COPPER IN IRON AND STEEL

Edited by Iain Le May and L. McDonald Schetky

COPPER IN IRON AND STEEL

Iain Le May

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FOREWORD

The beneficial effect of copper in improving the atmospheric corrosion resistance of steel was first exploited in the early 1930's. Today over 35 copper-containing "weathering steels" are manufactured by approximately 15 producers in the United States and Canada alone. If this were the only use of copper in iron and steel, it would be a most valuable alloying element. However, as this volume makes clear, copper has several important attributes including its use as a hardenability agent and for age hardening in structural, cast, and stainless steel, as a swelling agent during sintering in ferrous powder metallurgy, and as a graphitizing agent and for the refinement of pearlite in cast iron.

The present treatise is the first comprehensive updating in 35 years of information on copper in iron and steel. It differs from previous works on this subject in several respects: (1) the chapter on fundamental considerations goes beyond the fundamental considerations covered in the earlier volumes by discussing, in addition to phase equilibria, such subjects as hardenability and transformation kinetics, strengthening mechanisms, precipitation hardening and fatigue behavior of iron-copper alloys, (2) extensive information is included from recent work on a subject of great concern to users of copper in iron and steel, that of hot shortness, (3) in addition to reviewing earlier work, the latest work on each subject is thoroughly covered in the text and references, and (4) recognized experts have authored the individual chapters.

Drs. Le May and Schetky are to be congratulated for shepherding the assembly of such an authoritative and timely treatise on this important subject. The text will be found to be valuable to all steel and iron metallurgists who are finding increasing use of copper as a readily available and versatile alloying element.

H.W. Paxton
Vice President, Research
United States Steel Corporation

PREFACE

In the three decades leading us to the 80s we have seen an enormous change in the world's steel making capacity and an equally significant change in the manner in which the export and import trade in this most important commodity is carried out. From the development of new ore deposits ranging from the taconites to the enormous new deposits in Brazil and Australia, to the development of direct reduction processes, the technology of this industry is clearly in a dynamically changing state. With the extreme pressures on energy conservation from raw material to finished manufactured article, there is a constant search for organization of the performance of steel alloys, not just in terms of mechanical properties, but equally in terms of their life in service as defined by corrosion, creep, fatigue and stress rupture.

During the war years it was necessary to develop the lean alloys known as the National Emergency steels, and in this decade of increasing concern for the world supply of critically needed alloying elements a similar search for effective substitute alloys is underway.

Copper's use in steel has a long history, though in many ways a checkered one. Misconceptions abound as to its advantages and disadvantages, and it is the purpose of this book to bring into perspective the technical basis for exploiting copper in alloys where its benefits are real, and to more clearly define the areas where it is capable of causing problems in either steel making or steel fabrication.

The editors were extremely fortunate to obtain the services of the contributors who have prepared the various chapters. They represent an extraordinary range of experience, with an active role, past and present, in the development of many of the alloy systems described in these respective chapters. As the reader will see, the authors not only represent a broad cross section of the steel and iron industry, they also represent a large geographic spectrum.

To conserve space, chemical symbols have generally been used in the text to represent the metallic elements instead of writing these out in full, except at the beginning of a sentence. Similarly, abbreviations have been used for many organizations and these, together with other symbols utilized, are listed and identified in the Appendix.

Many people contribute to the preparation of a book such as this, but, in addition to the efforts of the contributors, we should like particularily to acknowledge the work of Mr. Alex Kozlow of ARK Enterprises Co. Ltd., who prepared all of the line drawings, and of the staff of the Printing Services

Department, University of Saskatchewan, who carried out the phototypesetting and page layout.

We wish to express our gratitude for support given to this work by the International Copper Research Association and the contributions of data, illustrations and information by the steel companies, foundries and technical associations of the United States, United Kingdom, Canada, Belgium and Japan.

Iain Le May
L. McDonald Schetky
1982

CONTENTS

List of Contributors .....
Foreword .....
Preface .....

1 INTRODUCTION - I. Le May and L.McD. Schetky 1

2 FUNDAMENTAL METALLURGICAL CONSIDUCTIONS - I. Le May and M.R. Krishnadev 5

2.1 Phase Equilibria 5
2.1.1 The Iron-Copper System 6
2.1.2 The Iron-Copper-Carbon System 9
2.1.3 Effect of Other Elements 9
2.2 Hardenability and Transformation Kinetics 14
2.2.1 Iron-Copper Alloys 17
2.2.2 Iron-Copper-Carbon Alloys 18
2.3 Strengthening Mechanisms 18
2.3.1 Solid Solution Strengthening 21
2.3.2 Precipitation Strengthening 21
2.4 Precipitation Hardening in the Iron-Copper System 23
2.4.1 Precipitate Morphology 23
2.4.2 Strengthening Mechanisms in Iron-Copper Alloys 23
2.4.3 Effect of Other Alloying Elements 26
2.4.4 Kinetics of Age Hardening 29
2.4.5 Effects of Cold Working on Precipitation 32
2.4.6 Effect of Plastic Deformation on Stability of Precipitates 33
2.4.7 Precipitation Strengthening at Low and Elevated Temperatures 34
2.5 Fatigue Behavior of Iron-Copper Alloys 37
2.5.1 Crack Growth Rate 38
2.5.2 Fatigue at Low Temperature 39
2.5.3 Effect of Other Variables on Fatigue Behavior 40
References 41

3 HOT SHORTNESS AND SCALING OF COPPER-CONTAINING STEELS - L. Habraken and J. Lecomte-Beckers 45

3.1 Definition 45
3.2 Copper in Iron and Steel 45
3.3 Scaling on Copper-Containing Steels 50
3.3.3 Scaling on Iron 50
3.3.2 Scaling on Copper-Containing Steel 50
3.3.3 Investigation of the Hot Shortness of Copper Containing Steels 57
3.3.4 Conclusion 72
3.4 Hot Working of Copper-Containing Steel 75
3.5 Improvements Relating to the Hot Shortness Phenomenon 76
3.5.1 Alloying Elements 79
3.5.2 Furnace Atmospheres 80
3.5.3 Conclusions 81
References 81

4 COPPER-CONTAINING STRUCTURAL STEELS - H. Okada, S. Sekino, Y. Hosoi and T. Murata 83

4.1 Problems in Production 83
4.2 Fundamentals 84
4.2.1 Tensile Properties and Toughness 84
4.2.2 Formability 86
4.2.3 Hardness 88
4.2.4 Hardenability and CCT Curves 89
4.2.5 Temper Embrittlement 89
4.2.6 Radiation Embrittlement 90
4.2.7 Other Mechanical Properties 94
4.3 Weldability 94
4.3.1 Hot Cracking 94
4.3.2 Cold Cracking 96
4.3.3 Toughness at the Fusion Line and Heat Affected Zone (HAZ) 96
4.3.4 Stress Relief Cracking 99
4.4 Structural Steels 100
4.4.1 Ultra-Low Carbon Steels 100
4.4.2 Low Carbon Steels 102
4.4.3 High Strength Structural Steels, Quenched and Tempered 105
4.4.4 Others 106
4.5 Corrosion Characteristics 111
4.5.1 Atmospheric Corrosion 111

4.5.2 Sea Water Corrosion 116
4.6 Copper in Pipeline Steels 117
4.6.1 Hydrogen Induced Cracking 117
4.6.2 Role of Copper in Pipeline Steels 119
References 128

5 ROLE OF COPPER IN WROUGHT STAINLESS STEELS - F.K. Bloom 135

5.1 History 135
5.2 Classification of Copper-Alloyed Grades 136
5.3 Phase Relationships and Microstructure 137
5.3.1 Solubility of Epsilon Phase 137
5.3.2 Plain Chromium, Low Nickel, Martensitic, Category A 139
5.3.3 Plain Chromium, Low Nickel, Ferritic, Category B 141
5.3.4 Chromium-Nickel, Borderline Austenitic-Martensitic, Precipitation Hardening, Category C 141
5.3.5 Chromium-Nickel, Austenitic-Ferritic, Sigma, Precipitation Hardening, Category D 142
5.3.6 Chromium-Nickel and Chromium-Nickel-Manganese, Stably Austenitic, Categories E & F 144
5.4 Physical Properties 145
5.5 Mechanical Properties 148
5.5.1 Plain Chromium, Low Nickel, Martensitic, Category A 148
5.5.2 Plain Chromium, Low Nickel, Ferritic, Category B 149
5.5.3 Chromium-Nickel, Borderline Austenitic-Martensitic, Precipitation Hardening, Category C 153
5.5.4 Chromium-Nickel, Austenitic-Ferritic, Sigma, Precipitation Hardening, Category D 158
5.5.5 Chromium-Nickel, Stable Austenitic, Category E 163
5.5.6 Austenitic Alloys with Copper Added for Low Cold Work Hardening 163
5.5.7 Austenitic Alloys with Copper Added for High Temperature Strength 166
5.5.8 Austenitic Alloys with Copper Added for Corrosion Resistance 167
5.5.9 Chromium-Nickel-Manganese, Stable Austenitic, Category F 167
5.6 Corrosion Resistance 170
5.6.1 Electrochemical Parameters 170
5.6.2 Resistance to General, Uniform Corrosion 173
5.6.3 Resistance to Pitting Type Attack 181
5.6.4 Resistance to Stress Corrosion Cracking 182

5.6.5 Corrosion by Oxidation and Scaling 187
5.7 Fabricating Properties 188
5.7.1 Melting 188
5.7.2 Hot Working 190
5.7.3 Cold Forming and Machining 191
5.7.4 Welding 193
5.8 Typical Applications 196
References 198

6 COPPER IN THE POWDER METALLURGY OF IRON AND STEELS - P.W. Taubenblat, A. Stosuy and M. Ohring 201

6.1 Introduction 201
6.2 The Iron-Copper System 202
6.2.1 Composition 202
6.2.2 Microstructure 203
6.2.3 Mechanical Properties 203
6.3 The Iron-Copper-Carbon System 209
6.3.1 Compositions 209
6.3.2 Microstructures 209
6.3.3 Mechanical Properties 212
6.4 The Iron-Copper-Nickel System 217
6.5 The Iron-Copper-Tin System 223
6.6 Machinability of Sintered Iron-Copper Alloys 225
6.7 Dimensional Changes During Sintering 226
6.7.1 Mechanisms of Shrinkage and Growth 228
6.7.2 Effect of Alloy Additions 232
6.7.3 Practical Control of Cu Growth 232
6.8 Infiltration of Iron Compacts 236
6.8.1 Infiltrant Properties 238
6.8.2 Properties of Infiltrated Compacts 240
6.9 Bearings 244
6.10 Applications 249
References 255

7 APPLICATIONS — L.McD. Schetky 259

7.1 Architectural and Structural Uses 259
7.2 Chemical Industry Applications 262
7.3 Transportation Applications 263
7.4 Applications in Energy-Related Industry 266
7.5 Applications of Copper-Containing Stainless Steel 267
7.6 Concluding Remarks 269
References 277

8 CAST COPPER-CONTAINING STEELS

Section I: Cast Carbon and Low Alloy Steels - W.K. Bock 279

8.1 Functions of Copper in Cast Steels 279
8.2 Analysis 280
8.3 Heat Treatment 281
8.4 Hardenability 282
8.5 Tensile Properties 284
8.6 Impact Properties 285
8.7 Weldability 286
8.8 Corrosion Resistance 287
8.9 Uses 288

Section II - Cast Stainless Steels - E.A. Schoefer 291

8.10 Description of Alloy Types 291
8.11 Mechanical Properties 295
8.12 Physical Properties 295
8.13 Design and Processing Considerations 297
8.14 Typical Applications 299
References 301

9 COPPER IN GRAY AND WHITE CAST IRONS - Josef A. Dilewijns 303

9.1 Copper in Gray Cast Irons 303
9.1.1 The Structure of Gray Cast Iron 303
9.1.2 Effects of Copper on the Structure 304
9.1.3 Effects of Copper on the Properties of Gray Cast Iron 308
9.2 Copper in White Cast Irons 322
9.2.1 White Cast Irons with a Pearlitic Matrix 322
9.2.2 White Cast Iron with a Martensitic Matrix 323
References 326

10 COPPER IN MALLEABLE AND DUCTILE CAST IRONS - John F. Wallace 329

10.1 Blackheart Malleable Iron 329
10.1.1 General Properties and Processing 329
10.1.2 Effect of Copper on Solidification and Annealing 331
10.1.3 Effect of Copper on the Mechanical Properties of Ferritic Blackheart Irons 332
10.1.4 Effect of Copper on Properties of Pearlitic Blackheart Malleable Iron 339

10.2 Other Types of Malleable Iron 340
10.2.1 Chill Cast 340
10.2.2 Alloy Irons 340
10.2.3 Whiteheart Malleable Iron 341
10.3 Spheroidal Graphite, Modular or Ductile Iron 342
10.3.1 General Properties and Processing 342
10.3.2 Effect of Copper on Spheroidization 343
10.3.3 Effect of Copper on Tensile Strength 343
10.3.4 Effect of Copper on Other Properties 348
10.3.5 Annealing of Ductile Irons Containing Copper 349
10.3.6 Precipitation Hardening 350
References 350

11 COPPER IN HIGH ALLOY IRONS - George A. Timmons 353

11.1 Introduction 353
11.2 High Alloy Gray Cast Iron 353
11.3 High Alloy White Irons 356
References 366

12 APPLICATIONS OF COPPER-CONTAINING CAST IRONS AND CAST STEELS - K. Bromage 367

12.1 Cast Irons 367
12.1.1 Gray Cast Irons 368
12.1.2 White Cast Irons 376
12.1.3 Nodular Irons 378
12.2 Cast Steels 382
12.2.1 17% Cr, 4% Ni, (2% Mo), 4% Cu Steel 382
12.2.2 20% Cr, 29% Ni, 3% Mo, 4% Cu Steel 382
12.2.3 25% Cr, 5% Ni, 3% Mo, 3% Cu Steel 384
12.2.4 14% Cr, 5% Ni, 1% Mo, 2% Cu Steel 387
12.2.5 Manganese-Copper Steels 388
References 390

13 RECYCLING AND RESEARCH - L.McD. Shetky and I. Le May 391

13.1 Recycling 391
13.2 Topics for Further Research 397
References 399

Appendices 401
A Conversion Factors 403
B List of Abreviations 405

Author Index 407

Subject Index 415

3

HOT SHORTNESS AND SCALING OF COPPER-CONTAINING STEELS

L. Habraken and J. Lecomte-Beckers

3.1 DEFINITION

Volume 5 of the *Metals Handbook* [1] gives the following definition of hot shortness: "Brittleness in metal in the hot forging range". It is a phenomenon which appears during hot forging, particularly in some types of steel containing low melting point elements, and especially Cu. It occurs commonly at the surface of these steels because, during the reheating before, or during forming, the content of non-oxidizable elements such as Cu is increasing, which is the reason why the name "surface hot shortness" is sometimes used. It is influenced strongly by the presence in the Cu-containing steel of residual elements such as Sb, Sn, and As, which are more soluble in Cu than in Fe, and also by Ni which forms complete liquid and solid solutions with Cu.

For the foregoing reasons, we shall examine the solubility of Cu in different Fe and mild steel systems in the following section.

3.2 COPPER IN IRON AND STEEL

The solubility of Cu in Fe is quite limited as shown in the phase diagram given in Chapter 2, Fig. 2.4. However, it must be mentioned that different

solubilities of Cu in Fe have been obtained by different authors. This solubility has been difficult to appreciate sometimes, as may be seen with respect to some experiments with the field ion microscope which have shown that fine Cu particles are often present in Fe or steels.

The ternary Fe-Cu-C system does not accurately give equilibrium conditions because of the influence of elements that are always present in steel. Fortunately, the Fe-Cu phase diagram gives useful information concerning the solidification of Cu-containing steels and shows well the presence of the phases γ and ϵ, the latter being the solid Cu-rich phase. However a certain number of studies have been made in order to define the Fe-Cu-C diagram [2], and this system is characterized by an extensive liquid miscibility gap, caused by small additions of graphite to the Fe-Cu binary system. Fundamental considerations have been dealt with in Chapter 2, to which the reader is referred.

The 1250°C isotherms proposed by Salter [3, 4] for mild steel-Cu ternary systems with Sn, Ni, Sb, Mn, As and Cr, are given in Figs. 3.1 to 3.6, respectively. In the ternary diagrams with As, Sb and Sn, the γ + liquid or $\gamma + \delta$ + liquid zones are extended to the axis mild steel-Sn (or Sb, As) showing the possibility of having a liquid Cu-rich phase even with very low Cu content in the steel. For the other elements, Ni, Mn and Cr (and especially Ni at a temperature of 1250°C), a liquid phase occurs only with high values of Cu content.

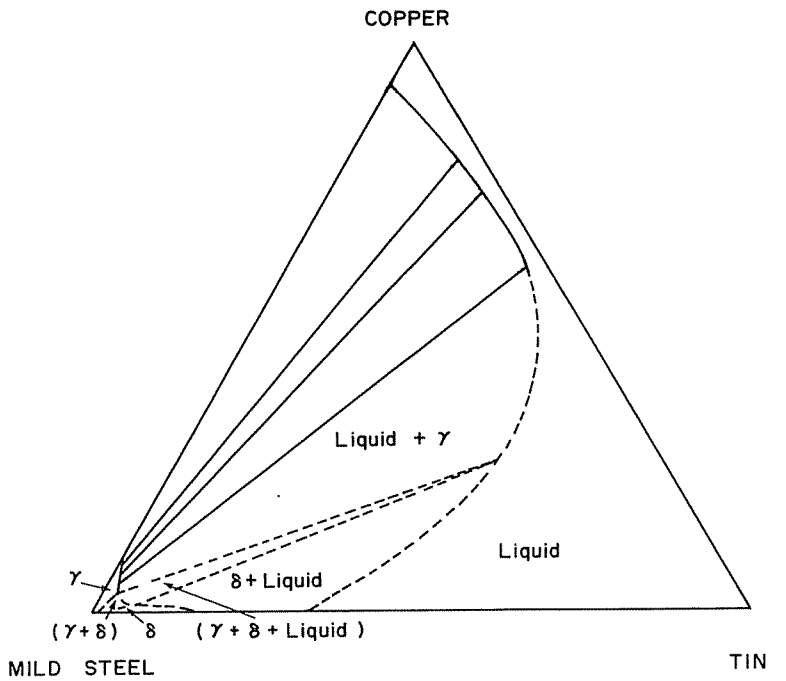


Fig. 3.1 Proposed 1250°C isotherm for the mild steel-Cu-Sn system [3].

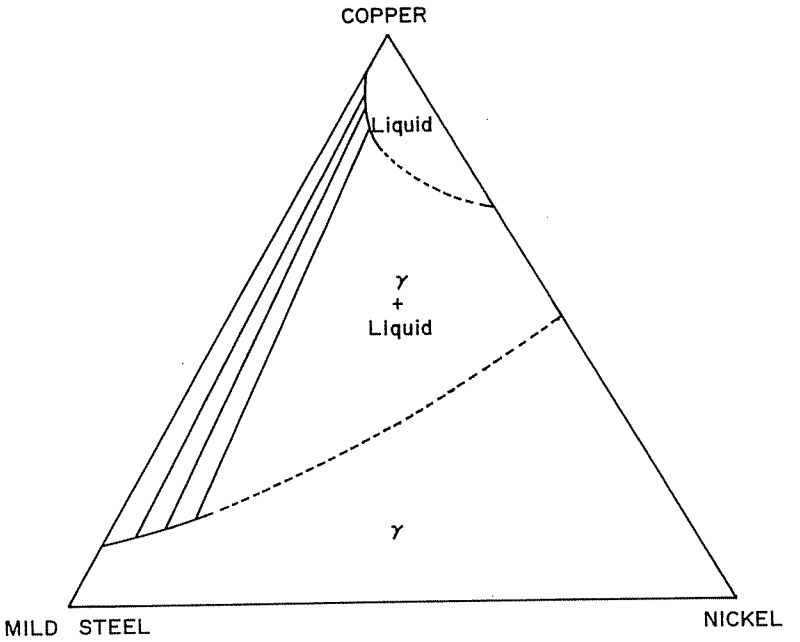


Fig. 3.2 Proposed 1250° C isotherm for the mild steel-Cu-Ni system [3].

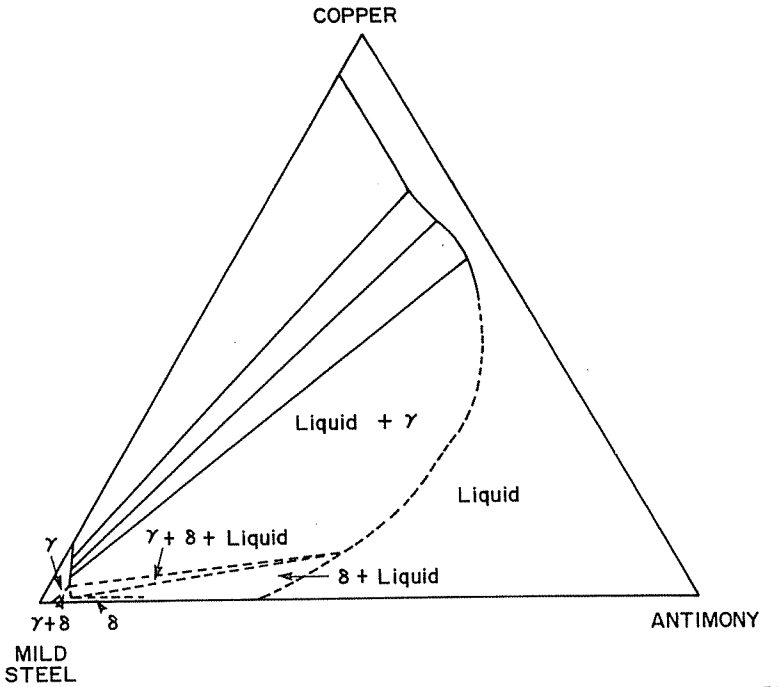


Fig. 3.3 Proposed 1250° C isotherm for the mild steel-Cu-Sb system [3].

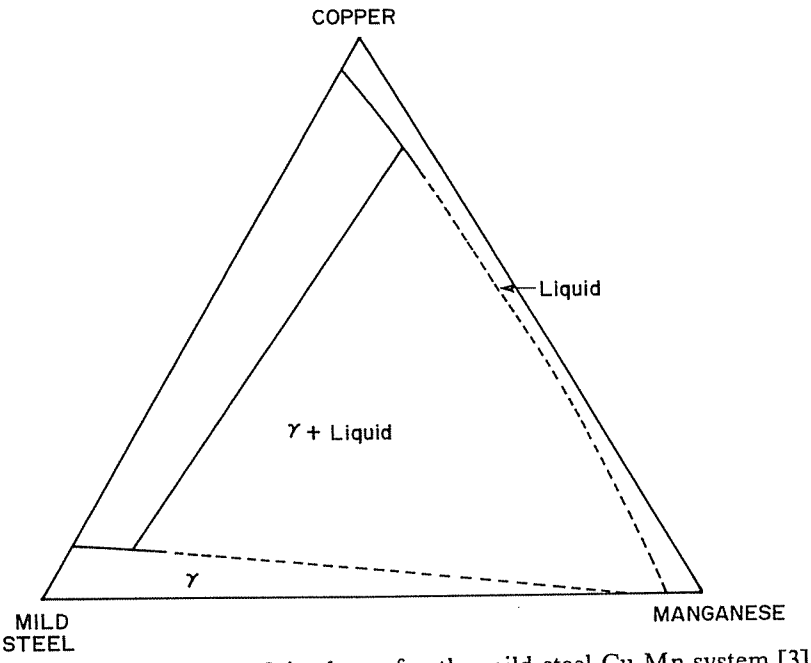


Fig. 3.4 Proposed 1250° C isotherm for the mild steel-Cu-Mn system [3].

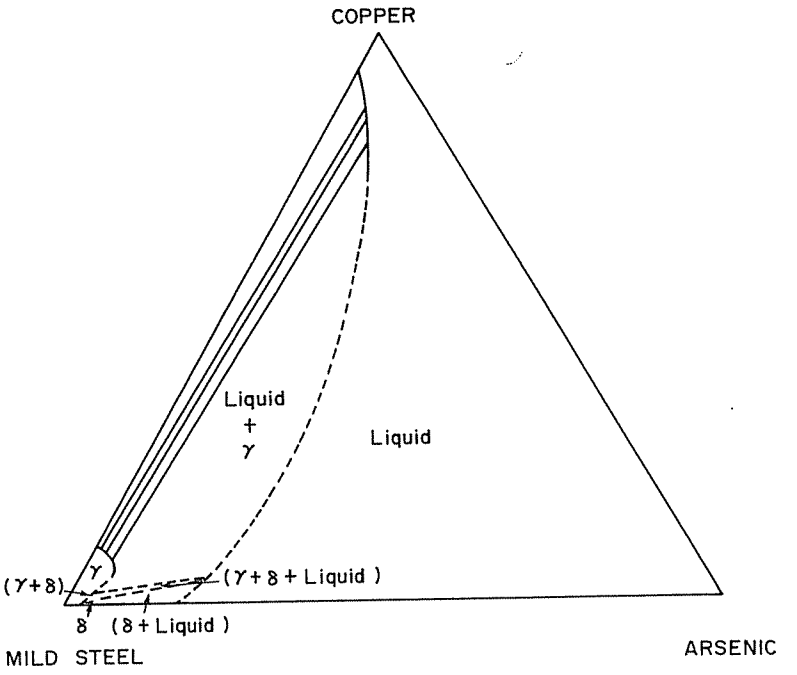


Fig. 3.5 Proposed 1250° C isotherm for the mild steel-Cu-As system [3].

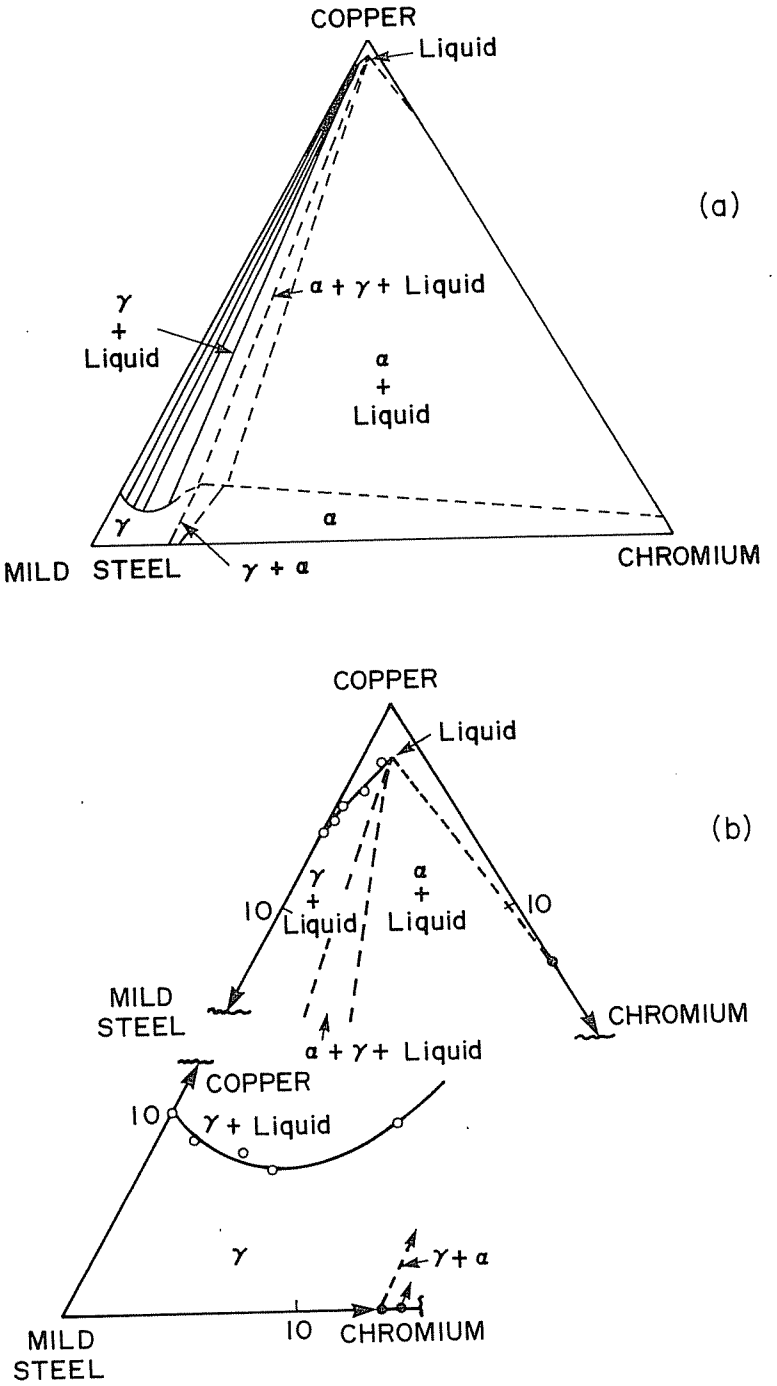


Fig. 3.6 Proposed 1250° C isotherm for the mild steel-Cu-Cr system [4]. *(a)* Complete isotherm; *(b)* enlarged corners.

3.3 SCALING ON COPPER-CONTAINING STEELS

The problem of hot shortness is not a new one, and it has been for a long time one of the more difficult problems encountered in steel production. In 1929, Pfeil [5] published a detailed study of hot oxidation and showed the deleterious influence of elements less prone to oxidation than Fe. At working temperature, the Fe oxidizes preferentially, leaving some alloying elements concentrated at the steel/oxide interface. When the melting point of the metallic phase is low, trouble may occur during hot working, Cu being the main detrimental element associated with the phenomenon.

3.3.1 Scaling on Iron

At temperatures higher than 400°C, the oxide scale is formed of three continuous and compact layers: namely hematite, Fe_2O_3; magnetite, Fe_3O_4; and wustite, FeO: the last mentioned is unstable below 570°C and theoretically will dissociate according to the reaction $4FeO \rightarrow Fe_3O_4 + Fe$. In the range 700-1250°C, the surface oxidation is due to the diffusion of the different ions. The relative thickness of the different layers is generally constant: Fe_2O_3, 1%; Fe_3O_4, 4%; and FeO, 95% of the total thickness of the scale.

3.3.2 Scaling on Copper-Containing Steel

A current steel oxidized at both 900°C and 1100°C produced outer scales similar to those formed on Fe: viz., a thin outer layer of Fe_2O_3 followed by a layer of Fe_3O_4, and a two-phase zone of FeO + Fe_3O_4, the Fe_3O_4 having precipitated during cooling because of the decreasing solubility of oxygen in FeO. The nobler elements remained unoxidized, as Pfeil predicted in 1929. In Cu-containing steel oxidized at 900°C, Cu was concentrated at the steel/oxide interface. During oxidation at higher temperatures large areas of relatively pure Cu were found, these being completely liquid at 1100°C.

Surface hot shortness in metals is caused by the penetration of liquid metal into cracks at the surface and along grain boundaries. Indeed, hot shortness depends strongly upon the products formed at the steel surface, and so may be adversely influenced by temperature, time, residual elements and atmosphere.

Influence of atmospheres

The atmosphere inside a reheating furnace is a complex mixture of continually varying composition, flowrate and pressure. To keep their investigation within reasonable limits, Nicholson and Murray [6] restricted it to a study of the effect of oxygen, water vapor and SO_2 contents. The specimens studied were transferred quickly from the scaling furnace and hot bent. To assess the severity of cracking the scale crack dimensions were compared with standard crack dimensions used by Born in similar work [7] (see Table 3.1).

(a) Effect of oxygen

Figure 3.7 shows typical results for a rimming steel. At low temperature hot shortness increases with oxygen content. At high temperature there is a peak

Table 3.1
Crack Dimensions (mm)

Code No.	0	1	2	3	4	4+
Depth	<0.23	0.23-0.36	0.36-0.51	0.51-0.76	>0.76	1.52
Width	<0.25	0.25-0.51	0.51-0.76	0.76-1.02	>1.02	1.78

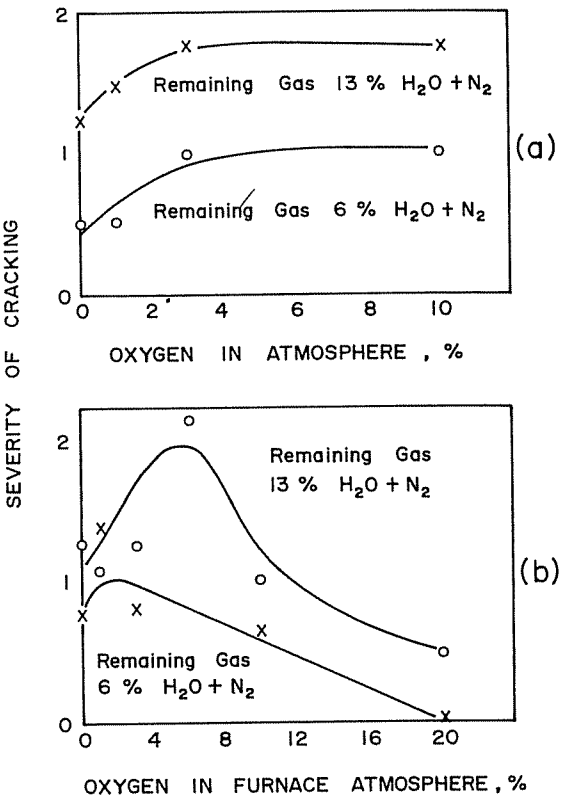


Fig. 3.7 Effect of furnace oxygen and water vapor on hot shortness in a 0.16 wt.% Cu-containing steel [6]. *(a)* Oxidized 1 h at 1000° C; *(b)* oxidized 1 h at 1250° C.

at an intermediate oxygen content.

(b) Effect of water vapor

As shown in Fig. 3.7, a high water vapor content is detrimental.

(c) Effect of sulfur dioxide

Sulfur dioxide was found to reduce hot shortness appreciably provided the oxygen content was low. Typical results are shown in Fig. 3.8 for a silicon

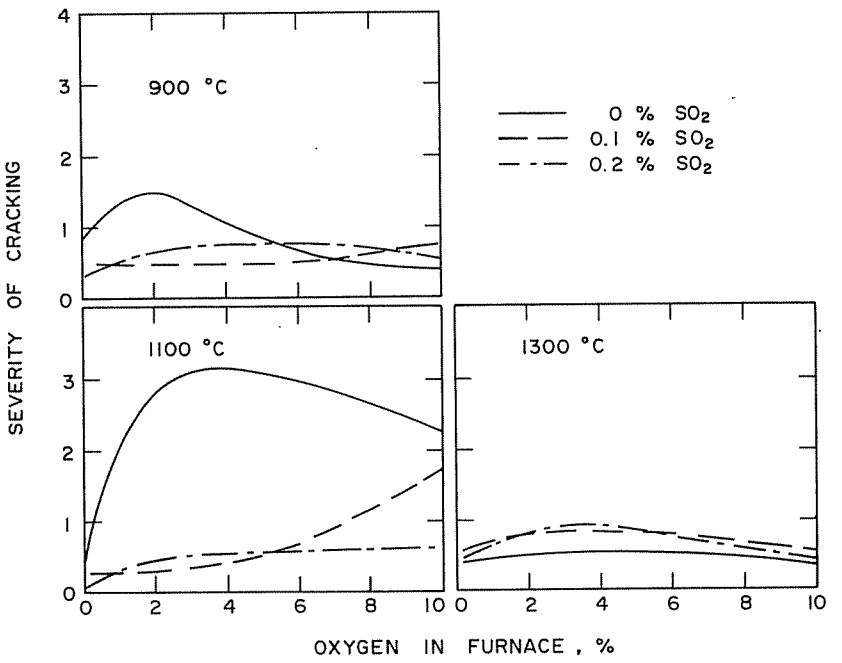


Fig. 3.8 Influence of furnace SO_2 content on surface hot shortness of Si-killed steel [6].

killed steel. Nicholson and Murray [6] obtained similar results for rimming steel, except that the beneficial effect of sulfur persisted up to 1300°C. Rolls and Preece [8] also showed that a Cu-containing steel treated in a neutral atmosphere containing SO_2 has a negligible tendency towards cracking.

Considering scale formation as a diffusion-controlled process, it would be expected that the scale formed and the metal/oxide interface would govern the process, in some measure. The importance of the furnace atmosphere lies in its influence on such physical and chemical properties of the scale as porosity, thickness, adherence, oxygen/sulfur potential and concentration of residuals.

The most significant feature of the influence of furnace atmosphere on cracking tendency appears to be the effect of sulfur. The affinity of sulfur for Cu is greater than for Fe in the range 600-1300°C. The sulfur reacts with the Cu at the metal surface to form copper sulfide, which is distributed into the scale. Analysis of the scales formed during oxidation shows that the amount of Cu occluded into the scale generally increases with increase in oxygen content. The effect of adding SO_2 is to increase Cu occlusion while, for a given oxidation rate, water vapor reduces this dispersion of Cu into the scale.

The effect of oxygen depends on the temperature. Indeed, at low temperature (~1100°C) hot shortness depends upon the balance between the rate of oxidation, causing enrichment in Cu, and the diffusion rate of Cu away

from the enriched region. Reduction of oxygen causes a reduction in oxidation rate and is generally accompanied by a reduction in hot shortness at this lower temperature.

However, at high temperature, the effect of increasing the oxygen content is to reduce hot shortness, usually after an initial increase. Depending on the temperature range, the major phenomenon is different; at low temperature (~1100°C), the number of occlusions is reduced and hot shortness depends only on the scaling rate, whereas at high temperatures (1250-1300°C) the process of Cu occlusion into the scale becomes increasingly important and hot shortness depends more on the proportion of Cu occluded.

Influence of additional elements

Salter [3, 4] examined the solubility of Cu in austenite and the surface energy properties of the Cu-rich phase in terms of the dihedral angle between austenite grains. He showed how these parameters are affected by the ternary additions of Sn, Ni, Sb, Mn, As and Cr, and measured the dihedral angle of the Cu-rich phase at the austenite grain boundaries to assess the effect of temperature on grain boundary penetration. Penetration was found to be inversely proportional to the dihedral angle.

The results of the dihedral angle measurements for a Cu-containing mild steel are shown in Fig. 3.9. They display a distinct minimum at about 1100°C. This means that the austenite will be most readily wet by the Cu-rich phase at about this temperature, causing maximum grain boundary penetration. Thus hot shortness will be a maximum at around 1100°C.

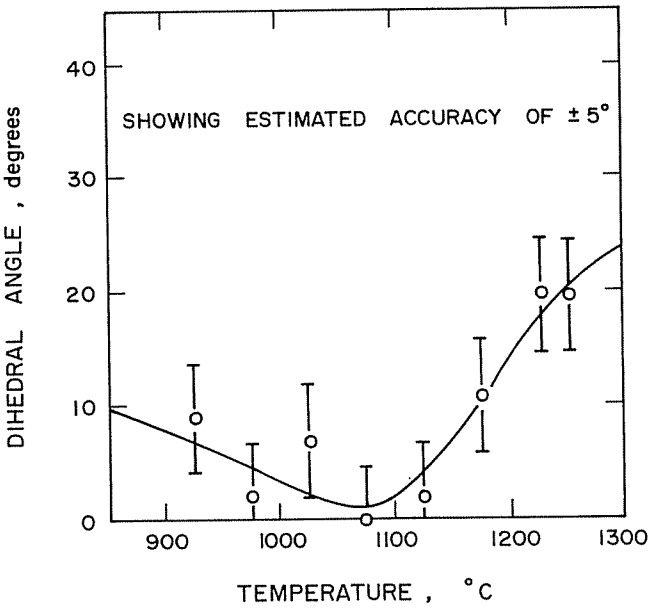


Fig. 3.9 Dihedral angle as a function of temperature for the mild steel-Cu system [3].

Mild steel-copper tin-alloys

Tin has been known for some time to be detrimental to hot shortness. The effect of Sn upon the dihedral angle as a function of temperature is shown in Fig. 3.10. Salter [3] showed that Sn is to some extent beneficial in decreasing wettability but the effect is not sufficient, particularly at 1050 to 1100°C where the minimum dihedral angle and, consequently, the maximum penetration are found; therefore, the maximum hot shortness will be observed at these temperatures.

Generally the solubility of Sn in austenite is low, and increasing Sn content results in an increase in the undissolved Cu-rich phase.

Mild steel-copper-nickel-alloys

Many investigations have shown that Ni can offset the detrimental effects of Cu. Salter [3] showed that Ni additions at all temperatures decrease the dihedral angle, this value reaching zero at and below 1100°C (see Fig. 3.11). At lower temperature, the Cu-rich phase is probably solid and thus grain boundary migration of the Cu atoms will decrease. At higher temperatures, however, there will be an increased susceptibility to grain boundary penetration even when Ni is present.

The solubility of Ni in austenite is high (almost equivalent to the Ni in the

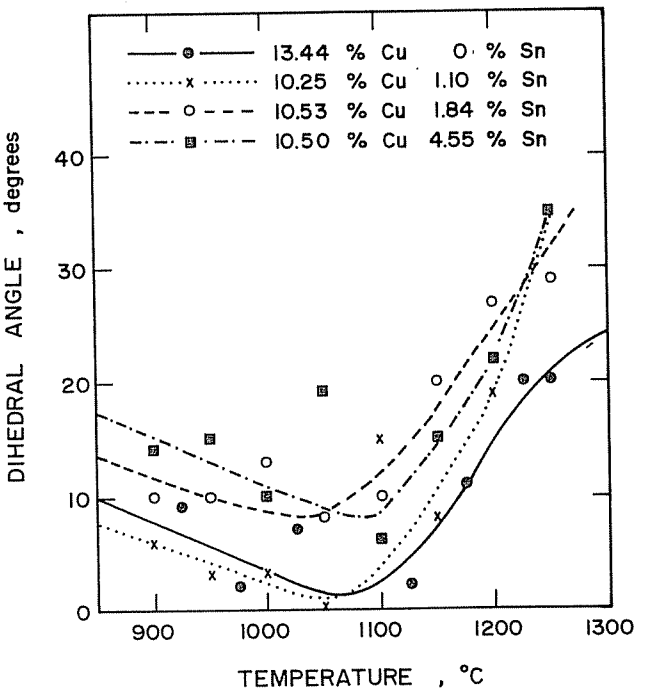


Fig. 3.10 Dihedral angle as a function of temperature for the mild steel-Cu-Sn system [3].

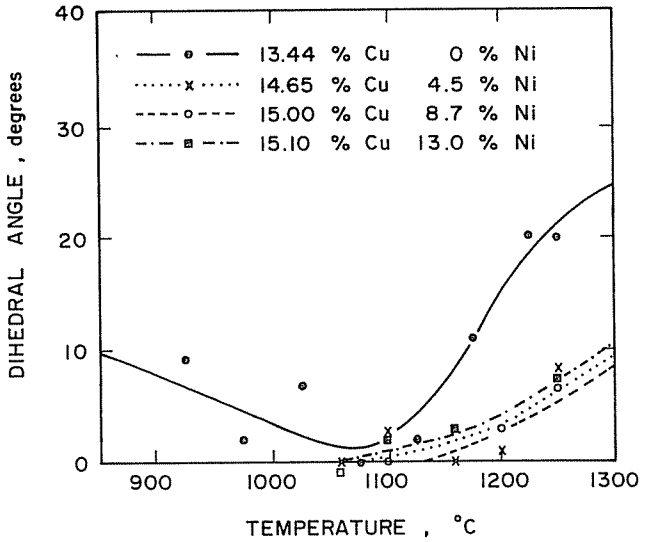


Fig. 3.11 Dihedral angle as a function of temperature for the mild steel-Cu-Ni system [3].

steel itself), while its solubility in the Cu-rich phase is relatively small (with a minimum at about 1100°C). An increasing Ni content in the alloy tends to cause an increase in both the Fe and Ni content of the Cu-rich phase.

Mild steel-copper-antimony alloys

It is to be expected that the effect of Sb will be similar to that of Sn. Its effect upon the temperature dependence of the dihedral angle was studied also by Salter [3] (see Fig. 3.12), and it may be seen that Sb causes an appreciable increase in the dihedral angle, particularly in the critical range 1050 to 1150°C.

Antimony has a more marked effect than Sn in reducing the solubility of Cu in austenite. Thus, the good effect on grain boundary penetration (which decreases with increasing Sb content) is prevented, and overall hot shortness increases with increasing Sb.

Mild steel copper-manganese-alloys

Manganese has little effect on hot shortness. The measurements of the dihedral angles reported by Salter [3] are shown in Fig. 3.13 and the effects of Mn are seen to be negligible in the critical range 1050-1150°C.

Manganese causes small reduction in the solubility of Cu in austenite. It is noticeable that it has a greater affinity for the Cu-rich phase than for austenite. It also lowers the melting point of the Cu-rich phase (when the Mn content is high).

Mild steel-copper-arsenic-alloys

Arsenic is detrimental for hot shortness but the effect is not so severe as with Sn or Sb. The form of the curves (dihedral angle as a function of temperature)

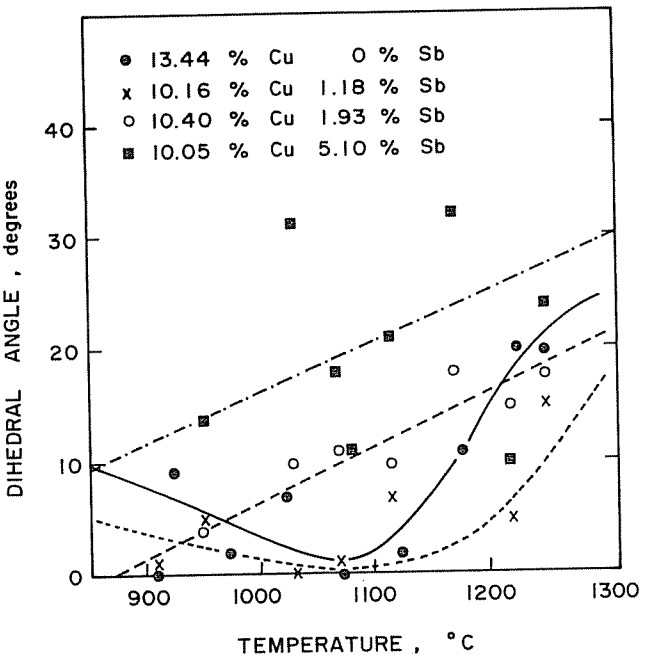


Fig. 3.12 Dihedral angle as a function of temperature for the mild steel-Cu-Sb system [3].

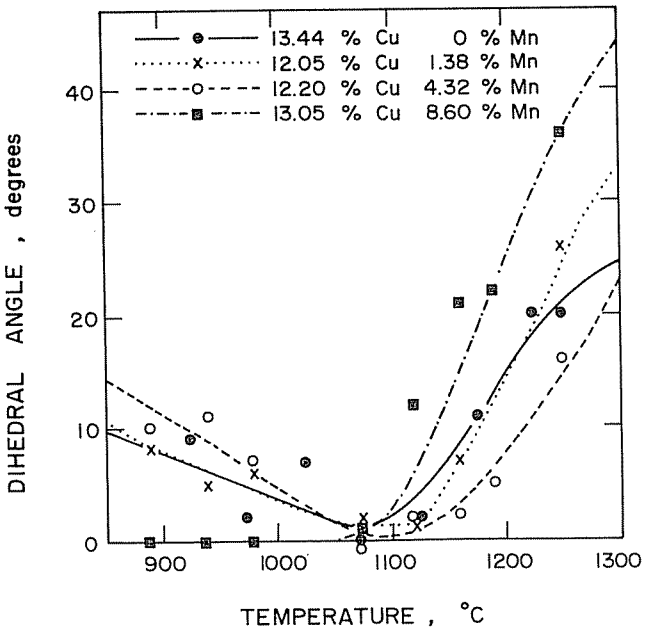


Fig. 3.13 Dihedral angle as a function of temperature for the mild steel-Cu-Mn system [3].

for the alloys containing 1% As is different because, as shown by Salter [3] (see Fig. 3.14), a maximum is produced at about 1100° C rather than a minimum. This indicates that the austenite will be less readily wet by the Cu-rich phase.

In general, As reduces the solubility of Cu in austenite. Arsenic lowers the melting point of the Cu-rich phase.

Mild steel-copper-chromium alloys

The effect of Cr on hot shortness is small. As found in the other systems examined, Salter [4] showed that there was a decrease in the value of dihedral angle with increasing temperature up to about 1100-1200° C, above which the dihedral angle increased (see Fig. 3.15). In the range 1075-1175° C there is a minimum dihedral angle and a maximum grain boundary penetration resulting in a maximum in hot shortness.

The solubility of Cr in the Cu-rich phase is low, and Cr decreases the solubility of Cu in austenite to a small extent.

3.3.3 Investigation of the Hot Shortness of Copper-Containing Steels

From time to time, with advances in analytical techniques, new conclusions concerning the problem of hot shortness may be drawn from the literature.

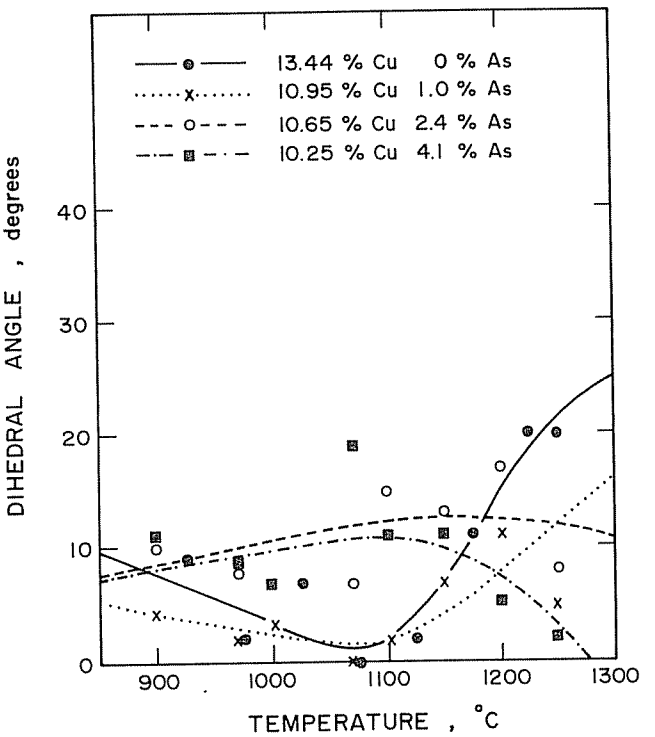


Fig. 3.14 Dihedral angle as a function of temperature for the mild steel-Cu-As system [3].

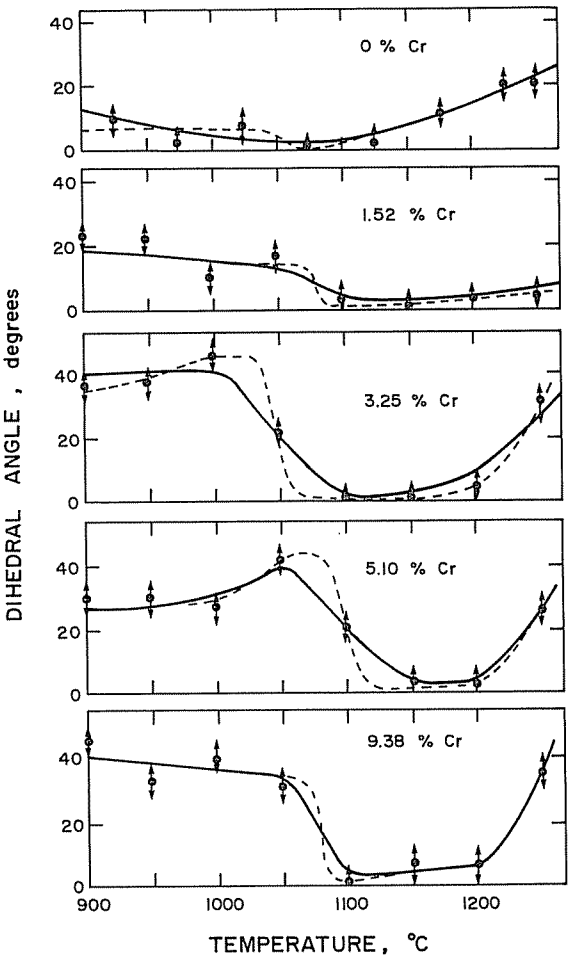


Fig. 3.15 Dihedral angle as a function of temperature for the mild steel-Cu-Cr system [4].

Generally, however, the literature deals with difficulties encountered in one or another application. Most of these have been solved and it can be concluded that Cu, in an amount not exceeding 0.4 to 0.5% by weight, may be added to constructional steels without difficulty. This was also pointed out in the study carried out by the Southern Research Institute [9]. In its report, however,the Institute has shown the great potential interest in any process allowing the prevention of hot shortness in steels containing from 0.5% to 1.5% Cu. The Centre de Recherches Métallurgiques (CRM) has investigated this matter, and examined the influence of additions of different elements to a Cu-containing steel [10], as reviewed in the following sections.

Experimental techniques

Oxidation tests were performed on the different types of alloys and steels

listed at Tables 3.2, 3.3, and 3.4. These tests were performed in an air atmosphere, generally under the following conditions: (a) 24 hours at 900° C; (b) 4 hours at 1100° C; (c) 2 hours at 1200° C. The time at temperature was chosen to provide the same weight gain at the three temperatures.

The specimens were examined metallographically in order to detect the presence of different phases and by electron microprobe to identify the compositions of these phases. Other tests, such as hot rolling and bend tests,

Table 3.2
Composition of Experimental Alloys

Alloy		Chemical Analysis, wt. %			
		C	Cu	Ni	Other
A1	Cu	0.108	3.04	-	-
A2	Cu+Ni	0.142	2.78	3.06	-
B1	Cu-Al	0.137	2.58	-	Al : 3.50
B2	Cu-Al + Ni	0.140	2.84	2.15	Al : 2.09
C1	Cu-Co	0.108	2.92	-	Co : 1.00
C2	Cu-Co + Ni	0.113	2.82	2.89	Co : 1.01
D1	Cu-Cr	0.117	3.01	-	Cr : 3.01
D2	Cu-Cr + Ni	0.122	2.93	2.89	Cr : 2.96
E1	Cu-Mn	0.150	2.68	-	Mn : 1.98
E2	Cu-Mn + Ni	0.117	2.80	2.68	Mn : 2.01
F1	Cu-Mo	0.162	2.04	-	Mo : 0.98
F2	Cu-Mo + Ni	0.148	1.80	2.10	Mo : 0.95
G1	Cu-Si	0.149	2.68	-	Si : 1.96
G2	Cu-Si + Ni	0.136	2.78	3.02	Si : 1.76
H1	Cu-P	0.116	2.92	-	P : 0.19
H2	Cu-P + Ni	0.116	2.85	3.12	P : 0.20
I1	Cu-Ti	0.174	1.95	-	Ti : 1.35
I2	Cu-Ti + Ni	0.166	1.80	1.35	Ti : 0.90

Table 3.3
Composition of High Purity Alloys

Alloy	Chemical Analysis, wt. %		
	C	Cu	Ni
HP 1	0.008	2.19	0.01
HP 2	0.006	2.37	3.35
HP 3	0.010	-	3.10
HP 4	0.010	-	1.10

Table 3.4
Analysis of Steels

Steel	Chemical Analysis, wt. %								
	C	Mn	Si	Al	Cu	Ni	As	Sn	P
S1	0.118	0.539	0.202	0.027	0.923	-	0.031	0.016	0.040
S2	0.149	0.755	0.325	0.009	1.080	1.070	0.029	0.013	0.040
S3	0.097	0.718	0.242	0.004	1.190	2.875	0.026	0.014	0.038
S4	0.127	0.758	0.304	0.004	2.970	0.050	0.031	0.021	0.039
S5	0.100	1.071	0.220	0.010	0.285	-	-	-	0.008
S6	0.087	1.196	0.270	0.032	0.420	0.450	-	-	0.008

were performed on the same alloys under particular conditions.

Figures 3.16 to 3.19 display the cracks which occurred during hot working of specimens by means of hot bending. No cracks could be detected when the temperature did not exceed 1000°C (Fig. 3.16). The degree of cracking depends on the composition of the steel, soaking time, soaking temperature and, obviously, the temperature during the bend test.

Influence of temperature and time

Temperature is one of the main parameters governing oxidation as shown in Fig. 3.20. As hot shortness depends upon the products formed at the steel

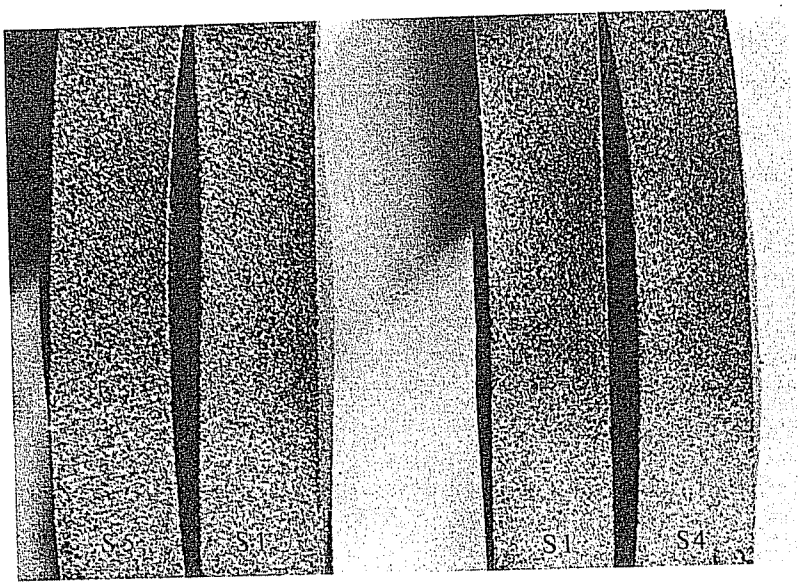


Fig. 3.16 Specimens of steels after hot bending. Test conditions 1000°C for 3 h [10].

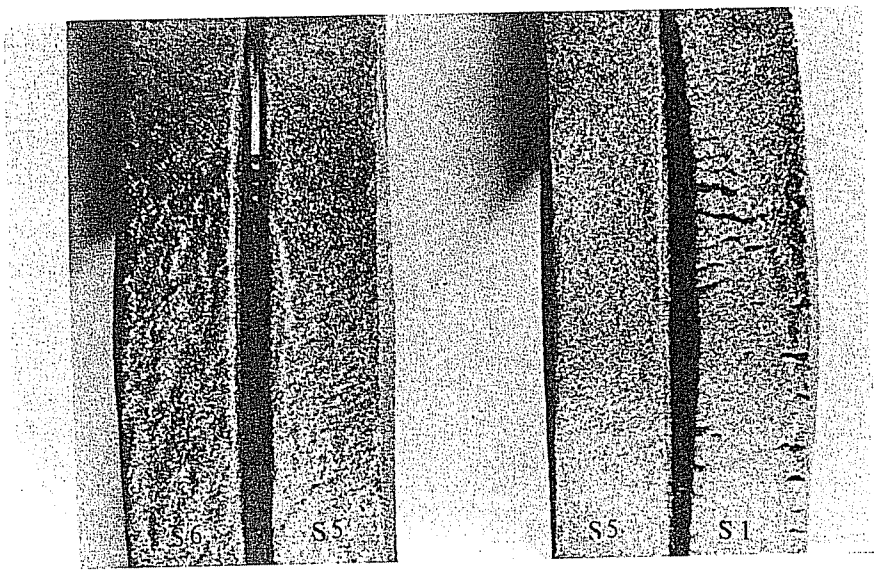


Fig. 3.17 Specimens of steels after hot bending. Test conditions 1200° C for 1 h [10].

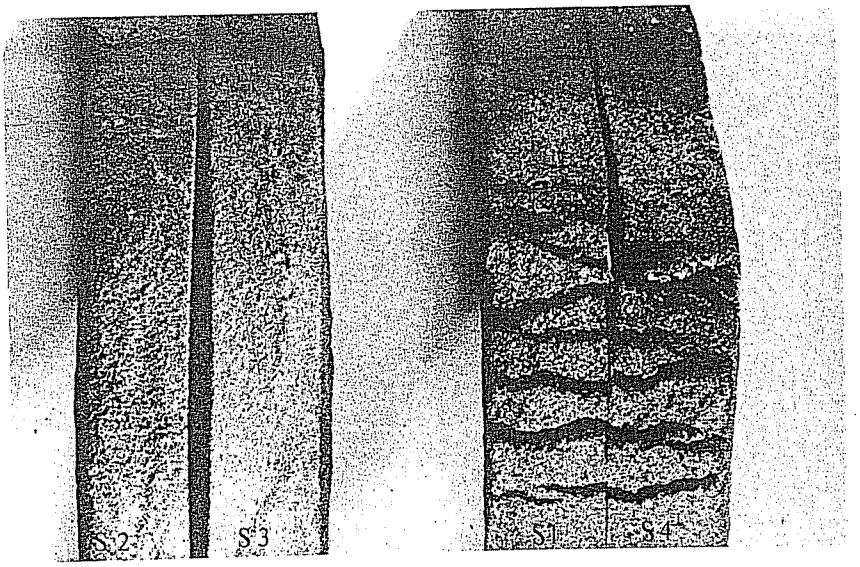


Fig. 3.18 Specimens of steels after hot bending. Test conditions 1200° C for 1 h [10].

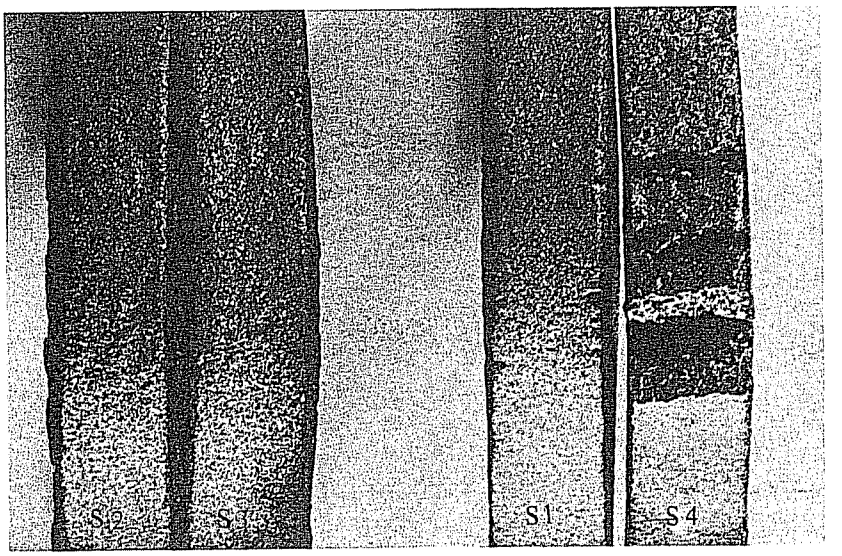


Fig. 3.19 Specimens of steels after hot bending. Test conditions 1200° C for 4 h [10].

surface, the range of temperature studied was restricted approximately to the range 900-1200° C (1100-1200° C is the approximate hot working temperature range and above the melting point of Cu, while 900° C is just below the austenitizing temperature and below the melting point of Cu).

In general, for most of the Cu-containing steels, the degree of cracking is more marked towards 1100-1150° C. The results of Nicholson and Murray [6] shown in Fig. 3.21 indicate a maximum in cracking (after oxidation and bending at different temperatures for some steels) obtained at 1100-1150° C.

Time is also of importance: severity of cracking increases with time but the rate of increase is shorter as the time is increased, the oxidation rate obeying a parabolic law.

Influence of addition elements

Enrichment of these elements and their precipitation with formation of a metallic phase in intermediate layers between the base metal and the oxide scale may be influenced by the alloying elements and principally by Cu. First, we must study the role of Cu in hot oxidation before investigating the influence of addition elements [9].

Behavior of copper-containing steels during hot oxidation

When the Cu content exceeds the solubility limit at room temperature, formation of numerous metallic precipitates is observed in the inner oxide scale (FeO). Their distribution in the ferritic matrix is uniform but their concentration is greater adjacent to the pearlite grains, as may be seen in Fig. 3.22.

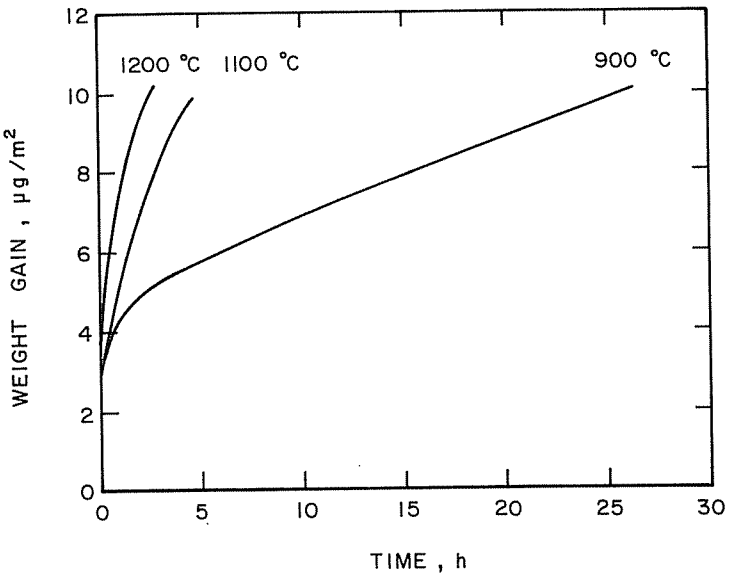


Fig. 3.20 Effect of temperature on oxidation of alloy A1 [10].

During oxidation at well defined temperatures (T), growth of the oxide scale leads to concentration of Cu atoms into a Cu-enriched phase along the metal/oxide interface. When $T < T_m$ ($\simeq$1083° C), where T_m is the melting point of the Cu-rich phase, the phase appears as a dispersion of metallic globules entrapped in an oxide layer along the interface (Fig. 3.23). When $T > T_m$, the liquid phase forms "lenses" in contact with the base metal (Fig. 3.24). The importance of these lenses depends on the composition of the alloy and on the oxidation time.

The liquid Cu-enriched phase penetrates along the austenite grain boundaries as shown in Figs. 3.25 and 3.26. The depth of penetration depends on the temperature and the composition of the Cu-enriched phase (the Cu content sometimes reaching 95%). Figure 3.26 shows also the segregation of the residual Ni in the liquid Cu-rich phase.

Behavior during hot oxidation of copper-containing steels containing other alloying elements

One can divide the alloying elements into two groups according to their affinity for oxygen:

1. Elements more oxidizable than Fe: Al, Mn, Mo, Si, P, Ti, Cr, Zr

Generally, as shown by the CRM experiments, elements of this class do not modify the general behavior of the Cu-rich phase: they usually occur as occlusions in the oxide scale or give rise to particular compounds. At low temperature (900° C) the effect on scale is not marked (the FeO zone often entraps some particles such as silicates and special spinels). Silicon additions,

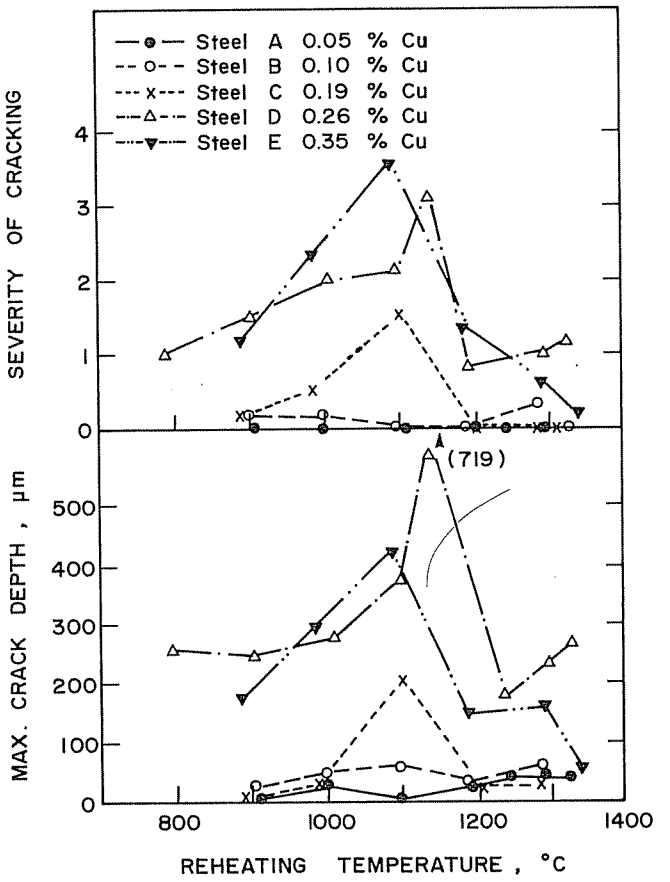


Fig. 3.21 Effect of Cu content on surface hot shortness [6].

however, seem to affect the oxidation process to some extent and give rise to a fine distribution of a metallic phase in the oxide scale (Figs. 3.27 *a* and *b*). In this case the Cu-enriched scale is dispersed in the inner layer, which reduces the oxidation rate and, in consequence, a smaller quantity of Cu is liberated. This suggests a convenient manner in which to reduce the presence of a metallic phase in the vicinity of the oxide scale/base metal interface.

Very often, especially for the most oxidizable elements such as Al, Si and Mn, the structure of the base metal near the interface is modified because of their affinity for oxygen and their more rapid diffusion towards the scale.

At high temperature (1100-1200° C) the results are as described above; however, now the metallic Cu-rich phase is a more or less continuous layer (Figs. 3.28 and 3.29). The situation is different when Si is present because at these high temperatures the inner oxide layer is viscous or perhaps liquid, and the oxidation rate increases rapidly. The beneficial effect of Si does not exist at high temperature. The same effect of depletion in highly oxidizable elements

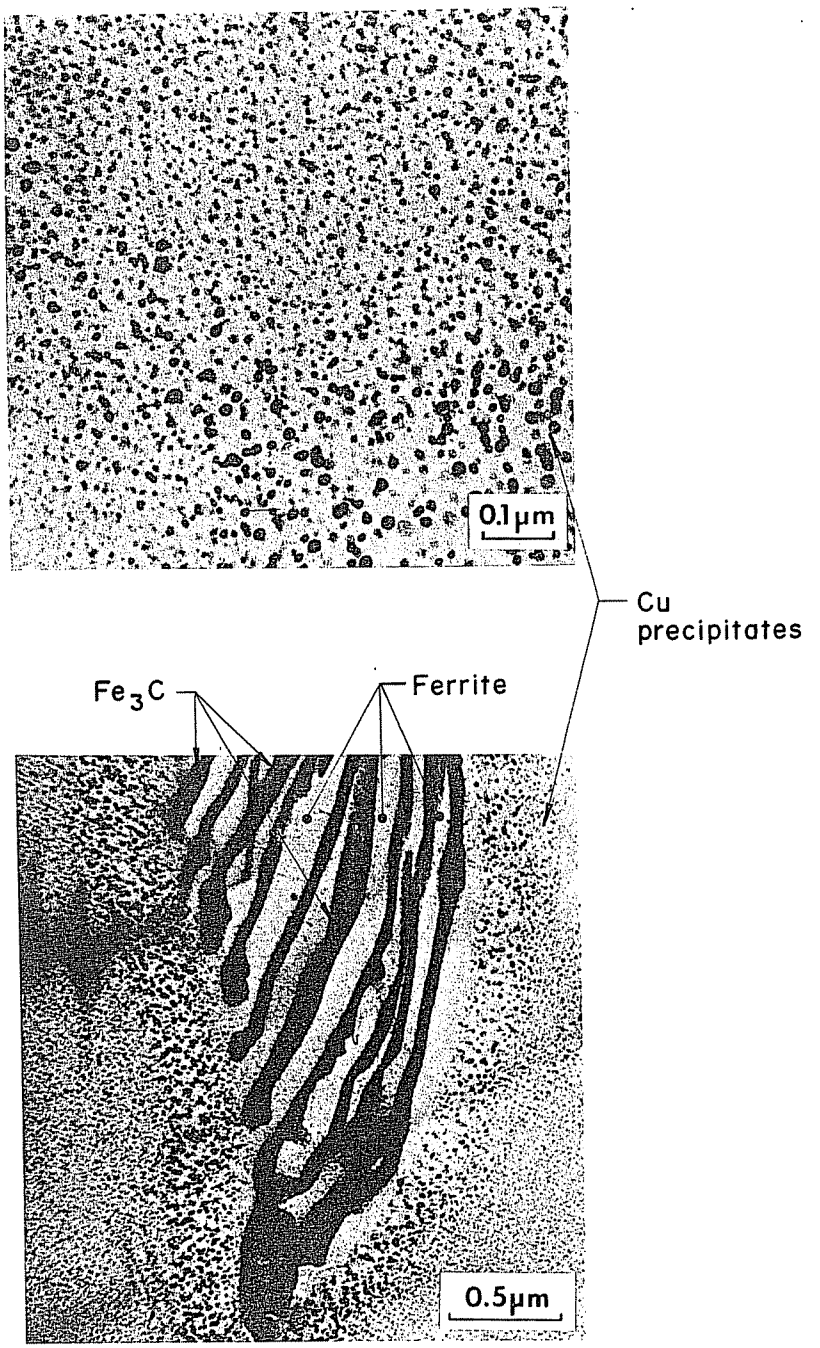


Fig. 3.22 Distribution of Cu precipitates showing greater concentration adjacent to pearlite in S4 steel after holding at 1100°C for 6 h [10].

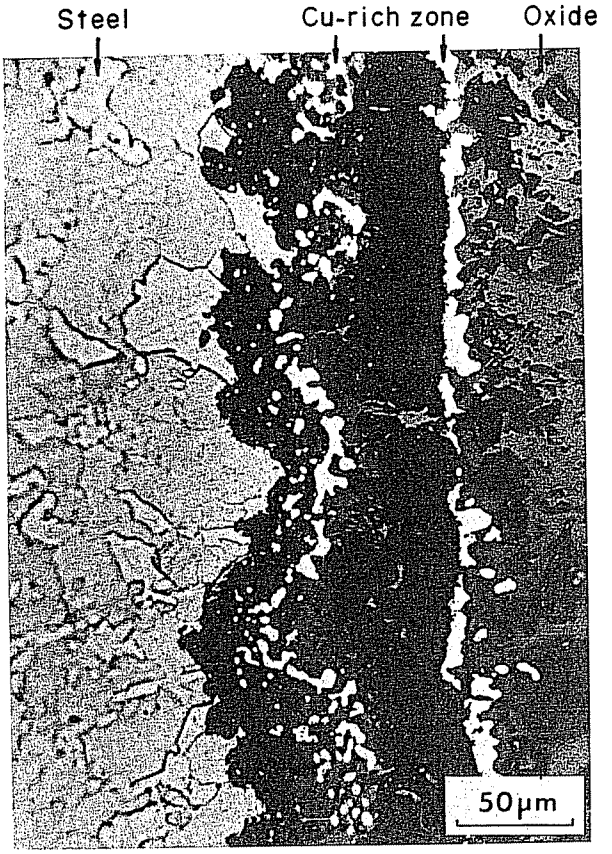


Fig. 3.23 Copper-enriched zone entrapped in oxide formed on alloy A1 held at 900° C for 24 h [10]. Etched in 2% nital.

as already mentioned at low temperature can be noted for Al- and Mn-containing alloys.

2. Elements less oxidizable than Fe: Co, Cu, Ni

At any temperature the behavior of Co is quite different. In fact, we obtain two metallic phases, the first being rich in Cu with a little Co, while near the metallic matrix a phase exists which becomes enriched in Co (an effect due to the low solubility of Co in Cu) (see Fig. 3.30).

The presence of Ni modifies the mechanism of oxidation and gives rise to *internal oxidation* (at all temperatures). This effect does not occur with Co and Cu. The austenite grain boundaries are oxidized, while at the scale/metal interface a two-phase zone composed of oxide and metallic globules (Fe + Ni + Cu) can be detected as shown in Fig. 3.31. The distribution of these elements varies with the oxidation temperature. In fact, the behavior of the Ni-containing steel oxidized at 1200° C (Fig. 3.31) is similar to that of a Ni-free

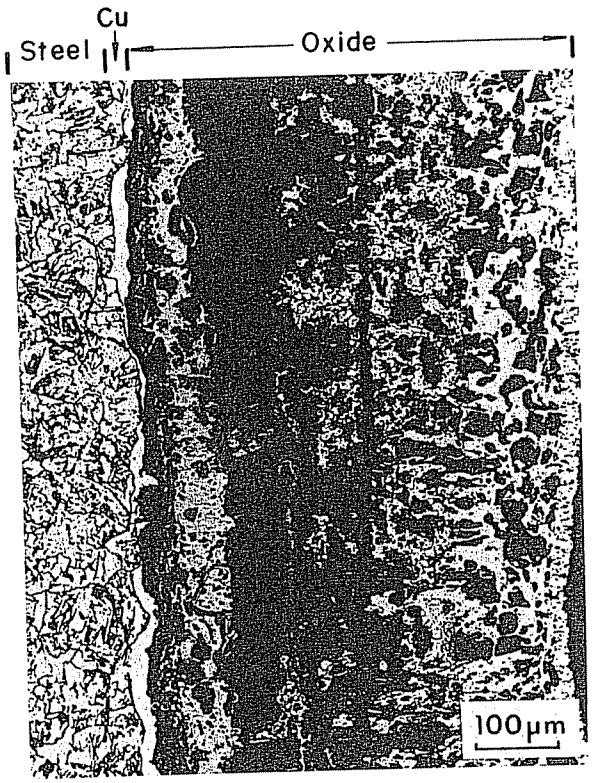


Fig. 3.24 Lenses of Cu at steel-oxide interface. Steel S4 held at 1100° C for 3 h [10].

steel oxidized at 900° C (Fig. 3.23). In both cases, the Cu-containing metallic phase is not molten and eventually becomes entrapped within the oxide scale, with a discontinuous distribution. This effect of internal oxidation remains predominant even if additional elements such as Co, Al or Cr are present.

According to the theory given by Benard [11], or the mechanism proposed by Bruckman [12], oxygen appears at the scale/metal interface by dissociation of complex $(Fe, Ni)_xO_y$ which liberates oxygen and gives a metallic Fe-Ni phase whose composition is roughly 60% Fe, 40% Ni. A second source of oxygen is by its penetration through the scale along cracks and porosity. Finally, the structure becomes as follows: in the base metal near the interface, oxidation of the grain boundaries; after that, a duplex zone of oxides and the metallic phase Fe-Ni; and, in contact with the atmosphere, the initial oxide layer relatively free of metallic particles and with some voids and porosity.

The solubility of Cu is higher when Ni is present in the alloy as has been verified by Salter [3]. One can estimate also that the metallic phase, which is

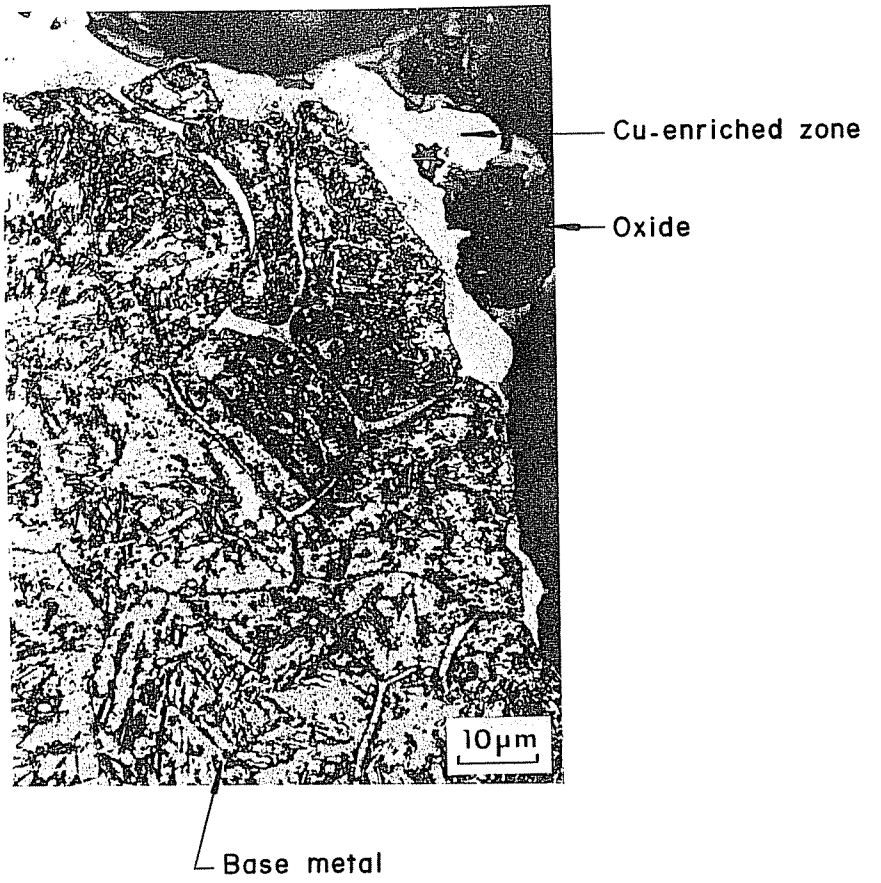


Fig. 3.25 Penetration of liquid Cu-enriched phase along austenite grain boundaries. Steel S4 held at 1100° C for 6 h [10].

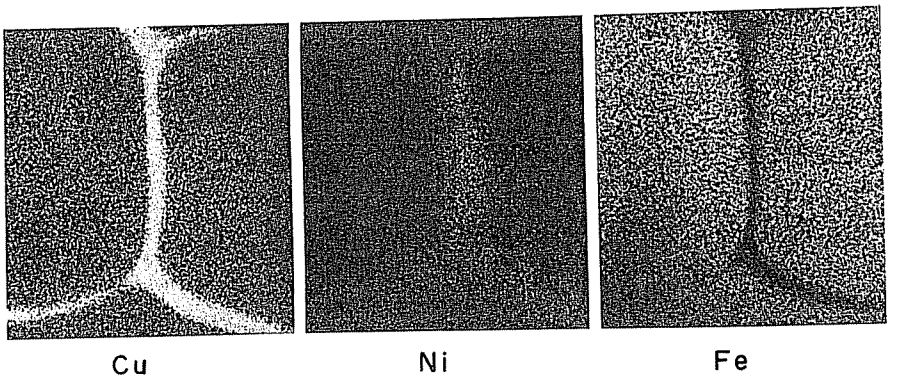
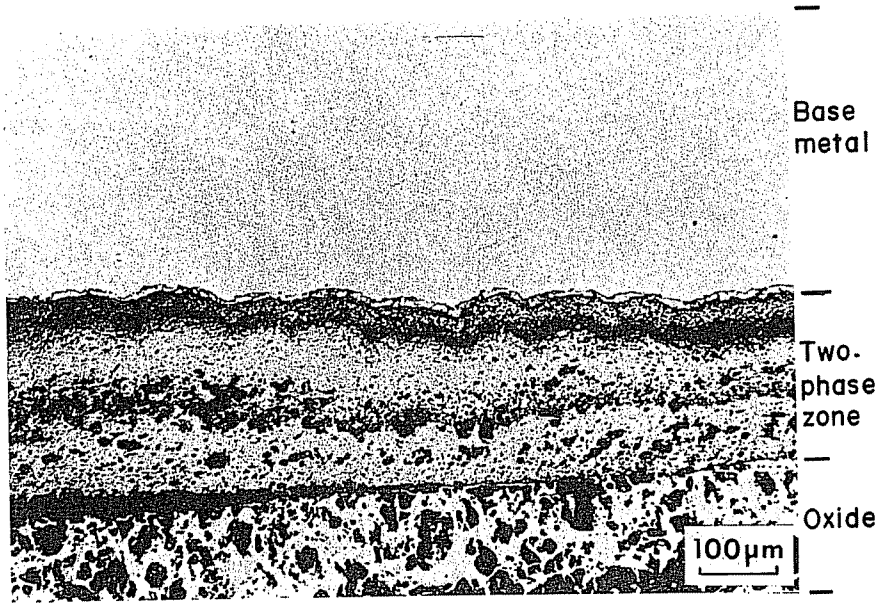
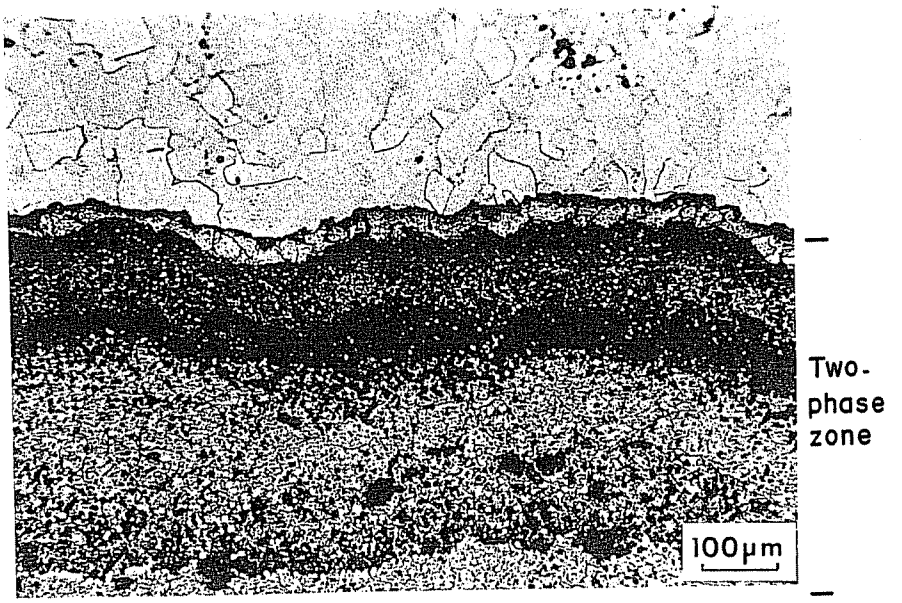


Fig. 3.26 Electron microprobe analysis of specimen shown in Fig. 3.25 showing x-ray images of Cu, Ni and Fe distribution around grain boundary penetration by Cu-rich phase [10].



(a)



(b)

Fig. 3.27 Alloy G1 (Cu-Si) after holding at 900° C for 24 h [10]. *(a)* Unetched; *(b)* etched in 2% nital.

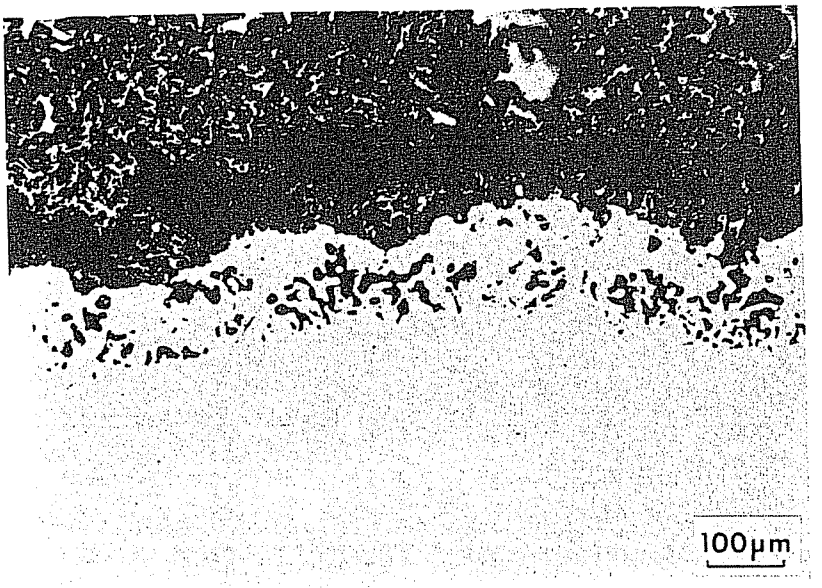


Fig. 3.28 Alloy E1 (Cu-Mn) after holding at 1200° C for 3 h. Unetched [10].

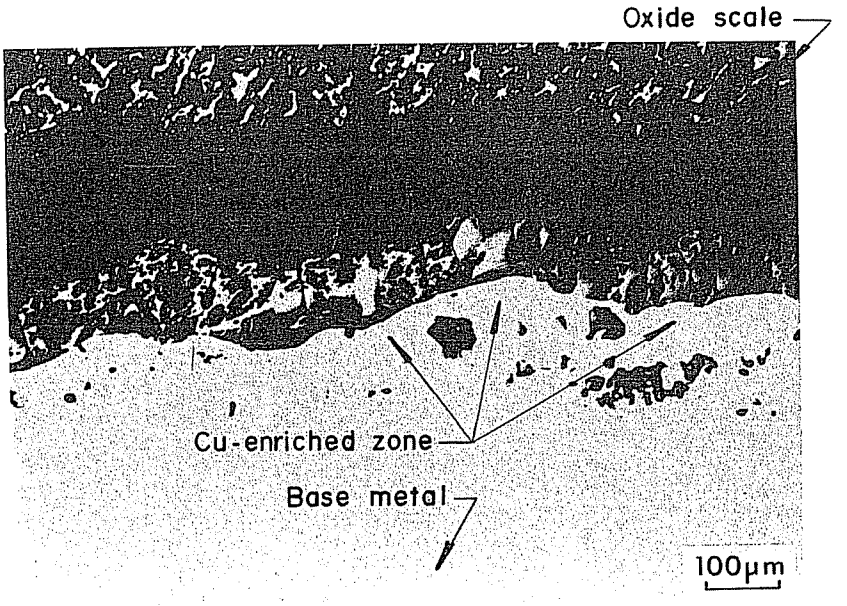
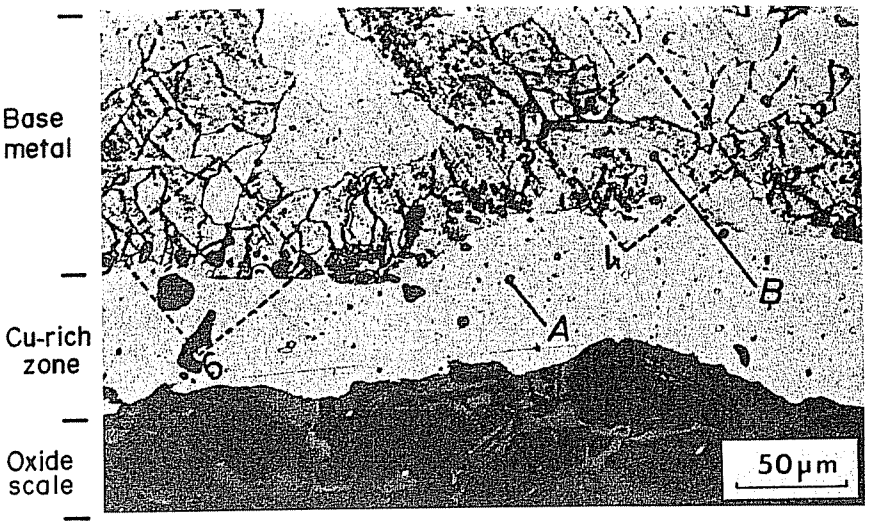


Fig. 3.29 Alloy H1 (Cu-P) after holding at 1200° C for 3 h. Unetched [10].



	Cu (%)	Co (%)	Fe (%)
A	95	1.2	3
B	11	14	75

Fig. 3.30 Alloy C1 (Cu-Co) after holding at 1200° C for 3 h [10].

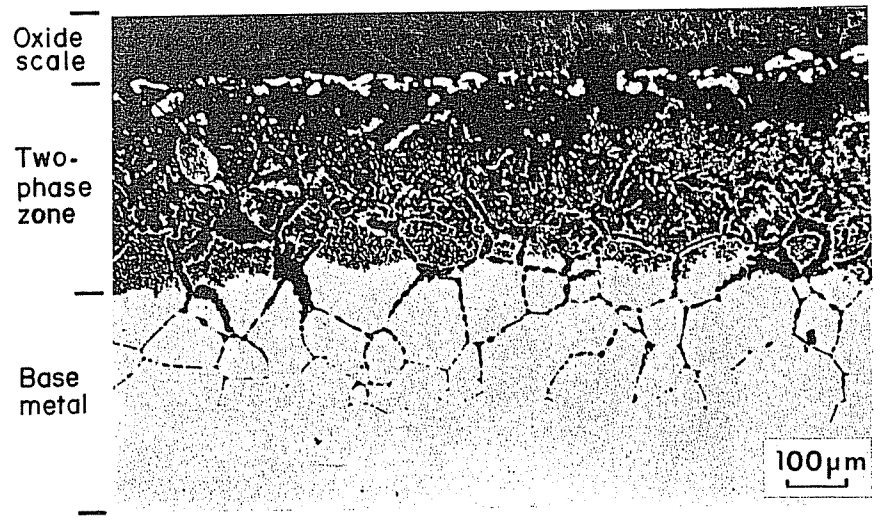


Fig. 3.31 Alloy A2 (Cu + Ni) after holding at 1200° C for 4 h [10].

enriched in Ni and Cu, in an amount of more or less 30% Cu, 30% Ni, has a melting point at least 200° C higher than in the Ni-free Cu alloy.

Figure 3.32 summarizes the two different processes of oxidation at high temperatures, for Cu-containing steel and steel containing Cu and Ni.

Behavior during hot oxidation of copper-nickel steels containing other alloying elements

Considering the quaternary alloys, for example a Ni-Co-Cu steel, we find again that there is internal oxidation of the grain boundaries after the first step of the oxidation. At 1100 to 1200° C, metallic globules appear in several parts of the oxide scale, their composition varying with position in the scale (see Fig. 3.33). The variation in Co may be explained by the small solubility of this element in the Cu-rich phase. For other quaternary elements, no special new effects have been found, internal oxidation again playing the major role.

Behavior during hot oxidation of complex copper-containing steels with silicon and manganese additions

Cox and Winn [13] studied the behavior of an RARDE* high tensile steel (2% Cu, 2% Si, 1% Mn and 0.8% Mo) during oxidation at 1100° C. They observed the formation of an additional layer under the oxide scale which greatly reduced the diffusion of Fe to the outside oxide. This layer consisted of a matrix of Fe_2SiO_4 and FeO containing Fe and Mo mixed-oxide crystals and dendrites of FeO. The Fe content of the Cu-rich phase of this complex steel was higher (15 to 60% Fe) than that of a plain Cu-containing steel (~5% Fe).

At 1100° C the phase containing only 5% Fe would be liquid, whereas for Fe contents of 15% and 60% the constitution would be liquid plus austenite. The reduced fluidity of the Cu-rich phase in the Cu-Si-Mn steel is considered to account for the improvement in hot working properties, and is derived from the addition to the steel of Mn, Si and Mo which, together with oxygen, form the additional layer.

3.3.4 Conclusion

The kinetics of the oxidation process in the Cu-containing steels are as follows: when the scale with the three iron oxides is formed, a metallic phase (95% Cu, 5% Fe) appears in the inner oxide (FeO). This phase remains dispersed in the oxide at low temperature (900° C) but is concentrated as a nearly continuous layer at high temperature (1050-1200° C) along the metal/oxide interface. The detrimental penetration within the austenite grain boundaries is rapidly observed. If Ni is present, the oxidation process is modified. Nickel promotes a second step in the oxidation; internal oxidation begins along the austenite grain boundaries together with a dissociation of iron and nickel oxides which liberates active oxygen at the interface. This effect is more important at high temperature.

*Royal Armament Research and Development Establishment

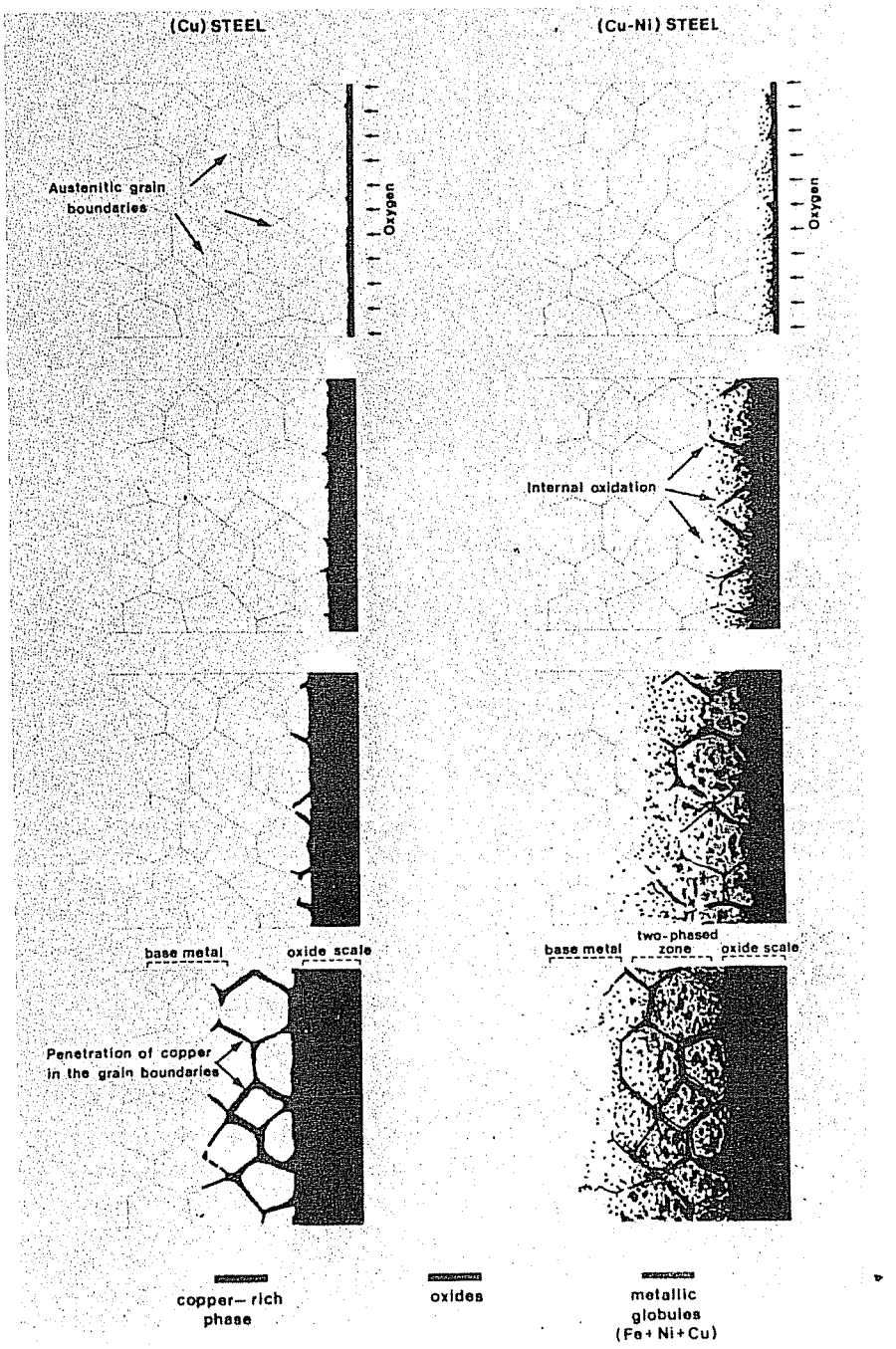
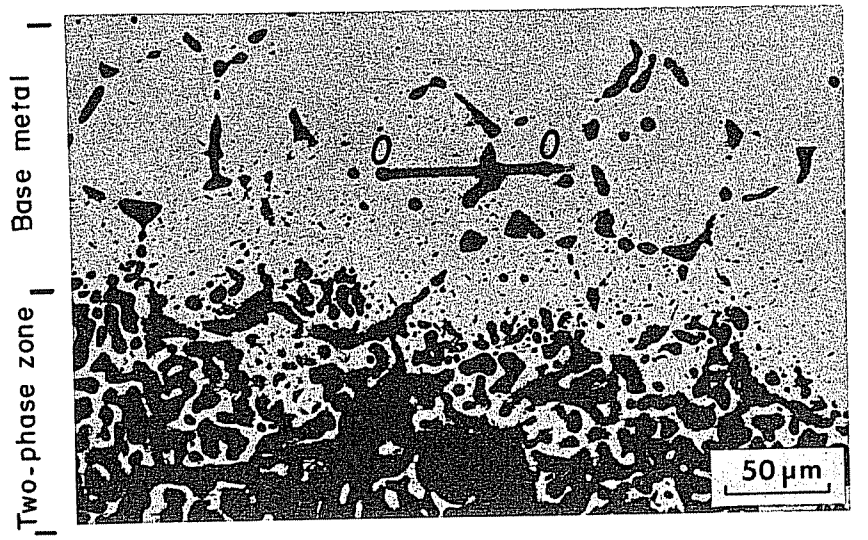
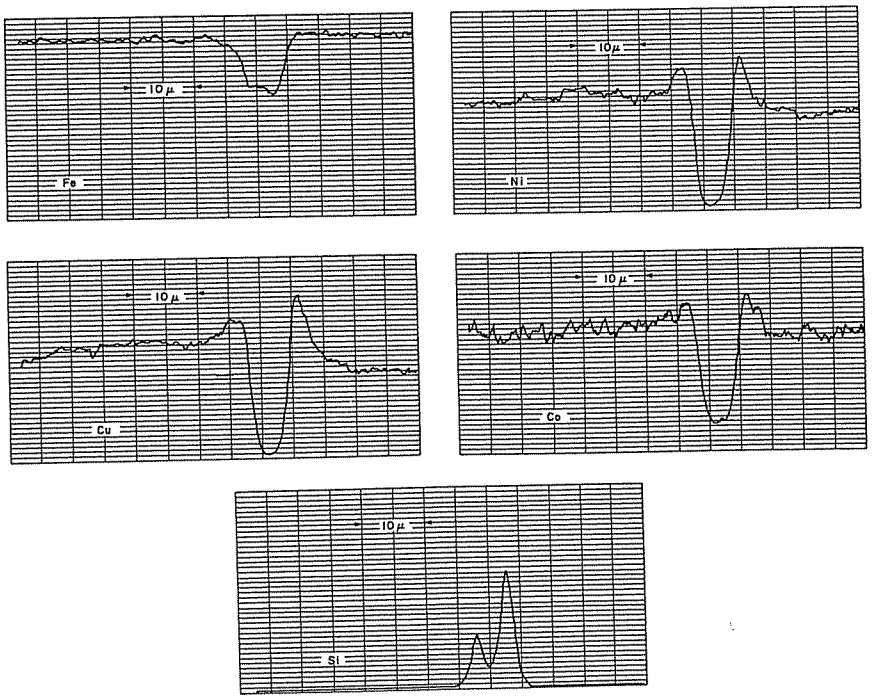


Fig. 3.32 The process of oxidation at high temperature (1100° C) for Cu-containing steel and Cu-Ni-steel [10].



(a)



(b)

Fig. 3.33 *(a)* Alloy C2 (Cu-Co-Ni) after holding at 1200° C for 3 h. *(b)* Electron microprobe line scan of 0-0 in *(a)* [10].

At the end of the first stage of oxidation, metallic globules (60% Cu, 30% Fe, 20% Ni) appear more or less aligned in the scale, especially when the temperature is high. During the course of internal oxidation, metallic globules of a high melting point intermediate phase (~30% Cu, 30% Ni, 30% Fe) appear dispersed in the oxide. The hot shortness phenomenon does not occur in this case, at least at normal working temperature, because the melting point of the metallic phase is high and the disposition of metallic particles is not favorable.

3.4 HOT WORKING OF COPPER-CONTAINING STEEL

The hot shortness phenomenon usually appears during forming at high temperatures. A typical example is the lack of reduction of area during tensile tests of Ni over a temperature range 750-1150° C . The segregation of specific minor residual elements to grain boundaries results in intergranular fracture with practically no elongation. Similar phenomena appear in alloys such as austenitic stainless steels, especially in high alloy grades. The low ductility at hot working temperatures causes cracking or tearing during rolling and forging operations.

The surface hot shortness of some steels is associated with weakness of the metal surface owing to cracks which developed on the ingot surface during furnace soaking at high temperature or during an intermediate reheating of the metal during hot rolling. As explained above, formation of an ϵ-Cu phase at the austenite grain boundaries is a major cause for the formation of such cracks.

Copper additions

Copper is a valuable addition in steel, as it increases the corrosion resistance and is responsible for precipitation hardening. Unfortunately, these benefits carry with them the problems of surface hot shortness. Nevertheless, numerous steels with residual or low Cu contents (~0.2 - 0.3%) are now produced and low alloy steels with Cu contents up to 1.5% are produced because of their high strength and good toughness. In such cases, a high Ni content is required and additional alloying elements such as Nb are normally added. In certain cases it is possible to use Si instead of Ni with good results, for example in the RARDE steel.

It should be mentioned also that the price of steels with low residual Cu is likely to increase. In fact, a "maximum copper" specification of 0.2% carried no extra charge in Europe until 1973 and cost an additional 5% in 1979. If the rise in melt-out-levels continues, it may become increasingly difficult to meet specifications calling for low Cu content without a premium on the price.

Hot rolling

Hot shortness surface defects originate in the slab reheating furnace and the actual surface break-up occurs in the hot rolling mill. The phenomenon starts with a small surface crack more or less normal to the surface which rotates into an orientation almost parallel to it, with successive reductions through the mill. The result is the formation of a sliver of metal at the surface of the hot

rolled strip which gives the characteristic surface blemish. In fact, any form of hot deformation of the grains, already weakened by intergranular penetration of the Cu-rich phase, may cause the grains to separate and surface tears to ensue.

During the process of hot rolling a Cu-containing steel, to a thickness of 2-3 mm, we may observe that the interface between oxide and metal is not regular (Fig. 3.34) and that pieces of scale can be present in the metallic zone. This is why, at the end of the rolling, it is possible to find some slivers embedded in the metal surface (see Fig. 3.35). If they are not numerous or large and if the interface is not too complex (with ϵ-Cu and oxides) their effects are small. But if the metal is subsequently cold or warm worked, these defects can spring out, giving an irregular surface with some roughness. In such cases, the addition of a small quantity of Ni leads to the surface appearance of Fig. 3.36, eliminating this difficulty during cold or warm forming. However, the addition of Ni gives rise to very adherent scales which are difficult to remove during hot rolling, the difficulties encountered in descaling Ni-containing steels being well-known [14].

3.5 IMPROVEMENTS RELATING TO THE HOT SHORTNESS PHENOMENON

Schematically, one can summarize the oxidation phenomena leading to hot shortness as follows: during oxidation, elements less oxidizable than Fe (e.g, Cu and Sn) remain unoxidized in the presence of Fe, or their oxides if eventually formed are quickly dissociated, as in the case of Ni and Co. This results in an enrichment of these elements in one or several intermediate layers between the base metal and the oxide scale. This effect is present when the element has reached its solubility limit in the alloy, for the particular temperature. On reaching their solubility limit these elements precipitate and form a second metallic phase. The composition of the latter is determined by the chemical analysis of the alloy. Our experiments have shown or confirmed that the composition and the distribution of the precipitated phase may be influenced by the alloying elements, and mainly by Cu, Ni and Co.

Numerous contradictory points of view have been expressed concerning the oxidation mechanisms; they concern mainly the problem of diffusion in the scale [11, 12]. The oxidation of most common metals such as Fe seems to proceed by diffusion of metal ions. The presence of oxygen at the metal/scale interface could be explained by the hypothesis of the dissociation of the scale [12]. From the literature [5, 11, 13] and also from our experiments, it appears that Ni alone gives rise to significant internal oxidation.

It appears also that the hot shortness problem can appear only when the temperature exceeds the melting point of the precipitated metallic phase. In some cases, this second phase penetrates into the austenite grain boundaries and weakens them. The "wettability" of a Cu-enriched phase — whose melting point is particularly low — is high, and its penetration into the austenite grain boundaries is known to be very rapid [10].

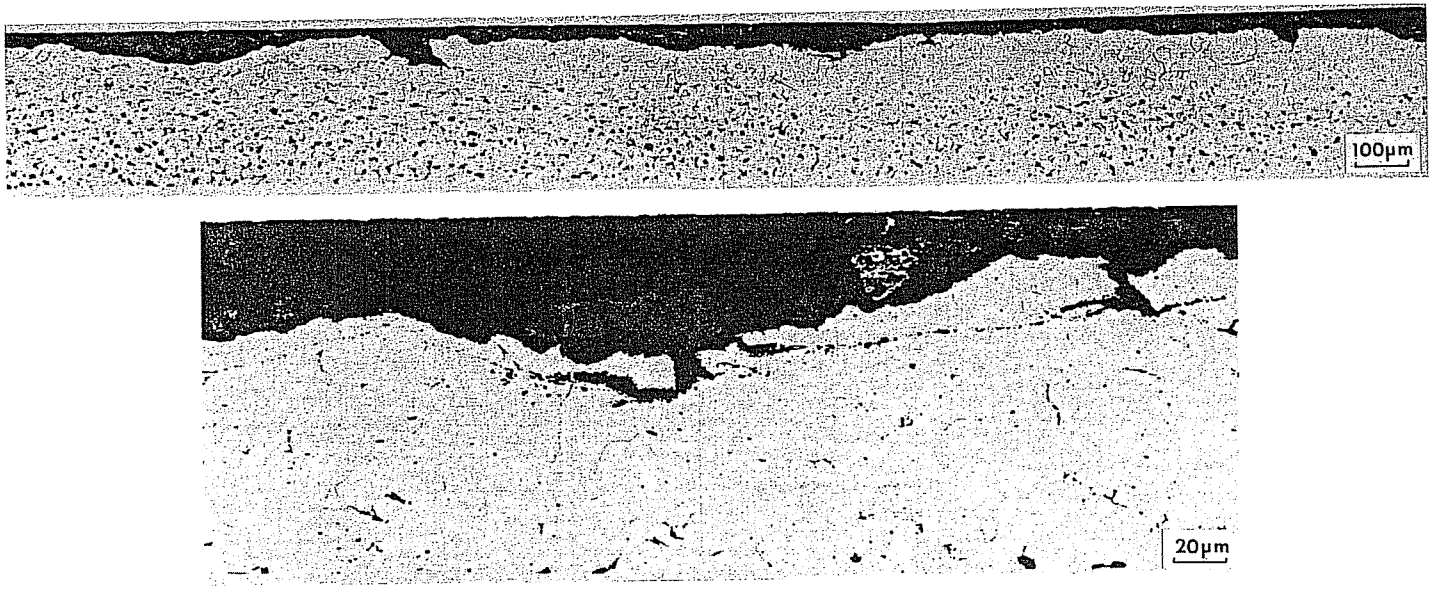


Fig. 3.34 Cor-Ten steel without Ni addition: 1280° C for 3 h, hot rolled at 1100-1125° C.

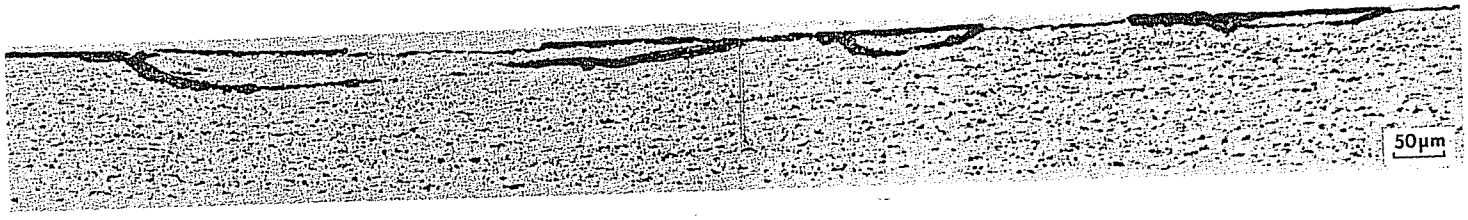


Fig. 3.35 Slivers on Cor-Ten hot rolled strip.

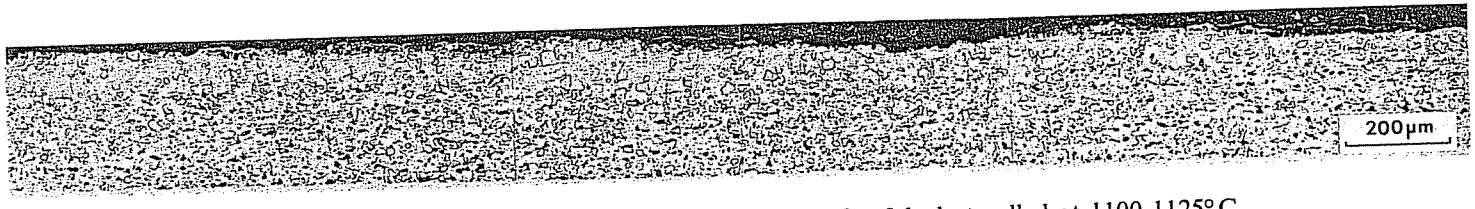


Fig. 3.36 Cor-Ten steel with Ni addition: 1280° C for 3 h, hot rolled at 1100-1125° C.

Therefore, the measures to prevent hot shortness should aim either at suppressing, or at least reducing, the precipitation of the Cu-rich phase, or at reducing the bad influence of that phase. Reducing the precipitation of the Cu-rich phase could be achieved by increasing the solubility of Cu in steel through the use of alloying elements; by reducing the oxidation and so reducing the amount of Cu-enriched phase, this being related to the atmosphere, temperature and soaking time; or by introducing Cu into the components of the oxide scale. The deleterious influence of the Cu-enriched phase could be reduced by increasing its melting point by the presence of elements of higher melting point; by isolating it from the austenite grain boundaries in the form of occlusions in the oxide scale; or by reducing the rate of penetration into these boundaries by increasing the dihedral angle.

3.5.1 Alloying Elements

To be effective, additional elements should be less oxidizable than Fe and should enhance the solubility of Cu in Fe, thus delaying the precipitation of the Cu-rich phase. They should also enhance the solubility of Fe in the Cu-rich phase to increase the melting point of the metallic phase; and increase the dihedral angle when this molten metallic phase penetrates along the austenite grain boundaries.

Figure 3.37 illustrates the effect of ternary additions on the solubility of Cu in austenite at 1250° C. It appears that Ni increases the solubility while other elements such as Sb, Sn, As, Mn and Cr decrease it.

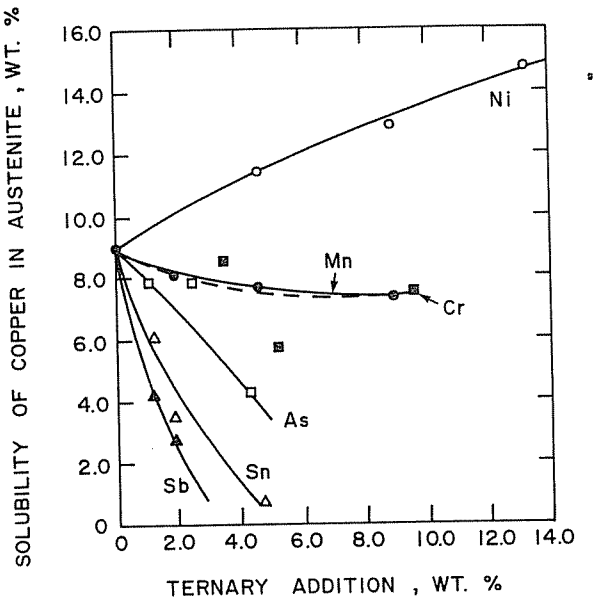


Fig. 3.37 Effect of ternary additions on solubility of Cu in austenite at 1250° C.

The elements more oxidizable than Fe have only a small effect on the process. Only Si enhances the dispersion of Cu globules. Unfortunately, this effect disappears at high temperatures because of the presence of an internal viscous phase which results in more rapid oxidation.

Among the elements less oxidizable than Fe are Co and Ni. However, Ni is highly soluble in Cu, while Co has only a small solubility. Of these two elements only Ni gives rise to metallic globules dispersed in the oxide. By additions of Ni and Co, one could enhance the solubility of Fe in the Cu-enriched phase and certainly increase the melting point of that phase. Cobalt gives a separate Fe-Co phase which concentrates along the Cu-rich phase and does not modify the phenomenon.

Another manner of increasing the melting point of the Cu-rich phase could be by introducing elements less oxidizable than Cu and miscible with this element, such as Pt and Pd, but these are too expensive and small additions do not greatly increase the melting point of the Cu-rich phase.

If Ni is present, the oxidation process is modified. Nickel promotes a second step in the process together with dissolution of iron and nickel oxides which liberates active oxygen at the interface. This effect is more important at high temperatures. According to many authors the quantity of Ni necessary to prevent hot shortness should be the same as that of Cu, however less Ni usually gives equivalent results. In some applications, for example those that require secondary hot forming, a steel more resistant to hot shortness will be required to avoid surface blemish.

It might be mentioned that Penning [15] studied the effect of Ni, not as an alloying element, but as a coating. He tested different coatings, viz., nickel oxide, nickel sulfide, Ni-20% Al, Ni-20% Cr, and Ni-Fe-Sn. Good results were obtained with Ni-20% Al powder protection and with ternary Ni-Fe-Sn. From industrial tests he showed that Ni-20% Al gave good results on a hot ingot, but that on a cold one an oxide scale formed rapidly. He suggested that this process is more economic than the use of Ni additions to the alloy.

3.5.2 Furnace Atmospheres

By operating the furnace at low oxygen contents and using air-atomized fuel oil to keep the water vapor content to a minimum, it should be possible to increase the acceptable Cu level in rimming steels. A further reduction in hot shortness has been obtained at low oxygen contents with the presence of sulfur in the furnace atmosphere originating from the fuel oil. However, the effect of sulfur is not entirely beneficial and some pitting and problems of adherent scales may arise. The effects of sulfur are reduced as the furnace oxygen content increases and disappear at about 6% oxygen. In any case, according to Rolls [16] the presence of sulfur may be deleterious if Ni is also present because of the formation and the intergranular penetration of liquid nickel sulfide during heating.

There appears to be little room for manoeuvre with regard to temperature. Low temperatures would permit a higher Cu level to be tolerated, but the reduced plasticity of the metal would increase the hazard of mill damage from higher loads.

Reheating time should always be kept to a minimum for orders requiring high surface quality, and careful selection of ingots and timing of their processing through the reheating furnace is important.

3.5.3 Conclusions

The problem of hot shortness can be solved:

- Over a limited temperature range by the presence in the scale of phases enriched in Si. Probably only specific compositions and working conditions are suitable.
- Commonly, without difficulty with Ni-containing steels due to the presence in the oxide layer of a metallic phase of high melting point, and the effects of the process of internal oxidation.
- Partial solutions might also be found by modifying the oxidation conditions, e.g., the temperature level, control of atmosphere, reduction of soaking time, and so on. These conditions should be defined in every case with relation to the composition of steel and, particularly, its Cu content.

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