Dental Materials Journal 4(1): 25–32, 1985

Electrochemical Measurement of Oxygen in Liquid Ni-based Alloys
— The effects of Cu and Cr as additive elements —

Kunio WAKASA and Masao YAMAKI

Department of Dental Materials, School of Dentistry, Hiroshima University, 1–2–3, Minami-ku, Kasumi-cho, Hiroshima 734, Japan

Received on March 14, 1985

The oxygen concentration in molten binary Ni-based alloys was estimated by an electrochemical method using solid electrolytes. The electrochemical cell was $Pt|Mo+MoO_2|ZrO_2(MgO)|\underline{O}$ (in liquid) $|Mo$. The activity of oxygen determined from the electromotive force (EMF) of the cell increased when Cu was added to pure Ni. Namely, the oxygen concentration was higher than that for pure Ni only when the amount of Cu was between 1wt% and 30wt%. In binary Ni-Cr alloys, it was deduced that the addition of 15 and 20 wt%Cr to pure Ni showed the lower oxygen concentration, although the liquid Ni-based alloys having 5, 7 and 10 wt%Cr tended to have higher oxygen concentrations than pure Ni.

Key Words: Oxygen, Ni-based alloy, Element

INTRODUCTION

Little is known about the thermodynamic behaviour of elements at diluted concentrations in liquid states in dental Ni-based cast alloys. In the Ni-based alloys, both Cr and Cu were constituted as main additive elements.1)-4) Thus, the thermodynamic properties of liquid Ni-based systems are of interest in the dental field, because the absorption and the dissolution of gases during melting and solidification seem to have an effect on the casting defects and the mechanical properties.5)-9) It is deduced that the dissolved gases in liquid metals and alloys occur as gas porosities and nonmetallic inclusions during their solidification of liquid ones. The liquid ones absorb some gases of oxygen, nitrogen and hydrogen.

The activity of oxygen dissolved in liquids has been recently estimated using solid anionic-conducting oxide electrolytes. The electrochemical method using solid electrolytes has been done to measure oxygen concentration in liquid Ni10)-12) and Ni-Cu binary alloys.13)-15) The method with $ZrO_2(CaO)$ solid electrolyte having an air/Pt reference electrode has been utilized,16) whereas another analysis by nitrogen/oxygen determinator which is used by Takahashi et al8) and Tajima et al9) has been carried out.17)-19) It was reported that the oxygen may escape from the sprue canal and outside from the mould, and the residual gases may exist within the casting, because the measured oxygen content was very small.8) Therefore, the oxygen concentration cell:

$$Pt|Mo+MoO_2|ZrO_2(MgO)|\underline{O}(\text{in liquid})|Mo,$$

involving a solid-oxide electrolyte was used in this study for the determination of the activity of oxygen dissolved in metals and alloys. The electromotive force (EMF) of the cell is given by the following equation.10)-16),20),21)

$$\mathrm{EMF}=(RT/4F)\ln[Po_2(\text{in liquid})/Po_2(\mathrm{Mo}+\mathrm{MoO_2})], \quad (1)$$

where R is the gas constant, F the Farady constant, T temperature, and Po_2 (in liquid) and Po_2 ($Mo+MoO_2$) are the oxygen partial pressure in equilibrium with dissolved oxygen in liquid metals and alloys and the oxygen dissociation pressure of MoO_2 that is oxygen partial pressure in equilibrium with Mo and MoO_2. In the present study, the experiment to estimate the oxygen concentration was performed and the effects of Cu and Cr addition to pure Ni on the activity and the concentration were discussed.

MATERIALS AND METHODS

The metals used to make the binary Ni-based alloys were two kinds of pure electrolytic Ni (≥99.9% purity; Katayama Chemical Co., Osaka, Japan and ≥99.95% purity; Bindura Nickel Co., Zimbabwe), electric Cu (≥99.9% purity; Katayama Chemical Co., Japan) and electrolytic Cr (≥99.9% purity; Rare Metallic Co., Tokyo, Japan). The Ni-based alloys were fused in a high-frequency induction furnace in a vaccum (about 10^{-5} torr) (Fuji Denpa Co., Osaka, Japan). In Ni-0.5, 1 and 2 wt%Cu binary alloys having perfect solid solution, the alloys were melted during the flow of Argon gas. The chemical components of the alloys are shown in Tables 1 and 2. Their main components were analyzed according to the methods described in JIS H 1101 (Cu) and JIS G 1217 (Cr).

The experimental apparatus is indicated in Figure 1. A ZrO_2-9mol% MgO tube containing a mixture of $Mo+MoO_2$ as a reference electrode was closed at one end, and it was dipped into liquid metals and Ni-based alloys. A Mo wire (0.5 mm diameter) was used to make electrical contacts to both liquid metals and alloys and the reference electrode. The apparatus including Al_2O_3-crusible was made every measurements. The electromotive force noted by EMF was then measured by a two-pen recorder with 0.5 mV/cm (It was also

Table 1 Copper levels of binary Ni-Cu alloys

Alloys (attempted)	Level achieved
Ni-10wt%Cu	9.40wt%
Ni-20wt%Cu	18.11wt%
Ni-30wt%Cu	28.47wt%

(Pure Ni; Katayama Chemical Co.)

Table 2 Chromium levels of binary Ni-Cr alloys

Alloys (attempted)	Level achieved
Ni-5wt%Cr	4.95wt%
Ni-7wt%Cr	6.30wt%
Ni-10wt%Cr	9.53wt%
Ni-15wt%Cr	15.00wt%
Ni-20wt%Cr	20.10wt%

(Pure Ni; Bindura Nickel Co.)

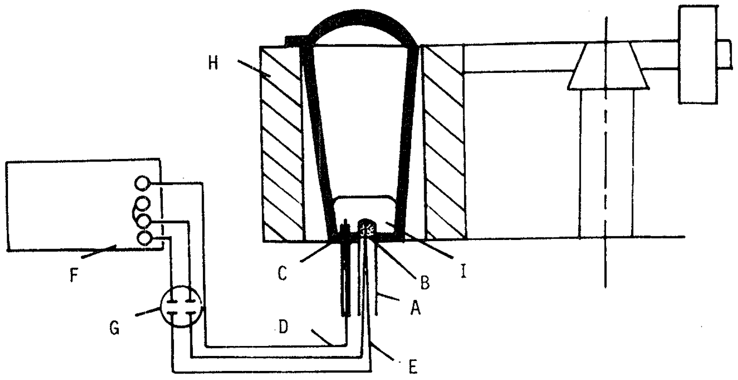


Figure 1 The experimental apparatus. A; solid electrolyte ($ZrO_2 \cdot 9$ mol% MgO)[a], B; MoO_2+Mo powder mixture[b], C; alumina crusible[c], D; Mo lead wire, E; Pt-to-(Pt+13wt%Rh) thermocouple, F; recorder to get electromotive force[d], G; recorder for zero junction, H; high-frequency centrifugal casting machine[e], I; molten metals and alloys.

a Nippon Kagaku Togyo Co., Nagoya, Japan. b Wako Pure Chemical Ind., Osaka, Japan. c TMC-102; Morita Co., Tokyo, Japan. d Type 3066–21; Yokogawa Hokushin Denki, Tokyo, Japan. e Castron-8; Yoshida Co., Osaka, Japan.

checked by a digital voltmeter with internal impeadance $10^8\ \Omega$. Type 1502A; Yokogawa Hokushin Denki, Tokyo, Japan).

The metals (Ni and Cu) and Ni-based binary alloys were melted using a high-frequency fusion and centrifugal casting during constant flow (5 litre/min) of Argon gas ($\geq 99.9\%$ purity). The weights melted was about 15 gram. The temperature was measured with a Pt-to (13wt%Rh·Pt) thermocouple.

RESULTS AND DISCUSSION

The changes in EMF values of the cell with the mass fraction of $\underline{O}$ in liquid Ni, Cu and Ni-Cu alloys is shown in Figure 2. The mass fraction of $\underline{O}$ is calculated by the following equation, using $a_{\underline{O}}=P_{O_2}$ (in liquid) $\exp(-\Delta G^0/RT)$:10)-13)

$$\ln a_{\underline{O}} = -\frac{\Delta G^0}{RT} - \frac{2EF}{RT} + \frac{1}{2} \ln \{P_{O_2}(Mo+MoO_2)\}, \qquad (2)$$

$$\text{where } \ln \{P_{O_2}(Mo+MoO_2)\} = -\frac{266.7 \pm 0.15\ ^{12)}}{4.1854RT}, \qquad (3)$$

$R=1.9865$ cal/mol·degree ,
$F=23066$ cal/mol·volt .

The Henrian activity coefficient of oxygen is related to the Henrian activity by $a_{\underline{O}}=[\underline{O}\,\%]\cdot f$ in the hypothetical liquid containing a low oxygen content (100 ppm) to higher content. It has been known that $a_{\underline{O}}$ corresponds to $[\underline{O}\,\%]$, because f is equal to 1.0.10)-12) This approach is considered to be real by analysing the oxygen concentration of the quenched samples obtained at each molten temperature by nitrogen/oxygen determinator.11),12) Thus, the oxygen concentration is deduced by calculating $a_{\underline{O}}$ according to the equation (2). In

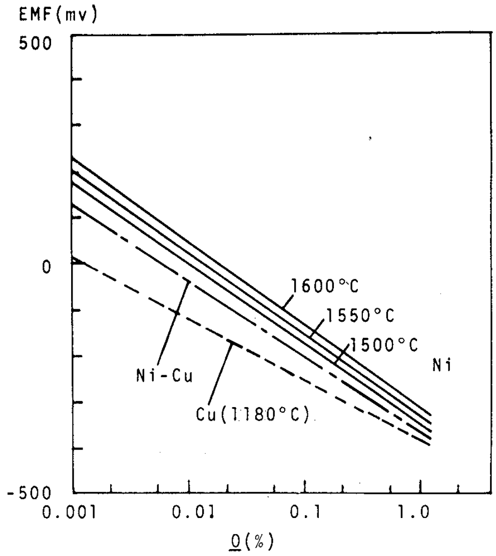


Figure 2 The EMF of the cell; $Pt|Mo+MoO_2|ZrO_2(MgO)|\underline{O}$(in liquid)$|Mo$ as a function of the logarithm of $\underline{O}$% in liquid Ni, Cu and Ni-Cu alloys.

this case, the standard Gibbs energy change for the reaction:

$$\frac{1}{2}O_2 \longrightarrow \underline{O} \text{ (in liquid states)}, \tag{4}$$

could be given as the temperature function as follows:

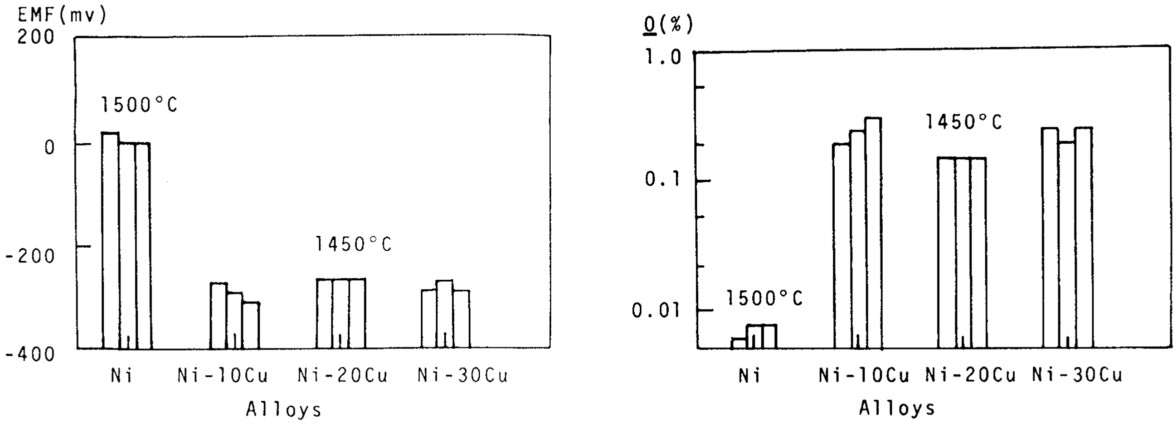
$$\Delta G^0(Ni) = -23200 + 3.93T^{10)}, \tag{5}$$

$$\Delta G^0(Cu) = -17500 + 2.22T^{10)}, \tag{6}$$

$$\Delta G^0(Ni\text{-}Cu) = 6530 - 11.5T^{14)}. \tag{7}$$

The value of $a_{\underline{O}}$ in the equation (2) is regarded a almost constant, even though the other equations of Gibbs energy change were used to measure the activity of oxygen.

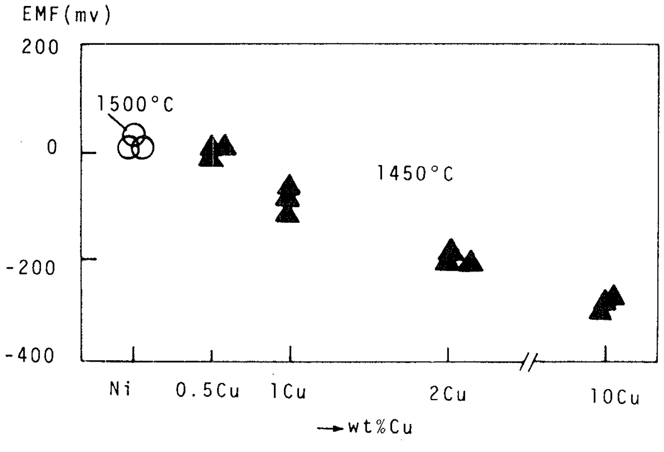
The changes in EMF values and oxygen concentration of the cell with different amounts of Cu added to Ni are shown in Figures 3(a) and (b). The EMF changes in liquid Ni at



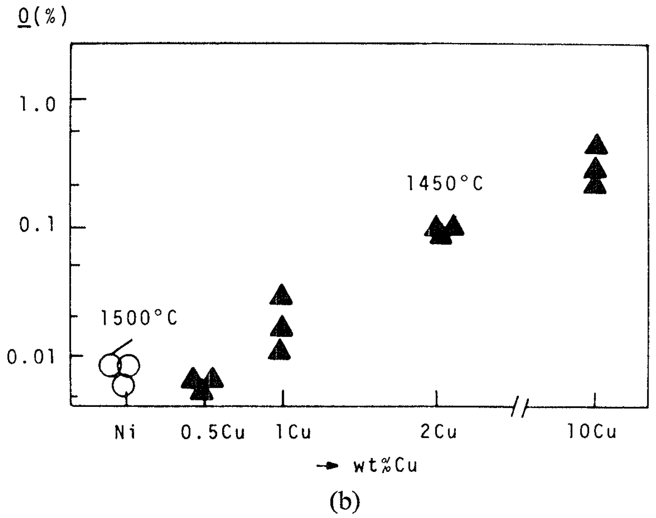
(a) (b)

Figure 3 (a) The EMF changes, and (b) The concentration of dissolved oxygen in pure Ni, and Ni-10, 20 and 30 wt%Cu binary alloys.

1500°C were about 4 mV, but the additions of 10, 20 and 30 wt%Cu to pure Ni lowered the respective mean values to −293, −265 and −282 mV. The oxygen concentrations corresponding to the EMF values, as shown in Figure 2, had larger mean values of 0.23 (10 wt%Cu), 0.156 (20 wt%Cu) and 0.196% (30 wt%Cu) than that of pure Ni (below 0.01%). Seeing the change of EMF values in liquid pure Ni by means of solid-oxide galvanic cell, which was shown in Figure 1, the present study showed a good agreement with that of Iwase et al.[12] In order to check the validity of ΔG^0(Ni), in addition, the equation (5) was used. The EMF values were almost found on the straight-line representing the relationship of EMF and oxygen concentration obtained by Iwase et al.[12] In Figures 4(a) and (b), the additive element of Cu (0.5, 1 and 2 wt%) was shown. The mean oxygen concentration increased by 0.017 and 0.09% with increasing 1 and 2 wt% as the amount of Cu. At 0.5 wt%Cu addition to pure Ni, the EMF values and oxygen concentration showed almost the same values (below 0.01%) as Ni. It is clarified that dissolved oxygens in liquid Ni-Cu binary alloys including additive elements of Cu lowers the activity and the oxygen concen-



(a)



(b)

Figure 4 (a) The EMF changes, and (b) The concentration of dissolved oxygen in pure Ni, and Ni-0.5, 1, 2 and 10 wt%Cu binary alloys.

tration decreased then.

Figure 5 shows the EMF changes with the decreasing molten temperatures after melting Ni-5 wt%Cr, Ni-7 wt%Cr and Ni-10 wt%Cr binary alloys. Different tendencies of EMF values were noted with the changes in their temperatures. In Ni-5wt%Cr binary alloy containing the lowest contents of Cr, the EMF values decreased markedly with the decrease of molten temperatures of 1550 to 1450°C, but the Ni-7wt%Cr alloy showed only a slight change with decreasing the temperatures. On the contrary, the Ni-10wt%Cr alloys having larger Cr content than the Ni-5wt%Cr and Ni-7wt%Cr binary alloys showed the lowest value of the Ni-based alloys at 1550°C, and a gradual change with decreasing temperatures up to 1450°C. Figure 6 presents the relation between EMF changes and molten temperatures in Ni-15wt%Cr and Ni-20wt%Cr binary alloys, similarly to Figure 5. The extent of EMF changes with the decrease of temperatures was very small in these binary alloys. Three specimens of binary Ni-20wt%Cr alloys had no difference at each molten temperature.

In Ni-based binary alloys containing Cr as an additive element, different thermodynamic behaviours for each binary alloy were observed in the variation of EMF values with molten temperatures (Figures 5 and 6). It is deduced that the activity of oxygen in the alloys indicates to change directly with different amounts of Cr. Consider the variation of EMF values with molten temperatures. The melting temperature of Cr is described to be about 1880°C in Ni-Cr equilibrium phase diagram,22) and the variation is, thus, not measured by this apparatus because of the absence of thermocouples. The EMF values, as has been reported,10) is decreasing with increasing the concentration of oxygen. In Figure 2, the higher EMF values were associated with the lower values of oxygen concentration in liquid

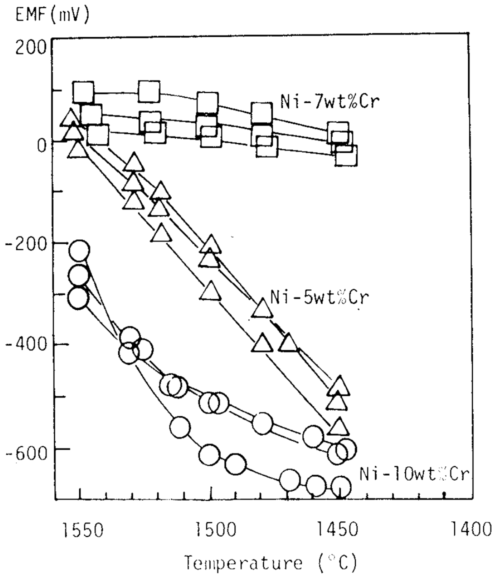


Figure 5 The EMF change with molten temperatures in Ni-5 wt%Cr (△), Ni-7 wt%Cr (□) and Ni-10 wt%Cr binary alloys (○).

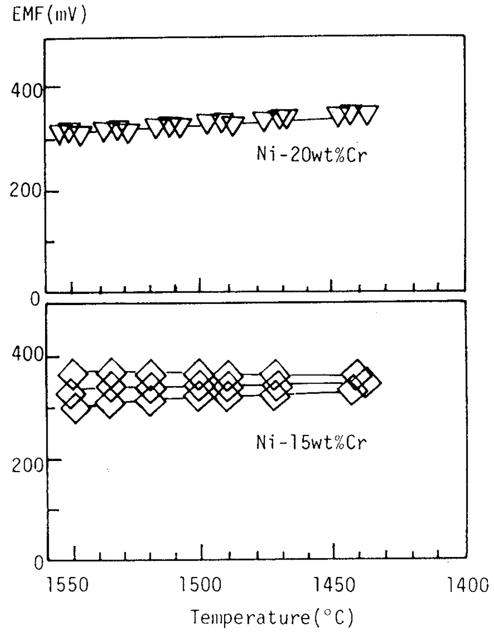


Figure 6 The EMF change with molten temperatures in Ni-15 wt%Cr (◇) and Ni-20 wt%Cr binary alloys (▽).

Ni, Cu and Ni-Cu binary alloys. It is, therefore, expected that the higher values of EMF in high contents of Cr in Ni-15 and -20wt%Cr alloys may have the lower concentration of dissolved oxygen in their alloys. Namely, the concentration of dissolved oxygen in Ni-5, 7 and 10wt%Cr alloys became higher than that of Ni-15 and 20wt%Cr alloys.

In the case of Ni-Cu binary alloys, the equilibrium phase diagram is known to be perfect solid solution.[23] The liquidus and solidus curves decrease continuously with increasing amounts of Cu added to pure Ni. Observing the changes of the EMF value and the oxygen concentration in Figure 4, the oxygen concentration had the larger values with increasing Cu element 1 and 2 wt% in comparison with that of pure Ni. As the standard free energy of formation of oxides is −29.53 (Cu_2O) and −53.09 (kcal/mol) (NiO) at 1200°C,[22] the binding energy of Ni works to became stronger than Cu. It is deduced that the addition of Cu element to pure Ni raises the activity coefficient of oxygen higher than pure Ni as well as the concentration of dissolved oxygen in liquid states.

Considering the validity of additive elements of Cu and Cr to pure Ni from these results, only the addition of 0.5 wt%Cu is needed to obtain the same oxygen concentration as pure Ni, but the addition of 1 wt%Cu may be necessary if the concentration of oxygen of about 0.02% is permitted. On the contrary, the addition of Cr to pure Ni may be valid for 15 and 20 wt%Cr. Further studies are needed to examine the relation between the EMF value and the concentration of dissolved oxygen of liquid Cr at molten temperatures above 1900°C in order to obtain the exact values of the oxygen concentration.

CONCLUSION

Using the oxygen concentration cell with a solid-oxide electrolyte, the activity of dissolved oxygen in liquid Ni, Cu and Ni-Cu binary alloys was examined, and the meaning of EMF values in liquid Ni-Cr binary alloys was discussed. The following results were obtained.

1. The addition of Cu to pure Ni increased the concentration of dissolved oxygen at 1180°C in liquid states of Ni-10, -20 and -30 wt%Cu binary alloys, compared with that of pure Ni. At 0.5 wt%Cu addition to Ni, the level of oxygen was almost the same value as pure Ni. In the Ni-Cu binary alloys having higher contents of 1 and 2 wt%Cu, the increased oxygen concentration was noted, similarly to the high concentrations of oxygen in the Ni-10, -20 and -30 wt%Cu binary alloys. Also, the concentration of oxygen at 1 wt%Cu was a lower value than those of the alloys with higher Cu contents.
2. With higher Cr contents of 15 and 20 wt%, it was expected from the EMF values that the lower concentration of oxygen was found in the Ni-15 and -20 wt%Cr alloys, compared with those of Ni-5, -7 and -10 wt%Cr alloys.

ACKNOWLEDGMENT

The authors give the grateful thanks to Mr. Yamada, H. and Mr. Ishigaya, F. at the Hiroshima City Art Direction Center for the permission to use the high-frequency vaccum-fusion furnace and the assistance to make the alloys.

REFERENCES

1) Ida, K.: Nonprecious alloys for crown and bridge applications and the casting, *J. Dental. Technics,* **4**(2): 36–42, 1976 (in Japanese).
2) Ito, M., Nagasawa, S., Ishii, K., Sugie, G., Miyazawa, T., Nakata, K. and Takahashi, S.: Testing cast Ni-Cr alloys for crown and bridge, *DE* **55**: 16–29, 1980 (in Japanese).
3) Yamane, M. and Hisatsune, K.: Dental cast base metals, ed. by Japan Soc. Dent. Appar. Mat., *Ishiyaku*, 1981, pp. 1–37 (in Japanese).
4) Hasegawa, J.: Properties of Ni-Cr alloys for castings, *J. J. Dent. Mat.*, **3**(5), 547–553, 1984 (in Japanese).
5) Noguti, H.: Symposium—Some problems on dental castings—II. Casting defects, ed. by Japan Soc. Dent. Appar. Mat., *Ishiyaku*, 1969, pp. 25–41 (in Japanese).
6) Nishimura, F., Oku, H. and Nomoto, S.: Effects of vaccum melting centrifugal casting on mechanical properties of Cobalt-Chromium alloy castings, *J. Japan. Res. Soc. Dent. Mat. Appl.*, **30**(3), 175–178, 1973 (in Japanese).
7) Levis, A.J.: Porosity in base metal partial denture casting alloys, related industrial alloys and pure metals, *Aust. D. J.*, **22**(3), 208–211, 1976.
8) Takahashi, J., Joshin, K., Okazaki, M. and Moriwaki, Y.: Oxygen contents and casting porosities in Ag alloys, *J. Japan. Soc. Dent. Appar. Mat.*, **20**(49), 1–7, 1979 (in Japanese).
9) Tajima, K., Kakigawa, H., Kozono, Y. and Hayashi, I.: Oxygen introduced by melting in Ni-Cr alloy castings, *J. J. Dent. Mat.*, **3**(3): 423–430, 1984 (in Japanese).
10) Fischer, W.A. and Ackermann, W.: Unmittelbare electrochemische Ermittlung des Sauerstoffgehaltes von Metallscchmelzen I. Untersuchungen an Eisen-, Kobalt-, Nickel-, und Kupferschmelzen, *Archiv. für Eisenhüttenw.*, **37**(1), 43–47, 1966.
11) Kemori, N., Katayama, I. and Kozuka, Z.: Activity measurements of oxygen in liquid Nickel by the E. M. F. method using the solid electrolyte, *J. Japan. Inst. Metals*, **40**(7), 751–757, 1976 (in Japanese)
12) Iwase, M., Miki, S. and Mori, T.: Electrochemical measurement of oxygen in liquid nickel, *J. Chem. Thermodynamics*, **11**: 307–315, 1979.
13) Oishi, T., Nagahata, T. and Moriyama, J.: The effects of Tin and Nickel to the thermodynamic properties of oxygen in molten Copper, *J. Japan. Inst. Metals.*, **34**(1): 1103–1107, 1970 (in Japanese).
14) Kurkarni, A.D. and Johnson, R.E.: Thermodynamic studies of liquid copper alloys by electromotive force method: Part II. The Cu-Ni-O and Cu-Ni systems, *Met. Trans.*, **4**(7): 1723–1727, 1973.
15) Sigworth, G.K. and Elliott, J.F.: The thermodynamics of dilute liquid copper alloys, *Canadian. Met. Quart.*, **13**(3), 455–461, 1974.
16) Fischer, W.A., Janke, D. and Ackermann, W.: Thermodynamik der Auflösung des Sauerstoffs in Fe-Co-, Fe-Ni-, Fe-Cu- und Co-Ni-Schmelzen, *Archiv. für Eisenhüttenw.*, **41**(4), 361–367, 1970.
17) Sakao, H. and Sano, K.: Activity of oxygen in liquid Fe-Ni, Fe-Co and Ni-Co alloys, *J. Japan. Inst. Metals*, **26**(1): 30–34, 1962 (in Japanese).
18) Dallmann, W.E. and Fassel, V.A.: Simultaneous determination of oxygen and nitrogenin metals by carrier-gas fusion extraction, *Anal. Chem.*, **39**(5), 133–142, 1967.
19) Hayashi, S. and Uno, T.: Activities of sulphur and oxygen in liquid Iron, *I. S. I. J.*, **68**(13): 1728–1736, 1982 (in Japanese).
20) Bowers, J.E.: The equilibrium between oxygen and molten Nickel and Nickel-Iron alloys, *J. Inst. Metals*, **90**: 321–328, 1961/62.
21) Tankins, E.S., Gokcen, N.A. and Belton, G.R.: The activity and solubility of oxygen in liquid Iron, Nickel, and Cobalt, *Trans. AIME*, **230**, 820–827, 1964.
22) Hansen, M.: Constitution of binary alloys, 2nd ed., *MacGraw-Hill Book Co. Inc.*, 1958, pp. 541–546.
23) Feest, E.A. and Doherty, R.D.: The Cu-Ni equilibrium phase diagram, *J. Inst. Metals.*, **99**: 102, 1971.

討を行った。

その結果によれば，いずれの材料にも時間—温度換算則が適用でき，重ね合わせの良好な合成曲線を作製することができた。パラフィンに，カルナウバワックスを添加した場合，高温側での応力緩和が著しく抑制されることがわかった。パラフィンにみつろうを添加すると，低温側の弾性率が低下することがわかった。またダンマルは混合物の応力緩和挙動にほとんど影響を与えないことが明らかになった。

溶融 Ni 基合金中の酸素の電気化学的測定

—添加元素としての Cu および Cr の影響—

若狭邦男，山木昌雄

広島大学歯学部歯科理工学講座

溶融2元系 Ni 基合金の酸素濃度を固体電解質を用いた電気化学的方法により評価した。そのセルは，Pt|Mo＋MoO_2|ZrO_2(MgO)|$\underline{O}$ (液体)|Mo である。熱起電力 (EMF) から決定する酸素活性は純 Ni に Cu を添加した時増加した。すなわち，酸素濃度は，その添加量が1 wt% 以上30 wt% までの時，純 Ni での値よりも大きくなった。2元系 Ni-Cr 合金では，5，7および10 wt%ほど Cr を含有すると，純 Ni よりも大きい酸素濃度を示すように思われ，15および20 wt% Cr の添加によって，純 Ni よりもより低い酸素濃度を呈するものと推測できる。

機能性モノマーの歯科的応用（その9）

各種 succinoxy methachylate の合成と無処理および酸処理歯質への接着性

福島忠男，川口　稔，井上勇介，宮崎光治，堀部　隆

福岡歯科大学　歯科理工学講座

レジンの歯質への接着性を改善するために，succinoxyethyl methacrylate (2SEM) に各種疎水基を導入した新しい succinoxy methacrylate (sSPrM, SPPM, Bis-SGMA) と 2SEM の4種を合成し，歯質への接着性と構造との関係を検討した。合成モノマーと BGDMA から調製した各種 bonding agent を無処理（最終研摩：サンドペーパー #600）と酸処理（37%リン酸，1分間処理）牛歯エナメルおよびデンチンに薄く塗布し，その上から即重レジンを塡入して作製した接着試料について，室温に10分間放置後（Dry：無処理），水中浸漬1日後（Wet：無処理と酸処理）に引張り接着試験を行った。無処理エナメルおよびデンチンへの接着性が Dry で最も優れていたのは，それぞれ Bis-SGMA (50 mol%) と 2SEM (55～65 mol%) であった。Wet では SPPM (40 mol%) と 2SEM (55～65 mol%) であった。酸処理エナメルおよびデンチンへの接着力が最も優れていたのは，それぞれ SPPM (40 mol%) と Bis-SGMA (15～25 mol%) であった。

合着用セメントの硬化後の寸法変化

蟹江隆人，西岡慎一，長岡成孝，劉　宏志，川越昌宜，
有川裕之*，藤井孝一*，上新和彦*，井上勝一郎*

鹿児島大学歯学部　歯科保存学 (1) 講座
*鹿児島大学歯学部歯科理工学講座

現在，市販されている4種類の系の合着用セメントについて練和比および試料寸法を変えた場合，硬化後の寸