Mechanical Properties and Oxidation Behavior of Hot Pressing Sintered Nb5Cr Superalloy

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Abstract—In this paper, an alloy with a group of Nb5Cr was prepared by hot pressing sintering and its phase composition was characterized. After hot pressing sintering, Cr element exists in the form of solid solution outside the Nb matrix, and a certain amount of $NbCr_2$ phase is formed. The bending strength of the obtained alloys is not less than 250 MPa, and the fracture toughness is close to that of H11 casting die steel. In addition to the mechanical properties of the alloy, the oxidation behavior of the alloy at different temperatures was also studied. The experimental results show that the change of the alloy is not obvious at 1000°C except for the dissolution of Cr element, and at 1000−1200°C, the alloy can spontaneously form a $CrNbO_4$ oxide film which is weakly bound to the alloy matrix. This is very conducive to the application of separation between the mold and the casting mold during casting. This product provides the casting industry with a material that can spontaneously form a Self-oxidizing film under high temperature oxidation environment and provides a usable choice for materials used in high temperature casting environment.

INTRODUCTION

Metal casting is a widely used and low-cost forming method for the processing of ferrous metals. It has the characteristics of several clean forming and is suitable for the forming of complex components and has been studied deeply and extensively for thousands of years. However, the casting process is relatively complex, especially the sand-casting process requires a lot of manpower, and the sand box must be reset every time the casting is done. The casting efficiency is relatively low. Therefore, fixed continuous casting has unique advantages.

In the past few years, many casting materials have been developed for continuous casting [1]. However, the casting materials developed in the past are not only easy to withstand high temperature, but also have a violent interaction with the casting mold in direct contact with the molten steel [2−4]. Therefore, it is necessary to add a large amount of release agent between the molten steel and the casting mold before casting [5]. The traditional fixed cavity continuous casting mold not only adds a process in the casting process, increases the cost of release agent, but also limits the complexity of the casting mold. It is not conducive to the industrial production of casting molds [6]. Therefore, the development of a mold that can isolate itself from the cast metal during the casting process and is easy to release during the separation process will greatly improve the efficiency of the casting process and provide more possibilities for the application of complex casting molds [7].

The selection of casting mold needs to consider the temperature, casting impact force [8], high temperature oxidation and molten steel erosion environment during the casting process [9]. So, in high-temperature resistant materials, superalloy with its good heat resistance, higher strength and better toughness occupy an important position [10]. With the development of modern metallurgical industry, a variety of high-temperature resistant superalloy systems have been developed. Such as Ni base superalloy, Mo base superalloy and Nb base superalloy. However, the melting point of the Ni-based superalloy is relatively low, and the superalloy will soften or even melt at about 1450°C [11, 12]. This temperature is far from the temperature of cast steel, and is not suitable for casting mold materials; The melting point of Mo-based superalloys usually exceeds 2000°C, while the metal Mo will be oxidized to MoO_3 at 600−700°C, MoO_3 will melt into a liquid at 795°C, and MoO_3 will boil at 1155°C [13]. Although the oxidation resistance at high temperatures can be improved by super alloying to form a protective film, the Mo-based superalloy will react violently with molten steel during the casting process. Therefore, it will cause extremely difficult to release the mold, and it is not suitable for steel casting [14, 15].

Nb−Cr superalloy with its very high melting point, and easy to form a thin layer of dense protective film in high temperature oxidation environment, and the protective film will be peeled from the matrix during cooling [16–18]. This can undoubtedly facilitate the demolding of the casting process. Moreover, hot pressing sintering process can avoid the problem of different melting points and uneven composition in the superalloy forming process of this system, which lays a solid foundation for the application of such materials [19, 20].

In this paper, a Nb5Cr superalloy was designed and prepared by vacuum hot pressing sintering method. The bending strength of the superalloy is close to 250 MPa, and a dense oxide film will be formed quickly under high temperature oxidation environment. After cooling, the oxide film will be separated from the substrate. It provides a new solution for the selection of casting mold.

2. MATERIALS AND METHODS

2.1. Materials Synthesis and Processing

In this paper, Nb powder (99.95%, 10 μm, Northwest Institute For Non-ferrous Mental Research, China) and Cr metal powder (99.0%, 30 μm, Jinzhou Institute of Metal Material, China) are mixed according to the molar ratio of NB-95% CR-5%, and placed in 250 mL graphite crucible and placed in a vacuum sintering furnace. The heating rate is 10°C per minute, and 30 MPa sintering pressure is applied after reaching the sintering temperature. The temperature is kept at 1500°C for 1 h, and then cooled to room temperature with the furnace.

After cooling and removing the pressure, the corresponding Nb5Cr superalloy sample can be obtained.

2.2. Materials Characterization

An electronic universal mechanical experimental machine DCS-250kN (Shimadzu, JAPAN) was used to measure the bending strength of $3 \times 4 \times 36$ mm^3 polished Nb5Cr standard specimen by three-point bending method. The effective span is set to 30 mm and the loading rate of the indenter is set to 0.5 mm/min. The bending strength of the material is calculated as shown in formula (1). The bending strength is measured three times to avoid accidental errors.

$$\sigma_f = \frac{3P_f L}{2h^2 W},\qquad(1)$$

where σ_f is the bending strength (mm); P_f is the load when the material is broken (N); L is the effective span (mm); h is Sample height (mm); W is sample width (mm).

The fracture toughness of the material was also tested on the standard sample of $2 \times 4 \times 24$ mm^3 with the same equipment, the fulcrum span was set at 16 mm, and the loading speed was set at 0.05 mm/min. The calculation method is shown in formula (2). Repeat the measurement three times to reduce the accidental error of the K_{IC}.

$$K_{IC} = Y \frac{3PL}{2B\omega^2} \sqrt{a},\qquad(2)$$

where K_{IC} is the Fracture toughness factor; P is the load when the material is broken (N); L is the effective span (mm); B is Sample width (mm); ω is Sample height (mm); a is the sample notch depth (mm); Y is the form factor, which can calculated by Eq. (3):

$$Y = \frac{1.1225\sqrt{\pi}}{\beta^{3/2}}$$
$$\times \left[\frac{5}{8} - \frac{5}{12}\alpha + \frac{1}{8}\alpha^3\beta^6 + \frac{3}{8}\exp\left(-\frac{6.1342\alpha}{\beta}\right) \right].\qquad(3)$$

This experiment used an X-ray diffractometer (XRD) of the type Empyrean (Panalytical, Netherlands) equipped with monochromatic $K\alpha$ radiation at a scan speed of 8°/min, in the 2θ range of 10°−70°. It was used for phase identification and simple quantitative analysis. The instrument has high information acquisition efficiency, sensitivity and measurement accuracy. Scanning electron microscopy(SEM) was performed on a VEGA3(TESCAN, Czech Republic) equipped with energy dispersive spectroscopy(EDS). It is used to identify morphology and element distribution by secondary electron. Secondary electron image resolution: magnification: 2.5−1 000 000; acceleration voltage: 0.2−30 kV, ion imaging resolution: 4 nm (30 kV) Acceleration voltage: 0.2−30 kV, Electron beam current 1 pA−2 μA. The oxidation process was simulated by Muffle furnace, and the surface morphology, post-oxidation phase and morphology of Nb5Cr superalloy were analyzed by SEM and XRD.

2.3. Static Oxidation Test

The static oxidation performance of $3 \times 4 \times 36$ mm Nb5Cr superalloy in Muffle furnace at 800, 1000 and 1200°C for 20 min was tested, and the unoxidized Nb5Cr superalloy was used as the control sample. After the furnace is heated to a predetermined temperature, the direct Nb5Cr sample is placed in the furnace, and then taken out at the same temperature for 20 min. The oxidation behavior of the Nb5Cr sample is compared by observing the surface morphology, mass changes and phase changes of the sample. At the same time, the phase and surface morphology of Nb5Cr superalloy before melting were observed as a contrast.
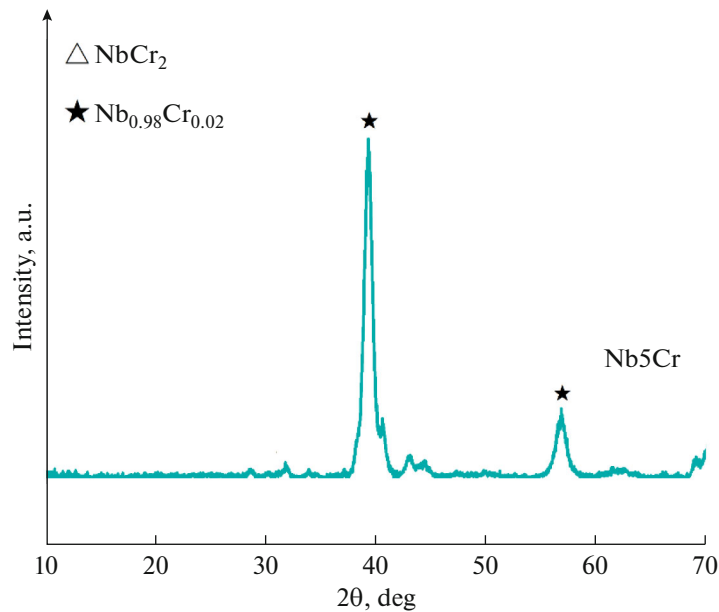
Fig. 1. XRD pattern of Nb5Cr superalloy.

3. RESULTS AND DISCUSSION

3.1. Structure and Mechanical Properties Characterization of Nb5Cr Superalloy

The XRD analysis of Nb5Cr superalloy is shown in Fig. 1. The phase composition shows that the Nb5Cr superalloy is mainly composed of $NbCr_2$ phase and $Nb_{0.98}Cr_{0.02}$ phase. Among them, $Nb_{0.98}Cr_{0.02}$ phase is the main component.

The XRD peak shape is inconsistent with the Nb metal peak shape. Combined with the PDF card, it is inferred that Cr changes the crystal structure of Nb through solid solution in Nb, making its lattice constant increase. In addition, Cr also forms a partial $NbCr_2$ phase with Nb, which is not completely in solid solution form in the Nb matrix.

The three-point bending test results of the standard sample of Nb5Cr superalloy are shown in Table 1, and the Nb5Cr superalloy obtained by the experiment shows a good bending strength. Three point bending test shows that the bending strength of the material is once higher than 250 MPa, It showed good strength.

Table 1. Sample's bending strength of Nb5Cr superalloy

Sample number	σ_f, MPa
01	255.61
02	282.62
03	265.34
04	257.88
05	267.24

The K_{IC} calculation results of Nb5Cr are shown in Table 2. The fracture toughness of the superalloy is close to that of H11 casting die steel [21, 22], and it can also resist certain impact as a die in the casting process.

3.2. High Temperature Oxidation Behavior of Nb5Cr Superalloy

We tested the oxidation behavior of Nb5Cr superalloy at 800, 1000 and 1200°C for 20 min, and recorded the mass changes during static oxidation respectively, as shown in Table 3.

Table 2. Sample's fracture toughness of Nb5Cr superalloy

Sample number	K_{IC}, MPa/m$^{1/2}$
01	36.72
02	35.83
03	35.84
04	36.88
05	35.24

Table 3. Mass change of superalloy before and after 20 min static oxidation

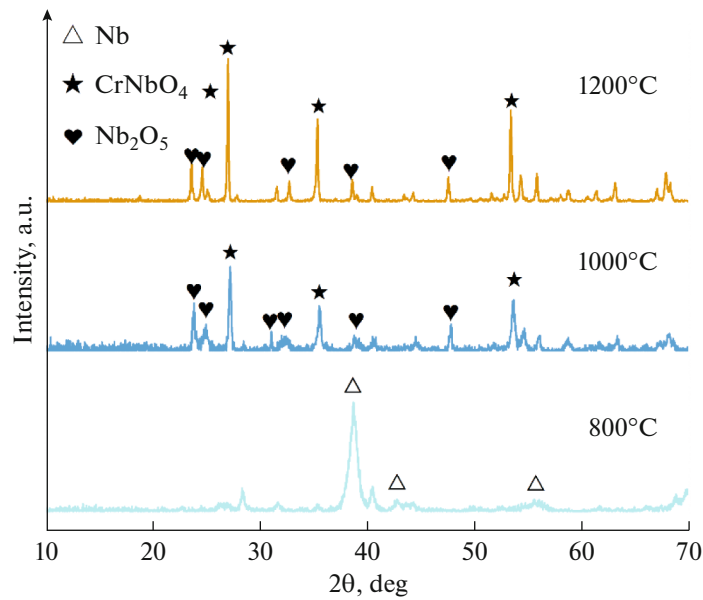| Temperature	Before oxidation mass, g	After oxidation mass, g
800°C	3.79	3.82
1000°C	3.80	3.91
1200°C	3.79	3.83

Fig. 2. XRD pattern of Nb5Cr after static oxidation at different temperatures.

As can be seen from Fig. 2, at 800°C static oxidation, the original peak value shifts to the left, which means the reduction of the original lattice constant. Combined with PDF card analysis, Cr single phase is formed at this time. This also shows that the $Nb_{0.98}Cr_{0.02}$ phase is a low temperature stable phase, and during the static oxidation process, Cr element will be dissolved out of the Nb matrix. At 800°C, a small amount of $NbCr_2$ remains, which indicates that $NbCr_2$ is still stable at this temperature. The XRD peaks change obviously after oxidation at 1000°C. The peak of metal Nb is almost undetectable on the surface, and becomes two phases of $CrNbO_4$ and Nb_2O_5.

Fig. 3. XRD pattern of the matrix after oxidation at 1200°C.

At 1200°C, the content of $CrNbO_4$ increases. This makes the ratio of Cr to Nb in the surface oxide significantly increase, which has exceeded the ratio of Cr to Nb in the matrix. Therefore, we speculated that at 1200°C, Cr element moved from the interior to the surface, forming a surface oxidation shell to protect the matrix.

After the Nb5Cr oxide layer oxidized at 1200°C was stripped and polished, the X-ray diffraction experiment was conducted, as shown in Fig. 3. After the static oxidation process, the Cr element below the surface still formed a solid solution structure with the Nb matrix. The solid solution of Cr element below the surface is higher. It shows that the diffusion rate of the surface Cr element is faster at high temperatures, forming a gradient structure from the surface to the interior and the concentration of Cr element from high to the end.
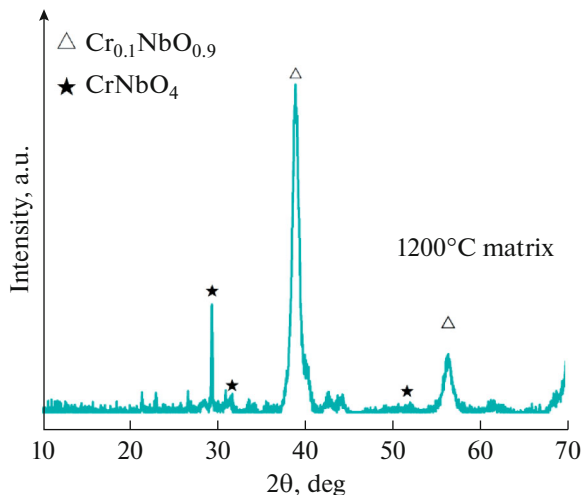
According to the images in Figs. 4a–4c, no obvious fluctuation occurred on the surface during the static oxidation experiment at 800°C, while only a small amount of foaming occurred on the surface with high magnification. It can be judged that at this temperature, Nb5Cr superalloy does not appear obvious oxidation, only Cr element has a dissolving phenomenon. The temperature can be maintained in a stable state for a long time. From the (d) (e) (f) image, it can be seen that Nb5Cr superalloy after oxidation at 1000°C, there is an obvious roughness under the low power microscope, and energy spectrum analysis shows that the surface oxygen content increases significantly. It can be seen from the energy spectrum that there is no obvious accumulation of Cr element on the surface. In combination with XRD analysis in Fig. 2, it is shown that $CrNbO_4$ phase is mainly formed on the surface, so
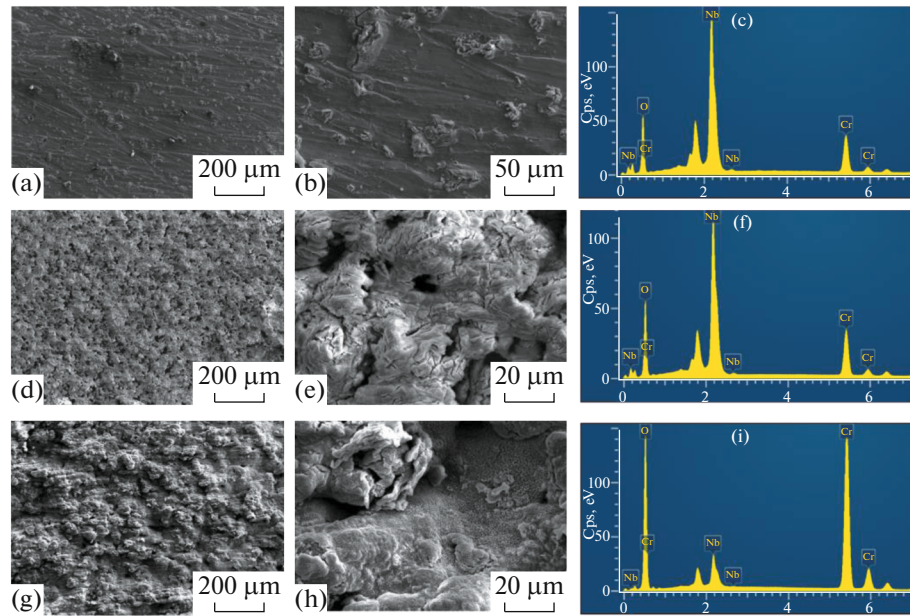
Fig. 4. SEM image and EDS analysis of Nb5Cr superalloy after static oxidation with different temperature: (a), (b), (c) 800; (d), (e), (f) 1000; (g), (h), (i) 1200°C.

the surface oxidation process at this temperature is mainly the co-oxidation of Nb and Cr elements. It can be seen from the (g, h) (i) image that after oxidation at 1200°C, there are obviously large particles on the surface of Nb5Cr superalloy, and the energy spectrometer also shows that the content of Cr on the surface increases sharply while the content of Nb decreases significantly. It is proved that the enrichment effect of Cr element appears on the surface, and the oxide shell of Nb−Cr is formed, which has a full protective effect on the metal matrix.

CONCLUSIONS

In this paper, Nb5Cr superalloy was prepared by vacuum hot pressing sintering method, and its mechanical properties and oxidation behavior were characterized. The superalloy shows good rigidity and toughness. Its bending strength exceeds 250 MPa, and the fracture toughness index K_{IC} exceeds 35 MPa/m$^{1/2}$. The static oxidation results show that at 800°C, Cr element comes out of the low temperature phase, and at 1000°C, there is a more violent oxidation on the surface, and the smooth surface appears fluctuation.

A certain amount of $NbCrO_4$ phase was oxidized and coated on the substrate. At 1200°C, the diffusion of Cr element is more intense, the surface fluctuation is very intense, and the content of $NbCrO_4$ is greatly increased, forming a protective shell that is easy to peel off, and playing a good role in protecting the matrix. Therefore, the material has suitable strength and toughness, can resist the external material depth in the high temperature environment of 1200°C, and can rely

on the characteristics of its surface oxide film easy separation, to provide a good mold for the casting release process.

CONFLICT OF INTEREST

As author of this work, I declare that I have no conflicts of interest.

REFERENCES

1. Cemernek, D. et al., Machine learning in continuous casting of steel: a state-of-the-art survey, *J. Intell. Manuf.,* 2022, vol. 33, no. 6, pp. 1561−1579.

2. Qian, F. et al., Corrosion mechanism of BN-ZrO$_2$ based side-dam by molten steel, *J. Eur. Ceram. Soc.,* 2022, vol. 42, no. 9, pp. 3996−4005.

3. Chen, J. et al., Formation of ferro-spinel layer at the corroded interface between Al$_2$O$_3$-spinel refractory and molten steel in RH refining ladle, *J. Am. Ceram. Soc.,* 2021, vol. 104, no. 11, pp. 6044−6053.

4. Pivano, A., Experiments on interactions of molten steel with suboxidized corium crust for in-vessel melt retention, *Nucl. Eng. Des.,* 2019, vol. 355, no. 8.

5. Nefedov, A.V., Novikov, E.G., Chicheneva, O.N., Gorovaya, T.Yu., and Fortunatov, A.N., Development of system for centralized supply of release agent to

molds of casting facilities of CJSC RIFAR, *Steel Transl.,* 2022, vol. 52, no. 7, pp. 651−655.

6. Hamasaiid, A. et al., Effect of mold coating materials and thickness on heat transfer in permanent mold casting of aluminum alloys, *Metall. Mater. Trans. A,* 2007, vol. 38, no. 6, pp. 1303−1316.

7. Li, T. et al., Formation of liquid-phase isolation layer on the corroded interface of MgO/Al_2O_3−SiC−C refractory and molten steel: Role of SiC, *J. Am. Ceram. Soc.,* 2021, vol. 104, no. 5, pp. 2366−2377.

8. Schurmann, D., Glavinić, I., Willers, B., Timmel, K., and Eckert, S., Impact of the electromagnetic brake position on the flow structure in a slab continuous casting mold: An experimental parameter study, *Metall. Mater. Trans. B,* 2020, vol. 51, no. 1, pp. 61−78.

9. Louhenkilpi, S., Continuous casting of steel, in *Treatise on Process Metallurgy,* Elsevier, 2014, pp. 373−434.

10. Gorr, B. et al., A new strategy to intrinsically protect refractory metal-based alloys at ultra-high temperatures, *Corros. Sci.,* 2020, vol. 166, p. 108475.

11. León-Cázares, F.D., Monni, F., Jackson, T., Galindo-Nava, E.I., and Rae, C.M.F., Stress response and microstructural evolution of nickel-based superalloys during low cycle fatigue: Physics-based modelling of cyclic hardening and softening, *Int. J. Plast.,* 2020, vol. 128, p. 102682.

12. Senkov, O.N., Gorsse, S., and Miracle, D.B., High temperature strength of refractory complex concentrated alloys, *Acta Mater.,* 2019, vol. 175, pp. 394−405.

13. Fu, T. et al., Microstructure and oxidation behavior of anti-oxidation coatings on mo-based alloys through HAPC process: A review, *Coatings,* 2021, vol. 11, no. 8, p. 883.

14. Fu, T. et al., Oxidation protection of high-temperature coatings on the surface of Mo-based alloys—A review, *Coatings,* 2022, vol. 12, no. 2, p. 141.

15. Zhu, Y., Schwam, D., Wallace, J.F., and Birceanu, S., Evaluation of soldering, washout and thermal fatigue resistance of advanced metal materials for aluminum die-casting dies, *Mater. Sci. Eng., A,* 2004, vol. 379, nos. 1−2, pp. 420−431.

16. Dovbenko, O.I., Bondar, A.A., Velikanova, T.Ya., and Sleptsov, S.V., The (Cr) + (NbC) quasi-binary eutectic in the Cr−Nb−C system, *Powder Metall. Met. Ceram.,* 2000, vol. 39, nos. 5−6, pp. 256−261.

17. Jiang, W., Li, M., Sha, J., and Zhou, C., Microstructure and oxidation resistance of composition gradients Nb−Si based alloy thin film, *Mater. Des.,* 2020, vol. 192, p. 108687.

18. Kuo, Y.-L., Hayashi, S., and Kakehi, K., The effects of Nb addition on the oxidation behavior of Ni−Fe−Cr alloys at 800°C, *Oxid. Met.,* 2021, vol. 95, no. 1−2, pp. 189−202.

19. Zhang, X. et al., Characterization of thermophysical and mechanical properties of hafnium carbonitride fabricated by hot pressing sintering, *J. Mater. Res. Technol.,* 2023, vol. 23, pp. 4432−4443.

20. Bocanegra-Bernal, M.H., Hot Isostatic Pressing (HIP) technology and its applications to metals and ceramics, *J. Mater. Sci.,* 2004, vol. 39, no. 21, pp. 6399−6420.

21. Leskovšek, V., Correlation between the K_{IC}, the HRc and the charpy V-notch test results for H11/H13 hot-work tool steels at room temperature, *Steel Res. Int.,* 2008, vol. 79, no. 4, pp. 306−313.

22. Leskovšek, V., Šuštaršič, B., and Jutriša, G., The influence of austenitizing and tempering temperature on the hardness and fracture toughness of hot-worked H11 tool steel, *J. Mater. Process. Technol.,* 2006, vol. 178, nos. 1−3, pp. 328−334.