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Concentration Dependence of the Spectral Emissivity of Liquid Binary Metallic Alloys

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A review is given on the literature data on the concentration dependence of the emissivity of liquid binary metallic alloys (Ni–Fe, Ce–Cu, Ni–Cr, Ti–Al). Our measurements at the liquidus temperatures are presented for the systems Ni–V, Fe–V, and Fe–Nb and the pure components at $\lambda = 547$ nm and $\lambda = 650$ nm. All available results are interpretated in comparison to the phase diagrams of the systems. This comparison indicates that the nonvariant liquidus temperatures have the highest deviation from a linear interpolation between the emissivity of the pure components. The corresponding concentration ranges are characterized by stronger atomic interactions in the melt. Therefore errors in noncontact temperature measurements occur if the concentration dependence is neglected or estimated from the pure components.

KEY WORDS: binary alloys; concentration dependence; emissivity; liquid metals; melting; pyrometry.

1. INTRODUCTION

One of the major prerequisites for using new contactless techniques for thermochemical and thermophysical measurements on liquid alloys is the availability of high-quality optical pyrometers. Similar it is necessary to have good data on the emissivity of metals and their temperature and concentration dependence. Until now such data are lacking. Only a few papers deal with this subject [1–5]. In this connection, it is of special importance to recognize that a linear interpolation between the emissivity of the pure components may result in significant errors. From this point of view we

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have reviewed the literature and determined the hemispherical spectral emissivity at selected liquidus temperatures of liquid Ni–V, Fe–V, and Fe–Nb alloys and the pure components at the wavelengths $\lambda = 547$ nm (green) and $\lambda = 650$ nm (red). The results have been used for temperature measurements during our electromagnetic levitation experiments about mixing enthalpies and heat capacities of high-melting liquid binary systems [6, 7].

2. LITERATURE OVERVIEW

Lange and Schenck [1] performed experiments on liquid and solid pure metals and binary alloys to investigate the temperature and the concentration dependence of emissivity. Their investigations included the liquid Ni–Al, Ni–Co, Ni–Fe, and Ni–Si systems. The real temperature of the melt T_r was measured by a thermocouple and the brightness (radiance) temperature of the surface T_b by a single color pyrometer (650 nm). The results for the alloys indicated that all values of $\varepsilon_{\lambda 650}$ were located between the emissivities of the pure components (Fig. 1; Fe–Ni). They suggested that for the systems investigated a linear interpolation between the emissivities of the pure components is adequate to calculate the emissivity of the alloys over the entire concentration range.

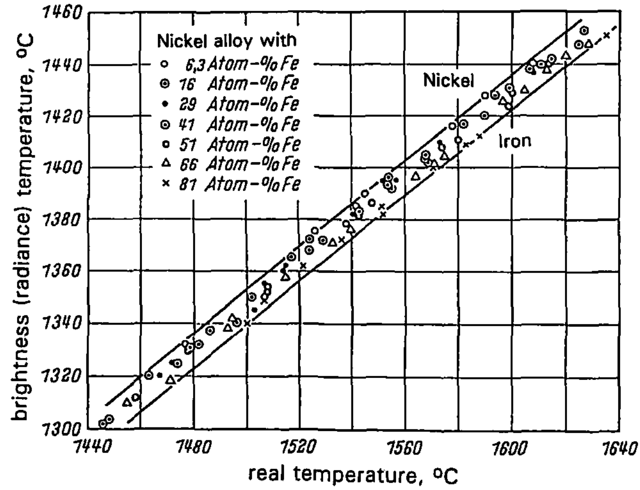

Fig. 1. The brightness (radiance) temperature, measured by optical pyrometry, versus the real temperature, measured by thermocouples, for nickel–iron alloys. The lines refer to the pure components. The figure is from Ref. 1.

This interpretation does not seem to be justified for the system Fe–Ni. A later investigation with an optical pyrometer of Ratanapupech and Bautista [2] (integral blackbody comparison method) described a distinctive concentration dependence. A temperature dependence (1810 to 1890 K) was not found. They presented their results with the following equation:

$$\varepsilon_{n645} = 0.3462 - 0.0506x_{\mathrm{Ni}} - 0.5009x_{\mathrm{Ni}}^2 + 0.5521x_{\mathrm{Ni}}^3 \tag{1}$$

where x_{Ni} is the mole fraction of nickel. Comparing Eq. (1) with the phase diagram (Fig. 2), one finds the lowest values of the emissivity in the concentration range near the liquidus temperature minimum of the Fe–Ni alloys.

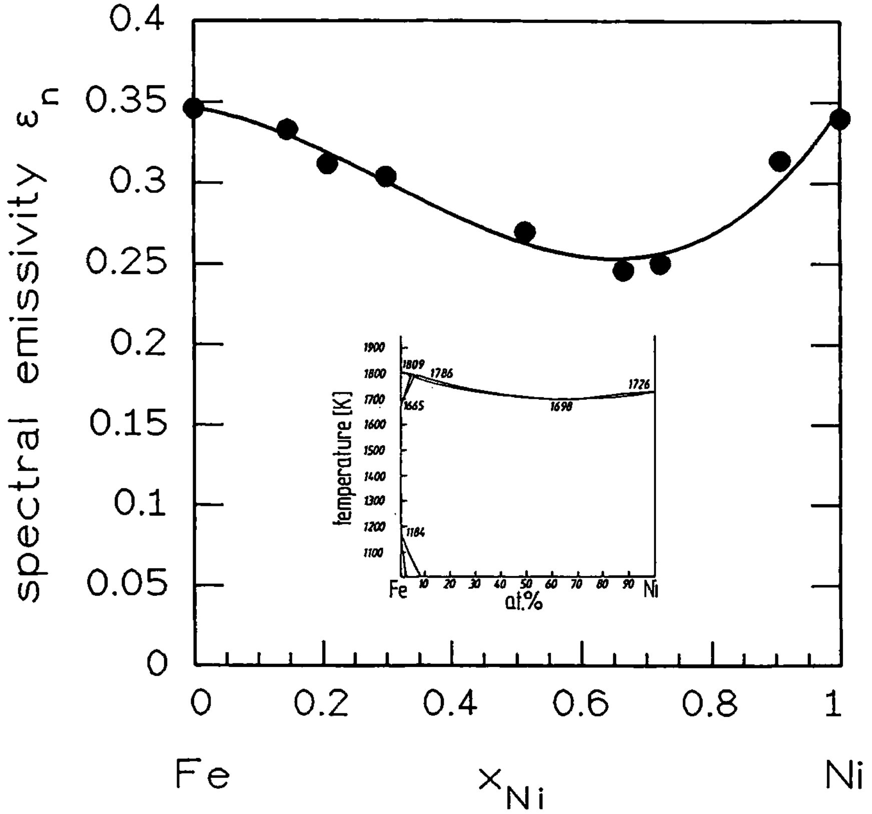

Fig. 2. Concentration dependence of the emissivity of iron–nickel alloys. Data points and curve are from Ref. 2; phase diagram is redrawn from Ref. 10.

With the same method Dokko and Bautista [3] investigated the emissivities of Ce–Cu alloys; the concentration dependence is significant, whereas the temperature dependence can be neglected (1376 to 1687 K). They presented their results with the following equation:

$$\varepsilon_{n645} = 0.292 - 0.065x_{\mathrm{Cu}} + 0.2242x_{\mathrm{Cu}}^2 + 1.1381x_{\mathrm{Cu}}^3 - 1.4773x_{\mathrm{Cu}}^4 \qquad (2)$$

The variation of the emissivity with composition corresponds to the phase diagram (Fig. 3). The maximum of the emissivity correlates with the congruent melting intermetallic phase $\mathrm{Cu_2Ce}$. The change of the emissivity in the cerium rich range is smooth, only a slightly marked minimum occurs. In this range the phase diagram shows an eutectic.

Shvarev et al. [4] investigated the normal spectral emissivity of Ni–Cr alloys by polarimetry over the wavelength range 0.37–2.65 μm up to $x_{\mathrm{Cr}} = 0.5$ at 1873 K. Measuring the refractive index (n) and the extinction coefficient (k), they obtained the normal spectral emissivity with the

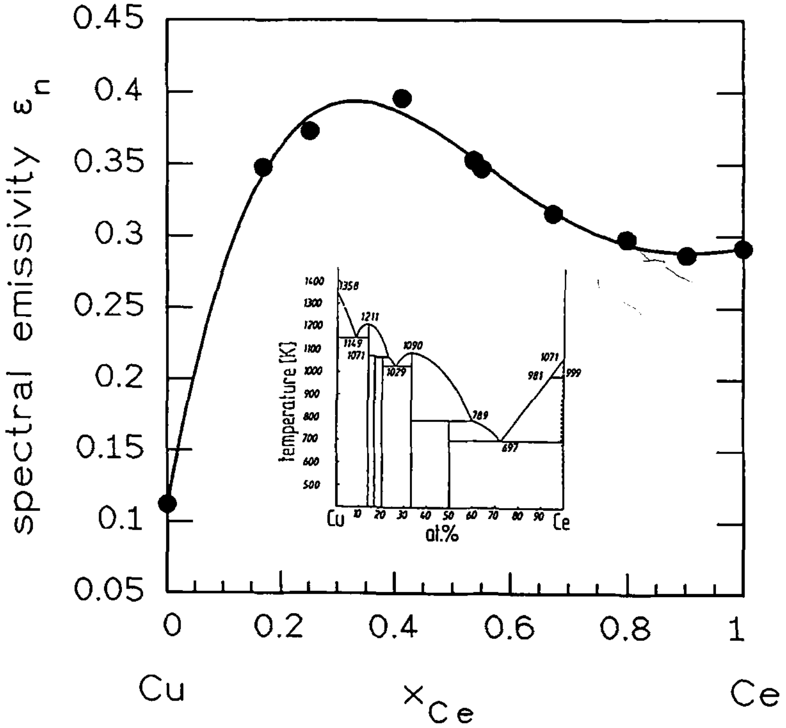

Fig. 3. Concentration dependence of the emissivity of copper–cerium alloys. Data points and curve are from Ref. 3; phase diagram is redrawn from Ref. 10.

Fresnel formula. Lin [8] determined the hemispherical spectral emissivity ε_{h650} of pure Cr ($\varepsilon_{h650} = 0.306$). Using the approximation [9]

$$\varepsilon_{h\lambda} = 1.07\varepsilon_{n\lambda} \tag{3}$$

one obtains the normal spectral emissivity $\varepsilon_{n650} = 0.286$. With this value a polynomial regression leads to the following function of the concentration dependence of the emissivity of Ni-Cr alloys:

$$\varepsilon_{n650} = 0.3665 - 0.2289x_{\mathrm{Cr}} + 1.5624x_{\mathrm{Cr}}^2 - 2.5892x_{\mathrm{Cr}}^3 + 1.1754x_{\mathrm{Cr}}^4 \tag{4}$$

The maximum of the graph is close to the eutectic and therefore again at a nonvariant crystallization point of the melt (Fig. 4).

Finally, Krishnan et al. [5] measured the optical properties (n and k) of liquid and undercooled liquid Ti–Al alloys by He–Ne laser ellipsometry

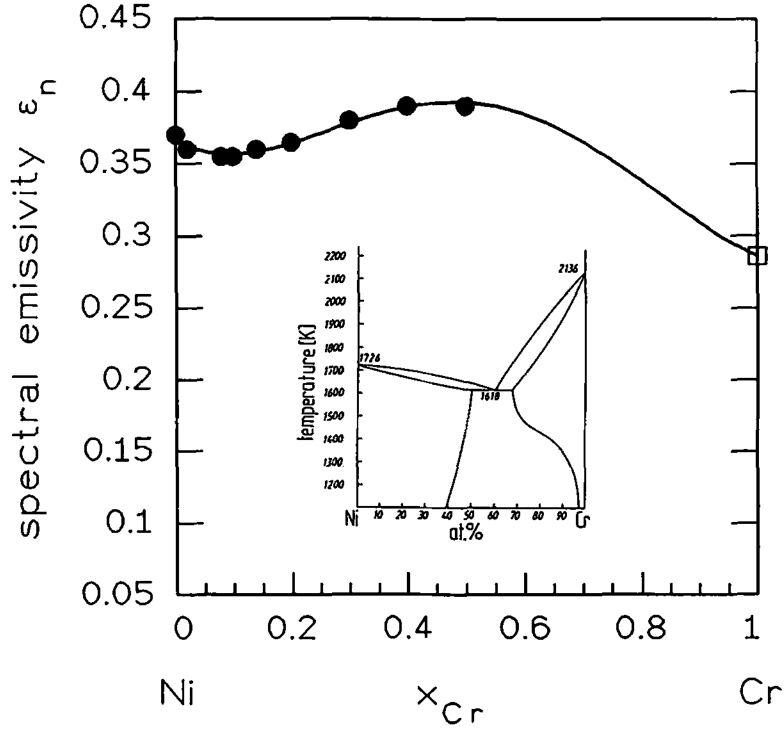

Fig. 4. Concentration dependence of the emissivity of nickel–chromium alloys. Data points and are from Ref. 4 (●) and 8 (□). The curve is according to Eq. (4). Phase diagram is redrawn from Ref. 10.

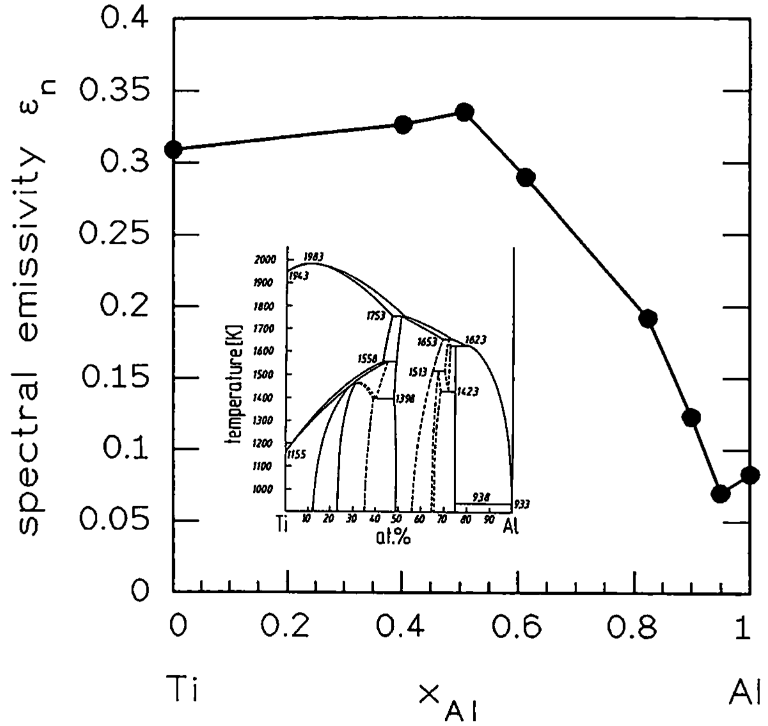

Fig. 5. Concentration dependence of the emissivity of titanium–aluminium alloys. Data points are from Ref. 5; phase diagram is redrawn from Ref. 10.

at $\lambda = 632.8$ nm. A function of the concentration dependence was not given. The highest emissivities correspond with the peritectic alloys, whereas the minimum is located at the aluminium-rich eutectic (Fig. 5). Moreover, a temperature dependence was determined. The curve refers to $T = 1800$ K.

3. MEASUREMENTS OBTAINED IN THIS WORK

Independently of one another, we used two optical pyrometers: a partial-radiation pyrometer and a quotient pyrometer. The partial-radiation pyrometer working at the wavelengths 547 nm (green) and 650 nm (red) was calibrated with tungsten lamps. The quotient pyrometer works simultaneously at 450 nm and 650 nm. The samples were electromagnetically levitated and melted under an inert gas atmosphere (He). The liquidus temperature was indicated by the quotient pyrometer as an arrest point in the time-temperature graph. Hereby the magnitude of the output value of the quotient pyrometer is of no consequence; the real liquidus temperatures T_r were taken from the literature. Due to this, the spectral emissivities measured were strongly influenced by the accuracy of literature data of the liquidus temperatures. Knowing that high-temperature phase boundaries are frequently inaccurate, we performed our measurements at nonvariant melting alloys. For the corresponding temperatures we assumed an error of ± 10 K for the literature data, resulting in an error of $\pm 10\%$ of the spectral emissivities obtained in this work. During the solidification of the sample we measured the brightness (radiance) temperature T_b with a partial-radiation pyrometer. With the help of a circulation gas cooling system which provides precise temperature control, we were able to expand the average period of solidification. We obtained the hemispherical spectral emissivity from Wien's approximation to Planck's law [Eq. (5)] and the normal spectral emissivity from Eq. (3). Wien's approximation is written as

$$\varepsilon_\lambda = \exp\left[\frac{C_2}{\lambda}\left(\frac{1}{T_r} - \frac{1}{T_b}\right)\right] \tag{5}$$

where ε_λ is the spectral emissivity, C_2 is Planck's second radiation constant ($C_2 = 1.4388 \times 10^{-2}\ \mathrm{m \cdot K}$), and λ is the effective wavelength of the pyrometer.

The following elements and alloys (at %) had been investigated at the liquidus temperature in the liquid state: Nb, V, Fe, Ni, the eutectic alloy $Ni_{49}V_{51}$, the concentration at the melting minimum $Fe_{69}V_{31}$, the eutectic alloys $Fe_{89,4}Nb_{10,6}$ and $Fe_{41}Nb_{59}$, and the intermetallic compound Fe_2Nb. The phase diagrams were taken from the literature: Ni–V [10], Fe–V [10], and Fe–Nb [11]. The determined emissivities of the pure liquid components are shown in comparison with the literature data in Table I. The values for the selected alloys are listed in Table II.

The Fe–V system shows a slightly increasing emissivity near of the lowest liquidus temperature of the system (Fig. 6). This may be due to small interactions between the atoms of the melt which were established by levitation alloying calorimetric measurements of the mixing enthalpy [6]. In the eutectic system nickel–vanadium one finds a stronger concentration dependence of the emissivity (Fig. 7). The incongruent melting σ phase causes stronger interactions. This fact is confirmed in a clear excess heat capacity [7]. In the system iron–niobium the influence of interactions between the atoms in the melt reflects in the temperature-dependent mixing enthalpy [12]. A clear decrease in the emissivity takes place at the iron-rich eutectic, whereas the compound Fe_2Nb is identified by the highest emissivity (Fig. 8).

Table I. Emissivity of the Pure Metals Niobium, Vanadium, Iron, and Nickel at Their Melting Points, T_m (Boldface and Normal Print Refer to the Hemispherical Spectral and Normal Spectral Emissivity, Respectively)

Metal, T_m, Ref.	This work	Literature values	References
Niobium, 2750 K [13]	$\varepsilon_{547}=$ **0.404** (0.3776)	$\varepsilon_{650}=0.35$	Touloukian et al., 1970 [15]
	$\varepsilon_{650}=$ **0.355** (0.332)	$\varepsilon_{650}=0.34$	Cezairliyan, 1972 [16]
		$\varepsilon_{645}=0.317$	Bonnell et al., 1972 [17]
		$\varepsilon_{650}=0.36$	Chekhovskoy et al., 1981 [18]
		$\varepsilon_{547}=$ **0.376**	Arpaci et al., 1985 [19]
		$\varepsilon_{650}=$ **0.36**	Arpaci et al., 1985 [19]
		$\varepsilon_{633}=0.321$	Krishnan et al., 1991 [20]
Vanadium, 2202 K [14]	$\varepsilon_{547}=$ **0.401** (0.375)	$\varepsilon_{650}=0.400$	Treverton et al., 1971 [21]
	$\varepsilon_{650}=$ **0.385** (0.36)	$\varepsilon_{650}=0.358$	Berezin et al., 1972 [22]
		$\varepsilon_{547}=$ **0.410**	Lin, 1991 [8]
		$\varepsilon_{650}=$ **0.402**	Lin, 1991 [8]
Iron, 1809 K [13]	$\varepsilon_{547}=$ **0.4535** (0.424)	$\varepsilon_{660}=0.36$	Bidwell, 1914 [23]
	$\varepsilon_{650}=$ **0.391** (0.365)	$\varepsilon_{650}=0.429$	Dastur et al., 1949 [24]
		$\varepsilon_{650}=0.384$	d'Entremont, 1963 [25]
		$\varepsilon_{650}=0.298$	Lange et al., 1968 [1]
		$\varepsilon_{650}=0.378$	Treverton et al., 1971 [21]
		$\varepsilon_{645}=0.357$	Bonnell et al., 1972 [17]
		$\varepsilon_{645}=0.346$	Ratanapupech et al., 1981 [3]
Nickel, 1726 K [13]	$\varepsilon_{547}=$ **0.492** (0.46)	$\varepsilon_{660}=0.221$	Bidwell, 1914 [23]
	$\varepsilon_{650}=$ **0.423** (0.395)	$\varepsilon_{650}=0.37$	Burgess et al., 1914 [26]
		$\varepsilon_{650}=0.355$	Lange et al., 1968 [1]
		$\varepsilon_{645}=0.346$	Bonnell et al., 1972 [17]
		$\varepsilon_{645}=0.34$	Ratanapupech et al., 1981 [3]
		$\varepsilon_{650}=0.366$	Shvarev et al., 1990 [4]
		$\varepsilon_{633}=0.40$	Krishnan et al., 1990 [27]

Table II. Hemispherical Spectral Emissivity of the Measured Liquid Binary Alloys (at %) in the Systems Ni–V, Fe–V, and Fe–Nb at Their Melting Points

		Hemispherical spectral emissivity	
Alloy	Liquidus temp. (K)	ε_{547}	ε_{650}
$Ni_{49}V_{51}$	1475	0.525	0.510
$Fe_{69}V_{31}$	1741	0.465	0.404
$Fe_{89,4}Nb_{10,6}$	1643	0.4127	0.3447
Fe_2Nb	1903	0.498	0.4175
$Fe_{41}Nb_{59}$	1773	0.4215	0.381

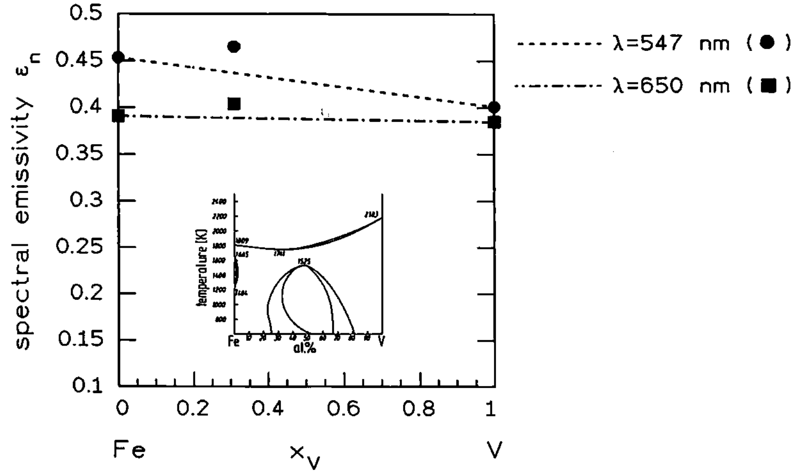

Fig. 6. Concentration dependence of the emissivity of iron–vanadium alloys. Data points are from the present work; phase diagram is redrawn from Ref. 10.

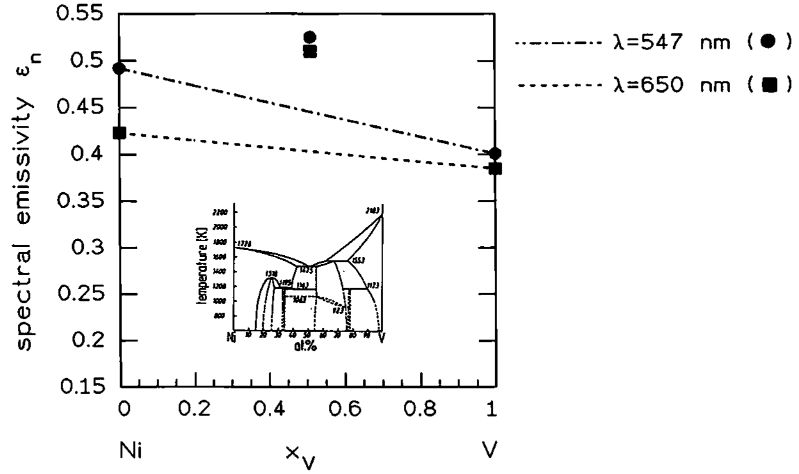

Fig. 7. Concentration dependence of the emissivity of nickel–vanadium alloys. Data points are from the present work; phase diagram is redrawn from Ref. 10.

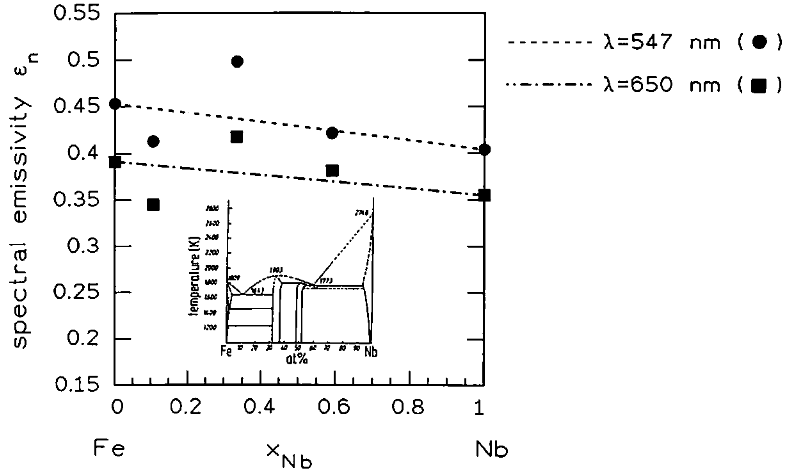

Fig. 8. Concentration dependence of the emissivity of iron–niobium alloys. Data points are from the present work; phase diagram is redrawn from Ref. 11.

4. CONCLUSIONS

The comparison between the concentration dependence of the emissivity of liquid binary alloys and the phase diagrams indicates the highest deviation of a linear estimation between the values of the pure components in the range of the nonvariant concentrations. These concentration ranges are characterized by stronger interactions of the atoms in the melt. The analysis of the data clearly points out that errors in noncontact temperature measurements result if the concentration dependence of the spectral emissivity is neglected or estimated from a linear interpolation between the pure components.

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REFERENCES

1. K. W. Lange and H. Schenck, *Arch. Eisenhüttenwesen* **39**:611 (1968).
2. P. Ratanapupech and R. G. Bautista, *High Temp. Sci.* **14**:269 (1982).
3. W. Dokko and R. G. Bautista, *Metall. Trans.* **11B**:309 (1980).
4. K. M. Shvarev, N. I. Vnukovskii, B. A. Baum, and P. V. Gel'd, *Teplofiz. Vysokikh Temp.* **20**:653 (1982).
5. S. Krishnan, C. D. Anderson, J. K. R. Weber, P. C. Nordine, W. H. Hofmeister, and R. J. Bayuzick, *Metall. Trans.* **24A**:67 (1993).

6. K. Schaefers, J. Qin, and M. G. Frohberg, *Steel Res.* **64**:229 (1993).
7. K. Schaefers, Dr.-Ing.-thesis (TU-Berlin, 1993), p. 57.
8. R. Lin, Dr.-Ing.-thesis (TU-Berlin, 1991), pp. 41–42.
9. D. N. Baria and R. G. Bautista, *Compilation of Experimental Work on Thermal Emittances of Materials*, Part I–Metals, USEORA Report IS-3346 (1975).
10. T. B. Massalski, J. L. Murray, L. H. Bennett, and H. Baker (eds.), *Binary Alloy Phase Diagrams, Vol. 2* (ASM, Metals Park, OH, 1986).
11. J. M. Z. Bejarano, S. Gama, C. A. Ibeiro, and G. Effenberg, *Z. Metallkunde* **84**:160 (1993).
12. K. Schaefers, J. Qin, M. Rösner-Kuhn, and M. G. Frohberg, *Steel Res.* **66**:183 (1995).
13. I. Barin, *Thermochemical Data of Pure Substances* (VCH Verlagsgesellschaft mbH, Weinheim, 1989).
14. P. D. Desai, *Int. J Thermophys.* **7**:213 (1986).
15. Y. S. Touloukian and D. P. DeWitt, in *Thermophysical Properties of Matter, Vol. 7, Thermal Radiation Properties: Metallic Elements and Alloys*; Y. S. Touloukian and C. Y. Ho, eds. (Plenum Press, New York; 1970).
16. A. Cezairliyan, *High Temp. High Press.* **4**:453 (1972).
17. D. W. Bonnell, J. A. Treverton, A. J. Valuga, and J. L. Magrave, in *Temperature: Its Measurement and Control in Science and Industry, Vol. 4*, H. H. Plumb, ed. (Instrument Society of America, Pittsburg, PA, 1972).
18. V. Ya. Chekhovskoi and S. A. Kats, *High Temp. High Press.* **13**:611 (1981).
19. E. Arpaci, G. Betz, and M. G. Frohberg, *High Temp. High Press.* **15**:519 (1985).
20. S. Krishnan, J. K. R. Weber, P. C. Nordine, R. A. Shiffman, R. H. Hauge, and J. L. Magrave, *High Temp. Sci.* **30**:137 (1991).
21. J. A. Treverton and J. L. Magrave, *J. Chem. Thermodyn.* **30**:473 (1971).
22. B. Ya. Berezin, V. Ya. Chekhovskoi, and A. E. Sheindlin, *High Temp. Sci.* **4**:478 (1971).
23. C. C. Bidwell, *Phys. Rev. Ser.* **3**:439 (1914).
24. M. N. Dastur and N. A. Gokcen, *J. Metals* **1**:665 (1949).
25. J. C. d'Entremont, *Trans. AIME* **227**:482 (1963).
26. G. K. Burgess and R. G. Waltenburg, *US National Bureau of Standards Scientific Paper No. 242* (Washington, DC, 1914), pp. 591–605.
27. S. Krishnan, G. P. Hansen, R. H. Hauge, and J. L. Magrave, *High Temp. Sci.* **29**:17 (1990).