

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(1): 0007-0012.

ARTICLE

Thermal Stability of Fine-Crystal Cr-NbCr₂ Alloy

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Abstract: Thermal stability of the fine-crystal Cr-NbCr₂ alloy prepared by mechanical alloying and hot pressing was researched. The results show that the grain size of Cr matrix has a certain degree of growing up after the thermal exposure, while the particle size of Laves phase NbCr₂ has no obvious change due to its high thermal stability. At the same time, the dislocation in the Cr matrix and the stacking faults/twins in the Laves phase NbCr₂ particles appear in the as-thermally exposed microstructure because of the increase of the compressive stress between Cr matrix and NbCr₂ particles. Due to the variation in particle size and the occurrence of crystal defects, the Cr-NbCr₂ alloy can keep higher compressive strength, yield strength and plastic strain after thermal exposure from 800 °C to 1200 °C for 50 h. However, the yield strength and plastic strain of the Cr-NbCr₂ alloy decline obviously by prolonging the thermal exposure because the growth of grains becomes the determining factor of properties.

Key words: Cr-NbCr₂ alloy; fine-crystal; thermal stability; crystal defects

Compared with traditional nickel-based alloy and titanium-based alloy, the Laves phase $X\text{Cr}_2$ alloy ($X=\text{Nb, Ta, Hf, Zr \dots}$) has been considered as a candidate material for high temperature structural applications due to its high melting temperature, good high temperature strength and good oxidation resistance, etc. Meanwhile, the main drawback of the Laves phase alloy is the poor ambient temperature toughness^[1-7]. One of the effective solutions to overcome the brittleness of Laves phase alloy is to fabricate in-situ composites containing reinforcing Laves phase in a relatively ductile matrix. Compared with Laves phase, Chromium has good ambient temperature ductility and toughness, moderate density, good high temperature oxidation and corrosion resistance, and thus Cr- $X\text{Cr}_2$ alloy has been studied widely^[8-14].

Earlier research results show that the ambient temperature toughness of Cr-NbCr₂ alloy can be improved by fine grain toughening and soft second phase toughening through mechanical alloying and hot pressing technology^[15]. The fine-crystal material has excellent strength due to high density of grain boundaries inside. However, these same grain boundaries lead to limit the thermal stability because they are

mostly in the metastable state at high temperature. Even without external force, the high temperature mechanical properties and the room temperature mechanical properties of the fine-crystal material will also change accordingly due to its instability of microstructure^[16-20], which is a potential danger in the practical engineering application. Thus, the thermal stability of fine-crystal Cr-NbCr₂ alloy is another key factor for its high temperature applications. In the present paper, the Cr-NbCr₂ alloy was prepared by mechanical alloying and hot pressing. Subsequently, the effect of thermal exposure from 800 °C to 1200 °C for 100 h on microstructure and properties of the Cr-NbCr₂ alloy was studied.

1 Experiment

The Cr-NbCr₂ alloy of composition Cr-12at% Nb was prepared by mechanical alloying and hot pressing with starting materials of 99.5 wt% Cr and 99.5 wt% Nb powders. The powders were mixed into a stainless steel jar with ball-to-material weight ratio of 13:1, rotating speed of 400 r/min and time of 20 h. Then, the mixed powders were placed in a graphite mould and hot pressed at 1250 °C for 30 min

Received date: January 14, 2017

Foundation item: National Natural Science Foundation of China (51074092); Natural Science Foundation of Jiangxi Province (2016BAB206113); KJLD Plan Projects of Jiangxi Provincial Education Department (KJLD14056)

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with a pressure of 45 MPa in a vacuum condition^[15].

Thermal exposure experimentations were performed in vacuum condition at 800, 1000 and 1200 °C for 10, 30, 50 and 100 h.

Phase composition of the Cr-NbCr₂ alloy was analyzed using a D-8 ADVANCE X-ray diffractometer. The relative density was determined based on Archimedean principle. The Vickers hardness testing was done by a HVS-1000 Vickers hardness tester with a load of 1 kg. Room temperature compression experiment was carried out with loading speed of 0.05 mm/min by WDW-50 electronic universal testing machine. The microstructure of the Cr-NbCr₂ alloy was investigated by a FEI QUANTA200 scanning electron microscopy (SEM) and a JEOL JEM-2100 transmission electron microscopy (TEM). Specimens for TEM were prepared by cutting thin slices using electrical discharge machining (EDM), grinding and polishing to a thickness of 100 μm and Ar⁺ ion beam thinning to perforation. TEM observations were carried out at 200 kV.

2 Results and Discussion

Fig.1 shows the X-ray diffraction patterns of the Cr-NbCr₂ alloy. The phase constituent consists of Laves phase NbCr₂ and Cr solid solution. In addition, the Cr-peaks are found to slightly shift to lower angles, which may be caused by the dissolution of Nb atoms into the Cr lattices. It shows no apparent phase change after the thermal exposure process.

The change of the relative density of the Cr-NbCr₂ alloy is shown in Fig.2. The relative density increases slightly with increase of thermal exposure time and thermal exposure temperature because of the disappearance of the small pore and the decrease of the amount of pores^[21]. After thermal exposure at 800, 1000 and 1200 °C for 100 h, the relative density varies from 97.5% to 98.4%, 98.6%, 98.8%,

respectively. Overall, the relative density of the Cr-NbCr₂ alloy is stable during the whole thermal exposure process.

Fig.3 shows the microstructure of the Cr/NbCr₂ alloy thermally exposed at 1000 °C for different time. Fig.4 shows the microstructure of the Cr/NbCr₂ alloy thermally exposed at

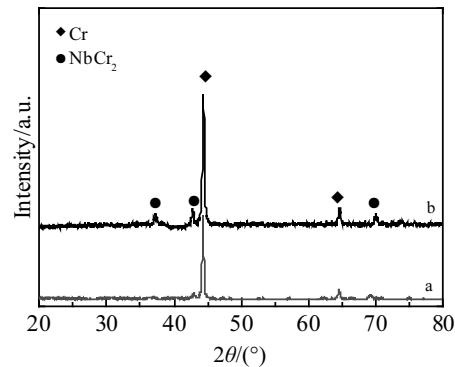


Fig. 1 XRD patterns of the Cr-NbCr₂ alloy (a-before thermal exposure and b-thermal exposure at 1200 °C for 100 h)

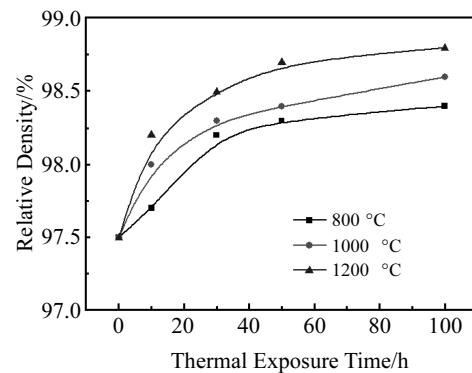


Fig. 2 Effect of thermal exposure time at different temperatures on relative density of the Cr-NbCr₂ alloy

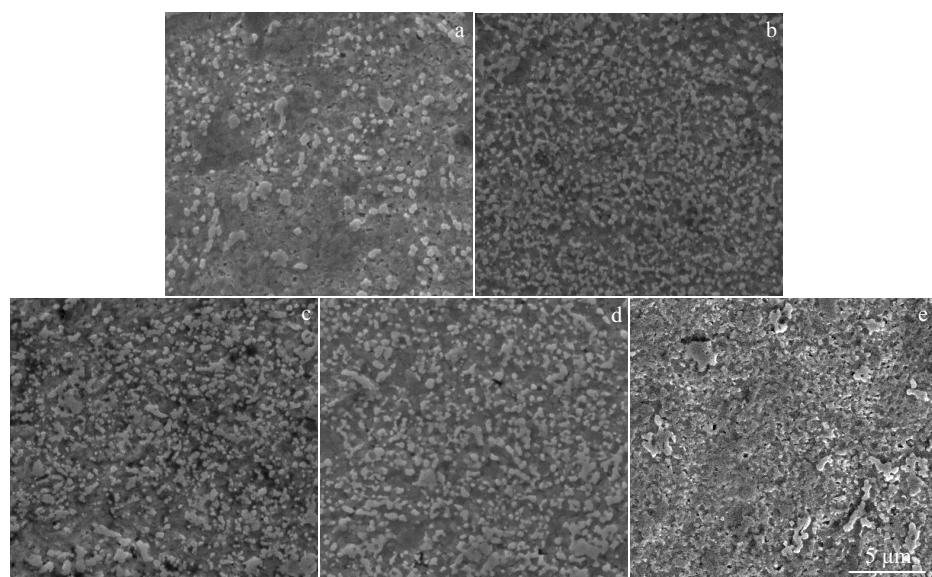


Fig.3 Microstructures of the Cr/NbCr₂ alloy thermally exposed at 1000 °C for different time: (a) 0 h, (b) 10 h, (c) 30 h, (d) 50 h, and (e) 100 h

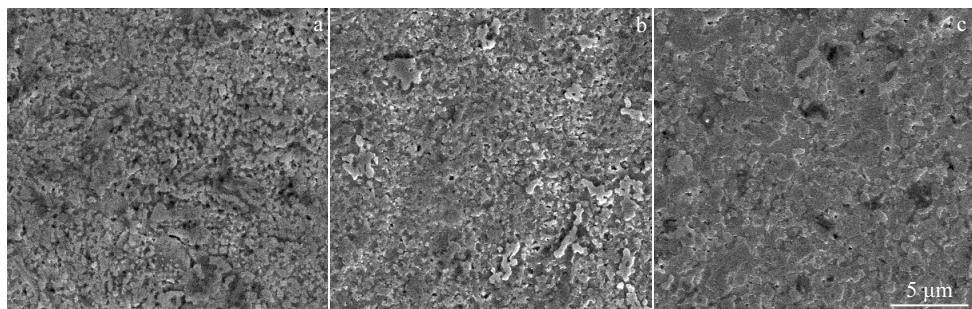


Fig.4 Microstructures of the Cr/NbCr₂ alloy thermally exposed at different temperatures for 100 h: (a) 800 °C, (b) 1000 °C, and (c) 1200 °C

different temperatures for 100 h. It shows that the Laves phase NbCr₂ particles has a certain degree of aggregation with the increase of thermal exposure temperature and thermal exposure time.

Fig.5 shows the variation of Vickers hardness of the Cr-NbCr₂ alloy. The Vickers hardness increases firstly and then decreases with increase of the thermal exposure time. After thermal exposure at 800, 1000 and 1200 °C for 100 h, Vickers hardness varies from 5.9 GPa to 5.6, 5.3 and 4.3 GPa, respectively.

Fig.6 shows the room-temperature compressive stress-strain curves of the Cr-NbCr₂ alloy after thermal exposure at different temperatures for different time. An obvious plastic deformation can be observed during the first 50 h thermal exposure process, which may be carried out by the good plasticity of chromium solid solution. But, the plastic deformation decreases obviously after thermal exposure for 100 h.

Fig.7 shows the change of the room temperature compressive properties of the as -thermally exposed Cr-NbCr₂ alloy, including compressive strength (Fig.7a), yield strength (Fig.7b) and plastic strain (Fig.7c). After thermally exposing at 800 °C for 10 h or at 1000 °C for 30 h, the compressive strength gets the maximum value. Prolonging the thermal exposure time, the compressive strength shows a downward trend. However, the compressive strength of the Cr-NbCr₂

alloy thermally exposed at 1200 °C increases with the thermal exposure time. The compressive strength of the Cr-NbCr₂ alloy varies from 1911 MPa to 1946, 2067 and 2463 MPa after it is thermally exposed at 800, 1000 and 1200 °C for 100 h, respectively. The compressive strength of the as- thermally exposed Cr-NbCr₂ alloys is no lower than the strength of the as-hot pressed Cr-NbCr₂ alloy.

The yield strength of the Cr-NbCr₂ alloy increases firstly and then declines with the thermal exposure time. The yield strength reaches the peak value after thermal exposure of 10 h at 800 °C and of 30 h at 1000 and 1200 °C. After thermally exposing at 800, 1000 and 1200 °C for 100 h, the

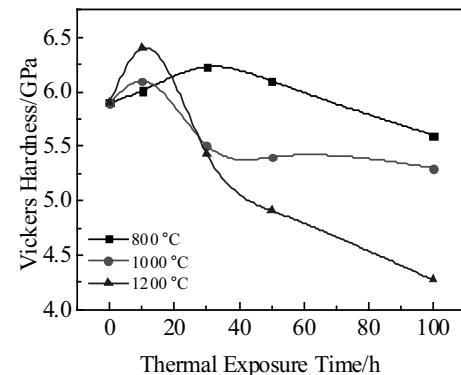


Fig.5 Effect of thermal exposure time at different temperatures on Vickers hardness of the Cr-NbCr₂ alloy

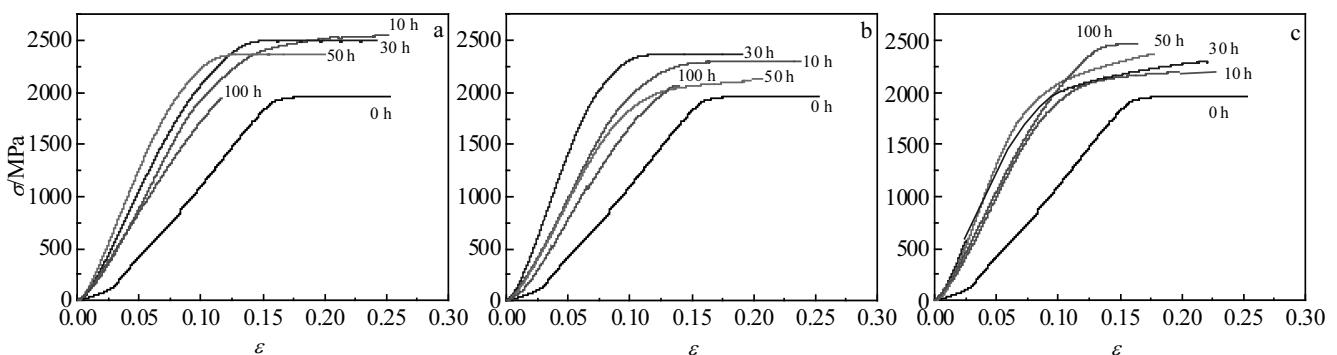


Fig.6 Room-temperature compressive stress-strain curves of the Cr-NbCr₂ alloy thermally exposed at 800 °C (a), 1000 °C (b), and 1200 °C (c) for different time

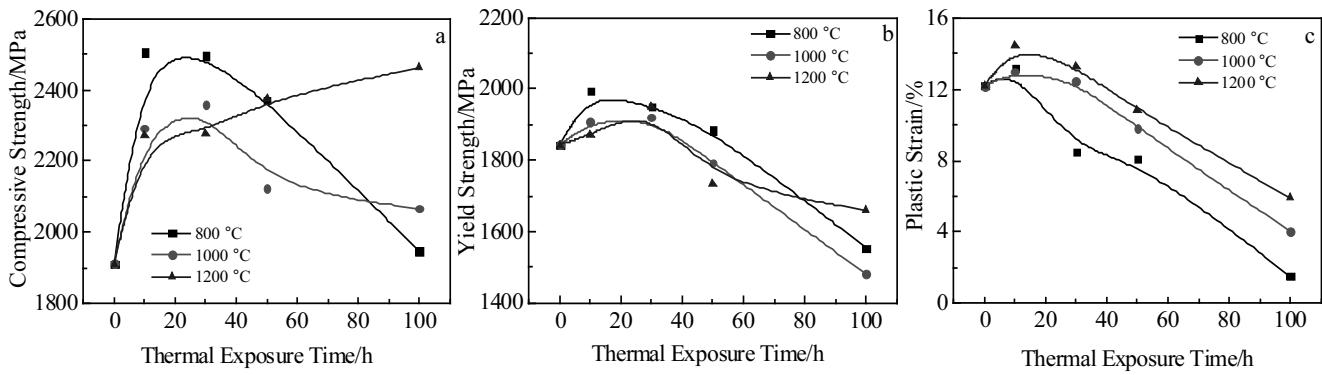


Fig.7 Effect of thermal exposure time at different temperatures on compressive strength (a), yield strength (b) and plastic strain (c) of the Cr-NbCr₂ alloy

yield strength of the Cr-NbCr₂ alloy varies from 1843 MPa to 1557, 1480 and 1659 MPa, decreased by 15.5%, 19.7% and 10.0%, respectively.

The change trend of the plastic strain is similar to the yield strength. After thermally exposing at different temperatures for 50 h, the Cr-NbCr₂ alloy can still keep high plastic strain more than 8%. While, the plastic strain decreases obviously after thermally exposed at 800, 1000 and 1200 °C for 100 h, which is 1.5%, 4.0% and 5.9%, respectively. It can be also seen that the plastic strain increases with the thermal exposure temperature.

Fig.8a shows the microstructure of the as-hot pressed Cr-NbCr₂ alloy. The particle size of Cr matrix and NbCr₂ particle is 250~375 nm and 125~225 nm, respectively. The selected area diffraction patterns (SADP, Fig.8b and Fig.8c) further confirm that the phase constituent is Cr matrix and C15 Laves phase NbCr₂. It shows no obvious faults/twins in the Laves phase. It is different from the as-vacuum arc-cast NbCr₂ alloy, accompanied with a number of micro twins/stack faults^[22-24]. Due to the synergistic effect of grain refinement and soft second phase, the as-hot pressed Cr-NbCr₂ alloy has high yield strength of 1911 MPa and good plasticity of 12.2%.

It is well known that the total free energy significantly increases with decrease of the grain size. Grain growth is inevitable owing to the reduction of the excess free energy with increase of thermal exposure time and thermal exposure

temperature. At the beginning of the thermal exposure process, the grain size of NbCr₂ particles and Cr matrix particles has no obvious increase. Meanwhile, the relative density of the Cr-NbCr₂ alloy increases slightly. It causes the slight increase of hardness, strength and plasticity of the Cr-NbCr₂ alloy. However, the main change of microstructure is the increase of grain size of Cr matrix as thermal exposure prolongs. At the same time, the thermal expansion coefficient of Cr matrix varies from $8.2 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at ambient temperature to $14.9 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ above 800 °C. Whereas, the particle size and the thermal expansion coefficient of NbCr₂ particle have no obvious increase due to its high thermal stability. With the change of grain size and thermal expansion coefficient of Cr matrix, it has larger compressive stress on the NbCr₂ particles by Cr matrix. It promotes the emergence of fault/twin in NbCr₂ particles. Meantime, it has some reverse compressive stress on Cr matrix by NbCr₂ particles, which promotes the presence of dislocation in the Cr matrix. By the change of the microstructure, the Cr-NbCr₂ alloy can keep higher plastic deformation ability after thermally exposing at high temperature for a long time. But, the properties of the Cr-NbCr₂ alloy, such as yield strength, plasticity and hardness etc, decline obviously by prolonging the thermal exposure because the coarsening of grain is the determining factor.

Fig.9a shows the microstructure of the Cr-NbCr₂ alloy thermally exposed at 1200 °C for 100 h. It can be seen that the

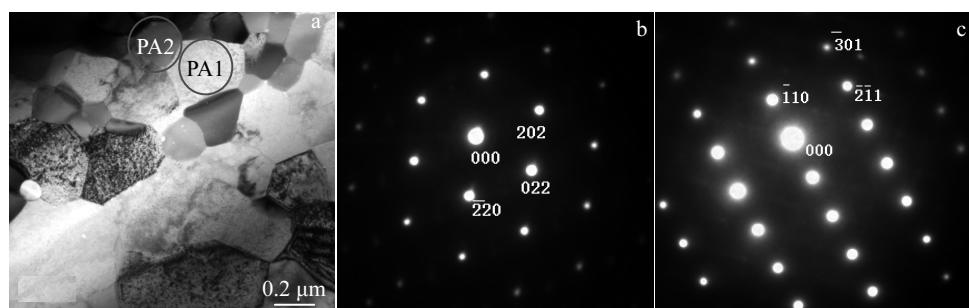


Fig.8 Microstructure of the as-hot pressed Cr-NbCr₂ alloy (a), SADP of Cr matrix (PA1) (b), and SADP of NbCr₂ particle (PA2) (c)

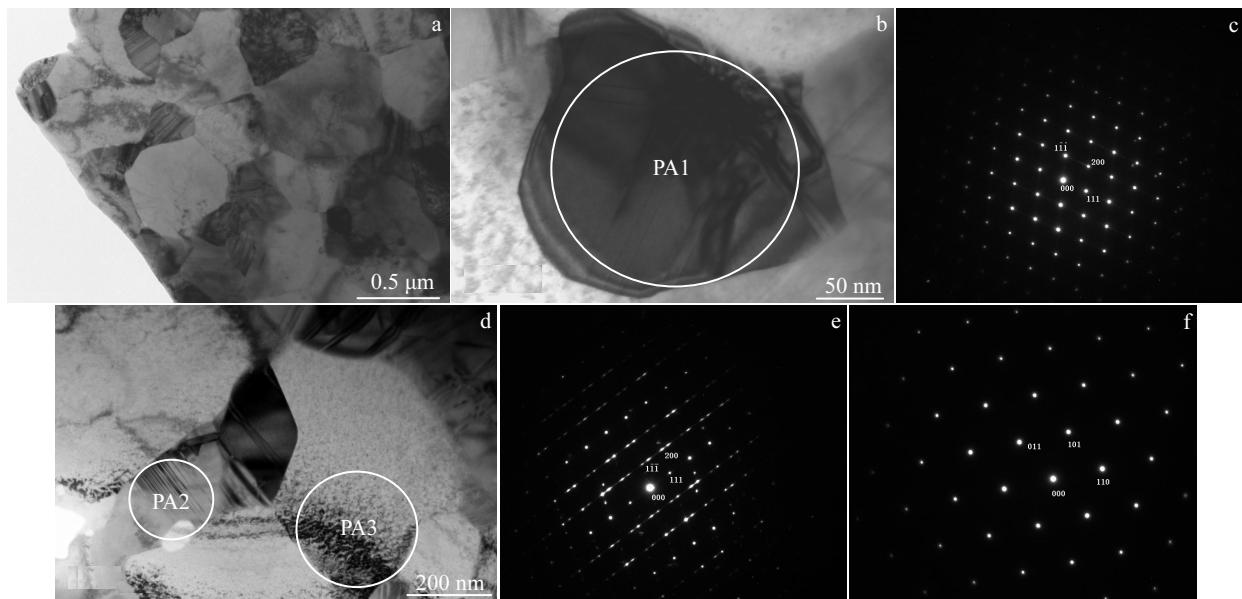


Fig.9 Microstructure of the Cr-NbCr₂ thermally exposed at 1200 °C for 100 h (a); the stacking faults in NbCr₂ (PA1) (b); the SADP of stacking faults at PA1 in NbCr₂ (c); twins in NbCr₂ (PA2) and dislocations in Cr matrix (PA3) (d); the SADP of twins at PA2 in NbCr₂ (e); the SADP of Cr matrix (PA3) (f)

grain sizes of Cr matrix increases to 570~620 nm. While, the grain size of NbCr₂ has no obvious change due to its high thermal stability and the stacking faults/twins can be seen in the Laves phase NbCr₂ particles. The C15 NbCr₂ phase has a complex fcc crystal structure containing 24 atoms in the unit cell. The stacking sequence of {111} atomic planes can be written ...ABCABC.... Here, each layer of ABC consists of four interpenetrating closely packed atomic plane. Under the compressive strain, the defects, such as stacking fault/twins, are easier to form. In fcc crystal structure, the stacking faults/twins can be obtained by shear a perfect crystal on {111} plane along 1/6<211>direction. Fig.9b and Fig.9d show the stacking faults and twins in NbCr₂ phase particles by a higher magnification, which are confirmed by SADPs (Fig.9c and Fig.9e). In Fig.9b, some thin stacking faults within Laves phase NbCr₂ are seen in the location of PA1. In Fig.9d, a twin cluster composed of many fine twin bands is found to extend across the entire grain in the location of PA2. In addition to the diffraction spots, some light streaking is seen in Fig.9c with the orientation of the streaks being a <111> crystallographic direction. It is confirmed by recording diffraction patterns at specimen orientations away from the <110> zone axes. The shape of the diffuse scattering confirms the occurrence of the stacking faults in the Laves phase NbCr₂ particles, which is lying parallel to the {111} plane. In Fig.9e, One set of twins reflections are seen and the twin plane is clearly the {111} crystallographic plane. The extensive diffuse streaks can also be seen running through the diffraction pattern aligned with the diffraction spots of the twin plane^[25,26]. The bcc Cr matrix at the lower right in Fig.9d (PA3)

confirmed by SADP (Fig.9f) shows evidence of extensive dislocation slip indicating that its deformation has occurred by dislocation glide.

3 Conclusions

1) During the thermal exposure process, the grain size of Cr matrix has a certain degree of growing up and some dislocations appear in the Cr matrix. At the same time, the particle size of Laves phase NbCr₂ has no obvious change due to its high thermal stability and some stacking faults/twins appear in the Laves phase NbCr₂.

2) The Cr-NbCr₂ alloy can keep higher compressive strength, yield strength and plastic strain after thermal exposure from 800 °C to 1200 °C for 50 h. However, the yield strength and plastic strain of the Cr-NbCr₂ alloy will decline obviously by prolonging the thermal exposure because the main determining factor is the growth of grain.

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细晶 Cr-NbCr₂ 合金的热稳定性

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摘要: 研究了通过机械合金化+热压工艺制备的细晶 Cr-NbCr₂ 合金的热稳定性。结果表明: 热暴露过程中, Cr 基体的颗粒尺寸有一定程度的长大, 而 Laves 相 NbCr₂ 颗粒由于其高热稳定性无明显变化。随着热暴露的进行, Cr 基体颗粒与 Laves 相 NbCr₂ 颗粒间压应力增加, 使得基体和 Laves 相中分别出现了位错和层错/孪晶结构。颗粒尺寸的变化和晶体缺陷的出现, 使得 Cr-NbCr₂ 合金在 800~1200 °C 热暴露 50 h 后仍具有较高的抗压强度, 屈服强度和良好的塑性。但随着热暴露的继续延长, 此时颗粒的长大成为主导因素, Cr-NbCr₂ 合金的屈服强度和塑性明显下降。

关键词: Cr-NbCr₂ 合金; 细晶; 热稳定性; 晶体缺陷

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