

THE THEORY
AND PROPERTIES
OF
THERMOCOUPLE
ELEMENTS



STP 492

AMERICAN SOCIETY FOR TESTING AND MATERIALS

THE THEORY AND PROPERTIES OF THERMOCOUPLE ELEMENTS

D. D. Pollock
Faculty of Engineering and Applied Science
State University of New York at Buffalo

ASTM SPECIAL TECHNICAL PUBLICATION 492

List price \$7.25

04-492000-40



AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race Street, Philadelphia, Pa. 19103

© BY AMERICAN SOCIETY FOR TESTING AND MATERIALS 1971
Library of Congress Catalog Card Number: 75-151771
ISBN 0-8031-0074-4

NOTE

The Society is not responsible, as a body,
for the statements and opinions
advanced in this publication.

Printed in Baltimore, Md.
May 1971
Second printing July 1975

Foreword

In this work, *The Theory and Properties of Thermocouple Elements*, Professor Pollock has written a singularly useful monograph which should appeal to a wide variety of readers, ranging from the advanced undergraduate or graduate student who is just beginning to get his feet wet in this area to the sophisticated specialist who wants to brush up on his fundamentals. More particularly, the work provides a worthwhile gathering of information of a theoretical nature on metallic thermocouples. Consider only the topics included: here, under one cover, we find the history, thermodynamics, mathematics, quantum mechanics, and physics of thermoelectricity, all neatly compiled and stored for us. A careful perusal of this material is bound to lead to a greater understanding of the behavior of thermoelectric metals in terms of the solid state physics involved.

R. P. Benedict

Westinghouse Electric Corp.

Related ASTM Publications

- Manual on the Use of Thermocouples in Temperature Measurement, STP 470 (1970), \$17.00**
- Specifications for Thermocouples, Sheathed, Type K, for Nuclear or for High Reliability Applications (E 235 - 67)**
- Liquid Baths for Thermocouple Measurements, Proposed Standard, 1970 Annual Book of ASTM Standards, Part 30**
- Preparation of Thermocouple Measuring Junctions, Proposed Standard, 1970 Annual Book of ASTM Standards, Part 30**
- Properties of Thermoelement Materials, Proposed Standard, 1970 Annual Book of ASTM Standards, Part 30**

Preface

This monograph was written in an attempt to fill a long standing void in the literature on thermoelectricity. The book by D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles*, Wiley, 1962, considers the theory and thermoelectric behavior of alloys below their characteristic temperatures. Other works, such as the *Manual on the Use of Thermocouples in Temperature Measurement, ASTM STP 470*, 1970, contain sections which are concerned primarily with the more practical and applied aspects of thermoelectric thermometry at elevated temperatures.

The present work attempts to explain the theory and the bases for the thermoelectric behavior of alloys in general and of those alloys commonly used for thermoelectric purposes at temperatures above their characteristic temperatures in particular. This is the range in which the vast preponderance of the applications have been and are being made. No single work which satisfies this need has yet come to my attention.

The text is designed to assist the novice, as well as the reader who has some familiarity with this field, to acquire a more fundamental understanding of this behavior in metallic conductors. Semiconductors are not included. It has been written so that only a knowledge of elementary calculus is required to follow the reasoning. All of the algebra is shown, and no steps in the derivations are considered to be "obvious" to the reader. Introductory material is provided in order to facilitate the understanding of the relevant concepts in thermoelectricity and solid state physics.

Most of the elementary knowledge required for the understanding of chapter 4 is given in the Introduction. However, chapters 2 and 3 will permit the novice to omit the derivations given in chapter 4. One may skip these and go on to the discussion at the end of that chapter with little loss in understanding. The Mott and Jones theory is given for the more sophisticated reader and because it does not appear to have been presented in elementary detail elsewhere. The combined presentations given in chapters 2, 3, and 4 are thought to provide a broader basis for the understanding of thermoelectric phenomena than is possible from any one explanation by itself.

Basic material already well represented in the literature is included in a minimal way for the sake of completeness. Other material, such as that presented originally by Bridgman or by Mott and Jones, is given in more detail than in the original. This has been done in an attempt to provide a simple and self-consistent presentation.

References have been provided so that additional information can be acquired by recourse to a minimum number of reliable sources.

The work will be of use to metallurgists and physicists. It details how thermoelectric properties can reflect the influence of factors such as composition and cold work on the behavior of the solid state. Descriptions such as these can be useful in the design of alloys for purposes other than thermoelectric ones.

D. D. Pollo

Buffalo, N.Y.
February 1971

Acknowledgments

The great assistance of Joseph K. Kielman of ASTM in the editing of this work is deeply appreciated.

I am indebted to Dr. H. Suprinick of the State University of New York and to Dr. C. Dean Starr and Dr. T. P. Wang of the Wilbur B. Driver Company for their valuable criticisms of work which has been incorporated into this monograph.

The efforts of Mr. R. H. Cherry and Mr. D. I. Finch of the Leeds and Northrup Company are acknowledged with sincere thanks.

Thanks are also due to Mr. R. P. Benedict of the Westinghouse Electric Corporation for contributing the Foreword of this edition.

Contents

Introduction	1
Thermocouples	1
Associated Thermoelectric Phenomena	2
Solid State Physics	6
Primary References	14
Other References	14
1. Elementary Concepts	15
1.1 The Seebeck Effect	15
1.2 The Peltier Effect	15
1.3 The Thomson Effect	15
1.4 Primary Reference	17
1.5 Other References	17
2. Thermodynamics of Thermoelectricity	17
2.1 Fundamental Theorem of Thermoelectricity	18
2.2 Entropy Considerations	19
2.3 The Peltier Effect	20
2.4 The Thomson Effect	20
2.5 The Concept of Absolute emf	21
2.5.1 Laws of Thermoelectric Circuits	22
2.6 Applications to Real Thermocouples	23
2.7 References	25
3. Combined Thermodynamic and Quantum Mechanic Model of Thermoelectricity	25
3.1 Noble Thermoelements	25
3.2 Transition Thermoelements	27
3.3 Summary	28
3.4 References	28
4. The Mott and Jones Theory of Thermoelectricity	28
4.1 Heat and Current Flow	29
4.2 The Effect of Heat and Current Flow on the Fermi Function	29
4.3 Integrals for the Electric and Heat Currents	33
4.4 Evaluation of j/e and $\partial Q/\partial x$	34
4.5 Evaluation of K_n	36
4.5.1 Evaluation of $\phi(E_F)$	39
4.5.2 Approximation of K_n and S	40
4.6 Noble Metals	41
4.7 Transition Metals	41
4.8 Comparison of Models	42
4.9 Thermoelectric Power and Electron Specific Heat	43
4.10 Comparison of Thermoelectric Powers	44
4.11 Summary	44
4.12 References	44

Contents

Introduction	1
Thermocouples	1
Associated Thermoelectric Phenomena	2
Solid State Physics	6
Primary References	14
Other References	14
1. Elementary Concepts	15
1.1 The Seebeck Effect	15
1.2 The Peltier Effect	15
1.3 The Thomson Effect	15
1.4 Primary Reference	17
1.5 Other References	17
2. Thermodynamics of Thermoelectricity	17
2.1 Fundamental Theorem of Thermoelectricity	18
2.2 Entropy Considerations	19
2.3 The Peltier Effect	20
2.4 The Thomson Effect	20
2.5 The Concept of Absolute emf	21
2.5.1 Laws of Thermoelectric Circuits	22
2.6 Applications to Real Thermocouples	23
2.7 References	25
3. Combined Thermodynamic and Quantum Mechanic Model of Thermoelectricity	25
3.1 Noble Thermoelements	25
3.2 Transition Thermoelements	27
3.3 Summary	28
3.4 References	28
4. The Mott and Jones Theory of Thermoelectricity	28
4.1 Heat and Current Flow	29
4.2 The Effect of Heat and Current Flow on the Fermi Function	29
4.3 Integrals for the Electric and Heat Currents	33
4.4 Evaluation of j/e and $\partial Q/\partial x$	34
4.5 Evaluation of K_n	36
4.5.1 Evaluation of $\phi(E_F)$	39
4.5.2 Approximation of K_n and S	40
4.6 Noble Metals	41
4.7 Transition Metals	41
4.8 Comparison of Models	42
4.9 Thermoelectric Power and Electron Specific Heat	43
4.10 Comparison of Thermoelectric Powers	44
4.11 Summary	44
4.12 References	44

x CONTENTS

5. Factors Affecting the Fermi Level	45
5.1 Effect of Temperature	45
5.2 Effects of Alloying Elements in Solution in Noble Metals	45
5.3 Effects of Alloying Elements in Solution in Transition Metals	47
5.3.1 Dilute Solutions	47
5.3.2 Concentrated Solutions of Noble Metals in Transition Elements	49
5.4 Effects of Stress or Working	50
5.5 Summary	51
5.6 References	51
6. Thermoelectric Behavior of Alloys	51
6.1 Alloys of Noble Metals	52
6.2 Alloys of Multivalent Metals	53
6.3 Alloys of Transition Elements	55
6.3.1 Solute Atoms with Completed Inner Electron Shells	55
6.3.2 Transition Metal Solutes	55
6.4 Summary	57
6.5 References	57
7. Low Alloy Thermoelements in Common Use	57
7.1 Platinum and Platinum Alloys	58
7.1.1 Platinum-Rhodium Alloys	59
7.2 Nickel and Nickel Alloys	59
7.2.1 Alumel-type Alloys	62
7.2.2 Chromel-type Alloys	63
7.3 Thermocouple Iron	64
7.4 Summary	65
7.5 References	65
8. High Alloy Thermoelements	65
8.1 Theory of Concentrated Solid Solutions	66
8.1.1 Effects of Ternary Elements in Concentrated Solid Solutions	68
8.1.2 Effect of Temperature upon $(E_0 - E_F)$	69
8.2 Thermoelectric Behavior of Concentrated Solid Solutions	69
8.3 ATP of Ternary Elements in Concentrated Solid Solutions	71
8.3.1 Scattering Parameter	74
8.4 Verification of the Temperature Dependence of $(E_0 - E_F)$	74
8.5 Design of Copper-Nickel Thermoelements	77
8.6 Summary	77
8.7 References	78
9. Some Other Applications of Thermoelectricity	79
9.1 Limits of Solid Solubility	79
9.2 Estimation of Imperfection Density	81
9.3 Summary	84
9.4 References	84

Electrical Properties. Electrical Properties. Thermocouples are commonly used in a wide range of applications. Due to their wide range of models and technical specifications, but it is extremely important to understand its basic structure, functionality, ranges as to better determine the right thermocouple type and material of thermocouple for an application. What are the elements of a common thermocouple design? The output of a thermocouple depends on the type of thermocouple it is. The normal thermocouple categories include Types J, K, T, E and N which are called "Base Metal" thermocouples, Types R, S and B which are called the "Noble Metal" thermocouples, and Types C and D which are called the "Refractory Metal" thermocouples.