Chromium – Copper – Nickel

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Introduction

A summary of experimental studies of phase equilibria is given in Table 1. [1909Jae] measured the melting point of a ternary alloy. [1923Sie] carried out extensive thermal analysis and reported a liquidus surface. [1955Mei1] reported an isothermal section at 930°C showing a "miscibility gap island" in the γ, (Cr,Ni,Cu) field. Since then a large number of studies have been carried out to understand the phase separation mechanism in ternary γ alloys, and the associated structure-property relationships. In addition, solubility of Cr in γ,(Ni,Cu) alloys as a function of temperature has also been reported [1939Ale, 1948Hib, 1967Zak]. Phase relations in the Cr-Cu-Ni system have been reviewed by [1949Jae, 1979Cha, 1979Dri, 1985Gup].

Binary Systems

The Cr-Cu binary phase diagram is accepted from [1993Cha1, 2002Ans]. The Cr-Ni binary phase diagram is accepted from [Mas2]. The Cu-Ni binary system is accepted from [2002Leb].

Solid Phases

The crystallographic data of the solid phases are listed in Table 2.
The solid solubility isotherms of Cr and Ni in (Cu) were investigated by [1967Zak] at 840, 910, 980, 1030 and 1070°C by means of X-ray diffraction and resistivity, and their results are shown in Fig. 1.
In the Cu-Ni system, the critical temperature of the miscibility gap is 354.5°C [1993Cha2]. With the addition of Cr phase separation in γ phase is thermodynamically favored, as a result the miscibility gap widens and the critical temperature increases significantly. Above 354.5°C, the miscibility gap is considered as an "island" as it does not extend up to the Cu-Ni binary edge. The locus of the miscibility gap island at a temperature other than 930°C is not known. The decomposition of Cu and Ni rich γ solid solutions, containing up to 16 mass% Cr, has been studied extensively in the temperature range of 500 to 850°C, as they undergo spinodal decomposition [1958Man, 1960Bad, 1973Kre, 1977Wu, 1978Cho, 1978Sau, 1978Wu, 1980Bow, 1983Rao, 1986Jia, 1986Rao, 1987Rao, 1991Abe, 1991Rao, 1992Fin, 1993Fin1, 1993Fin2, 1993Fin3, 1993Fin4, 1994Bha1, 1994Bha2, 1994Bha3, 1994Rag, 2001Lop, 2002Fin]. [1986Rao] reported that the coherent spinodal temperature for a Cu-26.7Ni-1.9Cr (mass%) alloy is 673°C. On the other hand, [1973Kni] observed that a Cu-29.45Ni-1.2Cr (mass%) alloy does not undergo spinodal decomposition in the temperature range of 500 to 750°C, rather the phase separation takes place by nucleation and growth mechanisms. Similarly, [1980Bow] found that the phase separation in a Cu-9Ni-2.5Cr (mass%) alloy also takes place by nucleation and growth processes in the temperature range of 550 to 850°C. [2001Lop] determined the composition of γ phases by analytical electron microscopy in two alloys that were aged at 800°C for more than 250 h. The compositions of Cu and Ni rich phases are listed in Table 3, and thus define only partly the locus of miscibility gap island at 800°C.

Liquidus, Solidus and Solvus Surfaces

The liquidus surface [1993Fin1] is shown in Fig. 2 along with selected isotherms. An earlier version of the liquidus by [1923Sie], accepted by [1985Gup], is thought to be unreliable, as it is based on a Cr-Cu phase diagram that is different from the one presently accepted. The drawbacks of experimental results of [1929Sei] and associated uncertainties of the Cr-Cu phase diagram have been discussed in detail [1993Cha1]. Specifically, the reported monotectic reaction $L_1 \rightleftharpoons \alpha + L_2$ at 1467°C in Cr-Cu system [1923Sie] could not be verified in subsequent investigations [1993Cha1]. [1985Gup] proposed a possible reaction scheme of the ternary system that includes the monotectic reaction. [1993Fin1] examined the as-solidified microstructures of four ternary alloys, Cu-31.7Ni-2.7Cr, Cu-28.5Ni-4.9Cr, Cu-44.2Ni-10.1Cr and Cu-45.1Ni-15.2Cr, and found primary dendrites of Ni rich γ phase and the eutectic mixture of α and

Cu rich γ phases in the interdendritic region. These results clearly demonstrate that the eutectic reaction originating from the Cr-Ni binary feeds directly into the eutectic in the Cr-Cu system, as shown in Fig. 2.

Isothermal Sections

Figure 3 shows the calculated isothermal section at 1200°C [1995Xia]. An isothermal section at 930°C [1955Mei1] is shown in Fig. 4, where minor adjustments are made along Cr-Ni edge to comply with the corresponding accepted phase diagram. It is characterized by the presence of a miscibility gap ($\gamma_1+\gamma_2$) island and a three-phase field ($\alpha+\gamma_1+\gamma_2$). This feature was confirmed by [1993Fin3]. However, phase compositions in the tie-triangle, which were determined by SEM and TEM X-ray energy-depressive analyses by [1993Fin3], differ by up to 4% compared to those by [1955Mei1]. In [1993Fin3] a conclusion was made that there were possibilities to be slightly wrong in the microanalysis.
The locus of the miscibility gap island at a temperature other than 930°C is not known. However, [2001Lop] determined the composition of γ phases by analytical electron microscopy in two alloys that were aged at 800°C for more than 250 h. The compositions of Cu and Ni rich phases are listed in Table 3, and thus define only partly the locus of miscibility gap island at 800°C.

Temperature – Composition Sections

Polythermal sections were reported by [1939Ale] and [1967Zak]. [1939Ale] determined the solubility of Cr in Cu-Ni alloys at a constant mass ratio of Cu:Ni as 70:30 and Cu:Ni as 80:20. Their results are shown in Figs. 5 and 6. In addition, [1948Hib] determined the solubility of Cr in Cu-10 mass% Ni, Cu-20 mass% Ni and Cu-30 mass% Ni, and the solubilities in these three alloys were reported to be 0.55 mass% Cr at 1065°C, 0.58 mass% Cr at 1075°C and 0.88 mass% Cr at 1120°C, respectively.
A polythermal section in the Cu corner was reported by [1967Zak], and it is shown in Fig. 7.

Thermodynamics

There is no experimental thermodynamic data of ternary alloys. However, since the discovery of phase separation of the γ phase [1955Mei1], thermodynamic modeling has been carried out to understand phase equilibria and phase separation mechanism [1955Mei2, 1957Mei, 1973Ans, 1981Gal, 1995Xia]. [1955Mei2, 1957Mei] used a regular solution model and calculated the isothermal section at 927 and 930°C that showed a remarkable agreement with the experimental isothermal section [1955Mei1]. In particular, both the three-phase field ($\alpha+\gamma_1+\gamma_2$) and the miscibility gap ($\gamma_1+\gamma_2$) were reproduced, whereas a simple graphical interpolation method did not yield any of the these results [1955Mei2, 1957Mei].

Notes on Materials Properties and Applications

A summary of experimental investigation of properties is given in Table 4. There has been a considerable interest in understanding the origin of strengthening mechanism in spinodally decomposed microstructures of ternary alloys. It has been shown that the increase in strength is proportional to the strain amplitude and independent of the wavelength of composition modulation [1986Rao, 1987Rao, 1992Fin, 1993Fin4]. Furthermore, prior deformation accelerates the spinodal decomposition kinetics, and also leads to a substantial increase in strength [1973Kre, 1994Rag]. The fatigue properties of ternary alloys, with and without spinodally decomposed microstructure, have also been reported [1992Wan, 1993Wan1, 1993Wan2, 1993Wan3, 1994Bom, 1994Wan]. Alloys with spinodally decomposed microstructures have higher fatigue strength [1992Wan].
The Cr impurity contribution to the resistivity and magnetoresistance was studied by [1972Eag]. These properties show a marked dependence on the Ni content, and the impurity contribution is proportional to the Cr content only in the alloys containing 23 at.% Ni. The results are consistent with the concept of spin-flip-scattering process.
Other properties investigated include corrosion and wear [1973And, 1988Qin, 1990Elb, 1990Sof], weldability [1969Pet], wettability [1995Xia, 2001Les], and oxidation [2003Cao1, 2003Cao2].
Ternary alloys have been used for decorative purposes by an electrodeposition process [1980Sri].

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Table 1: Investigations of the Cr-Cu-Ni Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1909Jae]	Thermal analysis	Cr-40.5Cu-19Ni (mass%)
[1923Sie]	Thermal analysis and optical metallography	1093-1498°C; Cu: 1.5-80 mass%, Ni: 5-80 mass%, Cr: balance
[1939Ale]	Hardness and optical metallography	400-1100°C; Cr: up to 0.5 mass%, Ni: up to 29.97 mass%, Cu: balance
[1948Hib]	Electrical resistivity, hardness and optical metallography	400-1075°C; Cr: 0.19-1.2 mass%, Ni: 10-30.3 mass%, Cu: balance
[1955Mei1]	Thermodynamic analysis	927°C; entire composition range
[1955Mei2]	Metallography and XRD	750-1120°C; entire composition range
[1957Mei]	Thermodynamic modeling	930°C; entire composition range
[1958Man]	XRD	550-800°C; Cr-46Cu-44Ni (mass%)
[1960Bad]	TEM, XRD and hardness	<980°C; Cu-(20.3-45.1)Ni-(0.75-3.6)Cr (mass%)
[1967Zak]	XRD	700-1070°C; Cr: 0.1-1.3 mass%, Ni: 0.35-1.45 mass%, Cu: balance
[1972Eag]	Resistivity and magnetometry	–271.65 to –173.15°C; 5.5-23 at.% Ni and $1.38 \cdot 10^{-3}$ - $1.21 \cdot 10^{-2}$ at.% Cr, Cu: balance
[1973Ans]	Thermodynamic modeling	930°C; entire composition range
[1973Kni]	TEM, hardness and electrical resistivity	500-750°C; Cu-29.45 mass% Ni and 1.2 mass% Cr
[1973Kre]	TEM, XRD and hardness	600-700°C; Cu-30.09Ni-2.94Cr (mass%)

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1977Wu]	TEM	600-700°C; Cu-28.9Ni-2.84Cr (mass%)
[1978Cho]	TEM	650°C; Cu-31.6Ni-1.7Cr (mass%)
[1978Sau]	TEM	300-900°C; Cu-(33.7-55.8)Ni-(3.8-15.5)Cr (mass%)
[1978Wu]	TEM	600-700°C; Cu-28.9Ni-2.84Cr (mass%)
[1980Bow]	TEM and hardness	550-850°C, Cu-(9-56)Ni-(2.5-16)Cr (mass%)
[1983Rao]	XRD	Cu-30Ni-5Cr (mass%)
[1986Jia]	TEM	580°C; Cu-36Ni-4Cr (mass%)
[1986Rao]	TEM, XRD and hardness	500-800°C; Cu-26.7Ni-1.9Cr (mass%)
[1987Rao]	TEM, SEM and XRD	500-650°C; Cu-44.8Ni-9.6Cr (mass%), Cu-51.9Ni-14.8Cr (mass%)
[1991Abe]	Atom-probe field ion microscopy	550-650°C; Cu-33.3Ni-1.7Cr (at.%)
[1991Rao]	TEM, XRD and hardness	500-800°C; Cu-26.73Ni-1.84Cr (mass%), Cu-44.78Ni-9.61Cr (mass%), Cu-51.91Ni-14.81Cr (mass%)
[1992Fin]	TEM, SEM, XRD and hardness	300-800°C; Cu-30Ni-2.5Cr (mass%), Cu-45Ni-10Cr (mass%)
[1993Fin1] [1993Fin2] [1993Fin3] [1993Fin4]	TEM, XRD and hardness	300-800°C; Cu-(28.5-45.1)Ni-(2.7-15.2)Cr (mass%)
[1994Bha1] [1994Bha2] [1994Bha3]	DSC, XRD and hardness	550-600°C; Cu-44.28Ni-5.4Cr (mass%)
[1994Rag]	XRD and hardness	500°C; Cu-31.8Ni-1.7Cr (mass%)
[1995Xia]	Thermodynamic calculations	1200°C; entire composition range
[2001Lop]	Atom-probe field ion microscopy, analytical TEM, SEM, XRD and hardness	600-800°C; Cu-34Ni-4Cr (mass%), Cu-45Ni-10Cr (mass%)
[2002Fin]	TEM and XRD	300-800°C; Cu-32.4Ni-3.4Cr (mass%), Cu-45.6Ni-17.4Cr (mass%)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, (Ni,Cu)	*cF*4 *Fm*$\bar{3}$*m*		
(Ni) < 1455	Cu	*a* = 352.32	pure Ni at 25°C [V-C2]
(Cu) < 1084.62		*a* = 361.46	pure Cu at 25°C [V-C2]
α, (Cr) < 1863	*cI*2 *Im*$\bar{3}$*m* W	*a* = 288.4	pure Cr at 27°C [V-C2]
$CrNi_2$	*oP*6 *Immm* $MoPt_2$	*a* = 252.4 *b* = 757.1 *c* = 356.8	60 to 76.5 at.% Ni [V-C2] [P]

Table 3: Composition of γ phases defining the miscibility gap boundary at 800°C

Alloy Composition (mass%)			γ_1 Composition (mass%)			γ_2 Composition (mass%)		
Cr	Cu	Ni	Cr	Cu	Ni	Cr	Cu	Ni
4	62	34	1.8	69.5	28.7	15.1	25.9	59.0
10	45	45	1.9	69.9	28.2	18.4	18.0	63.6

Table 4: Investigations of the Cr-Cu-Ni Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1960Bad]	Mechanical tests	Hardness, yield stress, tensile stress and elongation
[1969Pet]	Welding	Weldability
[1973And]	Wear/erosion	Sea water erosion
[1973Kre]	Mechanical tests	Tensile property
[1977Wu]	Mechanical tests	Yield stress
[1978Cho]	Mechanical tests	Yield stress
[1986Rao]	Mechanical test	Yield stress
[1987Rao]	Tensile test	Tensile properties
[1988Qin]	Electrochemical	Corrosion
[1990Elb]	Electrochemical	Corrosion
[1990Sof]	Electrochemical	Corrosion
[1991Rao]	Mechanical test	Hardness
[1992Fin]	Mechanical test	Hardness
[1992Wan]	Mechanical test	Fatigue

Reference	Method/Experimental Technique	Type of Property
[1993Wan1] [1993Wan2] [1993Wan3]	Mechanical test	Fatigue
[1994Bha1] [1994Bha2] [1994Bha3]	Mechanical test	Hardness
[1994Bom]	Mechanical test	Fatigue
[1994Wan]	Mechanical test	Low cycle fatigue, high cycle fatigue
[1995Xia]	Wettability	Joining
[2001Les]	Wettability	Joining
[2001Lop]	Mechanical test	Hardness
[2003Cao1] [2003Cao2]	Oxidation	Oxidation

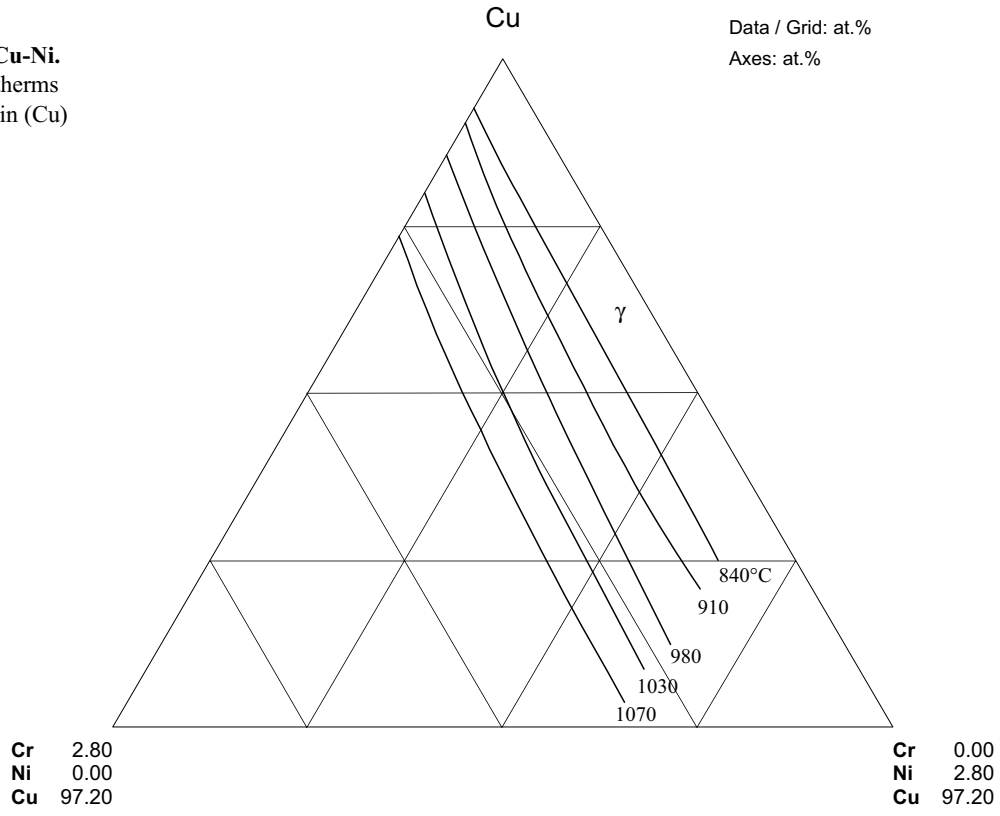

Fig. 1: Cr-Cu-Ni. Solubility isotherms for Cr and Ni in (Cu)

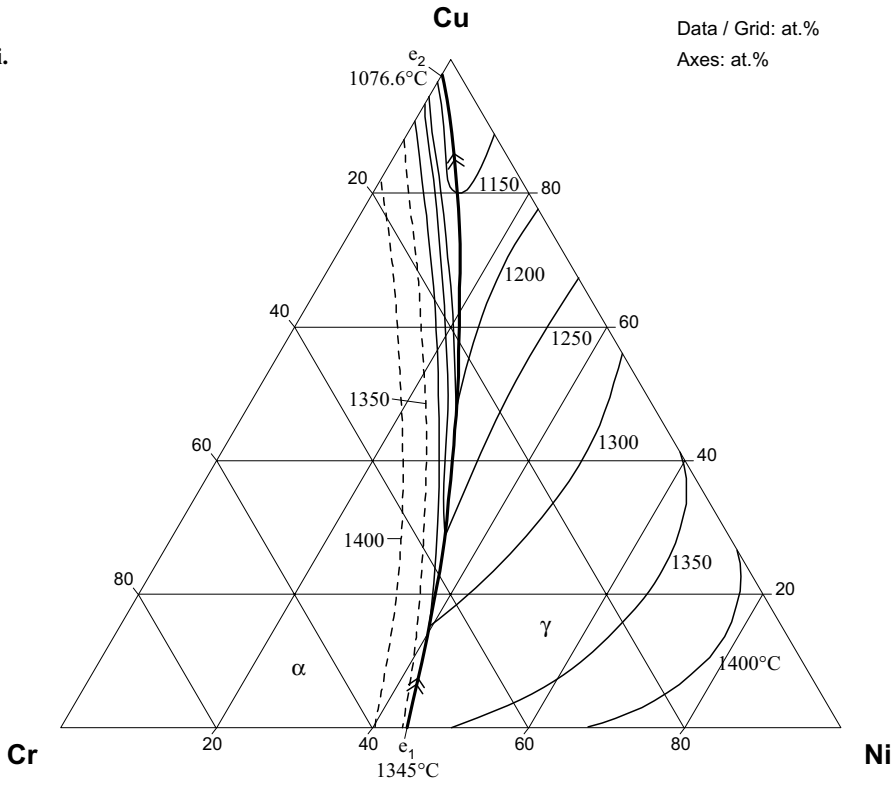

Fig. 2: Cr-Cu-Ni.
Liquidus surface

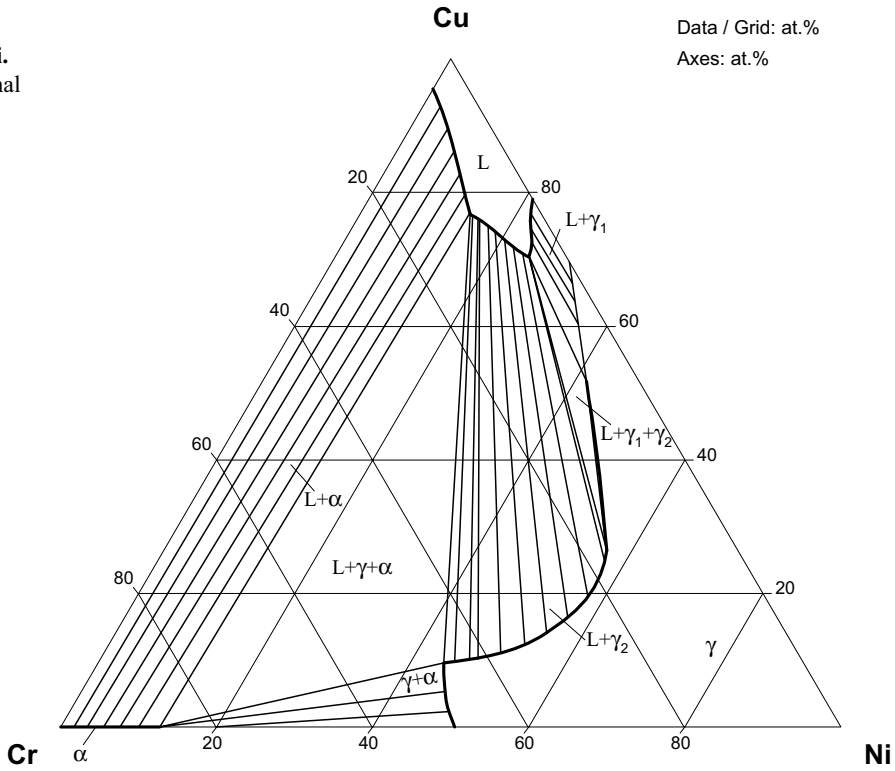

Fig. 3: Cr-Cu-Ni.
Calculated isothermal section at 1200°C

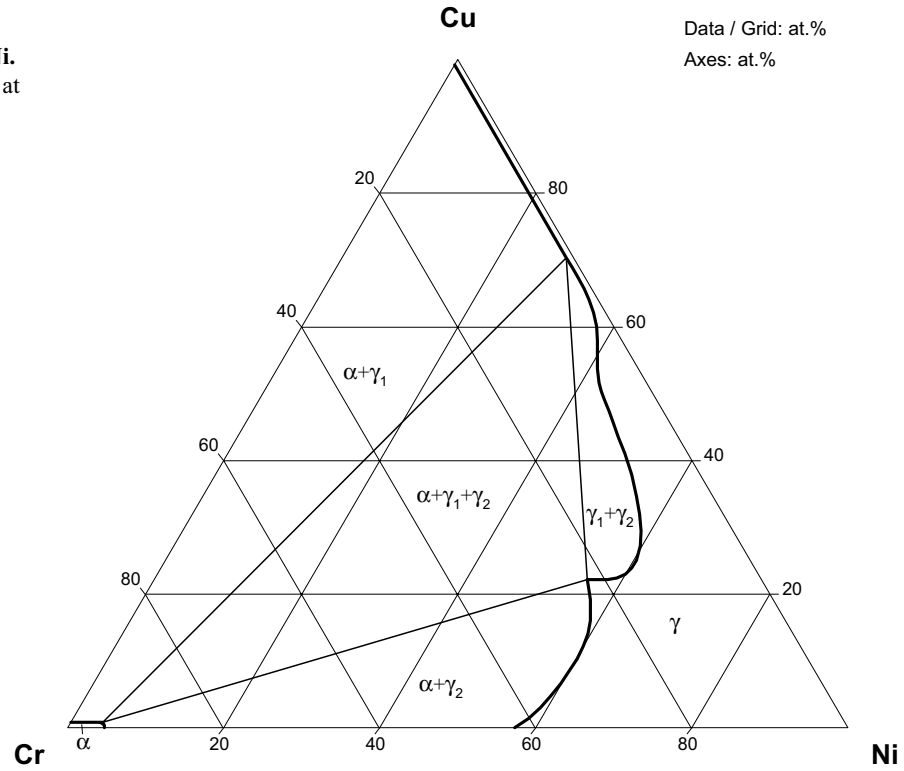

Fig. 4: Cr-Cu-Ni. Isothermal section at 930°C

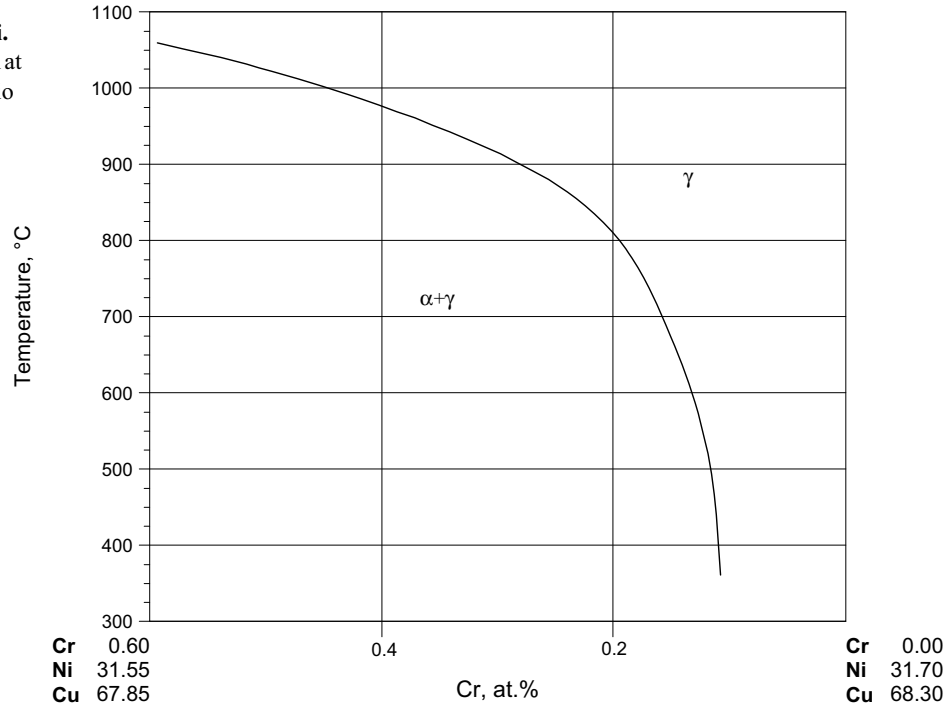

Fig. 5: Cr-Cu-Ni. Polythermal section at a constant mass ratio of Cu:Ni = 70:30, plotted in at.%

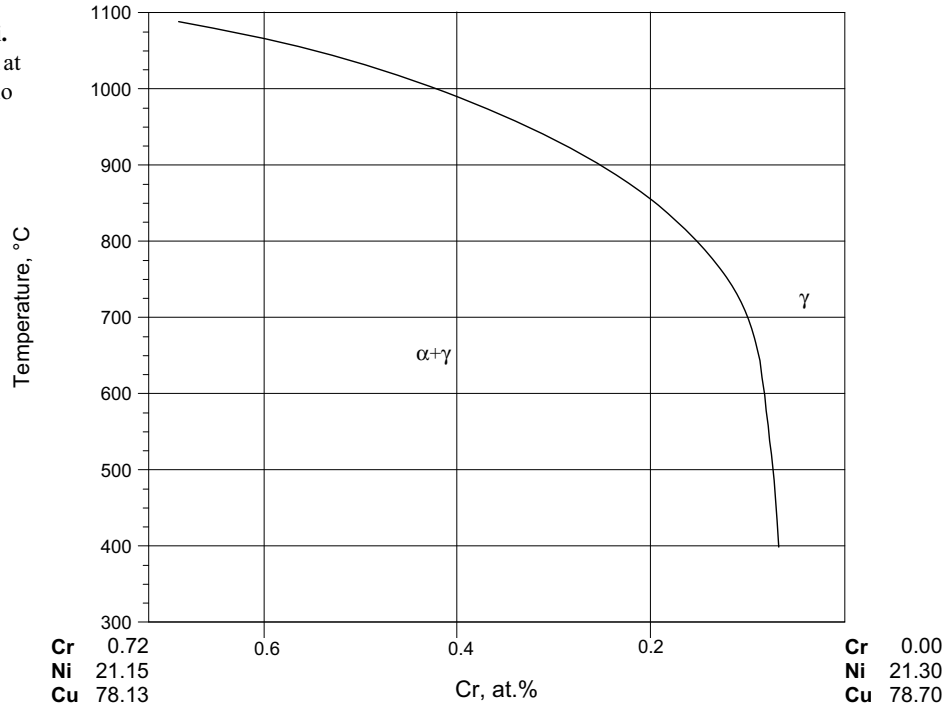

Fig. 6: Cr-Cu-Ni. Polythermal section at a constant mass ratio of Cu:Ni = 80:20, plotted in at.%

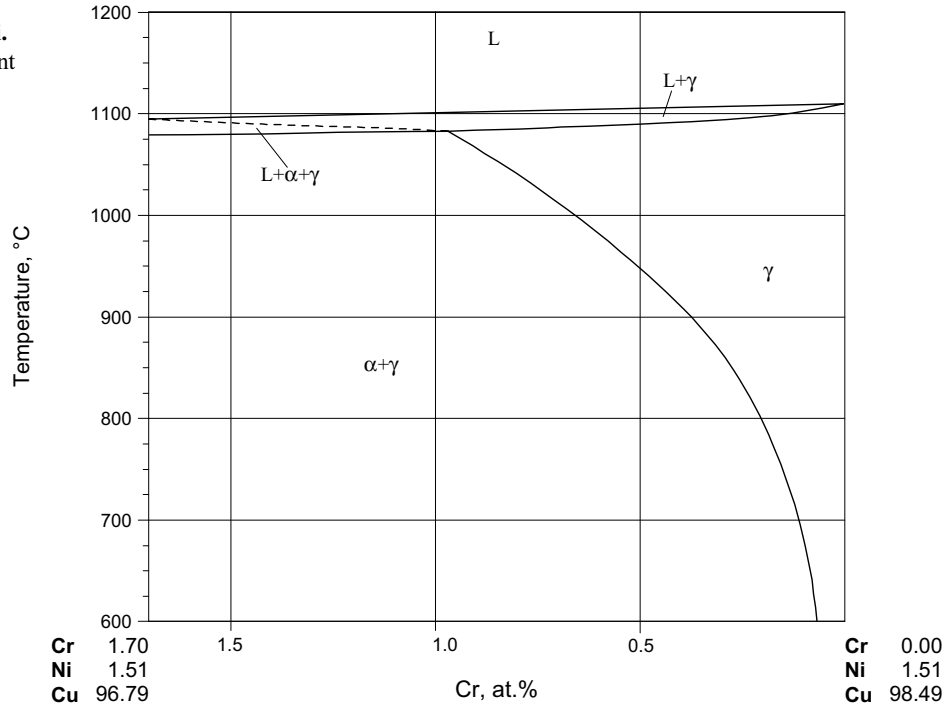

Fig. 7: Cr-Cu-Ni. Isopleth at a constant Ni content of 1.4 mass%, plotted in at.%