Eighth Quarterly Report
for
R&D AND EVALUATION OF A LIGHTWEIGHT, HIGH STRENGTH MAGNESIUM ALLOY
(May 1, 1969 - Aug. 1, 1969)

Contract No.: NAS5-10398
(Modification No. 2)

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ABSTRACT

The evaluation of Mg-30Sc has been completed. The extrusion of this alloy in the F temper had an excellent combination of properties with but one exception. It is stronger, tougher, stiffer (high modulus), and more cold formable than any other Mg alloy yet discovered. At elevated temperatures it is as strong and creep resistant as Mg-Th and may be heat treated to provide even better properties. The exception to this impressive list of properties is poor resistance to stress corrosion. Test bars stressed at less than half their tensile yield strength in a rural environment failed in about a week.

The search for a Mg-Sc ternary with high strength and low Sc content led to the selection of Mg-10Sc-5Li for evaluation on a normal laboratory scale. The CYS (51 ksi) of the 1/16" x 7/8" extrusion of this alloy in the T6 temper duplicated that obtained with 1/8" dia. wire in the mini-scale evaluation, but its TYS was found to be only 40 ksi. This large difference in yield strength is attributed to the poor creep resistance of the alloy even at room temperature.

Mg-15Sc-4Li was selected as the second ternary for evaluation on a normal laboratory scale because its higher Sc content and lower Li content provide higher strength (65 ksi CYS) and should provide better creep resistance. A 3" dia. billet of this alloy was prepared but was so badly contaminated with flux that it could not be extruded into good 1/16" x 1 1/4" strip. Remelting and settling of the alloy improved the quality of the billet, but significantly decreased the Sc and Li levels. Preparation of the alloy in an inert atmosphere is now planned.

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INTRODUCTION

Our research has shown that Mg-30Sc has an excellent combination of properties with but one exception-poor stress corrosion resistance. The possibility of improving this property by heat treatment was explored during this quarter. We have also found that ternary additions of Ag, Li, or Y are very beneficial to Mg-Sc. This work carried out on a mini-scale has shown that these ternaries containing only 10-15% Sc have properties comparable to those of Mg-30Sc. One of the ternaries, Mg-10Sc-5Li, was prepared during the last quarter and evaluated on a normal laboratory scale during this period. The mini-scale work was completed and a second Mg-Sc ternary was also evaluated on a larger scale.

SUMMARY OF EXPERIMENTAL RESULTS

1) Heat treatment of the Mg-30Sc extrusion at 950°F for one hour to convert the duplex α-β structure to α and furnace cooling to minimize residual stresses did not improve its poor stress corrosion resistance. Although the corrosion rate (0.6-1.0 mcd) of Mg-30Sc in salt water was relatively low, both samples from the quenched extrusion cracked during the 14 day test.

2) Small transverse test bars cut from the 1/16" x 1 1/4" extrusion of Mg-30Sc were about as strong as conventional longitudinal bars.

3) The properties of Mg-10Sc-5Li extruded into 1/16" x 7/8" strip were essentially the same as those obtained from 1/8" dia. wire. The TYS of this alloy in the T6 temper was well below its CYS (40 vs 51 ksi).

4) The Mg-10Sc-5Li extrusion experienced rapid primary creep at room temperature with a stress of 30 ksi, but creep rate decreased markedly with increasing time and was only 7×10^{-5}%/hour in the last 100 hours of the 1000 hour test. Rupture occurred within one minute at a stress of 40 ksi.

5) The corrosion resistance of Mg-10Sc-5Li in salt water was poor (5.6-6.6 mcd, compared to ~0.5 mcd for conventional Mg alloys).

6) Heat treatment of Mg-Sc-Y alloys containing 15-18%Sc and 12-21% Y indicated that Y was not as effective in producing β as Sc. Although the alloys containing 18-21% Y could not be converted entirely to β, they had very high strength (88-96 ksi CYS) but very limited ductility.

7) Decreasing the Sc content of Mg-16.9Sc-4.7Li to 13.6% and increasing its Li content to 5.3% decreased the amount of β that could be produced by heat treatment and markedly reduced its strength. Increasing the extrusion temperature of Mg-13.6Sc-5.3Li from 650 to 950°F did not significantly improve its poor ductility.

8) Melts of Mg-15Sc-4Li did not react with magnesia crucibles.

9) A five pound melt of Mg-15Sc-4Li was prepared and cast into a 3" diameter billet, but the metal was so badly contaminated with flux that the 1/16" x 1 1/4" extrusion made from it was too poor to test.

10) Remelting and settling improved the quality of the melt, but the Sc content was reduced to 13.2%, the Li level fell to 3.8%, and the metal was contaminated with Ca and Zn. The 1/16" x 7/8" strip extruded from this casting had only a fair surface and poor mechanical properties.

11) Heat treatment of the Mg-13Sc-4Li extrusion failed to produce an entirely β structure and caused melting at the grain boundaries, where the Ca impurity was concentrated.

CONCLUSIONS

1) Mg-30Sc has an excellent combination of properties except for its poor stress corrosion resistance.

2) Mg-10Sc-5Li is not strong enough to warrant further evaluation.

3) Small (≤5 pound) high quality melts of Mg-15Sc-4Li are difficult to prepare in air under a flux cover.

RECOMMENDATION

1) Mg-15Sc-4Li should be prepared in an inert atmosphere.

EXPERIMENTAL WORK

Mg-15Sc-4Li was prepared on a normal laboratory scale. Sublimed Mg (1345 grams) was melted in a magnesia crucible using a low density flux (85% KCl, 14% $MgCl_2$, 1% CaF_2) for melt protection. After melting, the flux was skimmed off and replaced with KCl. Metallic Sc (269 grams) was added, and the melt was held at 1500°F for five hours. About 223 grams of Mg-30Sc scrap was then added. A special flux designed for Li melts (45% KCl, 33.8% $LiCl_2$, 11.2% LiF, 10% $MgCl_2$) was added before 351 grams of Mg-10Sc-5Li scrap and then 82 grams of Li were alloyed. A small piece of paraffin was placed on top of the melt just before the melt was poured into a 3" diameter billet. Flow through the gate stopped before the mold cavity was completely filled. The remainder of the melt was then top poured. The casting (Figure 1) weighed 2040 grams compared to 2270 grams of metal charged. The billet was scalped and extruded into 1/16" x 1 1/4" strip (Fig. 1) at a container temperature of 750°F and a speed of 10 fpm. Extrusion speed was reduced to 1 fpm in an unsuccessful attempt to improve the poor surface of the strip. The container temperature was also decreased to 650°F without success.

The remaining billet and all but a small sample of the extrusion were later remelted in a magnesia crucible under KCl and the special flux for Li alloys. CaF_2 was added in an attempt to thicken the flux to facilitate separation from the metal. Since the melt was "sludgy" at 1400°F, temperature was increased to 1600°F. The melt was held at this temperature for 10 minutes to permit settling and then poured at 1550°F into the billet mold. The graphite mold was preheated to 600°F to ensure complete filling. A rather short billet (Figure 2) was obtained as a substantial part of the melt remained in the bottom of the crucible as sludge. The casting weighed 1340 grams. The billet was scalped and extruded into 1/16" x 7/8" strip (Figure 2) at 700°F and 1 foot per minute. The maximum pressure required for extrusion was 450 tons.

DISCUSSION

A) Evaluation of Mg-30Sc

The evaluation of Mg-30Sc has shown that this alloy has excellent properties with one exception—stress corrosion resistance. Test bars of the 1/16" x 1 1/4" strip failed at stresses of 15-30 ksi after a short exposure at a rural site. Since this might have been due to the duplex α-β structure of the extrusion as well as residual stress, we heat treated one sample at 950^{o}F for one hour and slowly cooled it in the furnace. This treatment should produce an α structure with little residual stress. However, this bar also failed in a few days at a stress of 30 ksi. The corrosion results (alternate immersion in 3% NaCl at 95^{o}F for two weeks) also reveal the susceptibility of Mg-30Sc to stress corrosion. Although the samples were not heavily attacked and had a respectable rate of 0.6-1.0 mcd (milligrams per square centimeter per day), both specimens taken from the quenched part of the extrusion cracked. The samples taken from the air cooled part of the extrusion did not crack, apparently because of lower residual stresses. The cracks tended to propagate primarily along the extrusion axis.

This tendency for cracks to propagate along the extrusion axis suggested the possibility of poor transverse properties. Although the strip is only 1 1/4" wide, we managed to prepare mini tensile bars with a reduced section 1/4" wide and 3/8" long. We tried to determine TYS from head travel, but the values were too low to be considered real. Small, free-standing compression bars were also tested. Transverse tests were also run on strip heat treated at 950^{o}F and furnace cooled. The results shown below indicate relatively little anisotropy of strength properties. Therefore, the cracking noted in Mg-30Sc cannot be attributed primarily to poor transverse properties.

	As-extruded				950^{o}F 1 hour			
Direction	%E	TYS	CYS	TS	%E	TYS	CYS	TS
Longitudinal	14	53	53	59	13	46	48	53
Transverse	5	--	52	53	8	--	56	52

The creep resistance at 500°F of Mg-30Sc in the as-extruded condition is comparable to that of Mg-Th and Mg-Y alloys but inferior to that of HM31A (Mg-3Th-1.5Mn). The Mg-30Sc test bar stressed at 2,000 psi in tension crept 0.08% in 10 hours, 0.188% in 100 hours, and 0.357% in 1000 hours. The creep curve was entirely primary; that is, creep rate continued to decrease with increasing time. Creep rate after 1000 hours was 1.1×10^{-4}%/hour.

B) Evaluation of Mg-10Sc-5Li

The evaluation of Mg-10Sc-5Li in the form of extruded 1/16" x 7/8" strip has been completed. Mechanical properties have been determined as-extruded and after heat treatment at 1050°F for 6 minutes, quenching, and aging at 250°F for 24 hours in order to form and harden β. As shown below, the results compare quite well with those obtained earlier with 1/8" diameter wire.

	1/16" x 7/8" Strip					1/8" Dia Wire				
Condition	%E	TYS	CYS	TS	E	%E	TYS	CYS	TS	E
As-extruded	8	30	36	39	5.7	2	29	33	37	6.0
Heat Treated	3	40	51	50	6.3	--	--	52	--	---

The modulus of the strip determined with Tuckerman gauges was ∽6.5×10^6 psi for both tempers. The relatively low TYS of the heat treated strip was unexpected. This is the first Mg alloy we've seen with a TYS 11 ksi lower than its CYS. We have noticed a tendency for the TYS to be somewhat lower than the CYS when a fine-grained alloy is tested at a temperature where creep is a significant factor. This suggests that Mg-10Sc-5Li has poor creep resistance even at room temperature.

Creep tests at room temperature tend to corroborate this hypothesis. A tensile bar of Mg-10Sc-5Li in the T6 temper crept rapidly (0.08% in only 30 minutes) when stressed at only 30,000 psi. Creep extension increased much more slowly with increasing time to 0.138% after 10 hours, 0.185% after 100 hours and 0.232% after 1000 hours. Creep rate in the last 100 hours of the test was only 7×10^{-5}%/hour. Another tensile bar stressed at 40,000 psi ruptured within one minute. Although the creep rate at the end of the test is low, the initial rate is high enough to influence the yield strength at the relatively low strain rate (0.02"/"/min) used in the tensile test.

The salt water corrosion resistance of Mg-10Sc-5Li in the T6 temper was also determined. Samples of the 1/16" x 7/8" extrusion about 1 1/2" long were subjected to alternate immersion in 3% NaCl at 95^{o}F for 11 days. We initially planned a test period of 14 days, but severe pitting through the specimens prompted termination of the test. Corrosion rates of 6.2, 6.6, and 5.6 mcd were obtained with the three samples. This is well above the rate of 0.2-1.0 mcd for most commercial Mg alloys. Further testing of Mg-10Sc-5Li was halted because its TYS (40 ksi) is not higher than that of the Mg-Y alloys now under development.

C) Mini-Scale Evaluation of Mg-Sc Ternaries

Failure of Mg-10Sc-5Li to achieve the high level of strength we anticipated focused attention on the mini-scale evaluation of other Mg-Sc ternaries. Three systems appear to be particularly promising-Mg-Sc containing Ag, Li, or Y. The exploratory work on the first two systems was completed during the last quarter. Maximum CYS (58 ksi) in the Mg-Sc-Ag system was obtained with Mg-15Sc-9Ag in the T6 temper. Even higher CYS (65 ksi) was obtained with Mg-15Sc-4Li in the T6 temper. The Li alloy is particularly interesting because its density (1.7g/cc) is well below that of the Ag alloy (2.0gm/cc).

Since the properties of the Mg-Sc-Y ternaries are also impressive, the selection of a second ternary for evaluation on a normal laboratory scale was deferred until the mini-scale work on this alloy system was completed. The previous work indicated that Y can be substituted for a substantial part of the Sc without impairing the high strength obtained with Mg-Sc alloys (e.g., Mg-30Sc). However, the more recent results shown below indicate that ductility is impaired if the Y content is too high. Y also appears to be less effective than Sc in forming the β phase. As much as 21% Y was added to Mg-15Sc without completely converting the structure to β by heat treatment at 1150^{o}F. In spite of this, the CYS of these alloys is extremely high when the alloy is quenched from 1150°F and aged to decompose the β. Ductility, however, is very limited. Three bars of Mg-15Sc-18Y and two bars of Mg-18Sc-18Y fractured after less than 0.5% compression, while two bars of Mg-15Sc-21Y failed before the 0.2% offset was reached. The low strength of Mg-18Sc-12Y is due to the formation of a small amount of β.

	Nominal		CYS (ksi) after 24 Hour Age at					
Alloy No.	%Sc	%Y	75°F	300°F	350°F	400°F	450°F	500°F
102,277	15	18	42	86	91	90	93	84
102,292	15	21	53	90	96	--	96	--
102,259	18	12	36	39	40	42	41	39
102,304	18	18	43	82	86	87	86	88

Review of the mini-scale work led to the selection of Mg-15Sc-4Li for more extensive evaluation on a larger scale. Since the five pound melt of Mg-10Sc-5Li reacted with the alumina crucible, another small (100 gram) melt of Mg-15Sc-4Li (alloy No. 102,354) was prepared in a magnesia crucible. Careful examination of the crucible after the melt was poured revealed no evidence of attack. Magnesia was therefore selected as the crucible material for the five pound melt of this alloy. When this alloy was extruded and heat treated, its properties were found to be markedly inferior to those of the first alloy (No. 102,222) of the same nominal composition. As shown below chemical analysis revealed that the second alloy (102,354) was much lower in Sc and somewhat higher in Li. Relatively little β was formed by heat treatment, and its properties therefore suffered.

	Analyzed		Ext.	F (As Extruded)				CYS (ksi)	
					ksi				
Alloy No.	%Sc	%Li	Temp.	%E	TYS	CYS	TS	T4	T6
102,222	16.9	4.7	750°F	--	--	50	41	45	65
102,354	13.6	5.3	650	--	--		39	25	31
			800	1	32	36	36		
			950	1	32	37	37		

Since the best properties of Mg-30Sc are obtained in the as-extruded condition, the extrusion temperature of Mg-14Sc-5Li (102,354) was varied in an attempt to obtain a better combination of strength and ductility. As shown on the preceding page, ductility was low regardless of extrusion temperature. This may be due primarily to the poor quality of the melt, which was heavily contaminated with flux.

D) Evaluation of Mg-15Sc-4Li

The five pound melt of Mg-15Sc-4Li was prepared without incident and was poured into a 3" diameter billet. Examination of the magnesia crucible revealed no obvious attack. The pouring and/or mold temperatures were too low because the casting solidified at the gate before the mold cavity was filled (Figure 1). This necessitated top pouring the remaining metal. Recovery was excellent - 2040 grams of casting from an initial charge of 2270 grams. Metallographic examination and chemical analysis (Table I) indicated the composition of the alloy was close to the desired level. The quality of the casting, however, was very poor due to flux contamination. The billet was scalped and extruded into 1/16" x 1 1/4" strip. As shown in Figure 1, the quality of the extrusion was also poor. Varying the container temperature from 650 to 750°F and the speed from 1 to 10 fpm had little effect on extrusion appearance.

Since extrusion quality was too poor to warrant testing, we decided to remelt the alloy and try to decrease flux contamination by settling. All of the metal from the first melt except a sample of the extruded strip was remelted. CaF_2 was added to thicken the flux and thereby aid in its separation from the metal. Since the melt was "sludgy" at 1450°F, it was heated to 1600°F and held there for 10 minutes. After settling, the melt was poured into the mold heated to 600°F to prevent premature solidification at the gate. The casting, shown in Figure 2, appeared to be much better than the first one; in fact, its quality appeared comparable to that of conventional Mg alloys prepared on this scale. When the billet was scalped, however, numerous flux spots were discovered. The recovery from the second melt was relatively poor-only 1[illegible]40 grams from the initial charge of ~2000 grams.

The limited length of the billet necessitated a change in strip size to 1/16" x 7/8" in an attempt to provide sufficient material for the evaluation planned. As shown in Figure 2, the quality of the strip was much better than that of the first extrusion (Figure 1) but was still not good. A tensile bar of the strip in the as-extruded condition failed at a stress of 39 ksi just before the 0.2% offset (yield strength) was reached. Another test bar had a CYS of 41 ksi. The poor ductility of the extrusion is attributed primarily to its poor quality. Heat treatment of the extrusion at 950°F produced only a limited amount of β (compared to an all-β structure from the first melt). Increasing the solution temperature to 1100°F increased the amount of β to about half the microstructure but caused melting at the grain boundaries.

These results indicated a significant drop in Sc and/or Li content as well as the presence of metallic impurities. This was confirmed by chemical and spectrographic analyses. Note in Table I that the Sc content (13.2%) and even the Li level (3.8%) are well below the nominal composition and the actual composition of the first melt (alloy No. 102,424). Spectrographic analysis of the second melt (102,456) indicated the probability of contamination with Ca and Zn. Since interference from Sc impairs the accuracy of the spectrographic analysis, the alloy was analyzed chemically for these elements as well as K, a major constituent of the flux. Substantial quantities of each of these elements were detected chemically.

Since Ca and K could be present in the flux inclusions and not alloyed in the metal, it was necessary to examine the microstructure of the alloy with the electron probe. A sample of the extrusion heat treated at 1100°F was selected in order to maximize the area of eutectic melting at the boundaries. The probe examination revealed the presence of α, β, undissolved particles of Sc dispersed in the structure, and high Ca concentration at the boundaries. Since these areas contained little Sc, they are believed to be primarily Mg-Ca eutectic. The melting point of this eutectic (961°F) agrees well with the metallographic observations.

The concentration of K in all the metallic phases was nil. The sample was not probed for Zn because its presence was not suspected nor revealed until a later date.

Contamination of the sample with Ca is very surprising. We must conclude that the Ca is produced by reduction of CaF_2 with Sc. Since the free energy of formation of LiF is essentially half that of CaF_2, it is reasonable to assume that LiF may also be reduced by Sc. This may explain why the Li level of the Mg-Sc-Li ternaries is usually higher than the nominal value. The lower Li level of the remelted alloy is probably due simply to oxidation losses during holding. The presence of K probably reflects severe flux contamination. The presence of Zn is baffling.

The unexpected contamination of the Mg-15Sc-4Li melt with Ca and Zn prompted the spectrographic analysis of the other two large scale melts. As shown in Table I, small amounts (~0.05%) of Ca were found in both alloys, while Al and Zn were also detected in the Mg-30Sc binary. Because these results could be caused by Sc interference, it was necessary to analyze for these elements chemically. The results in Table I show that Mg-30Sc was contaminated with 0.25% Al and Mg-10Sc-5Li contained 0.03% Ca. The indications of Ca and Zn in the spectrographic analysis of Mg-30Sc were apparently caused by interference since they were detected in only trace amounts by chemical analysis.

E) Future Work

Preparation of high quality Mg-15Sc-4Li melts in air under a flux cover is obviously a difficult task. The best solution may simply be to avoid it and prepare the alloy in an inert atmosphere. This approach will obviously eliminate flux contamination but is complicated by the vaporization of Mg. This may also be a serious problem because molten Mg must be held for a long time at relatively high temperatures in order to dissolve the Sc. We hope that this problem can be minimized by placing a lid on the crucible and using an induction field to stir the melt and accelerate dissolution of the Sc. In the preliminary work Y will be substituted for Sc, and a Mg-15Y alloy will be prepared in an argon atmosphere.

The melt will be allowed to solidify in the crucible, which is about 2 3/4" in diameter and 9" high. The billet so formed may be suitable for extrusion without scalping. If this run is successful, we will try to prepare Mg-15Sc. A second short run will then be required to alloy the Li. This two-step procedure should minimize loss of Li due to vaporization and greatly reduce the hazard of opening the furnace to air.

TABLE I

Analysis of Mg-Sc Alloys

A) Spectrographic

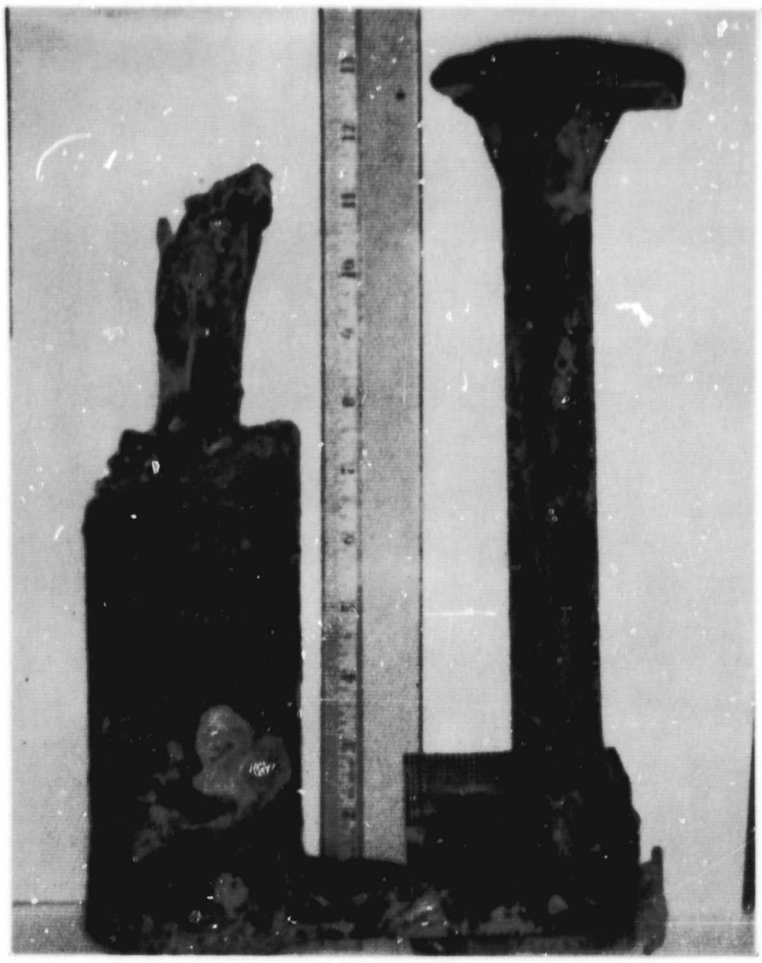
	Alloy No.		
	101,805	102,223	102,456
%Al	0.36	<0.03	0.07
%Ca	0.06	0.05	0.8
%Cu	0.015	0.011	0.007
%Fe	0.035	0.005	0.017
%Mn	0.06	<0.02	0.02
%Ni	0.05	0.004	0.018
%Pb	>0.1	0.03	0.09
%Si	0.10	<0.01	0.01
%Sn	>0.02	0.01	0.02
%Zn	0.32	<0.02	0.26

B) Chemical

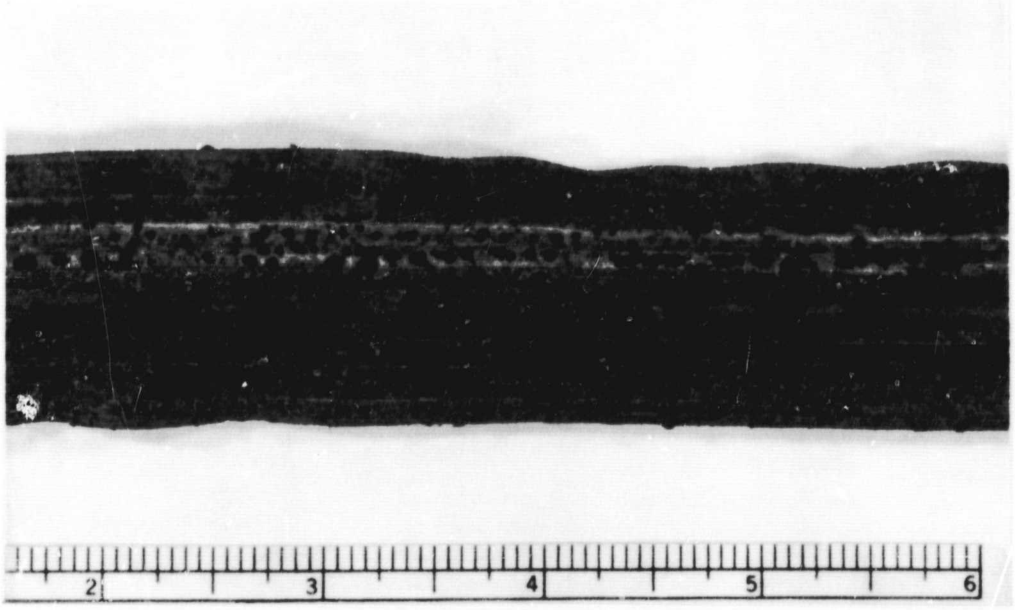
	Nominal		Analyzed		
Alloy No.	%Sc	%Li	%Sc	%Li	%Other
101,805	30	--	31.4	--	0.016 Fe
102,223	10	5	10.8	5.42	0.041 Al
102,424	15	4	15.8	5.38	
102,456*	15	4	13.2	3.85	0.52 Ca, 0.18 Zn, 0.86 K

*Remelt of 102,424

Figure 1
Mg-15Sc-4Li-First Melt (Alloy No. 102,424)



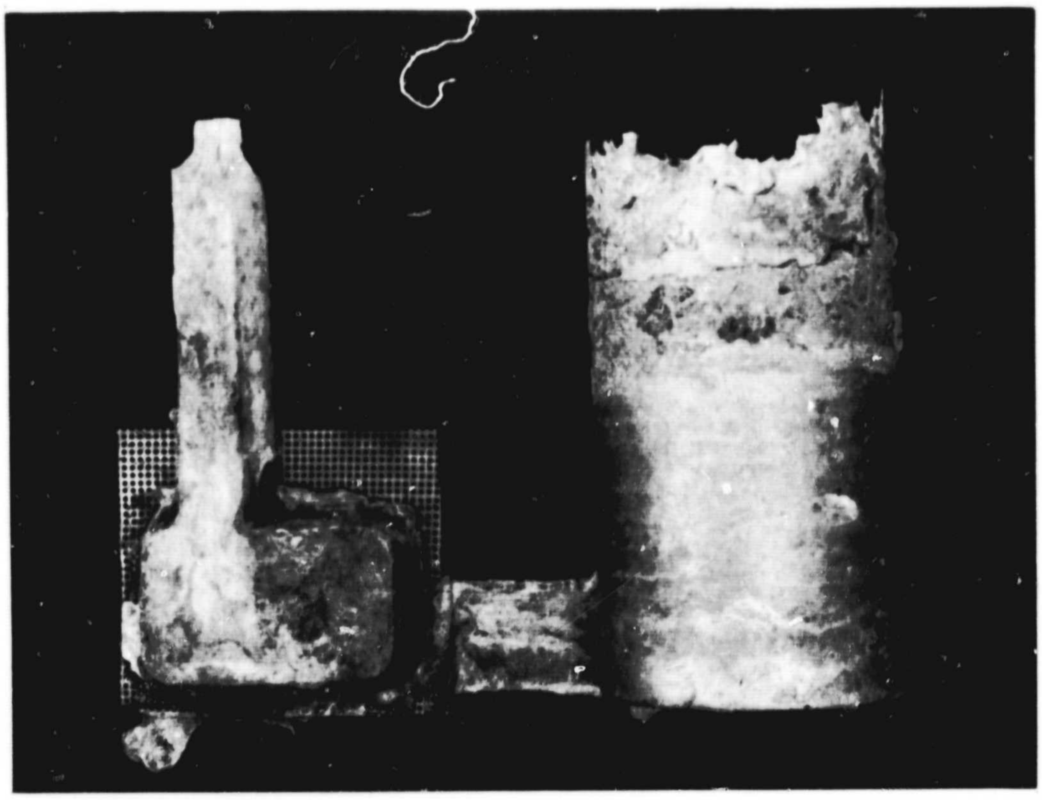
Negative No. 66473
Casting - 3" Diameter Billet



Negative No. 66471
Extrusion - 1/16" x 1 1/4" Strip

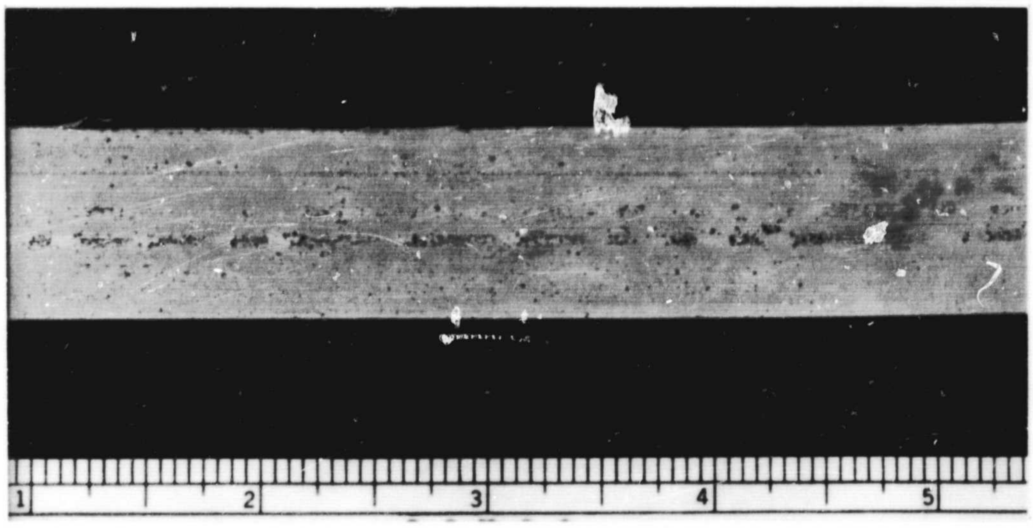
Figure 2

Mg-15Sc-4Li-Remelt (Alloy No. 102,456)



Negative No. 66369

Casting - 3" Diameter Billet



Negative No. 66472

Extrusion - 1/16" x 7/8" Strip