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AN X-RAY DIFFRACTION TECHNIQUE FOR THE STUDY OF HIGH-PRESSURE PHASE CHANGES IN IRON ALLOYS

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ABSTRACT

Static high-pressure x-ray diffraction experiments on metals and alloys are the only means available for simultaneously determining: (a) the structures of martensitic phases formed at high pressure, (b) the fraction of the sample which these phases represent, (c) the pressures at which they begin to form, and (d) the pressures at which the high-pressure phases begin to return to the original crystallographic structure. While employing a combination of existing techniques, the present investigation developed modifications in the experimental procedures as well as improvements in the diffraction recording technique. It was found that the body-centered-cubic to hexagonal close-packed martensitic transformation in pure iron occurs at 70 kilobars rather than at the 130 kilobars reported by previous high-pressure x-ray investigations[1-5], and agrees more closely with values of 80 and 50 kbar recently determined by electrical resistivity[6-7]. In addition, some common interpretation difficulties, concerning primarily pressure determination and phase fraction estimation are discussed.

INTRODUCTION

High-pressure x-ray diffraction studies are used principally to detect any phase change that may be occurring at high-pressure and to determine the crystallographic structure of phases involved.

High-pressure studies are also of interest because they give a qualitative measure of the relative stability of phases which could not otherwise be studied because the phases do not coexist at ambient pressure. These high-pressure studies add a third dimension to the standard temperature-composition equilibrium diagrams, thus permitting a more complete understanding of the nature of the equilibrium between phases. Of course, in the study of martensitic transformation, the diagrams are metastable equilibrium diagrams because of the nonequilibrium nature of the martensitic transformation.

The application of high pressure to induce phase changes in metals has been carried out for the past several decades. But it is only within the past 10 years that the use of x-ray diffraction at pressures above 30 kilobars (kbar) has enabled investigators to determine the nature of the change taking place and the crystal structure of the resulting phase[1-5,8-9].

Measurements using x-ray diffraction are capable of determining the structure of the phases present, the fraction of the sample that they represent, the pressure at which the new phases begin to form, and the pressure at which they begin to return to the original structure. The three other techniques used to study high-pressure transformations under static or incrementally increased pressurization conditions are electrical resistivity, volume change, and Mossbauer spectroscopy. Although all three of these techniques are capable of determining transition pressures, none is capable of determining the structure of the phases and the fraction of the sample that has transformed.

EXPERIMENTAL TECHNIQUE

By incorporating improvements into existing techniques for obtaining and interpreting high-pressure x-ray diffraction patterns, the experimental program described in the present paper makes it possible to more closely monitor phase changes

as a function of pressure. This improved method includes modified beam collimation, sample mounting and diamond alignment procedures and the use of a high-speed, high-contrast Polaroid film to significantly reduce exposure times and errors due to cassette placement and film shrinkage.

Sample Preparation

High-purity commercial iron powder and vacuum-melted iron alloys were used throughout this study. Filings from the iron alloys were annealed in evacuated Vycor capsules at 1900°F. Thin sheets of some of the alloys were produced by "pack-rolling"[10] to thicknesses ranging from 0.002 to 0.006 inch. The problem in using samples produced by this method is the preferred orientation or texture present in the thin sheets even after annealing. The resulting difficulties in diffraction-pattern interpretation will be discussed later.

Equipment and Procedure

A schematic drawing of the commercially available high-pressure x-ray camera[11] used to obtain the high-pressure x-ray diffraction patterns in shown in Figure 1. The unit consists essentially of a cylinder inside which a piston is free to move. A flat-faced piston diamond is attached to one end of the piston, and a similar anvil diamond is attached to a demountable anvil assembly that is held in place by a backing plate during operation. The diameter of the anvil diamond face, 0.040 inch, is approximately twice that of the piston diamond. The sample is placed between the two diamond surfaces. Pressure is applied to the sample using a known gas pressure on the back surface of the piston assembly. The gas is fed through a high-pressure gas line and pressure regulator attached to a tank of dry nitrogen. The high ratio - approximately 10.000 to 1 - of the surface area of the back of the piston assembly to that of the piston diamond face made it possible to generate the high pressures required to induce transformations in the specimen.

X-rays leaving the source are collimated using a tube having restricted openings at either end. The opening at the x-ray source-end is approximately 0.02 inch, while that at the sample end is about 0.01 inch. During the course of this study it was found that better beam definition could be achieved and spurious x-ray lines on the pattern could be eliminated by placing a 0.015-inch-thick piece of lead containing a pinhole approximately 0.008 inch in diameter over the sample end of the collimator.

It was also found that alignment of the x-ray beam relative to the center of both the piston and anvil diamonds was important. Since pressure gradients increase with distance from the center of the diamond faces, the x-ray beam should pass as close to the center of the diamond faces as possible. Alignment can be determined by placing a sheet of standard x-ray film wrapped in aluminum foil between the diamond faces, applying a force of about 2 lb, and turning on the x-ray beam for less than a second[3]. This procedure produces an image of the outside edges of both diamond faces superimposed on the image of the beam. Measurements showed that the piston diamond diameter was 0.022 inch, the avil diamond 0.040 inch, and the beam diameter 0.012 inch where it passed through the sample.

Since the chances of developing destructive fracture in the diamonds at high loads are greatly increased if the piston and anvil diamond faces are not strictly parallel, one should determine the extent of non-parallelism before beginning the high-pressure experiments. Interference microscopy can be used for this purpose, and Figure 2 is an interference photomicrograph of the high-pressure surface of a piston diamond taken at 170X. In this case, the diamond surface was misaligned by 1.7 degrees relative to a plane perpendicular to the axis of the piston assembly.

Two problems encountered in diffraction-pattern interpretation are "nonsample" diffraction lines and low diffraction line intensity. Nonsample diffraction lines are caused by lead between the anvils getting into the path of the x-ray beam. Low diffraction line intensity is due to extrusion, at high pressure, of copper from behind the face of either diamond into the path of either the main x-ray beam or the diffracted x-rays. The copper which is used to fasten the diamonds to their assemblies, can be easily removed with a long needle or razor blade.