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METASTABLE PHASES PRODUCED BY ION IMPLANTATION
IN METALS*

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ABSTRACT

Experimental evidence for the formation of metastable phases in metals using ion implantation is reviewed. Ion channeling and transmission electron microscopy are the main experimental techniques which have been used to investigate these materials. For heavy metallic implanted species at low implanted concentrations (≤ 1 at.%), the materials are generally substitutional solid solutions, often exceeding equilibrium solid solubilities. At higher concentrations both metastable solid solutions and amorphous structures can be produced. Examples from the Ag:Cu, Ta:Cu, Dy:Ni, and Au:Pt systems are shown to illustrate specific points. A thermal spike-type mechanism has been proposed to explain these behaviors.

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I. INTRODUCTION

The physical properties of metals have always been of high interest and an area of continuing study. These metals are usually alloys and not pure metallic elements. Perhaps one of the largest areas of development has involved investigation of the physical properties of alloys as a function of composition, where alloys have been tailored to enhance a given physical parameter or minimize a parameter of deleterious effect. Summaries of equilibrium phase diagrams are available which show the phases formed between two metallic elements as a function of temperature and composition. These phase diagrams, however, are for equilibrium and it is possible to form nonequilibrium or metastable alloys which could not exist in thermal equilibrium. Actually some very common alloys, the steels for example, are nonequilibrium or metastable alloys and if an infinite amount of time were available a different system would be formed.

Metastable alloys can be formed by quenching from a liquid state and may have unusual and useful properties. Very rapid quenching techniques are often required; the two most commonly used methods are splat cooling and vapor quenching. The quenching speed of these techniques is such that the atoms of the alloy do not have time to diffuse and form the equilibrium alloys as the temperature is being lowered. In general, the maximum rate of temperature decrease is of the order of 10^6 - 10^8 °C/s. Using these techniques Duwez at Caltech² and others³⁻⁵ have succeeded in forming metastable alloys in systems which generally have not been amenable to nonequilibrium alloy formation.

Ion implantation is a relatively new technique for introducing impurities into a solid in a nonequilibrium fashion. It is clean and versatile in that any element can be introduced into any solid material. The energetic ion enters, is slowed and comes to rest in the solid very rapidly ($\leq 10^{-12}$ sec. for the ion-target combinations discussed in this paper). During this slowing process energy is lost to the atoms of the solid in the form of a collision cascade or thermal spike.⁶ Thus as an implanted impurity comes to rest, it is generally located in a region of high lattice temperature. If one calculates the decay of the thermal spike in a material such as copper at room temperature, one finds that the appropriate cooling rates are of

the order of 10^{12} - 10^{14} °C/s.⁷ This is assuming that the thermal conduction takes place almost entirely by the atoms of the solid and there is no contribution from the electronic component.

Ion implantation is a proven technique in semiconductor technology. It is used for controlled doping of a large variety of transistor and microcircuit applications. However, the use of ion implantation in metals and insulators is just beginning to be studied. One area that is just opening up is the use of ion implantation in metallurgical studies. For this purpose I would like to divide the use of ion implantation metallurgy into two areas. The first is equilibrium studies. These studies, which have been pioneered by S. M. Myers at Sandia Laboratories,⁸ will be described in a later paper at this symposium. The second area is that of nonequilibrium metallurgy, and will be discussed here.

II. SUBSTITUTIONAL SOLID SOLUTIONS

The silver-copper metallurgical system is a classic example used to illustrate the failure of the Hume-Rothery rules⁹ for predicting solid solubilities in metals. Whereas, the Hume-Rothery rules would predict complete solid solubility across the range of the binary phase diagram, the actual equilibrium phase diagram shows that the ranges of solid solubility in pure Ag or Cu, or the α phases, are quite limited. It was with the system silver-copper that Duwez² showed that splat cooling could be used to generate metastable phases in metals. Using this technique he was able to create silver-copper alloys of any composition which were completely substitutional. Thermal annealing of such samples when the composition was within the miscibility gap produced precipitation, indicating that these were indeed metastable phases.

The first results using ion implantation to create metastable phases in these systems were obtained using He ion channeling techniques by Borders and Poate¹⁰ who showed that 100% substitutional solutions of silver and copper could be obtained by ion implantation. Subsequently, Poate, Borders, Cullis, and Hirvonen¹¹ examined the substitutionality of implanted Ag in Cu as a function of implantation dose for peak concentrations up to 17 at.% silver. These results showed that the silver is indeed

100% substitutional at concentrations far beyond the maximum equilibrium concentration to which silver can be dissolved in copper at room temperature (≤ 0.1 at.%) or even the maximum Ag solubility in Cu (≈ 5 at.%). These results then show that implanted Ag in Cu behaves similarly to samples created by splat cooling or vapor quenching at least up to 17 at.% which was as high as could be obtained using the ion implantation technique due to sputtering.

The same samples were investigated using transmission electron microscopy (TEM) to examine the microstructure of the implanted alloys. The results were consistent with the ion channeling data. After implantation, diffraction patterns showed only faint evidence of metallic silver and some Cu_2O and the corresponding dark field micrographs showed fairly uniform contrast with both the silver and the oxide occupying small, (≤ 25 Å) irregularly shaped regions, probably on the surface. This suggests that most of the Ag is in solution.

Since the Ag-Cu alloy is a metastable phase, thermal annealing should return the samples to the equilibrium phase (precipitated α -Ag in α -Cu). This is clearly shown by parallel studies¹² again using TEM and ion channeling. Electron diffraction patterns in the TEM indicate that Ag precipitates out after annealing at 200°C and that by 400°C, Ag precipitates with well-defined crystallographic orientations can be imaged in bright field. Moire fringes can be imaged at these positions with the proper spacing for overlapping Ag and Cu reflections (15.7 Å for the 200). These precipitates are hundreds of angstroms in lateral extent and the existence of Moire fringes indicates that the planes of Ag atoms in the precipitates are parallel to the planes of Cu atoms in the host matrix. Thus the precipitates are at least partially coherent.

The channeling data support the TEM results. Angular distributions after thermal annealing indicated that the Ag atoms are more than 90% substitutional up to 300 C but by 380 C, the substitutionality of the Ag as measured by $\langle 110 \rangle$ channeling is $\approx 60\%$. These data confirm that implanted Ag in Cu is indeed a metastable solid solution and that thermal annealing returns the system to its equilibrium state.

III. AMORPHOUS ALLOYS

The production of amorphous alloys using ion implantation is an intriguing possibility. While it is quite easy to produce amorphous phases in semiconductors by the use of ion implantation, most metals tend to reorder, even at very low temperatures, and until recently the production of amorphous phases had not been observed. Evidence for such phases was observed by Borders and Poate¹⁰ in the W-Cu system. They have recently investigated the Ta-Cu¹² system rather extensively and found it to be very similar to W-Cu.

High fluence, implants of Ta into Cu are 100% substitutional at low concentrations (≤ 0.1 at.%). As the concentration is increased, He ion channeling measurements indicate that 1) the Ta becomes less substitutional, 2) Cu atoms are displaced (or strained) from normal lattice sites and are seen as direct backscattering centers, and 3) the Ta depth distribution narrows as a disordered layer near the surface dechannels the incident Ta thereby decreasing its range in combination with the removal of surface atoms by sputtering. Thus, between 1 and 10 at.% Ta in Cu, the substitutionality of the Ta falls from 90% to 0%.

Ta implanted copper samples were also examined using TEM. In the as-implanted condition and after thermal annealing at or below ~ 400 C, two distinct bands of diffuse scattered intensity are observed in electron diffraction. Diffuse bands are characteristic of amorphous microstructure or at least of very small microcrystallites. From the breadth of the diffuse band and use of the Scherrer equation which relates the variation in d-spacing to particle size, it was determined that the size of any crystallites contributing to the diffuse band was ≤ 6 Å. For clusters of this diameter it is probably meaningless to differentiate between amorphous and microcrystalline structures.

As previously stated, these amorphous structures as evidenced by the diffuse bands were stable up to 400 C. Annealing at $\sim 600^\circ\text{C}$, however, produced definitive evidence of elemental Ta and dark field micrographs showed Ta microcrystallites of about 30 Å in extent. Even after this anneal, there was some evidence of the diffuse band attributed to an amorphous structure. Annealing at ~ 750 C produced much larger Ta precipitates and the diffuse band disappeared. These results indicate that high implanted concentrations of Ta or W in copper produce a

metastable amorphous phase stable to temperatures between 400 and 600 C.

The Salford group has produced a noncrystalline metastable phase by implantation of Dy into Ni.¹³⁻¹⁵ In this system an amorphous Ni phase, probably stabilized by the Dy, is observed using TEM. This phase was more unstable than that observed in the Ta:Cu work; thermal annealing to ~ 300 C or bombardment by electrons in the electron microscope both produced a widening and sharpening of the diffuse band and microcrystallites of 30-100 Å diameter are observed. They have contrasted the behavior of Ni implanted with Dy to that of Ni implanted with Pb where no such amorphous phase is produced. Both TEM and channeling measurements were used to correlate microstructural changes with changes in the depth profile of the implanted species and its substitutionality.

Recently, workers at Stony Brook and NRL have succeeded in forming an alloy of Pt and Au¹⁶ which exhibits spinoidal composition variations on a 50 Å scale but when examined using electron diffraction is found to be amorphous.

IV. DISCUSSION

The ability to create substitutional metastable phases using ion implantation suggests that a thermal-spike type mechanism may be appropriate when modeling the behavior of these implanted heavy metallic ions. After the implanted ion has come to the end of its range, it is located in a region of high lattice temperature for the duration of the thermal spike. It is free to move diffusively during this short time and can sample the local atomic environment. After the decay of the thermal spike the implanted atom will tend to be located in the lowest energy location in the volume it was able to sample. For metallic atoms in copper at low concentrations, this location is a copper vacancy as is evidenced by the high substitutionality of metallic impurities implanted in copper. As the concentration of the implanted atoms rises, the probability increases that an implanted atom will encounter a previously-implanted atom, before the thermal spike decays. If this is a lower energy state, the implanted atoms will tend to be located adjacent to one another. Thus the transition to

nonsubstitutional behavior as a function of dose for Ta and W in Cu can be explained by a model in which isolated Ta or W atoms in Cu reside in Cu lattice sites because that is the lowest energy configuration available. At higher concentrations the impurity atoms locate near each other, trapping or straining Cu atoms from their normal sites. This results in the observed amorphous phase formation.

Phenomenological models such as these are fine, but they cannot predict which systems will produce noncrystalline structures such as Ta-Cu and Dy-Ni and which result in solid crystalline solutions, such as Ag-Cu. Nagel and Tauc¹⁷ have related the tendency to form noncrystalline alloys with an effective valence of the combination. They predict an increase in the stability of a noncrystalline form when the Fermi level lies at a minimum in the density of states. Andrew et al¹⁸ have discussed this hypothesis as applied to alloys formed using ion implantation and it has worked on the few systems for which there are experimental data. An alternative approach based on the multiplicity of polymorphic forms has been suggested by Wang and Merz.¹⁹ However, there is clearly much room for further work.

Perhaps the most neglected area of research has been the investigation of the physical properties of implanted alloys and the relationship of changes in these properties to changes in microstructure. The unusual properties of metallic glasses formed using more conventional techniques suggests that research in this area may be unusually profitable.

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