氏　　　　　名	Lopez Hirata Victor Manuel（ロペス・ヒラタ・ビクトル・マヌエル）
授与学位	工学博士
学位授与年月日	平成2年3月28日
学位授与の根拠法規	学位規則第5条第1項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）材料物性学専攻
学位論文題目	Study on Phase Transformations in Cu－Ni, Cu－Ni－Fe and Cu－Fe Alloys by AP－FIM（アトム・プローブ電界イオン顕微鏡による Cu－Ni, Cu－Ni－Fe および Cu－Fe 合金の相変態の研究）
指導教官	東北大学教授　平野　賢一
論文審査委員	東北大学教授　平野　賢一　東北大学教授　木村　宏 東北大学教授　深道　和明

論文内容要旨

CHAPTER I GENERAL INTRODUCTION

The Atom-Probe Field Ion Microscope (AP-FIM) is constituted of a Field Ion Microscope (FIM) which enables us to observe the microstructure of materials with a magnification as high as one million times and of a time-of-flight mass spectrometer, the Atom-Probe (AP), which permits us the chemical analysis of materials in an area less then a 10 nm scale. This feature of AP-FIM makes it a very special experimental method compared with other methods such as TEM, SANS, etc. In addition, the selected area analysis and random area analysis convert AP-FIM into a very powerfull tool to study atomistic mechanism of phase transformations in alloys.

AP-FIM has been applied successfully to analyse whether a phase decomposition in a given metallic system takes place by the nucleation and growth process or by the spinodal decomposition process. Besides, the high-resolution of FIM provides an excellent tool to study the morphology of very fine precipitates and its crystallographic orientation with the matrix phase. Therefore, if the AP-FIM analysis is properly performed, several metallurgical problems can be successfully elucidated. The general purpose of the present work is to carry out a study on phase transformations in copper alloys taking the above mentioned advantages of AP-FIM.

CHAPTER II THEORETICAL ASPECTS OF PHASE TRANSFORMATIONS

Dealing with the thermodynamic stability of binary solution, Gibbs discerned two different kinds of fluctuations, one corresponding to fairly drastic atomic rearrangement with very small localized volumes, and the other corresponding to very small rearrangements extend over large volumes. The former concerns with the nucleation and growth theory and the later concerns with the spinodal decomposition theory. So far, it has been interesting to probe wheather an alloy decomposes by the spinodal decomposition or by the nucleation and growth process. Experimental verification has been carried out in some alloy systems, but the early stages of the phase decomposition have not been well understood. In this chapter, some important decomposition theories including its most recent advances are critically reviewed. In addition, the theories on coarsening of the decomposed phases are also described briefly.

CHAPTER III THEORETICAL ASPECTS OF AP-FIM

For FIM, needle-like specimen is used and it is usually called "tip" and prepared by electropolishing wires of 0.1 to 0.3 mm diameter. The tip is prepared,after the phase decomposition treatment and introduced into the FIM chamber with a background pressure better than 1x 10^{-8} toor. To obtain the atomic image of the tip surface, an imaging gas such as He, Ne, Ar or H_2 is introduced in the FIM chamber to a pressure up to 8×10^{-5} torr, subsequently a positive high-voltage, which typically ranges between 3 and 15 KV is applied on the tip. The imaging gas atoms are positively ionized in the so-called ionization zone near the tip surface and will be accelerated along almost radial trajectories towards the grounded imaging screen which is lightened up at the points of the impact.

A time-of-flight atom-probe FIM consists of two parts; one is the FIM to image the atomic arrangement of the specimen and the other is the time-of-flight spectrometer in which each individual atoms are field evaporated from the FIM tip and identified. The chemical identification of a single ion is achieved by measuring its time of flight, t, and subsequently evaluating its mass to charge ratio, m/n.

CHAPTER IV PHASE SEPARATION IN Ni-Cu ALLOYS

The heat of mixing in Ni-Cu system has been shown to be positive and thus the Ni-Cu system has a tendency towards clustering of solute atoms, that is, a preference for making the nearest neighbours of like atoms. In addition, the existence of a miscibility gap at a rather low temperature range, i.e., 600K, has been suggested in the equilibrium phase diagram of the Ni-Cu system theoretically on the basis of the thermodymanical data. On the other hand, the experimental determination of both the miscibility gap and spinodal, so far, has not been possible because of the low diffusivities ($10^{-28}-10^{-31}$ ㎡/sec) at lower temperatures then 600K, and of the experimental difficulty due to the nearly same atomic numbers of Cu and Ni.

In the present work, the coherent spinodal of the Ni-Cu system could be estimated by analysing the electrical resistivity with the Cahn-Kolometz equation. In addition, it has been shown by the AP analysis that the amplitude of the composition modulation increases with ageing time without any practically change in the wavelength. This is a clear evidence for the spinodal decomposition.The concentration profiles of fully aged specimens obtained by AP analysis are analysed by the Fourier transformation. This analysis enabled us to determine the diffusion coefficient of the system inside the coherent spinodal to be negative, -3.54×10^{-28} ㎡/sec, as predicted by Cahn's theory.

CHAPTER V PHASE SEPARATION IN Cu-Ni-Fe ALLOYS

The spinodal decomposition in Cu-Ni-Fe alloy has been extensively studied by the previous workers by the methods such as magnetic analysis, X-ray diffration, TEM, Small Angle Neuton Scattering SANS and Anomalous Small Angle X-ray scattering ASAX.

In the present work, kinetics of growth of the decomposed phase, the coherent spinodal temperature and morphology of the decomposed phases as well as the composition of the decomposed phases in Cu-46at%Ni-4at%Fe and Cu-48at%Ni-8at%Fe alloys are analysed by an AP-FIM. It is found that growth of the wavelength of the composition modulation in the early stage of the decomposition occurs more slowly than in the later stage of the decomposition where the Ostwald ripening according to the LSW theory is observed. FIM observation of the decomposed alloys shows that phase decomsition takes place in the ⟨100⟩ directions and that the decomposed phases are coherent each other even in the later stage. Besides, AP analysis showed that composition of the decomposed phases is in agreement with that expected from the calculated Cu-Ni-Fe phase diagrams.

CHAPTER VI PHASE TRANSFORMATION OF γ-Fe PRECIPITATES IN A Cu-1.5 at%Fe ALLOY

The transformation of the γ-Fe phase precipitate to the α-Fe phase precipitate is expected to occur during coarsening of the precipitate in Cu-Fe alloys. However, it has never been observed if the alloy is subjected to the thermal treatment alone. The γ-Fe precipitates in Cu-Fe alloys have been observed to transform martensitically to α-Fe by action of any of the following: a) Cold rolling of the alloy, b) Extraction of precipitate from the alloy and c) Ion-bombarding the alloy. This transformation has been classified as a martensitic type because of its diffusionless nature.

In the present work, the mechanism of the martensitic transformation and the influence of the γ-Fe particle size on the martensitic transformation induced by cold working, the transformation of γ-Fe into α-Fe by thermal treatment alone, as well as the ripening of the γ-Fe precipitates in a Cu-1.5 at%Fe alloy, are studied using FIM and TEM observations.

It is found that the γ-Fe precipitates smaller than about 10 nm can not be transformed martensitically to α-Fe by plastic deformation. The transformation in the precipitates larger then 10 nm follows the Kurdjumov-Sach relationship. Dislocations are found in the matrix near the transformed α-Fe particles, suggesting that the dislocation cutting mechanism proposed for the transformation is working. No transformation from the γ-Fe to α-Fe can be generated by thermal treatment alone for the γ-Fe precipitates as large as about 50 nm. The ripening of the γ-Fe precipitates follows the coarsening theory of LSW for the diffunsion-controlled growth.

CHAPTER Ⅶ SUMMARY

An atom-probe study on the phase decomposition in Ni-Cu, Cu-Ni-Fe and Cu-Fe alloys was carried out and following conclusions were attained.

1. Phase decomposition in Ni-Cu alloys occurs by the spinodal decomposition process which follows Cahn's theory of the spinodal decomposition. The coherent spinodal temperature has been determined experimentally.
2. Variation of the wavelength of the composition modulation with ageing time in the studied Cu-Ni-Fe alloy in the early stage of the decomposition is slower than in the later stage. The coarsening stage follows the LSW theory for thermally activated growth. Composition of the Cu-rich and Ni-rich phase have been determined to be in agreement with the theoretical miscibility gap.
3. In Cu-Fe alloys, the transformation of the γ-Fe precipitates into the γ-Fe precipitates does not occur even by prolonged ageings. However, it can be generated when the alloy having the γ-Fe precipitate larger then 10nm is cold worked.

審　査　結　果　の　要　旨

典型的な相分解の殆どすべてのものがCu合金において見られ，実用的にも重要であるため，Cu合金の相変態については多くの研究がなされて来た。しかしCu-Ni合金など実験上の困難性のため解明すべき問題を残したままになっているCu合金もいくつかある。本研究はアトム・プローブ電界イオン顕微鏡（AP・FIM）の高倍率，高分析性能に着目し，これと透過電子顕微鏡を併用することによって，Cu-Ni合金およびCu-Ni-Fe合金の相分解過程およびその速度論的挙動，およびCu-Fe合金における準安定γFe析出相の挙動を明らかにしたものである。本論文はその成果をまとめたもので全編7章よりなる。　第1章は緒論であり，本研究の目的と意義を述べている。

第2章では本研究の理論的背景を論じており，特にスピノーダル分解，核生成と成長およびオストワルド成長理論について問題点を明らかにしている。

第3章は本研究の主要実験手段であるAP・AIM装置について説明し，FIM像およびAP分析結果の解析法について述べたものである。

第4章ではCu-Ni合金の相分解過程をAP・FIMによって調べ，スピノーダル分解を確認すると共に，電気抵抗測定法によって整合スピノーダル温度を決定した成果を述べている。この合金のスピノーダル分解を極めて明確に検証することに成功したことは本研究の主要成果の一つである。

第5章はCu-Ni-Fe合金の相分解過程をAP・FIMによって詳しく調べた結果を述べたものである。分解生成相の＜100＞方向の配向性，生成相の間の整合性，オストワルド成長期における生成相の挙動などについて原子的尺度での新しい知見を得ている。

第6章ではCu-Ni合金における核生成－成長型析出過程の初期において形成される準安定γFe析出相の安定性や母相との整合性をFIM観察によって原子的尺で調べた結果を述べている。準安定γFe析出相は粒子径が10nm以上に成長したものであれば，試料を冷間加工することによって平衡αFe相へと変態できることを見いだしている。

第7章は結論である。

以上要するに本論文は，AP・FIMを駆使してCu-Ni，Cu-Ni-FeおよびCu-Fe合金の相分解過程を研究し，多くの新しい知見を得たものであり，材料物性学の発展に寄与するところが少なくない。

よって，本論文は工学博士の学位論文として合格と認める。