

MODIFICATION OF SILICON IN EUTECTIC AND HYPER-EUTECTIC Al-Si ALLOYS

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Abstract

Tableted FeP, NiP, CuP, and FeP+CuP as well as granular CuP were evaluated for modification of primary Si in several Al-Si foundry alloys. Virgin A390, 392, and 393 alloys and secondary aluminum-based B390.1 and 339.1 alloys were studied in this investigation. Tableted FeP (-100 mesh sizing) proves to be a more potent modifier than conventional CuP. Primary Si grain size of below 40-microns is achieved at 50ppm P-addition rate and short contact times for alloy temperature range of 1350-1470°F. Phosphorus treatment of eutectic alloys result in formation of primary Si and reduction in size and volume of eutectic Si.

Introduction

The hyper-eutectic Al-Si alloys exhibit a highly desirable combination of characteristics, such as castability, low coefficient of thermal expansion, weldability, corrosion resistance, machinability, abrasion resistance, good sliding properties, and high temperature strength. The high silicon concentration in these alloys is primarily responsible for many of these characteristics. However, small sizing and highly uniform distribution of Si particles in the alloy is essential for attainment of optimum alloy properties. Because of these desirable characteristics, the hyper-eutectic Al-Si alloys find widespread usage in automotive applications. For example, the Aluminum Association (AA) registered 390 alloys are used as material of choice for engine blocks, cylinders, and brake parts. For higher wear resistance and lower thermal expansion AA registered 392 and 393 alloys are used for heavy duty pistons, brake parts, clutches, and pumps. The eutectic and near eutectic Al-Si alloys constitute even a larger share of the commercial Al-Si foundry alloys. Alloys such as AA registered 339 alloy are also widely used in automotive applications such as pistons.

The eutectic in the Al-Si alloy system occurs at 12% Si. The microstructure of alloys containing greater than about 15% Si generally contains primary Si grains along with Al+Si eutectic. Alloys containing between 12-15% Si although hyper-eutectic by definition, may not contain primary Si grains because of presence of other elements and non-equilibrium conditions.

For similar reasons, and on the contrary, alloys containing 8-12% Si may contain Al+Si eutectic, primary Al, as well as primary Si grains. Extensive use of secondary Al and recycled Al scrap in production of Al-Si foundry alloys introduce many other elements such as Fe,

Cu, Mn, Mg, Ni, Zn, Ti, Cr, and Sn into these alloys and along with non-equilibrium cooling, influence the microstructure expected from the equilibrium phase diagram.

The primary silicon in hyper-eutectic alloys is not readily nucleated by the usual impurities which are usually present in these alloys. Refinement of primary silicon is usually achieved by the addition of phosphorus to the melt. Phosphorus reacts with liquid aluminum to produce a fine dispersion of aluminum phosphide (AlP) which has a crystal structure very similar to that of silicon, and acts as an effective heterogeneous nucleant for silicon. Other elements such as Mg, W, S, and La have been reported to be effective modifiers but none has achieved commercial importance^(1,2).

The eutectic Al-Si alloys on the other hand are refined by addition of Sr, Na, or Sb. These elements affect the growth and branching of eutectic Si crystals during solidification and thus influence their size and morphology. However, the microstructure of eutectic alloys will also be altered by presence of phosphorus through formation of primary Si crystals and change in size and morphology of eutectic Si.

The two most common techniques to add phosphorus to Al-Si is usage of copper-phosphorus (CuP) master alloys (such as 1% P-Cu, 8% P-Cu, and 15% P-Cu granules, shots, nuggets, and rod) and specialty commercial fluxes. Use of Cu-P master alloys adds considerable amounts of copper to the alloy. A number of Al-Si alloys (such as the AA registered 392 and 393 alloys) have a limited tolerance for copper concentrations thus restricting CuP usage at large addition rates. Most fluxes contain red phosphorus as the active agent (typically 1-2% P) and other salts to prevent rapid oxidation/combustion of elemental phosphorus. Safety and environmental concerns, low phosphorus concentration, and degree of effectiveness are a number of drawbacks of these fluxes.

Nickel-Phosphorus (NiP) containing 20% P is an effective silicon modifier and is available in ingot and lump form. However, its high price prohibits its wide spread application. Ferrophosphorus (FeP) containing 25% P is also an effective lower cost silicon modifier which is available in lump or granular form. However, low tolerance for iron in a number of Al-Si alloys, such as the AA registered A390 alloys, limit widespread application of FeP.

Recently developed high performance phosphorus additives which utilize FeP, NiP, CuP or a combination of these in powder form as source of phosphorus have been extensively reviewed by the

author³⁾. Comparison of the performance of these new additives with that of conventional CuP shot in modification of secondary Al-based B390.1 and 339.1, and virgin A390, 392, and 393 alloys is the subject of this investigation.

Experimental

Commercially available FeP (25.0% P) in lump form, CuP (15.0% P) as 1/32" x D granules, and NiP (20.0% P) in lump form were granulated and screened to -100 mesh sizing for this study. Atomized aluminum powder of 99.9% purity at 30 mesh x D sizing was used as the binding agent. The following formulations were prepared and tableted via cold compaction at 15,000 psi.

15% P	:	60% FeP-40% Al
12% P	:	60% NiP-40% Al
12% P	:	30% FeP-30% CuP-40% Al
12% P	:	80% CuP-20% Al

CuP granules was used directly without compaction in evaluation of secondary aluminum-based B390.1 and 339.1 alloys. These two alloys were supplied by a secondary aluminum ingot manufacturer. The virgin A390, 392, and 393 alloys were prepared directly from 99.99% purity Al, Si, Fe, Cu, Mn, Mg, Ni, Zn, Sn, and Ti.

The alloy for each test, weighing approximately 10kg was prepared by melting in a ceramic coated steel pot via a resistance heated furnace. A melt sample was taken prior to addition and at 1, 2, 3, 4, 5, 10, 30, and 60 minutes after addition of phosphorus additive. The alloy was stirred for 30-seconds after the initial addition of phosphorus additive and for 10-seconds prior to each sampling. Samples were taken using a ceramic coated steel cone sampler (AA TP-1 grain refining test⁴⁾ sampler, 2.5" large diameter x 1" small diameter x 2.5" height) which was heated to 200°C prior to each sampling. Upon sampling, each sample was air cooled to full solid form prior to extraction from the cone sampler. These samples were sectioned (perpendicular to cone axis) 0.3 inches from the bottom (small diameter end) of each sample cone. The cut surface was mounted and polished for metallographic examination. Average primary silicon grain size was measured via standard ASTM grain size measurement technique.

Results and Discussion

The extent of primary Si modification in virgin A390 alloy, when tableted CuP, CuP+FeP, NiP, and FeP (all at -100 mesh sizing) were used as modifiers are presented in Figure 1.a&b for 730°C and 800°C alloy temperatures, 100ppm P-addition rate, 5-minutes and 60-minutes after modifier addition. Figure 2 and 3 show the primary Si grain size for alloy A390 as a function of P-addition rate and time from addition when tableted CuP and tableted FeP (both at -100 mesh sizing) are used as modifiers. The results indicate that CuP produce little or no modification at 730°C alloy temperature at 100ppm P-addition rate while some modification takes place at 800°C alloy temperature. A mixed FeP+CuP additive shows significantly better modification effect while NiP and FeP produce the best modification. Primary Si grain size of 40-microns is readily achieved with both NiP and FeP-based additives at very short contact times.

The effectiveness of tableted CuP, NiP, and FeP (all at -100 mesh sizing) in modification of 392 and 393 alloys at 730°C and 800°C

alloy temperatures and 100ppm P-addition rate were also investigated. Again, CuP produces no modification at these addition level and temperature in both alloys while NiP results in some modification, with FeP producing a better refining effect. The 393 alloy with a higher Si content proves to be more difficult to modify than the 392 alloy.

The modification effects for secondary-based B390.1 alloy using tableted FeP and CuP granules are shown in Figure 4.a and 4.b. It is shown that tableted FeP (-100 mesh sizing), in contrast to granular CuP, is a far better Si modifier at both low and high alloy temperatures, low addition rates, and short contact times. At 50ppm P-addition rate, primary Si grain size of below 50 microns is readily achievable with tableted FeP while no modification is achieved with CuP granules at this addition rate for both high and low alloy temperatures.

Addition of phosphorus to unmodified/as cast secondary based 339.1 alloy results in precipitation of primary Si grains in this eutectic alloy. Formation of primary Si is also accompanied by reduction in width and thus volume of acicular eutectic Si in this alloy. Both FeP and CuP produce this result with FeP being a more potent modifier. Figure 5 shows the results for CuP modified alloy.

Summary and Conclusion

Tableted FeP (-100 mesh sizing) and tableted NiP (-100 mesh sizing) are far more potent primary Si modifiers than tableted or granular CuP. This was demonstrated for virgin alloys A390, 392, and 393 and for secondary-based B390.1 and 339.1 alloys. Tableted FeP produces below 40 micron primary Si grain size in 390 alloys at 50ppm P-addition rate, short contact time and at both low and high alloy temperatures.

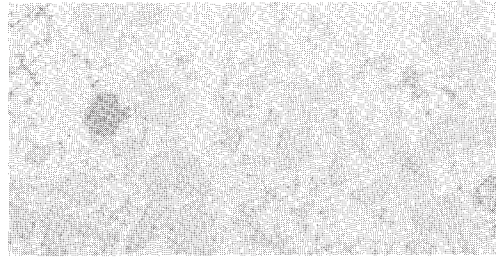
Addition of phosphorus to 339.1 alloy results in formation of primary Si grains and reduction in size and volume of eutectic Si.

Acknowledgments

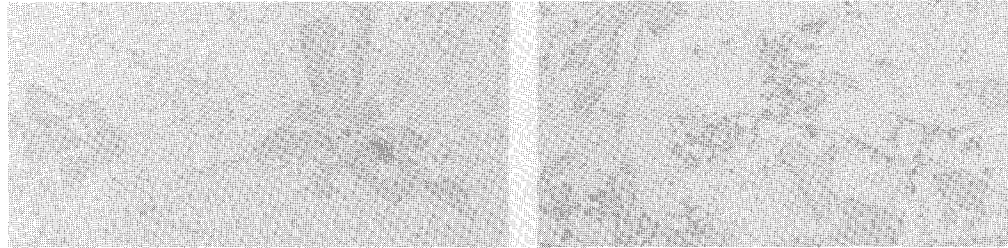
The author wishes to thank many of his colleagues at Shieldalloy Metallurgical Corporation for their support and assistance with this work. Special thanks to Glenn D. Lucas and Michael Borrero for their effort with the experimental runs and analysis, and to Janet B. Heck for her invaluable work in preparing the manuscript.

References

1. J.R. Davis, et al, eds., Metals Handbook, Vol. 15 (Metals Park, OH; American Society for Metals, 1988), 161-753.
2. J.E. Gruzleski and B.M. Closset, "The Treatment of Liquid Aluminum-Silicon Alloys" (DesPlaines, IL; American Foundrymen's Society, 1990) 13-126.
3. B. Heshmatpour, "High Performance Phosphorus Additives for Modification of Silicon in Al-Si Alloys", Light Metals 1996 (Warrendale, PA; The Minerals, Metals & Materials Society), 687-695.
4. TP-1 Standard Test Procedure for Aluminum Alloy Grain Refiners, 1995 (Washington, D.C.; The Aluminum Association.)

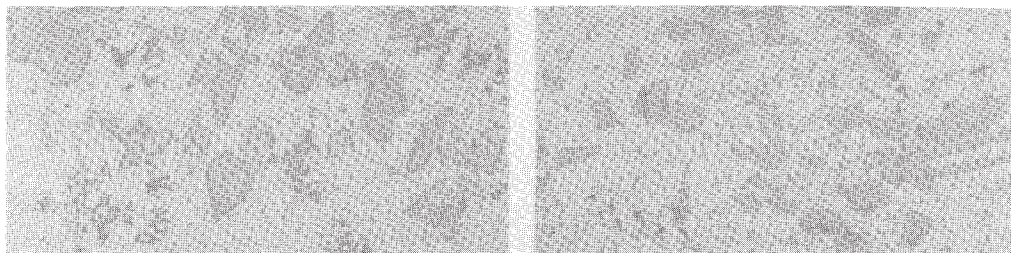


A390 ALLOY BEFORE MODIFICATION



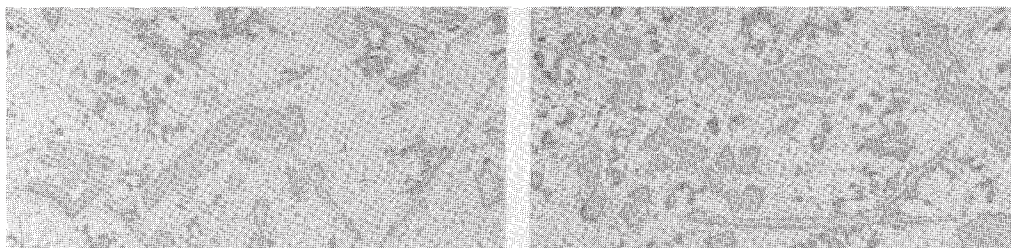
CuP - 730°C, 5-minutes after addition

CuP - 730°C, 60-minutes after addition



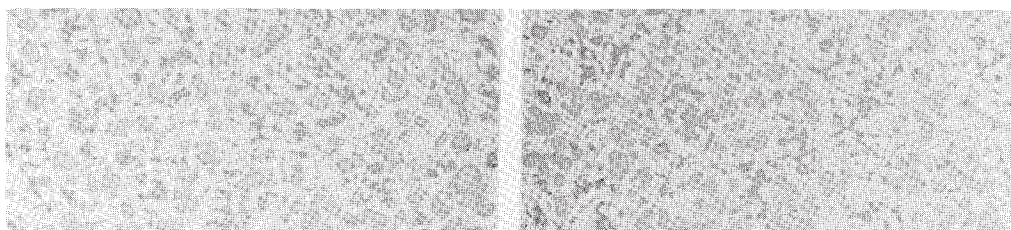
CuP - 800°C, 5-minutes after addition

CuP - 800°C, 60-minutes after addition



CuP+FeP - 730°C, 5-min. after addition

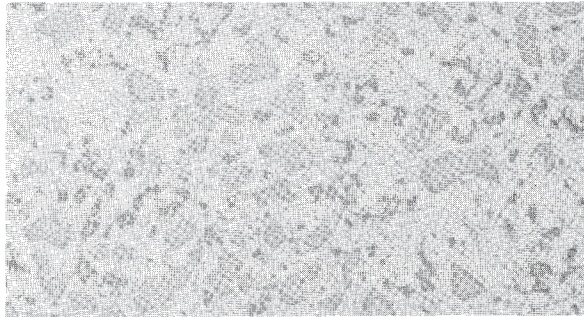
CuP+FeP - 730°C, 60-min. after addition



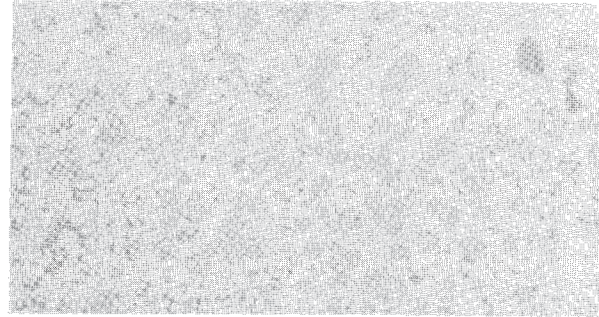
CuP+FeP - 800°C, 5-min. after addition

CuP+FeP - 800°C, 60-min. after addition

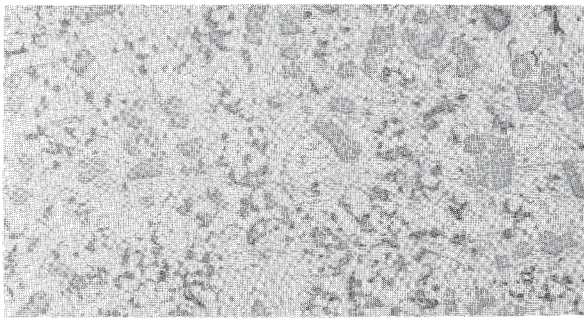
Figure 1.a - Modification of virgin A390 alloy using CuP, CuP+FeP, NiP, and FeP at 100 ppm phosphorus addition rate (magnification 50x).



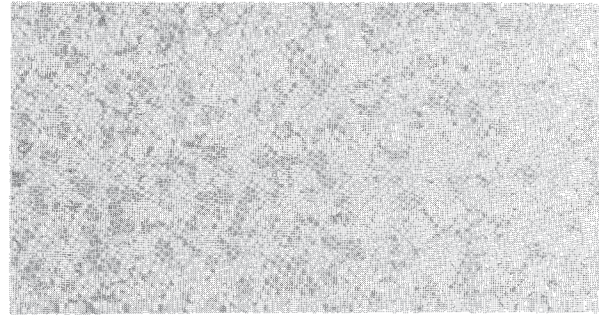
NiP - 730°C, 5-minutes after addition



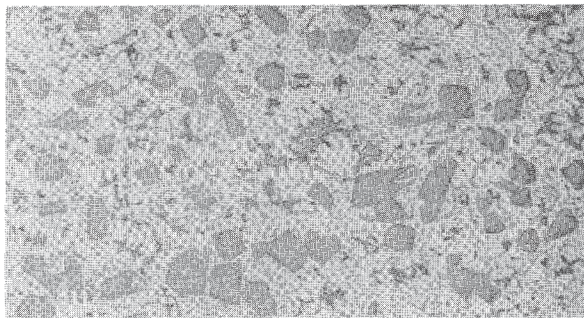
NiP - 730°C, 60-minutes after addition



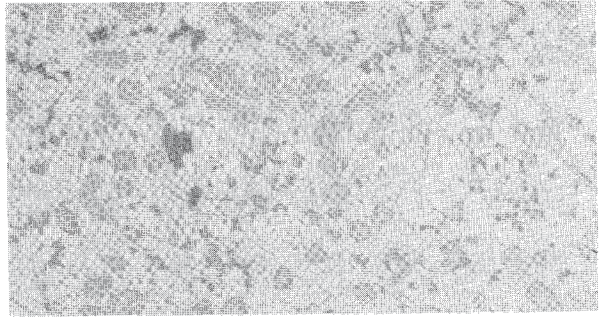
NiP - 800°C, 5-minutes after addition



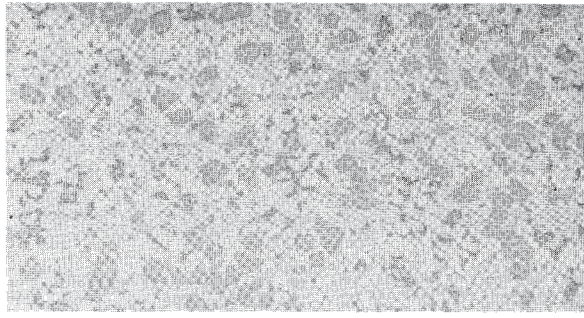
NiP - 800°C, 60-minutes after addition



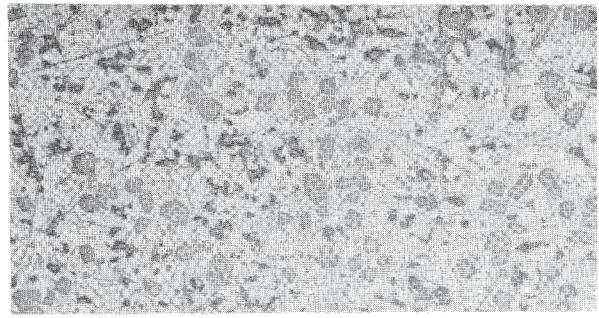
FeP - 730°C, 5-minutes after addition



FeP - 730°C, 60-minutes after addition



FeP - 800°C, 5-minutes after addition



FeP - 800°C, 60 minutes after addition

Figure 1.b - Modification of virgin A390 alloy using CuP, CuP+FeP, NiP, and FeP at 100ppm phosphorus addition rate (magnification 50x).

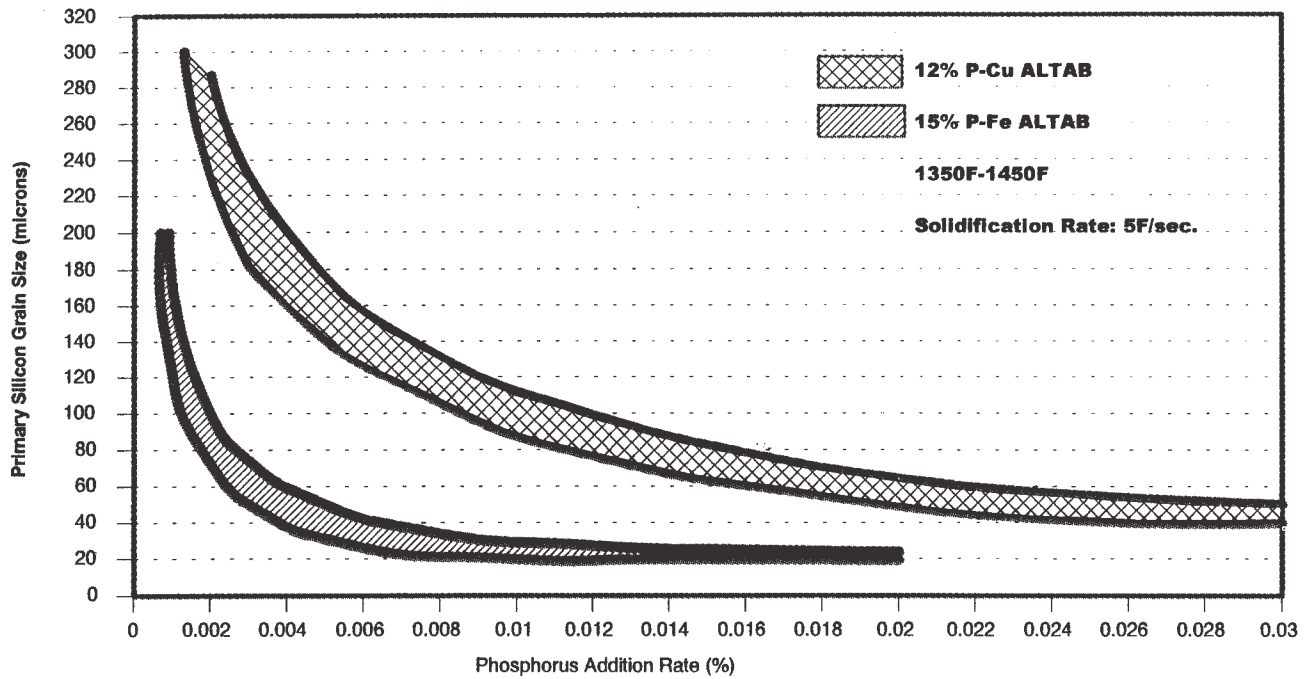


Figure 2 - Primary silicon grain size for alloy A390 for various phosphorus addition rates.

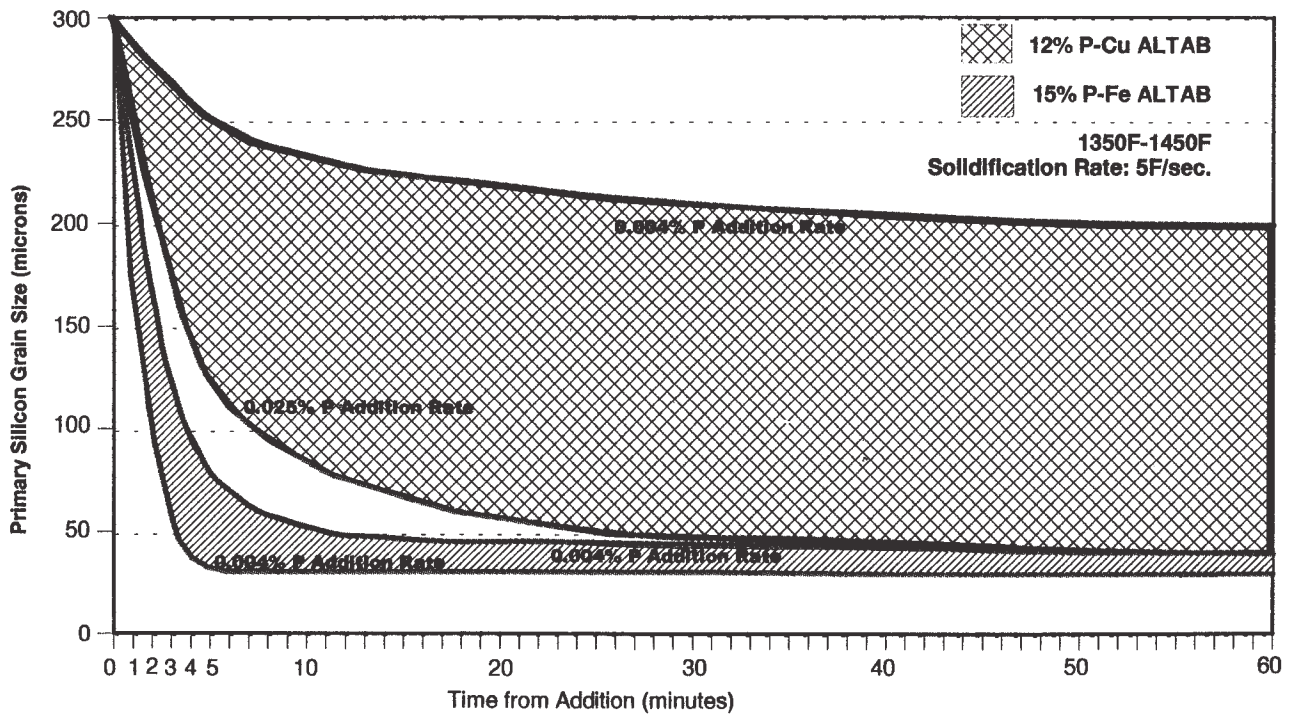
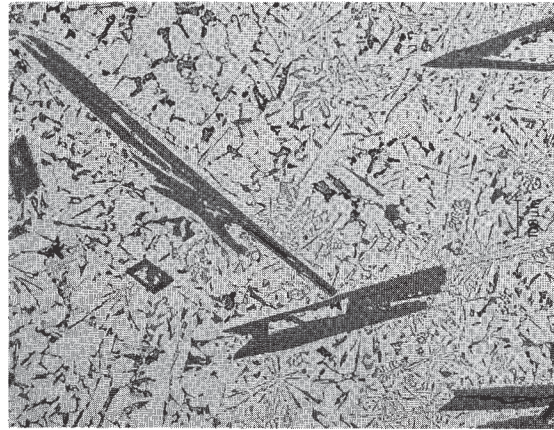
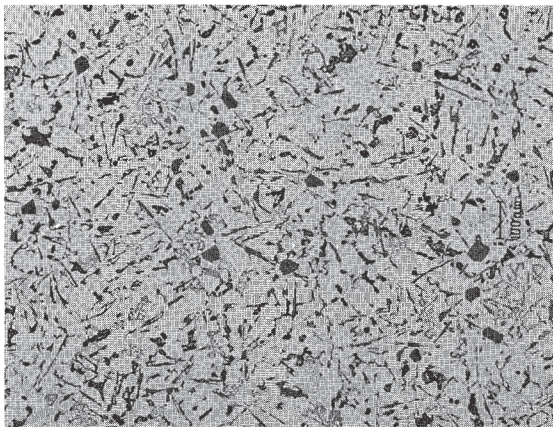


Figure 3 - Primary silicon grain size in alloy A390 as a function of time after addition of P-ALTAB.



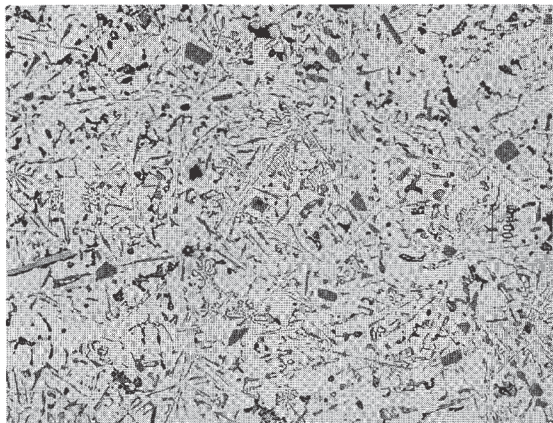
Alloy B390.1 before modification



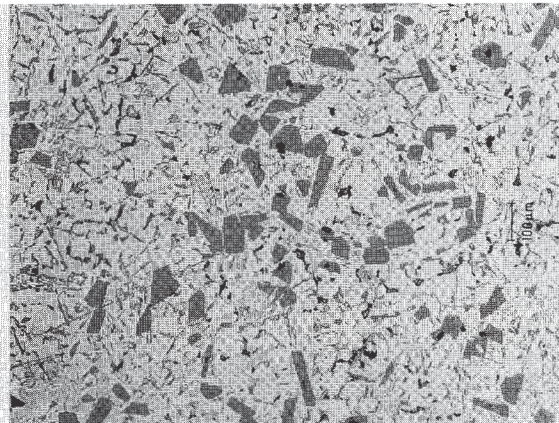
**FeP - 50ppm P-addition, 730°C
30-minutes after addition**



**FeP - 50ppm P-addition, 730°C
60-minutes after addition**



**FeP - 50ppm P-addition, 790°C
30-minutes after addition**



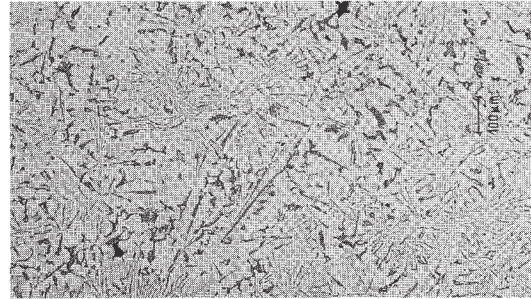
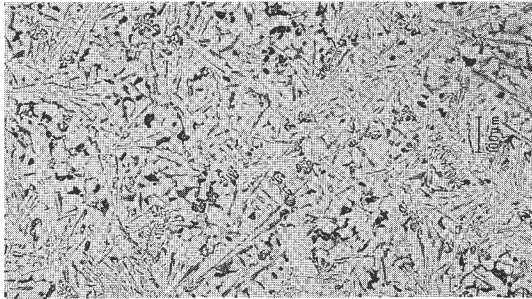
**FeP - 50ppm P-addition, 790°C
60-minutes after addition**

**Figure 4.a - Modification of secondary Al-based B390.1 alloy using FeP.
(magnification 100x).**

CuP Modified Alloy

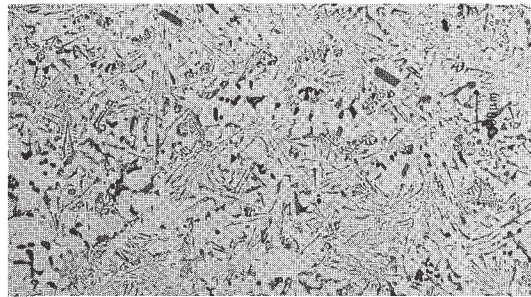
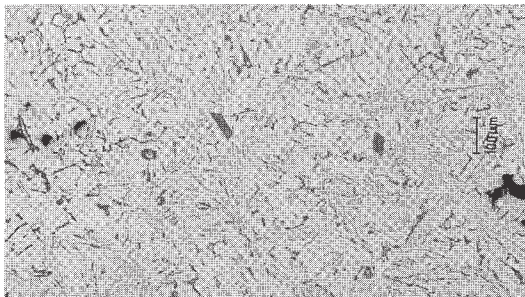
30-Minutes After Addition

60-Minutes After Addition



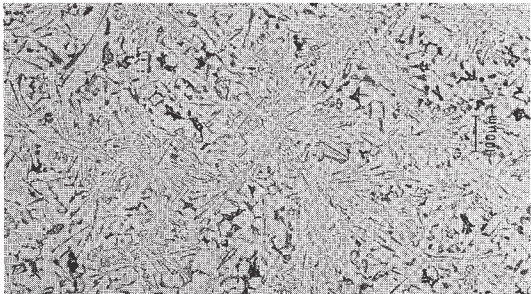
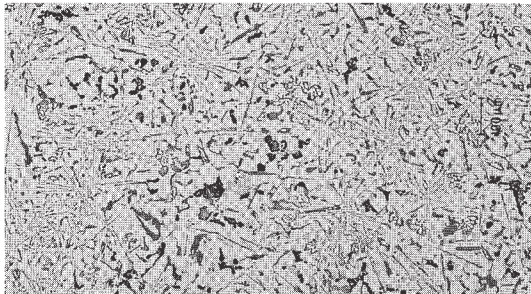
50ppm P-addition - 730°C

50ppm P-addition - 730°C



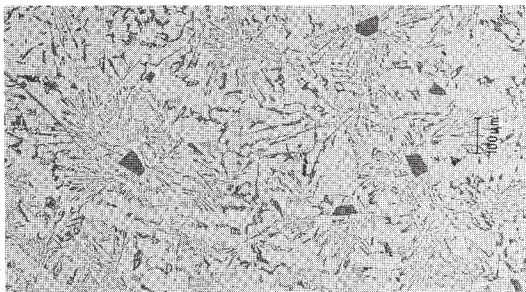
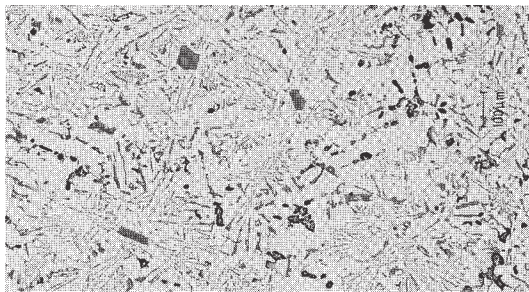
100ppm P-addition - 730°C

100ppm P-addition - 730°C



50ppm P-addition - 790°C

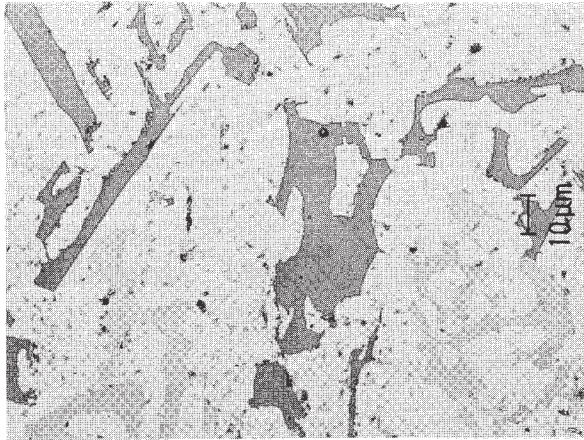
50ppm P-addition - 790°C



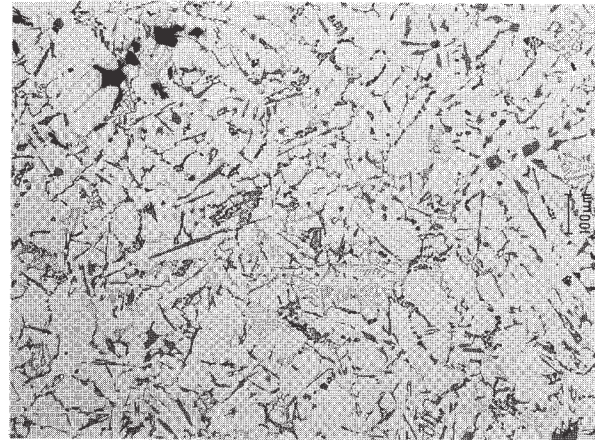
100ppm P-addition - 790°C

100ppm P-addition - 790°C

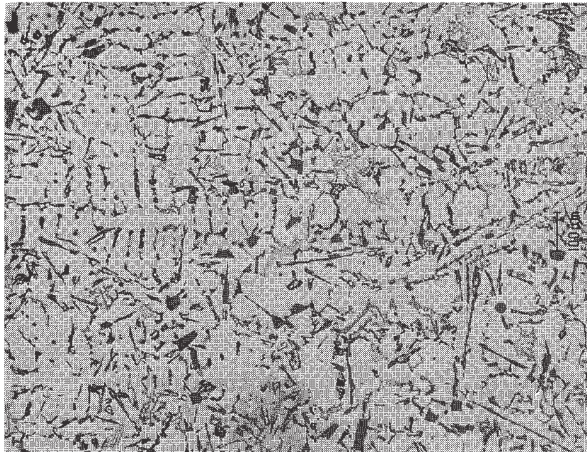
Figure 4.b - Modification of secondary Al-based B390.1 alloy using CuP. (magnification 100x).



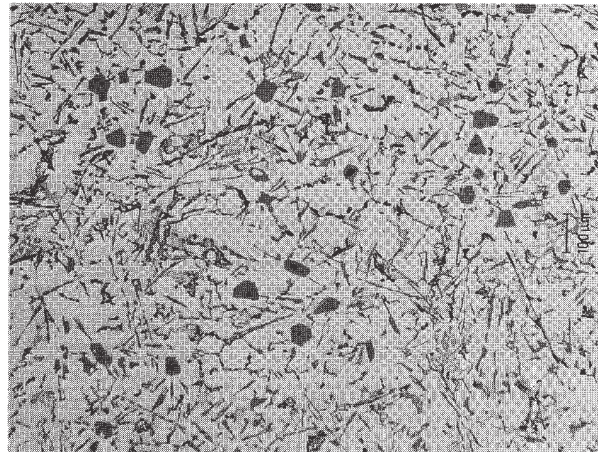
Before Modification , 500x



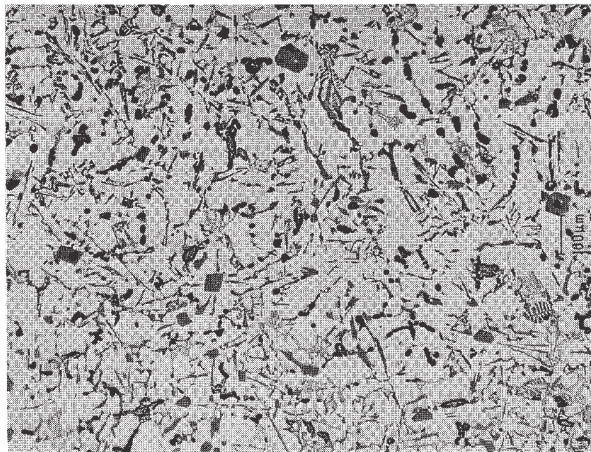
Before Modification, 100x



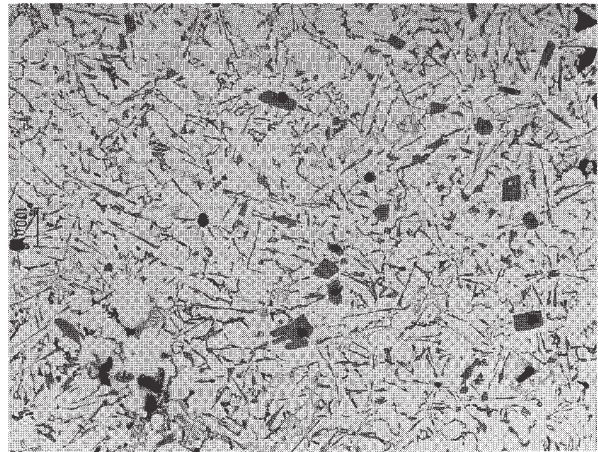
CuP - 50ppm P-addition, 730°C, 100x



CuP - 100ppm P-addition, 730°C 100x



CuP - 50ppm P-addition, 790°C, 100x



CuP - 100ppm P-addition, 790°C, 100x

Figure 5 - Modification of secondary Al-based 339.1 alloy using CuP, 60-minutes after addition.