LASER/ULTRASONIC NDE OF MELT SPUN RIBBONS

John J. Smith*, Moshe Rosen*, and Haydn N.G. Wadley**

*Center for Nondestructive Evaluation, The Johns Hopkins University, Baltimore, MD, USA
**Metallurgy Division, National Bureau of Standards, Gaithersburg, MD, USA

INTRODUCTION

One of the most important methods of rapidly solidifying metal alloys is the melt spinning process, first patented in 1958\(^1\). Melt spinning is the technique by which alloys are continuously cast into ribbon form by squirting a molten stream onto a rotating metal wheel. Cooling rates up to one million degrees per second can be achieved. Improvements of the mechanical, chemical, electrical, and magnetic properties of many alloys are associated with microstructures that can result from these high cooling rates. As a result of the improvements to material properties that are possible, rapidly solidified metallic alloys have been the subject of an extensive number of scientific studies during the past 10 years.

It is well known that many microstructural features, such as alloy element content and changes of metallurgical phase, can affect the elastic properties of materials. Since knowledge of the microstructural state is essential in determining the success of preparation of rapidly solidified alloys, a method of measuring elastic moduli, such as Young's modulus, would be a useful tool for quality control. Accurate values of the elastic moduli can be provided by measurements of ultrasonic velocity in a material. In this paper, an ultrasonic method that is especially suitable for measurements on melt-spun specimens is described. The use of this ultrasonic technique to characterize melt-spun specimens, both before and after subsequent thermal processing, is demonstrated with an investigation of some aluminum-manganese alloys.

ULTRASONIC CHARACTERIZATION

For a bulk specimen, both longitudinal and shear wave velocities must be known to calculate Young's modulus. Only the longitudinal velocity need be known, however, to calculate the Young's modulus of a bar with lateral dimensions less than 1/10 the longitudinal sound wavelength. In this case, transverse contractions (i.e., Poisson's ratio effects) occur in phase with longitudinal motions and a longitudinal wave is called an extensional wave. In an isotropic bar of constant cross-section, the extensional velocity is related to Young's modulus by the equation

\[ v = \left( \frac{E}{\rho} \right)^{\frac{1}{2}} \]  \( (1) \)

where \( E \) is Young's modulus, \( v \) is the extensional wave velocity, and \( \rho \) is the density. It is not necessary for the bar to have a circular cross-section for Eq. 1 to hold\(^2\). Thus, Eq. 1 can be used to determine the Young's modulus of a melt-spun specimen with a ribbon geometry if the sound wavelength is at least 10 times the largest dimension of the ribbon cross-section. The ribbons prepared for the present
investigation were 1 to 1.5 mm wide, about 40 μm thick, and at least 15 cm long.

It is difficult to characterize rapidly solidified materials in their initial state with conventional ultrasonic techniques (i.e., with piezoelectric transducers) because the efficiency of energy transfer from transducer to specimen and back is low due to the small cross-sectional area that can be exposed to the transducer. However, it is precisely in the initial ribbon form, before bulk pieces have been formed by expensive consolidation operations, that it is most economical to test the rapidly solidified alloys. Therefore, a new technique in which a high-power pulsed laser induced extensional sound waves in a ribbon was used. The ultrasonic velocity measuring system is illustrated in Fig. 1. A single shot from a 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 about 1.7 cm in aluminum (11 to 17 times the specimen ribbon width), satisfying the dimensional requirement discussed above. 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 simultaneously and displayed on the oscilloscope 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 Fig. 2.

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,

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**Fig. 1 - Ultrasonic measuring system setup with laser generation and piezoelectric detection.**
Fig. 2 - Typical laser generated ultrasonic signal (top) and trigger signal (bottom)

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. The sound velocity in each ribbon was calculated simply by dividing the difference of the two travel distances by the difference of the two travel times, i.e., $\Delta \text{distance}/\Delta \text{time}$. This differential technique 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. The experimental error of the ultrasonic velocity measurements was estimated to be approximately 1%.

NDE OF A MELT-SPUN ALLOY: ALUMINUM-MANGANESE

The production of alloys with enhanced concentrations of alloy elements in solution is an area of research that has been attracting substantial interest. The aluminum-manganese system was chosen for investigation because significant extension of the equilibrium solubility limit of about 0.5 wt.% Mn is possible upon rapid solidification\textsuperscript{3–11}. Under conditions of rapid solidification, microcrystalline solid solutions containing up to 15 wt.% Mn reportedly have been formed. Thus, the properties of aluminum-manganese solid solutions could be studied over a wide range of manganese concentrations. Increases of hardness\textsuperscript{5–7} and ultimate tensile strength\textsuperscript{11} which are proportional to manganese content have been observed for these nonequilibrium solid solutions.

Ultrasonic Examination of Al–Mn

In order to examine the elastic properties of the rapidly solidified Al–Mn alloys, the extensional sound wave velocity of alloys containing from 0.1 wt.% Mn to 12 wt.% Mn was measured. The effects of high temperature on the alloys was studied
by annealing the as-spun specimens isothermally at 450°C for varying lengths of time and then re-examining them.

In Fig. 3 the ultrasonic velocity as a function of manganese content and heat treatment is shown. The Young's modulus data shown in Fig. 4 were calculated from the velocities measured and the specimen densities in accordance with Eq. 1. It can be seen that the manganese concentration had a much larger effect on velocity and Young's modulus than did the heat treatment of a particular alloy composition. The initial decrease of velocity and modulus vs. composition and the subsequent increase was unexpected. One would have expected that for a solid solution the curves would change monotonically with increasing solute content. In order to understand the cause of the modulus effects, electrical resistivity measurements, metallography, and x-ray diffractometry were performed.

Corroborative measurements

Metallography - Optical micrographs of ribbons with 1, 5, and 12 wt.% Mn are shown in Figs. 5, 6, and 7 respectively. In the micrographs the straight edge of each sample is the side of the ribbon that contacted the spinning wheel during solidification. The grain boundaries of the 1 wt.% Mn ribbon are accentuated after annealing for 3 hours at 450°C (Fig. 5b). In addition, a roughened surface is observed, which could be due to precipitates. The as-spun 5 wt.% Mn specimen in Fig. 6a appears inhomogeneous only in the center, where the presence of a cellular solidification microstructure indicates a decreased temperature gradient. Substantial precipitation exists in the specimen annealed 3 hours at 450°C (Fig. 6b). Figure 7a reveals the microstructure of the as-spun 12 wt.% Mn alloy. Some primary

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Fig. 3 - Extensional sound wave velocity of as-spun and annealed Al-Mn alloys

Fig. 4 - Young's modulus of as-spun and annealed Al-Mn alloys
Fig. 5 - Al-1 wt.% Mn ribbon edge as quenched (a) and annealed 3 hours at 450°C (b)

Fig. 6 - Al-5 wt.% Mn ribbon edge as quenched (a) and annealed 3 hours at 450°C (b)

Fig. 7 - Al-12 wt.% Mn ribbon edge as quenched (a) and annealed 3 hours at 450°C (b)

Fig. 8 - Lattice parameter variation of as-spun and annealed Al-Mn alloys
precipitation exists along the grain boundaries. Evidently, the quench rate was not sufficient to retain all 12 wt.% Mn in solution. A large amount of second phase precipitated after annealing at 450°C for 3 hours (Fig. 7b).

X-ray diffraction - The solubility of manganese in the alloys could be determined by lattice parameter measurements done with an x-ray diffractometer. Since manganese has a smaller atomic volume than aluminum, the lattice parameter of the alloy should decrease if manganese is in substitutional solid solution with the aluminum. The effect of composition on lattice parameter is illustrated in Fig. 8. In the as-spun specimens containing less than 5 wt.% Mn the lattice parameter decreased linearly with increasing manganese concentration, indicating fairly complete solubility of manganese in the aluminum. Above 5 wt.% Mn 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. 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 Al-Mn phase, were seen on the diffraction patterns of the alloys containing greater than 5 wt.% Mn. For alloys containing less than 2 wt.% Mn only a small change in the lattice parameter was seen after annealing, 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.

Electrical resistivity - The electrical resistivity of a metal depends on the ease with which its electrons can move. The solute atoms of a solid solution disturb the periodicity of the crystal lattice by straining it, leading to higher electrical resistivity. Precipitation of the solute in the form of a second phase removes this strain and thus decreases the resistivity. The dependence of resistivity on the composition and annealing time of the Al-Mn alloys, measured by a 4 point probe potentiometric technique, is shown in figure 9. Between 0.1 wt.% and 9 wt.% Mn in the as-spun state, the resistivity increased linearly, as expected of the

![Graph showing electrical resistivity vs weight percent manganese]

Fig. 9 - Electrical resistivity of as-spun and annealed Al-Mn alloys
solid solutions. Above 9 wt.% Mn the resistivity leveled off, indicating that a complete solid solution did not exist in the as-spun 12 wt.% Mn specimen. Annealing at 450°C for periods as short as 5 minutes had a large effect on the electrical resistivity of the alloys with higher manganese content. After 3 hours at 450°C the resistivity of those alloys decreased to the resistivity of the annealed 2 wt.% Mn specimen, consistent with the view that the Al-Mn precipitates seen with x-ray diffraction, contribute little to the electrical resistivity.

Interpretation of the ultrasonic results

The sound velocity and Young’s modulus data can be largely understood by combining the information gained from the different measurement results. Between compositions of 3 and 9 wt.% Mn the elastic modulus increases fairly linearly. This composition range was seen to correspond to solid solution by the metallography, resistivity, and x-ray observations. A constant change of modulus with solute content is normal and well understood. At concentrations above 9 wt.%, the leveling of the Young’s modulus is explained by the fact that a pure solid solution was not obtained, as was shown by the corroborative measurements. Due to the high concentration of manganese near one side of the ribbon seen in Fig. 7b, 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. Zener proposed a model that predicted, from thermoelastic considerations, an elastic modulus decrease in substitutional solid solutions because of solute induced lattice strain. 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. 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. This leads one to consider the possibility that the nature of the solid solution itself undergoes a transition around 2 wt.% Mn, perhaps to a semi-ordered solution. The critical composition of 2 wt.% Mn also corresponds to the onset of instability of the supersaturated solid solution, as indicated by the sharp changes of the lattice parameter and electrical resistivity upon annealing (Figs. 8 and 9). Furthermore, 2 wt.% Mn 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 (Fig. 4) could be due to the elimination of disorder from the lattice by precipitation or clustering, thus removing 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. 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 value is relatively independent of manganese content.
CONCLUSIONS

The results of this investigation show that the effect of alloying elements on the physical properties of rapidly solidified alloys can be investigated with ultrasonic velocity measurements. In fact, the technique could be used to detect metallurgical phase changes in any material with a ribbon geometry, whether or not it is a product of rapid solidification. At the moment, the type of ultrasonic measurement described in this paper is primarily of scientific interest. With further development, however, it could be refined to the point where it would have industrial applications for continuously testing flat ribbons or sheets of metal.

REFERENCES