

Phase equilibria in the Ni–Cr–Zr₂Ni₇ partial system

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Alloys from the Ni–Cr–Zr₂Ni₇ partial system have been studied using optical microscopy, X-ray diffraction, DTA, electron microprobe analysis and microhardness measurements. The existence of two quasibinary sections was established. The projection of the liquidus and solidus of the partial Ni–Cr–Zr system in the composition range Ni–Cr–Zr₂Ni₇ was constructed and isopleth 8.8 at.% Zr was built.

Quasibinary section / Binodal curve / Isopleth / Equilibria / U-type reaction

Introduction

The aim of the earliest studies of Cr–Ni–Zr alloys was concerned with the search for new materials for high operating temperatures in gas turbine engines, namely quasibinary eutectics between the Ni-based solid solution and intermetallic compounds forming in the Ni–Zr system [1,2]. [1] reported about the eutectic formed between (Ni) and the Zr(Ni,Cr)₅ intermetallic phase at the composition 67.9Ni–22.3Cr–9.8Zr (at.%). The melting point was about 1270 °C. This result was confirmed by [2], who found that the eutectic in this system has a melting point of 1255 °C and a composition of 67.1Ni–22.3Cr–10.6Zr (at.%). The reinforcing intermetallic phase was not identified. The isothermal section of the Cr–Ni–Zr ternary system in the ZrCr₂–ZrNi–Ni–Cr region was determined at 1000 °C by [3]. It is shown in Fig. 1a. The characteristic features of this isothermal section are the existence of the binary ranges (Ni)–Zr₂Ni₇ and (Ni)–ZrNi₅, the presence of two ternary intermediate phases, λ₁ (C14) and λ₂ (C15), and a solid solution based on the λ₂ ZrCr₂ modification of the Laves phase existing in the Cr–Zr binary system from room temperature to 1560 °C. The Ni solubility in the phase with MgCu₂ structure type reaches ~10 at.%. The λ₁ (C14, MgZn₂ structure type) ternary phase, also reported by [4], was found to extend from ~16 to 36 at.% Ni, the phase region being only ~2 at.% Zr wide. The λ₂ (C15) ternary phase exists between ~38 and ~70 at.% Ni, has a narrow phase region and deviates from the AB₂ stoichiometry line towards the Cr–Ni side with increasing Ni content.

Based on these experimental results, a thermodynamic study of the Cr–Ni–Zr system was

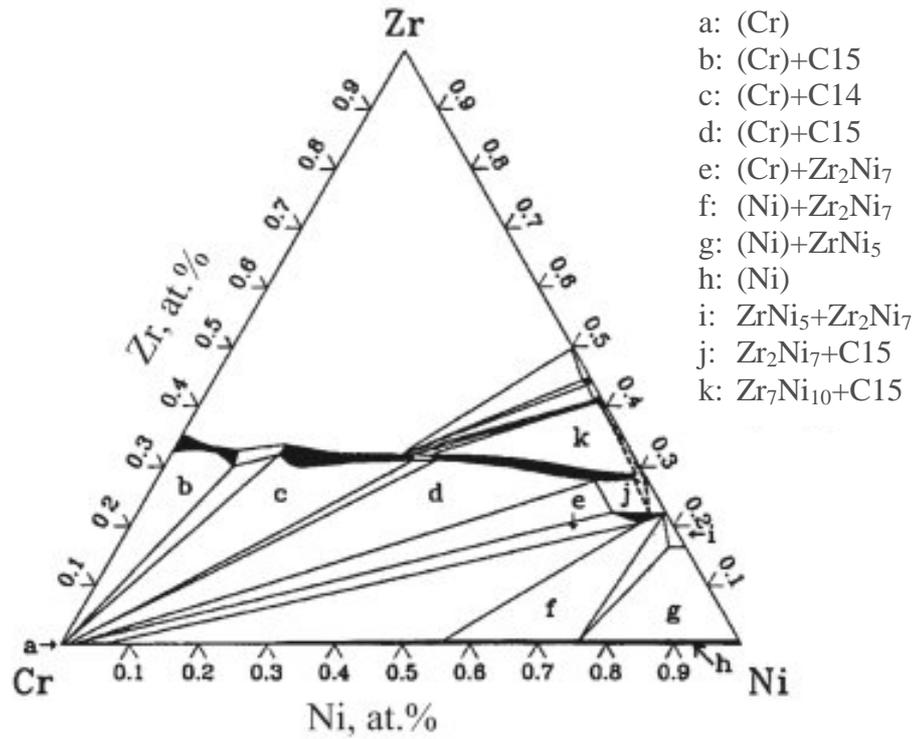
performed by [5] and calculated isothermal sections at 1000 and 500 °C were presented. The 1000 °C isothermal section agrees well with the part that had been experimentally determined by [3] and shows also phase equilibria above 40 at.% Zr. The calculated isothermal section at 500 °C [5] is shown in Fig. 1b. The characteristic feature of this isothermal section is the absence of the λ₁ (C14) ternary intermediate phase and the extension of the λ₂ (C15) phase region from the Cr–Zr system almost to the Ni–Zr system. The equilibrium between Zr₂Ni₇ and (Ni) is absent, but a sizeable expansion of the binary range (Ni)+ZrNi₅ takes place. It was shown by [6] that a (Ni)+ZrNi₅ eutectic is formed in the composition range from 9.5 to 10 at.% Zr and a Cr content of up to 11.5 at.%. Simultaneously, it was shown that a eutectic between (Ni) and Zr₂Ni₇ exists in the composition range 17–28.5 at.% Cr.

The following tasks were formulated for this work:

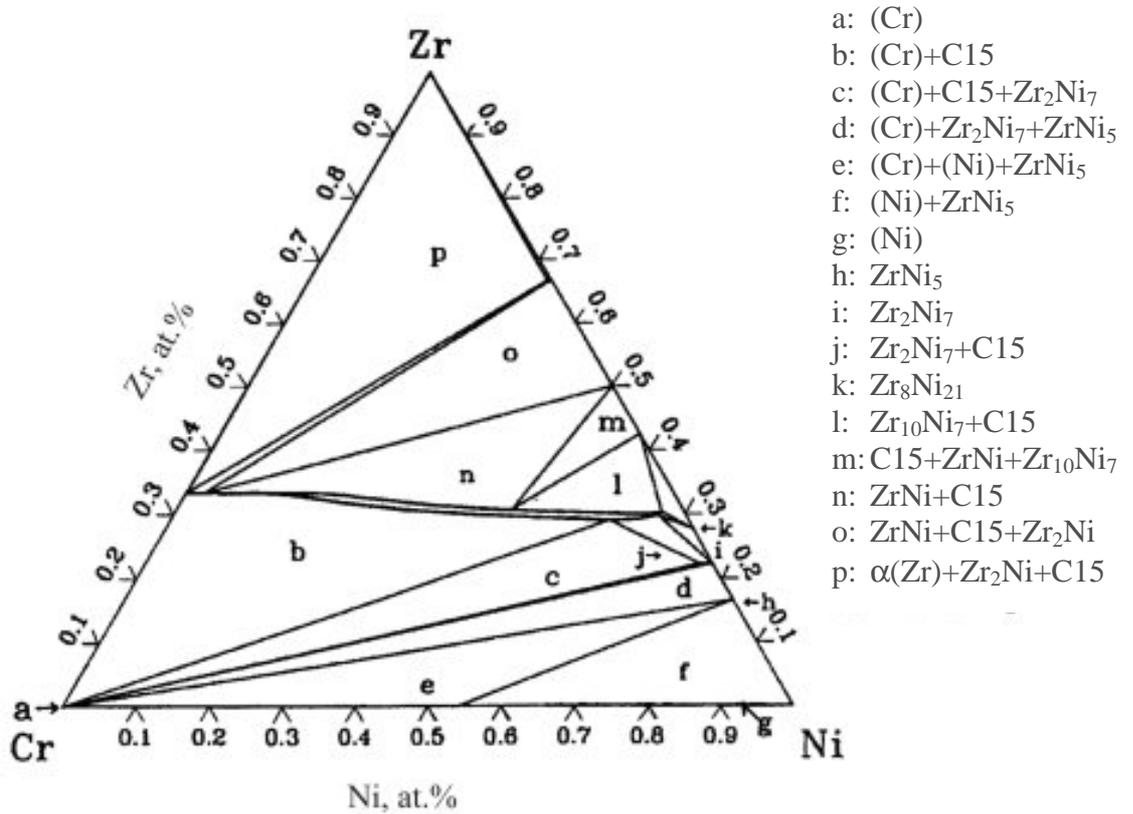
- confirm the existence of pseudobinary sections between Zr₂Ni₇ and (Ni) and (Cr), and determine their type and parameters;
- build the projection of the liquidus and solidus of the partial Ni–Cr–Zr system in the composition range Ni–Cr–Zr₂Ni₇;
- build a more complete isothermal section for the aforementioned concentration range.

Sample preparation and experimental procedure

Alloys were prepared as 50 g ingots using components with the following purity: 99.95 mass% Ni, 99.98 mass% Cr and 99.9 mass% Zr, by arc melting under an atmosphere of purified argon in a laboratory



(a)



(b)

Fig. 1 Isothermal sections of the Ni–Cr–Zr system: (a) at 1000 °C [3], (b) at 500 °C [5].

furnace with a non consumable tungsten electrode. For a better homogenization all specimens were melted 6 times with overturning and cast into a copper mould with a diameter of 15 mm.

The alloy composition was controlled by X-ray fluorescent analysis using a spectrometer VRA-30. The difference between the results of the analysis and the nominal compositions of the alloys did not exceed 0.2%, therefore the nominal alloy compositions were used later.

The specimens were examined by means of optical microscopy, X-ray diffraction, DTA and electron microprobe analysis. The phase microhardness was measured by indentation of a standard diamond pyramid with 100 g (0.98n) load. Solidus and liquidus temperatures were determined using a DTA-8M3 thermoanalyzer with the accuracy of ± 5 °C at heating and cooling rates of 0.7 °C/s in Al₂O₃ and Y₂O₃ crucibles in an atmosphere of high-purity helium for specimens of 0.8–1.2 g. X-ray patterns of the alloys were obtained using a diffractometer DRON-3M (Co K α radiation).

48 alloys were investigated. 7 of them had a constant concentration of 8.8 at.% Zr. This corresponds to the Zr concentration in the (Ni)+ZrNi₅ eutectic of the binary system according to [3,7]. The other alloy compositions were located in the regions of the probable existence of invariant and monovariant equilibria and supposed location of quasibinary sections. Furthermore, the binary compounds ZrNi₅ and Zr₂Ni₇ were prepared. The composition of the alloys and the results of the DTA study are presented in Table 1.

Experimental results and discussion

There are two quasibinary sections in the domain delimited by (Ni)+Zr₂Ni₇ and (Cr)+Zr₂Ni₇, namely Cr₃₂Ni₆₈–Zr₂Ni₇, and Cr₉₈Ni₂–Zr₂Ni₇. They are shown in Fig. 2 and Fig. 3. These sections are of a eutectic type. The structure of the (Ni)+Zr₂Ni₇ eutectic depends on the cooling rate. A higher cooling rate leads to a less regular structure. The structure of the alloy #4, which was crystallized in a 15 mm copper mould with a cooling rate of about 40 °C/s, is presented in Fig. 4a. The eutectic grains have a length of up to 200 μ m and a width of up to 50 μ m with a regular lamellar structure. In contrast, the eutectic of alloy #38, that has nearly the same composition, but was cooled at a rate of up to 150 °C/s, has an equiaxed structure with about 30 μ m-wide grains, which consist of plume-like particles of Zr₂Ni₇ embedded in a (Ni) matrix (Fig. 4b).

The alloys with compositions located along the Cr₉₈Ni₂–Zr₂Ni₇ join have a structure typical for a eutectic-type quasibinary section (Fig. 5). The primary Zr₂Ni₇ crystals have faceted form (Fig. 5a,b), whereas the primary crystals of (Cr) have a dendritic form typical for primary crystals of pure metals and metal-

based solid solutions (Fig. 5d). The structure of the eutectic colonies shows that the leading phase in the eutectic crystallization is Zr₂Ni₇ (Fig. 5c).

The combination of the eutectic-type quasibinary section between the (Ni)-based solid solution and Zr₂Ni₇ with the peritectic formation of ZrNi₅ leads to the U-type reaction L+Zr₂Ni₇⊕(Ni)+ZrNi₅. The boundaries of the phase domains were determined by X-ray phase analysis and microhardness measurements of the constituent structures and discrete phases. The results are presented in Table 2.

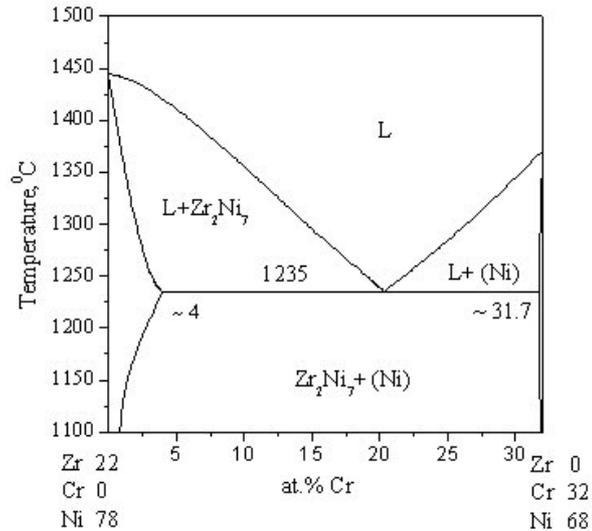


Fig. 2 The Cr₃₂Ni₆₈–Zr₂₂Ni₇₈ quasibinary section.

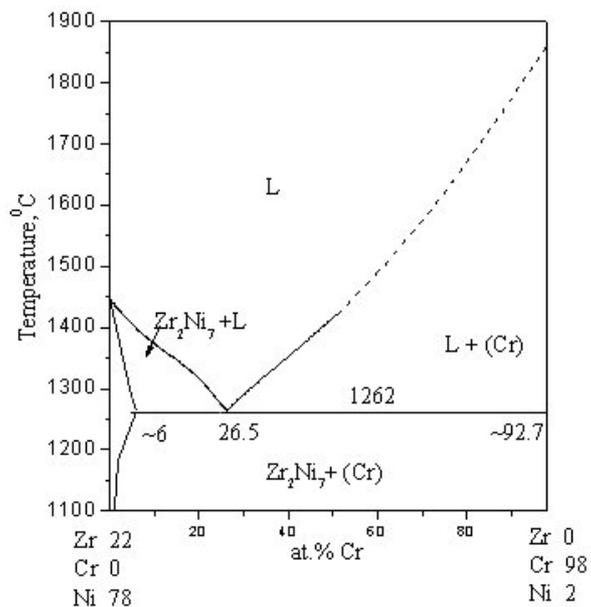


Fig. 3 The Cr₉₈Ni₂–Zr₂₂Ni₇₈ quasibinary section.

Table 2 Crystal structure of phases and microhardness of phases and structural components.

# alloy	Composition, at. %			Microhardness, (·HV)	Crystal structure and lattice parameters of the phases, nm, °			
	Ni	Cr	Zr		γ f.c.c ±0.0003	α b.c.c ±0.0003	ZrNi ₅ , cubic ±0.0005	Zr ₂ Ni ₇ , monoclinic ±0.0005
7	91.2	0.0	8.8	352, eut.	0.3528	-	0.6716	fixed <i>a</i> = 0.4697 <i>b</i> = 0.8231 <i>c</i> = 1.2185 <i>β</i> = 95.5±0.05
1	86.2	5.0	8.8	480, eut.	0.3539	-	0.6732	
2	81.2	10.0	8.8	501, eut.	0.3555	-	0.6728	
3	76.2	15.0	8.8	442, eut.	0.3561	-	0.6725	
4	71.2	20.0	8.8	317, eut.	0.3567	-	-	
39	66.2	25.0	8.8	417, eut.	0.3593	0.2883	-	<i>a</i> = 0.4698 <i>b</i> = 0.8230 <i>c</i> = 1.2186 <i>β</i> = 95.5±0.05
40	61.2	30.0	8.8	535, eut.	0.3592	0.2882	-	<i>a</i> = 0.4698 <i>b</i> = 0.8235 <i>c</i> = 1.2186 <i>β</i> = 95.5±0.05
8	83.3	0.0	16.7	500, intermetallic	-	-	0.6726	
9	77.8	0.0	22.2	460, eut. 181, intermetallic	-	-	-	<i>a</i> = 0.4690 <i>b</i> = 0.8277 <i>c</i> = 1.2180 <i>β</i> = 95.6±0.05
10	72.8	5.0	22.2	286, intermetallic	-	-	-	<i>a</i> = 0.4697 <i>b</i> = 0.8235 <i>c</i> = 1.2187 <i>β</i> = 95.5±0.05

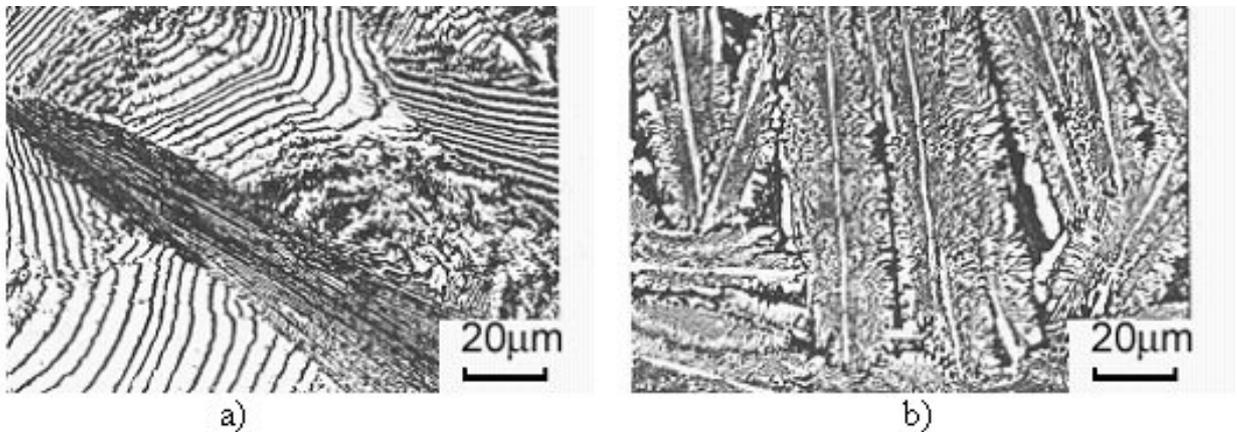


Fig. 4 Microstructure of a Ni–20Cr–8.8Zr eutectic alloy crystallized a) in a copper mould, b) on a water-cooled copper hearth.

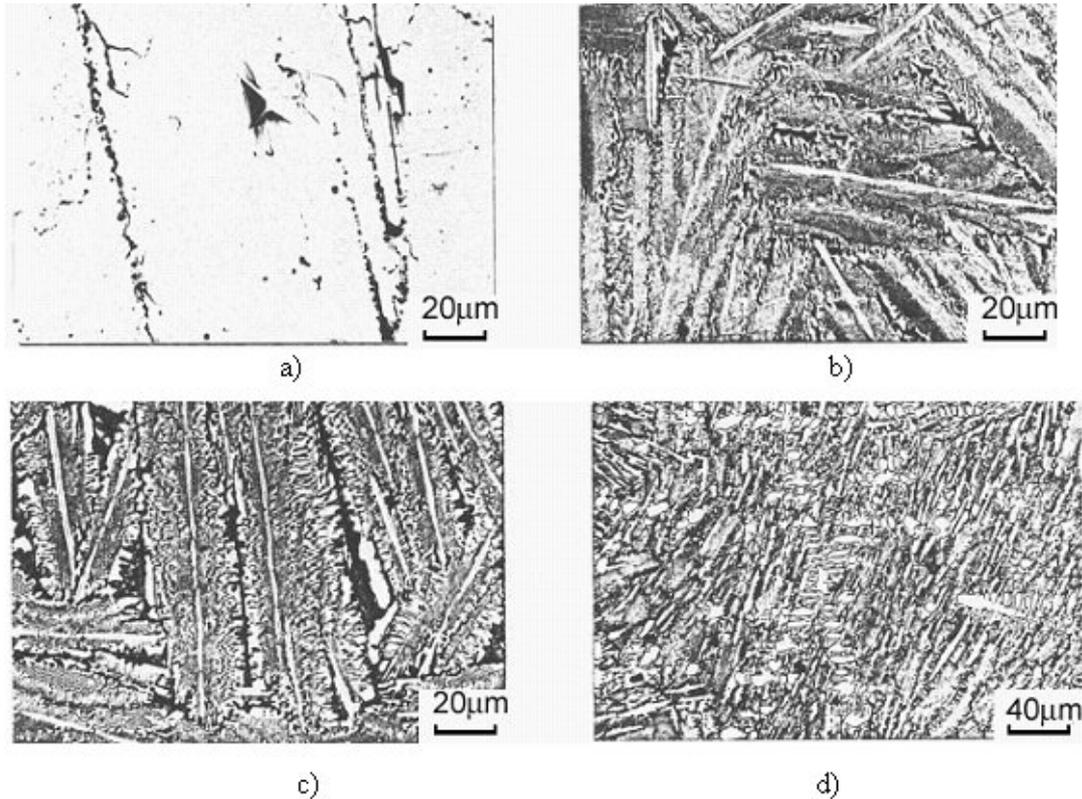


Fig. 5 Microstructure of alloys located in the (Cr)–Zr₂Ni₇ quasibinary section. a) #10, Ni-5Cr-22.2Zr; b) #13, Ni-25Cr-16.7Zr; c) #43 Ni-26.5Cr-15.5Zr; d) #14 Ni-30Cr-15.5Zr.

At the borders of the phase region (Ni)+ZrNi₅, a rise of the chromium content leads to an increase of the Zr concentration in the eutectic. In the (Cr)+Zr₂Ni₇ phase region, an increase of the Zr content has the opposite effect. Microstructures of alloys from the isopleth 8.8 at.% Zr are presented in Fig. 6. Measurements of the lattice parameters show that the solubility of Cr in ZrNi₅ does not exceed 1 at.%, but up to 6 at.% Cr can be dissolved in Zr₂Ni₇. The change of the microhardness of Zr₂Ni₇ from 181 HV to 286 HV upon alloying with 5 at.% Cr confirms this result. Since the microhardness of Zr₂Ni₇ is more than half of that of ZrNi₅, it defines the dependence of the microhardness in the alloys in the isopleth 8.8 at.% Cr (Table 2). In the phase region γ -Ni+ZrNi₅ an increase of the Cr content from 0 to 10 at.% is accompanied by solid solution strengthening of γ -Ni, and the microhardness of the eutectic increases from 352 HV to 501 HV. The appearance of Zr₂Ni₇ in the structure leads to a decrease of the microhardness, which in the range from 15 to 20 at.%Cr is not compensated by a strengthening of (Ni) because of the constant composition of γ -Ni in the ternary phase region (Ni)+ZrNi₅+Zr₂Ni₇. The minimum value of the microhardness (317 HV) was observed in the point of cross-section of the (Ni)-Zr₂Ni₇ pseudobinary section (alloy #4). Subsequent increase of the Cr content leads

to solid solution strengthening of (Ni) and Zr₂Ni₇ and to appearance of a hard (Cr) phase in the structure of the ternary eutectic ((Cr)+(Ni)+Zr₂Ni₇). The microhardness of the eutectic increases to 535 HV.

The location of the eutectic binodal curves in the ternary range (Ni)+(Cr)+Zr₂Ni₇ was determined by examination of the alloys #44, #45, and #46. Their structures are presented in Fig. 7. The alloy #44 has primary crystals of Zr₂Ni₇ with faceted forms that are typical for intermetallics (Fig. 7a). The alloy #45 has primary crystals of (Cr) in form of dendrites (Fig. 7b), which is typical for metal-based solid solutions, and the alloy #46 has a practically eutectic structure (Fig. 7c). In morphology it is similar to the structure of the alloy #43 (Fig. 5c). The location of the L \oplus (Ni)+Zr₂Ni₇ eutectic binodal curve was determined by examination of the alloys #22, #39, #40, and #41. The alloys #22 and #39 have a eutectic structure (Fig. 8), which is similar in morphology to the eutectic in the pseudobinary section Ni₆₈Cr₃₂–Zr₂Ni₇ (alloy #38, Fig. 4b). Traces of (Ni) primary crystals were observed in the microstructure of the alloy #40, which is presented in Fig. 8c. The alloy #41 has already eutectic structure (Fig. 8d). Combining this fact with the DTA results, the conclusion was made that the composition of this alloy corresponds to the composition of the ternary eutectic (Cr)+(Ni)+Zr₂Ni₇.

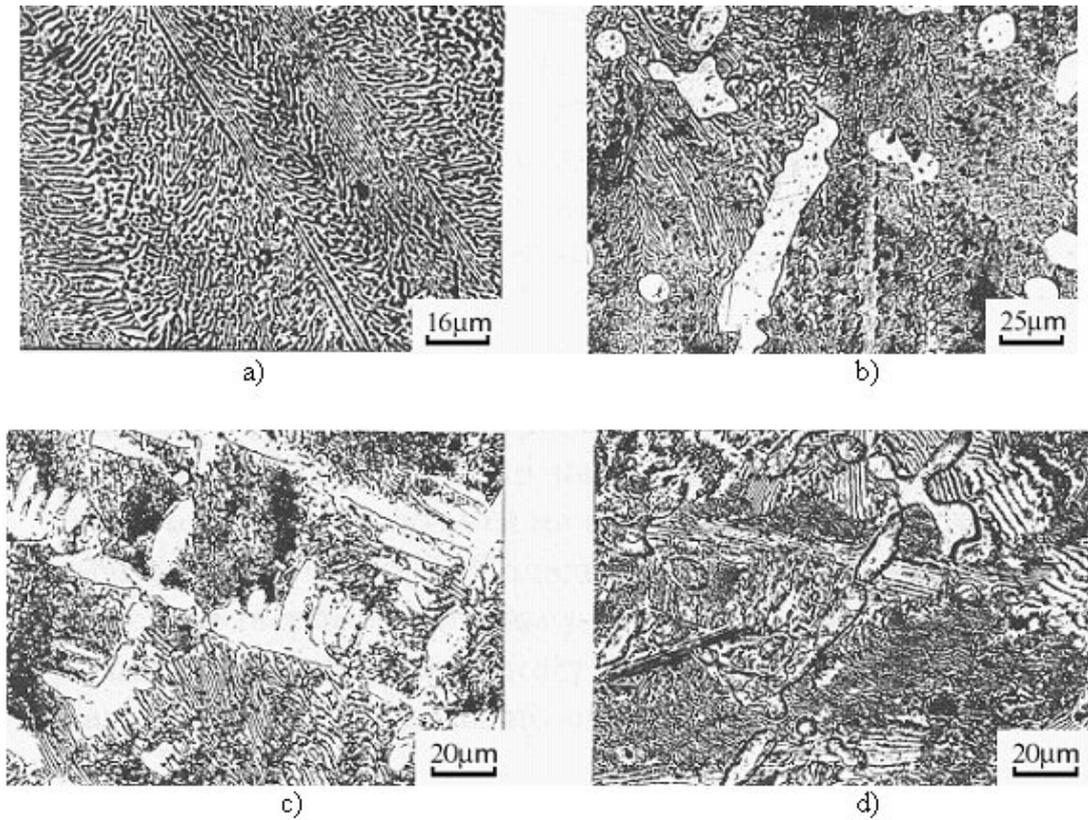


Fig. 6 Microstructure of alloys located in the isopleth 8.8 at.% Zr: a) #7, Ni-8.8Zr; b) #1, Ni-5Cr-8.8Zr; c) #2 Ni-10Cr-8.8Zr; d) #3 Ni-15Cr-8.8Zr.

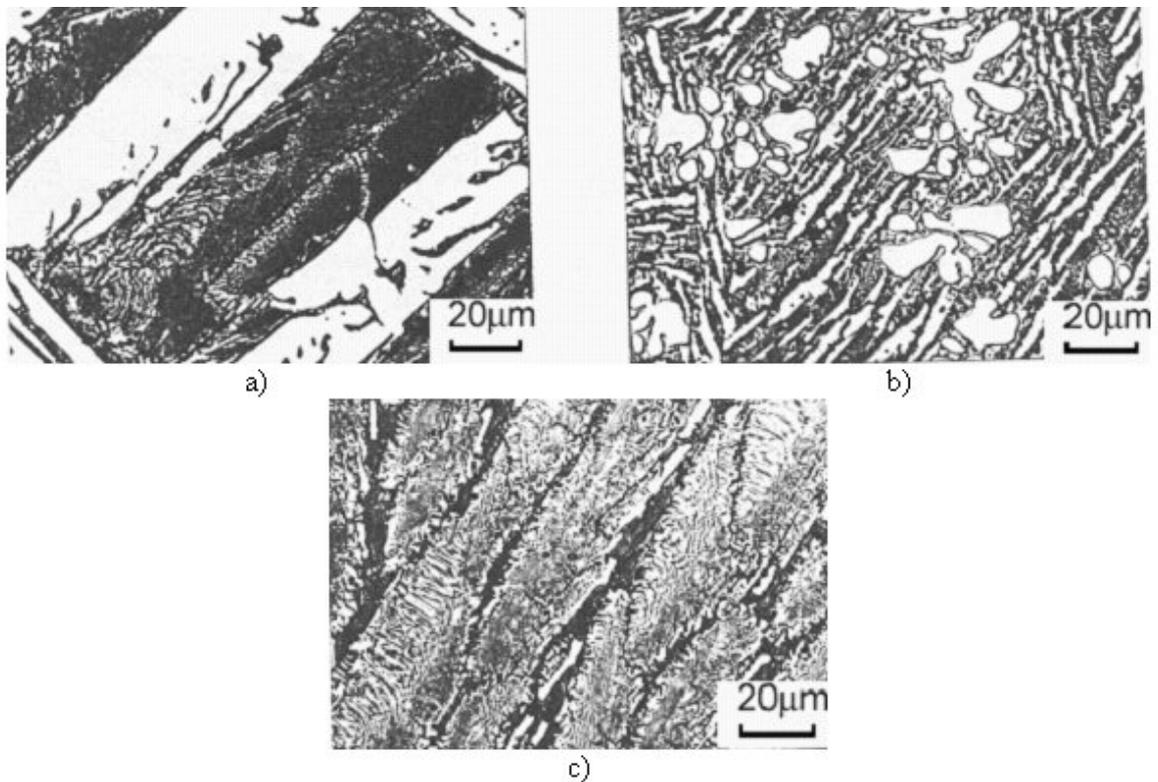


Fig. 7 Microstructure of alloys located close to the binodal $L^{\oplus} (Ni)+(Cr)+Zr_2Ni_7$: a) #44, Ni-26Cr-13Zr; b) #45, Ni-30Cr-13Zr; c) #46, Ni-34Cr-13Zr.

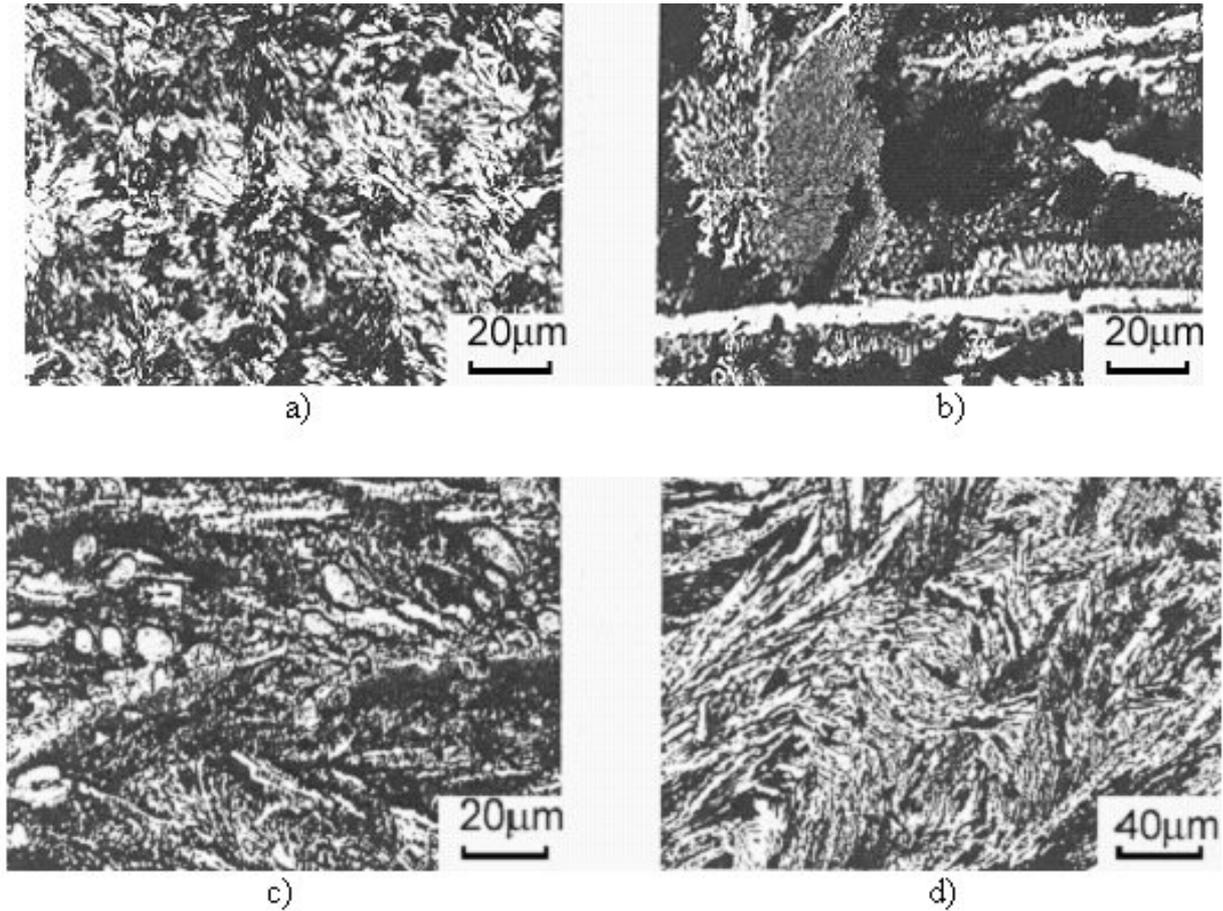


Fig. 8 Microstructure of alloys located close to the binodal $L^{\oplus}(\text{Cr})+\text{Zr}_2\text{Ni}_7$: a) #22, Ni–30Cr–6Zr; b) #39, Ni–25Cr–9Zr; c) #40 Ni–30Cr–9Zr; d) #41 Ni–37Cr–9Zr.

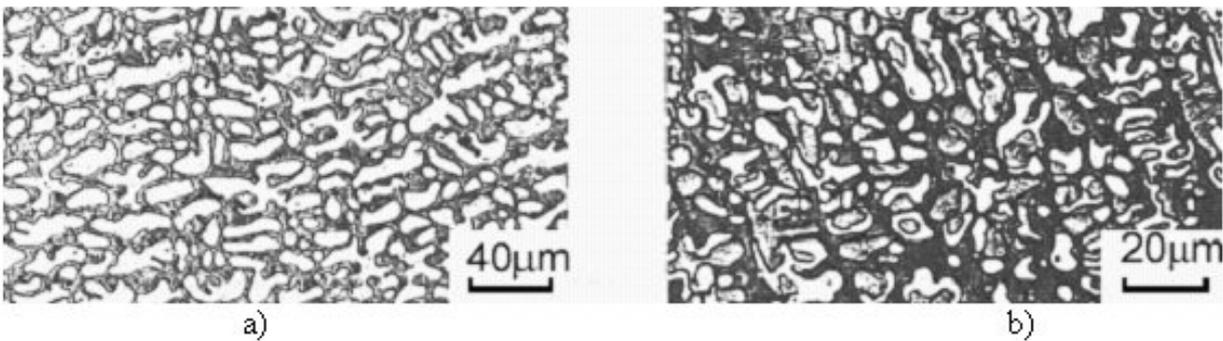


Fig. 9 Microstructure of alloys located on the binodal $L^{\oplus}(\text{Cr})+(\text{Ni})$: a) #18, Ni–42.5Cr–4Zr; b) #37, Ni–46Cr–4Zr.

The location of the binodal curve $L^{\oplus}(\text{Cr})+(\text{Ni})$ was determined by microscopy study of the alloys #18 and #37. Their microstructures are shown in Fig. 9.

The projection of the liquidus and solidus of the partial Ni–Cr–Zr system in the investigated range of composition Ni–Cr–Zr₂Ni₇ is presented in Fig. 10.

There are 5 two-phase regions: (Ni)+(Cr), (Ni)+Zr₂Ni₅, Zr₂Ni₅+Zr₂Ni₇, (Ni)+Zr₂Ni₇, (Cr)+Zr₂Ni₇; and 2 three-phase regions: (Ni)+ZrNi₅+Zr₂Ni₇, (Ni)+(Cr)+Zr₂Ni₇. The isopleth with 8 at.% Zr is shown in Fig. 11. The parameters of the invariant equilibria are presented in Table 3.

Table 3 Invariant equilibria.

T, °C	Type of reaction	Composition, at. %			
		Phase	Ni	Cr	Zr
1195	L ≡ (Ni) + ZrNi ₅ e ₁	L	91.2	-	8.8
		(Ni)	99.7	-	0.3
		ZrNi ₅	83.3	-	16.7
1345	L ≡ (Ni) + (Cr) e ₂	L	46	54	-
		(Ni)	50	50	-
		(Cr)	38	62	-
1310	Zr ₂ Ni ₇ + L ≡ ZrNi ₅ P ₁	L	83.8	-	16.2
		Zr ₂ Ni ₇	77.8	-	22.2
		ZrNi ₅	83.4	-	16.2
1262	L ≡ (Cr) + Zr ₂ Ni ₇ e ₃	L	58	26.5	15.5
		(Cr)	2	97.7	0.3
		Zr ₂ Ni ₇	75.7	3.1	21.2
1235	L ↔ (Ni) + Zr ₂ Ni ₇ e ₄	L	71.2	20	8.8
		(Ni)	67.7	32	0.3
		Zr ₂ Ni ₇	76	3	21
1200	L ≡ (Ni) + (Cr) + Zr ₂ Ni ₇ E	L	54	37	9
		(Ni)	57.7	42	0.3
		(Cr)	17	82.7	0.3
		Zr ₂ Ni ₇	75.7	3.2	21.1
		ZrNi ₅	82.5	<1	16.6
1220	L + Zr ₂ Ni ₇ ≡ (Ni) + ZrNi ₅ U	L	83.5	6.5	10
		(Ni)	73.2	26.5	0.3
		Zr ₂ Ni ₇	76.5	(3)	20.5
1440	congruent	L	77.8	-	22.2
		Zr ₂ Ni ₇	77.8	-	22.2

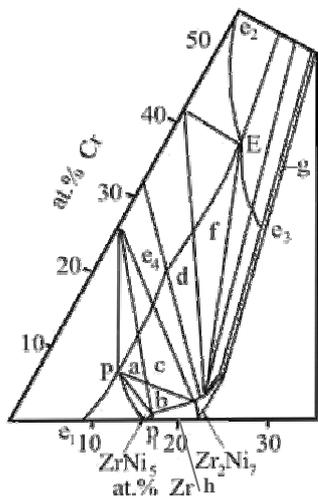


Fig. 10 Projection of the liquidus and solidus of the partial Cr–Ni–Zr system.

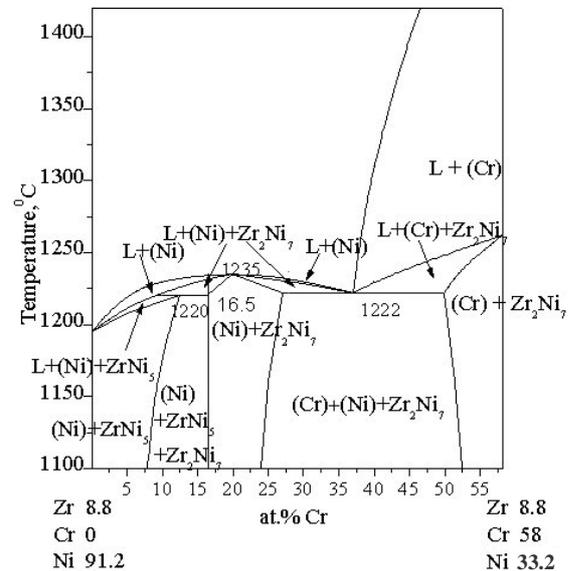


Fig. 11 Isoleth 8.8 at.% Zr.

Conclusions

There are two quasibinary sections in the domain delimited by (Ni)+Zr₂Ni₇ and (Cr)+Zr₂Ni₇, namely Cr₃₂Ni₆₈–Zr₂Ni₇, and Cr₉₈Ni₂–Zr₂Ni₇. In addition to the two three-phase eutectic-type invariant equilibria

realised in the quasibinary sections, two four-phase invariant equilibria exist in the Cr–Ni–Zr₂Ni₇ partial system. The combination of the eutectic-type quasibinary section between the (Ni)-based solid

solution and Zr₂Ni₇ with the peritectic formation of ZrNi₅ leads to the U-type reaction L+Zr₂Ni₇⊕(Ni)+ZrNi₅. In the (Cr)+(Ni)+Zr₂Ni₇ three-phase region, crystallization is finished by an E-type reaction: L⊕(Cr)+(Ni)+Zr₂Ni₇.

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