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Al-Cr-Ti (Aluminum-Chromium-Titanium)

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The previous review of this system by [1992Hay] presented a partial reaction scheme and isothermal sections for Ti-rich alloys at 1200, 1100, 1000, 800, and 600 °C, based mainly on the results of [1960Enc]. A number of studies were reported since then, extending the phase equilibria to the other regions of the composition triangle. The existence of the $L1_2$-type phase in Al-rich alloys of this ternary system has attracted much attention due to their low density, good oxidation resistance, and the somewhat better mechanical properties associated with the cubic symmetry, in comparison with those of the tetragonal $TiAl_3$.

Binary Systems

The Al-Cr phase diagram by [2000Mah] includes a thermodynamic assessment and depicts a number of intermediate phases with significant ranges of homogeneity: $CrAl_7$ (V_7Al_{45}-type monoclinic); Cr_2Al_{11} ($CrAl_5$-type monoclinic); $CrAl_4$ (monoclinic); Cr_2Al ($MoSi_2$-type tetragonal); and an unconfirmed low-temperature phase X at 75 at.% Cr. Between 30 and 41 at.% Cr, five phases have been reported (αCr_4Al_9, βCr_4Al_9, γCr_4Al_9, αCr_5Al_8, and βCr_5Al_8), with no well-established phase boundaries between them [2000Mah]. A report by [1999Hel] discussed a possible *B*2-ordering of the Cr-rich body-centered cubic (bcc) phase. The updated version of the Al-Ti phase diagram [2005Rag] depicts a number of intermediate phases. $TiAl_3$ has two crystal modifications. $TiAl_3$ ([high temperature (HT)] ($D0_{22}$-type tetragonal) forms peritectically at 1387 °C and decomposes eutectoidally at 735 °C. $TiAl_3$ [low temperature (LT)] (tetragonal) forms at ~950 °C and is stable at low temperatures. Ti_5Al_{11} is a superstructure based on the AuCu-type tetragonal phase. It forms peritectically at 1416 °C and decomposes eutectoidally at 995 °C to $TiAl_2$ and $TiAl_3$ (HT). $TiAl_2$ ($HfGa_2$-type tetragonal) forms congruently at 1215 °C from Ti_5Al_{11} and is stable at low temperatures. $Ti_{1-x}Al_{1+x}$ (AuCu-type tetragonal) is stable between 1445 and 1170 °C. Ti_3Al_5 is an LT phase stable below 810 °C. TiAl, often designated γ, has the $L1_0$, AuCu-type tetragonal structure and forms peritectically at 1460 °C. (βTi) (bcc, also denoted β) and liquid undergo a peritectic reaction at 1490 °C to yield (αTi) (close-packed hexagonal, also denoted α). Ti_3Al, commonly labeled α_2, has the $D0_{19}$, Ni_3Sn-type hexagonal structure and forms congruently from (αTi) at 1176 °C. The Cr-Ti phase diagram [2000Zhu] depicts a continuous bcc solid solution between βTi and Cr. The only intermediate phase of this system, Cr_2Ti, exists in all three Laves modifications. At 1359 °C, γCr_2Ti (*C*14-type hexagonal) forms congruently at 64.6 at.% Cr from the bcc phase. It transforms at 1271 °C to βCr_2Ti (63.8 – 66.7 at.% Cr, *C*36-type hexagonal), which decomposes eutectoidally at 804 °C. αCr_2Ti (62.7 – 66.5 at.% Cr, *C*15-type cubic) forms peritectoidally at 1223 °C, and is stable at low temperatures.

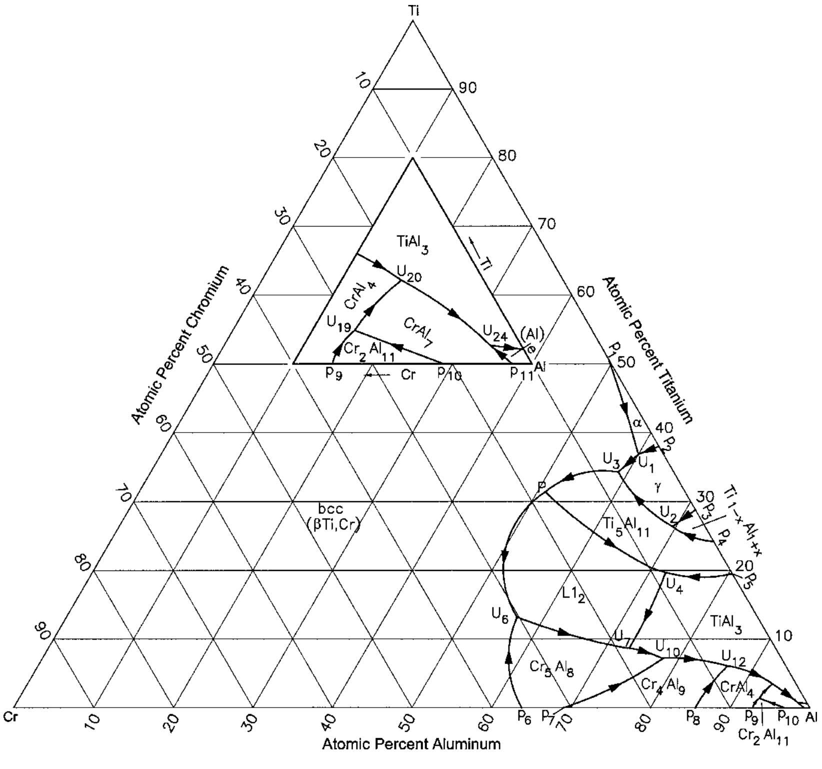


Fig. 1 Al-Cr-Ti schematic liquidus projection. The inset is an enlarged version of the Al corner

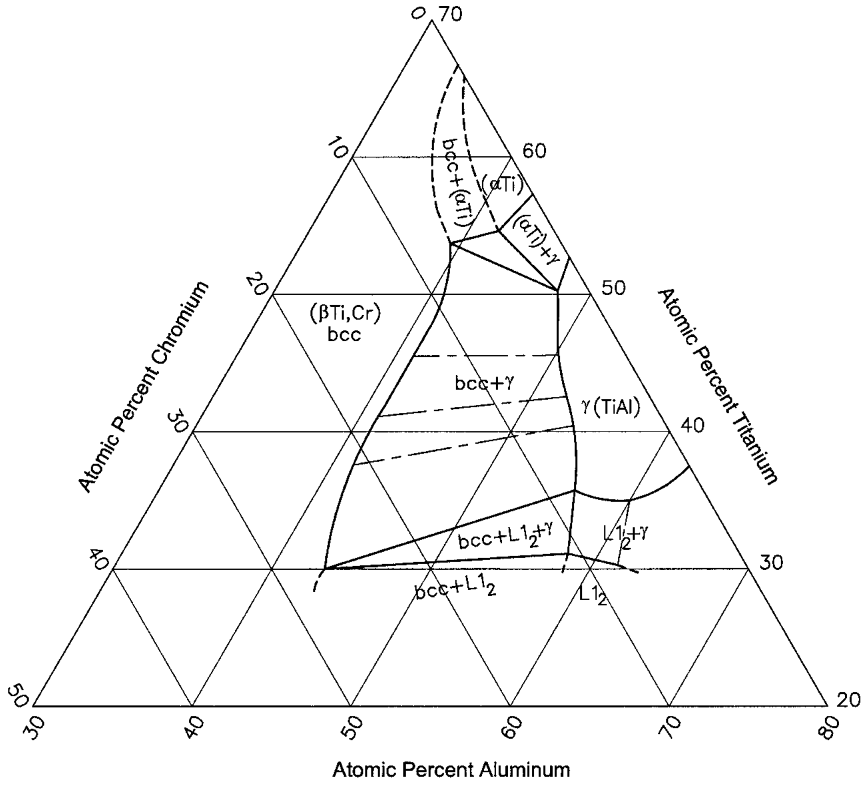


Fig. 2 Al-Cr-Ti partial isothermal section at 1200 °C [2001Fuj]

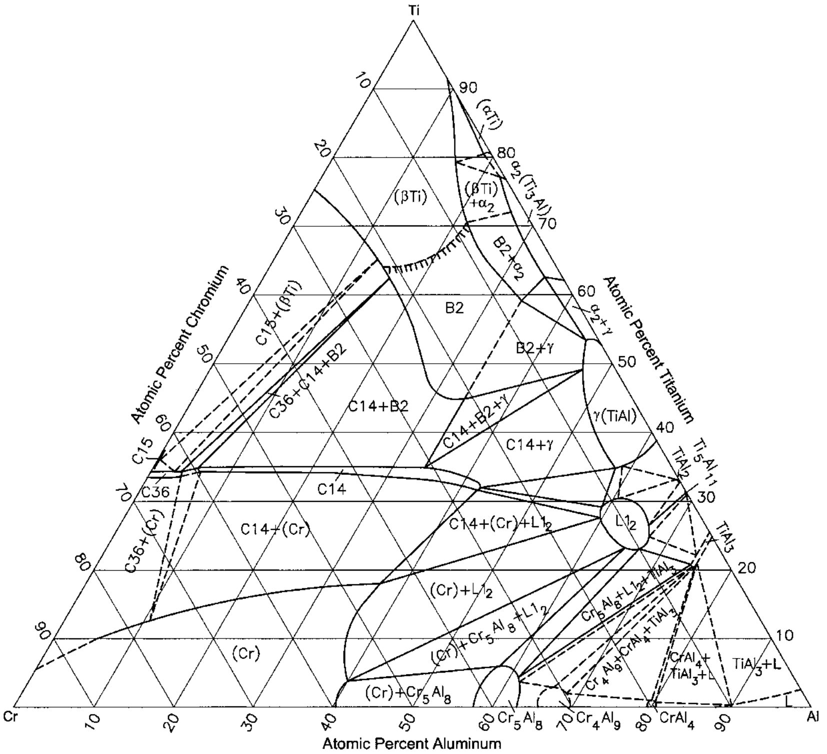


Fig. 3 Al-Cr-Ti isothermal section at 1000 °C [1996Jew2, 1996Jew3, 2000Kai]

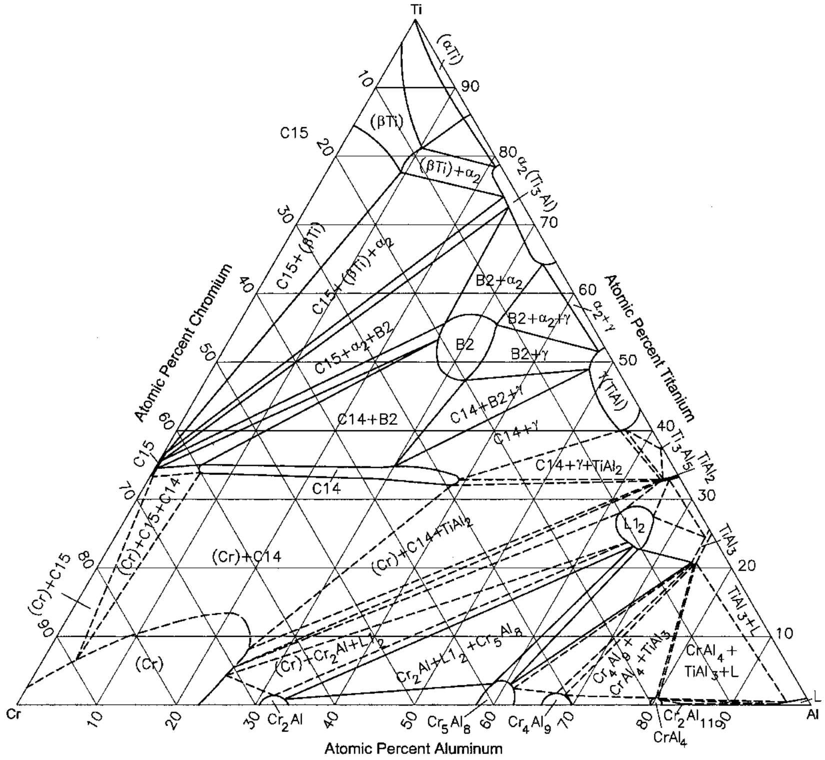


Fig. 4 Al-Cr-Ti isothermal section at 800 °C [1996Jew2, 1996Jew3]

Ternary Phases

In Al-rich compositions, it is now well established that the $L1_2$, $AuCu_3$-type cubic phase (denoted τ in some reports) exists in the ternary range near the structurally related $D0_{22}$ tetragonal binary compound $TiAl_3$ [1990Mab, 1990Zha, 1992Nic, 1993Kum, 1993Nak, 1995Bra, 1996Jew1, 1996Jew3, 1997Mab, 1997Xu, 2001Fuj, 2002Kau, 2003Bar, 2003Lee, 2003Oh]. It is stable at temperatures below ~1370 °C [1997Mab] and has a composition range of ~59 to 68 at.% Al and ~6 to 13 at.% Cr. Its lattice parameter is in the range of 0.3943 to 0.3957 nm [1996Jew3]. [2003Lee] observed that a rather small shift in the $L1_2$ phase field toward the Al corner seen with decreasing temperature could be effective in enhancing its stability and providing the key for higher fracture toughness.

The other ternary phase is the $C14$-type Laves phase. The binary $C14$-type compound γCr_2Ti, which is present above 1271 °C, is stabilized at lower temperatures by the addition of a few percent of Al. It has a composition range of ~5 to 42 at.% Al at 1000 and 800 °C at approximately constant Ti content [1996Jew2]. The width of the field is about 1 at.% Ti at the low Al end and increases to ~3 at.% Ti at 35 at.% Al. The lattice parameters of the $C14$ phase increase linearly from $a = 0.4931$ nm and $c = 0.8031$ nm at 5 at.% Al to $a = 0.5055$ nm and $c = 0.8247$ nm at 35 at.% Al. At 1050 °C, [1997Xu] noted that the extent of the (βTi) field increases at the expense of the $C14$ field, which dissolves <20 at.% Al at this temperature.

At 1000 °C, Cr additions induce the $B2$ ordering in (βTi). At 800 °C, the $B2$ field is separated from (βTi) and is present as an island around 30at.%Al-20at.%Cr-50at.%Ti. Cr appears to stabilize the $B2$ phase at lower temperatures [1994Gao, 1994Zha]. [2000Sha] and [2002Sha] reported on the characteristics of the metastable ω phase formed after quenching and retaining the $B2$ phase at room temperature in alloys with 10 at.% Cr and 20 to 40 at.% Al.

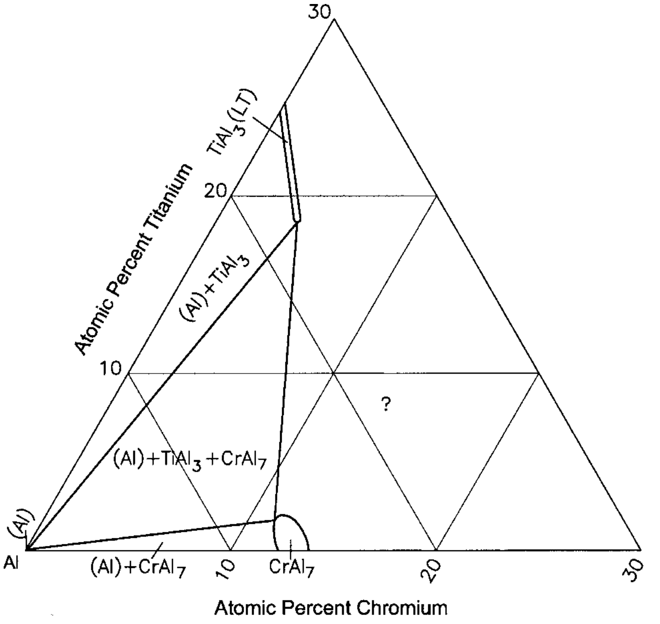


Fig. 5 Al-Cr-Ti partial isothermal section at 497 °C [1994Sok]

Table 1 Al–Cr–Ti tentative reaction sequence down to 600 °C

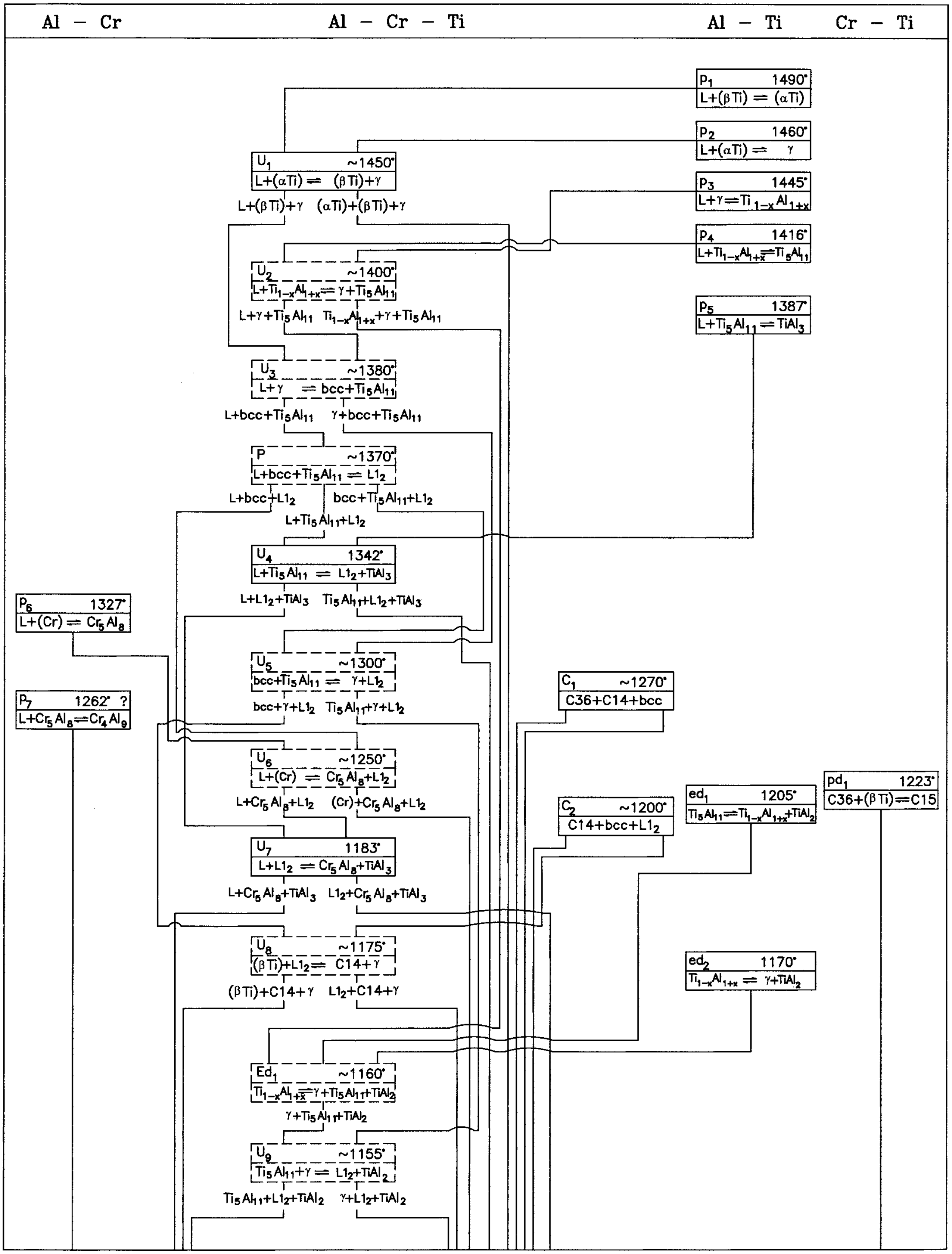


Table 1 Al–Cr–Ti tentative reaction sequence down to 600 °C (contd.)

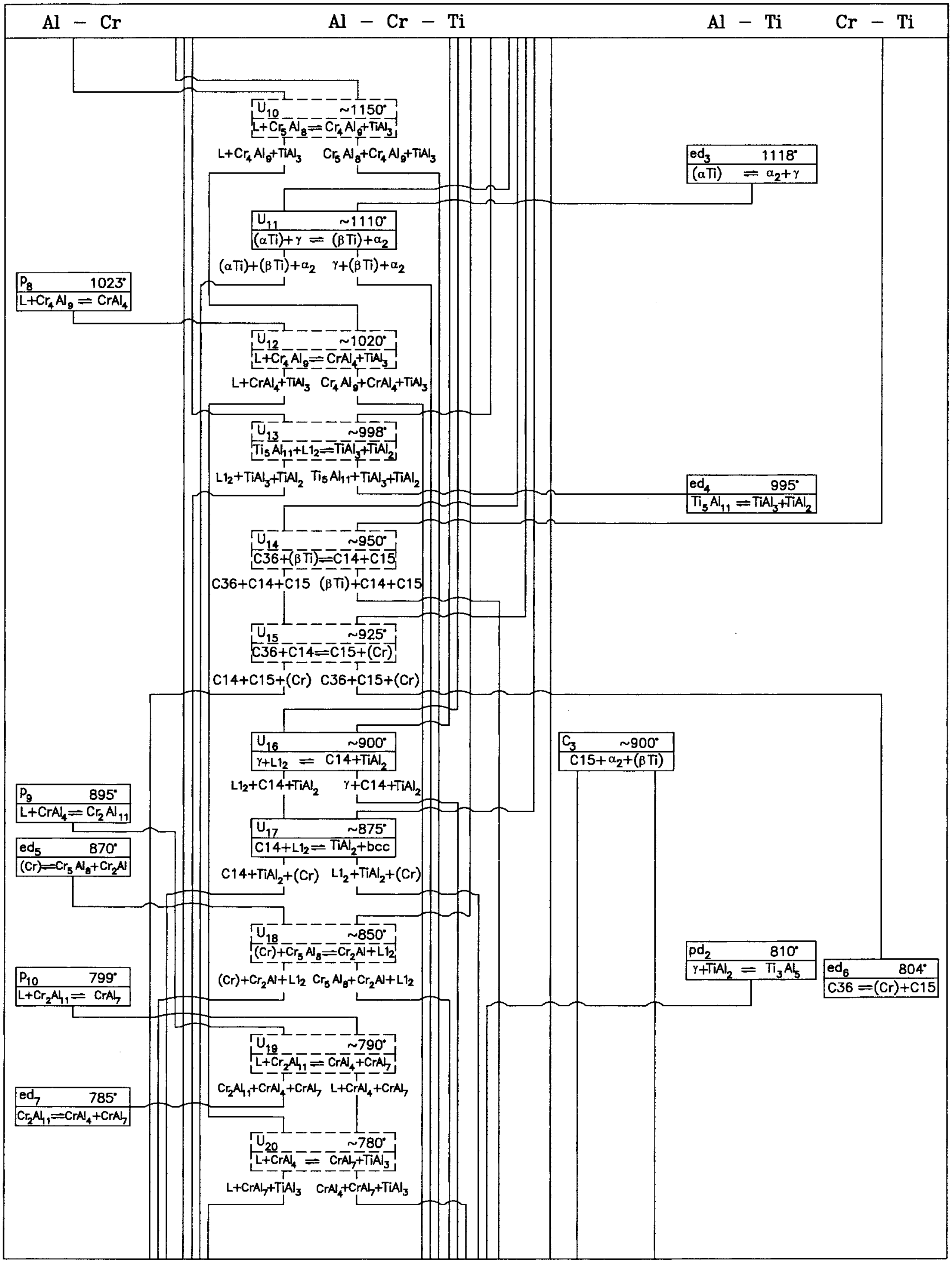
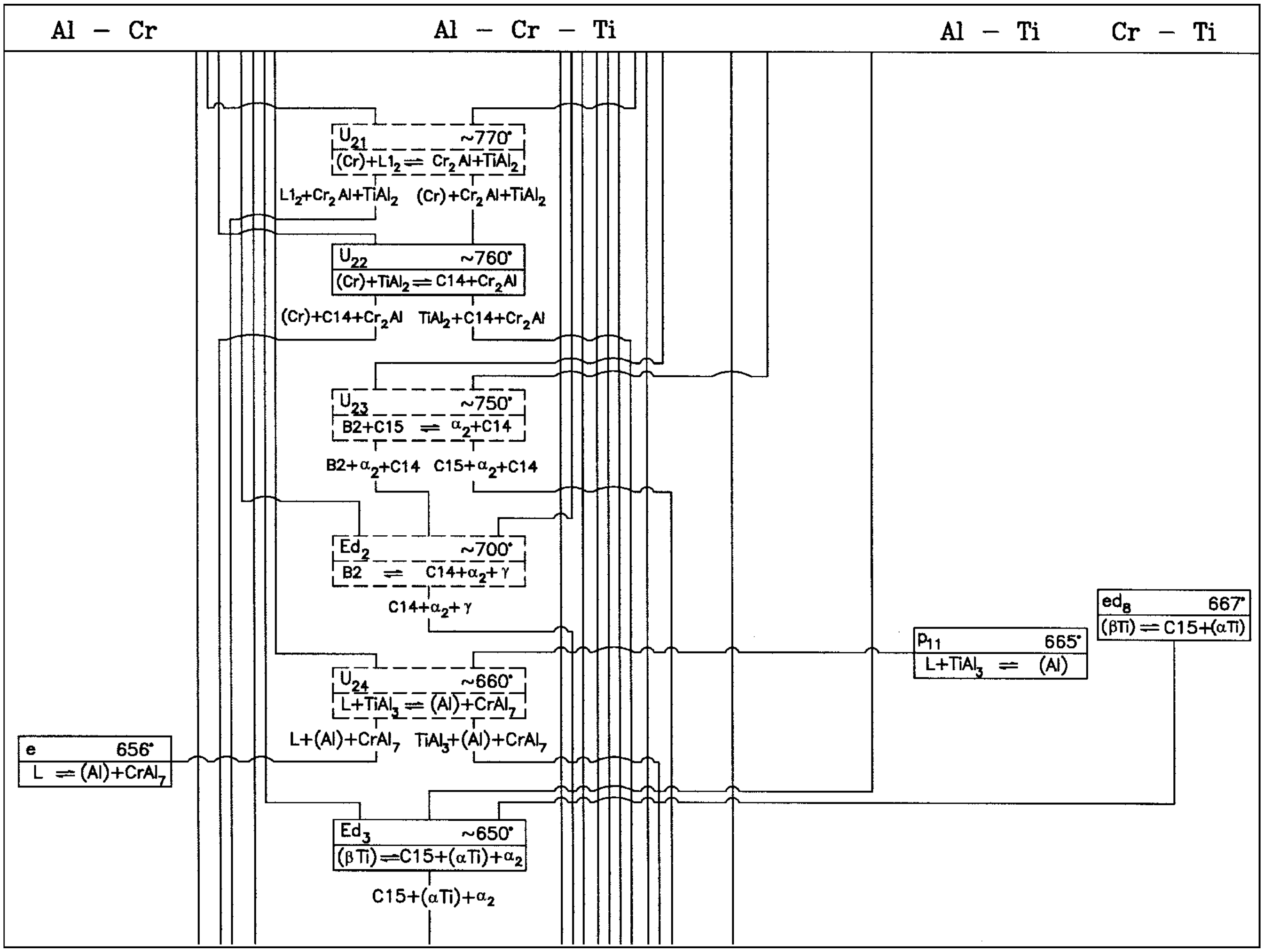


Table 1 Al–Cr–Ti tentative reaction sequence down to 600 °C (contd.)



Liquidus Projection

Very limited information is available regarding the solidification characteristics of this system [1997Mab, 2001Ich]. [1997Mab] determined a partial vertical section at 25 at.% Ti, depicting the solidus and liquidus of the $L1_2$ phase. [2001Ich] determined a partial liquidus projection showing the equilibrium between $L1_2$ and the surrounding phases, which included Cr_2Al and presumably $C14$ (labeled AlCrTi by [2001Ich]). Cr_2Al is an LT phase that is present below 910 °C and is not expected to be in equilibrium with the liquid. The Al solubility in the $C14$ phase decreases with increasing temperature and is <20 at.% at 1050 °C. With the intervening dominant bcc field, it is unlikely that the $C14$ phase comes into equilibrium with the liquid. Figure 1 shows a schematic liquidus projection. $L1_2$ is postulated to form through a ternary peritectic reaction P at ~1370 °C: $L + bcc + Ti_5Al_{11} \rightarrow L1_2$. The four-phase invariant reactions U_4 and U_7 are those given by [2001Ich]. The other reactions are postulated here to be consistent with the isothermal sections discussed below.

Isothermal Sections

Isothermal sections of this ternary system have been reported in a number of studies: [1993Nak] (partial at 1000 °C); [1994Has] (partial at 1200 °C); [1994Kla] (1200 °C); [1994Sok] (partial at 497 °C); [1995Bra] (partial at 1000 °C); [1995Hao] (1000 °C); [1995Jew], [1996Jew2], and [1996Jew3] (partial at 1000 and 800 °C); [1997Jew] (1000 and 800 °C); [1997Mab] (partial at 1150 °C); [1997Xu] (partial at 1050 °C); [2000Kai] (partial at 1000 °C); [2001Fuj] (partial at 1200 and 1000 °C); and [2001Has] (1200 °C).

With starting metals of 99.99 at.% Al, 99.99 at.% Cr, and 99.5% Ti, [2001Fuj] melted 13 ternary compositions in an arc furnace. The alloys were annealed at 1200 and 1000 °C for four to seven days and quenched. The phase equilibria were studied by metallography, selected area electron diffraction, and quantitative x-ray microanalysis. The partial isothermal section constructed by [2001Fuj] at 1200 °C is redrawn in Fig. 2. Most of experimental tie lines fall in the (βTi) + TiAl (γ) region.

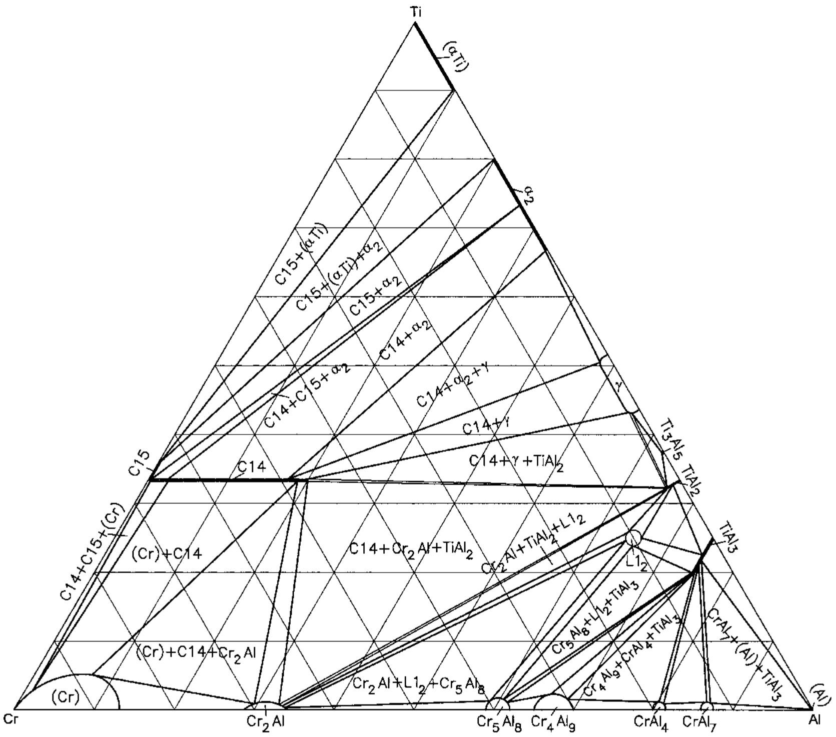


Fig. 6 Al-Cr-Ti schematic isothermal section at 600 °C

With starting metals of 99.99 at.% Al, 99.5 at.% Cr, and 99.98% Ti, [1996Jew2] arc-melted 13 alloy compositions under Ar atmosphere. After homogenization, the alloys were annealed at 1000 and 800 °C for 500 and 1000 h and were quenched in water. The phase equilibria were studied by optical and scanning electron microscopy, energy-dispersive x-ray analysis, and differential scanning calorimetry. Partial isothermal sections were constructed at 1000 and 800 °C for Al-lean alloys. Using the same starting materials as above, [1996Jew3] arc-melted 11 Al-rich alloys, which were annealed at 1000 and 800 °C for 100 to 500 h and were quenched in water. Using the same experimental techniques as above, [1996Jew3] listed the measured compositions and lattice parameters of the identified phases. Partial isothermal sections were constructed at 1000 and 800 °C. [2000Kai] used 99.99% Al, 99.3% Cr and 99.7 at.% Ti as starting metals to melt seven Ti-rich alloys in an arc furnace under Ar atmosphere. The alloys were annealed at 1000 °C for 168 h and were quenched in ice water. The phase equilibria were studied with diffusion couples along with energy-dispersive spectroscopy and electron microscopy. Combining the partial sections determined by [1996Jew2], [1996Jew3], and [2000Kai], a full isothermal section at 1000 °C is constructed in Fig. 3. It is in reasonable agreement with the partial section determined by [2001Fuj] at 1000 °C. The ternary phases $C14$, $L1_2$, and $B2$ are present. Their characteristics were summarized in the preceding section. The binary phase TiAl (γ) dissolves up to 8 at.% Cr [1997Jew]. Cr_5Al_8 dissolves 6.2 at.% Ti. Cr dissolves up to 18 at.% Ti at 37 at.% Al. $TiAl_3$ dissolves about 5 at.% Cr. In Fig. 4, a full isothermal section at 800 °C is constructed from the results of [1996Jew2] and [1996Jew3]. The three ternary phases are present. The solubility of Cr in γ and of Ti in Cr_5Al_8 is 4.5 and 3.9 at.%, respectively. The solubility of Ti in (Cr) is 13.5% at 20 at.% Al.

Using starting metals of 99.9 at.% Al, 99.9 at.% Cr, and 99.5% Ti, [1994Sok] melted 14 Al-rich compositions in an arc furnace under Ar atmosphere. The samples were annealed at 497 °C (770 K) for 1000 h and were quenched in an ice-water mixture. The phase equilibria were studied by metallography and x-ray powder diffraction. The partial isothermal section constructed by [1994Sok] is redrawn in Fig. 5 to agree with the accepted binary data. The binary compound Cr_2Al_{11} shown by [1994Sok] is omitted, as this phase decomposes eutectoidally at 785 °C [2000Mah]. $TiAl_3$ dissolves up to 4 at.% Cr. $CrAl_7$ dissolves up to 2 at.% Ti.

A Tentative Reaction Scheme

A tentative reaction sequence down to ~600 °C is written for this ternary system in Table 1, which is consistent with the liquidus projection and the isothermal sections. The allotropic transitions in Cr_5Al_8, Cr_4Al_9, and $TiAl_3$ are not considered. The bcc phase in the ternary region may be denoted as bcc, (βTi), (Cr), or $B2$. The $L1_2$ phase is assumed to form peritectically at ~1370 °C. The nucleation of $C14$ in the ternary region at ~1270 °C (critical point C_1 in Table 1), creates two three-phase fields of ($C36$ + $C14$ + bcc). The coalescence of the ($C14$ + bcc) and ($L1_2$ + bcc) fields [2002Kau] postulated here at ~1200 °C (C_2 in Table 1) results in the formation of the three-phase fields of $C14$ + (βTi) + $L1_2$ and $C14$ + (Cr) + $L1_2$. The formation of a miscibility gap in the bcc ($B2$) region at ~900 °C (C_3 in

Table 1) creates the three-phase fields of $C15 + \alpha_2 + (\beta Ti)$ and $C15 + \alpha_2 + B2$. Below 800 °C, the island-like region of $B2$ probably vanishes (Ed_2 in Table 1). The reactions postulated here are placed in broken boxes. The temperatures shown for these reactions are notional values. They merely indicate the probable sequence of the reactions with falling temperature. Reactions U_1, U_{11}, Ed_3, and C_3 were given by [1992Hay]. U_4 and U_7 were determined by [2001Ich]. Reactions U_{16}, U_{17}, and U_{22} are those suggested by [1996Jew3]. The lower temperature limit of stability of the $C14$ and $L1_2$ phases is not known. Assuming that $C14$ and $L1_2$ are present, a schematic sketch of the phase equilibria at ~600 °C is shown in Fig. 6.

References

1960Enc: E. Ence, P.A. Farrar, and H. Margolin, "Binary and Ternary Diagrams of the Ti-Al-Cr and Ti-Al-V Systems," Wright Air Development Division Technical Report No. 60-316, 1960, p 1-20

1990Mab: H. Mabuchi, K. Hirukawa, H. Tsuda, and Y. Nakayama, Formation of Structural $L1_2$ Compounds in the Ternary Al-Ti-Cr System, *Scr. Metall. Mater.,* Vol 24, 1990, p 505-508

1990Zha: S. Zhang, J.P. Nic, and D.E. Mikkola, New Cubic Phases Formed by Alloying Al_3Ti with Mn or Cr, *Scr. Metall. Mater.,* Vol 24, 1990, p 57-62

1992Hay: F.H. Hayes, The Al-Cr-Ti (Aluminum-Chromium-Titanium) System, *J. Phase Equilib.,* Vol 13 (No. 1), 1992, p 79-86

1992Nic: J.P. Nic, J.L. Klansky, and D.E. Mikkola, Structure-Property Observations for Al-Ti-Cr Alloys near the Cubic $(Al,Cr)_3Ti$ Phase, *Mater. Sci. Eng. A,* Vol A152, 1992, p 132-137

1993Kum: K.S. Kumar, Microstructure and Mechanical Properties of Ternary $L1_2$ Al-Rich Intermetallics, *Structural Intermetallics, Proc. Int. Symp. 1st,* R. Darolia, Ed., Miner. Metals Mater. Soc., Warrendale, PA, 1993, p 87-96

1993Nak: Y. Nakayama and H. Mabuchi, Formation of Ternary $L1_2$ Compounds in Al_3Ti Based Alloys, *Intermetallics,* Vol 1, 1993, p 41-48

1994Gao: Y. Gao, J. Zhu, and Q.G. Cai, Microstructure of the Ordered β Phase in Ti-Al Alloy with Chromium and Vanadium, *Scr. Metall. Mater.,* Vol 31 (No. 5), 1994, p 571-575

1994Has: K. Hashimoto and Y. Mizuhara, Phase Stability of Ti-Al-X at High Temperatures, *Microstruct. Prop. Relations Ti Alloys Proc Harold Margolin Symp.,* S. Ankem and J.A. Hall, Ed., Miner. Met. Mater. Soc., Warrendale, PA, 1994, p 225-234

1994Kla: J.L. Klansky, J.P. Nic, and D.E. Mikkola, Structure/Property Observations for Al-Ti-Cr Intermetallic Alloys, *J. Mater. Res.,* Vol 9 (No. 2), 1994, p 255-258

1994Sok: E.M. Sokolovskaya, E.F. Kazakova, E.I. Poddyakova, V.K. Portnoi, and A.A. Temirbaeva, Phase Composition of Alloys of the Al-Cr-Ti System at 770 K, *Vestn. Mosk. Univ. Ser. 2: Khim,* Vol 35 (No. 5), 1994, p 453-454 (in Russian); TR: *Moscow Univ. Chem. Bull.,* Vol 49 (No. 5), 1994, p 53-55

1994Zha: B. Zhang, J. Wang, X. Wang, and W. Chen, A Study on the β and ω Phases in a Ti-Al-Cr Alloy, *Scr. Metall. Mater.,* Vol 30 (No. 4), 1994, p 399-404

1995Bra: M.P. Brady, J.L. Smialek, and F. Terepka, Microstructure of Alumina-Forming Oxidation Resistant Al-Ti-Cr Alloys, *Scr. Metall. Mater.,* Vol 32 (No. 10), 1995, p 1659-1664

1995Hao: S. Hao and N. Zeng, Isothermal Section of the Phase Diagram of the Ti-Al-Cr Ternary System at 1000°C, *Jinshu Xuebao,* Vol 31 (No. 4), 1995, p B152-B158 (in Chinese)

1995Jew: T.J. Jewett and M. Dahms, Investigation of the γ-$Ti(Cr,Al)_2$ Phase at 800°C and 1000°C, *Scripta Metall. Mater.,* Vol 32 (No. 10), 1995, p 1533-1539

1996Jew1: T.J. Jewett, B. Ahrens, and M. Dahms, Stability of the $L1_2$ Phase at 800°C in the Ti-Al-Cr System, *Scr. Mater.,* Vol. 34 (No. 3), 1996, p 395-399

1996Jew2: T.J. Jewett and M. Dahms, Stability of the $Ti(Cr,Al)_2$ Phase, *Z. Metallkd.,* Vol 87 (No. 4), 1997, p 254-261

1996Jew3: T.J. Jewett, B. Ahrens, and M. Dahms, Phase Equilibria Involving the τ-$L1_2$ and $TiAl_2$ Phases in the Ti-Al-Cr System, *Intermetallics,* Vol 4, 1996, p 543-556

1997Jew: T.J. Jewett, B. Ahrens, and M. Dahms, Stability of TiAl in the Ti-Al-Cr System, *Mater. Sci. Eng. A,* Vol A225, 1997, p 29-37

1997Mab: H. Mabuchi, H. Tsuda, T. Matsui, and K. Morii, Microstructure and Mechanical Properties of Ternary $L1_2$ Intermetallic Compound in Al-Ti-Cr System, *Mater. Trans., JIM,* Vol 38 (No. 6), 1997, p 560-565

1997Xu: H. Xu, Z. Jin, and R. Wang, Study on the Phase Equilibria of the Al-Cr-Ti System at 1050°C, *Scr. Mater.,* Vol 37 (No. 10), 1997, p 1469-1473

1999Hel: T. Helander and O. Tolochko, An Experimental Investigation of Possible $B2$ Ordering in the Al-Cr System, *J. Phase Equilib.,* Vol 20 (No. 1), 1999, p 57-60

2000Kai: R. Kainuma, I. Ohnuma, K. Ishikawa, and K. Ishida, Stability of $B2$ Ordered Phase in the Ti-Rich Portion of Ti-Al-Cr and Ti-Al-Fe Ternary Systems, *Intermetallics,* Vol 8, 2000, p 869-875

2000Mah: K. Mahdouk and J.C. Gachon, Thermodynamic Investigation of the Aluminum-Chromium System, *J. Phase Equilib.,* Vol 21 (No. 2), 2000, p 157-166

2000Sha: G. Shao and P. Tsakiropoulos, On the ω Phase Formation in Cr-Al and Ti-Al-Cr Alloys, *Acta Mater.,* Vol 48, 2000, p 3671-3685

2000Zhu: W. Zhuang, J. Shen, Y. Liu, L. Ling, S. Shang, Y. Du, and J.C. Schuster, Thermodynamic Optimization of the Cr-Ti System, *Z. Metallkd.,* Vol 91 (No. 2), 2000, p 121-127

2001Fuj: T. Fujita, H. Ikeda, S. Tanaka, and Z. Horita, Construction of Ti-Al-Cr Phase Diagram Using Quantitative X-ray Microanalysis in Analytical Electron Microscope, *Nippon Kinzoku Gakkaishi,* Vol 65 (No. 5), 2001, p 382-388 (in Japanese)

2001Has: K. Hashimoto, Alloy Design of γ Titanium Aluminides, *LiMAT-2001, Proc. Int. Conf. Light Materials for Transportation Systems,* 2nd ed., N.J. Kim, C.S. Lee, and D. Eylon, Ed., Pohang Univ. Sci. Technol., Pusan, Korea, Vol 2, 2001, p 799-804

2001Ich: M. Ichimaru, N. Mori, and Y. Miura, Al-Ti-Cr Ternary Phase Diagram and Solidification Structure of $(Al,Cr)_3Ti$ Alloys, *Keikinzoku,* Vol 51 (No. 2), 2001, p 640-645 (in Japanese)

2002Kau: L. Kaufman, Calculation of Multi-Component Phase Diagrams for Niobium Alloys, *Niobium Sci. Technol. Proc. Int. Symp., Niobium 2001, Orlando,* Niobium 2001 Ltd., Bridgeville, PA, 2002, p 107-120

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

2003Bar: O.M. Barabash, Yu.V. Milman, D.V. Miracle, M.V. Karpets, N.P. Korzhova, T.N. Legkaya, N.M. Mordovets, Yu.N. Podrezov, and V.I. Voskoboinik, Formation of Periodic Microstructures Involving the $L1_2$ Phase in Eutectic Al-Ti-Cr Alloys, *Intermetallics,* Vol 11 (No. 9), 2003, p 953-962

2003Lee: J.K. Lee, M.W. Oh, M.H. Oh, and D.M. Wee, Phase Stability of $L1_2$ Based Alloys in Al-Ti-Cr Systems, *Intermetallics,* Vol 11, 2003, p 857-865

2003Oh: M.W. Oh, J.K. Lee, M.H. Oh, and D.M. Wee, Phase Stability of $L1_2$ Based Alloys at 800°C in Al-Cr-Ti System, *Taehan Kunsok Chaeryo Hokkoechi,* Vol 41 (No. 1), 2003, p 1-7 (in Korean)

2005Rag: V. Raghavan, Al-Ti (Aluminum-Titanium), *J. Phase Equilib. Diffusion,* Vol 26 (No. 2), 2005, p 171-172