AI-Ti-V (Aluminum-Titanium-Vanadium)

V. Raghavan

The room temperature ductility of TiAl is significantly improved by V. The previous review of this system by [1995Hay] presented a schematic liquidus projection, a partial reaction scheme, isothermal sections at 1400, 1200, 1100, 1000, and 800 °C, and partial isothermal sections for Ti-rich alloys at 900, 800, 700, and 600 °C. The work of [1991Par], [1994Ahm1], and [1994Ahm2] (not covered in the review of [1995Hay]) is discussed in this update, adding two full isothermal sections at 900 and 600 °C and clarifying the liquidus projection near the Al corner.

Binary Systems

The updated version of the Al-Ti phase diagram [2005Rag] depicts a number of intermediate phases. TiAl₃ has two crystal modifications: TiAl₃ (high temperature [HT]) ($D0_{22}$ -type tetragonal) forms peritectically at 1387 °C and decomposes eutectoidally at 735 °C; and TiAl₃ (low temperature [LT]) (tetragonal) forms at ~950 °C and is stable at low temperatures. Ti₅Al₁₁ is a superstructure based on the AuCu-type tetragonal phase. It forms peritectically at 1416 °C and decomposes eutectoidally at 995 °C to TiAl₂ and TiAl₃ (HT). TiAl₂ (HfGa₂-type tetragonal) forms congruently at 1215 °C from Ti₅Al₁₁ and is stable at low temperatures. $Ti_{1-x}Al_{1+x}$ (AuCu-type tetragonal) is stable between 1445 and 1170 °C. Ti₃Al₅ is a low-temperature phase that is stable below 810 °C. TiAl, often designated γ , has the $L1_0$, AuCu-type tetragonal structure and forms peritectically at 1460 °C. (βTi) (body-centered cubic [bcc], also denoted β) and liquid undergo a peritectic reaction at 1490 °C to yield (aTi) (close-packed hexagonal, also denoted α). Ti₃Al, commonly called α_2 , has the $D0_{19}$, Ni₃Sntype hexagonal structure and forms congruently from (αTi) at 1176 °C. The Al-V diagram [2000Ric] depicts five intermetallic compounds: V₅Al₈ (D8₂, Cu₅Zn₈-type cubic); VAl₃ ($D0_{22}$, TiAl₃-type tetragonal); V₄Al₂₃ (hexagonal); V₇Al₄₅ (monoclinic); and V₂Al₂₁ (cubic). The results of [2000Ric] give lower peritectic formation temperatures of 1408 °C (1670 °C in [Massalski2]) for V₅Al₈ and 1270 °C (1360 °C in [Massalski2]) for VAl₃. [1994Ahm1] considered VAl₃ to be distinct from TiAl₃, quoting the results of [1955Car] of a "face-centered tetragonal" structure for VAl₃. In a bodycentered tetragonal setting (which is the correct unit cell), the lattice parameters given by [1955Car] tally with those listed by [Pearson3]. TiAl₃ and VAl₃ are isomorphous $D0_{22}$ compounds. The Ti-V phase diagram [1981Mur] has no intermediate phases. BTi and V form a continuous solid solution $(\beta Ti, V)$ over a wide range of temperatures. It is not clear whether a stable miscibility gap (shown in [Massalski2]) exists in this solid solution at lower temperatures [1989Wei].

Liquidus Projection

With starting metals of 99.999% Al, 99.98% Ti, and 99.7% V, [1991Par] induction-melted 28 alloy composi-

tions under an Ar atmosphere and used 10 additional alloys obtained from other sources. The phase equilibria were studied by metallography, x-ray diffraction (XRD), scanning electron microscopy with the inclusion of energy-dispersive analysis, and differential thermal analysis at a heating/cooling rate of 25 °C/min. A liquidus projection was constructed, depicting four U-type transition reactions. Also, an isothermal section at 900 °C was presented.

The liquidus projection reviewed by [1995Hay] requires a revision near the Al corner. According to [1995Hay], the continuous solid solution between TiAl₃ and VAl₃ forms below 1100 °C. Further, the isothermal section at 1200 °C by [1994Ahm2] does not depict a continuous solid solution. This implies that a three-phase equilibrium between the Alrich liquid and the two solid solutions based on TiAl₃ and VAl₃, respectively, will continue down to <1200 °C. In Fig. 6 of [1995Hay], on the other hand, the liquidus line from p_5 (1387 °C) along the Al-Ti side terminates on the Al-V side at p₆, which is located at 1360 °C [1995Hay], 1215 °C [1991Par], or 1270 °C [2000Ric]. [1994Ahm1] proposed an additional invariant reaction, U_5 , on the liquidus surface at lower temperatures and extended the liquidus line resulting from this reaction toward the Al corner. At the temperature at which the solid solution based on TiAl₃ and VAl₃ merge to form a continuous solution, this extended liquidus line should terminate. This is indicated as a lower critical point C in the revised (tentative) liquidus projection shown in Fig. 1 [1994Ahm1]. The binary and ternary invariant reactions in Fig. 1 are denoted the same way as in [1995Hay] and [1994Ahm1], except that an additional reaction U' has been introduced to account for the primary crystallization of $Ti_{1-x}Al_{1+x}$. It must be pointed out that the liquidus surface is tentative and that the extent of the primary fields shown in Fig. 1 is only approximate. The solidification reactions at the Al-end are shown schematically in the inset in Fig. 1.

Isothermal Sections

With starting metals of 99.999% Al, 99.6% Ti, and 99.7% V, [1992Ahm] and [1994Ahm2] melted 36 ternary alloys in an arc furnace under an Ar atmosphere. The samples were given a final anneal at 1200, 900, 800, 700, and 600 °C for 1 day, and 2, 4, 6, and 8 weeks, respectively. The phase equilibria were studied by scanning and transmission electron microscopy and by XRD. The compositions of the phases were determined by energy-dispersive x-ray analysis. [1994Ahm2] constructed five isothermal sections at 1200, 900, 800, 700, and 600 °C. At all these temperatures, [1994Ahm2] found that a significant fraction of the area occupied by (BTi) (bcc) is in the form of the ordered B2 (CsCl-type) structure. Two of these isothermal sections at 900 and 600 °C are redrawn in Fig. 2 and 3 to agree with the accepted binary data. The triangulations in Fig. 2 and 3 are identical to those seen in the isothermal



Fig. 1 Al-Ti-V tentative liquidus projection



Fig. 2 Al-Ti-V isothermal section at 900 °C [1994Ahm2]

sections at 1000 and 800 °C of [1985Has] (reviewed in [1995Hay]) and at 900 °C of [1991Par]. The homogeneity ranges of the phases are, however, significantly different.

The *B*2-ordered region found by [1994Ahm2] in the temperature range of 1200 to 600 $^{\circ}$ C was not reported in earlier studies. From the absence of antiphase boundaries in



Fig. 3 Al-Ti-V isothermal section at 600 °C [1994Ahm2]

samples annealed at 1200 °C, [1994Ahm2] concluded that the B2 region is present at this temperature and does not form during quenching. The region, where the antiphase boundaries are observed, was taken to be in the disordered bcc form at the annealing temperature.

[1992Cha1] investigated five Ti-rich alloys by HT x-ray diffraction. Combining their results with those of [1985Has], they constructed partial isothermal sections at 1100, 1000, and 800 °C. [1992Cha2] studied three alloys with 4, 7, and 15 at. % V, respectively, and a constant Al content of 44 at. %, by means of HT XRD and differential scanning calorimetry. They found the $(\alpha Ti) + (\beta Ti) \rightarrow (\beta Ti)$ transition temperature decreases from 1457 °C for the binary alloy to 1370 °C for the alloy with 14 at. % V. The V addition has no significant effect on the $(\alpha Ti) \rightarrow \alpha_2 + \gamma$ eutectoid temperature [1992Cha2]. [1998Cha] studied the solidification characteristics of alloy compositions $Al_{71}Ti_{25}V_4$ and $Al_{66}Ti_{25}V_9$. The occurrence of the ω -phase and other metastable phases was reported by [1995Sha], [2002Sha], [2003Cha], and [2003Hu].

[1997Zha] made a thermodynamic evaluation of this system, using new experimental results for the phase equilibria at 1100 and 1000 °C in the optimization. [2001Kan] computed the boundaries between the (β Ti), α_2 , and γ -phases by the cluster-variation method. The thermodynamic parameters of molten Ti-Al-V alloys were calculated by [2003Che].

References

1955Car: O.N. Carlson, D.J. Kenney, and H.A. Wilhelm, The Aluminum-Vanadium Alloy System, *Trans. Amer. Soc. Metals*, Vol 47, 1955, p 520-542

- 1981Mur: J.L. Murray, The Ti-V (Titanium-Vanadium) System, Bull. Alloy Phase Diagrams, Vol 2 (No. 1), 1981, p 48-55
- **1985Has:** K. Hashimoto, H. Doi, and T. Tsujimoto, Reexamination of the Ti-Al-V Ternary Phase Diagram, *J. Jap. Inst. Metals*, Vol 49, 1985, p 410-416 (in Japanese); TR: *Trans. Jap. Inst. Metals*, Vol 27 (No. 10), 1986, p 741-749
- 1989Wei: F. Wei and H.M. Flower, Phase Separation Reactions in Ti-50V Alloys, *Mater. Sci. Technol.*, Vol. 5, 1989, p 1172-1177
- **1991Par:** M. Paruchuri and T.B. Massalski, Phase Diagram Relationships in the Ternary System Ti-Al-V, *MRS Symp. Proc.*, L. Johnson, Ed., Materials Research Society, Vol. 213, 1991, p 143-149
- **1992Ahm:** T. Ahmed and H.M. Flower, The Phase Transformations in Alloys Based on Ti₃Al-V and TiAl-V, *Mater. Sci. Eng.*, *A*, Vol A152 (No. 1-2), 1992, p 31-36
- **1992Cha1:** P.K. Chaudhury and H.J. Rack, Ti-Al-V Ternary Phase Stability at Elevated Temperatures, *Scripta Metall. Mater.*, Vol 26, 1992, p 691-695
- **1992Cha2:** P.K. Chaudhury, M. Long, and H.J. Rack, Effect of Vanadium on Elevated Temperature Phase Relations in Titanium Aluminides Containing 44 At. % Al, *Mater. Sci. Eng. A*, Vol A152, 1992, p 37-40
- 1994Ahm1: T. Ahmed, H.J. Rack, and H.M. Flower, Liquidus Projection of Ti-Al-V System Based on Arc Melted and Cast Microstructures, *Mater. Sci. Technol.*, Vol 10, 1994, p 681-690
- 1994Ahm2: T. Ahmed and H.M. Flower, Partial Isothermal Sections of Ti-Al-V Ternary Diagram, *Mater. Sci. Technol.*, Vol 10, 1994, p 272-288
- **1995Hay:** F.H. Hayes, The Al-Ti-V (Aluminum-Titanium-Vanadium) System, *J. Phase Equilib.*, Vol 16 (No. 2), 1995, p 163-176
- **1995Sha:** G. Shao, A.P. Midownik, and P. Tsakiropoulos, ω-Phase Formation in V-Al and Ti-Al-V Alloys, *Philos. Mag. A*, Vol 71 (No. 6), 1995, p 1389-1408

- 1997Zha: F. Zhang, "A Thermodynamic Study of the Ti-Al-V Ternary System," Ph.D. dissertation, University of Wisconsin, 1997
- **1998Cha:** W.S. Chang and B.C. Muddle, Intermediate Phases and Phase Relation in the Composition Range Al₃(Ti,V) to TiAl in the Al-Ti-V System, *Mater. Sci. Eng., A*, Vol A251 (No. 1-2), p 232-242
- **2000Ric:** K. W. Richter and H. Ipser, The Al-V Phase Diagram Between 0 and 50 Atomic Percent Vanadium, *Z. Metallkd.*, Vol 91 (No. 5), 2000, p 383-388
- **2001Kan:** S.Y. Kang and H. Onodera, Analyses of $HCP/D0_{19}$ and $D0_{19}/L1_0$ Phase Boundaries in Ti-Al-X (X = V, Mn, Nb, Cr, Mo, Ni, and Co) Systems by the Cluster Variation Method, *J. Phase Equilib.*, Vol 22 (No. 4), 2001, p 424-430
- 2002Sha: G. Shao and P. Tsakiropoulos, Prediction of ω Phase

Formation in Ti-Al-X Alloys, *Mater. Sci. Eng.*, A, Vol A329-A331, 2002, p 914-919

- **2003Cha:** W.S. Chang and B.C. Muddle, Structure and Stability of a New Ternary Hexagonal Phase in Al₃Ti-Based Al-Ti-V Alloys, *Metall. Mater. Trans. A*, Vol 34A (No. 3), 2003, p 491-501
- **2003Che:** Z.Y. Chen and L.J. Xu, Thermodynamic Parameter Calculation and Evaporation Behavior of Elements in the Ti-Al-V Alloys, *Trans. Nonferrous Met. Soc. China*, Vol 13, 2003, p 119-123
- **2003Hu:** Q.M. Hu and R. Yang, Geometric and Electronic Structure of Ti₂AlX (X = V, Nb or Ta), *Phys. Rev. B: Condens. Matter*, Vol 68 (No. 5), 2003, p 054102/1-054102/7
- 2005Rag: V. Raghavan, Al-Ti (Aluminum-Titanium), J. Phase Equilib. Diffus., Vol 26 (No. 2), 2005, p 171-172