The Cr-Ni-Zr (Chromium-Nickel-Zirconium) System

K.P. Gupta, The Indian Institute of Metals, India

Introduction

The Cr-Ni-Zr system was reviewed by [2000Gup]. In developing high temperature resistant brazing material, the Cr-Ni-Zr system has been studied at the Ni-corner. The results are given here.

In order to discuss the new results on Cr-Ni-Zr system, it is necessary to recapitulate the binary systems. The Cr-Ni system [1991Nas] (Fig. 1) is a simple eutectic system, the eutectic reaction L $\leftrightarrow \alpha + \gamma$ occurring at 1345 °C, where α and γ are the terminal solid solutions of body centered (bcc) Cr and face centered cubic (fcc) Ni, respectively. At the eutectic reaction temperature, the γ phase extends to \sim 50 at.% Cr and the α phase extends to \sim 32 at.% Ni. Solubility of Ni in Cr decreases with decrease in temperature reasonably fast down to ~1100 °C. A Ni₂Cr ordered phase forms in the γ phase region below ~ 600 °C. The Cr-Zr system [Massalski2, 1993Oka] shows (Fig. 2) the presence of only one intermediate phase Cr2Zr which occurs in three polymorphic forms, the $\alpha Cr_2 Zr(\psi_1)$ exists below ~1592 °C, the $\beta Cr_2 Zr(\beta_1)$ exists between 1592 and 1622 °C, and the $\gamma Cr_2 Zr(\gamma_1)$ exists between 1622 and 1673 °C. Two eutectics, $L \leftrightarrow \alpha + \beta_1$ and $L \leftrightarrow \psi_1 + \alpha'$ occur at 1592 and 1332 °C, respectively. The α' phase is the

terminal solid solution of β Zr. A eutectoid reaction $\alpha' \leftrightarrow$ $\omega + \psi_1$ occurs at 831 °C with ω representing the α Zr phase. The solubility of Zr in Cr is negligible at room temperature and is ~ 1.5 at.% Zr at the eutectic temperature 1592 °C. The Ni-Zr system [1991Nas] (Fig. 3) has eight intermediate phases Ni₅Zr(ε), Ni₇Zr₂(π), Ni₃Zr(λ), Ni₂₁Zr₈(θ), Ni₁₀Zr₇(β), Ni₁₁Zr₉(ν), NiZr(ϕ), and NiZr₂(ξ). The π , ϕ , and ξ phases melt congruently at 1440, 1260, and 1120 °C, respectively. All the other intermediate phases form through peritectic or peritectoid reactions: $L + \pi \leftrightarrow \varepsilon$, $L + \pi \leftrightarrow \theta$, $\pi + \theta \leftrightarrow \lambda$, $L + \eta \leftrightarrow \lambda$ $\phi \leftrightarrow v_1$ and L + v $\leftrightarrow \beta$ occurring at 1300, 1180, 920, 1170, and 1160 °C, respectively. Five eutectic or eutectoid reactions: $L \leftrightarrow \gamma + \varepsilon, L \leftrightarrow \theta + \beta, L \leftrightarrow \phi + \xi, L \leftrightarrow$ $\xi + \alpha'$, and $\alpha' \leftrightarrow \xi + \omega$ occur at 1170, 1070, 1010, 960, and 845 °C, respectively. The v phase undergoes eutectoid transformation $v \leftrightarrow \beta + \phi$ at 978 °C. The phases and their structure data are given in the review paper [2000Gup].

[1999Kho] reinvestigated the Cr-Ni-Zr system at the Ni-rich corner, up to \sim 40 at.% Cr and up to \sim 30 at.% Zr. The alloys were melted in a water cooled copper hearth, tungsten electrode arc furnace under argon atmosphere. The component elements were Ni of 99.95 mass% purity, Cr of 99.98 mass% purity, and Zr of 99.95 mass% purity. The alloys in cast condition were used for this investigation.



Fig. 1 The Cr-Ni system [1991Nas]



Fig. 2 The Cr-Zr system [1993Oka]



Fig. 3 The Ni-Zr system [1991Nas]

Ten alloys were prepared, of which seven contained 8.8 at.% Zr with Cr varying from 0-30 at.% in steps of 5 at.%, two alloys were binary Ni-Zr alloys containing

16.67 and 22.22 at.% Zr and one alloy with 5 at.% Cr and 22.22 at.% Zr. Metallography, x-ray diffraction (XRD), and thermal analysis were used for characterization of the alloys.



Fig. 4 (a) A partial liquidus projection at the Ni-corner of Cr-Ni-Zr system. (b) Reaction scheme for liquidus projection of (a)

Isothermal section established by [1995Jou] at 1000 °C showed that Cr solid solution (α phase) was in equilibrium with the π phase. In the present investigation the alloy with 5 at.% Cr and 22.22 at.% Zr showed that a eutectic type pseudobinary exists between the π and α phase with a eutectic temperature of 1285 °C, the eutectic composition is given to be at a composition of near Cr₂₄Ni₆₀Zr₁₆. Another eutectic type pseudobinary was reported between the γ and π phase with eutectic temperature and composition of 1235 °C and Cr₂₀Ni_{71.2}Ze_{8.8}, respectively. Phase analysis of the cast alloys with compositions of 25 and 30 at.% Cr and both containing 8.8 at.% Zr were found to show 3 phases $\gamma + \pi + \alpha$. The three phase equilibrium solidus temperature for the two alloys was found to be 1220 °C, indicating the existence of a ternary eutectic reaction E. The ternary reaction E arises due to the liquid compositions coming down from the three eutectic reactions e_1 , e_2 , and e_3 occurring at the Cr-Ni binary and the pseudo-binaries $\alpha - \pi$ and $\gamma - \pi$, respectively. The alloy with 15 at.% Cr and 8.8 at.% Zr was found to have 3 phases $\gamma + \pi + \varepsilon$ below the solidus temperature 1220 °C. This 3 phase region arises due to a U-type four phase reaction U:L + $\pi \leftrightarrow \gamma$ + ε . The four phase reaction arises due to the interaction of the liquid compositions coming down from the eutectic point e2 at the $\gamma - \pi$ pseudobinary and a liquid composition coming down from the peritectic reaction p: $L + \pi \leftrightarrow \varepsilon$ occurring at

the Ni-Zr binary. The four phase reaction also gives a 3 phase equilibrium $L + \gamma + \varepsilon$ at 1220 °C which finally terminate at the eutectic point $e_4:L \leftrightarrow \gamma + \varepsilon$ at the Ni-Zr binary. The liquidus projection for the investigated composition of the Cr-Ni-Zr system is given in Fig. 4(a), and the corresponding reaction scheme is given in Fig. 4(b).

References

- **1991Nas:** P. Nash, *Phase Diagrams of the Binary Nickel Alloys*, ASM International, Materials Park, OH, 1991 (Review)
- **1993Oka:** H. Okamoto, J. Phase Equilib., 1993, **14**(b), p 768 (Review)
- **1995Jou:** J.M. Joubert, M. Latroche, A. Percheron-Guegan, and I. Ansara, The Zr-Ni-Cr System at 1000 °C in the ZrCr₂-ZrNi-Ni-Cr Region, *J. Phase Equilib.*, 1995, **16**(6), p 485-492 (Phase Equilibria, #)
- **1999Kho:** V.F. Khorunov, V.G. Ivanchenko, and V.K. Kvashitskil, Structure and Phase Composition of Ni-Cr-Zr and Ni-Cr-Hf Alloys and as Brazes, *Avotom. Svarka*, 1999, **11**, p 14-22 (Phase Equilibria, #), in Russian
- 2000Gup: K.P. Gupta, The Cr-Ni-Zr (Chromium-Nickel-Zirconium) System, J. Phase Equilib. Diffus., 2000, 21(4), p 402-407

indicates presence of phase diagram.

Cr-Ni-Zr evaluation contributed by **K.P. Gupta**, the Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1996. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary nickel alloys.