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Undercooling and rapid solidification of Nb-Si eutectic alloys studied by long drop tube

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Abstract: Niobium-silicide alloys have great potential for high temperature turbine applications. The two-phase Nb/Nb_5Si_3 in situ composites exhibit a good balance in mechanical properties. Using the 52 m drop tube, the effect of undercooling and rapid solidification on the solidification process and micro-structural characterization of Nb-Si eutectic alloy was studied. The microstructures of the Nb-Si composites were investigated by optics microscope (OM), X-ray diffraction (XRD) and scanning electron microscope (SEM) equipped with X-ray energy dispersive spectrometry (EDS). Up to 480 K, deep undercooling of the Nb-Si eutectic samples was successfully obtained, which corresponds to 25% of the liquidus temperature. Contrasting to the conventional microstructure usually found in the Nb-Si eutectic alloy, the microstructure of the undercooled sample is divided into the fine and coarse regions. The most commonly observed microstructure is Nb+Nb_5Si_3, and the Nb_3Si phase is not be found. The change of coarseness of microstructure is due to different cooling rates during and after recalescence. The large undercooling is sufficient to completely bypass the high temperature phase field.

Key words: Nd-Si eutectic alloys; intermetallics; long drop tube; undercooling; rapid solidification

1 Introduction

With the development of the aerospace technology, it required more powerful and efficient turbine which can work at a higher working temperature. Nb-Si alloys and their composites have excellent high temperature properties, especially for Nb/Nb_5Si_3 in situ composite, which has good plasticity at low temperature and high strength at high temperature[1−4]. However, it is far away from practical application for this kind of material. Many problems, such as the control of the in situ processing of the composite material and the structure optimizing, need to be solved. Utilizing rapid solidification techniques, we can obtain various microstructures of the materials. This is a possible way to control the microstructures of the Nb/Nb_5Si_3 in situ composite. Therefore, many researches studied the non-equilibrium solidification of the Nb-Si alloy system. SPAEPEN[5] studied Nb-Si system by utilizing a pulse laser quenching technique. Amorphous microstructure was obtained under the cooling rate in a range from 10^9 K/s to 10^{12} K/s. BERTERO et al [6, 7] studied the solidification process of Nb-Si system with the magnetic levitation and the splat quenching methods. They found that the microstructures were mainly composed of fine grains of Nb and Nb_3Si phases. Utilizing melt spinning method, BENDERSKY et al[8] found that only Nb and Nb_5Si_3 phases could be obtained in the Nb-Si system. In contrast, BOWDEN et al[9] got the results different from those of BENDERSKY et al[8] through the electronic beam heating and the splat quenching studies. They found that the quenched foil contained a lot of Nb_3Si and Nb_5Si_3.

Microgravity condition could provide a unique experimental environment to make the bulk metallic liquid solidify in vacuum [10]. Therefore, container-less solidification can be realized. The large supercooling could be obtained through the solidification in microgravity because the heterogeneous nucleation rate could be largely suppressed in the container-less solidification process. In this paper, we studied the solidification process of Nb-Si alloy system by utilizing the 52 m long drop-tube. The effects of undercooling and rapid solidification on the solidification process and microstructures of Nb-Si eutectic alloy were studied.

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2 Experimental

Nb-18.7%Si master ingot was synthesized from the highly purified Nb (99.9%) and Si (99.99%). The alloy cylinder with the diameter of 2 mm was got through the remelting and the suction casting of the master ingot in a vacuum arc-melting furnace. The cylinder samples were used for the drop-tube solidification experiment. The 52 m long drop-tube employed an electron beam heating furnace to melt the sample. The molten sample experienced 3.26 s free falling in the drop tube with microgravity of 10^{-7} g. Various supercooled spherical samples could be obtained. The recalescence point could be recorded by the temperature measurement system. The sample was etched in the acid solution of H_2O-HNO_3-HF with the volume ratio of 5∶2∶1. The microstructures and the constitution of the sample were analyzed by optical microscope, XRD, SEM and EDS.

3 Results and discussion

3.1 Microstructures of as-casting samples

Fig.1 shows the phase diagram of the binary Nb-Si system. It can be seen from Fig.1 that there exists a wide range of two phase coexistence region between the end compound and intermetallic compound Nb_5Si_3. This indicates that it is possible to synthesize the composite material containing the refractory metal (Nb solid solution) and the intermetallic compound Nb_5Si_3. It should be noted that Nb_5Si_3 phase has the very high melting point (2 520 ℃) , hardness and strength, while Nb solid solution has excellent room temperature plasticity. The composite material with the excellent mechanical properties could be synthesized through controlling the constitution and the ratio of Nb and Nb_5Si_3 in the composite. Therefore, it is very important to study the microstructures of the composite material synthesized under the various conditions. Under equilibrium solidification condition, Nb-18.7%Si(mole fraction) alloy contains a stable Nb+Nb_5Si_3 micro-structure. This could be changed through the variation of the solidification condition.

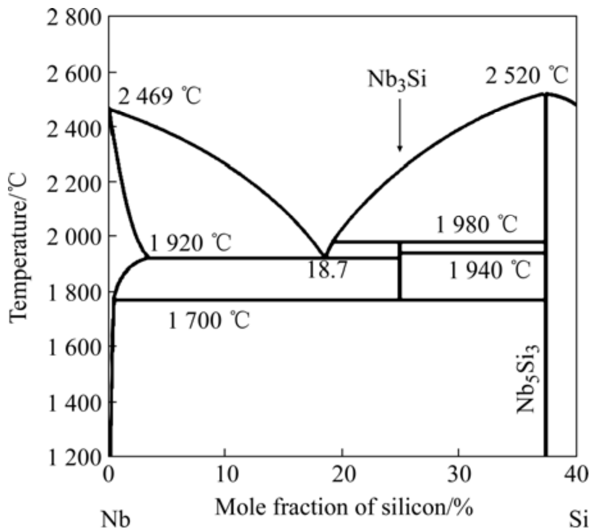

Fig.1 Nb-Si binary phase diagram

Fig.2 shows the microstructure of the suction-cast Nb-18.7%Si(mole fraction) alloy. The dark phase is Nb_3Si primary phase, while the light gray one is Nb-Nb_3Si eutectic structure. This implies that there is no Nb_5Si_3 phase in the as-casting sample. This result can be understood from the difference in the reactions occurred at the equilibrium and the non-equilibrium solidification conditions, as shown in Fig.3. In the case of the equilibrium solidification, the following eutectic and eutectoid reactions are occurred.

$L \rightarrow Nb+Nb_3Si$

$Nb_3Si \rightarrow Nb+Nb_5Si_3$

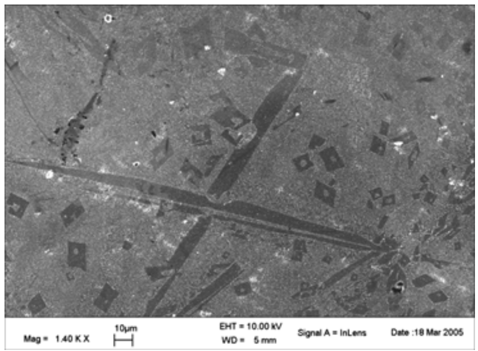

Fig.2 SEM image of as-casting Nb-18.7%Si alloy

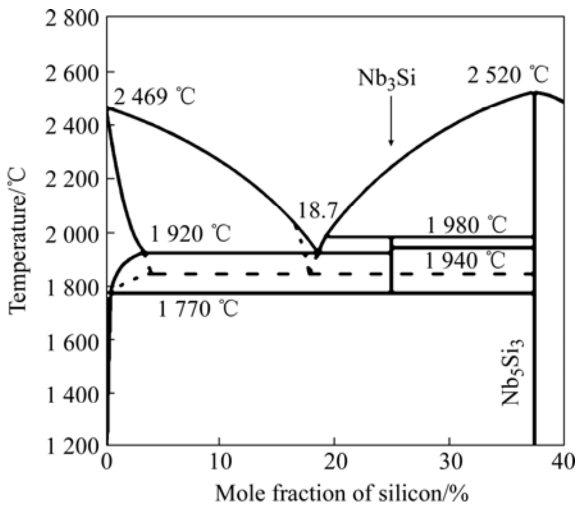

Fig.3 Binary Nb-Si phase diagram under rapid solidification

In the case of the non-equilibrium solidification, however, the eutectic point might deviate from the equilibrium eutectic point due to the large cooling rate and the large supercooling. Instead of the above reactions for the equilibrium solidification, the following reactions will occur for the non-equilibrium solidification.

$L\rightarrow Nb_3Si$

Beneath the eutectic point, the residual melt will perform the following reaction.

$L\rightarrow Nb+Nb_3Si$

From above, it can be known that Nb_3Si phase in the as-casting sample do not change into the eutectoid structure of $Nb+Nb_5Si_3$.

MENDIRATTA et al[11], BEWLAY et al[12, 13] and ZHAO et al[14] analyzed the kinetics of the eutectoid reaction. It was known that the decomposition of the Nb_3Si phase was very slow. This also implied that primary phase Nb_3Si and the eutectic phase $Nb+Nb_3Si$ could be preserved in the rapid solidification process. The eutectic composition in our suction-cast condition was around Nb-18.0%Si(mole fraction) which was deduced from the analysis of samples with the different compositions.

3.2 Microstructures of drop-tube samples

The spherical samples with the diameters of 2−4 mm were obtained in the drop-tube experiment. The maximum supercooling of 480 K could be obtained in our experiment. The microstructures of Nb-18.7%Si (mole fraction) alloys are shown in Fig.4. The dark phase is Nb_5Si_3 phase, while the heavy-gray phase is Nb phase and the white one comes from the Nb-Nb_5Si_3 eutectic phase. All of the samples are composed of the coarse domains and the fine grains. In contrast to the results of the as-casting samples, the drop-tube samples do not contain Nb_3Si phase. Only Nb and Nb_5Si_3 phases are found in these samples. This result is consistent with that of BENDERSKY's experiment, while it has a big difference from that of BOWDEN and MENDIRATTA's experiment. It should be noted that the thickness of sample in BENDERSKY's experiment is about 20−30 μm which is much thinner than that in BOWDEN and MENDIRATTAS's experiment (100 μm). Therefore, it is reasonable to deduce that the cooling rate in BENDERSKY's experiment was higher than that in BOWDEN and MENDIRATTA's experiment. Combined with our experimental results, it can be concluded that Nb-Si melt can be cooled down directly into $Nb+Nb_5Si_3$ region at the high enough cooling rate or at the large supercooling. The $Nb+Nb_3Si$ eutectic region is not necessary to be experimented in such case.

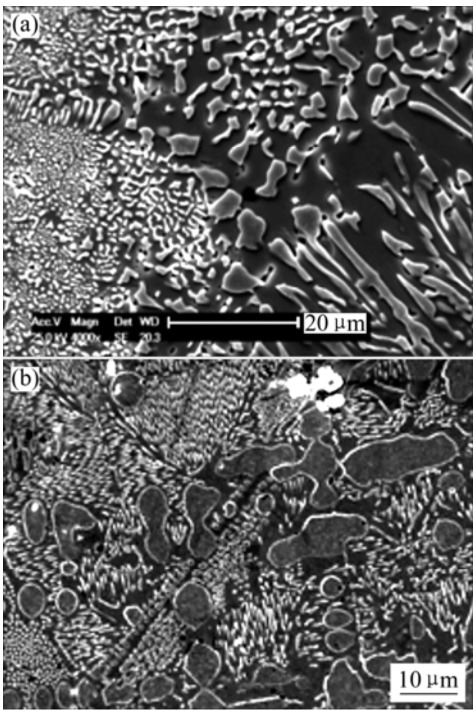

Fig.4 SEM images of drop-tube samples with diameters of 2.6 mm(a) and 3.4 mm(b)

The results show that all of drop-tube samples contained both of the coarse structure regions and the fine structure regions. As mentioned above, the large supercooling can be obtained in our experiment. This induces the formation of the fine microstructure of $Nb+Nb_5Si_3$ phase in the sample. However, large amount of heat flux is released during the recalescence process. It reduces the cooling rate in the solidification process. The residual melt remained after the recalescence will solidify into the coarse $Nb+Nb_5Si_3$ structure. This result, from another aspect, demonstrats that the supercooling impacts large influence on the formation of the microstructures.

4 Conclusions

Up to 480 K, deep undercooling is successfully obtained for the Nb-Si eutectic samples, which corresponds to 25% of the liquidus temperature. Contrasting to the conventional microstructure usually found in the Nb-Si eutectic alloy, the microstructure of the undercooled sample is divided into the fine and coarse regions. The most commonly observed microstructure is Nb + Nb_5Si_3, and the Nb_3Si phase can not be found. The change of coarseness of microstructure is due to different cooling rates during and after recalescence. The large undercooling is sufficient to completely bypass the high temperature phase field.

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