness of ternary Laves phase $\text{C15}-\text{Cr}_2(\text{Nb,Ti})$ is about $3.0 \text{ MPa m}^{1/2}$, much larger than $1.4 \text{ MPa m}^{1/2}$ for binary Laves phase Cr_2Nb . The addition of Ti is effective in toughening binary Laves phase Cr_2Nb , and thus toughening Laves phase-based alloys.

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