Nondestructive Characterization of Rapidly Solidified Alloys

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ABSTRACT

The enhancement of certain material properties by rapid solidification is closely related to the novel microstructures that can result from high cooling rates. Since small variations in processing greatly affect these microstructures, NDE sensors are required to detect and monitor these microstructural features during processing. An ultrasonic technique, utilizing laser generated ultrasound has been developed to detect changes of sound velocity associated with microstructural transformations occurring in rapidly solidified melt-spun ribbon specimens. Elastic moduli, calculated from the ultrasonic measurements, were used to characterize the decomposition of extended solid solutions of aluminum-manganese alloys and the crystallization of amorphous metal alloys.

RAPIDLY SOLIDIFIED METALLIC ALLOYS have been the subject of an extensive number of scientific studies in the last 10 years. By virtue of their different and often enhanced physical properties (as compared to conventionally solidified alloys) both scientific and commercial interest are warranted. These enhancements are achieved by more homogeneous alloy element distribution, reduced grain size, nonequilibrium microstructural constituents, and, sometimes, a noncrystalline (amorphous) microstructure. In order to achieve high cooling rates the methods of rapid solidification results in fine powder or thin ribbon samples. Thus, it is difficult to characterize rapidly solidified materials in their initial state with traditional nondestructive techniques designed for bulk geometries. However, it is precisely in the initial powder or ribbon form, that it is essential to ensure that the desired metastable microstructures have formed. Ideally, these characterizations should be in-process, making possible closed loop control of the production processes.

In this paper, ultrasonic velocity measurements are used to characterize (both before and after thermal processing designed to decompose metastable microstructure constituents) rapidly solidified microcrystalline and amorphous alloys that were prepared by melt spinning. The experimental advantages and disadvantages of some ultrasonic methods will be discussed. Both a microcrystalline alloy system (aluminum-manganese) and amorphous systems are examined.

The amorphous structure that results when some alloys are correctly melt-spun is caused by the large quench rates (up to \(10^4\) K/sec) that are attainable by melt spinning. A most important need in the case of the amorphous alloys is a nondestructive method of determining whether any crystallization has occurred during solidification or during subsequent processing. Conversely, in other alloys such as some in the Al-Mn system, the intent is not to create an amorphous structure but rather to extend the solubility of a solute (Mn) in the matrix (Al) beyond that achievable under conventional (equilibrium) processing conditions. The resulting product is crystalline with a grain size of 10 to 40 microns. It is essential to develop a means of ensuring that a sufficient concentration of alloy elements is retained in solid solution both during solidification and during subsequent thermo-mechanical treatments.

EXPERIMENTAL PROCEDURES

In the thin narrow (e.g., 2 mm x 50 \(\mu\)m) ribbons of melt spun material, only guided ultrasonic waves are propagated. There are several ways of generating and receiving these guided ultrasonic waves. Two will be discussed here: piezoelectrically generated and detected signals in a pitch - catch mode.
and laser generated signals in a pitch -piezoelectric catch mode. The first represents only a slight modification to conventional ultrasonic techniques. The second method is not traditional and was especially developed for measurements on specimens with ribbon geometries, and may ultimately be capable of noncontact application by replacing the detecting piezoelectric transducer with an EMAT or laser interferometer.

PIEZOELECTRIC METHOD - For acoustically two-dimensional samples the group velocity of the fundamental longitudinal Lamb wave and the fundamental horizontally polarized shear wave (SH(0)) were measured using piezoelectrically generated waves. Commercial longitudinal transducers with nominal frequencies of 1, 2.25, 5, and 10 MHz were used for generation and detection of the fundamental longitudinal Lamb wave. AC-cut quartz or Parametrics (V155) normal beam (0.5 in.) shear wave transducers operating at 5 MHz were used to generate and receive the SH(0) wave. The quartz crystal transducers required impedance matching networks whereas the commercial transducers did not. For both wave types a viscous silicone fluid was used as an acoustic couplant between the transducer and the ribbon specimen. A two transducer pitch-catch arrangement was used for the time-of-flight measurements instead of the single transducers pulse-echo method due to the absence of at least two echoes of appreciable amplitude.

The orientations of the generating and receiving transducers relative to the ribbon specimen proved to be an extremely important consideration. The transducer-specimen configurations used in this study are based on those reported by Gelles (1, 2) in his work on films, foils, thin plates, whiskers, fibers and fine wires. In particular, two transducer positions for each type of wave were found to yield the largest received signal amplitudes. The longitudinal Lamb wave transducer-specimen configuration is shown in Figure 1 and the SH(0) wave transducer-specimen configuration is shown in Figure 2. In both cases the "a" configuration was used for samples that could not support their own weight but could be easily bent around a sharp corner. The "b" configuration was used for stiffer samples that could support their own weight but could not be easily bent around a sharp corner. For generation and detection of the SH(0) type wave the transducers were positioned in such a manner as to orient the shear particle displacements parallel to the width direction in the plane of the ribbon or sheet specimen.

A schematic diagram of the experimental apparatus used for velocity measurements is shown in Figure 3. The apparatus is essentially equivalent to that used for the pulse-echo overlap method (3).

The generation of longitudinal sound waves in specimens with ribbon geometries by conventional techniques (i.e. with piezoelec-
Q-switched Nd:YAG laser (wavelength = 1.064 μm) was directed at the ribbon surface. A fraction of the electromagnetic pulse was absorbed, heating the ribbon and thereby thermoelastically generating an ultrasonic pulse at one end of the ribbon. The pulse propagated the length of the ribbon and was detected by a 3 mm diameter acoustic emission transducer. The frequency of the detected waves was below 300 kHz, corresponding to an extensional wavelength of ≈ 1.7 cm in aluminum (11 to 17 times the specimen ribbon width), satisfying the dimensional requirement for extensional wave propagation. The amplified transducer signal was digitally recorded at a 50 ns sampling rate with a 2 channel digital storage oscilloscope. A silicon photodiode, activated by the scattering of the light pulses from the sample was used to trigger the oscilloscope. The trigger and transducer signals were recorded si-

Fig. 3 - Schematic diagram of conventional through-transmission time-of-flight measuring system using piezoelectric generation and detection

Fig. 4 - Schematic diagram of time-of-flight measurement apparatus using pulsed laser generation and piezoelectric transducer (itself is difficult). The efficiency of energy transfer from transducer to specimen and back is low because the small cross-sectional area that can be exposed to the transducer allows only a small fraction of the sound energy radiated from the transducer to be passed into the ribbon. The ribbon specimens examined in this study typically had a thickness of only 40 microns. Furthermore, it would be extremely difficult to apply this technique in-process.

LASER ULTRASOUND GENERATION - The ultrasonic velocity measuring system is illustrated in Figure 4. A single shot from a simultaneously and displayed on the oscillo-
scope screen. Transit time was determined by reading the time difference between the trigger signal and the arrival of the ultrasonic pulse at the transducer. A typical oscilloscope display is shown in Figure 5.

A number of procedures were followed to ensure accurate measurements: the laser pulse that launched the ultrasonic wave was shaped into a line by a 0.5 mm wide slit; the ribbon was held flat on a PMMA (Plexiglass) sheet; and measurements of transit time were taken at two different propagation distances for each specimen. This differential tech-
Fig. 5 - Typical ultrasonic signal (top) and trigger signal (bottom) recorded and displayed.

nique eliminated ambiguities about distance (i.e., to what part of the transducer should distance be measured) and about time (i.e., where the leading edge of the sound wave is). The ribbon was mounted on a calibrated translation stage that allowed distances to be measured to a precision of 0.001 inches. Reproducible time measurements were made by choosing a distinctive part of the initial wave arrival to find the time of flight. The experimental error of the ultrasonic velocity measurements was estimated to be approximately 1%.

NDE EXAMINATION OF THE AMORPHOUS TO CRYSTALLINE TRANSITION

Amorphous alloys, or glassy metals, are solids with frozen-in liquid structures. The absence of translational periodicity in the amorphous state along with the macroscopic compositional homogeneity are the main reasons for their improved properties, e.g., high mechanical strength, good corrosion resistance, and excellent magnetic behavior. Their unusual mechanical, chemical, and physical properties have stimulated extensive scientific and technological interest. One serious problem in the processing and utilization of amorphous alloys that may limit their future technological applications is their low thermal stability. When thermo-mechanical conditions are appropriate, metallic glasses relax structurally and ultimately crystallize into more stable structures resulting in drastic variation in properties. The factors governing the thermal stability of these alloys and their effect on properties are not well understood. For example, upon crystallization, amorphous alloys undergo very large changes in the elastic and anelastic properties with accompanying reduction in plastic properties (embrittlement). For this reason, the availability of a nondestructive ultrasonic characterization technique for both property determination and metallurgical process control could be extremely useful.

Metallic glasses are not thermodynamically stable, and they tend to structurally relax and finally crystallize upon appropriate heat treatment. Waseda et al. (4) showed that annealing metallic glasses increased the short-range order. Egami (5) used energy-dispersive methods to confirm the log-time kinetics of the relaxation process. His work indicated that the activation energy for relaxation continuously increased with time, which may correspond to the removal of quenched-in defects. Although changes in density and electronic structure associated with the crystallization process are rather minute (6), appreciable variations were observed in several physical properties, including the elastic moduli (7-9). The crystallization behavior of metallic glasses was examined by several workers (10-13). It was found that small additions of noble metals (Cu, Ag) to Pd-Si greatly stabilizes the amorphous phase, and particularly in Pd$_{77.5}$Cu$_{0.06}$Si$_{0.165}$ glass (14) which became the subject of numerous investigations. The effect of isothermal annealing on the crystallization kinetics of Pd$_{77.5}$Cu$_{0.06}$Si$_{0.165}$ was determined by differential scanning calorimetry (14). Associated with relaxation and crystallization of metallic glasses are variations in the elastic and mechanical properties. Young's modulus E and shear stiffness generally increase by 20-40% but the bulk modulus K increases by only about 7% upon crystallization (8). Kurusmovic and Scott (15) found that E for Cu$_{40}$Zr$_{60}$ increased by about 10% due to structural relaxation and another 15% upon crystallization. In contrast, the density of glassy metals generally changes by only 0.3-1.5%.

The main objectives of the present investigation were as follows:

- Determination of the isothermal transformation kinetics from the amorphous to the crystalline state by means of monitoring changes in sound wave velocity (elastic modulus).
- Study of the relaxational changes occurring in the amorphous state, prior to crystallization.

Metallic glass ribbons of PdCuSi and CuZr alloys were prepared by the melt spinning technique. A small charge of a casting was melt spun from a fused quartz tube. The alloys were melted inductively and the molten metal was ejected from the fused quartz tube onto the outside of a rotating copper wheel. The samples were approximately 40 µm thick and 1.25 mm wide. Ultrasonic, x-ray, and metallographic examination prior to the crys-
Table 1 - Physical properties of ribbon samples

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>$v_{\text{Ext.}}$ (m/sec)</th>
<th>$v_{\text{Lamb}}$ (m/sec)</th>
<th>$v_{\text{Shear}}$ (m/sec)</th>
<th>$v_{\text{long.}}$ (m/sec)</th>
<th>E (GPa)</th>
<th>G (GPa)</th>
<th>k (Gpa)</th>
<th>v</th>
</tr>
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<tr>
<td>Pd-Cu-Si</td>
<td>2970</td>
<td>(3290)</td>
<td>1787</td>
<td>4495</td>
<td>94.5</td>
<td>33.6</td>
<td>167.8</td>
<td>0.41</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>(1)</td>
<td>(3585)</td>
<td>1980</td>
<td>(4670)</td>
<td>79.8</td>
<td>28.7</td>
<td>121.5</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>(3560)</td>
<td>1950</td>
<td>(4777)</td>
<td>78.1</td>
<td>27.8</td>
<td>154.2</td>
<td>0.40</td>
</tr>
<tr>
<td>Metglas</td>
<td>(1)</td>
<td>4640</td>
<td>4900</td>
<td>2680</td>
<td>(5560)</td>
<td>157.2</td>
<td>59.7</td>
<td>145.6</td>
</tr>
<tr>
<td></td>
<td>2605-SC</td>
<td>4460</td>
<td>4720</td>
<td>2750</td>
<td>(5345)</td>
<td>145.6</td>
<td>55.4</td>
<td>134.8</td>
</tr>
<tr>
<td>Metglas</td>
<td>2605-GO</td>
<td>4490</td>
<td>4730</td>
<td>2770</td>
<td>(5279)</td>
<td>152.4</td>
<td>58.8</td>
<td>133.7</td>
</tr>
</tbody>
</table>

Crystallization treatment revealed no crystallinity. Crystallization was performed in evacuated borosilicate glass capsules at predetermined isothermal holding temperatures. Optical metallography indicated that the crystallization process in PdCuZrSi ribbon is not homogeneous in the bulk. Two coexisting growth processes were observed: frontal growth from the free surfaces of the ribbon towards the interior, and homogeneous nucleation and growth in the bulk.

Using the piezoelectric pitch-catch technique in conjunction with equations listed in the Appendix, values for the Young’s, shear, and bulk moduli and Poisson’s ratio were calculated for Pd-Cu-Si, Cu-Zr, and Metglas in the as-spun state, before they were crystallized. In addition, values for the velocity of the bulk longitudinal wave, $v_L$, the longitudinal type extensional wave, $v_E$, and the velocity of the type extensional wave, $v_E$, were calculated for Metglas from $v_L$ and $v_E$. For Pd-Cu-Si and aluminum, $v_L$, $v_E$, and $v_E$ were obtained from direct measurements. Finally, for Cu-Zr, $v_L$, $v_E$, and $v_E$ were determined by direct measurements and $v_E$ was calculated. Table 1 summarizes the results obtained for elastic moduli, Poisson’s ratio, and sound wave velocities.

The variation of extensional velocity of Pd$_{77.5}$Cu$_{3}$Si$_{16.5}$ with annealing times was determined with the laser-generation ultrasound technique. Figure 6 shows the variation of the extensional wave velocity, $v_E$, as a function of crystallization time at three isothermal holding temperatures, 380, 390, and 400 °C. The initial sound-wave velocity, in the amorphous state, was found to be 2970 m sec$^{-1}$, whereas in the fully crystallized state it reached an asymptotic value of 3490 m sec$^{-1}$. Taking 10.52 and 10.69 g cm$^{-3}$ as the density of the amorphous and crystalline Pd$_{77.5}$Cu$_{3}$Si$_{16.5}$, respectively, the Young moduli could be calculated. They were found to be 9.46 x 10$^3$ kg-mm$^{-2}$ for the amorphous state and 13.27 x 10$^3$ kg-mm$^{-2}$ for the crystalline state, i.e., a difference of about 40%. Figure 6 exhibits a relatively sharp increase in the sound velocity during the first five minutes of the isothermal holding. The variation of the extensional wave velocity with crystallization time manifests the dramatic changes in the elastic properties with an increase of about 40% in Young’s modulus. The sigmoid curves represent the crystallization kinetics which are typical of a thermally activated process. Thus, the kinetic parameters, i.e., activation energy and the growth rate parameters can be determined from this nondestructively gathered data (16, 17). Furthermore, the time dependence of the crystallized volume fraction was found to be compatible with a diffusion controlled growth mechanism (18, 19) for a plane boundary growth that is preceded by a rapid nucleation process (20).

The effect of copper content on the Young’s modulus of ZrCu alloys in the crystalline and amorphous state indicates that the lowest value of the Young’s modulus is

![Sound Wave Velocity vs. Crystallization Time](image-url)
for pure crystalline zirconium, whereas the highest value is for pure crystalline copper (Figure 7). A maximum and a minimum are found for alloys and compositions near the intermetallic compounds Zr$_2$Cu and ZrCu, respectively. The variations of the Young's modulus with composition of the amorphous alloys, between 30 and 70% copper, is a smooth S-curve with an inflection point at 50% copper. It is conjectured that the amorphous state can be interpreted in terms of short range order structure where the mixing pairs Zr-Zr, Cu-Cu, and Cu-Zr are of equal probability at the composition of 50% Cu. The inflection point on the Young's modulus versus composition curve will then represent the point for maximal configurational entropy of the metallic glass. Analysis of the temperature dependence of the sound wave velocity of Zr-Cu alloys in the composition range between 30 and 70% Cu allowed determination of the activation energies of the diffusional processes governing the crystallization kinetics. The activation energy increased from 90 to 110 kcal/mole as copper content exceeds 50%. The change in crystallization mechanism as copper content exceeds 50% may be related to the configurational entropy change as the population of Cu-Cu pairs increases. The relationship is of basic importance in the understanding of the transformation of the amorphous state into coexisting compounds upon isothermal crystallization (21).

The initial increase in the extensional sound velocity, of about 3.7% (i.e., 7.4% in the Young's modulus) of PdCuSi and a similar increase in the Zr-Cu amorphous alloys, appears to be related to a structural relaxation that precedes the crystallization process in the amorphous state (15, 19). Structural relaxation was found to be particularly enhanced in glasses obtained at high quenching rates, where greater structural disorder is to be expected (27). The lower elastic stiffness in the glassy state has been attributed to the interatomic displacements inherent in a disordered structure (23). The elastic stiffness should, therefore, increase with increased local ordering as a consequence of the structural relaxation. Initially, the amorphous alloy has a disordered packing of the constituent atoms. Heat treatment in the amorphous region at temperatures below the glass transition temperature, $T_g$, or for relatively short periods of time at temperatures above $T_g$ causes structural and compositional relaxation. The free volumes are redistributed by short range shuffling of the atoms, thus a more rigid close-packed atomic distribution of high coordination is achieved.

EXTENDED SOLID SOLUTIONS: Al-Mn

The aluminum-manganese system was chosen for investigation because significant extension of the equilibrium solubility limit is possible upon rapid solidification (24–32). Thus, the properties of aluminum-manganese solid solutions could be studied over a wide range of manganese concentrations. The equilibrium solubility of manganese in aluminum is 2 wt.% at the eutectic temperature of 657 °C (930 °K) as shown in Figure 8. At higher Mn concentrations an intermetallic compound (Al$_x$Mn) is formed by a peritectic transformation. Under conditions of rapid solidification this reaction is bypassed and microcrystalline substitutional solid solutions containing up to 15 wt.% Mn reportedly have been formed (30). Increases of hardness (26, 28, 29, 31) and ultimate tensile strength (32) which are proportional to manganese content have been observed for these nonequilibrium solid solutions. To explore the physical basis of the ultrasonic phenomena observed x-ray diffraction, electrical resistivity, and optical microscopy measurements were made.

Aluminum-manganese alloys were prepared by melting 5N purity aluminum and 4N purity manganese and casting under 0.5 atmospheres (380 torr) or argon. Rapidly solidified ribbons were then prepared from these alloys by melt spinning. Thin ribbon specimens, 1 to 1.5 mm wide and 30 to 50 μm thick with continuous lengths of >1 meter were produced. For thermal stability experiments the as-spun specimens were annealed isothermally at 450 °C (723 °K) for varying lengths of time. Each ribbon was encapsulated in a borosilicate glass tube, in the same manner as the amorphous alloys during annealing.

The effect of composition and heat treatment on the lattice parameter is illustrated in Figure 9. In the as-spun specimens containing less than 5 wt.% Mn the lattice parameter decreased linearly with increasing manganese concentration. Above 5 wt.% Mn
Fig. 8 - Partial phase diagram of the aluminum-manganese system with the region around the eutectic point enlarged.

The slope of the relation changed. This deviation from linearity suggested that the solubility of manganese in aluminum may not have been complete in the higher Mn content (9 and 12 wt.% Mn) alloys. The as-spun lattice parameters are consistently above the values Jones (32) derived by averaging data reported in the literature. From 0 to 5 wt.% Mn, the difference is less than .003 Å. Beyond 5 wt.% Mn, the deviation between the values of Jones and Figure 9 increases with manganese content.

After annealing for 1 hour at 450 °C the lattice parameter increased from that of the as-spun condition for all compositions above 1 wt.% Mn and peaks, identified as the AlMn phase, were seen on the diffraction patterns of the alloys containing > 5 wt.% Mn. For alloys containing less than 2 wt.% Mn only a small change in the lattice parameter was seen, indicating a more thermally stable solid solution. Annealing for a further 2 hours resulted in a small additional lattice parameter increase in the alloys with less than 3 wt.% Mn.

Optical micrographs of ribbons with 1, 5, and 12 wt.% Mn are shown in Figures 10, 11, and 12 respectively. In the micrographs the straight edge of each sample is the side of the ribbon that contacted the spinning wheel during solidification.

A columnar microstructure, indicative of through thickness directional solidification, is seen in the 1 wt.% Mn sample. In the as-spun state, grain boundaries are slightly visible. Darkish spots seen in the structure are small pores, which may have caused the

Fig. 9 - Lattice parameter variation of as-spun and annealed Al-Mn alloys.

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Fig. 10 - Al-1 wt.% Mn ribbon edge as quenched (a) and annealed 3 hours at 450 °C (b) calculated densities to be somewhat overestimated. The grain boundaries are accentuated after annealing for 3 hours at 450 °C. In addition, a roughened surface is observed, which could be due to precipitates.

The as-spun 5 wt.% Mn specimen appears inhomogeneous only in the center, where the presence of a cellular solidification microstructure indicates a decreased temperature gradient (33). Substantial precipitation exists in the specimen annealed 3 hours at 450 °C (Fig. 11), consistent with the large resistivity decrease and lattice parameter increase reported above.

Figure 12 reveals the microstructure of the as-spun 12 wt.% Mn alloy. Some primary precipitation exists along the grain boundaries. Directional solidification is indicated by the columnar grain structure and by the solute segregation at the edge of the ribbon opposite the wheel side. Evidently, the quench rate was not sufficient to retain all 12 wt.% Mn in solution. A large amount of $\text{Al}_6\text{Mn}$ precipitated after annealing at 450 °C for 3 hours (Fig. 12).

In Figures 13 and 14 the ultrasonic velocity and Young's modulus as a function of manganese content are shown. The velocity and modulus curves have essentially the same shape, although the slope of the modulus curve is increased because Young's modulus is proportional to the square of the velocity, and the density increases linearly with manganese content (0.02 gm-cm$^{-3}$/wt.% Mn). It can be seen that manganese concentration had a much larger effect on velocity and Young's modulus than did the heat treatment of a particular alloy composition.

Pure aluminum ribbons had a modulus of $6.93 \times 10^{11}$ dynes/cm$^2$ (69.3 GPa). Upon the addition of 0.1 wt.% Mn the modulus decreased sharply to $6.35 \times 10^{11}$ dynes/cm$^2$ (63.5 GPa). The modules decreased more slowly with increasing manganese content up to 1.2 wt.% Mn. Above 1.2 wt.% Mn the modulus increased. Above 9 wt.% Mn the rate of increase abated. The Young's modulus of the heat treated alloys was always higher than in the as-spun state. The difference due to annealing was not a simple function of concentration.

The statically determined Young's modulus of conventionally cast Al-Mn alloys has been reported to increase linearly for compositions between 1.7 and 14.5 wt.% Mn (34). This suggests that the $\text{Al}_6\text{Mn}$ phase has a substantially higher modulus than aluminum. Between manganese concentrations of 3 and 9 wt.% Mn the elastic modulus results of the present study confirm this finding, even though the rapidly solidified ribbons are expected to contain much higher concentrations of Mn in solution and, thus, a smaller volume fraction of $\text{Al}_6\text{Mn}$. The leveling of Young's modulus above 9 wt.% Mn could be a manifestation of manganese segregation. Due to the high concentration of manganese near

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Fig. 12 - Al-12 wt.% Mn ribbon edge as quenched (a) and annealed 3 hours at 450 °C (b)

The ribbon side not exposed to the melt spinning wheel, a substantial fraction of the specimen volume was depleted of manganese. Therefore, the bulk of the ultrasonic pulse may have propagated in material containing much less than 12 wt.% Mn.

The cause of the abrupt decrease of Young's modulus upon the addition of 0.1 wt.% Mn to pure aluminum is at this time unclear and is still under investigation. Several comments can be made, however about the continued decrease of Young's modulus upon the addition of more Mn to aluminum. A similar decrease in Young's modulus with increasing solute content has been observed in substitutional solid solutions of some other alloy systems, notably ones based on copper and silver (35). Zener proposed a model that predicted, from thermodynamic considerations, an elastic modulus decrease in substitutional solid solutions because of solute induced lattice strain (36). Support for the notion that this can occur in Al-Mn alloys comes from a slight dip of longitudinal sound velocity that was observed in hot pressed Al-Mn alloys at a very low Mn concentration corresponding to a solid solution (37). The extreme conditions of rapid solidification extend the solubility limit and, thus, would be expected to magnify any effect seen in equilibrium solid solutions.

According to Zener's model, Young's modulus would be expected to continue to decrease monotonically with increasing Mn solute in the as-spun ribbons. This was not observed here. Instead, the modulus rose sharply with the addition of manganese above 3 wt.% Mn. Although some precipitation was seen in as-spun alloys containing more than 3 wt.% Mn, the lattice parameter and resistivity results indicate that most of the manganese was quenched in solution. It seems surprising, therefore, that the small volume fraction of Al12Mn that may have existed in the as-spun state could so strongly increase the modulus. Moreover, the precipitation of much more Al12Mn during annealing treatments caused only a relatively small modulus increase. This leads one to speculate the possibility that the nature of the solid solution itself undergoes a transition at around 20 wt.% Mn. Interestingly, this is the eutectic composition, at which the equilibrium solubility of manganese in aluminum is maximum.

The rise of Young's modulus caused by annealing at 450 °C (Figure 14) could be due to the elimination of disorder from the lattice by precipitation or clustering, thus annihilating the modulus-decreasing effect of lattice strain which Zener's theory addresses. Another effect of annealing could be precipitation hardening, which is known to increase slightly the Young's modulus of some Al-Cu alloys (38). The contribution of precipitation to the elastic modulus increase is most likely minor, however, because the increase of Young's modulus over the as-spun
wave velocity measurements had to be made at several frequencies and the data fitted to the proper dispersion curve corresponding to a fixed Poisson’s ratio.

3. The low frequency Lamb wave velocity, $V_L$, could not be determined for narrow ribbons whose width was on the same order as the acoustic wavelength. Instead, the longitudinal extensional wave velocity, $V_E$, was obtained by the laser generation method and it was used for elastic modulus determination. In addition, wide ribbons could be cut down after $V_L$ measurement for $V_E$ measurement.

4. The thermal stability of Pd-Cu-Si was evaluated. The initial increase in the extensional velocity appears to be related to a structural relaxation that precedes the crystallization process in the amorphous state. The crystallization process obeys conventional kinetics for a thermally activated process.

5. Young's modulus and X-ray diffraction lattice parameter measurements have been made nondestructively on rapidly solidified ribbons of Al-Mn supersaturated solid solutions.

6. In both the as-spun and annealed alloys, Young's modulus has a maximum at a composition around 2 wt. % Mn.

The percentage of manganese present in Al-Mn alloys appears to have a greater effect on Young's modulus than the state in which manganese is distributed (as solid solution or as part of a precipitate).

The physical processes that are responsible for the softening and stiffening of the crystal lattice as the Mn concentration increases are at present not fully understood.

ACKNOWLEDGMENTS

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REFERENCES

The equations that relate the isotropic elastic moduli to the measured guided wave velocities and to each other are listed below.

\[ G = \rho V_g^2 \]

\[ E = 4G \left[ 1 - \left( \frac{V_s}{V_L} \right)^2 \right] = \rho V_g^2 = \rho V_L^2 (1 - \nu^2) \]

\[ \nu = 1 - 2 \left( \frac{V_s}{V_L} \right)^2 = \frac{V_s^2}{2V_L^2} - 1 = \left[ 1 - \left( \frac{V_s}{V_L} \right)^2 \right]^{1/2} \]

\[ V_E = \left( \frac{E}{\rho} \right)^{1/2}, \quad V_L = \left( \frac{E}{\rho (1-\nu^2)} \right)^{1/2}, \quad V_s = \left[ \frac{G}{\rho} \right]^{1/2} \]

\[ \nu = \frac{E}{2G} - 1, \quad k = \frac{E}{3(1-2\nu)}, \quad G = \frac{E}{2(1+\nu)} \]

\[ \text{Where:} \]
\[ G = \text{Shear Modulus} \]
\[ \rho = \text{Mass Density} \]
\[ E = \text{Young's Modulus} \]
\[ \nu = \text{Poisson's Ratio} \]
\[ k = \text{Bulk Modulus} \]
\[ V_s = V_{SH0} = \text{Velocity of fundamental horizontally polarised shear wave} \]
\[ V_L = \text{Velocity of fundamental longitudinal wave at zero frequency} \]
\[ V_E = \text{Velocity of fundamental extensional wave at zero frequency} \]