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Microstructure evolution of as-cast Nb-Ti-C alloys

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Abstract: Nb-Ti-C alloys with different Ti contents (4%−16%, mole fraction) were fabricated by vacuum non-consumable arc-melting method. The results indicate that the alloys contain niobium solid solution (Nb_{ss}), carbides (Nb_2C, (Nb, Ti)C) and eutectic of Nb_{ss}/MC. Carbides in the Nb-Ti-C alloys change from Nb_2C to (Nb, Ti)C with the increase of titanium content. Microstructures in the as-cast state include primary plate-like Nb_2C, eutectic of Nb_{ss}/Nb_2C, Nb_{ss} and secondary needle-like Nb_2C in Nb-5Ti-4C alloy, and other microstructures are primary Nb_{ss}, eutectic of Nb_{ss}/(Nb, Ti)C. Morphology of carbides are changed apparently through adding different Ti contents, and morphology of Nb_{ss} changes from the cellular structure to dendrite.

Key words: Nb-Ti-C alloy; carbide transformation; niobium solid solution

1 Introduction

Niobium-based alloys have been investigated as next generation high-temperature structure materials in place of current Ni-based or Co-based superalloys, which have a maximum operating temperature of about 1 400 K[1−3]. As one of refractory metal, pure niobium has a relatively low density, a very high melting point (2 741 K) and good room temperature ductility. However the strength of pure Nb decreases substantially as temperature is above 1 200 K[4]. Pure Nb has higher solid solubility of C, N, O compared with other superalloys, which suggests that Nb based alloys have great effect of solid solution strengthening[5−6]. Solid solution strengthened Nb alloys with V, Ta, Mo, Hf and W have been reported[7−9], and also some two-phase in-situ composites containing a BCC Nb solid solution (Nb_{ss}) and an intermetallic compound such as Nb_3Al[10−12] or Nb_5Si_3[13]. The strength of Nb-10Mo-(10−15)W-10Ti-18Si alloy which was developed by Japan can reach 800 MPa even at 1 773 K[2].

Traditional Nb alloys suffer from some problems[2−3], such as high density and poor oxidation resistance. The superalloy can keep low temperature plastic property of niobium, and hold low density, high strength, and high oxidation resistance. For Nb-Ti-C alloys the Ti reacts with oxygen to form selective oxides[10, 14], which can decrease the oxygen diffusion rate. Moreover, Ti and C can decrease the density of Nb based alloys[1, 6]. High temperature strength of the alloys can be improved by the generating of uniformly distributed carbides[15]. No systematic studies of microstructure evolution of Nb-Ti-C alloys have been reported. So, the purpose of this work is to investigate the phase composition, the distribution of carbides and Nb_{ss}, and microstructure evolution of as-cast Nb-Ti-C alloys.

2 Experimental

The composition design of Nb-Ti-C alloys in this work was based on binary phase diagram of Nb-C. High purity Nb, sponge Ti and TiC powder were used as raw materials. The alloys were prepared by vacuum non-consumable arc-melting method and cast into buttons. The starting materials were treated by acid washing and water scrubbing, and then uniformly mixed. The buttons were melted three times with electromagnetic mixing to ensure chemical homogeneity. The mass of buttons is about 30 g. The nominal compositions of the alloys in this work are Nb-5Ti-4C, Nb-20Ti-4C, Nb-47Ti-4C and Nb-58Ti-4C (mole fraction, %), and the precision contents are listed in Table 1. Their microstructures and compositions of the alloys were characterized using a combination of X-ray

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diffraction analyzer (XRD), scanning electron microscope (SEM) and energy dispersive spectroscope (EDS).

Table 1 Composition of Nb-Ti-C alloy (mole fraction, %)

Alloy	Nb	Ti	C
Nb-5Ti-4C	91.25	4.47	4.28
Nb-20Ti-4C	74.58	21.30	4.12
Nb-47Ti-4C	48.39	47.60	4.01
Nb-58Ti-4C	37.93	58.17	3.90

3 Results and discussion

3.1 Phase identification

The XRD patterns of samples are shown in Fig.1. It is found that the alloys contain three different phases: Nb_{ss}, Nb_2C and (Nb, Ti)C. Nb-5Ti-4C alloy contains Nb_{ss} and Nb_2C; other alloys (Nb-20Ti-4C, Nb-47Ti-4C and Nb-58Ti-4C) contain Nb_{ss} and (Nb, Ti)C.

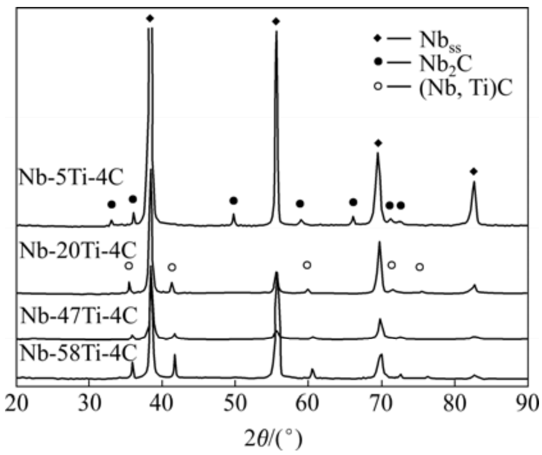

Fig.1 XRD patterns of as-cast samples

The lattice parameters calculated from the XRD data are 0.330 52, 0.330 05, 0.329 63 and 0.329 42 nm for the Nb_{ss} in Nb-5Ti-4C, Nb-20Ti-4C, Nb-47Ti-4C and Nb-58Ti-4C alloys. More Ti elements dissolve in Nb_{ss} as Ti content increases, and the solid solubility of Ti in Nb_{ss} is improved. This phenomenon is caused by Ti element, which has little atomic radius, in place of Nb element with a BCC structure.

3.2 Microstructure evolution of Nb-Ti-C alloys with Ti content

SEM micrographs of each alloy in the as-cast state are shown in Fig.2. The compositions measured by EDS of Nb_{ss} and carbides of each alloy are shown in Table 2. The molar ratio of C/M (Nb, Ti), calculated from EDS data, in deep color zone of Fig.3(a), is higher than that in bright part. So it can be known that the deep color phase is carbides and the bright color phase is Nb_{ss}.

Fig.2(a) shows the microstructure of the Nb-5Ti-4C alloy, and a two-phase microstructure consisting of Nb_{ss} and Nb_2C can be observed. One kind of plate-like primary Nb_2C phase distributes uniformly in grains; and another eutectic of Nb_2C/ Nb_{ss} phase distributes in grain boundary (Fig.2(a)). It is excited that the third kind of needle-like carbides distributes in grains from the high magnification images of Fig.3(b).

Therefore, it can be concluded that plate-like carbides nucleate and grow up from liquid alloy firstly under the condition of non-equilibrium solidification according to binary alloy phase diagram of Nb-C; and then Nb_{ss} grains grow up around primary carbides, which are used as effective nucleating particles; the eutectic of Nb_{ss} and Nb_2C precipitates from remnant liquid in grain boundary lastly. The secondary needle-like Nb_2C with the length of 8−10 μm and width of about 1 μm, precipitates during cooling from the solidification temperature due to supersaturation of C in the Nb_{ss} phase because of the solubility limit of carbon reducing.

Table 2 EDS analysis of each alloy

Alloy	Element	Nb_{ss}		Carbides	
		w/%	*x*/%	*w*/%	*x*/%
Nb-5Ti-4C	C	9.47	44.24	14.76	56.63
	Ti	1.95	2.28	2.36	2.27
	Nb	88.58	53.48	82.88	41.10
Nb-20Ti-4C	C	11.09	47.01	14.68	50.50
	Ti	8.29	8.81	27.70	23.89
	Nb	80.62	44.18	57.62	25.62
Nb-47Ti-4C	C	7.88	34.53	12.29	40.73
	Ti	24.97	27.44	53.81	44.74
	Nb	67.15	38.03	33.90	14.53
Nb-58Ti-4C	C	3.93	18.84	15.40	46.09
	Ti	36.96	44.48	58.25	43.71
	Nb	59.11	36.68	26.35	10.19

As indicated from the XRD analysis, the alloys of Nb-20Ti-4C, Nb-47Ti-4C and Nb-58Ti-4C consist of Nb_{ss} with BCC structure and (Nb, Ti)C with FCC NaCl structure. It is noted that more carbides are got compared with Nb-5Ti-4C alloy, carbide network becomes densely and complex, and the primary dendrite becomes more developed with the increase of Ti content in alloys.

In Nb-20Ti-4C alloy (shown in Fig.3(a)), the eutectic structure of intermediate phase is observed, in which Nb_{ss} and (Nb, Ti)C are alternatively distributed.

Carbides are in the majority in this eutectic zone. There is no significant secondary needle-like carbides precipitation. Secondary carbides also cannot be observed in Nb-47Ti-4C and Nb-58Ti-4C (shown in Figs.3(c) and (d)), and also plate-like precipitate carbides becomes less. The phenomenon indicates that eutectic temperature of the alloys decreases and rich carbon zone in Nb_{ss} disappears.

The Nb_{ss} becomes a coarse dendritic morphology with the increase of Ti content observed from Figs.2(b), (c) and (d), which indicates that this phase solidifies first, and then an eutectic mixture of carbide and Nb_{ss} phases

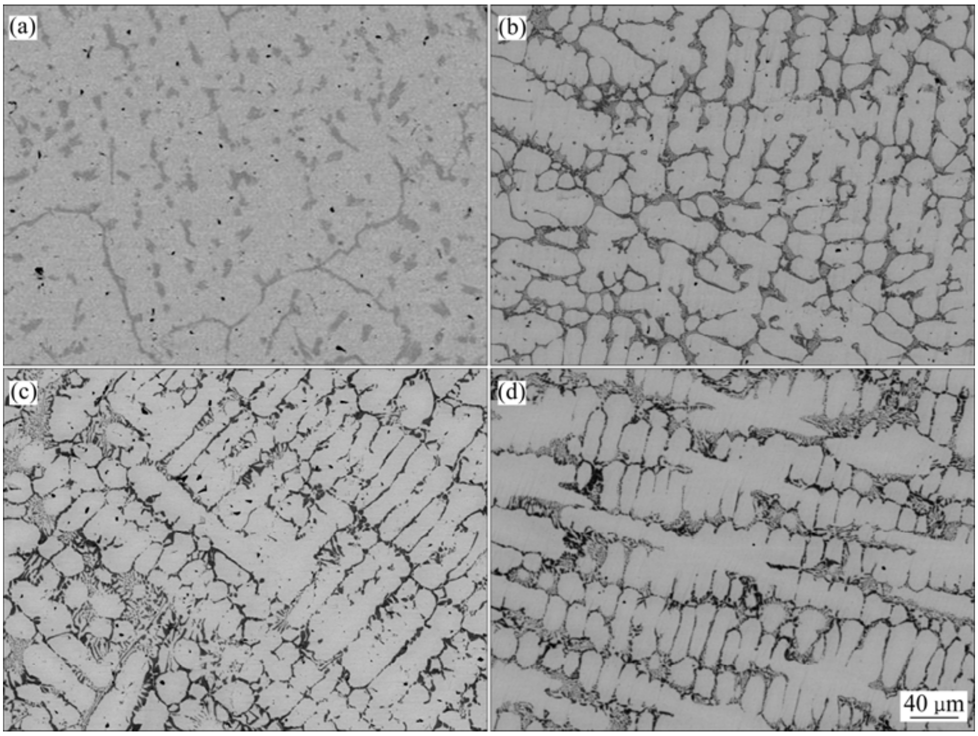

Fig.2 SEM micrographs of each alloy in as-cast state: (a) Nb-5Ti-4C alloy; (b) Nb-20Ti-4C alloy; (c) Nb-47Ti-4C alloy; (d) Nb-58Ti-4C alloy

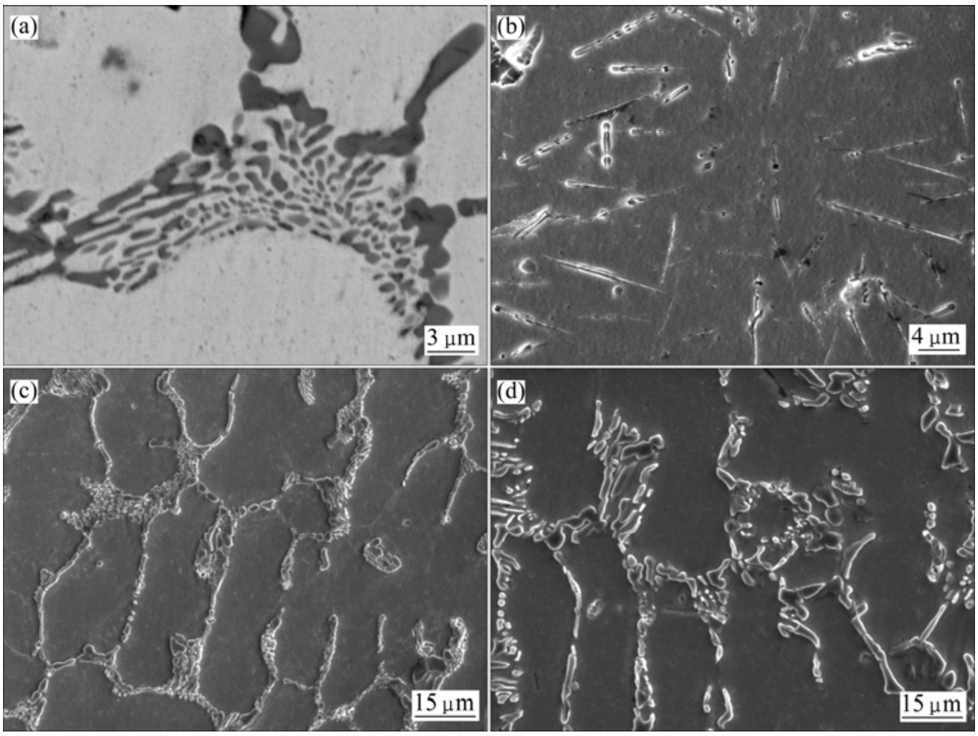

Fig.3 SEM images with high magnification: (a) Nb-20Ti-4C alloy; (b) Nb-5Ti-4C alloy; (c) Nb-47Ti-4C alloy; (d) Nb-58Ti-4C alloy

forms from the interdendritic liquid finally. The atomic ratio of Nb/Ti in Nb_{ss}, as shown in Table 2, decreases obviously with changing Ti element content. There are also more Ti elements dissolving in Nb_{ss}. The increase of solid solubility of Nb_{ss} is beneficial to oxidation resistance of the alloys. It is noted, however, that carbides are developed observing from Fig.3(d). The atomic ratio of M(Nb, Ti)C in carbides is approximately 1 based on the calculation from Table 2 in Nb_{ss} of Nb-20Ti-4C, Nb-47Ti-4C, and Nb-58Ti-4C alloy.

Above all, the volume fraction, structure and style of carbides change with changing Ti content. The reaction of carbon with Ti is easier than with Nb. Carbides include Nb_2C, growing up mainly in grains as primary phase, and (Nb, Ti)C, precipitating mainly in grain boundary as secondary phase. These carbides are contributive to improve high temperature mechanical properties through dispersion strengthening, solution strengthening and boundary strengthening. We know, however, that the temperature of eutectic transformation decreases as Ti with low melting point is added. The range of crystallizing increases. So, Nb_{ss} has more cooling time for crystal growth. Cellular structure is obtained in Nb-5Ti-4C alloy and coarse dendritic morphology is obtained in other alloys. Moreover, this also make secondary carbide disappear, and the most carbides solidify in boundary finally.

4 Conclusions

1) Ternary Nb-Ti-C alloys consist of niobium solid solution (Nb_{ss}), carbides including Nb_2C and (Nb, Ti)C and eutectic of Nb_{ss}/MC. The styles of carbides change from Nb_2C to (Nb, Ti)C with the increase of Ti content. The atomic ratio of Ti element in Nb_{ss} and MC increases with the increase of Ti content.

2) Primary Nb_2C, Nb_{ss}, eutectic of Nb_{ss} and Nb_2C and secondary Nb_2C are included in Nb-5Ti-4C alloy, and the other Nb-Ti-C alloys consist of primary Nb_{ss} and eutectic of Nb_{ss} and (Nb, Ti)C.

3) Nb is effective on the solubility of Ti in Nb_{ss}, but the temperature of eutectic transformation decreases with the increase of Ti content. Morphology of carbides is changed apparently by adding different Ti contents. The crystallization morphology of Nb_{ss} changes from the cellular to dendrite.

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