

High Temperature Oxidation of Cr-25Nb Alloy Synthesized by Mechanical Alloying and Hot Pressing

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Abstract: Cr-25Nb alloy was prepared by mechanical alloying (MA) and hot pressing (HP), and the influences of milling time on the density and oxidation property of samples were investigated. During the studying of the effect of different ball grinding time on oxidation resistance, we discover that the relative density of the Cr-25Nb alloy would increase with the ball grinding time increasing, but when it was oxidized at 1200°C for 5 h in the air, the gain weight rate of the oxidized samples does not only decreased with the ball milling time increasing. In the period of MA 0 to 20 h, the gain weight rate of the oxidized samples reduced with the ball milling time increasing. When the ball milling time further increased, the gain weight rate increased and the oxidation resistance of samples went down. Thus, the oxidation resistance of sample of MA 20 is best. The oxide layer appearance of MA 15 h, MA 20 h, MA 35 h were observed by SEM, respectively. It is found that the oxide layer thickness of specimen of MA 20 hour is thinnest. From the result of EDS and XRD, Cr₂O₃ was formed on the outer oxide layer. However, the oxides in the inner layer were mainly Cr₂O₃ and CrNbO₄.

Keywords: Cr-25Nb alloy, mechanical alloying, oxidation behavior.

1. INTRODUCTION

The Laves phase NbCr₂ alloy has a great potential for high temperature structural applications due to its high melting temperature, appreciable creep resistance, relatively low density (7.7g/cm³), and high strength [1-5]. However, there has been a wide research activity in intermetallics in the last years, commercial utilization of NbCr₂ was hampered because it is very brittle at low temperature, like other intermetallics. Therefore, many researches have been done to improve fracture toughness of NbCr₂ in material design and preparing technique. As reported by Takasugi *et al.* [6-8], one route to improve the deformability of NbCr₂ is through alloy additions. For example, the addition of Mo to NbCr₂ Laves phase compound was shown to be effective in improving the compressive deformability at high temperature [6]. In the past few decades, some attempts to improve the mechanical properties of NbCr₂ Laves phase alloys have been performed, such as the ductile-phase [9], addition of other elements [10-12], and so on. Especially, the ambient fracture toughness has been achieved 20MPa • m^{1/2} for Ti-modified Nb(Cr)-NbCr₂ in-situ composites [9]. However, although the Nb(Cr, Ti) matrix phase is ductile, it is not oxidation resistant and, furthermore, is likely susceptible to oxygen embrittlement during elevated temperature exposure in air [13].

A number of studies mentioned above have been conducted using arc-melted buttons. It is well known that mechanical properties of alloys are affected by adopted fabrication technique. Mechanical alloying (MA) has shown to be a promising synthesis technique for materials with high-melting temperature [14]. MA is a high-energy ball milling technique for production of microscopically homogeneous

materials starting from blended elemental powder mixtures. Many high temperature melting intermetallics that are difficult to prepare by conventional processing techniques could be easily synthesized with better mechanical properties by the MA process followed by hot pressing (HP). In this method, it is easy to realize the approaches of controlling the microstructure to enhance the ductility of Laves phase NbCr₂. There are a large number of reports on behavior of conventionally cast NbCr₂ in the past decades, but few studies have been carried out on MA and HP materials consolidated [15, 16].

In this study, the fabrication of Cr-25Nb alloy by HP from mechanically alloyed powders and the influence of milling time on the oxidation resistance of alloy at 1200°C were investigated.

2. EXPERIMENTAL

High-purity crystalline powders of Nb (99.9%, -200mesh) and Cr (99.9%, -200mesh) in a molar ratio of 1: 3 (i.e., 75Cr-25Nb) were milled in vacuum for periods up to 50 h. The milling was carried out in a planetary ball-mill (QM-1SP) with both vial and balls made of hardened steel. To reduce oxidation of powders during mechanical alloying, the mechanical alloying was performed in vacuum. Milling parameters such as ball-to-powder mass ratio (13: 1) and speed rotation (400 rpm) were kept constant throughout the experiments. During the milling, the powders are liable to adhere to the wall of the pot due to the so called cold welding effect, causing the decreased milling efficiency or even uncompleted milling. The pot was therefore taken into a glove box every 5 h to remove the adherent powders from the pot wall and to break the agglomerated powders. The powders were taken in a graphite mould with 14 mm diameter and hot-pressed under 45 MPa for 0.5 h at 1523 K in conditions of vacuum.

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The density of the hot pressed samples was determined by the immersion method in distilled water, based on Archimedes principle. The relative density has been calculated by relating these values to the theoretical density. The powder samples were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Cross-section of the oxidized specimens was investigated by SEM. XRD data was collected at a slow scan rate of $0.005^\circ/\text{s}$ for the careful determination of average crystallite size and internal strain using Williamson-Hall method and the method is suggested by Ungar *et al.* [17, 18].

Oxidation property was evaluated using the hot pressing specimens. Their surfaces were abraded on fine SiC paper, and were washed in running water and ultrasonically cleaned with alcohol. Oxidation tests were performed in air at 1473 K until 5 h. The samples were placed in an alumina crucible (30mm diameter), and the weight changes were monitored by a balance of Sartorius Type BT224S (sensitivity 0.1mg).

3. RESULTS AND DISCUSSION

3.1. Analysis of Powders

The diffraction patterns of elemental mixture powders and as-milled powders are shown in Fig. (1). At the early stage of milling, crystalline Nb and Cr peaks were observed. It can be seen that mechanical alloying leads to significant broadening of X-ray diffraction peaks after 20 h milling, indicating the formation of fine grain and a high density of defects caused by large local strains in the powder particles (as shown in Fig. 2a, b). The broadening of X-ray diffraction peaks is associated with the refinement of grain size. At the very beginning of milling, MA leads to a fast decrease of the grain size. XRD patterns do not exclude an amorphous structure (especially MA 35).

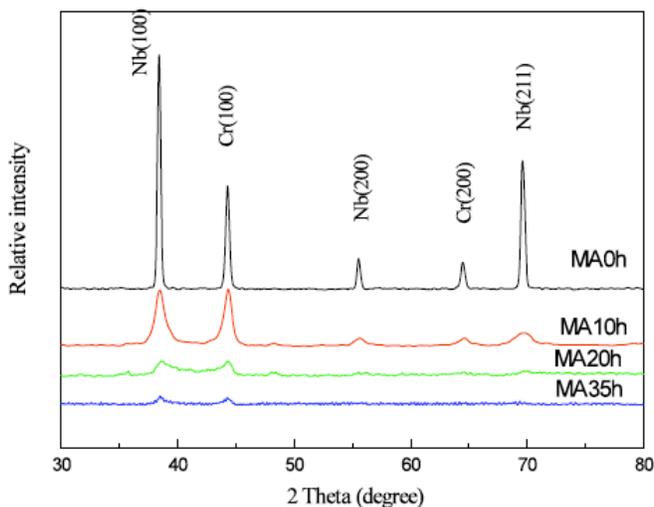


Fig. (1). X-ray diffraction patterns of elemental mixture powders and as-milled powders.

Because a part of Nb atoms dissolved into the Cr lattices, the peaks of Cr were lightly shifted to low angle (the lattice constants changed from 2.8845 \AA to 2.8901 \AA , calculated from XRD results) and the Nb peaks were weakened. It agrees with the previous results that supersaturated solution Cr(Nb) had been formed by mechanical alloying.

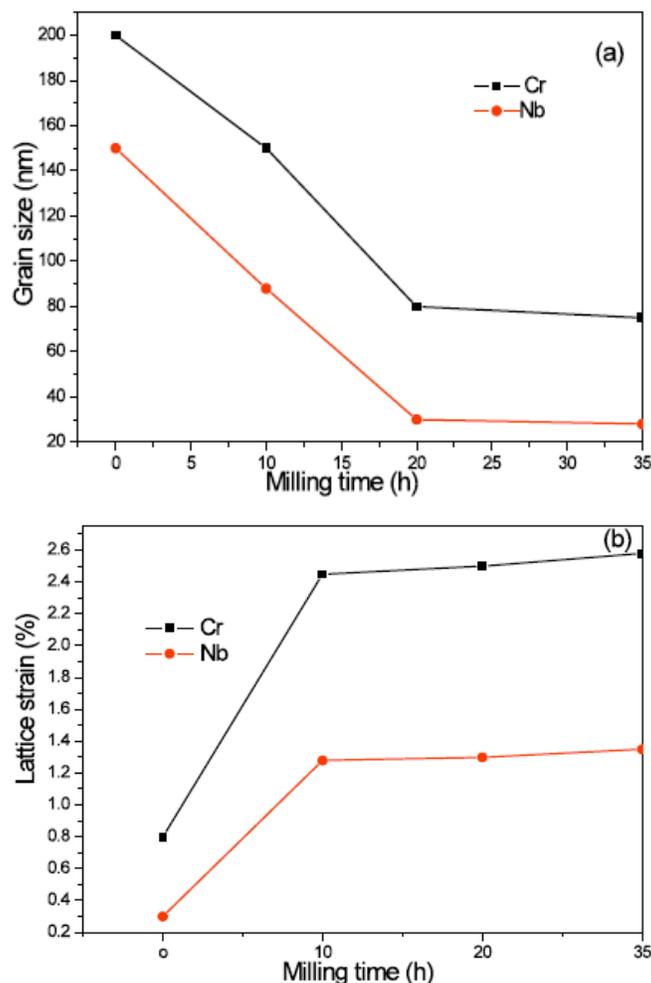


Fig. (2). Variation of grain size (a) and lattice strain (b) with MA time.

The typical SEM micrograph of elemental mixture powders is shown in Fig. (3a). The powders have irregular shapes and various sizes. The mean size of particles is about $20 \mu\text{m}$. Fig. (3b) shows the micrograph of as-milled powders. It can be seen that the size of particles is about $3 \mu\text{m}$, which tend to be uniform. After 20 h milling, the particles are refined, but some of particles appear large blocks. During the ball milling, the Nb particles were collided into slices due to their excellent ductility. The Nb slices gradually turn large through welding fine Cr particles around them. Though refining action occurs simultaneously, the welding plays a dominant role in this procedure. The milled powders are more homogenous than elemental powders from the EDX analysis. The distributions of elements of Nb and Cr are similar for all milled powders.

3.2. Density of Hot-Pressed Samples

Fig. (4) shows the influence of milling time on the relative density of samples. It can be clearly seen that all of the densities of the samples is above 94% of the theoretical density of Cr-25Nb and the relative densities increase with the milling time increasing. Till to 50 h, the relative density is up to 98%. The results indicate the specimens are more and more compact with longer milling time under the same hot

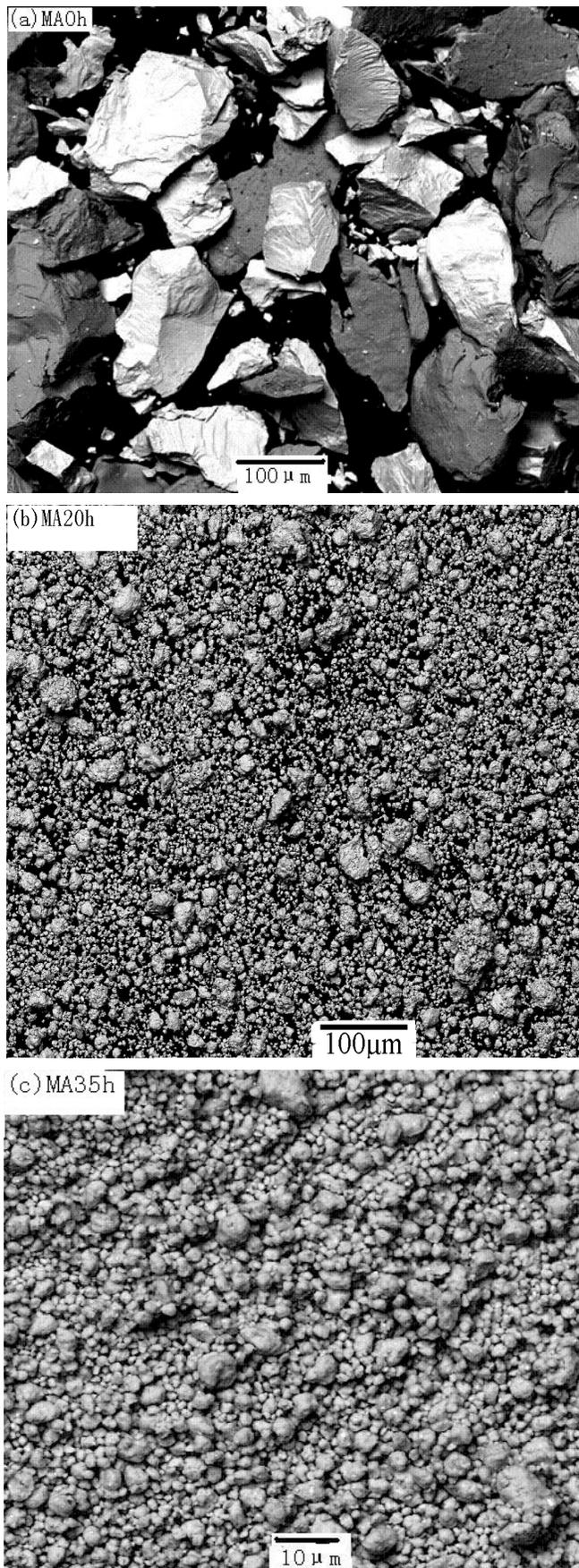


Fig. (3). The SEM micrographs of powders. (a) Elemental powders; (b) ball milling for 20 h; (c) ball milling for 35h.

pressing condition. The increase of densities is possibly attributed to the powders refined with the milling time increasing, the particles are smaller, which leads to easy diffusion in the hot pressing process. Consequently, the relative densities increase with the milling time increasing.

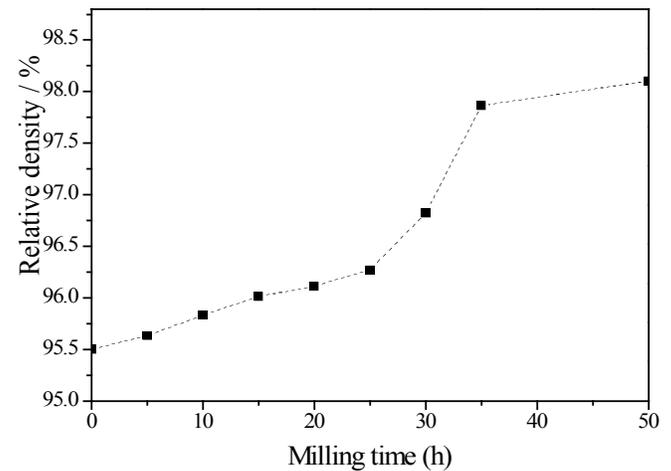


Fig. (4). Relative density of samples as a function of milling time.

3.3. Oxidation

Fig. (5) shows the influence of milling time on the weight changes of Cr-25Nb alloys in air at 1473K for 5h. As can be seen from Fig. (5), the weight gain reduces and reaches its minimum when the milling time is for 20h, followed increase. This can be explained by the following: Firstly, Kofstad and Lillerud [19] considered the microcracks transport processes are concluded to be significant during the initial oxidation period. However, as have been known the density of specimens increase with increasing milling time during the hot pressing process, seen in Fig. (4). This is attributed to that there are few microcracks, that is to say few diffusion paths for Cr or Nb and oxygen. So, the weight gain reduces with increasing the density of specimens. Secondly, mechanical alloying can be used to produce materials with extremely fine grain sizes. The most direct effect of the strong reduction of the grain size obtainable by this method is the appearance of large concentrations grain boundaries that act as diffusion paths and increase the rate transportation of the alloy components in the presence of chemical potential gradients. In addition, a possible additional effect of mechanical alloying in the case of Cr-Nb alloys is related to an increase of the mutual solubility of the alloy components, as observed in a number of cases. This trend to reduce the critical content of the most reactive component Cr required to sustaining the exclusive external growth of its oxide. All these factors can contribute to provide a more efficient supply of Cr to the alloy/scale interface needed to form and to maintain protective external Cr_2O_3 scales. However, in the early stages (transient oxidation) before the steady-state scale is achieved, both Cr and Nb oxidize. With the reducing of the grain size, the grain boundary diffusion of Nb is enhanced. Based on the aforesaid reasons, the weight gain reduces with the milling time increasing before 20h, and followed increase. It can be concluded fine grain can improve the oxidation resistance, and maybe has a negative influence on the oxidation resistance when the grain size is more refined.

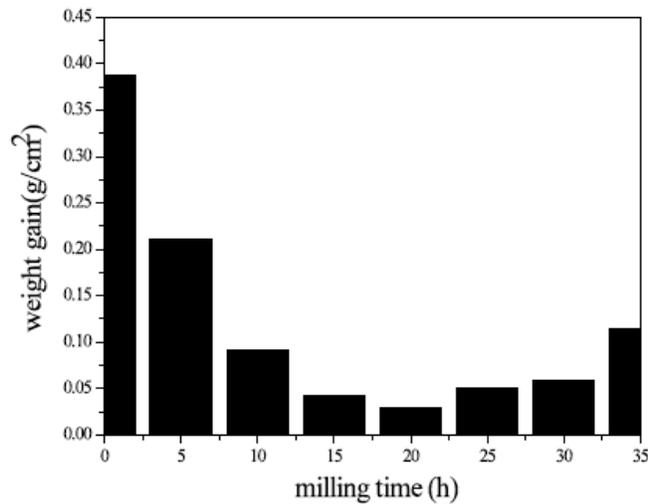


Fig. (5). Weight change versus milling time for Cr-25Nb alloys isothermally oxidized at 1473 K in air.

3.4. SEM Image of Oxidized Specimens

Oxidized cross-section images of Cr-25Nb alloy milled for 15, 20 and 35h, respectively, are shown in Fig. (6). It can be clearly seen that the oxidation layers of the three specimens are like plate and porous. With the EDX, it can be known that the predominately oxide phase of a compositional corresponding to CrNbO₄. The outer scale spilt is Cr₂O₃. The difference in SEM images is the thickness of the oxidized layer. The thick of these three specimens is about 60μm, 40μm and 50μm, respectively. It can be seen that the oxidized layer thick of the as-MAed specimen for 20 h is thinner than those of the other specimen. The result is consistency with the influence of milling time on the weight gain shown in Fig. (5). To interpret this, an effective diffusivity of Cr (D_{eff}) is proposed, which is a summation of lattice diffusivity (D_L) and grain boundary diffusion (D_{GB}) of Cr in the alloy as given below [20]

$$D_{eff} = (1 - f)D_L + fD_{GB} \quad (1)$$

where, f is the area proportion of grain boundary. Assuming the grains are cubic, $f=2\delta/d$ (δ is the GB width and d is the grain size). Also, considering $D_{GB} \gg D_L$, Eq. (1) can be simplified as

$$D_{eff} = D_L + \frac{2\delta}{d} D_{GB} \quad (2)$$

Hence, D_{eff} increases with decreasing d . The enhanced grain boundary diffusion prevented the Cr depletion at the scale-metal interface due to the Cr consumption by oxidation and simultaneously by vaporization.

4. CONCLUSION

In the study of the effect of milling time on oxidation resistance, the results show that the relatively density of Cr-25Nb alloy increases with the ball grinding time increasing. When it was oxidized at 1200°C for 5h in the air, the gain weight rate of the oxidized samples does not only decreased with the ball milling time increasing. In the period of MA 0 to 20 h, the gain weight rate of the oxidized samples reduced with the ball milling time increasing, that is to say, the

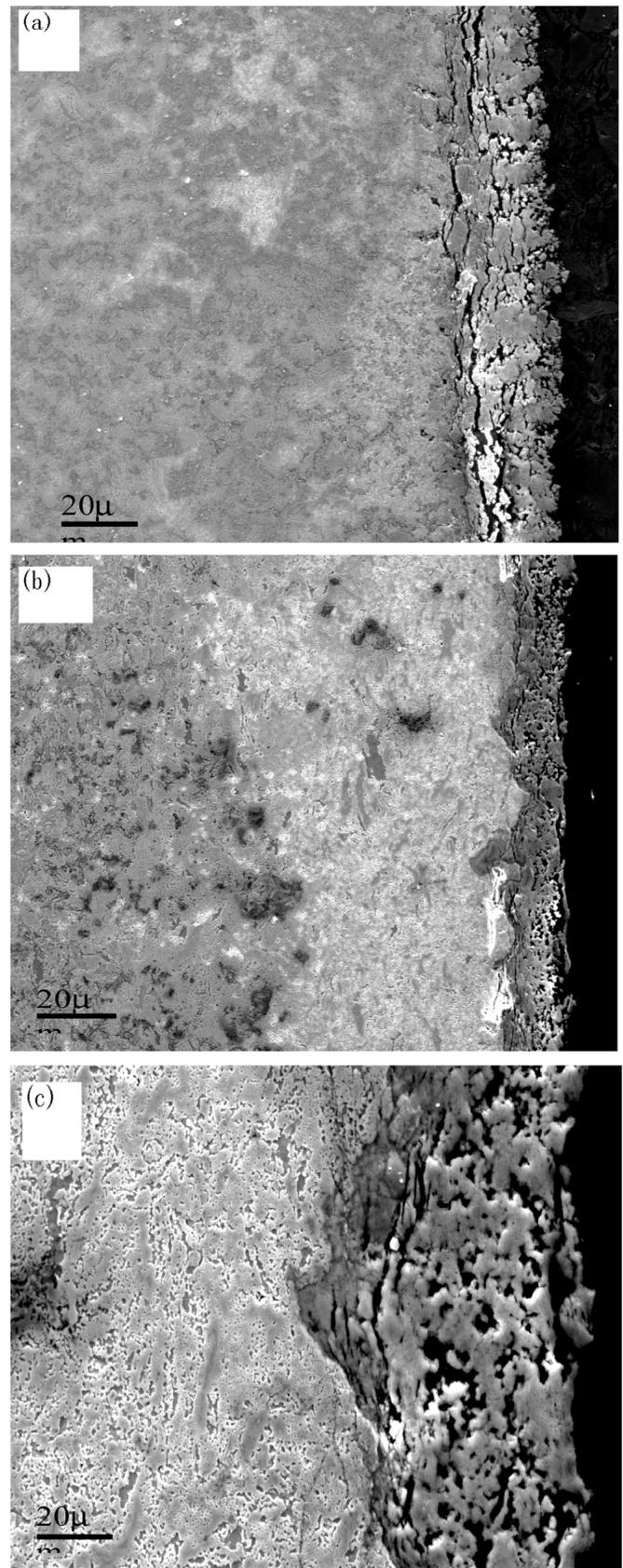


Fig. (6). SEM (secondary electron) cross-section micrograph of the oxide layer of Cr-25Nb alloys milled for (a) 15h; (b) 20h; (c) 35h.

oxidation resistance has been improved. When the ball milling time further increased, the gain weight rate increased and

the oxidation resistance of samples went down. Thus it is showed that the oxidation resistance of sample of MA 20 is best. The oxide layer appearance and the structure of specimens of MA15, MA 20, MA 35 h were observed by SEM, respectively. It is found that the oxide layer thickness of specimen of MA 20 hour is thinnest, which displayed the high temperature oxidation resistance was better; From the results of energy spectrum analysis and XRD, Cr_2O_3 was formed on the outer oxide layer and in the inner layer the oxides were mainly Cr_2O_3 and CrNbO_4 .

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REFERENCES

- [1] Liu CT, Zhu JH, Brandy MP. Physical metallurgy and mechanical properties of transition-metal Laves phase alloys. *Intermetallics* 2000; 8: 1119-29.
- [2] Thoma DJ, Nibur KA, Chan KC. The effect of alloying on the properties of (Nb,Ti) Cr_2 C15 Laves phases. *Mater Sci Eng A* 2002; 329-331: 408-15.
- [3] Bewlay BP, Lewandowski JJ, Jackson MR. Refractory metal-Intermetallic *in situ*. Composites for aircraft engines. *JOM* 1997; 40: 44-67.
- [4] Jiang Chao. Site preference of early transition metal elements in C15 NbCr₂. *Acta Mater* 2007; 55(5): 1599-05.
- [5] Kazantzis VA, Aindow M, Jones IP, Triantafyllidis GKM De, Hosson JTH. The mechanical properties and the deformation microstructures of the C15 Laves phase Cr₂Nb at high temperatures. *Acta Mater* 2007; 55: 1873-89.
- [6] Takasugi T, Yoshida M, Hanada S. Deformability improvement in C15 NbCr₂ intermetallics by addition of ternary elements. *Acta Mater* 1996; 44(2): 669-74.
- [7] Yoshida M, Takasugi T. The alloying effect on the high temperature deformation of Laves phase intermetallic compound. *Mater Sci Eng A* 1997; 234-236: 873-6.
- [8] Takasugi T, Yoshida M. The effect of ternary addition on structure and stability of NbCr₂ Laves phases. *J Mater Res* 1998; 13(9): 2505-13.
- [9] Chan KS. Alloying effects on fracture mechanisms in Nb-based intermetallic *in situ* composites. *Mater Sci Eng A* 2002; 329-31: 513-22.
- [10] Davidson DL, Chan KS. The Effect of microstructure on the fracture resistance of Nb-Cr-Ti *in situ* composites. *Scr Mater* 1998; 38: 1155-61.
- [11] Yao Q, Sun J, Zhang Y, Jiang B. First-principles studies of ternary site occupancy in the C15 NbCr₂ Laves phase. *Acta Mater* 2006; 54: 3585-91.
- [12] Yoshida M, Takasugi T. Phase relation and microstructure of the Nb-Cr-W alloy system. *Mater Sci Eng A* 1999; 262: 107-14.
- [13] Brady MP, Pint BA, Tortorelli PF, Wright IG. High-temperature oxidation and corrosion of intermetallics, In: Schutze M, Ed. Corrosion and environmental degradation of materials. Weinheim, Wiley-VCH, Germany 2001.
- [14] Kang PC, Yin ZD. Phase formation during annealing as-milled powders of molybdenum disilicide. *Mater Lett* 2003; 57: 4412-7.
- [15] Ohta T, Nakagawa Y, Kaneno Y. Microstructures and mechanical properties of NbCr₂ and ZrCr₂ Laves phase alloys prepared by powder metallurgy. *J Mater Sci* 2003; 38: 657-65.
- [16] Davidson DL, Chan KS. Microstructural and fracture characterization of Nb-Cr-Ti mechanically alloyed materials. *Metal Mater Trans A* 2002; 33: 401-16.
- [17] Nie XW, Lu SQ, Wang KL. Phase transformations of NbCr₂ intermetallics produced by mechanical alloying followed by hot-pressing consolidation. *Mater Charact* 2008; 59: 816-9.
- [18] Nie XW, Lu SQ, Wang KL. Effect of mechanical alloying on the structure and properties of NbCr₂ Laves phase fabricated by hot pressing. *Powder Technol* 2008; 184: 333-6.
- [19] Lillerud KP, Kofstad P. On high temperature oxidation of chromium. *J Electrochem Soc* 1980; 127: 2397-409.
- [20] Hart EW. On the role of dislocation in bulk diffusion. *Acta Met* 1957; 5: 597-9.

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