

# UTLENIANIE MATERIAŁÓW METALICZNYCH

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2. A.S. Khanna, „Introduction to High Temperature Oxidation and Corrosion”, ASM International, Materials Park, 2002.
3. S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982.
4. S. Mrowec, Kinetyka i mechanizm utleniania metali, 1980.
5. Wei Gao and Zhengwei Li ”Developments in high-temperature corrosion and protection of metals”, Ed, Woodhead Publishing Limited, Cambridge, England, 2008.
6. R. Cottis, M. Graham, R. Lindsay, S. Lyon, J. Richardson, J. Scantlebury, F. Stott, „Basic Concepts, High Temperature Corrosion, tom I” w „Shreir’s Corrosion”, Elsevier, Amsterdam, 2010.

# Własności wybranych tlenków metali

| Oxide                                    | Structure   | Melting point, °C           | Boiling point, °C | Molar volume, cm <sup>3</sup> | Volume ratio (oxide/metal) |
|--|---|-----------------------------|-------------------|-------------------------------|----------------------------|
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> | D5 <sub>1</sub> (corundum)                                  | 2015                        | 2980              | 25.7                          | 1.28                       |
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | (defect spinal)   | $\gamma \rightarrow \alpha$ | ...               | 26.1                          | 1.31                       |
| BaO                                      | B1 (NaCl)   | 1923                        | ~2000             | 26.8                          | 0.69                       |
| BaO <sub>2</sub>                         | Tetragonal (CaC <sub>2</sub> )                              | 450                         | d.800             | 34.1                          | 0.87                       |
| BeO                                      | Br (ZnS)  | 2530                        | ~3900             | 8.3                           | 1.70                       |
| CaO                                      | B1 (NaCl)   | 2580                        | 2850              | 16.6                          | 0.64                       |
| CaO <sub>2</sub>                         | CII (CaC <sub>2</sub> )                                     | ...                         | d.275             | 24.7                          | 0.95                       |
| CdO                                      | B1 (NaCl)   | ~1400                       | d.900             | 18.5                          | 1.42                       |
| Ce <sub>2</sub> O <sub>3</sub>           | D5 <sub>2</sub> (La <sub>2</sub> O <sub>3</sub> )           | 1692                        | ...               | 47.8                          | 1.15                       |
| CeO <sub>2</sub>                         | CI (CaF <sub>2</sub> )                                      | ~2600                       | ...               | 24.1                          | 1.17                       |
| CoO                                      | B1 (NaCl)   | 1935                        | ...               | 11.6                          | 1.74                       |
| Co <sub>2</sub> O <sub>3</sub>           | Hexagonal   | ...                         | d.895             | 32.0                          | 2.40                       |
| Co <sub>3</sub> O <sub>4</sub>           | HI <sub>1</sub> (spinal)                                    | $\rightarrow$ CoO           | ...               | 39.7                          | 1.98                       |
| Cr <sub>2</sub> O <sub>3</sub>           | D5 <sub>1</sub> ( $\alpha$ Al <sub>2</sub> O <sub>3</sub> ) | 2435                        | 4000              | 29.2                          | 2.02                       |
| Cs <sub>2</sub> O                        | Hexagonal (CdCl <sub>2</sub> )                              | ...                         | d.400             | 66.3                          | 0.47                       |
| Cs <sub>2</sub> O <sub>3</sub>           | Cubic (Th <sub>3</sub> P <sub>4</sub> )                     | 400                         | 650               | 70.1                          | 0.50                       |
| CuO                                      | B26 monoclinic  | 1326                        | ...               | 12.3                          | 1.72                       |
| Cu <sub>2</sub> O                        | C3 cubic  | 1235                        | d.1800            | 23.8                          | 1.67                       |
| FeO                                      | B1 (NaCl)   | !420                        | ...               | 12.6                          | 1.78 on $\alpha$ -iron     |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | D5 <sub>1</sub> (Haematite)                                 | 1565                        | ...               | 30.5                          | 2.15 on $\alpha$ -iron     |
| $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> | D5 <sub>7</sub> cubic                                       | 1457                        | ...               | 31.5                          | 2.22 on $\alpha$ -iron     |
| Fe <sub>3</sub> O <sub>4</sub>           | HI <sub>1</sub> (spinel)                                    | ...                         | d. 1538           | 44.7                          | 2.10 on $\alpha$ -iron     |
| Ga <sub>2</sub> O <sub>3</sub>           | Monoclinic  | 1900                        | ...               | 31.9                          | 1.35                       |
| HfO <sub>2</sub>                         | Cubic   | 2812                        | ~5400             | 21.7                          | 1.62                       |

# Własności wybranych tlenków metali

| <i>Oxide</i>                   | <i>Structure</i>                                  | <i>Melting point, °C</i> | <i>Boiling point, °C</i> | <i>Molar volume, cm<sup>3</sup></i> | <i>Volume ratio (oxide/metal)</i> |
|--------------------------------|---|--------------------------|--------------------------|-------------------------------------|-----------------------------------|
| In <sub>2</sub> O <sub>3</sub> | D5 <sub>3</sub> (Sc <sub>2</sub> O <sub>3</sub> ) | ...                      | d.850                    | 38.7                                | 1.23                              |
| IrO <sub>2</sub>               | C4 (TiO <sub>2</sub> )                            | ...                      | d.1100                   | 19.1                                | 2.23                              |
| La <sub>2</sub> O <sub>3</sub> | D53 (Sc <sub>2</sub> O <sub>3</sub> )             | ...                      | d.850                    | 38.7                                | 1.23                              |
| Li <sub>2</sub> O              | C1 (CaF <sub>2</sub> )                            | ~1700                    | 1200                     | 14.8                                | 0.57                              |
| MgO                            | B1 (NaCl)   | 2800                     | 3600                     | 11.3                                | 0.80                              |
| MnO                            | B1 (NaCl)   | ...                      | ...                      | 13.0                                | 1.77                              |
| MnO <sub>2</sub>               | C4 (TiO <sub>2</sub> )                            | ...                      | d.535                    | 17.3                                | 2.37                              |
| Mn <sub>2</sub> O <sub>3</sub> | D53 (Sc <sub>2</sub> O <sub>3</sub> )             | ...                      | d.1080                   | 35.1                                | 2.40                              |
| Mn <sub>3</sub> O <sub>4</sub> | H1 <sub>1</sub> (spinel)                          | 1705                     | ...                      | 47.1                                | 2.14                              |
| MoO <sub>3</sub>               | Orthorhombic                                      | 795                      | ...                      | 30.7                                | 3.27                              |
| Na <sub>2</sub> O              | C1 (CaF <sub>2</sub> )                            | Subl. 1275               | ...                      | 27.3                                | 0.57                              |
| Nb <sub>2</sub> O <sub>5</sub> | Monoclinic  | 1460                     | ...                      | 59.5                                | 2.74                              |
| Nd <sub>2</sub> O <sub>3</sub> | Hexagonal   | ~1900                    | ...                      | 46.5                                | 1.13                              |
| NiO                            | B1 (NaCl)   | 1990                     | ...                      | 11.2                                | 1.70                              |
| PbO                            | B10 tetragonal                                    | 888                      | ...                      | 23.4                                | 1.28                              |
| Pb <sub>3</sub> O <sub>4</sub> | Tetragonal  | ...                      | d.500                    | 75.3                                | 1.37                              |
| PdO                            | B17 tetragonal                                    | 870                      | ...                      | 14.1                                | 1.59                              |
| PtO                            | B17 (PdO)   | ...                      | d.550                    | 14.2                                | 1.56                              |
| Rb <sub>2</sub> O <sub>3</sub> | (Th <sub>3</sub> P <sub>4</sub> )                 | 489                      | ...                      | 62.0                                | 0.56                              |
| ReO <sub>2</sub>               | Monoclinic  | ...                      | d.1000                   | 19.1                                | 2.16                              |
| Rh <sub>2</sub> O <sub>3</sub> | D51 ( $\alpha$ -Al <sub>2</sub> O <sub>3</sub> )  | ...                      | d.1100                   | 31.0                                | 1.87                              |
| SiO                            | Cubic   | ~1700                    | 1880                     | 20.7                                | 1.72                              |

# Własności wybranych tlenków metali

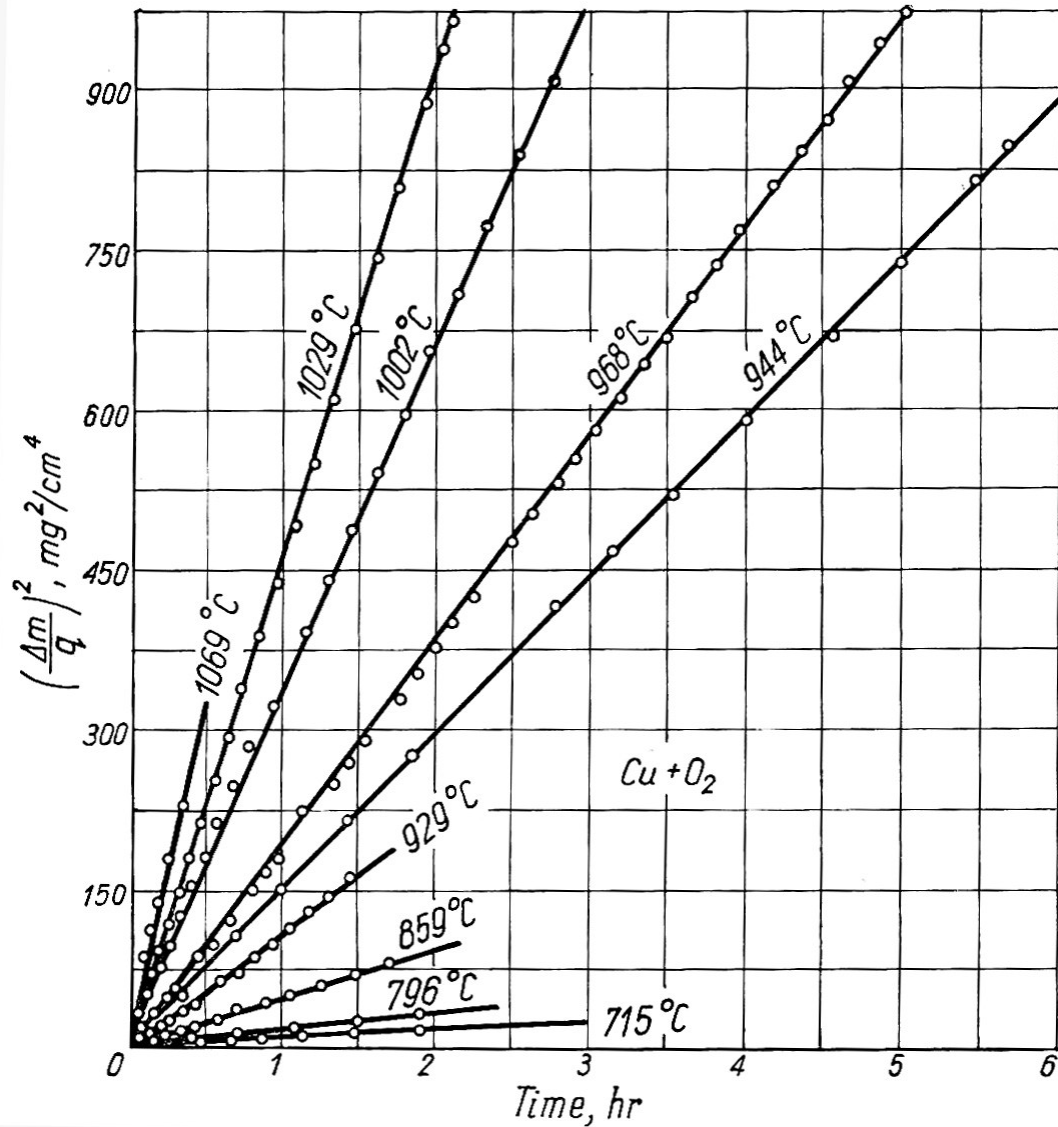
| <i>Oxide</i>                   | <i>Structure</i>                                    | <i>Melting point, °C</i> | <i>Boiling point, °C</i> | <i>Molar volume, cm<sup>3</sup></i> | <i>Volume ratio (oxide/metal)</i> |
|--------------------------------|---|--------------------------|--------------------------|-------------------------------------|-----------------------------------|
| SiO <sub>2</sub>               | β cristobalite C9                                   | 1713                     | 2230                     | 25.9                                | 2.15                              |
| SnO                            | B10 (PbO)   | ...                      | d.1080                   | 20.9                                | 1.26                              |
| SnO <sub>2</sub>               | C <sub>4</sub> (TiO <sub>2</sub> )                  | 1127                     | ...                      | 20.9                                | 1.26                              |
| SrO                            | B1 (NaCl)   | 2430                     | ~3000                    | 22.0                                | 0.65                              |
| Ta <sub>2</sub> O <sub>5</sub> | Triclinic   | 1800                     | ...                      | 53.9                                | 2.47                              |
| TeO <sub>2</sub>               | C <sub>4</sub> (TiO <sub>2</sub> )                  | 733                      | 1245                     | 28.1                                | 1.38                              |
| ThO <sub>2</sub>               | Cl (CaF <sub>2</sub> )                              | 3050                     | 4400                     | 26.8                                | 1.35                              |
| TiO                            | B1 (NaCl)   | 1750                     | ~3000                    | 13.0                                | 1.22                              |
| TiO <sub>2</sub>               | C4 (Rutile)   | 1830                     | ~2700                    | 18.8                                | 1.76                              |
| Ti <sub>2</sub> O <sub>3</sub> | D5 <sub>1</sub> (α-Al <sub>2</sub> O <sub>3</sub> ) | ...                      | d.2130                   | 31.3                                | 1.47                              |
| Tl <sub>2</sub> O <sub>3</sub> | D5 <sub>3</sub> (Sc <sub>2</sub> O <sub>3</sub> )   | 717                      | d.875                    | 44.8                                | 1.30                              |
| UO <sub>2</sub>                | Cl (CaF <sub>2</sub> )                              | 2500                     | ...                      | 24.6                                | 1.97                              |
| U <sub>3</sub> O <sub>8</sub>  | Hexagonal   | ...                      | d.1300                   | 101.5                               | 2.71                              |
| VO <sub>2</sub>                | C4 (TiO <sub>2</sub> )                              | 1967                     | ...                      | 19.1                                | 2.29                              |
| V <sub>2</sub> O <sub>3</sub>  | D5 <sub>1</sub> (α-Al <sub>2</sub> O <sub>3</sub> ) | 1970                     | ...                      | 30.8                                | 1.85                              |
| V <sub>2</sub> O <sub>5</sub>  | D8 <sub>7</sub> Orthorhombic                        | 690                      | d.1750                   | 54.2                                | 3.25                              |
| WO <sub>2</sub>                | C4 (TiO <sub>2</sub> )                              | ~1550                    | ~1430                    | 17.8                                | 1.87                              |
| B-WO <sub>3</sub>              | Orthorhombic  | 1473                     | ...                      | 32.4                                | 3.39                              |
| W <sub>2</sub> O <sub>5</sub>  | Triclinic   | Sub.~850                 | ~1530                    | 29.8                                | 3.12                              |
| Y <sub>2</sub> O <sub>3</sub>  | D5 <sub>3</sub> (Sc <sub>2</sub> O <sub>3</sub> )   | 2410                     | ...                      | 45.1                                | 1.13                              |
| ZnO                            | B3 (wurtzite)                                       | 1975                     | ...                      | 14.5                                | 1.58                              |
| ZrO <sub>2</sub>               | C4 <sub>3</sub> monoclinic                          | 2715                     | ...                      | 22.0                                | 1.57                              |

# Przebieg procesu utleniania wybranych metali

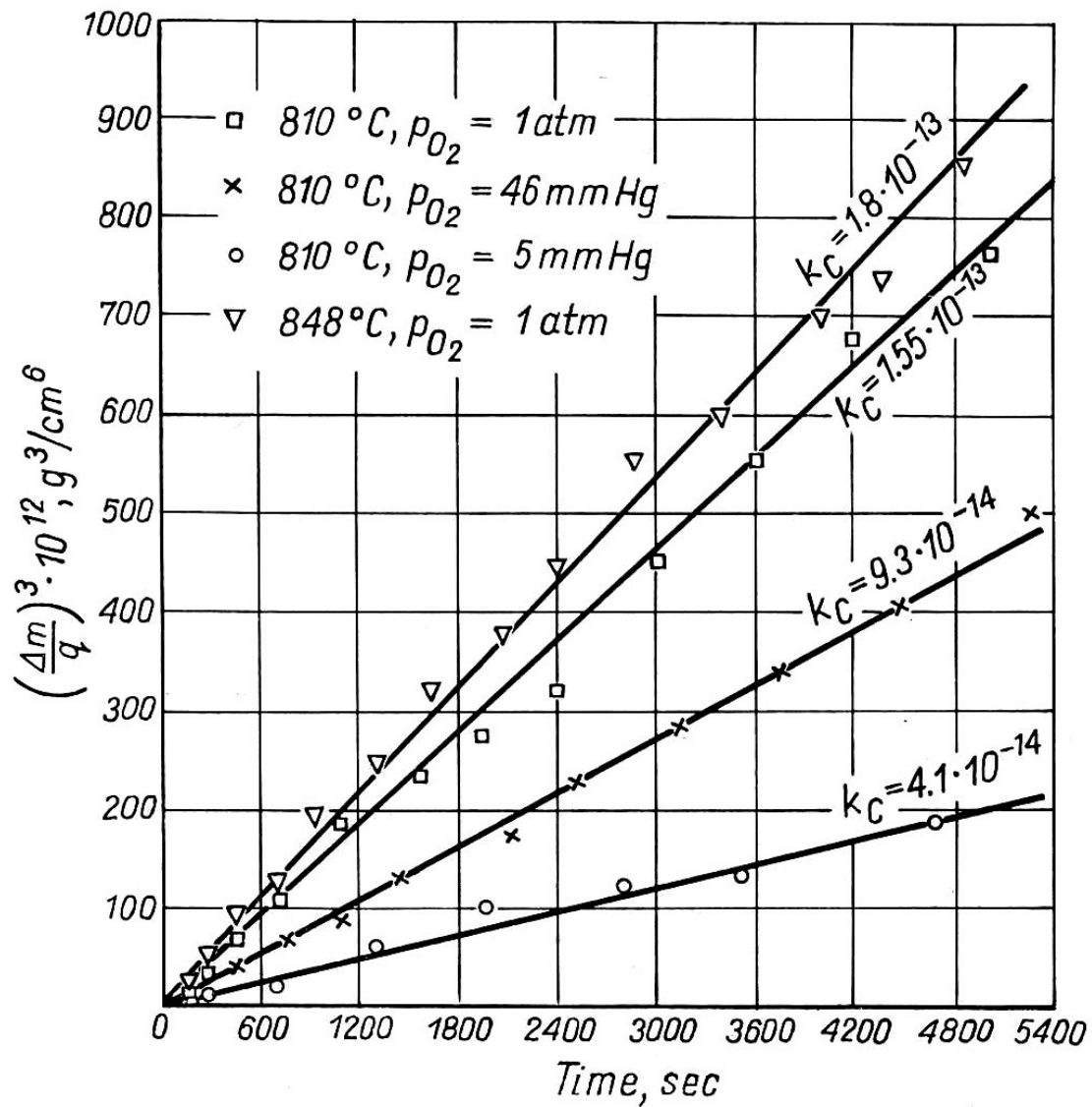
| Metal | Temperature, °C |          |           |          |          |          |      |          |      |          |       |          |
|-------|-----------------|----------|-----------|----------|----------|----------|------|----------|------|----------|-------|----------|
|       | 100             | 200      | 300       | 400      | 500      | 600      | 700  | 800      | 900  | 1000     | 1100  |          |
| Mg    | log.            |          | par.      | paralin. | lin.     |          |      |          |      |          |       |          |
| Ca    | log.            |          | par.      | lin.     | lin.     |          |      |          |      |          |       |          |
| Ce    | log.            | lin.     | incr.     |          |          |          |      |          |      |          |       |          |
| Th    |                 |          | par.      |          | lin.     |          |      |          |      |          |       |          |
| U     | par.            | paralin. | lin.      | incr.    |          |          |      |          |      |          |       |          |
| Ti    |                 |          | log.      | cu.      | cu.      | paralin. |      |          |      | paralin. |       |          |
| Zn    |                 |          | log. cu   |          | cu.      |          |      |          | cu.  | cu.      | lin.  |          |
| Nb    |                 |          | par.      | par.     | paralin. |          |      | lin.     | lin. |          | incr. |          |
| Ta    | log. inv.       | log.     |           | par.     | paralin. |          |      | lin.     |      | lin.     |       |          |
| Mo    |                 |          | par.      | paralin. | paralin. |          |      | lin.     |      | lin.     |       |          |
| W     |                 |          | par.      | par.     | par.     |          |      | paralin. |      | paralin. |       | paralin. |
| Fe    | log.            | log.     | par.      | par.     | par.     |          |      | par.     |      | par.     |       | par.     |
| Ni    |                 | log.     | log.      | cu.      | par.     |          |      |          |      | par.     |       | par.     |
| Cu    |                 | log. cu. | cu.       |          | par.     |          | par. |          | par. |          |       |          |
| Zn    |                 | log      | log. par. |          |          |          |      |          |      |          |       |          |
| Al    | log. inv.       | log.     | log.      | par.     |          | lin.     |      |          |      |          |       |          |
| Ge    |                 |          |           | par.     |          | paralin. |      |          |      |          |       |          |

Denotations: log. — logarithmic law; inv. log. — inversely logarithmic law; cu — cubic law; par. — parabolic law; paralin. — paralinear law; lin. — linear law; incr. — increased oxidation rate.

# Kinetyka utleniania miedzi

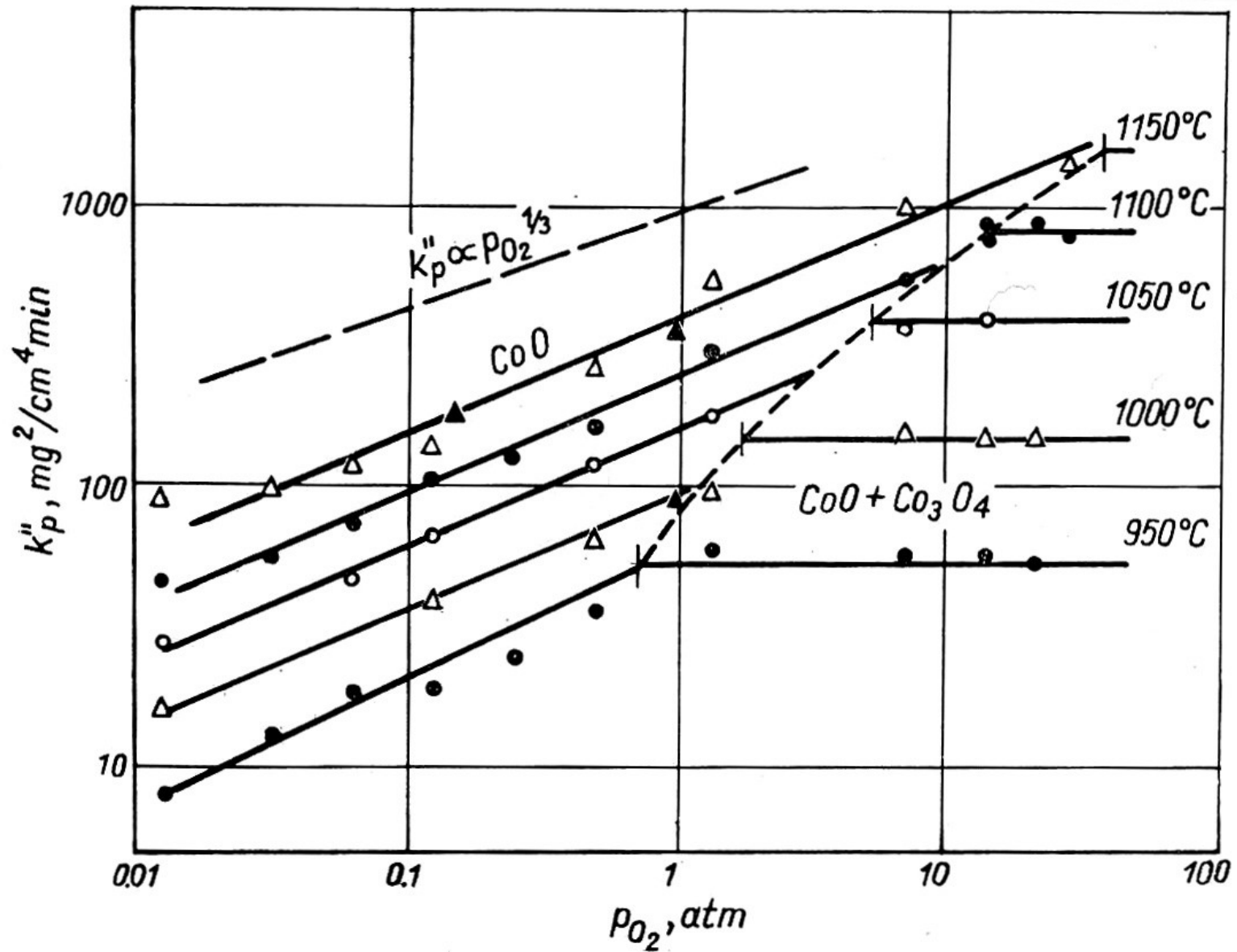


# Kinetyka utleniania CuO

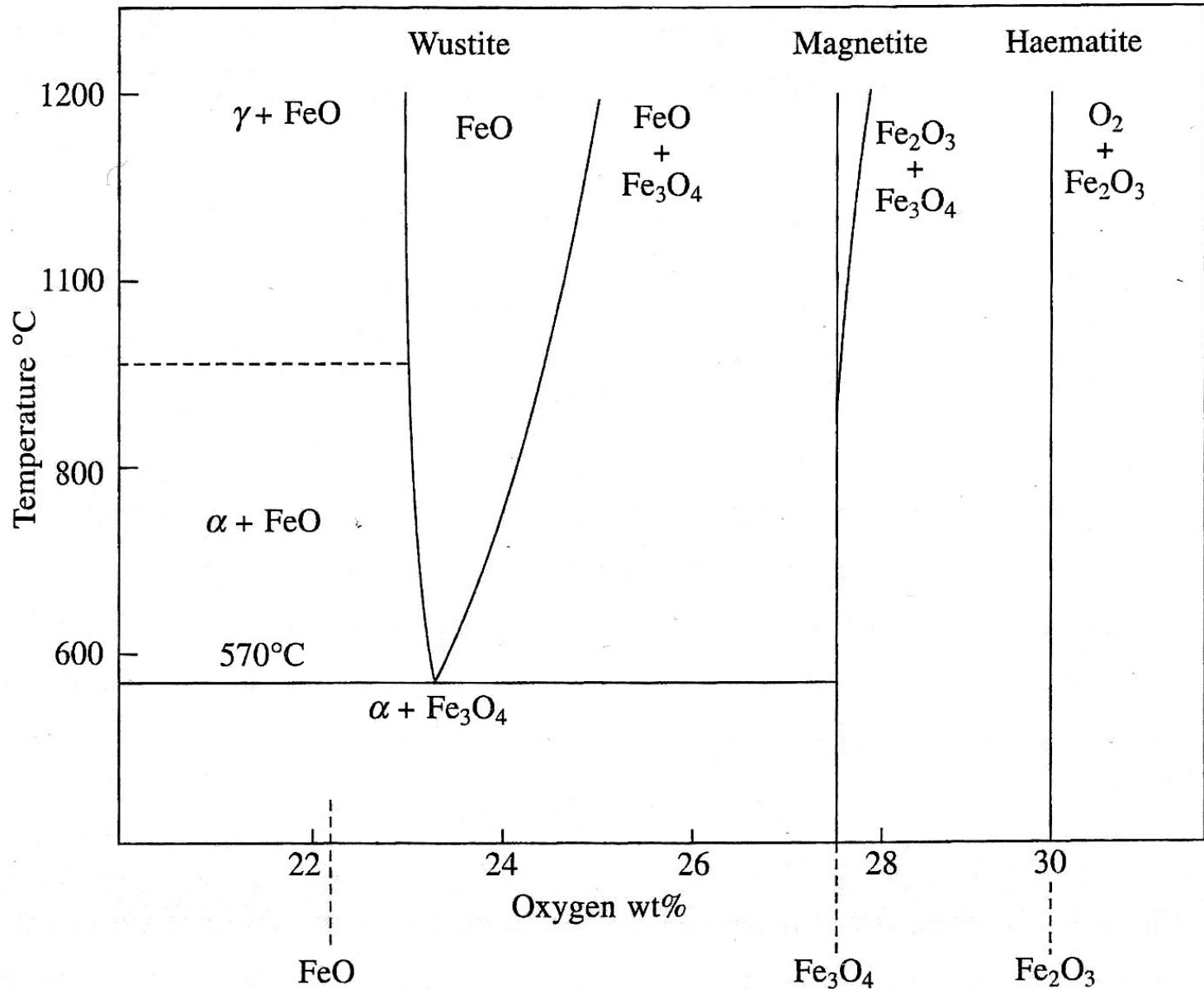




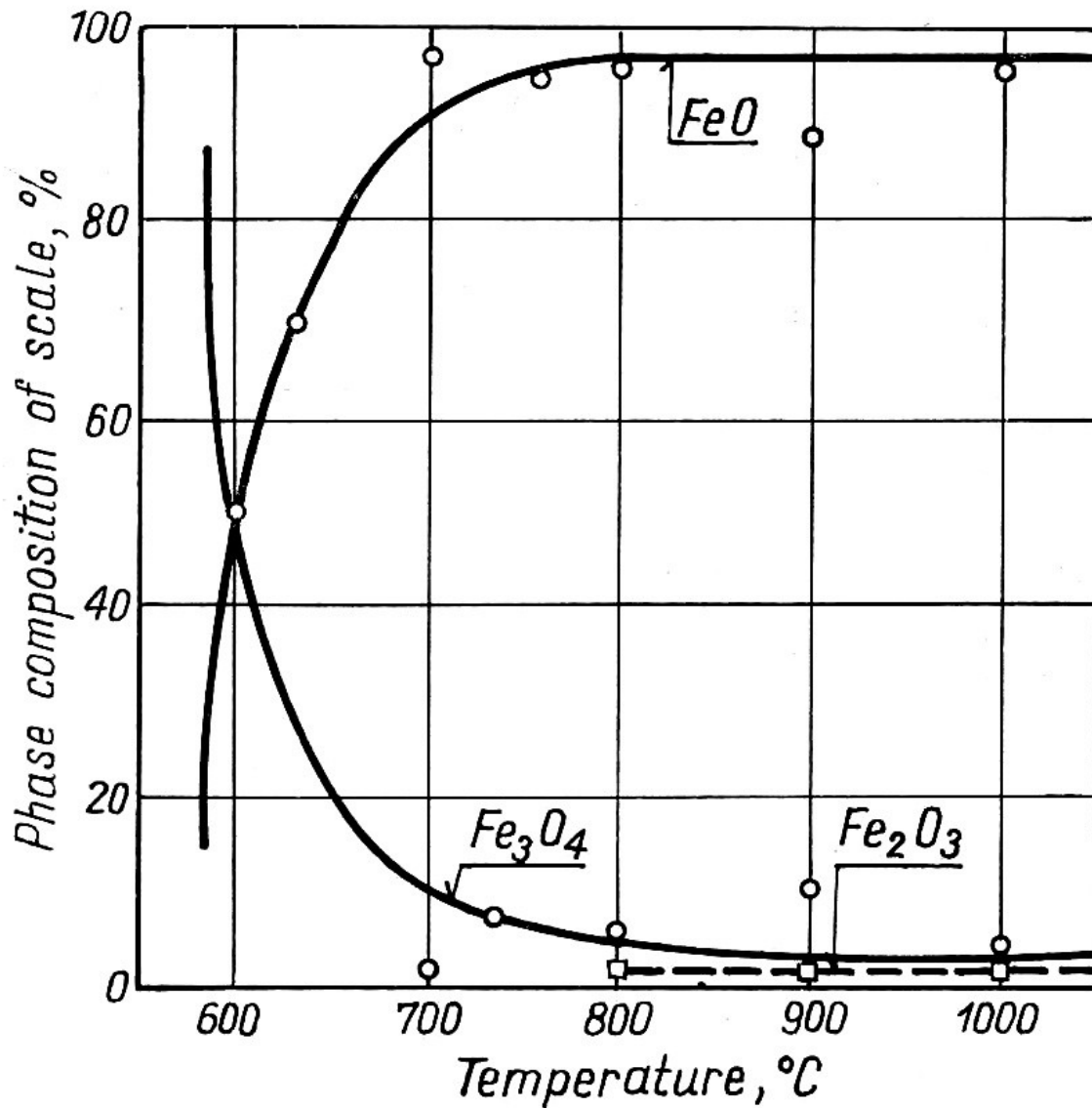
# Zależność szybkości utleniania kobaltu od ciśnienia



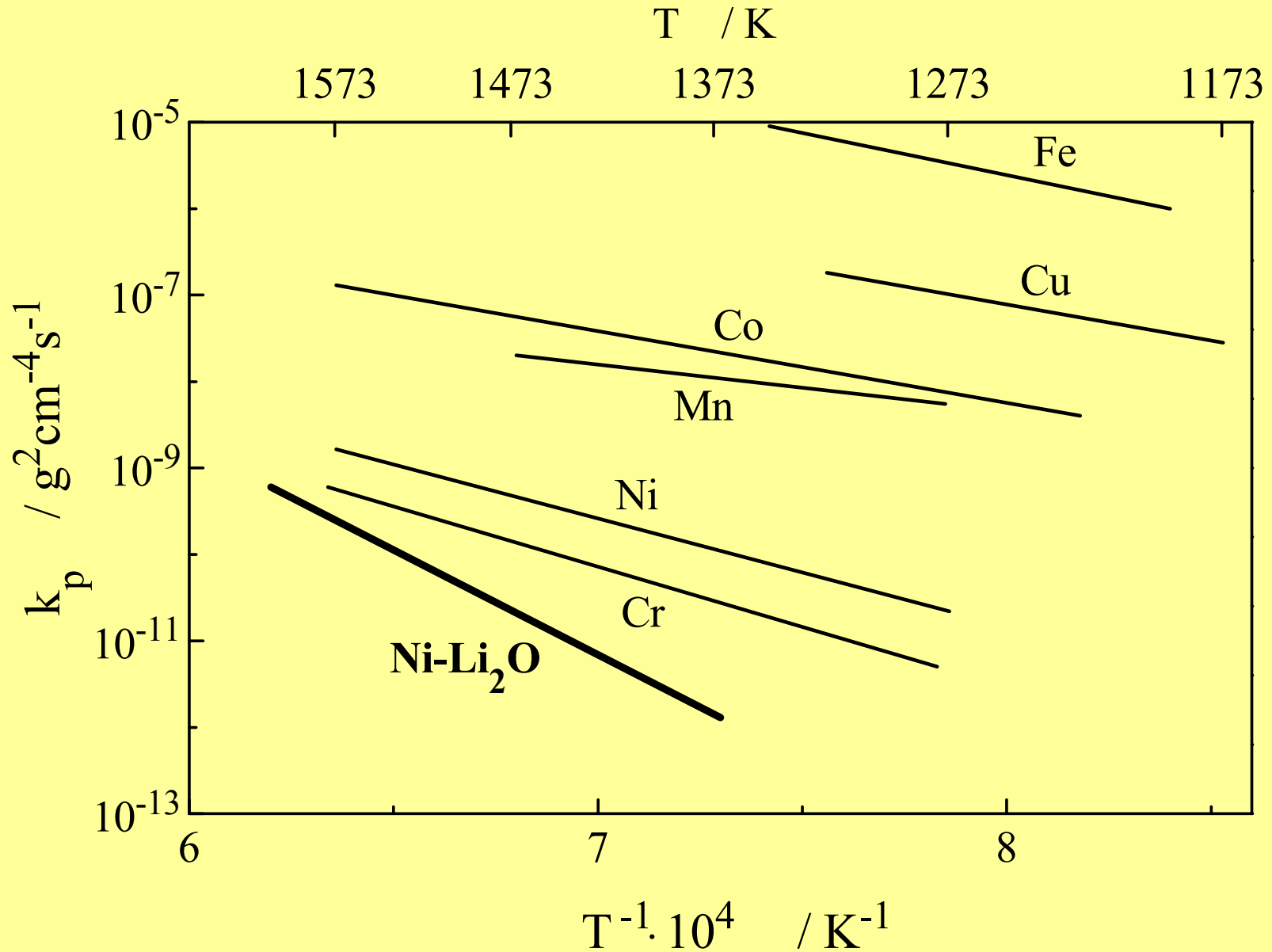
# Diagram fazowy układu Fe-O<sub>2</sub>



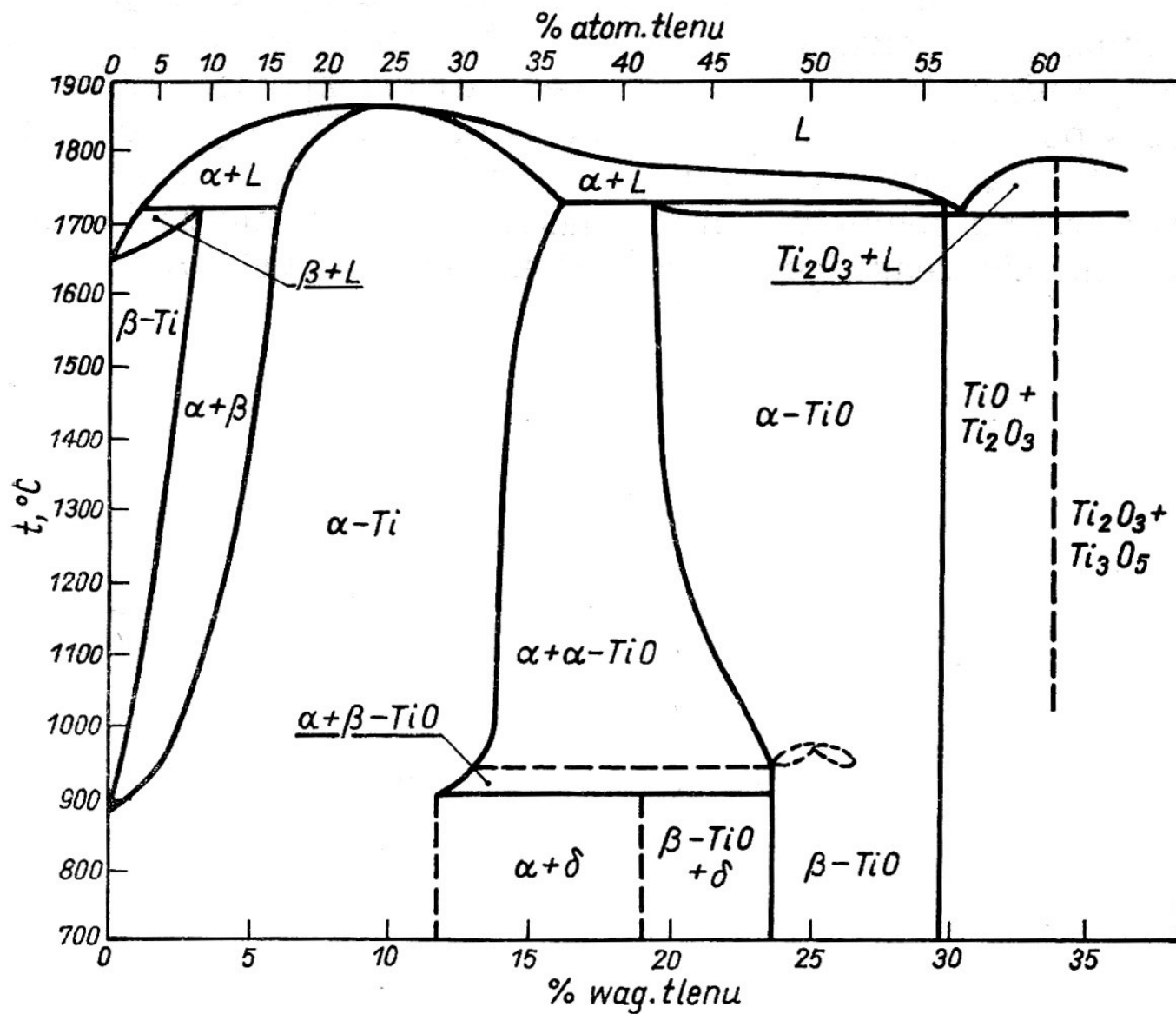
# Wpływ temperatury na skład zgorzeli tlenkowej narastającej na żelazie



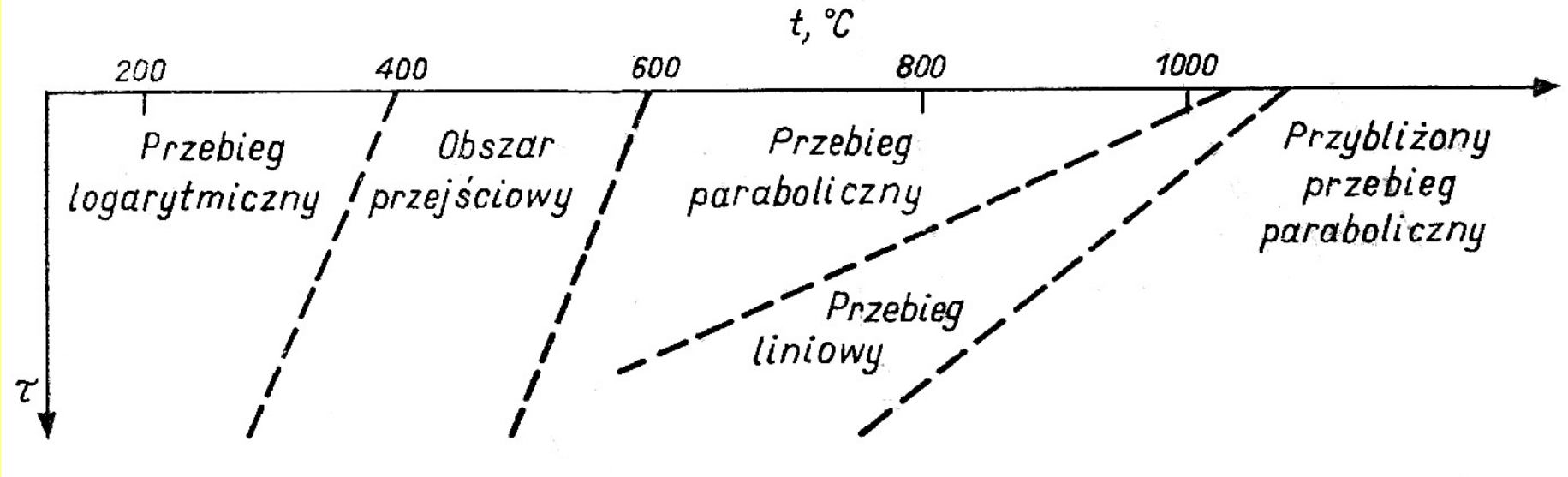
# Szybkości utleniania wybranych metali



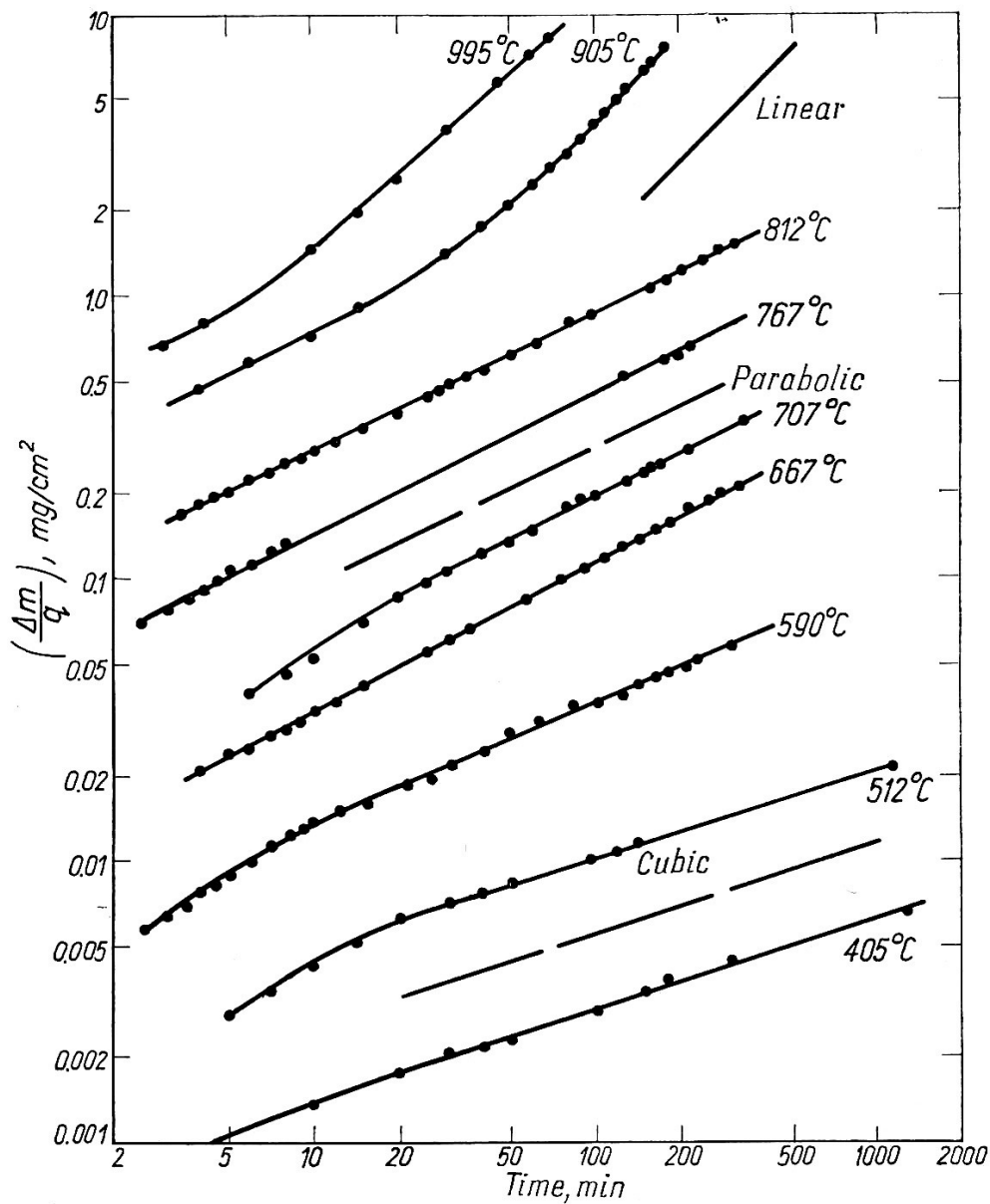
# Diagram fazowy układu $\text{Ti-O}_2$



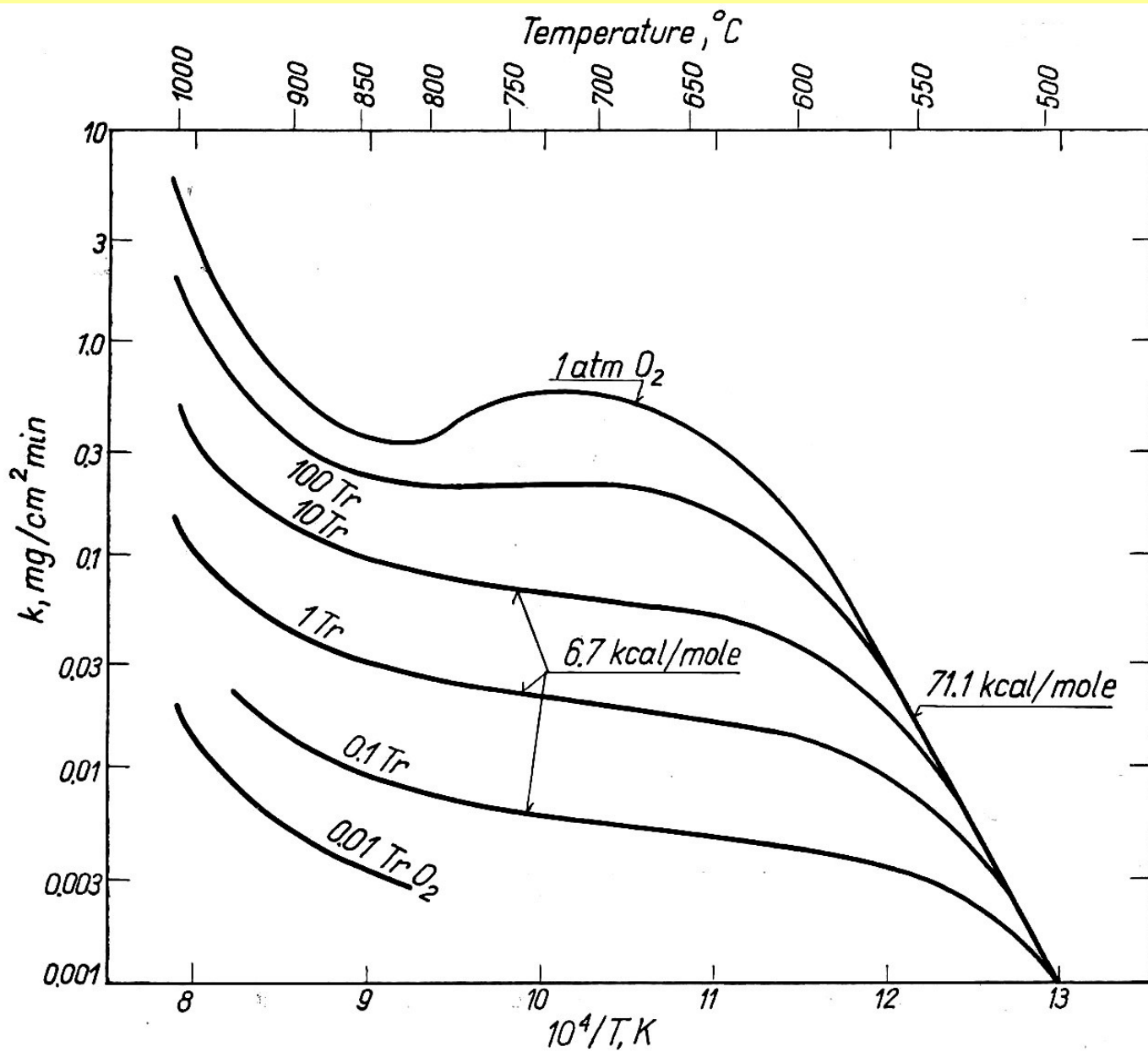
# Schemat wpływu temperatury i czasu na kinetykę utleniania Ti



# Wpływ temperatury na kinetykę utleniania Ti

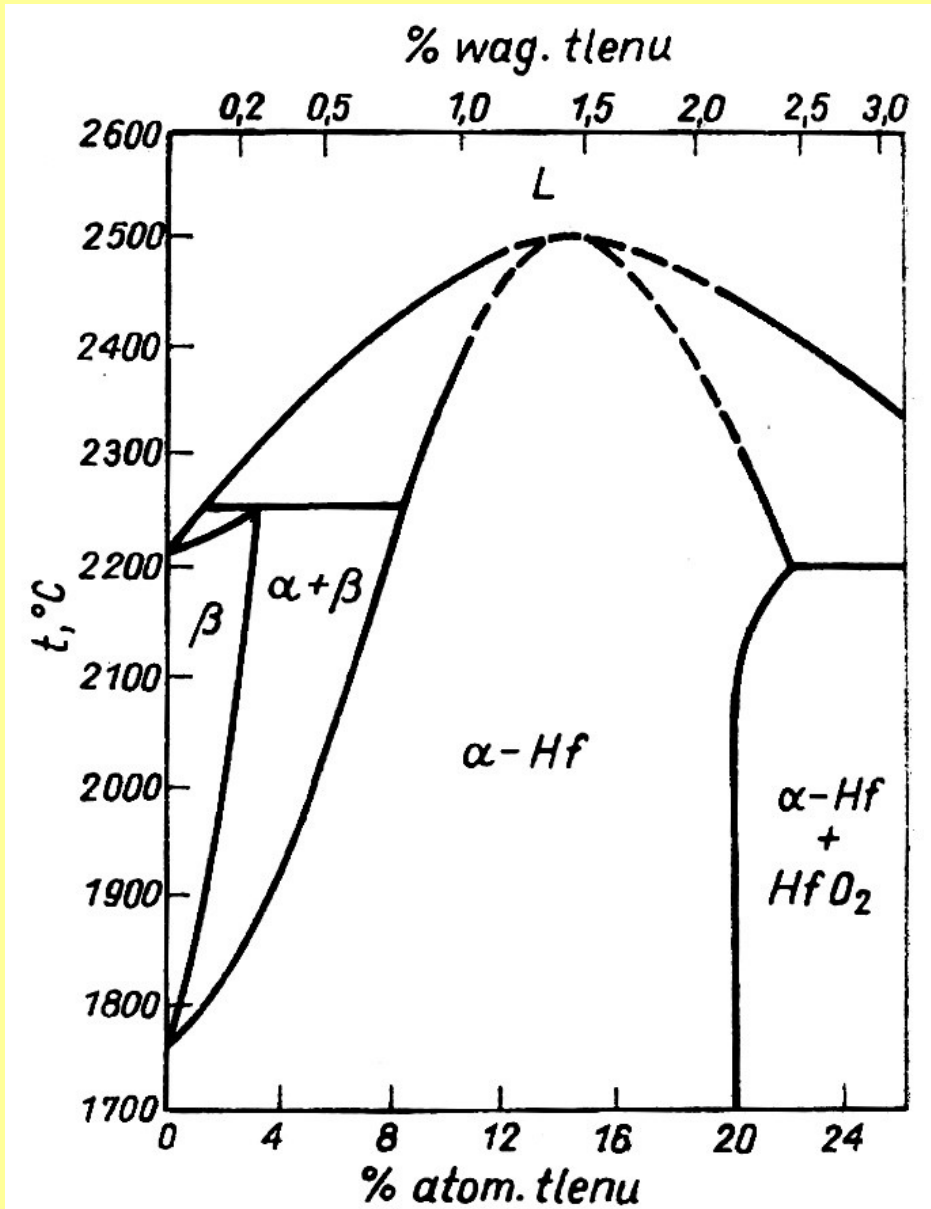


# Wpływ temperatury i ciśnienia tlenu na kinetykę utleniania Ti

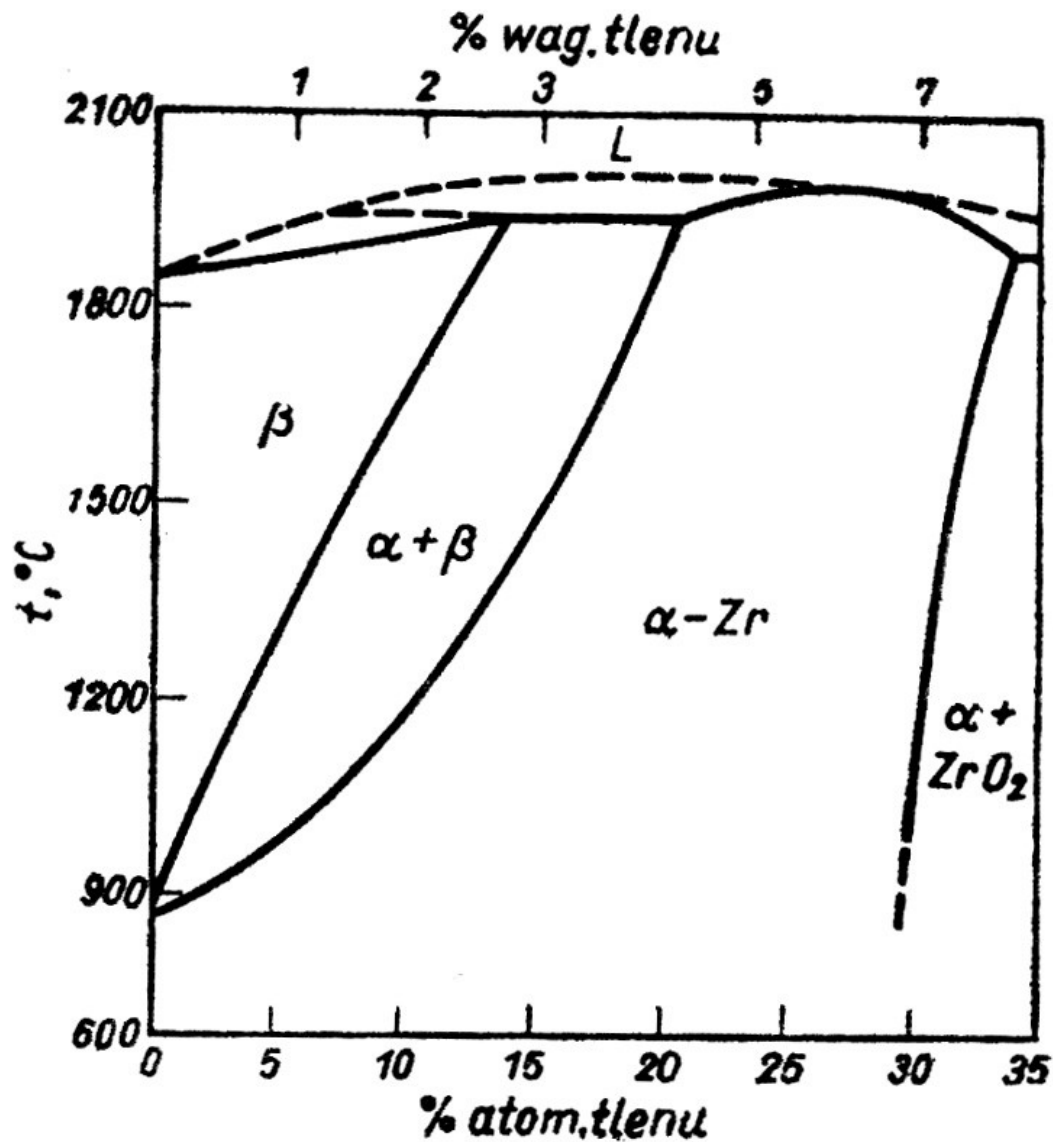




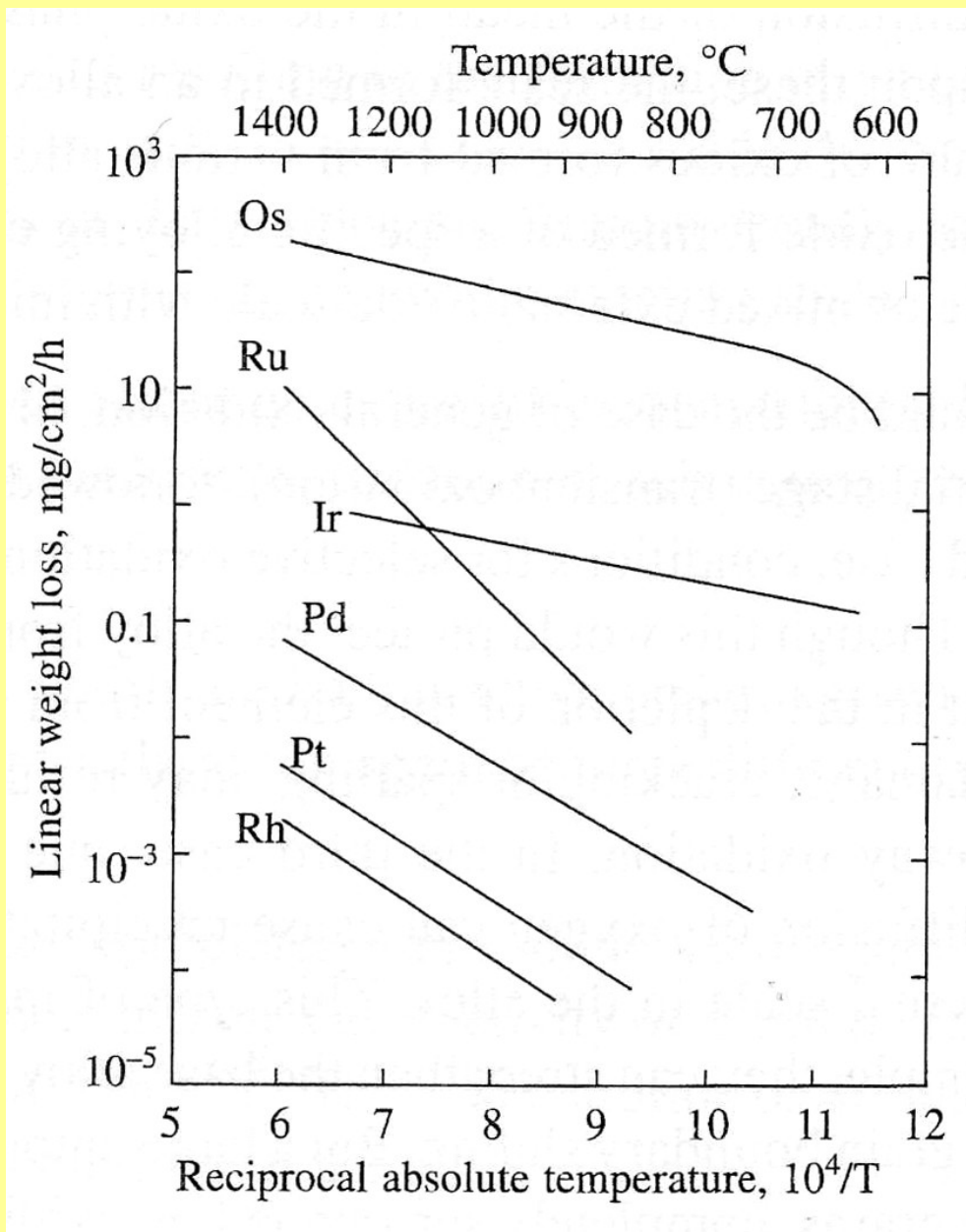
# Diagram fazowy układu Hf-O<sub>2</sub>



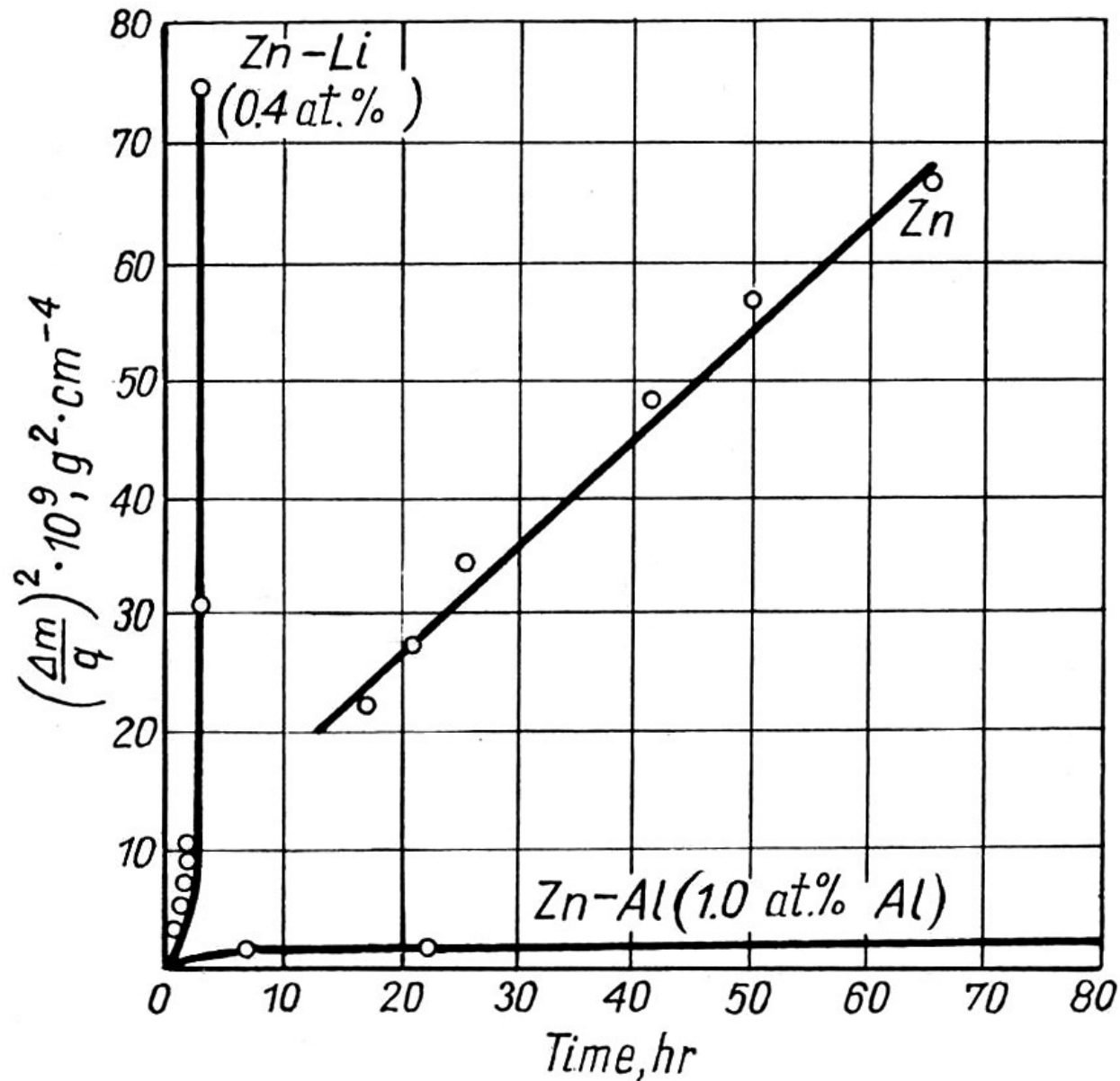
# Diagram fazowy układu Zr-O<sub>2</sub>



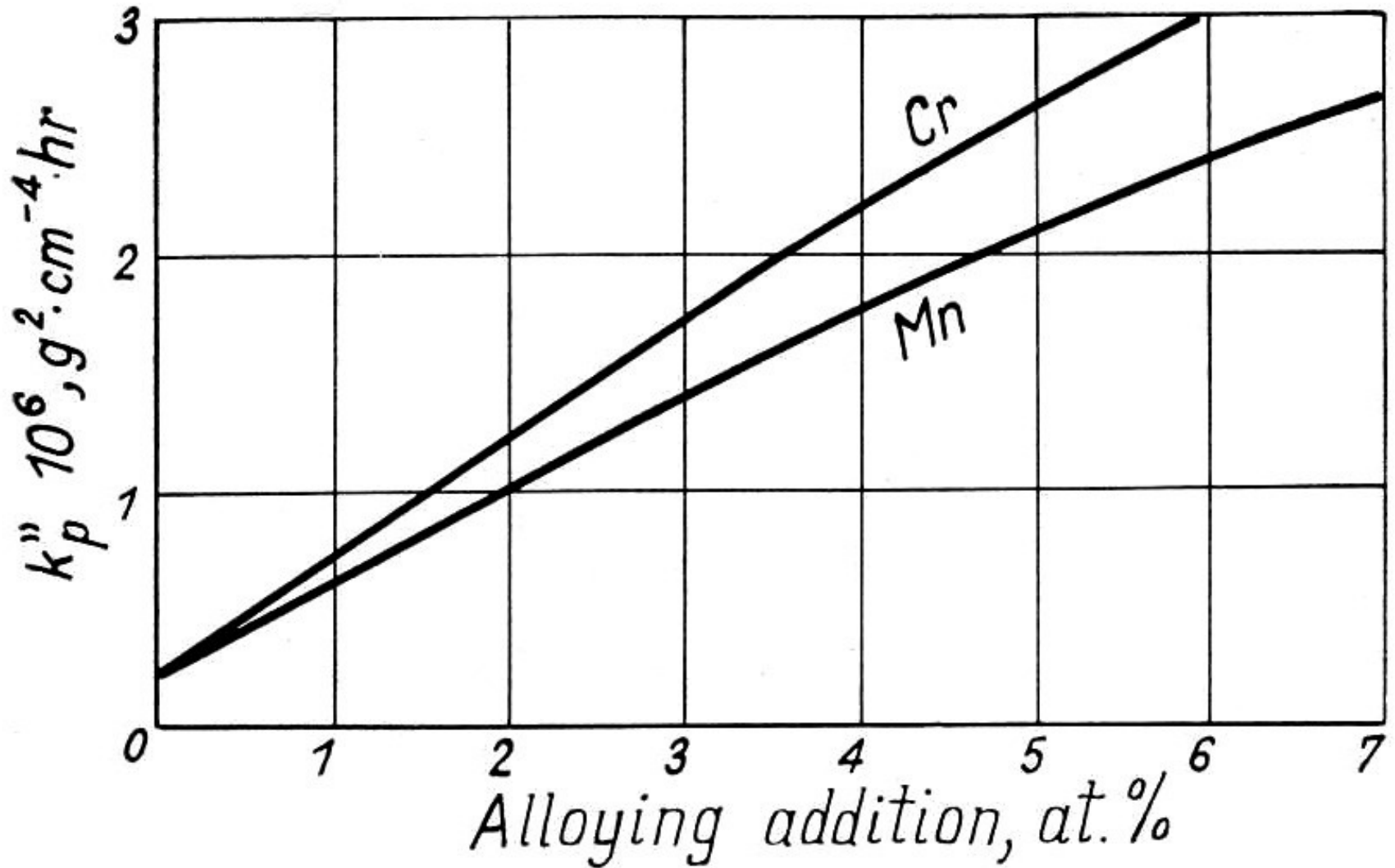
# Wpływ temperatury na szybkość degradacji metali szlachetnych



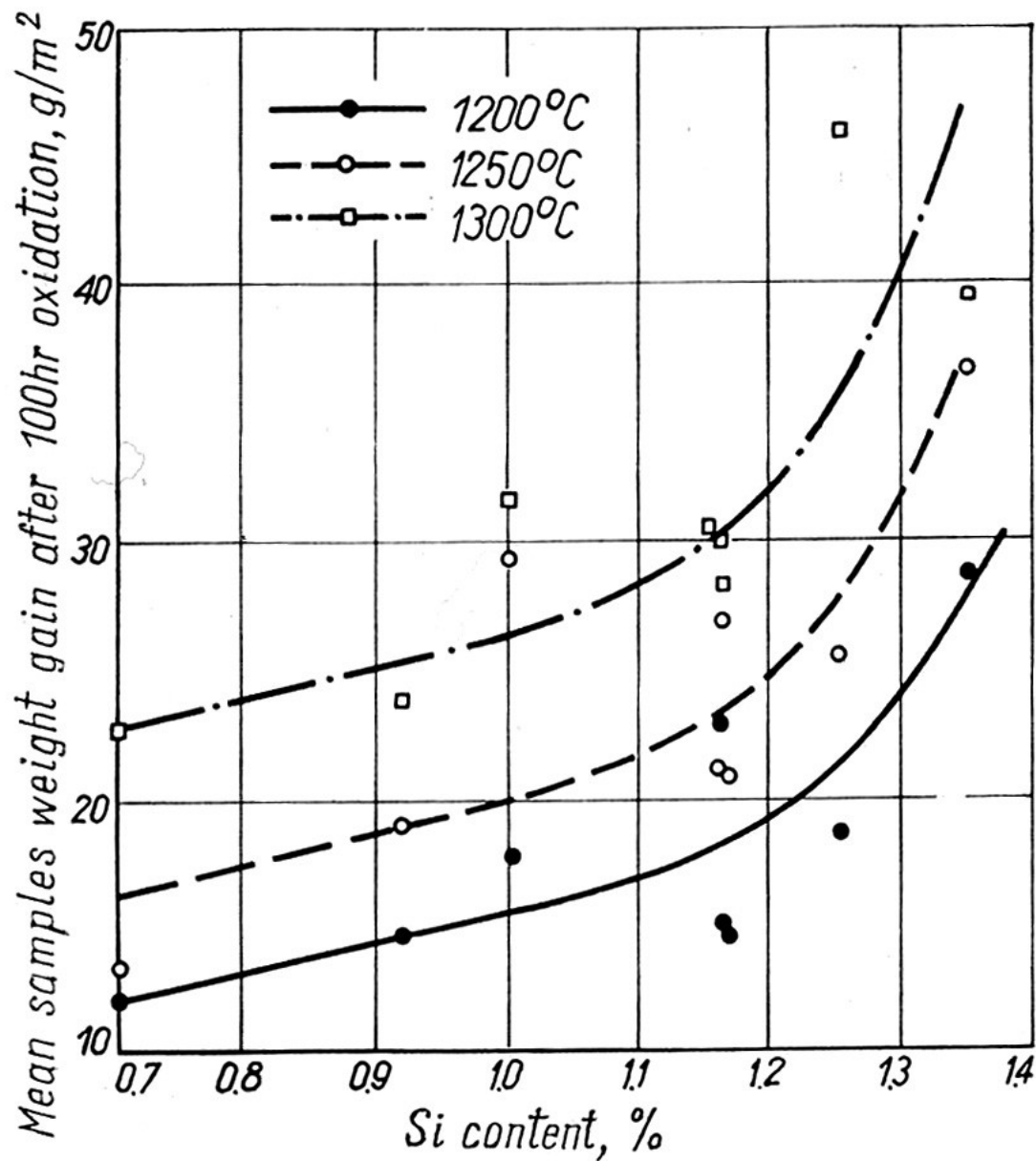
# Wpływ różnowartościowych domieszek na szybkość utleniania Zn



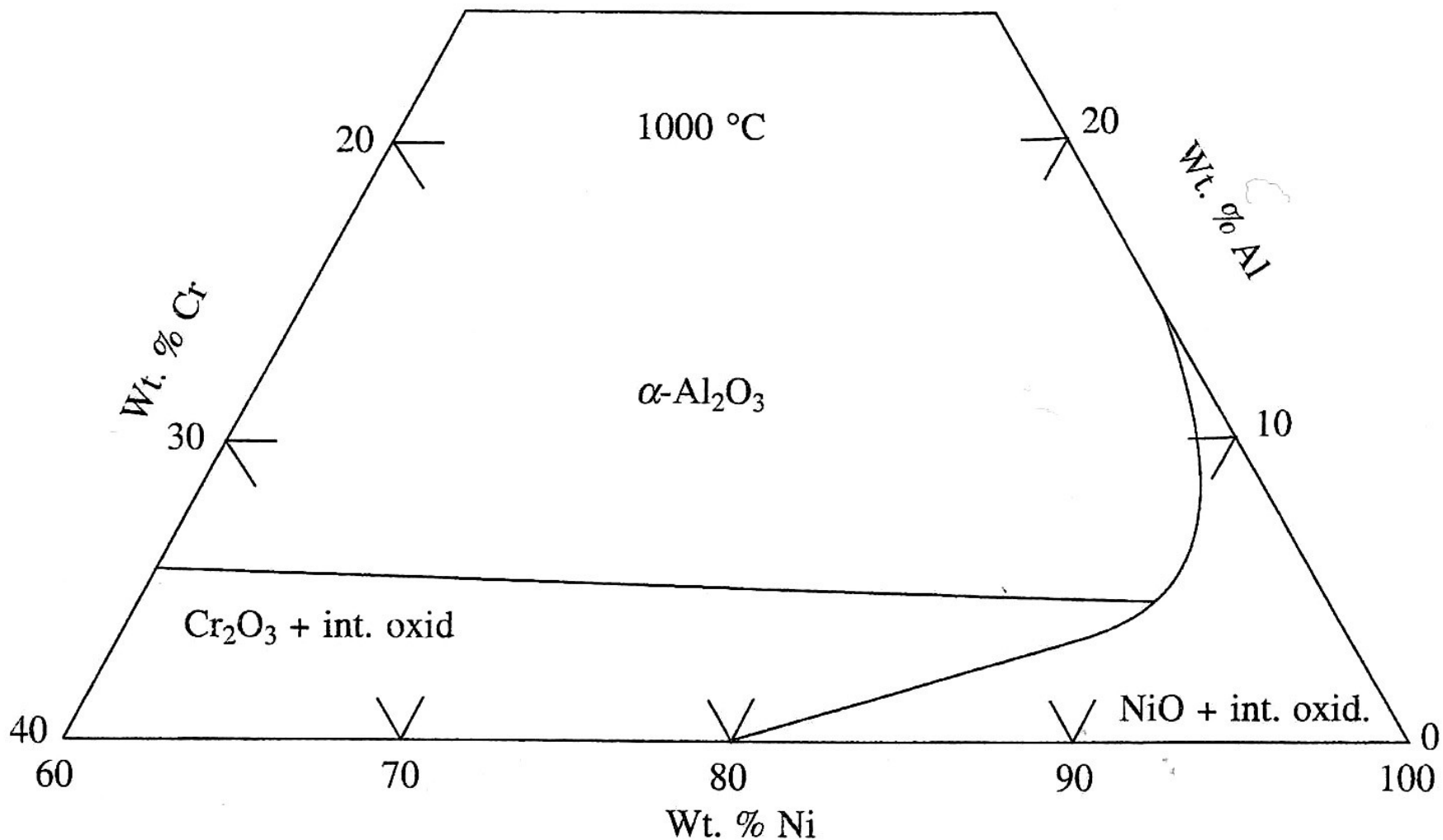
# Wpływ różnowartościowych domieszek na szybkość utleniania Ni



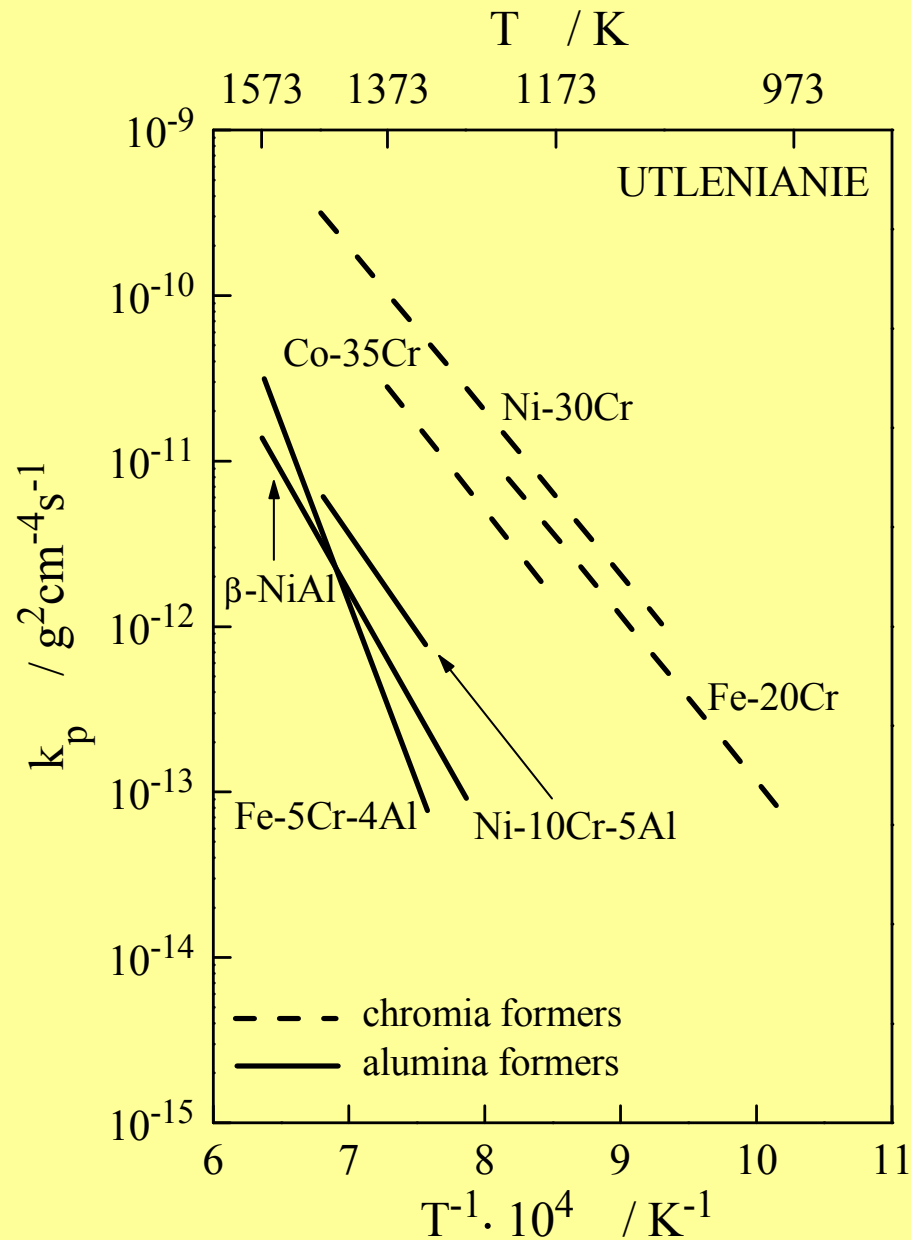
# Wpływ Si na szybkość utleniania stopów typu *kanthal* (Fe-Cr-Al)



# Diagram fazowy układu $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$ -NiO

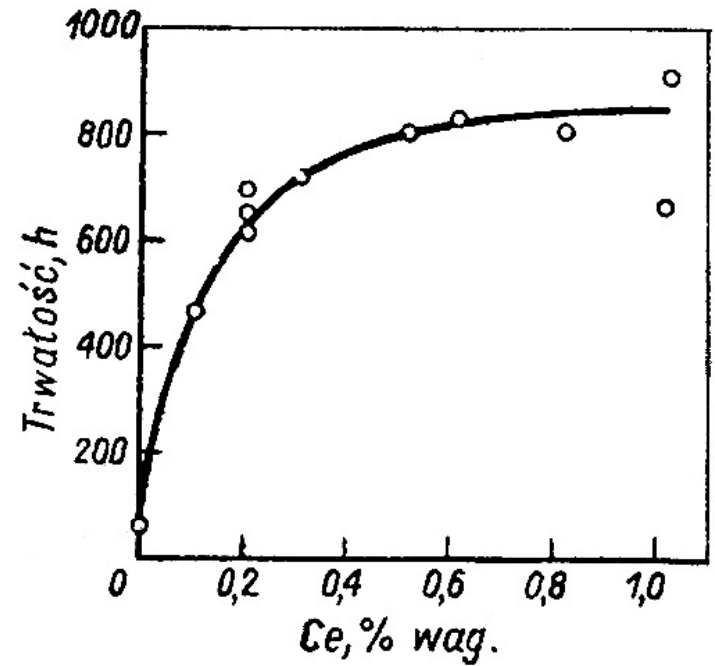
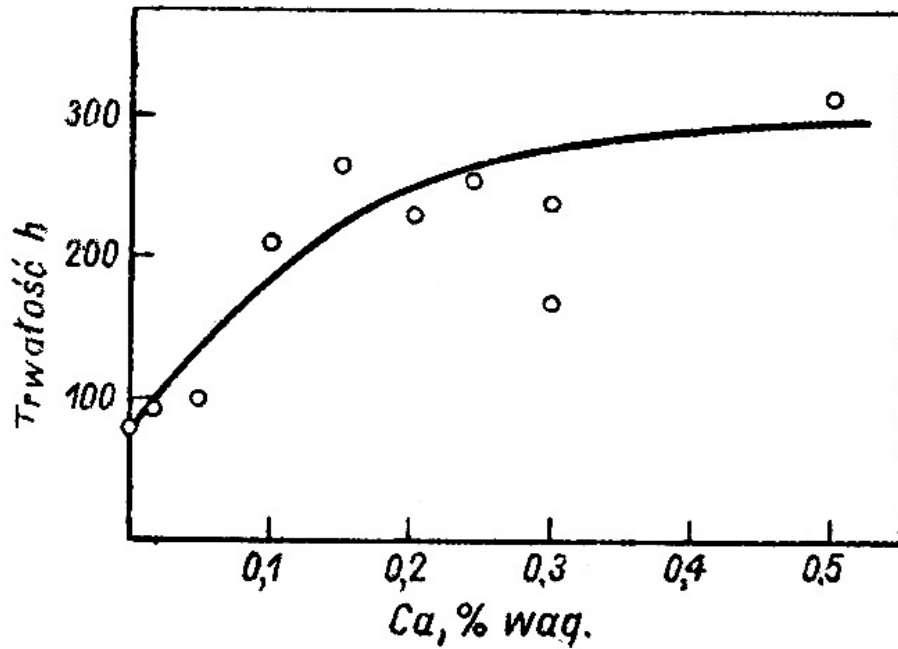


# Szybkości utleniania wybranych stopów

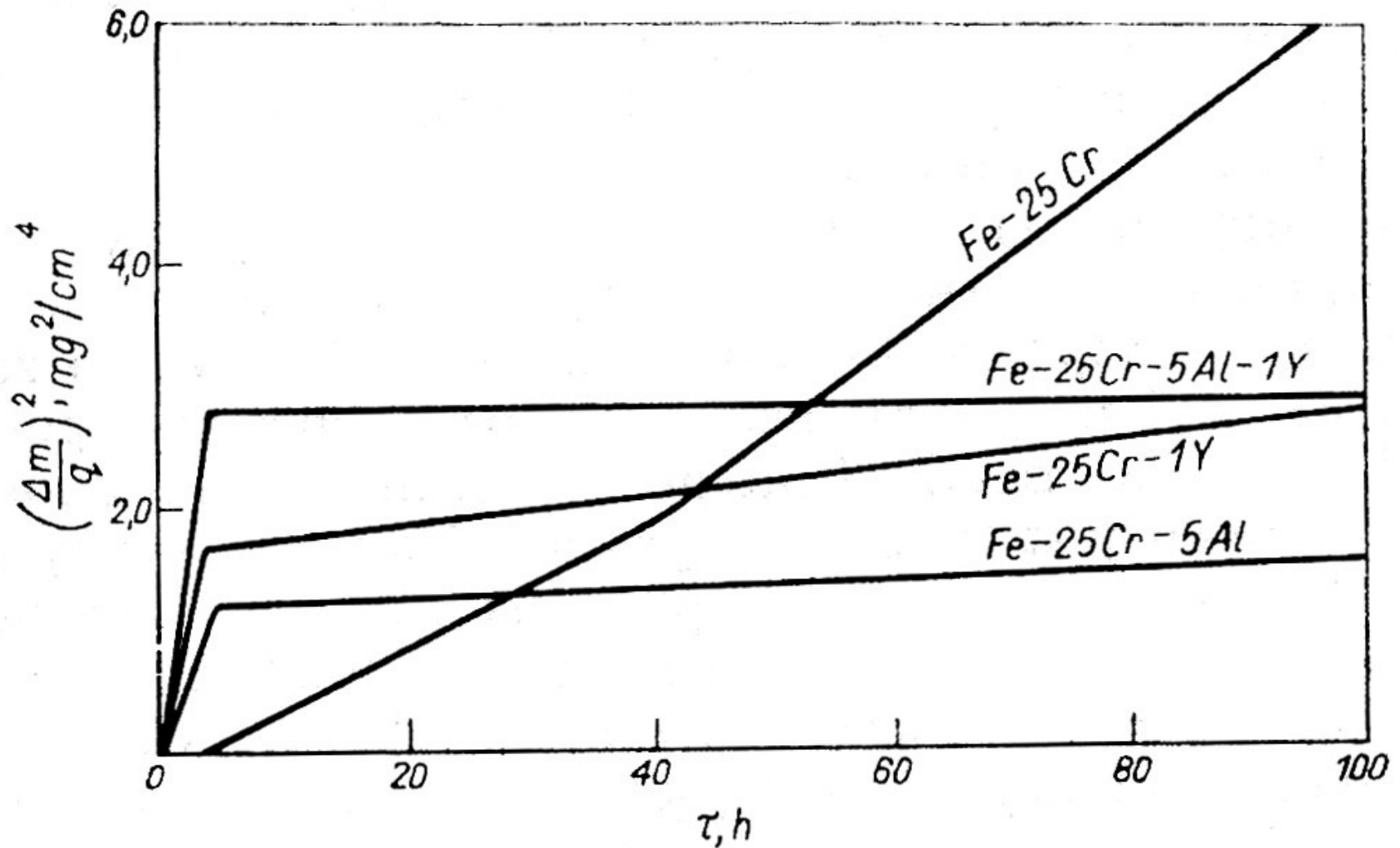




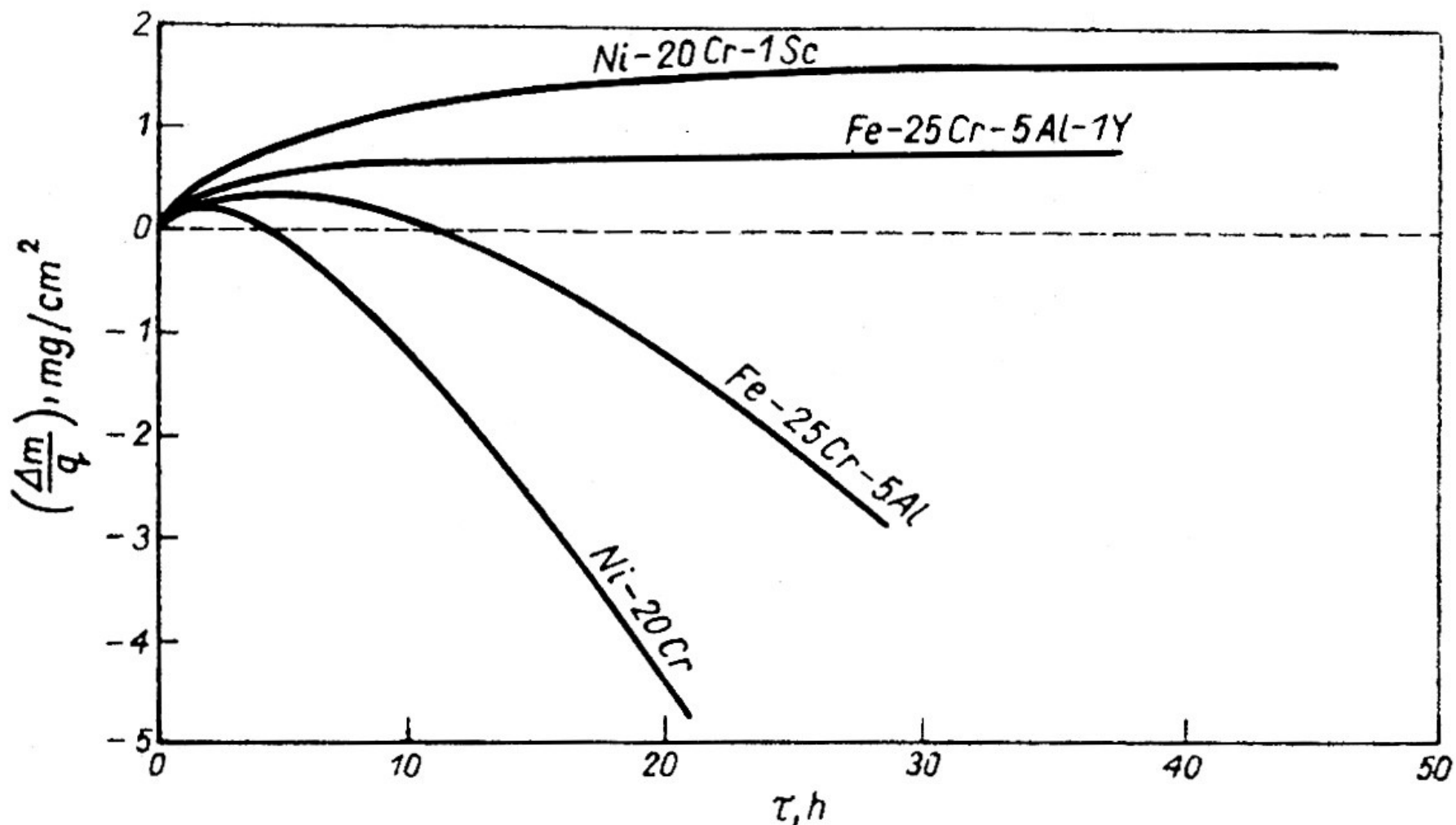
# Wpływ Ca i Ce na trwałość stopu Ni-20Cr w temp. 1050 °C



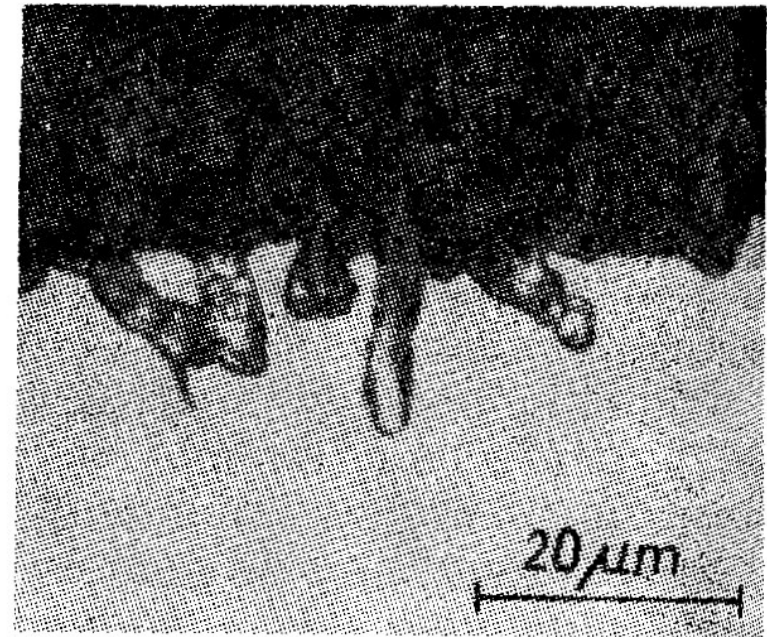
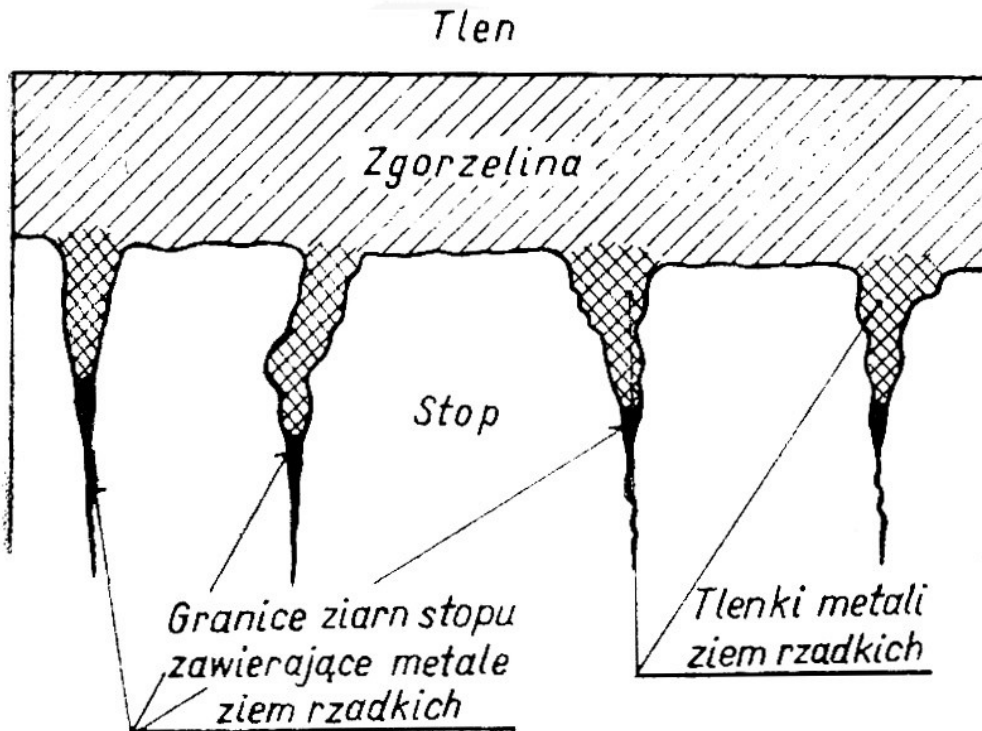
# Wpływ Y na szybkość utleniania stopu Fe-25Cr-5Al



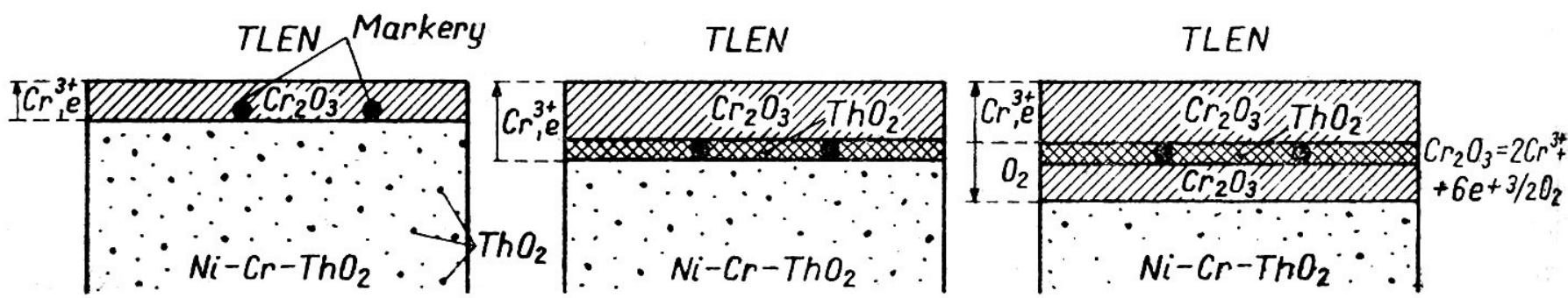
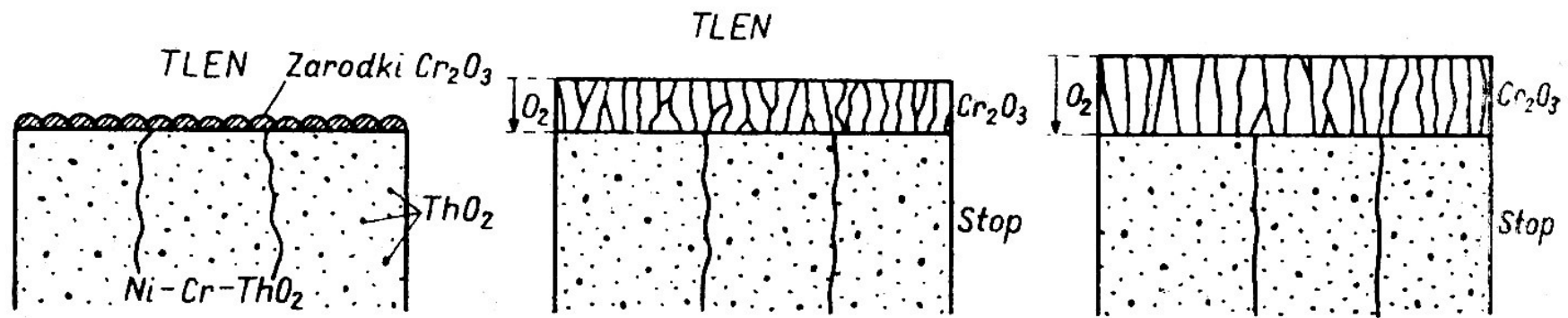
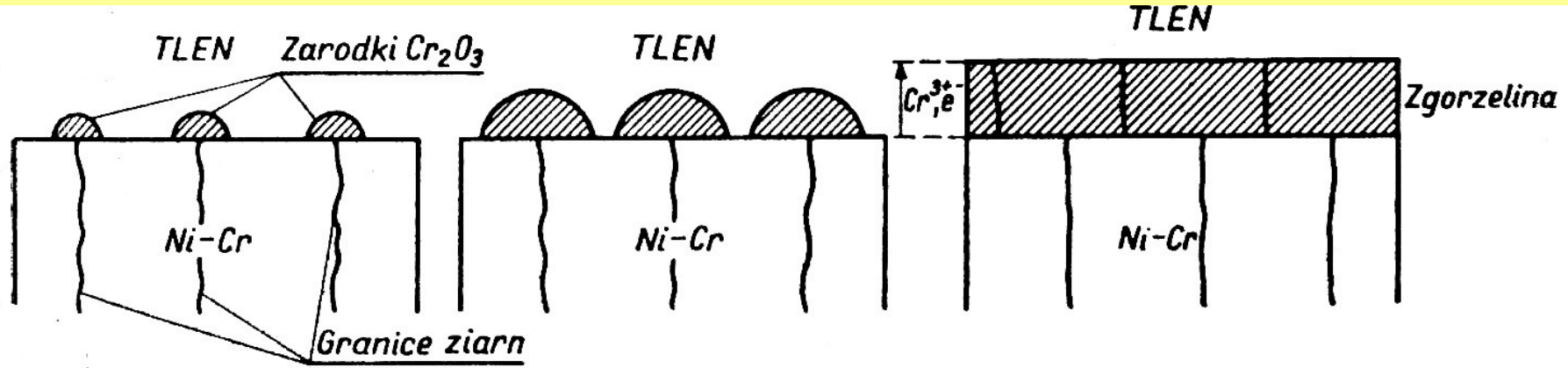
Wpływ Y i Sc na szybkość degradacji stopów Fe-25Cr-5Al oraz Ni-20Cr w warunkach cyklicznego utleniania



Schemat mechanicznego wiązania zgorzeliny z podłożem za pośrednictwem utlenionych wewnątrz metali ziem rzadkich, zgromadzonych na granicach ziarn stopu



# Schemat formowania się zgorzeliny $Cr_2O_3$ na wysokoprocentowych stopach Ni-Cr



**KONIEC**