

Microstructure and hardness of binary Cr-Ta alloys^①

ZHANG Zhao-sen(张兆森), HE Yue-hui(贺跃辉),

HUANG Bai-yun(黄伯云), PENG Chao-qun(彭超群)

(State Key Laboratory for Powder Metallurgy, Central South University,
Changsha 410083, China)

[Abstract] The dependences of the microstructure and hardness of the binary Cr-Ta alloys [Cr-9.0, -9.2, -9.4, -9.6, -9.8, and -13.0 Ta] (mole fraction, %) were investigated. When Ta content of the alloy is less than 9.4%, there are primary dendrite grains of a Cr solid-solution phase existing in the matrix of Cr-Cr₂Ta eutectic colonies in the alloy. Moreover, the regular polygon grains of the primary Cr₂Ta Laves-phase are surrounded by the Cr-Cr₂Ta eutectic colony in the hyper-eutectic Cr-9.4% Ta alloys. The scanning electron microphotograph shows that one of the Cr₂Ta phase plates of an eutectic colony always connects with the primary Cr₂Ta Laves-phase grain in a hyper-eutectic alloy. The eutectic colony size of Cr-Ta alloys decreases with increasing Ta. In addition, the macrohardness of Cr-Ta alloys is influenced by the chemical composition at room temperature. The binary eutectic Cr-Ta alloy presents the lowest hardness on a macrohardness scale.

[Key words] binary Cr-Ta alloys; Ta content; Laves-phase

[CLC number] TG 144

[Document code] A

1 INTRODUCTION

The Cr₂X (X= Nb, Zr, Ta, Ti, etc.) Laves-phase based alloys are the candidate materials for the ultrahigh temperature structural applications, because they possess the combination of high-melting points, good oxidation resistance and great high-temperature strength^[1, 2]. However, they are very brittle at room temperature^[3], which prohibits their commercial applications. One of the potential solutions to overcome this brittleness is to fabricate the in-situ composites reinforced by the Laves-phase^[4, 5].

Limited work has been done on the in-situ composites reinforced with Laves-phase, such as Cr-Cr₂Ta and Cr-Cr₂Nb^[6, 7]. The existence of a Cr-Cr₂Ta eutectic reaction provides a good opportunity for the formation of a Cr solid solution matrix composite reinforced by the Cr₂Ta Laves-phase. In addition, the material possesses a high-melting point greater than 1760 °C so that the material shows excellent mechanical properties at high temperatures. The Cr matrix phase exhibits some ductility higher than the Cr₂Ta Laves-phase at room temperature^[8, 9], good oxidation resistance at high temperatures and good corrosion resistance at room and elevated temperatures^[10- 12]. The mechanical properties of the Cr matrix can be further improved by the mechanical treatments and alloying-element additions^[9, 13, 14]. The fracture-toughness improvement of the Cr-Ta alloy could be expected by the introduction of the boundaries between the Cr matrix phase and

Cr₂Ta laves phase, which may deflect the cracks. Thus, the aligned microstructure of Cr-Ta alloys, which will induce a great amount of crack deflection, attracts the researchers' interest. In order to obtain the alloy with an aligned microstructure, it is important to determine the chemical composition of the eutectic Cr-Ta alloy. In this paper, the relationship among the microstructure, hardness, and chemical composition of the binary Cr-Ta alloys was investigated.

2 EXPERIMENTAL

The Cr-Ta alloy samples weighing approximately 70 g were prepared by an arc-melting furnace. High-purity Cr and Ta chips were used as charge materials in order to prevent the effect of impurities on the microstructure of alloys. The nominal chemical compositions of the alloys studied are shown in Table 1. The alloys were inverted and re-melt ten times in a pure argon environment in order to improve the homogeneity of the chemical composition of the materials. During the final solidification of the alloys, the electronic power was reduced slowly during the solidification of the alloys so that a metastable-equilibrium microstructure can be obtained. The total mass loss less than 0.6% (mass fraction, %) of each button-shaped sample, which is mainly due to the evaporation of Cr, was ensured by the correct operations.

Microstructures of the Cr-Ta alloy samples were examined using optical and scanning electron microscopies (SEM: Cambridge Instrument S360). The

Table 1 Nominal chemical compositions of materials studied (mole fraction, %)

Sample number	Chemical composition	Sample number	Chemical composition
1	Cr-9.0% Ta	4	Cr-9.6% Ta
2	Cr-9.2% Ta	5	Cr-9.8% Ta
3	Cr-9.4% Ta	6	Cr-13.0% Ta

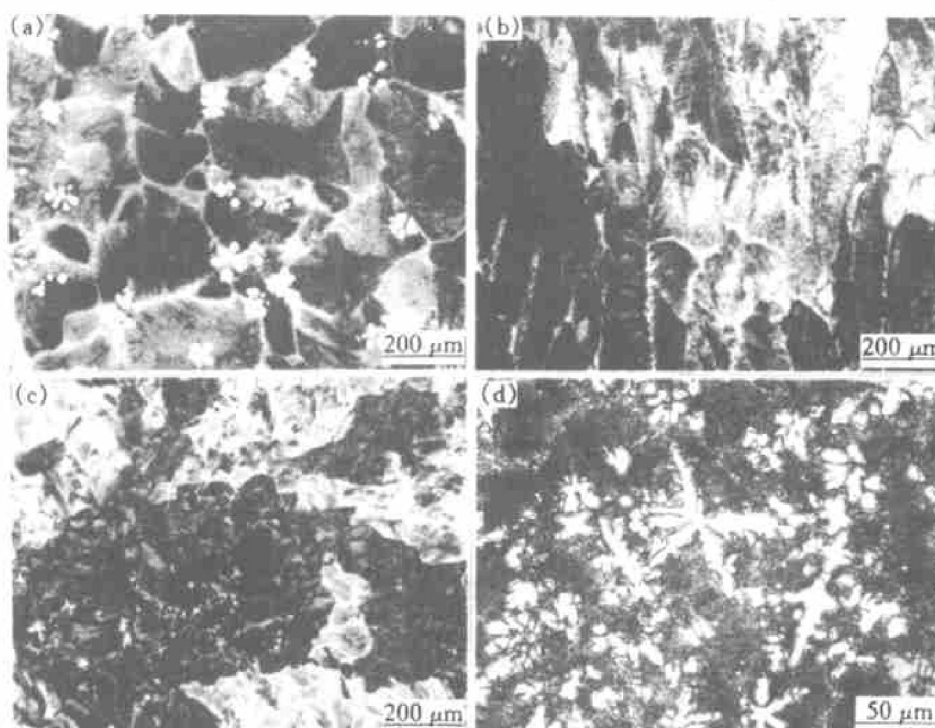
samples for microstructural examinations were cut from the same place of alloy buttons by electrical spark machine, and electrically etched in a solution of 100 g oxalic acid and 1000 mL pure water for 30 s. The chemical compositions of phases were analyzed using the scanning electron microscopy with an energy-dispersion X-ray spectroscopy (EDX). Hardness measurements were conducted on the macrohardness scales using a Micronet 2001 Microhardness Tester.

3 RESULTS

Fig. 1 exhibits the micrographs of the microstructures of the binary Cr-Ta alloys studied. It can be found that the Cr-9.4% Ta alloy presents a full eutectic microstructure which shows mainly a lamella morphology, as shown in Fig. 1(b). When Ta content of the alloys is less than 9.4% Ta (mole fraction, %), the microstructure consists of the primary dendrite grains and the eutectic colonies as shown in Fig. 1(a). The EDX analyses revealed that the primary dendrite grain is a Cr solid solution containing 4% Ta. Thus, the Cr-9.0% and Cr-9.2% Ta alloys were identified to be the hypo-eutectic al-

loys. The amount of the primary dendrite grains decreases with increasing Ta of these hypo-eutectic alloys. However, when the Ta content of Cr-Ta alloy is greater than 9.4%, for example in the Cr-9.6% Ta alloy, the microstructure is mainly composed of the primary regular polygon grains and the eutectic colonies, as shown in Fig. 1(c). The composition analyses explain that this primary phase is a Cr_2Ta Laves phase. Moreover, a large amount of primary Cr_2Ta exists in the as-cast ingot of Cr-13% Ta alloy, as shown in Fig. 1(d), which indicates that the alloy is of typical hypo-eutectic alloy. The amount of the primary Cr_2Ta increases with increasing Ta. At a high magnification, it could be clearly seen that there is a Cr_2Ta phase plate of the eutectic colonies, which always connects with the primary Cr_2Ta grain surrounded by the eutectic colony, as shown in Fig. 2. Fig. 3 shows the dependence of the eutectic microstructure on the chemical composition of the binary Cr-Ta alloys. It demonstrates that the chemical composition of the binary eutectic Cr-Ta alloy is Cr-9.4% Ta, which is in contrast with the literature results of Cr-13% Ta^[15]. The effect of Ta on the average eutectic colony size of the Cr-Ta alloys was studied. It can be observed that the eutectic colony size decreases with increasing Ta. The hyper-eutectic Cr-Ta alloy has the fine microstructure with an average colony size approximate less than 150 μm .

The effect of Ta on the macrohardness of the as-cast binary Cr-Ta alloys is shown in Fig. 4. Compared with hypo- and hyper-eutectic Cr-Ta alloys studied in this paper, the binary eutectic Cr-Ta alloy exhibits a

**Fig. 1** Optical micrographs of as-cast alloys

(a) —Cr-9.2% Ta; (b) —Cr-9.4% Ta; (c) —Cr-9.6% Ta; (d) —Cr-13.0% Ta

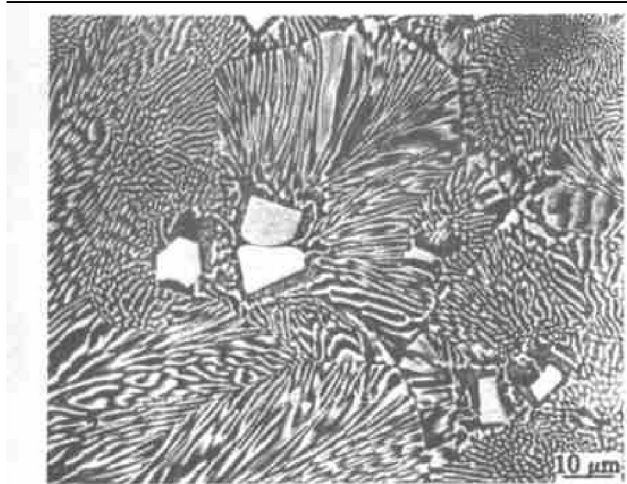


Fig. 2 SEM micrograph of as-cast Cr-9.6% Ta alloy

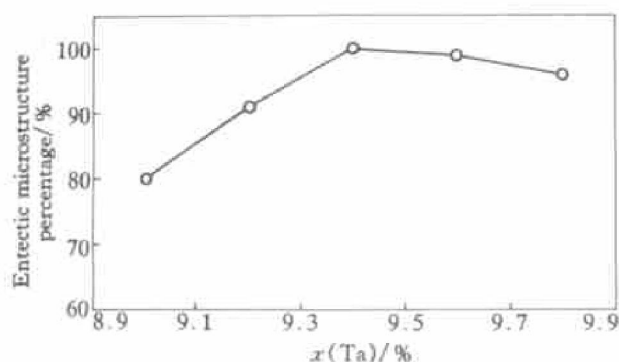


Fig. 3 Dependence of lamellar microstructure on Ta content of Cr-Ta alloys

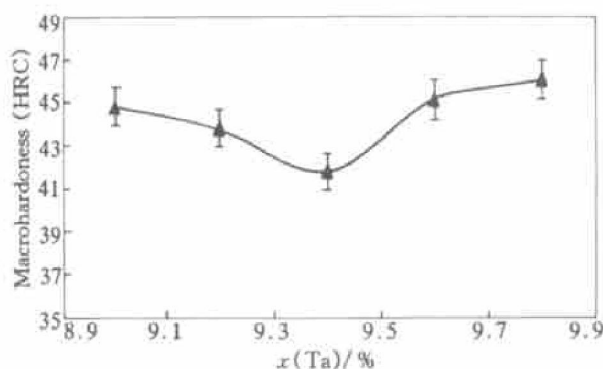


Fig. 4 Effect of Ta on hardness of Cr-Ta alloys

minimum macrohardness. In addition, Ta influences the hardness of both hypo- and hyper-eutectic alloys. The macrohardness of the binary Cr-Ta alloys increases with increasing the primary dendrite phase in a hypo-eutectic Cr-Ta binary alloy or the primary Cr_2Ta Laves phase in a hyper-eutectic alloy, respectively.

4 DISCUSSION

In Refs. [15, 16], the phase diagrams of the binary Cr-Ta alloy and ternary Cr-Ta-Zr alloy were given. They indicated that the binary eutectic Cr-Ta alloy is Cr-13% Ta. However, in this paper, the Cr-

9.4% Ta alloy possesses a full eutectic microstructure, as shown in Fig. 1(b), which means that the accurate chemical composition of binary eutectic Cr-Ta alloy should be considered to be subject to correction.

The eutectic colony size of the binary Cr-Ta alloys studied decreases with increasing Ta. Specially, the hyper-eutectic Cr-Ta alloys possess fine eutectic colonies. It is possible that the primary Cr_2Ta Laves phase could work as the crystallization nuclei for the formation of eutectic colonies of the Cr-Ta alloy during the solidification, as shown in Fig. 2, which promotes the number of eutectic colonies in the binary hyper-eutectic Cr-Ta alloys. Therefore, the eutectic colony size of the binary hyper-eutectic Cr-Ta alloy decreases with increasing primary Cr_2Ta Laves phase.

The binary hypo- and hyper-eutectic Cr-Ta alloys exhibit greater macrohardness than the binary eutectic Cr-Ta alloy, as shown in Fig. 4, which is associated with the strengthening of the Cr solid solution containing Ta in hypo-eutectic alloys and the harder secondary-phase Cr_2Ta Laves grains in hyper-eutectic alloys, respectively.

5 CONCLUSIONS

1) The chemical composition of the binary eutectic Cr-Ta alloy was found to be Cr-9.4% Ta (mole fraction, %), rather than Cr-13% Ta reported in prior literatures. The Cr-Ta alloy with Ta content less than 9.4% is a binary hypo-eutectic Cr-Ta alloy, and the Cr-Ta alloys studied with Ta content greater than 9.4% is a binary hyper-eutectic Cr-Ta alloy.

2) The microstructure of the Cr-Ta alloys with less than 9.4% consists of the primary dendrite grains of a Cr solid solution phase and eutectic colonies. And the microstructure of Cr-Ta alloys with greater than 9.4% was composed of the primary Cr_2Ta Laves phase and eutectic colonies. For the hyper-eutectic Cr-Ta alloys, the eutectic colonies always nucleate attaching self to the primary Cr_2Ta phase grains.

3) The eutectic colony size of the binary Cr-Ta alloys decreases with increasing Ta. The hyper-eutectic Cr-Ta alloy exhibits fine microstructures due to the existence of the primary Cr_2Ta Laves phase grain which could act as the crystallization nuclei of eutectic colonies.

4) Among the Cr-Ta alloys studied in this work, the macrohardness of the binary eutectic Cr-Ta alloy is the lowest.

[REFERENCES]

- [1] Livingston J D. Refractory and silicide laves phases, high temperature silicides and refractory alloy [A]. Brinant C L, et al. Proceedings of Materials Research Society

- Symposium [C]. Pittsburgh: MRS, 1994. 395– 406.
- [2] Kumar K S. Laves phase-based materials: microstructure, deformation modes and properties, high-temperature ordered intermetallic alloy [A]. Koch C C, et al. Proceedings of Materials Research Society Symposium [C]. Pittsburgh: MRS, 1997. 677– 688.
- [3] Zhu J H, Liu C T, Liaw P K. Phase stability and mechanical behavior of NbCr₂ based Laves phases [J]. Intermetallics, 1999, 7(9): 1011– 1016.
- [4] Bewlay B P, Sutliff J A, Jackson M R, et al. Microstructural and crystallographic relationships in directionally solidified Nb-Cr₂Nb and Cr-Cr₂Nb eutectics [J]. Acta Metallurgica et Materialia, 1994, 42(8): 2869– 2878.
- [5] Anderson K R, Groza J R, Dreshfield R L, et al. High performance dispersion strengthened Cu-8 Cr-4 Nb alloy [J]. Metall Mater Trans, 1995, 26(9A): 2197– 2206.
- [6] Takeyama M, Liu C T. Microstructure and mechanical properties of Laves-phase alloys based on Cr₂Nb [J]. Mater Sci Eng, 1990, 132A: 61– 66.
- [7] Liu C T, Tortorelli P F, Horton J A, et al. Effect of alloy additions on the microstructure and properties of Cr-Cr₂TaNb alloys [J]. Mater Sci Eng, 1996, 214A: 23– 32.
- [8] Kumar K S, Liu C T. Precipitation in Cr-Cr₂Nb alloy [J]. Acta Mater, 1997, 45(9): 3671– 3686.
- [9] Matsumoto Y, Fukumori J, Morinaga M, et al. Alloying effect of 3D transition elements on the ductility of chromium [J]. Scripta Materialia, 1996, 34(11): 1685 – 1689.
- [10] Skeldon M, Calvert J M, Lees D G. Investigation of the growth mechanism of Cr₂O₃ on pure chromium in 1 ATM oxygen at 950 °C [J]. Oxidation Metallurgy, 1987, 28(1– 2): 109– 125.
- [11] Navinsek B, Panjan P. Oxidation resistance of PVD Cr, Cr-N, Cr-N and Cr-N-O hard coatings [J]. Surface and Coating Technology, 1993, 59(1– 3): 244– 248.
- [12] Zheng X G, Young D J. High temperature corrosion of pure chromium in CO-CO₂-2SO₂-N₂ [J]. Corrosion Science, 1994, 36(12): 1999– 2015.
- [13] Morinaga M, Nambu T, Morinaga M, et al. Effect of surface imperfections on the ductility of pure chromium [J]. Journal of Materials Science, 1995, 30(4): 1105 – 1110.
- [14] Provenzano V, Valiev R, Rickerby D G, et al. Mechanical properties of nanostructured chromium [J]. Nanostructured Materials, 1999, 12(5): 1103– 1108.
- [15] Villars P, Prince A, Okamoto H. Handbook of Ternary Alloy Phase Diagrams [M]. Metals Park: American Society for Metals, 1995. 9254.
- [16] Massalski T B, Murray J L, Bennett L H, et al. Binary Alloy Phase Diagrams [M]. Metals Park: American Society for Metals, 1986. 867.

(Edited by HE Xue-feng)