

Processing and Microstructure of Cr-Ta and Cr-Ta-Mo Composites Reinforced by the Cr₂Ta Laves Phase *

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Abstract

The Cr-Ta alloy with an eutectic structure has a good combination of high strength and oxidation resistance at elevated temperatures up to 1,200°C. It is an ideal candidate for ultrahigh-temperature applications. However, the material shows low ductility and fracture toughness at room temperature. An effective way to improve the ductility and fracture toughness is to obtain an aligned microstructure of eutectic Cr-based alloys, using a directional-solidification (DS) process, in which the feed materials with eutectic compositions are preferred. In the present work, a quantitative technique was developed to assist in monitoring and controlling the composition of the Cr-based alloys throughout the processing at elevated temperatures. The eutectic compositions of the Cr-Ta and Cr-Ta-Mo alloy systems were determined to be Cr-9.7 at. % (atomic percent) Ta and Cr-9.7 at. % Ta-1.0 at. % Mo, respectively.

* Research sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U. S. Department of Energy, under subcontract, 11X-SP173V, to the University of Tennessee, and by the AR&TD Materials Program, under contract with DE-AC05-000R22725 with UT-Battelle, LLC.

Introduction

The Cr_2X ($\text{X} = \text{Ti}, \text{Hf}, \text{Zr}, \text{Nb}, \text{Ta}, \text{etc.}$) Laves-phase alloys are candidate materials for applications at temperatures greater than $1,200^\circ\text{C}$, because these alloys have good oxidation resistance and strength at elevated temperatures [1-10]. However, these alloys are very brittle at room (24°C) and moderately high temperatures (approximate 400 to 800°C), which prohibits their commercial application as structural materials. One of the potential solutions to overcome the brittleness of Laves-phase alloys is to fabricate *in situ* composites reinforced by Laves phases in a relatively ductile matrix [11-18]. The presence of a $\text{Cr-Cr}_2\text{Ta}$ eutectic reaction provides a good opportunity for the formation of the Cr solid solution alloy reinforced with the Cr_2Ta Laves phase [19]. The $\text{Cr-Cr}_2\text{Ta}$ alloy has a high melting point greater than $1,700^\circ\text{C}$, and the Laves phase has an ordered crystal structure so that it shows excellent mechanical properties at elevated temperatures. In addition, the Cr matrix phase exhibits some ductility, which is greater than the Cr_2Ta Laves phase at room temperature [3, 20], and good oxidation resistance at high temperatures. The mechanical properties of the Cr matrix can be improved by the mechanical treatment and alloying-element additions [20-22]. Thus, the Cr solid solution matrix composite reinforced by Laves phases makes the material attractive. Our previous research showed that aligned lamellar structures obtained by directional solidification (DS) using a High-Temperature Optical-Floating-Zone Furnace could improve the strength and toughness of the $\text{Cr-Cr}_2\text{Ta}$ *in situ* composites [23].

Eutectic compositions of the Cr -based alloys are critical for obtaining well-aligned lamellar structures using DS. It is worth noting that the published data of the eutectic composition of the Cr-Ta binary system range from 9.8 atomic percent (at. %) Ta [10] to 13 at. % Ta [19], and molybdenum alloying is thought to be capable of solid solution hardening of the Cr -rich phase [24]. Determining the eutectic compositions of the Cr-Ta and Cr-Ta-Mo alloy systems are of interest in the present study. To achieve the desired compositions, proper masses of the raw materials are calculated prior to processing. However, there is a large difference between the melting points of Cr and Ta , and the boiling point of Cr is lower than that of Ta . Thus, the vaporization of chromium during the processing, especially at the initial stage, should be taken into account. Moreover, a considerable weight loss due to the Cr evaporation could occur during directional solidification, where the molten alloy is exposed to ultrahigh temperatures for long time. To assist in monitoring and controlling the compositions of the Cr -based materials, a quantitative tracking technique was employed in the present study and has given satisfying results.

Experimental

High-purity Cr , Ta , and Mo chips were used as charge materials in order to avoid deleterious effects of impurities on the microstructure and mechanical properties of the alloys. The nominal compositions of the alloy studied are shown in Table 1. Unless specified otherwise, the compositions mentioned are in atomic percent (at. %) hereafter. Button-shaped samples of the alloy were obtained by arc-melting in argon. Every sample was inverted and remelted eight to ten times in order to improve the homogeneity of the microstructure and chemical composition of the alloy. Then cylindrical ingots with a length of 60 mm and a diameter of 9 mm were obtained by drop-casting. Selected samples were further processed by directional solidification in a flowing argon atmosphere using a High-Temperature Optical-Floating-Zone Furnace. Details of the directional solidification processing can be found elsewhere [23]. At each stage of the processing, weight loss was carefully measured and tracked for the ingot (Figure 1). The evaporation of the chromium was assumed to be the only source of the weight loss, and the corresponding actual composition was calculated and recorded for tracking purposes, as illustrated in Figure 1. The actual masses of the alloying elements prior to each processing stage except the raw materials were calculated by the derived actual composition of the last stage,

and then were converted to concentrations in atomic percentages to reflect the composition deviations during the processing (Figure 1).

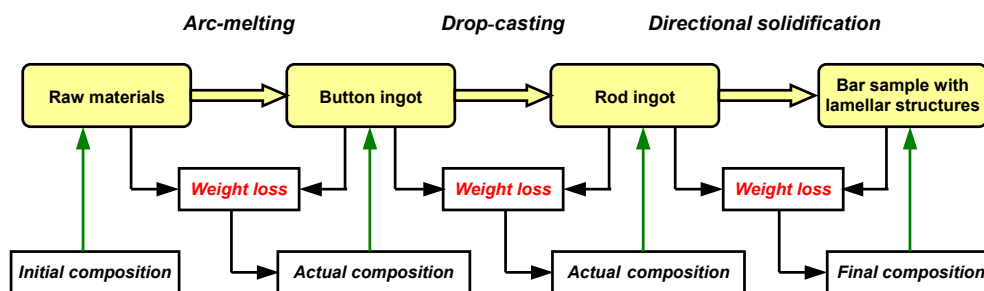


Figure 1 Composition monitoring and tracking during different stages of the processing.

For a binary Cr-X alloy system, the actual concentration of an alloying element, X, after a certain processing stage was calculated by the following equation:

$$X \text{ at. \%} = \frac{W_X/M_X}{W_X/M_X + (W_{Cr} - \Delta W)/M_{Cr}} \times 100\% \quad (1)$$

where, M_X and M_{Cr} are the atomic weights of the alloying elements, X and Cr, respectively, W_X and W_{Cr} the masses of X and Cr prior to the processing stage, and ΔW is the weight loss that equals the sum of W_X and W_{Cr} minus the ingot mass. The actual composition in a ternary Cr-X-Y alloy system can be calculated in a similar way, as shown in Equation 2:

$$\begin{cases} X \text{ at. \%} = \frac{W_X/M_X}{W_X/M_X + W_Y/M_Y + (W_{Cr} - \Delta W)/M_{Cr}} \times 100\% \\ Y \text{ at. \%} = \frac{W_Y/M_Y}{W_X/M_X + W_Y/M_Y + (W_{Cr} - \Delta W)/M_{Cr}} \times 100\% \end{cases} \quad (2)$$

where, M_Y and W_Y are the atomic weight and mass of the ternary alloying element, Y, respectively. Following the processing, the microstructures of the samples were examined using optical microscopy (OM).

Table 1 Nominal compositions of the Cr-Ta and Cr-Ta-Mo alloys (at. %)

Alloy system	Nominal compositions
Cr-Ta	Cr-9.6Ta, Cr-9.7Ta, Cr-9.8Ta
Cr-Ta-Mo	Cr-9.7Ta-1.0Mo, Cr-9.7Ta-3.0Mo, Cr-9.7Ta-5.0Mo

Results and discussion

1. Composition deviations of the Cr-based alloys during processing

The compositions of the Cr-Ta and Cr-Ta-Mo samples throughout the processing are calculated by Equations 1 and 2, and

are listed in Table 2. Note that surplus chromium was added prior to arc-melting to compensate for the Cr evaporation, and the initial Ta and/or Mo concentrations were lower than the nominal values. It was found that for the drop-cast Cr-Ta alloys, the actual composition could be controlled to a level very close to the nominal value. However, a more significant increase in the Ta content occurred in the DS sample (Figure 2), which can be attributed to the long-time exposure of the sample to ultrahigh temperatures during DS processing. Meanwhile, composition deviations in the Cr-Ta-Mo alloys were slightly higher than those in the Cr-Ta alloys. The possible reason is that the molybdenum alloying had changed the vapor pressure of the Cr-rich phase, which should be considered while preparing Cr-Mo-Ta DS samples.

Table 2 Composition deviations during different stages of the processing (at. %)

Nominal composition	Processing stages			
	Raw materials	Arc-melting	Drop-casting	Directional solidification
Cr-9.6Ta	Cr-9.50Ta	Cr-9.57Ta	Cr-9.58Ta	/
Cr-9.7Ta	Cr-9.63Ta	Cr-9.70Ta	Cr-9.71Ta	/
Cr-9.8Ta	Cr-9.74Ta	Cr-9.81Ta	Cr-9.83Ta	/
Cr-9.6Ta	Cr-9.37Ta	Cr-9.46Ta	Cr-9.49Ta	Cr-9.60Ta
Cr-9.7Ta-1.0Mo	Cr-9.58Ta-0.99Mo	Cr-9.64Ta-0.99Mo	Cr-9.70Ta-1.00Mo	/
Cr-9.7Ta-3.0Mo	Cr-9.60Ta-2.97Mo	Cr-9.65Ta-2.99Mo	Cr-9.67Ta-2.99Mo	/
Cr-9.7Ta-5.0Mo	Cr-9.60Ta-4.95Mo	Cr-9.67Ta-4.99Mo	Cr-9.71Ta-5.01Mo	/

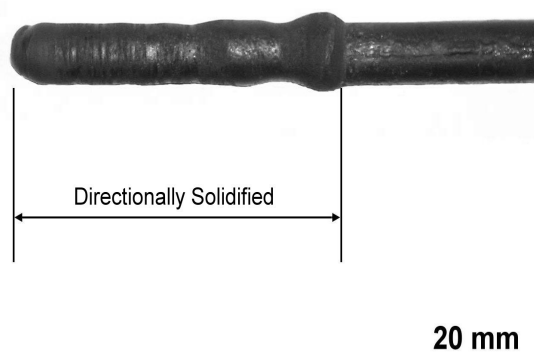


Figure 2 Cr-Ta samples directionally solidified at a growth speed of 40 mm/h and a rotation rate of 20 rpm.

2. The eutectic composition of the binary Cr-Ta alloys

Microstructures of the binary Cr-Ta alloys prepared by drop-casting are shown in Figure 3. It could be found that the Cr-9.71 at. % Ta alloy possessed a virtually fully eutectic microstructure, which shows mainly a lamellar colonies morphology [Figure 3(b)]. Occasionally the Cr_2Ta primary phase surrounded by well-developed eutectic colony was found at a higher magnification [Figure 3(d)]. In the Cr-9.83 at. % Ta alloy, the microstructure consisted of the primary Cr_2Ta phases with angular shapes and eutectic colonies [Figure 3(a)], while the microstructure in the Cr-9.58 at. % Ta alloy was mainly composed of the primary regular Cr-rich dendrite grains and eutectic colonies [Figure 3(c)]. Thus, the eutectic composition of the binary Cr-Ta alloy system was identified to be Cr-9.7 at. % Ta.

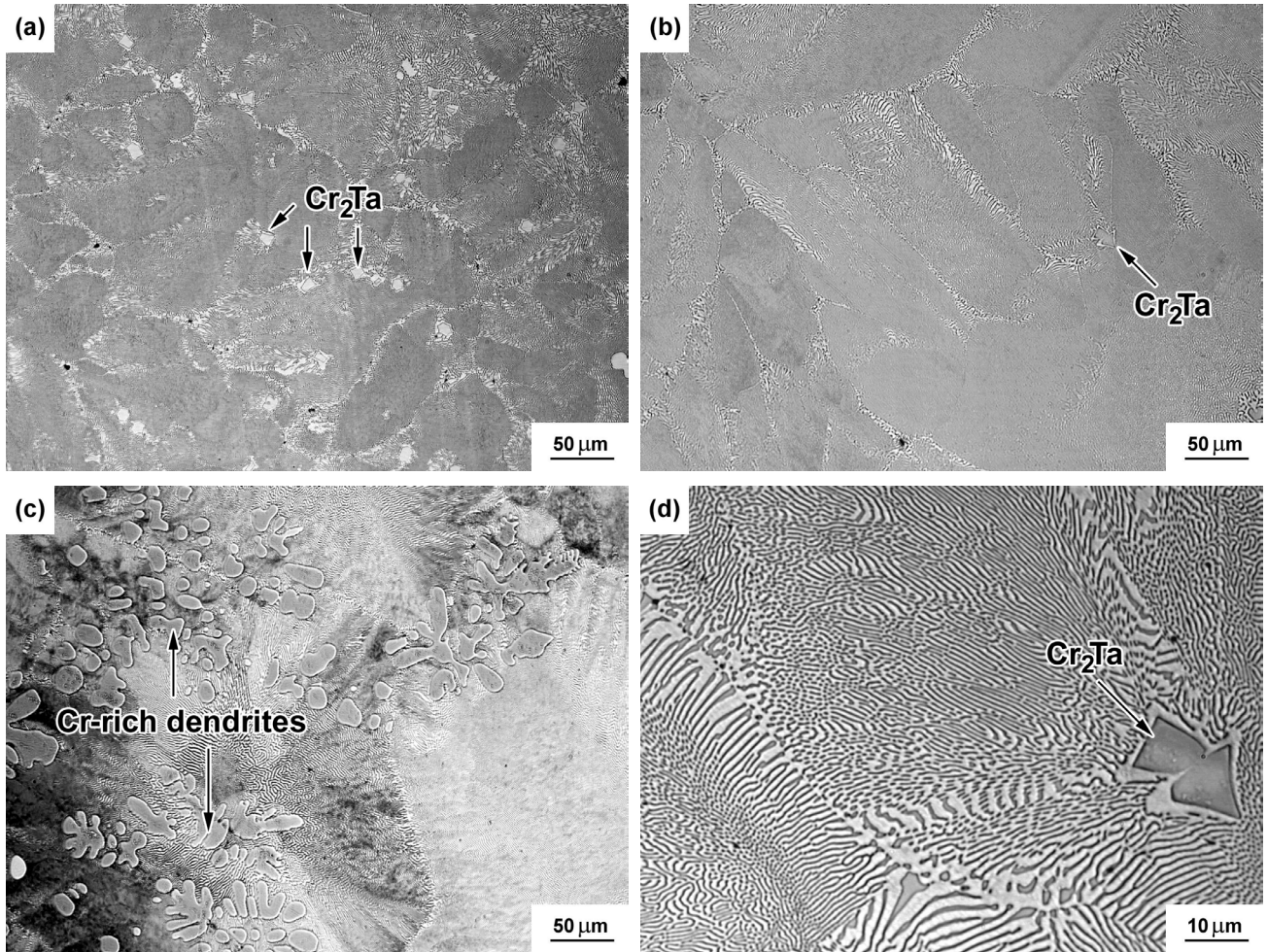


Figure 3 Optical micrographs of the drop-cast Cr-Ta alloys: (a) Cr-9.83 at. % Ta; (b) and (d) Cr-9.71 at. % Ta; (c) Cr-9.58 at. % Ta.

3. The eutectic composition of the Cr-Mo-Ta alloys

The eutectic Cr-9.7 at. % Ta alloy was selected as the base composition for alloying with Mo, and various levels of molybdenum were added. Microstructures of the drop-cast Cr-Ta-Mo alloys are shown in Figure 4. It was found that the Mo addition at levels of 3.0 at. % and 5.0 at. % had significantly modified the eutectic point of the Cr-9.7 at. % Ta alloy, which led to a large amount of pro-eutectic dendrites throughout the microstructure [Figures 4(a) and 4(b)]. However, a fully eutectic structure was obtained in the sample with the lowest Mo concentration (1.0 at. %) studied, as shown in Figures 4(c) and 4(d). A comparison of the microstructures of the eutectic Cr-Ta [Figure 3(d)] and Cr-Mo-Ta [Figure 4(d)] samples indicates that the Mo-containing alloy possessed a better developed lamellar structure with finer lamellar spacing than the Cr-Ta base alloy, which might facilitate the attainment of well-aligned lamellar structure using DS. It is interesting to note that the as-cast CN-151 alloy with multiple alloying elements (Cr-9.75Ta-5Mo-0.5Ti-0.01Ce, at. %) was reported to have a fully lamellar structure, and the mechanical properties were improved [24]. The solid solution hardening effects in the Cr-9.7 at. % Ta-1.0 at. % Mo alloys will be investigated later.

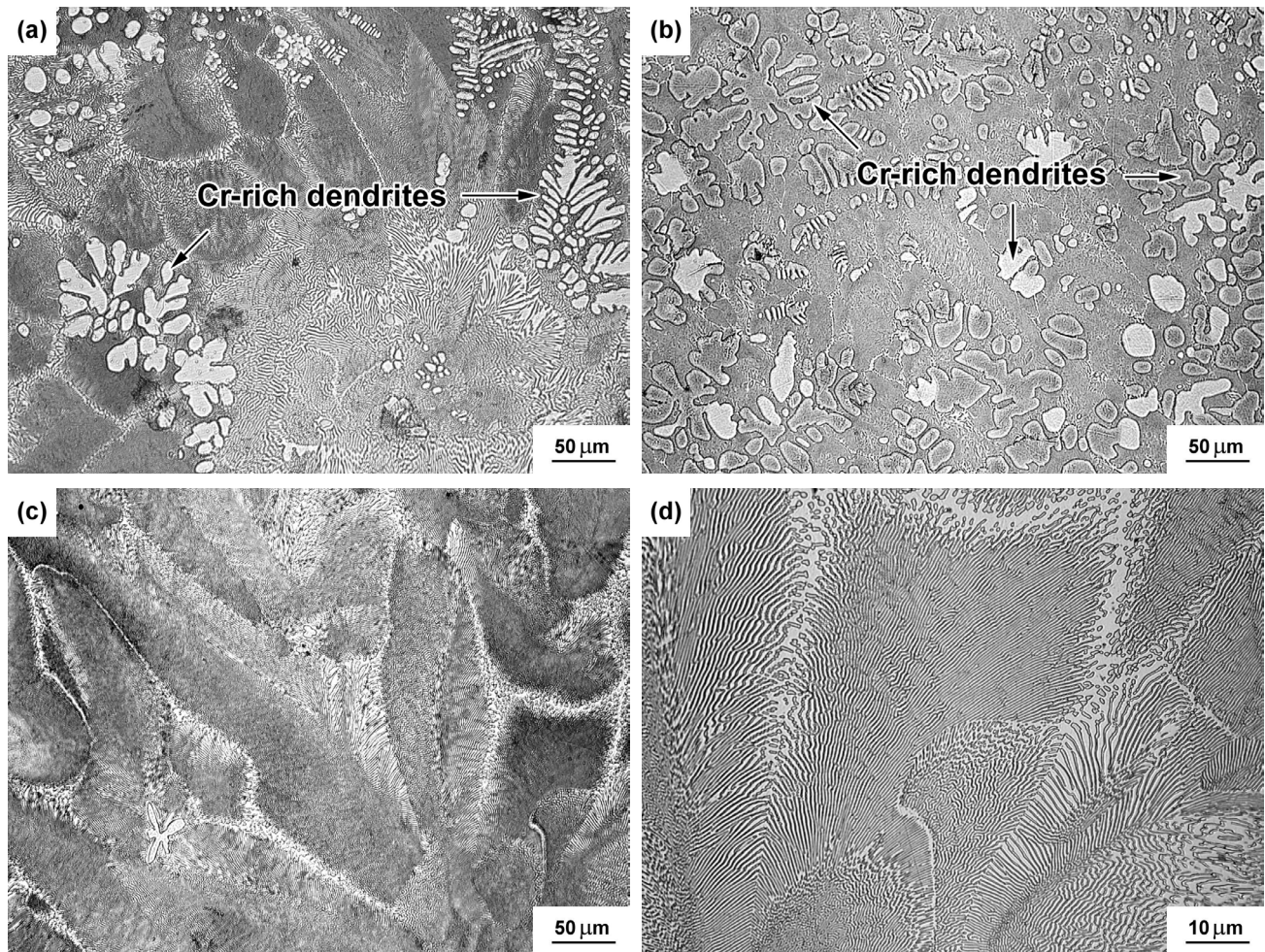


Figure 4 Optical micrographs of the drop-cast Cr-Ta-Mo alloys: (a) Cr-9.71 at. % Ta-5.01 at. % Mo; (b) Cr-9.67 at. % Ta-2.99 at. % Mo; (c) and (d) Cr-9.70 at. % Ta-1.00 at. % Mo.

Conclusions

1. A quantitative tracking technique was developed to monitor and control the compositions of Cr-based alloys during processing at elevated temperatures. Evaporation of chromium was assumed to be the only source of the weight loss, which was carefully measured at each stage of the processing, thus allowing the calculation and tracking of the compositions.
2. The eutectic composition of the drop-cast Cr-Ta binary alloy was determined using the tracking technique mentioned above. While the primary Cr_2Ta phase and Cr-rich dendrite phase appeared in the alloys with the tantalum concentrations of 9.83 at. % and 9.58 at. %, respectively, a virtually fully eutectic structure was present in the Cr - 9.71 at. % Ta alloy. Thus, the eutectic composition of the Cr-Ta system was determined to be 9.7 at. % Ta.
3. In the Mo content range investigated (from 1.0 at. % to 5.5 at. %), it was found that the Mo additions of 3 at. % and 5 at. % significantly modified the eutectic composition of the Cr-9.7 at. % Ta alloy, which led to a large amount of pro-eutectic dendrites. A fully eutectic structure was obtained only at the lowest Mo level (1.0 at. %) studied.

Acknowledgment

The present research is sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U.S. Department of Energy, under subcontract No., 11X-SP173V, to the University of Tennessee, and by the AR&TD Materials Program, under contract No., DE-AC05-000R22725 with UT-Battelle, LLC. Dr. R. Judkins and Dr. P. Carlson are the contract monitors. One of the authors (DFW) thanks C.A. Carmichael, E. Lee, J.L. Wright, and Hongbin Bei for their kind help in the preparation and characterization of the alloys.

References

1. Livingston J. D., Refractory and Silicide Laves Phases, in High-temperature silicides and refractory alloy, Briant C. L., Petrovic J. J., Bewlay B. P., Vasudevan A. K., and Lipsitt H. A., (eds.), Pittsburgh, MRS, 1994, 395-406.
2. Kumar K. S., Laves Phase-based Materials: Microstructure, Deformation modes and properties, in High-temperature ordered intermetallic alloy, Koch C. C., Liu C. T., Stoloff N. S., and Wanner A., (eds.), Pittsburgh, MRS, 1997, 677-688.
3. Kumar K. S. and Liu C. T., Precipitation in a Cr-Cr₂Nb alloy, *Acta Materialia*, **45**(1997), 3671-3686.
4. Ravichandran K. S., Miracle D. B., and Mendiratta M. G., Microstructure and mechanical Behavior of Cr-Cr₂Hf *in-situ* intermetallic composites, *Metallurgical and Materials Transactions*, **27**(1996), 2583-2592.
5. Zhu J. H., Liu C. T., and Liaw P. K., Phase stability and mechanical behavior of NbCr₂-based Laves phase, *Intermetallics*, **7**(1999), 1011-1016.
6. Zhu J. H., Liu C. T., Pike L. M., and Liaw P. K., Thermodynamic interpretation of the size ratio limits for Laves phase formation, *Metallurgical and Materials Transaction*, **30**(1999), 1449-1452.
7. Zhu J. H., Pike L. M., Liu C. T., and Liaw P. K., Point defects in binary Laves phase alloys, *Acta Materialia*, **47**(1999), 2003-2018.
8. Zhu J. H., Pike L. M., Liu C. T., and Liaw P. K., Point defects in binary NbCr₂ Laves-phase alloys, *Scripta Materialia*, **39**(1998), 833-838.
9. Zhu J. H., Liaw P. K. and Liu C. T., Effect of electron concentration on the phase stability of NbCr₂-based Laves phase alloys, *Materials Science and Engineering A*, **A240**(1997), 260-264.
10. Brady M. P., Zhu J. H., Liu C. T., Tortorelli P. F., and Walker L. R., Oxidation resistance and mechanical properties of Laves phase reinforced Cr *in-situ* composites, *Intermetallics*, **8**(2000), 1111-1118.
11. Aoyama N. and Hanada S., Microstructure and strength of NbCr₂/Cr composites, *Materials Transaction - JIM*, **38**(1997), 155-162.
12. Reviere R., Sauthoff G., Jonson D. R., and Oliver B. F., Microstructure of directionally solidified eutectic based Fe(Al, Ta)/Fe₂Ta(Al) alloys as a function of processing condition, *Intermetallics*, **5**(1997), 161-172.
13. Liu C. T., Tortorelli P. F., Horton J. A., and Carmichael C. A., Effects of alloy additions on the microstructure and properties of Cr-Cr₂Nb Alloys, *Materials Science and Engineering A*, **A214**(1996), 23-32.
14. Bewlay B. P. and Jackson M. R., Effect of Hf and Ti additions on microstructure and properties of Cr₂Nb-Nb *in situ* composites, *Journal of Materials Research*, **11**(1996), 1917-1922.
15. Takeyama M. and Liu C. T., Microstructure and mechanical properties of Laves phase alloys based on Cr₂Nb, *Materials Science and Engineering A*, **A132**(1991), 61-66.
16. Kumar K. S., Pang L., Liu C. T., Horton J., and Kenik E. A., Structural stability of the Laves phase Cr₂Ta in a two-phase Cr-Cr₂Ta alloy, *Acta Materialia*, **48**(2000), 911-923.
17. Tagasugi T., Kumar K. S., Liu C. T., and Lee E. H., Microstructure and properties of two-phase Cr-Cr₂Nb, Cr-Cr₂Zr

and Cr-Cr₂(Nb, Zr) alloys, *Materials Science and Engineering A*, **A260**(1999), 108-123.

18. Brady M. P., Zhu J. H., Liu C. T., Tortorelli P. F., Walker L. R., McKamey C. G., and Wright J. L., Intermetallics reinforced Cr Alloy for high-temperature use, *Materials at High Temperatures*, **16**(1999), 189-193.
19. Massalski T. B., Murray J. L., Bennett L. H., and Baker H. (eds.), Binary alloy phase diagram, American Society for Metals, Metals Park, OH, 1986, 867.
20. Matsumoto Y., Fukumori J., Morinaga M., Furui M., Nambu T., and Sakaki T., Alloying effect of 3D transition elements on the ductility of chromium, *Scripta Materialia*, **34**(1996), 1685-1689.
21. Provenzano V., Valiev R., Rickerby D. G., and Valdre G., Mechanical properties of nanostructured chromium, *Nanostructured Materials*, **12**(1999), 1103-1108.
22. Morinaga M. and Nambu T., Effect of surface imperfections on the ductility of pure chromium, *Journal of Materials Science*, **30**(1995), 1105-1110.
23. He Y. H., Wang D. F., Liaw P. K., Liu C. T., Heatherly L., and George E. P., Processing, microstructure and mechanical properties of the Cr-Ta composites reinforced by the Cr₂Ta Laves phase, 15th Annual Conference on Fossil Energy Materials, Knoxville, Tennessee, 2001.
24. Liu C. T., Zhu J. H., Brady M. P., McKamey C. G., and Pike L. M., Physical metallurgy and mechanical properties of transition-metal Laves phase alloy, *Intermetallics*, **8**(2000), 1119-1129.