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Part IV

# EFFECT OF BASIC PHYSICAL PARAMETERS ON ENGINEERING PROPERTIES OF INTERMETALLICS
## Part IV



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J.H. Westbrook and D.L. Wood, authors)

## NOTICES

## FOREWORD

This report was prepared by the General Electric Research Laboratory under USAF Contract No. AF 33(616)-7714. This contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," and Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Lt. Jacobsen acting as project engineer.

This report covers work conducted from December 1961 to December 1962.

A. J. Peat assisted in many phases of the experimental program; L. C. Cook performed the tensile tests; W. J. Baxter carried out the extrusion of materials to specimen shape. For these contributions, the authors express their gratitude.

# ABSTRACT

This report is a continuance of the authors' mechanical property measurements and grain boundary studies on AgMg. A general survey of the effects of dilute ternary solute additions on the flow stress of AgMg has been made. A unique, efficient device to measure ductile-brittle transition temperatures on wire specimens has been designed and built. Using this device, the effects of composition, grain size, strain rate, and ternary solute additions on the transition temperature have been documented for AgMg. Further studies of the kinetics of solute-induced grain boundary hardening indicate that the phenomenon is much more complex than previously supposed.

This technical documentary report has been reviewed and is approved.

W G Ramke

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

## LIST OF TABLES

EFFECT OF BASIC PHYSICAL PARAMETERS
ON ENGINEERING PROPERTIES OF INTERMETALLICS

J. H. Westbrook and D. L. Wood

## I. INTRODUCTION

There are among the intermetallic materials several compounds which are of considerable potential for high-temperature structural applications. The use of intermetallics as structural materials, however, as well as their mechanical fabrication for experimental and other uses has been hindered by the general absence of knowledge or understanding of their mechanical behavior. This contract is directed toward filling this gap with particular attention to what is probably the most serious mechanical shortcoming of intermetallics: their lack of ductility at ordinary temperatures.

The program seeks the establishment of correlations of structural, compositional, and physical parameters of intermetallic compounds with their mechanical properties. It is hoped that such correlations will lead to an elucidation of the factors affecting the flow process in such materials, and particularly to a better understanding of the source of brittleness in polycrystalline intermetallics.

From December 1958 to December 1960, techniques were developed for producing suitable test specimens of both AgMg and NiAl, methods for testing were devised, and the tensile behavior of the CsCl structure compound AgMg was extensively documented in terms of strain, strain rate, temperature, grain size, composition, and metallurgical processing treatment. These results are summarized in WADD Technical Report 60-184--Part I, August 1960, and Part II, September 1961.

From December 1960 to December 1961, a study was made of the grain boundary hardening which was found to occur in many intermetallic compounds having a stoichiometric excess of active metal component. This grain boundary hardening was shown to be associated both with the anomalously high ductile-brittle transition temperatures common in these materials and with the "pest" phenomenon occurring in certain intermetallics. The results of this study are described in WADD Technical Report 60-184--Part III, July 1962.

On the basis of an evaluation of these results, the program was directed during the current work period toward an evaluation of the effects of dilute ternary solute additions on the mechanical properties, toward a more

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direct study of the effects of metallurgical and process variables on the ductility, and toward an improved understanding of the grain boundary segregation phenomenon.

## II. MECHANICAL PROPERTY STUDIES

An extensive study of the tensile flow stress of the binary compound AgMg has been carried out previously under this contract.[1] In that study an evaluation was made of the effects of binary composition, temperature, strain and strain rate. This accumulated information has made possible extensions of the exploration in directions which contribute not only to the fundamental understanding of the mechanical behavior of intermetallics but also to enlightened considerations of the potential capabilities of such materials to meet the requirements imposed in practical structural applications.

One of the primary objectives of the program has been, from the outset, an elucidation of the brittleness problem in intermetallics, and the formulation of a solution to the problem if such be possible. Practical realization of an intermetallic structural material will require, in addition, improvements in strength level and improved understanding of strengthening mechanisms. Specific attacks on these objectives during the past year have included studies of the effect of dilute ternary additions on the flow stress and the effects of metallurgical variables on the ductile-brittle transition temperature. As with the previous study of tensile behavior, the experimentally attractive compound AgMg has served as a material for the initial phase of the program.

### A. Experimental Observations

#### 1. Effect of Ternary Additions on the Flow Stress of AgMg

A group of AgMg alloys of various base compositions and containing dilute ternary solute additions of either Cu, Zn, Sn, Al, or Ce were processed by the usual methods[2] into 0.040-inch-diameter tensile specimens which were then strained at various temperatures. Examination of the flow stress data for these single-phase ternary compounds shows that analysis of the solid solution strengthening imparted by ternary solutes is more difficult than previously reported. The reason is as follows: although regular increases in flow stress with ternary additions are observed at all temperatures for bases containing silver in excess of the stoichiometric composition, compounds containing an excess of magnesium may exhibit either an increase, a decrease, or no significant change in flow stress upon ternary alloying according to the temperature and ternary solute employed.

Table I gives the values of flow stress for the dilute ternary AgMg base alloys and Table II the corresponding lattice parameter data. It may be seen from Table I, for example, that with an addition of 1 A/o Zn, a base

TABLE I

Flow Stress at Various Temperatures for Dilute Ternary AgMg Base Alloys Annealed at 400°C, with Values for the Flow Stress of the Binary Base, Which are Interpolations of Previous Data, Shown for Comparison

| Composition | | | Flow Stress (1000 psi) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Binary Base | | | | Ternary Alloy | | | | |
| Alloy No. | Binary Base (A/o Mg) | Ternary Solute (A/o) | RT | 100°C | 200°C | 250°C | RT | 100°C | 150°C | 200°C | 250°C |
| 11 | 49.6 | 1.0 Sn | 21.0 | 17.0 | 10.5 | 6.4 | 32.2 | 28.0 | 27.2 | 25.4 | 21.2 |
| 12 | 49.8 | 2.0 Sn | 17.1 | 14.5 | 8.7 | 5.2 | * | * | * | * | * |
| 13 | 50.7 | 1.0 Zn | * | * | 24.5 | 12.0 | 24.4 | 20.4 | -- | 16.0 | 11.2 |
| 14 | 50.8 | 2.0 Zn | * | * | 25.5 | 12.8 | 29.4 | 28.9 | -- | 20.2 | -- |
| 38 | 49.8 | 1.0 Zn | 17.1 | 14.5 | 8.7 | 5.2 | 30.0 | 26.0 | 23.6 | 20.8 | 11.2 |
| 20 | 50.2 | 1.0 Cu | * | * | 16.0 | 8.0 | 33.6 | 28.6 | -- | 25.2 | 18.8 |
| 29 | 50.7 | 1.1 Cu | * | * | 24.5 | 12.0 | 25.0 | 22.0 | -- | 16.8 | -- |
| 34 | 52.0 | 1.0 Cu | * | * | 34.5 | 16.8 | * | * | * | 34.6 | -- |
| 23 | 50.5 | 1.2 Al | * | * | 22.5 | 11.0 | 33.3 | 33.0 | -- | 27.8 | -- |
| 35 | 48.3 | 1.3 Al | 32.0 | 28.4 | 16.2 | 9.6 | 34.8 | 33.6 | 31.6 | 26.7 | 18.0 |
| 36 | 49.3 | 2.5 Al | 25.0 | 20.5 | 12.5 | 7.5 | 32.4 | 32.4 | -- | 32.8 | 27.5 |
| 27 | 50.7 | 0.05 Ce | * | * | 24.5 | 12.0 | * | 34.8 | -- | 25.6 | 18.4 |

*Denotes insufficient ductility to permit testing.

TABLE II

Lattice Parameters for Dilute Ternary AgMg Base Alloys Annealed at 400°C with Values for the Lattice Parameter of the Binary Base, Which Are Interpolations of Previous Data, Shown for Comparison

| | Composition | | $a_0$ | |
|---|---|---|---|---|
| Alloy No. | Binary Base (A/o Mg) | Ternary Solute (A/o) | Binary Base (A) | Ternary Alloy (A) |
| 11 | 49.6 | 1.0 Sn | 3.3127 | 3.3163 |
| 12 | 49.8 | 2.0 Sn | 3.3130 | 3.3202 |
| 13 | 50.7 | 1.0 Zn | 3.3158 | 3.3132 |
| 14 | 50.8 | 2.0 Zn | 3.3166 | 3.3120 |
| 38 | 49.8 | 1.0 Zn | 3.3130 | 3.3105 |
| 20 | 50.2 | 1.0 Cu | 3.3142 | 3.3099 |
| 29 | 50.7 | 1.1 Cu | 3.3158 | |
| 34 | 52.0 | 1.0 Cu | 3.3210 | 3.3158 |
| 23 | 50.5 | 1.2 Al | 3.3154 | 3.3123 |
| 35 | 48.3 | 1.3 Al | 3.3100 | 3.3086 |
| 36 | 49.3 | 2.5 Al | 3.3121 | 3.3076 |
| 27 | 50.7 | 0.09 Ce | 3.3158 | 3.3143 |

containing 49.8 A/o Mg (No. 38) is strengthened while a base containing 50.7 A/o Mg (No. 13) is weakened by the addition. Similarly, the addition of 2 A/o Zn weakens a base containing 50.8 A/o Mg.

Although in all Ag-rich bases of Table I, a ternary addition resulted in strengthening, it would appear that the effect of ternary additions to Mg-rich bases cannot be easily predicted. Table I shows, for example, that 1 A/o Cu increases the flow stress of a base containing 50.2 A/o Mg (No. 20), while a base containing 50.7 A/o Mg is weakened by a similar addition of Zn. Furthermore, such an addition to 52.0 A/o Mg appears to have little effect, at least at 200°C. The lattice parameter data in Table II were originally obtained with the intention of correlating solute-induced changes in flow stress with lattice strain. However, as was reported previously,[3] and is established more completely in a later section of the present report, the effects of solute additions on flow stress are rendered ambiguous by their concomitant interaction with the grain boundary hardening phenomenon. Therefore, no further attempts were made to utilize the lattice parameter data in a quantitative way.

## 2. Effect of Metallurgical Variables on the Ductile-Brittle Transition Temperature of AgMg

Brittleness at very low temperatures is a normal property of most metals and alloys having a body-centered cubic or hexagonal crystal structure. In such materials it is not uncommon to observe a so-called ductile-brittle transition temperature, at which there is a marked change in the ductility. At temperatures above the ductile-brittle transition temperature the material behaves in a ductile manner; below, it behaves in a brittle manner.

Although determination of the temperature at which a material no longer behaves in a ductile fashion has been in large part connected with assessment of suitability of a material for service, the transition temperature has also proved to be a useful parameter in fundamental explorations of the effects of metallurgical variables on ductility. The types of test employed for determination of the change from ductile to brittle behavior, as well as the criteria for defining the transition temperature, vary widely. All of the conventional methods of determination of transition temperatures involve rather time-consuming and tedious testing of large numbers of specimens. Furthermore, variation in material from specimen to specimen necessarily contributes to the scatter and thus limits the usefulness of such tests in studies of the effects of metallurgical variables on the transition temperature. It is desirable, therefore, to employ a method for measuring transition temperatures which involves only one test on a single specimen. A device capable of such measurements has been designed and built, and the effects of composition, grain size, thermal treatment, and strain rate on the transition temperature of AgMg have been measured.

(a) The Bend-Test Apparatus. The apparatus illustrated schematically in Fig. 1 is designed to bend a wire or strip specimen at a constant rate around a drum of uniform diameter while the temperature of the specimen is being decreased. The "transition temperature" is that temperature at which the specimen will no longer tolerate bending at a given rate to the fixed strain determined by the diameter of the drum and the diameter or thickness of the specimen.

Variation in relative strain rate from 1 to 180 is accomplished by various combinations of motor speed and drive gears. At the slowest rate the specimen is bent around the drum at 1 linear inch per 18 minutes; at the fastest rate, 1 linear inch of specimen is bent every 6 seconds. Further variation in strain rate could be accomplished either by changing the diameter of the drum (2 inches in diameter in the present case) or the diameter of the specimen (0.040 inch in the present case) if these parameters were changed proportionately so as to maintain a constant strain.

Control of temperature is obtained by immersing the mechanical apparatus in a silicone oil bath. A motor-driven stirrer contributes to the

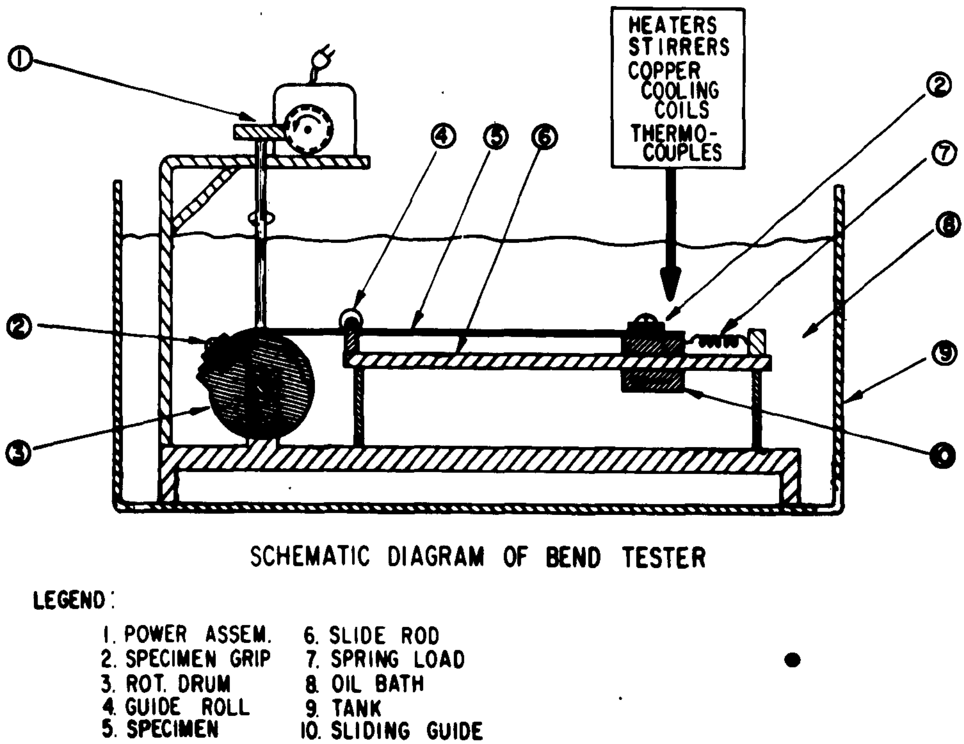



Fig. 1 Schematic diagram of bend tester.

maintenance of uniform bath temperature. The bath is heated initially to a temperature sufficient to permit bending of the specimen without fracture. After this condition has been established, the drum is set in continuous rotation and cooling is initiated by shutting off the thermal power input to the bath. Bath cooling rates faster than natural cooling are obtained by forced water cooling through a number of copper coils immersed in the bath. In the present apparatus, some examples of cooling rates available are shown in Table III. As the bath and specimen cool, bending is continued until fracture occurs; the temperature of the bath at the time of fracture is recorded. The reproducibility of measured transition temperatures is found to be of the order ±10°C at a level of 170°C and ±2° at a level of 60°C.

(b) Effects of Prior History and Composition. Although no transition temperature measurements were made on cast material because of the extreme difficulty of producing satisfactory test specimens, it would appear that the entire range of compositions of AgMg will not withstand any plastic deformation at room temperature in the as-cast state. This statement is based on qualitative observations of the ability of the material to be deformed by bending by hand at room temperature. At temperatures of the order of

TABLE III

Examples of Cooling Times and Corresponding Rates Available in Bend Test Apparatus

| | Cooling Condition | | | | | |
|---|---|---|---|---|---|---|
| | Fast | | Intermediate | | Slow | |
| Temp Range (°C) | Time (min) | Rate (°C/min) | Time (min) | Rate (°C/min) | Time (min) | Rate (°C/min) |
| 200-160 | 1.5 | 27 | 6 | 6.5 | 28 | 1.4 |
| 160-120 | 3.5 | 11 | 10 | 4.0 | 40 | 1.0 |
| 120-80 | 6 | 6.5 | 14.5 | 2.8 | --* | --* |
| 80-40 | 11.5 | 3.5 | 30 | 1.3 | --* | --* |

*Impractical because of the minimum strain rate presently available.

0.5 of their absolute melting temperature, on the other hand, all compositions can be made to flow readily at moderately fast strain rates. It is this high-temperature ductility that permits the extrusion of cast billets to the 0.040-inch-diameter wires that were used in the present study.

Once some deformation has been performed, however, the mechancal behavior is markedly changed. A considerable enhancement of the low-temperature ductility of Ag-rich compositions by extrusion is evidenced by the fact that the extruded wires can be bent severely and rapidly, even at temperatures as low as that of liquid nitrogen. The extent to which Mg-rich compounds are "enductiled" by extrusion is more difficult to ascertain. It seems clear, however, that at least for compounds containing only very small concentrations of excess Mg a significant enhancement of ductility is also achieved; e.g., an extruded wire of 50.1 A/o Mg can be bent at room temperature.

Figure 2 shows the relation of the transition temperature to the logarithm of the Mg concentration in excess of the stoichiometric composition, 50 A/o. These same data are replotted in a different manner in Fig. 3 which also shows the related dependence of grain boundary hardening on composition. The effects of stoichiometry are very striking. Unfortunately, the observed effects of composition on transition temperature are obviously due at least in part to the grain boundary hardening phenomenon. The effects of composition, per se, on the transition temperature are further complicated by an apparent variation with composition of the beneficial effects imparted by extrusion. New and ingenious experiments must be designed to separate these various factors.

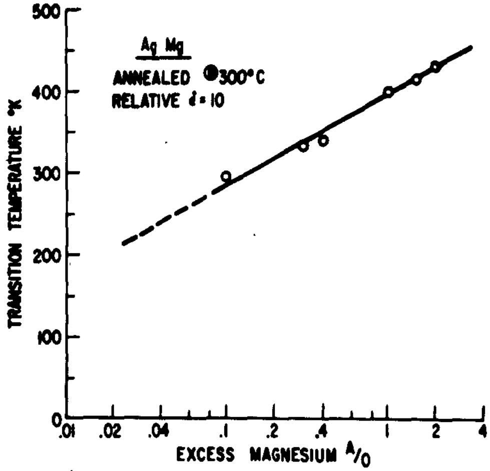
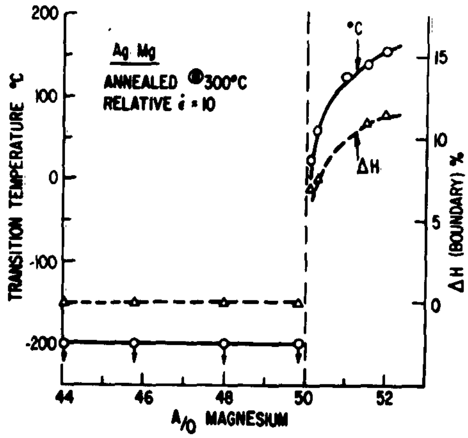



Fig. 2 Ductile-brittle transition temperature for Mg-rich AgMg compounds as a function of the logarithm of the concentration of magnesium in excess of the stoichiometric composition (50 A/o).

Fig. 3 Ductile-brittle transition temperature and increment of grain boundary hardening for AgMg compounds as a function of composition.




(c) Effect of Dilute Ternary Additions. Previous work on grain boundary hardening showed that various additions of ternary solute elements could either remove the hardening from compounds which once had it or cause it to occur in compounds originally free from it. In view of the good correlation in the foregoing section between grain boundary hardening and transition temperature, it is of interest to consider the effects of dilute ternary solute additions on the transition temperature.

Although quantitative data are not complete at the time of writing of this report, those which are available, together with some additional qualitative observations, are of sufficient import to warrant inclusion here. Table IV shows the composition of the binary base, the ternary solute concentration, the presence or absence of grain boundary hardening in both binary and ternary, and the measured transition temperature of both the binary and the ternary compounds.

TABLE IV

| Alloy No. | Binary Base (A/o Mg) | Transition Temp °C of Binary Base | Room Temp Grain Boundary Hardening in Binary Base | Ternary Solute (A/o) | Transition Temp (°C) | Room Temp Grain Boundary Hardening in Ternary $\left[\frac{\Delta H}{H}(\%)\right]$ |
|---|---|---|---|---|---|---|
| 11 | 49.6 | <-195 | No | 1.1 Sn | 83 | 18 |
| 12 | 49.8 | <-195 | No | 2.0 Sn | 200 | 17 |
| 38 | 49.8 | <-195 | No | 1.0 Zn | <-195 | 0 |
| 13 | 50.7 | 105 | Yes | 1.0 Zn | 40 | 8 |
| 14 | 50.8 | 110 | Yes | 2.0 Zn | <-195 | 0 |
| 20 | 50.2 | 45 | Yes | 1.0 Cu | <-195 | 0 |
| 29 | 50.7 | 105 | Yes | 1.1 Cu | <-195 | 0 |
| 34 | 52.0 | 157 | Yes | 1.0 Cu | 171 | 12 |
| 35 | 48.3 | <-195 | No | 1.3 Al | <-195 | 10 |
| 36 | 49.3 | <-195 | No | 2.5 Al | <-195 | 24 |
| 23 | 50.5 | 88 | Yes | 1.2 Al | <-195 | 15 |
| 27 | 50.6 | 97 | Yes | 0.09 Ce | 35 | 0 |

Additions of Sn to Ag-rich material cause grain boundary hardening to occur and cause the transition temperature to be increased to values considerably above room temperature. Additions of Zn, on the other hand, do not promote grain boundary hardening or brittleness in Ag-rich compounds. In fact, in some instances, additions of Zn or of Cu to Mg-rich material eliminate grain boundary hardening and cause the transition temperature to be decreased to a value below room temperature. Additions of Al cause grain boundary hardening to occur even in Ag-rich material, but for some reason do not cause the transition temperature to rise above room temperature.

It is interesting to note that in alloy No. 13 the addition of 1 A/o Zn is apparently not sufficient to depress the transition temperature below room temperature, as is the case for the addition of 2 A/o Zn, in alloy No. 14. Another interesting observation is that the addition of about 1 A/o Cu to a base containing 50.7 A/o Mg caused the transition temperature to be below room temperature while the addition of a similar amount of Cu to a base containing 52.0 A/o Mg does not remove grain boundary hardening and actually increases the transition temperature above that which would occur normally for the binary alloy.

(d) Effects of Thermal Treatment. Studies of thermal treatment were carried out largely on a single Mg-rich composition, 50.3 A/o Mg. Extrusion to 0.040-inch-diameter wire results in a relatively fine grain size ($1.7 \times 10^{-3}$ cm diameter). During a 1-hour anneal of extruded wires, grain growth does not occur at temperatures below about 300° to 350°C. However, significant changes in the transition temperature of Mg-rich compounds result from annealing at temperatures below that necessary for grain growth. Figure 4 shows the transition temperature as a function of annealing temperature; also included are curves for both bulk and boundary hardness. The effect of heat treatment on the detailed course of the initial decrease in

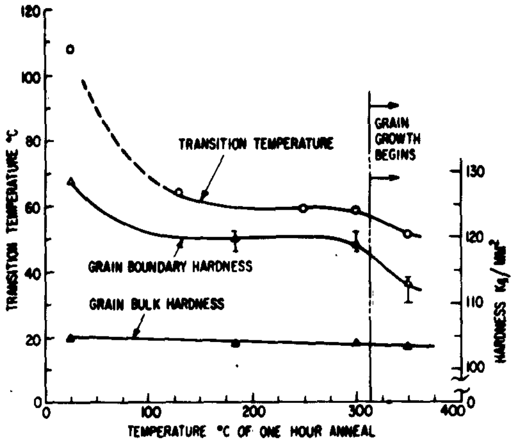



Fig. 4 Transition temperature and hardness (grain boundary and grain center) as a function of annealing temperature for Ag + 50.3 A/o Mg.

transition temperature from the as-extruded value cannot be simply determined. This is a result of the fact that the as-extruded wire itself must be heated in the oil bath to a temperature of about 120°C in order to be tested. This treatment itself is sufficient for some annealing to occur. The datum point at the annealing temperature of 125°C was obtained by annealing the wire <u>in situ</u> in the oil bath immediately prior to testing. Thus, this point is a valid point and corresponds to the lowest annealing temperature at which the effect can be precisely documented. Nevertheless, the transition temperature curve of Fig. 4 shows clearly that during annealing at temperatures below about 100° to 125°C a significant decrease occurs in transition temperature from that of the as-extruded material. Only a slight further decrease in transition temperature occurs until an annealing temperature is approached at which grain boundary migration occurs. During the early stages of annealing, a corresponding decrease in grain boundary hardness with increased annealing temperature is also noted, although the grain center hardness remains relatively unchanged.

Specimens were annealed for grain growth for 1 hour in argon at 400°, 450°, 500°, and 600°C. Figure 5 shows the linear dependence of the inverse of the absolute transition temperature on the reciprocal of the square root of the average grain diameter; an increase in grain size is seen to result in an increase in transition temperature. A transition temperature of 130°C is implied for single crystals of the 50.3 A/o Mg composition. However, the apparent effects of grain size are rendered somewhat ambiguous by the concomitant phenomenon of grain boundary hardening. This follows from the previous observation[3] that the amount of grain boundary hardening increases with annealing temperature because of the enhanced kinetics for oxygen/nitrogen contamination.

(e) <u>Effect of Strain Rate.</u> It has been known qualitatively since the earliest part of the present investigation that the ductility of AgMg compounds

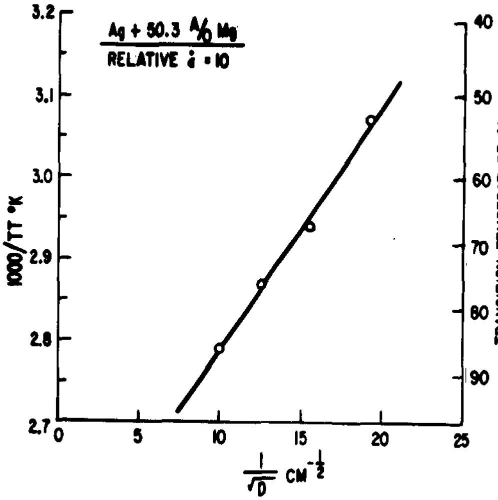



Fig. 5 The inverse of the absolute transition temperature as a function of the reciprocal of the square root of the average grain diameter.

was particularly sensitive to strain rate. A quantitative measure of this sensitivity now has been made possible with the measurement of transition temperature. Fugure 6 shows for Mg-rich compounds the variation in

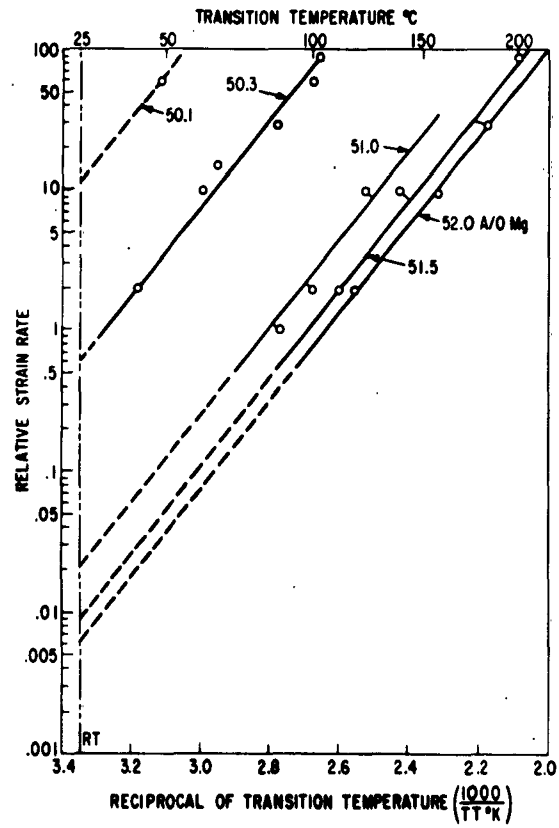



Fig. 6 Logarithm of relative strain rate as a function of the reciprocal of absolute transition temperature.

transition temperature with strain rate. The linear relation shown between log strain rate and reciprocal transition temperature is in accord with similar observations for metals.[4-6]

## B. Discussion of Results

### 1. Consideration of the Effects of Dilute Ternary Solute on Flow Stress

An evaluation of the effects of dilute ternary solute additions shows clearly that any study of the mechanisms of solid solution strengthening in intermetallics must be carried out within quite restrictive limitations. Since the flow stress is most certainly influenced by the presence of grain boundary hardening, consideration of effects of ternary additions on the flow stress cannot be made in a simple, straightforward manner in compounds in which grain boundary hardening normally exists or in those in which such hardening is induced by the addition of the ternary element. Obviously such limitations apply as well to studies of the effect of annealing treatment or of grain size on the flow stress. This follows from the fact that in material of a given composition, the degree of grain boundary hardening is changed as the annealing treatment is varied.

The data shown in Table I point up two facts of great importance in any consideration of intermetallics as a structural material. The first of these is that significant strengthening can be produced by relatively dilute ternary solute additions without impairment, and indeed sometimes with improvement, of low-temperature ductility. This is evidenced, for example, in that 1 A/o Zn increases the flow stress at RT for a near stoichiometric compound (No. 38) by 75 per cent.

The second important fact to be gained from the observations is the marked retention of strength with increasing temperature which is produced by ternary additions. At 200°C (0.43 $T_{mp}$) the addition of 1 A/o Zn to a base containing 49.8 A/o Mg (No. 38) produced a strength 140 per cent greater than that of the binary alloy. At the same temperature a 1 A/o Cu addition (alloy No. 20) increased the flow stress by 50 per cent with a simultaneous improvement in low-temperature ductility. In alloy No. 35 the addition of 2.5 A/o Al to a base containing 49.3 A/o Mg causes a retention of the RT stress value at a temperature of more than 200°C; at 250°C (0.48 $T_{mp}$) the ternary is about 270 per cent stronger than the base binary alloy.

### 2. Considerations of Transition Temperature

(a) Effect of Composition. Because of the occurrence of grain boundary hardening in Mg-rich AgMg it is not possible to draw conclusions from the present study as to the manner in which excess Mg atoms affect the transition temperature. An experiment can be designed, however, to yield this information. In such an experiment a series of specimens of Mg-rich compositions would be treated in an oxygen-bearing atmosphere so as to attain a range of grain boundary hardening in each series. Extrapolation from a plot of the transition temperature as a function of amount of grain boundary hardening for each composition would enable determination of the value of the transition temperature at zero grain boundary hardening. The fundamental relation between composition and characteristic transition temperature could then be obtained. Although the available data are few and scattered, an approach along these lines has been made in Fig. 7. It appears that Mg-rich binaries as well as Mg-rich ternaries with Zn or Cu should show transition temperatures near liquid $N_2$ if grain boundary hardening were removed (i. e., a behavior similar to Ag-rich binaries). Most Ag-rich ternaries have lower transition temperatures than the Mg-rich binaries at equivalent levels of boundary hardening.

It would also be of interest to determine the manner in which the transition temperature varies with composition on the Ag-rich side of stoichiometry. This relationship can be established with adaptation of the present experimental apparatus to subnormal temperatures. Such information would be meaningful not only in fundamental considerations of the brittleness problem, but also in considerations of optimum composition of potentially practical materials such as NiAl, etc.

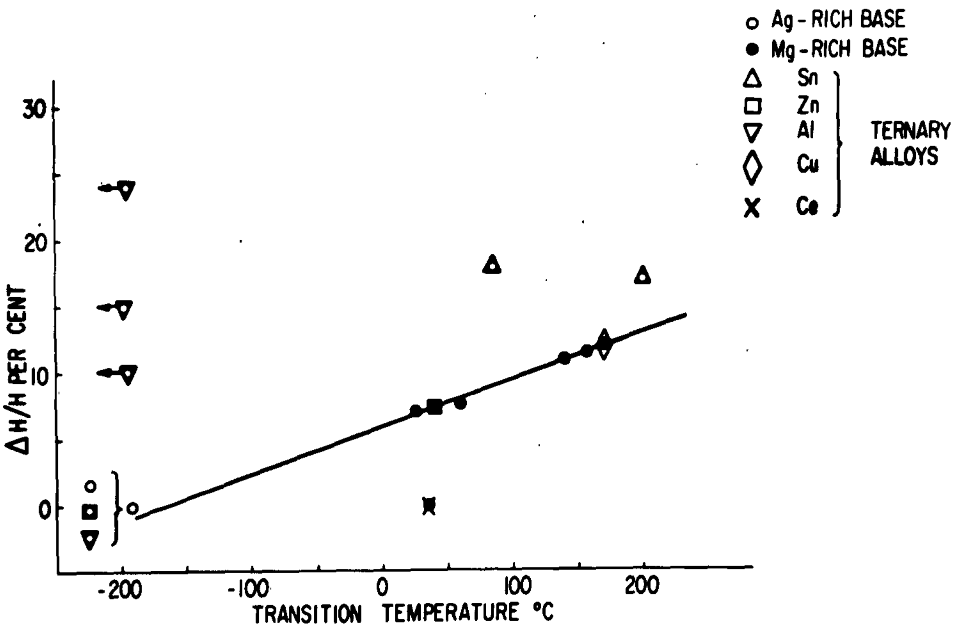



Fig. 7 The relation of the amount of grain boundary hardening, $\Delta H/_H$ to the transition temperature of both binary and ternary AgMg compounds.

Small ternary solute additions impart effects of the greatest importance to the ultimate practical utilization of intermetallics. For example, an addition of 1 A/o Zn, Cu, or Al to a near stoichiometric base has been shown to lower the transition temperature by ~400°C. Furthermore, as was pointed out in the preceding section, such additions may simultaneously cause an increase in the flow stress of the base material.

In contrast to the apparent direct correlation between grain boundary hardening and transition temperature shown in Fig. 3, gross exceptions to such a relationship are noted for the ternary compounds shown in Table IV. This is particularly evidenced by the fact that additions of Al, although they promote grain boundary hardening (and cause an increase in flow stress), cause a lowering of the transition temperature.

It appears, therefore, that the grain boundary brittleness of these materials has a more subtle and complex basis than that which can be detected by means of the microhardness test. It is found, for example, that using a base of near stoichiometric composition, additions of either Sn or Mg tend to embrittle the material, while additions of Zn, Cu, Al, or Ag do not cause embrittlement but rather often result in "enductilement." It of interest to note that additions of Sn and Mg expand the AgMg lattice, while additions of Zn, Cu, Al, and Ag contract the lattice.

(b) Effect of Thermal Treatment. The observation that the transition temperature of AgMg is affected by annealing of extruded material at temperatures below those necessary for grain growth cannot be explained simply on the basis of a stress-relief anneal. This statement is based on the fact that only small differences are found to exist between the bulk hardness values of as-extruded material and material annealed at 300°C. The decrease in transition temperature may be due to the observed decrease in grain boundary hardening resulting perhaps from an alteration of the substructure of the material; e.g., rearrangement of the subgrains or a redistribution of impurities.

The increase in transition temperature which is brought about by annealing at temperatures above about 350°C arises from at least two (perhaps related) sources: that of the increased grain size itself and that of the increased boundary hardening that is a result of the higher annealing temperature. It is interesting to speculate as to how much the often observed and generally accepted dependence of ductility on grain size in metals is due to impurity segregation to grain boundaries.

(c) Effect of Strain Rate. The effects of composition on transition temperature have been demonstrated in Figs. 2 and 3. Alternatively the effects of composition on deformability can be viewed in terms of the strain rate corresponding to a constant transition temperature. The curves of Fig. 6 were extrapolated to room temperature and the corresponding strain rates were plotted against composition in Fig. 8. The logarithm of the strain rate is seen to be a steep hyperbolic function of composition. It is not yet clear whether or not a discontinuity exists in this function at the stoichiometric composition.

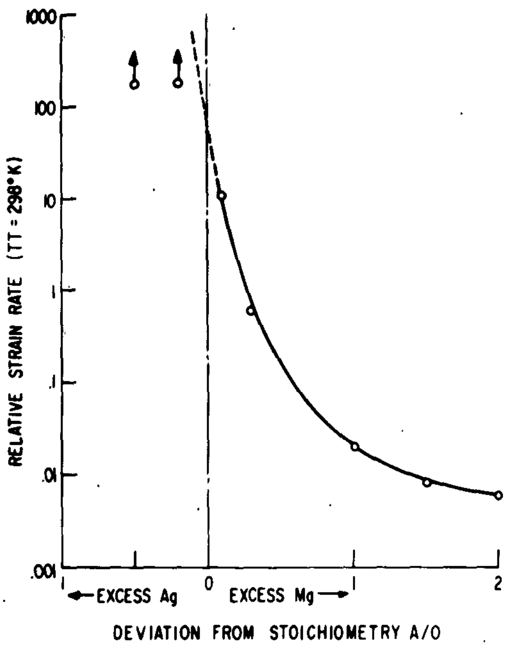



Fig. 8 Values of relative strain rate corresponding to a transition temperature of 298°K, extrapolated from Fig. 7, as a function of compositional deviation from stoichiometry.

## III. GRAIN BOUNDARY STUDIES

The last summary report(3) as well as the current studies reported above, demonstrated that intermetallic compounds with an excess of the electropositive element exhibit grain boundary hardening which can be associated with the anomalously high ductile-brittle transition temperatures in these materials. This hardening has been further shown to result from grain boundary concentrations of oxygen and nitrogen although no second phase can be detected at grain boundaries even with the electron microscope. During the present period, the effects of composition, temperature, and heat treatment on the steady-state hardening of both bulk and grain boundary were studied. In addition, some kinetic studies of the hardening reaction were performed.

Typical time dependence of hardening of both bulk and boundary in a Mg-rich AgMg composition following a quenching heat treatment is reproduced in Fig. 9. In the previous work the grain boundary effect was demonstrated to be due to the local presence of solute oxygen, but the bulk effect could only be surmised to result possibly from analogous interaction of solute with internal defects in the bulk lattice. The kinetics of the rehardening following quenching have been examined from -70°C to room temperature. An Arrhenius plot of such data for the grain boundary hardening is shown in Fig. 10. A parallel and almost coincident straight line was also found for the bulk hardness. The low slope observed corresponds to such a low activation energy, 1.3 kcal, that it does not seem likely that it characterizes a single process.

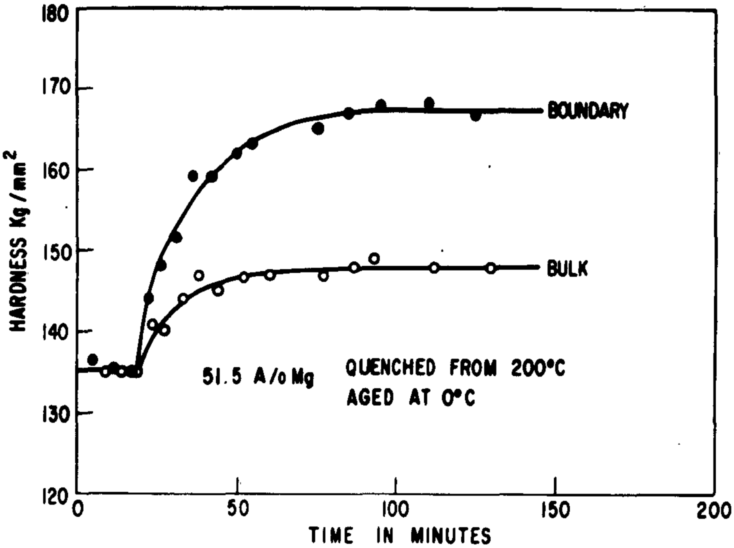



Fig. 9 Boundary and bulk hardness of Ag + 51.5 A/o Mg quenched from 200°C as a function of aging time at 0°C.

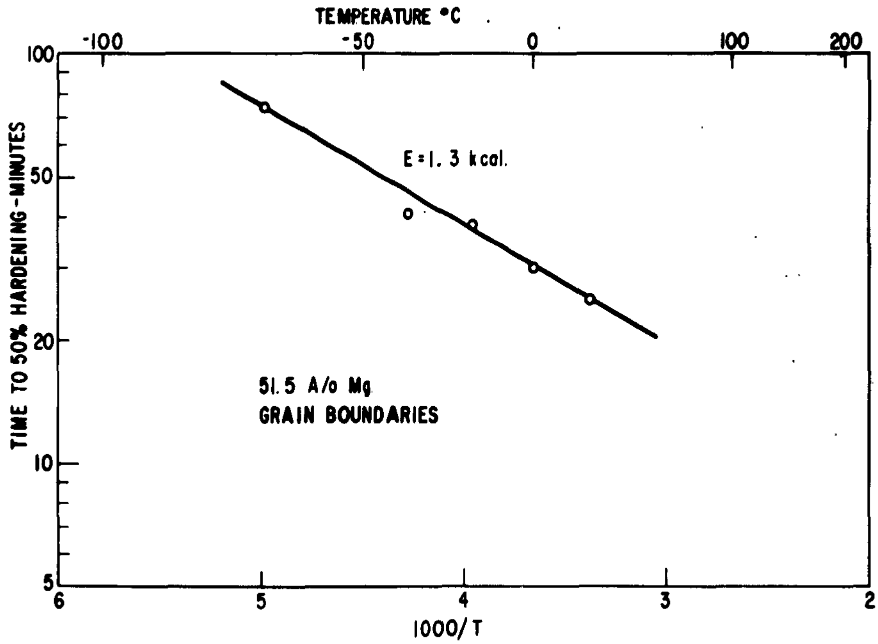



Fig. 10 Time to 50 per cent hardening (grain boundaries) of Ag + 51.5 A/o Mg as a function of the reciprocal of aging temperature.

Studies were also carried out in which the temperature of the initial anneal was varied but with all "aging" following quenching carried out at a constant temperature (RT). A set of such results for the 51.5 A/o Mg composition is shown in Fig. 11. Some aging effect is found for all annealing temperatures except the lowest, 125°C. Saturation hardness levels are approximately the same in all cases but the incubation time for initial hardening increases with decreasing temperature. The significance of these observations is not yet apparent.

In an attempt to gain further insights into the phenomena occurring in the temperature range from 125° to 200°C in the 51.5 A/o Mg alloy, equilibrium hardness values were determined at temperature for both bulk and boundary. The results are shown in Fig. 12. An abrupt discontinuity is observed in both curves between 125° and 130°C. At higher temperatures both curves pass through maxima but remain separated until about 200° as observed previously. Although these results are consistent with one another, they do not yet afford a clue to a reasonable model.

More limited studies have been done on an Ag-rich composition. A series of hardening curves for a 49.0 A/o Mg alloy annealed at various temperatures and aged at room temperature are shown in Fig. 13. Surprisingly, this composition is observed to harden following quenching although no ultimate hardness difference results between bulk and boundary. Saturation

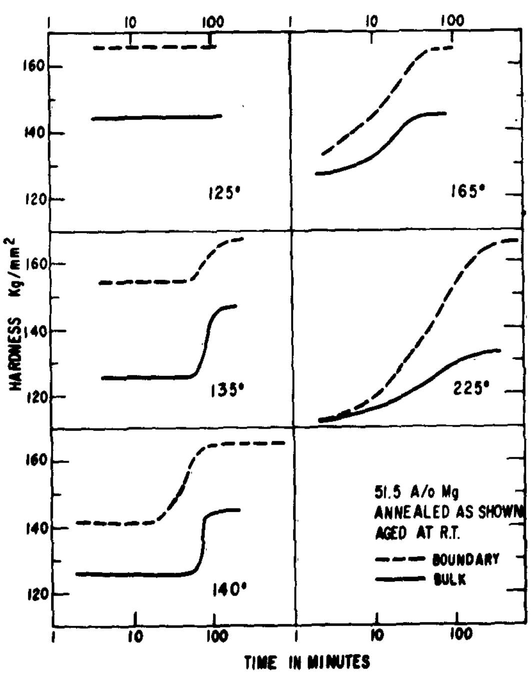



Fig. 11 Boundary and bulk hardness vs aging time for Ag + 51.5 A/o Mg aged at room temperature after quenching from various temperatures.

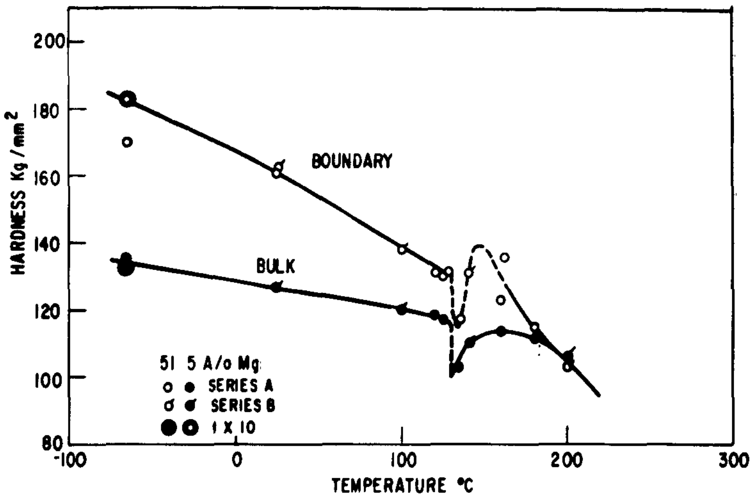



Fig. 12 Boundary and bulk hardness as a function of temperature for Ag + 51.5 A/o Mg.

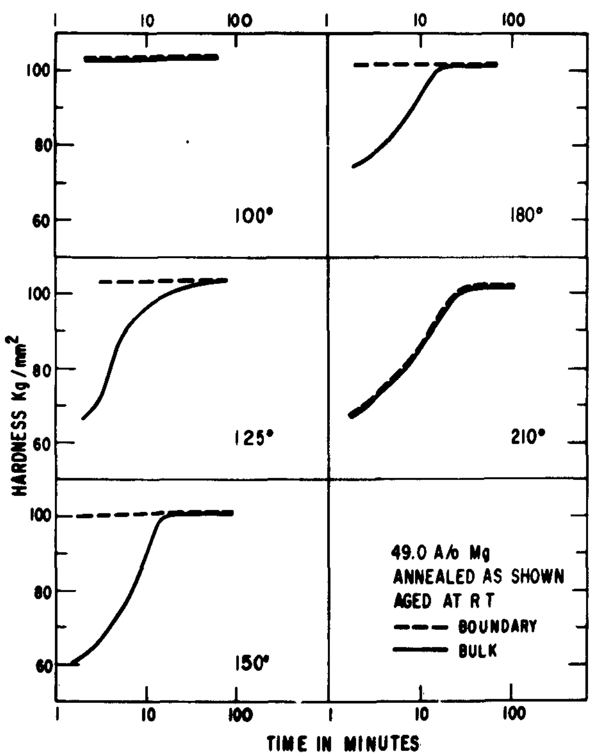



Fig. 13 Boundary and bulk hardness vs aging time for Ag + 49.0 A/o Mg aged at room temperature after quenching from various temperatures.

hardness values are independent of annealing temperature. For annealing temperatures of 180°C and below, the bulk material does not age, and for 100° neither bulk nor boundary age.

## IV. CONCLUSIONS

### A. Mechanical Property Studies

Significant strengthening can be produced in AgMg compounds by relatively dilute ternary additions; instances are observed in which there is retention of such increased strength at temperatures of 0.5 $T_{mp}$. Some ternary solutes in addition to increasing the flow stress decrease the ductile-brittle transition temperature by as much as 400°C.

The transition temperature of Mg-rich compounds is sharply dependent on composition; it is not clear whether or not a discontinuity exists in this relation at the stoichiometric composition.

The transition temperature is found to be inversely proportional to the logarithm of the strain rate for AgMg. The transition temperature also varies linearly with the reciprocal square root of the grain size; this dependence, however, may be complicated by the presence of grain boundary hardening.

### B. Grain Boundary Studies

The effects of composition, time, temperature, and heat treatment are much more complex than was previously imagined. No model is yet apparent which will account for all of the observations.

## V. FUTURE WORK PLANNED

Evaluation of the results obtained in the current work period together with the information gained in previous work under this contract suggest a number of areas requiring further study. The properties of intermetallics have been shown to be influenced by grain boundary hardening, a phenomenon which is exhibited in many classes of intermetallics and structure. It is apparent, therefore, that attention should be given to gaining a better understanding of the grain boundary hardening mechanism, *per se.*

Furthermore, in order to determine the true effects of basic physical parameters on the engineering properties of intermetallics, it is necessary to examine these effects in the absence of grain boundary hardening. Such a study might be approached by:

(a) Measurement of the properties of material treated so as to provide varying degrees of grain boundary hardening among test specimens. Extrapolation of the quantity $\Delta H/H$ to zero would provide a property value characteristic of any given composition.

(b) Elimination of grain boundary hardening in the materials to be tested. This might be accomplished by purification techniques or by high-temperature homogenization techniques.

(c) Consideration of the properties of a new base material which is not subject to the grain boundary hardening phenomenon.

(d) Measurement of the properties of single crystals to remove the complication of grain boundary effects.

In addition, there is a need for a quantitative study of the observed beneficial effects of prestrain on the low-temperature ductility of the compound AgMg. Since there appears to be nothing unique of restrictive about AgMg it might be expected that with sufficient understanding appropriate processing might be employed to produce similar "enductilement" or other, perhaps more potentially practical, compounds.

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2. Grain Structure
3. Intermetallic Compounds
4. AgMg
5. Stresses

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