AD-A158 612 PROCESS VARIABLE-STRUCTURE RELATIONSHIPS IN MECHANICAL ALLOYING(U) NORTH CAROLINA STATE UNIV AT RALEIGH C C KOCH 30 JUN 85 N00014-84-K-0253 1/1

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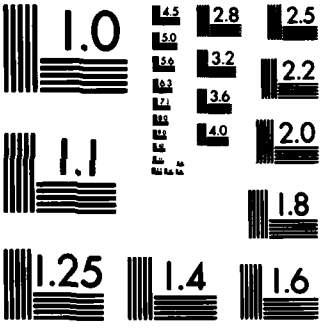

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Annual Report to the

Office of Naval Research

for

The Period July 1, 1984 to June 30, 1985

for

Contract: N00014-84-K-0253

Process Variable-Structure Relationships in Mechanical Alloying

C. C. Koch

North Carolina State University

Raleigh, N.C. 27695-7907

Background

Mechanical alloying is a high energy ball milling technique for producing composite metal powders with controlled microstructures by the repeated cold welding and fracture of free powder particles. Mechanical alloying (MA) has been mainly applied to the oxide dispersion strengthening of a variety of nickel-base, cobalt-base, iron-base, aluminum, and titanium alloys (1). Most of this MA technology was developed by the International Nickel Company. While some limited academic studies (2, 3, 4) have been made, the mechanisms controlling MA are not well understood nor has MA been used as a general non-equilibrium processing method (5, 6) as, for example, rapid solidification.

Research Objectives

The goal of this research is to elucidate the mechanism(s) controlling Mechanical Alloying (MA) and the alloy structures so formed. The experimental approach is to systematically study process variables such as temperature, energy input, environment, and starting material and relate such variables to the structure produced by MA. Microanalytical and structure determinations emphasize electron microscopy and x-ray diffraction methods. Quantification of the mechanism(s) is sought.

Progress During the Period July 1, 1984 to June 30, 1985

I. Personnel

Professor C. C. Koch is the Principal Investigator on this program. Two graduate students, Mr. Brian McDermott and Mr. Kevin Aldrich were hired to work on the program starting September 1, 1984. Unfortunately, Mr. Aldrich had difficulty with several graduate courses and dropped out of school after the Fall semester. To replace Mr. Aldrich, Mr. Robert Davis, one of our outstanding Seniors, joined the program in January, 1985 and will continue as a graduate student starting in August, 1985.

II. Equipment

The MA studies carried out during this reporting period were all done in a SPEX mixer/mill model number 8000. This small high energy mill is capable of MA about 10 cm^3 of material and is very convenient for the process variable studies such that large quantities of powder are not needed. Two materials were used as the milling medium in the form of ball bearings (7.9 mm diameter). The ball bearing steel AISI 52100 was initially used, but most of the work was carried out with martensitic stainless steel balls (AISI 440C) which appear to minimize iron contamination of the MA powders.

An attritor mill (model number 1-SDG) was acquired from Union Process Inc. which has a tank capacity of 1.5 gallons and a powder-milling medium capacity of 0.8 gallons. While it is a laboratory model it is large enough to closely duplicate production conditions. This attritor was specially designed with an extended frame for possible incorporation of a torque meter. The attritor mill is now in place in our laboratory.

III. Selection of Model Materials

A. Ductile-Ductile Powders

The first class of model materials to be studied contain elemental powders in which both exhibit a large degree of plastic deformation at room temperature. Several criteria were used to select the components including cost, phase relationships, and reactivity with the environment. Copper and zinc were selected for study. Copper (fcc) and zinc ($_{hcp}$), with different crystal structures, can be used to conveniently monitor the progress of MA by x-ray diffraction measurements. In addition Cu and Zn form "electron compounds" such as bcc β brass at given concentrations, the structure and occurence of which are well documented. Compared to some transition metal systems, Cu and Zn are relatively inert and inexpensive.

B. Ductile-Brittle Powders

Copper and silicon have been tentatively selected as the "ductile-brittle" components. Cu and Si also form the same sequence of electron-compounds as Cu-Zn and Si is readily available and inexpensive. Preliminary tests with Cu and Si will be reported below along with the more extensive data on Cu-Zn.

C. Brittle-Brittle Powders

While it is not obvious that mechanical alloying could occur between brittle components, there is evidence of material transfer during dynamic friction tests of brittle WC (7) and evidence of major structural changes on grinding of brittle compounds (8). Selection of brittle-brittle model systems will be made for studies in the coming year. Possibilities are Cr-Si or Mo-Si.

IV. Process Variables

The tests conducted during this reporting period used a constant ball to powder weight ratio of 5:1. Therefore, the kinetic energy of the impacting medium was kept constant.

The vial temperature increases from room temperature at the start of milling to about 65°C after approximately 90 minutes. The macroscopic temperature was measured by thermocouples both external and internal to the vial. Changing the average temperature of the vial by either forced air convection (a fan), to about 35°C, or by blowing liquid nitrogen on the vial, to about -15°± 5°C, made substantial changes in the powder yield by modifying the degree of cold-welding to the vial walls and milling medium. The change in average temperature with milling time is illustrated in Figure 1a, b, and c for the three above cases.

The average temperatures described above do not indicate what the instantaneous temperature of the powder surfaces may attain during impact. There are some upper limits to what this temperature might be. Amorphous Ni_{60} Nb_{40} powders don't crystallize during MA (5), therefore, the crystallization temperature is not reached. The melting point is not reached since the powder surface morphology, as determined by scanning electron microscopy, remains jagged and angular after MA. Experiments are planned, and will be described below in which changes in the powder structure during MA will provide information on the temperature increases that occur.

The most interesting result of our study of MA of the Cu-Zn powders was the observation of the formation of bcc β brass at 50 and 52.5 weight percent Cu from MA of elemental Cu and Zn powder mixtures. X-ray diffraction analysis indicated the β brass formed in about three hours of MA under ambient conditions with a complete disappearance of Cu and Zn diffraction lines. Besides the bcc lines, the possible presence of an fct martensitic structure was also observed. (9) Confirmation of the martensite will require TEM study. When the powder was MA in air, ZnO lines were also present.

Electron probe analysis of the MA Cu-Zn powders revealed iron contamination from the vial and/or milling medium of the order of 0.5 weight percent maximum after MA for three hours. The formation of the bcc structure from the fcc and hcp starting components gives a very clear probe of the extent of MA and will be used extensively in our studies of process variables. A short note describing the formation of β brass and possible mechanisms will be prepared shortly.

Preliminary studies of the formation of bcc β-phase in the ductile-brittle case of Cu-Si has focused on Cu-8 weight percent Si mixtures. After about ten hours of MA, βCu-Si lines appeared along with the Cu lines. Further work on this system is continuing.

V. Macroscopic Cold-Welding

The effort during the reporting period on the macroscopic cold-welding studies to parallel the MA work has been confined to a study of the extensive literature on this subject. It would appear that a dynamic friction experiment would more closely duplicate the action during MA than a static compressive test. Such experiments will be planned for the next year's research.

VI. Visits from INCO

On May 23, 1985 we were visited by Dr. John J. deBarbadillo, R and D Department Manager, and Dr. John H. Weber, R and D Fellow, of INCO Alloys International, Huntington, West Virginia. The INCO MA research and development is now located at Huntington since the closing of the Sterling Forest research laboratory. Drs. deBarbadillo and Weber were very interested in our work on MA and supplied us with a number of their reports which are not easily obtainable in the open literature. We agreed to keep each other informed on our research in this area. C. C. Koch will visit the Huntington laboratories later this year.

VII. Transmission Electron Microscopy of MA Powders

A significant aid to understanding the mechanism of MA should come from the direct observation of the powder microstructure as it develops. While optical microscopy and scanning electron microscopy illustrate the development of the powder morphology during MA, only TEM can reveal the internal structure. Of special interest is the structure at the transition from an intimate mixture of dissimilar powders to an "alloy". Techniques for thinning the MA powders were explored during the reporting period. The most promising method appears to be mixing the powders with a special epoxy in a 3 mm diameter tube, sectioning the tube and thinning the composite wafer by ion-milling or electrochemically.

Research Planned for the Period July 1, 1985 - June 30, 1986

The experiments to determine the local powder temperatures during MA will be conducted. One approach will be to monitor the structural changes - tempering - of Fe-C martensite during MA of a fresh, brittle, martensite. Probes of the tempering reaction will include microhardness, x-ray diffraction, and thermal response measured in a differential scanning calorimeter. The other method will involve commercial melting point standard crystals that melt at different temperatures. These are supplied in powder from Omega.

Once the powder temperature has been measured and calibrated to the average vial temperature, the influence of temperature on the structural changes during MA will be followed. These changes will be followed by transmission electron microscopy along with x-ray diffraction.

More extensive work on the ductile-brittle system will be pursued and a brittle-brittle system will be explored.

The attritor mill will be used and results from the SPEX mill will be checked with the larger volume of powder MA in the attritor. This will give data which can be scaled to production processes.

A device for studying the macroscopic cold welding will be built to try to understand the variables which influence the movement of material at the surface. These results will be compared to the MA parameters.

Comparisons between both MA and macroscopic cold welding experiments will be made as a function of environment - air vs. inert atmosphere.

With the experimental results obtained, a first attempt to model the mechanical alloying process will be made. Models for cold welding and dynamic friction will be used for guidance.

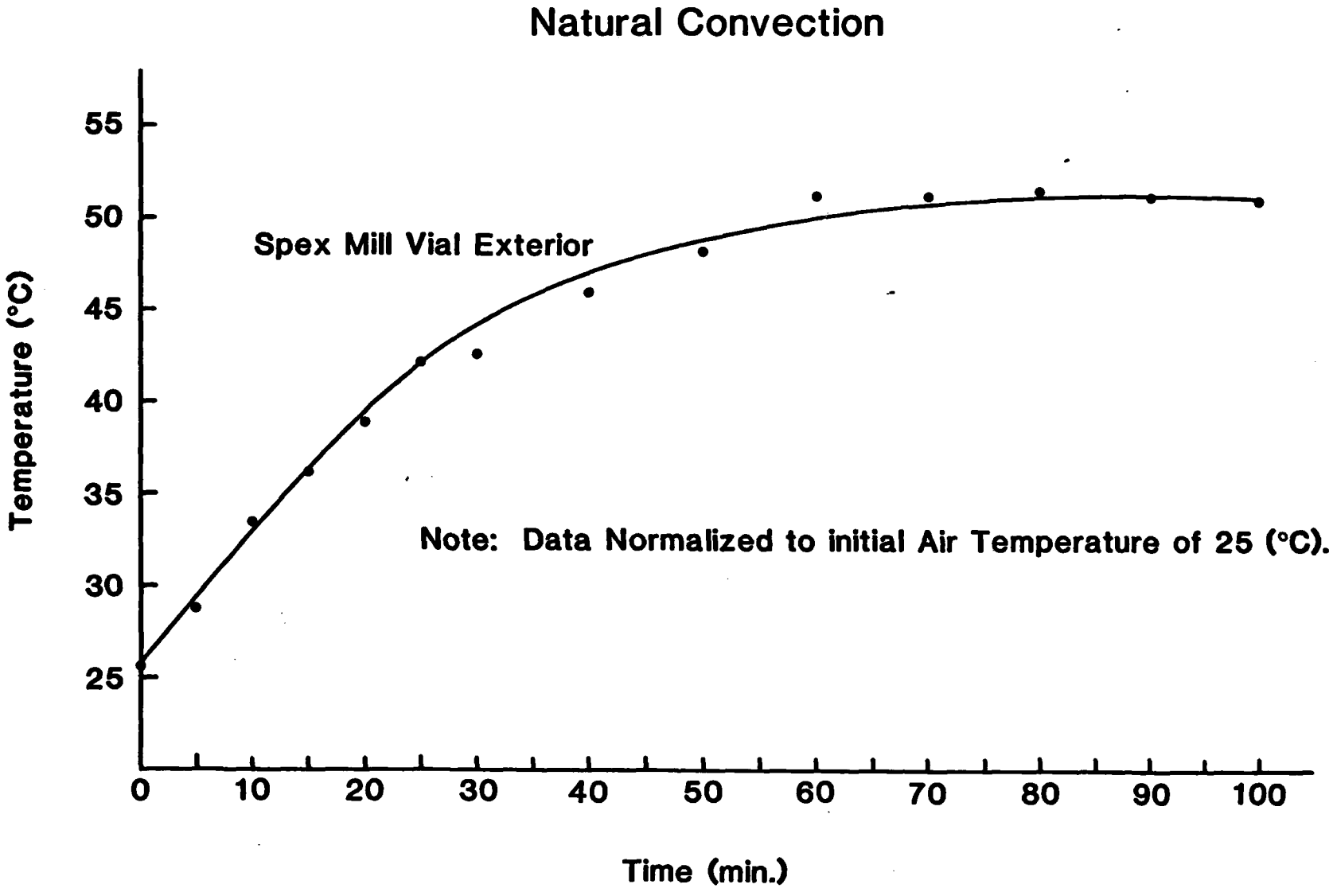
Natural Convection
Spex Mill Vial Exterior
Note: Data Normalized to initial Air Temperature of 25 (°C).
Temperature (°C)
55
50
45
40
35
30
25
0
10
20
30
40
50
60
70
80
90
100
Time (min.)

Figure 1a

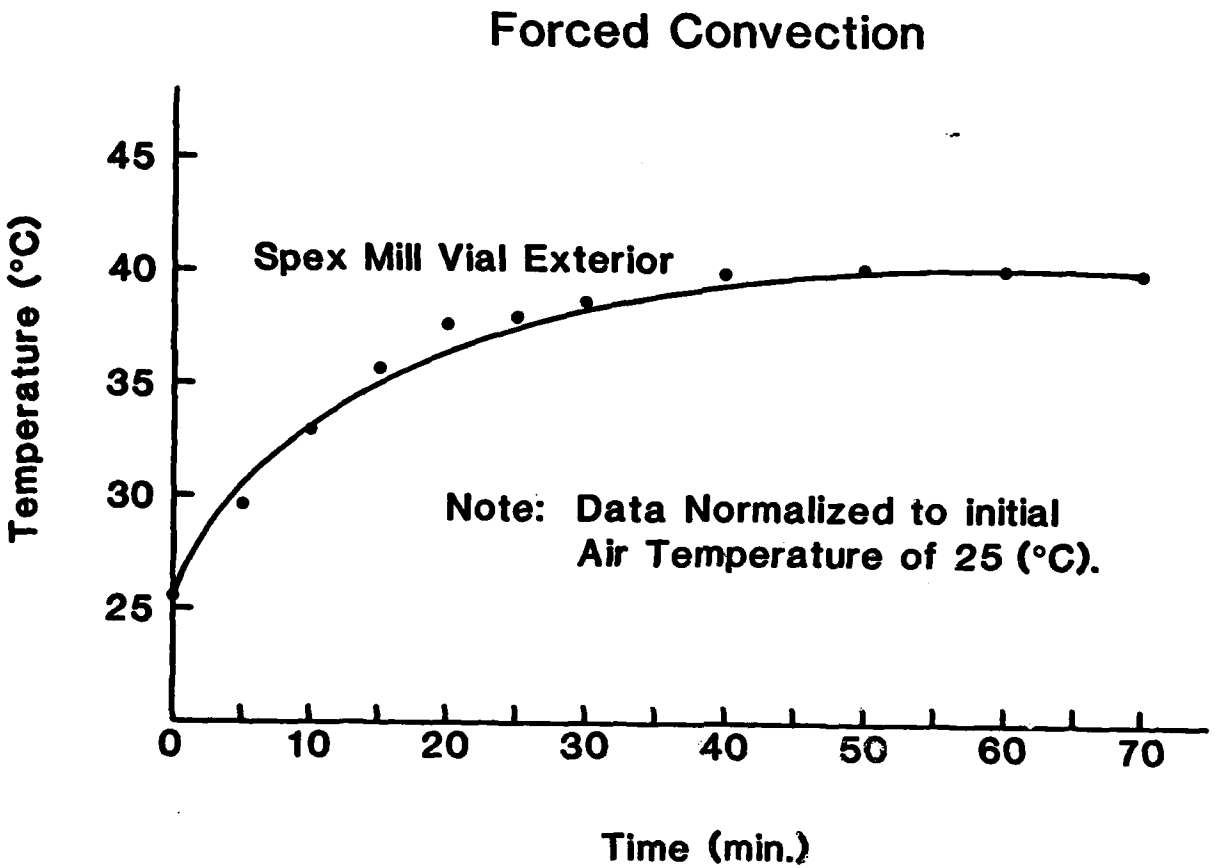
Forced Convection
Temperature (°C)
45
40
35
30
25
Spex Mill Vial Exterior
Note: Data Normalized to initial
Air Temperature of 25 (°C).
0
10
20
30
40
50
60
70
Time (min.)

Figure 1b

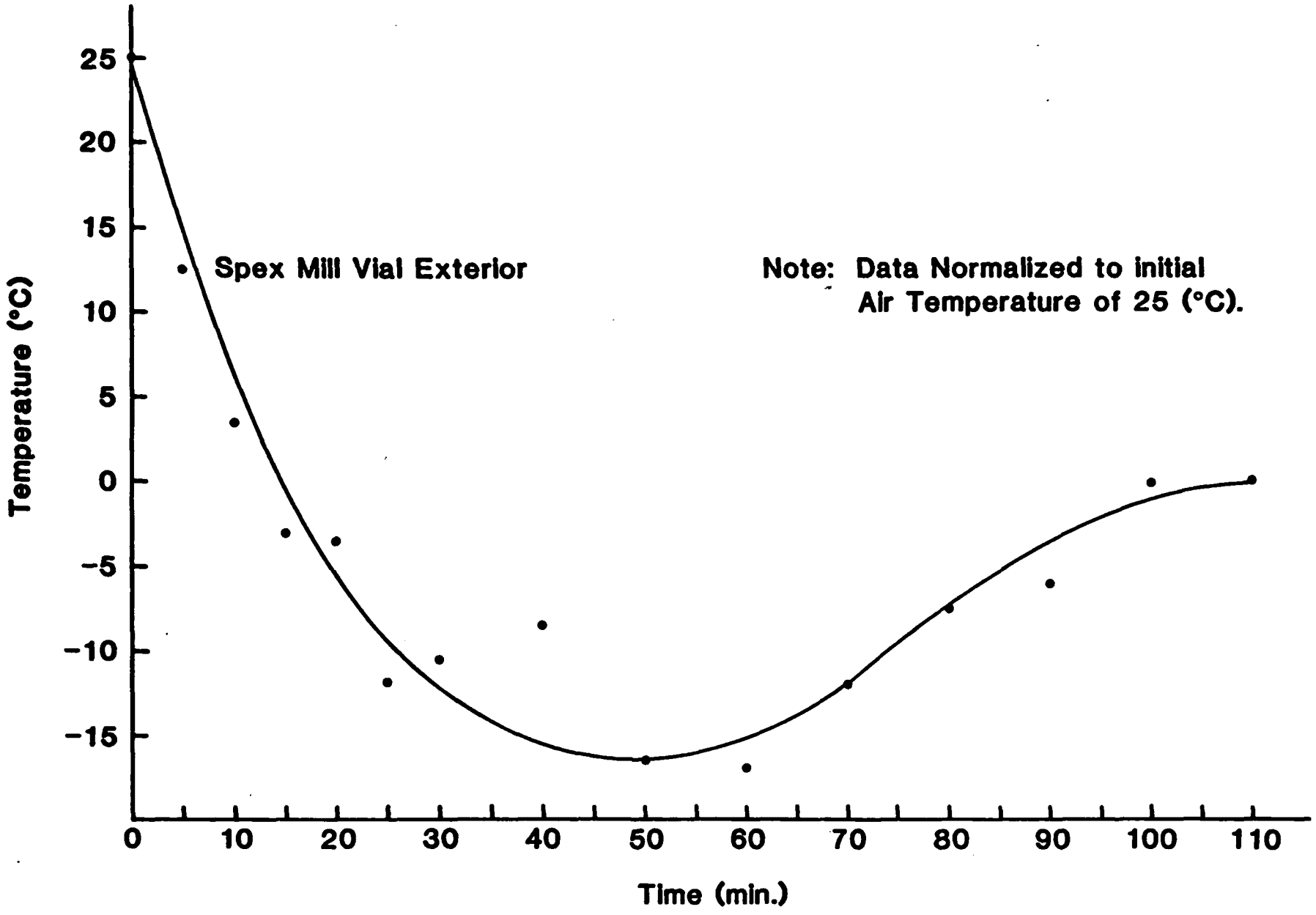
Liquid Nitrogen Chilled
Spex Mill Vial Exterior
Note: Data Normalized to initial
Air Temperature of 25 (°C).
Temperature (°C)
25
20
15
10
5
0
-5
-10
-15
0
10
20
30
40
50
60
70
80
90
100
110
Time (min.)

Figure 1c

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