

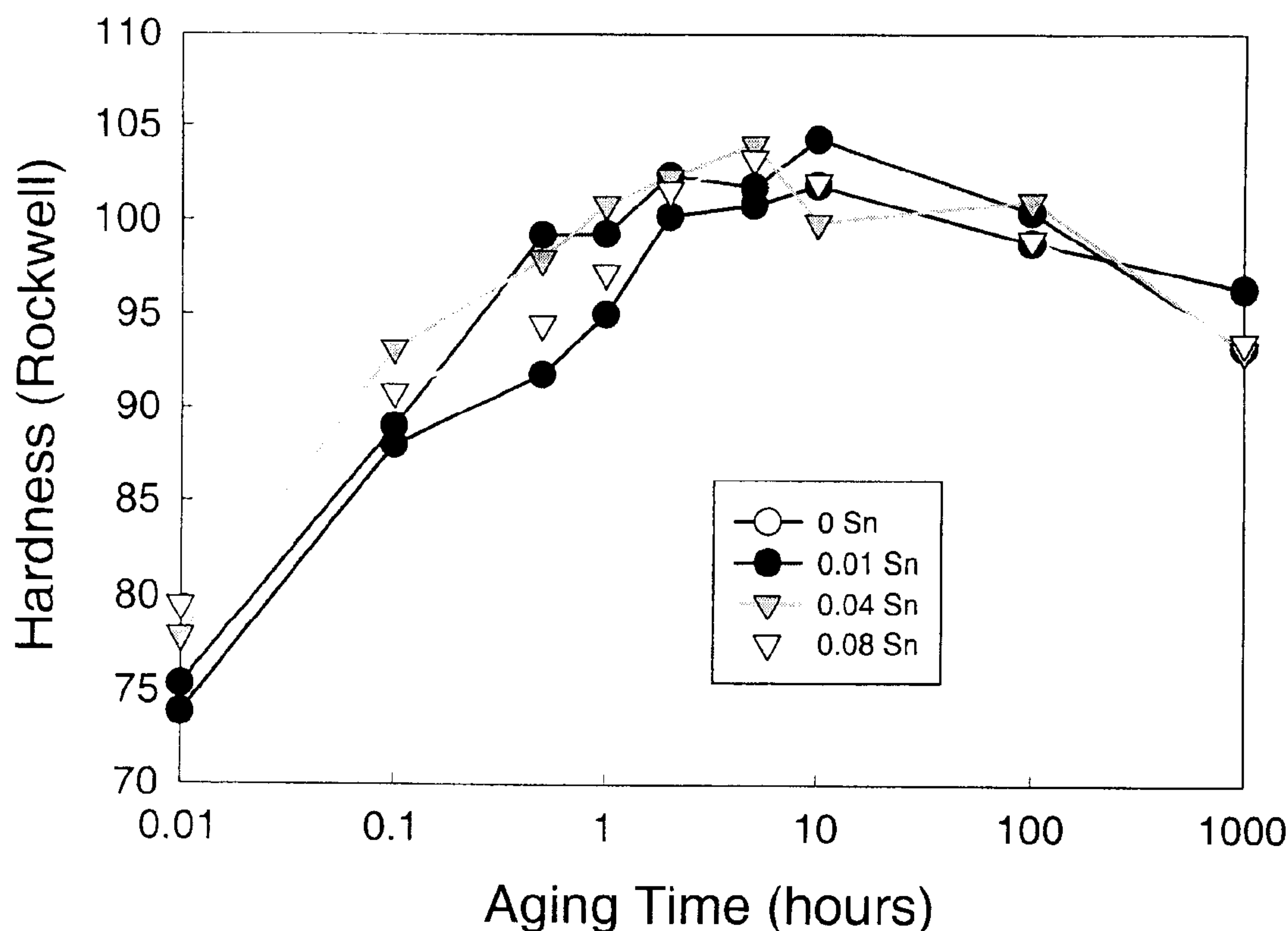
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(19) **United States**(12) **Patent Application Publication**
Wolverton et al.(10) **Pub. No.: US 2004/0213694 A1**(43) **Pub. Date: Oct. 28, 2004**(54) **A HIGH STRENGTH CAST ALUMINUM
ALLOY WITH ACCELERATED RESPONSE
TO HEAT TREATMENT**(75) Inventors: **Christopher Wolverton**, Saline, MI
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24, 2003.**Publication Classification**(51) **Int. Cl.⁷** **C22C 21/04**(52) **U.S. Cl.** **420/530; 420/537**(57) **ABSTRACT**

The invention relates to an improved cast Al alloy designed to provide an accelerated response to heat treatment; specifically, the alloy's response to thermal growth during aging is accelerated, leading to a dimensionally more stable casting. This improvement is achieved by the addition of trace amounts of Sn, In, Ge or Cd to an Al—Si—Cu cast alloy. The improved alloy has particular application for cast Al engine blocks and cylinder heads.

**Effect of Sn Additions on Hardness
Aging at 180C**

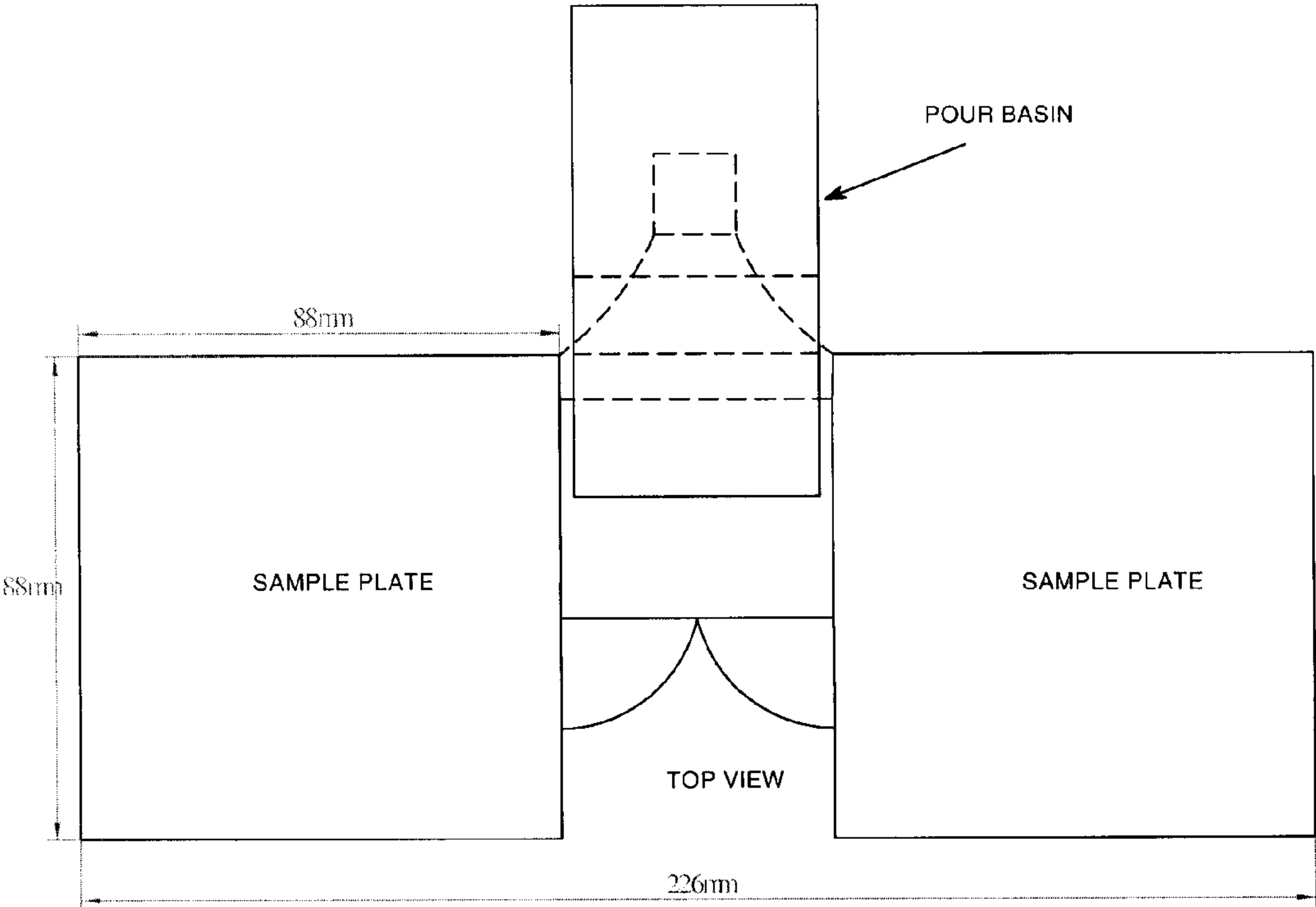


Fig. 1

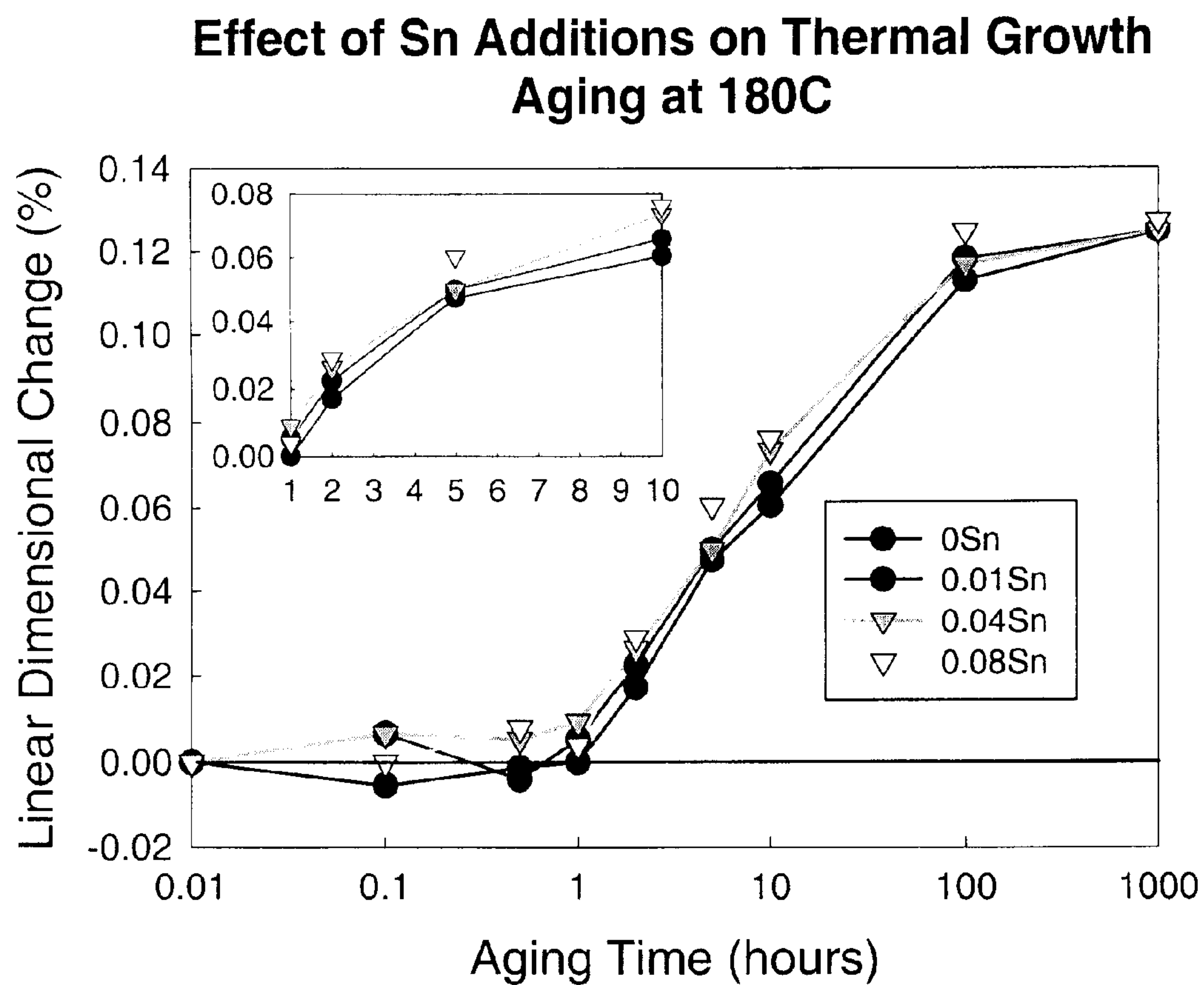


Fig. 2

**Effect of Sn Additions on
Kinetics of Precipitate Growth
Aging at 180C**

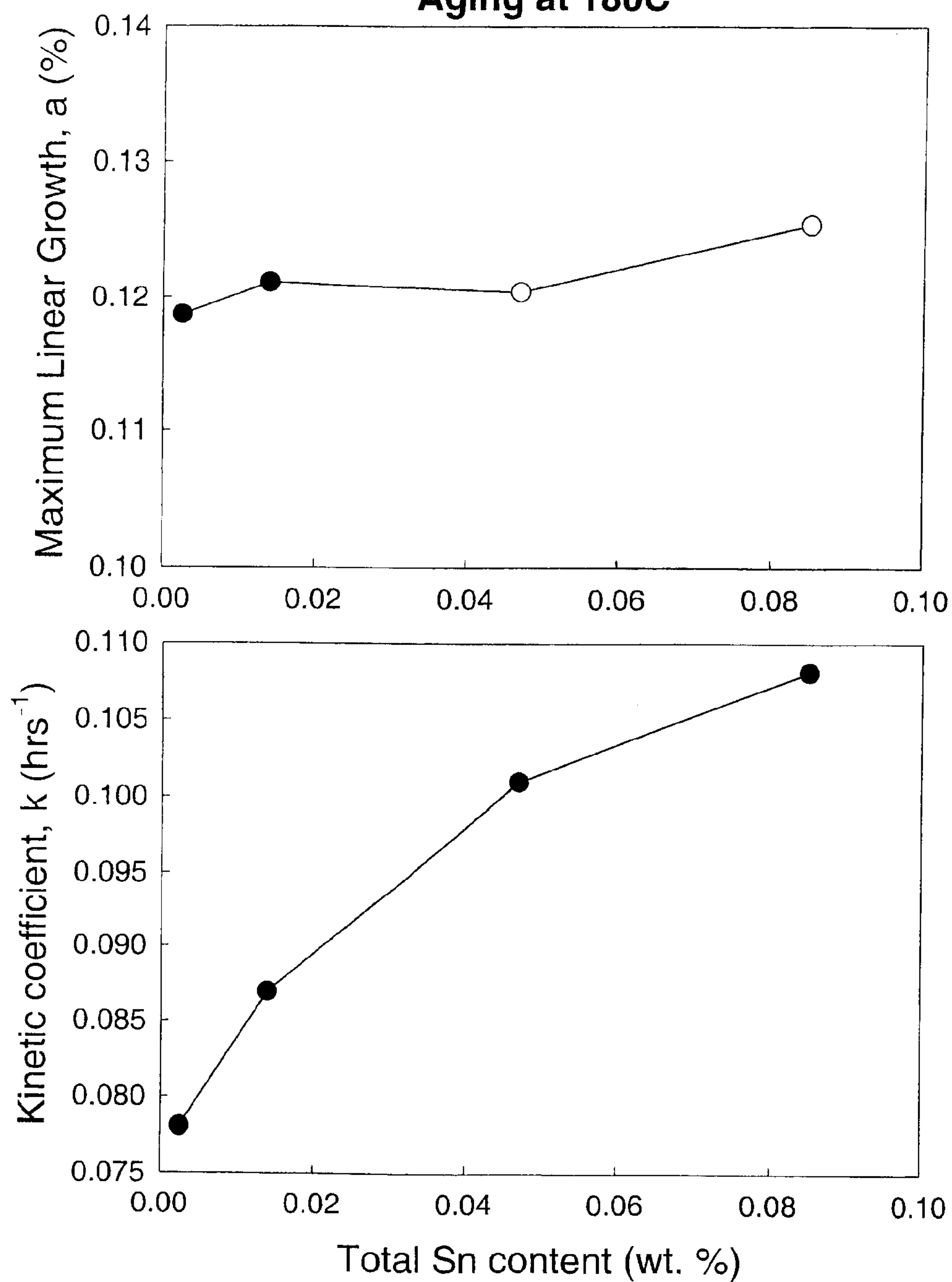
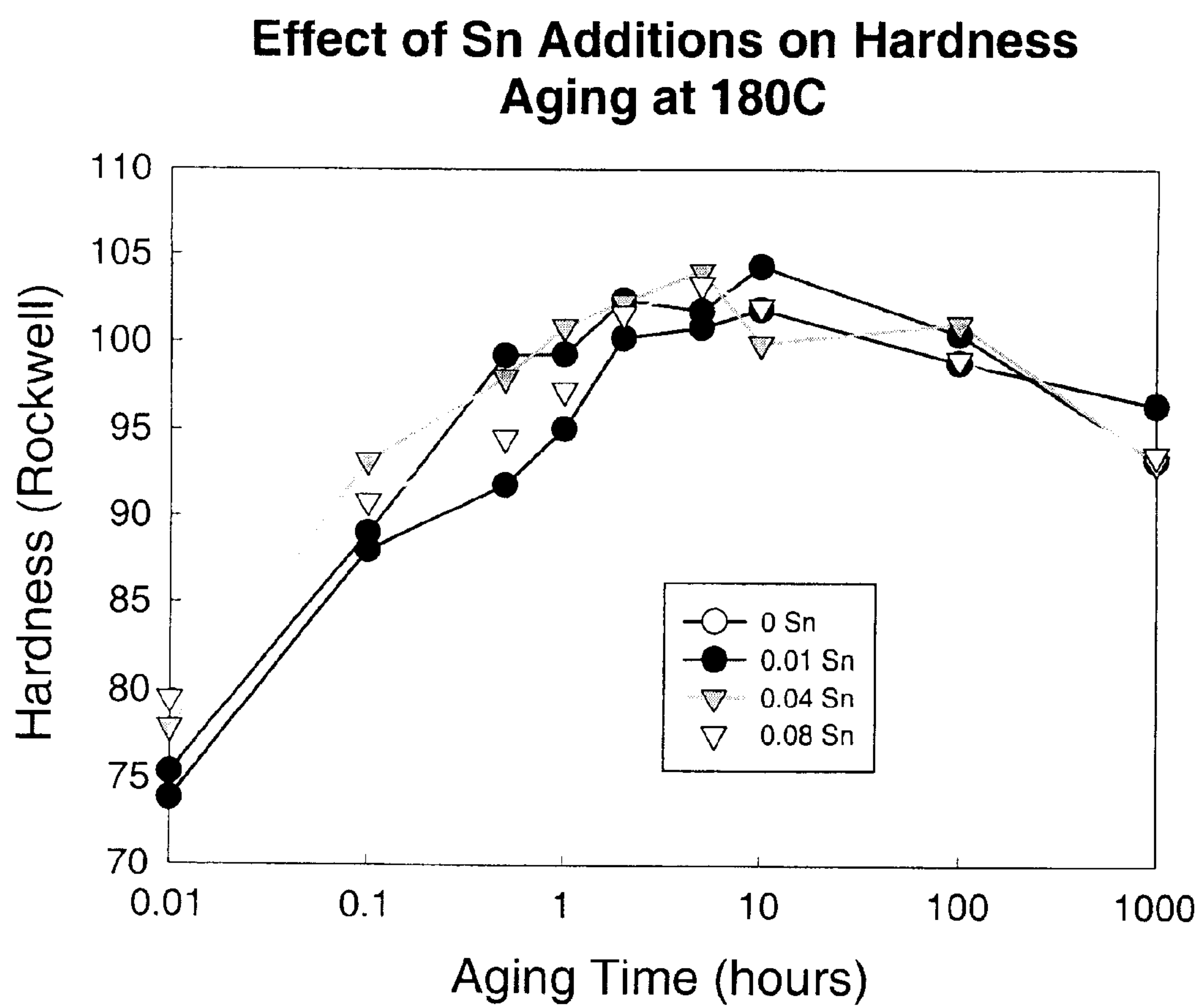


Fig. 3

**Fig. 4**

Effect of Sn Additions on Thermal Growth Aging at 240C

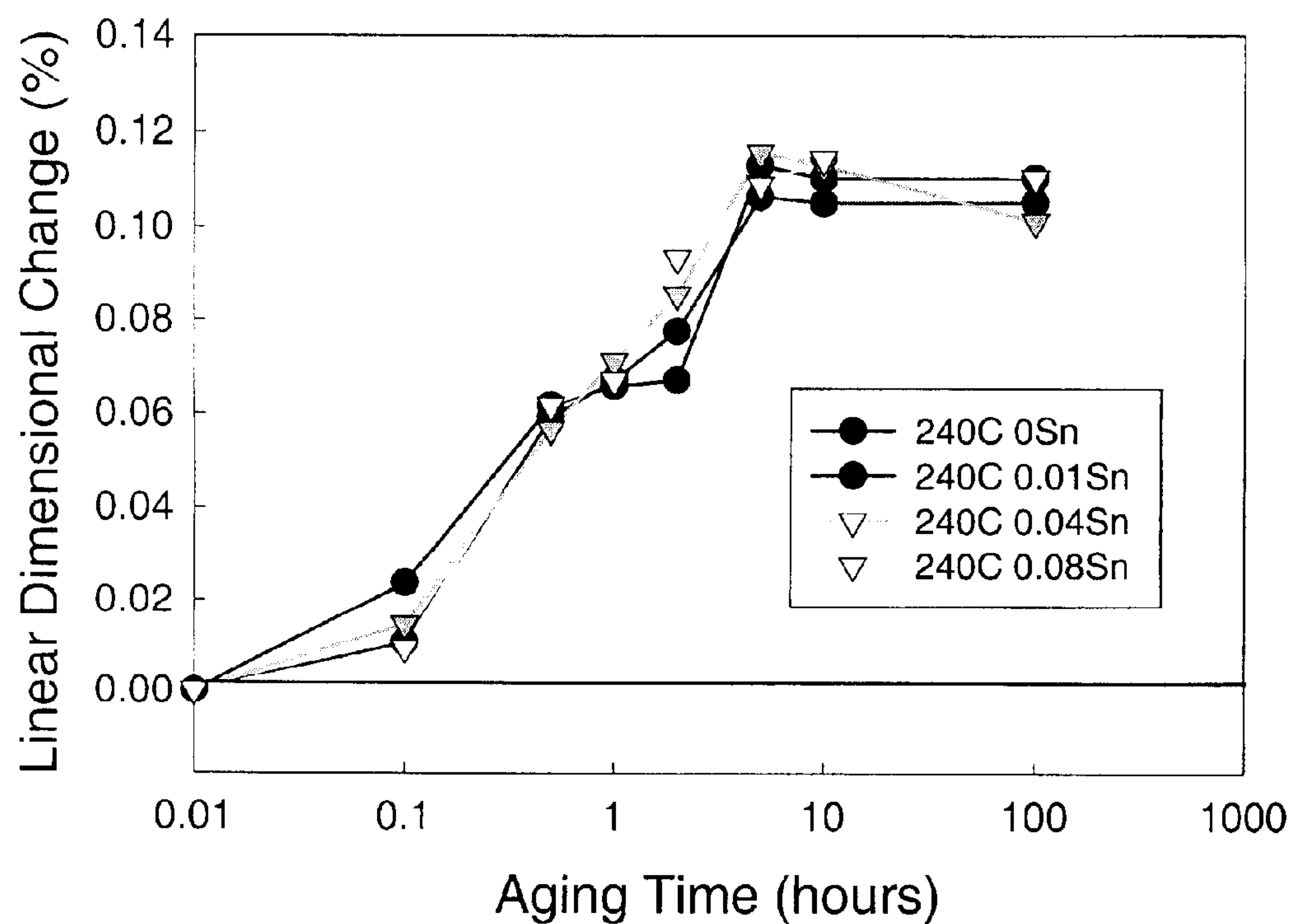
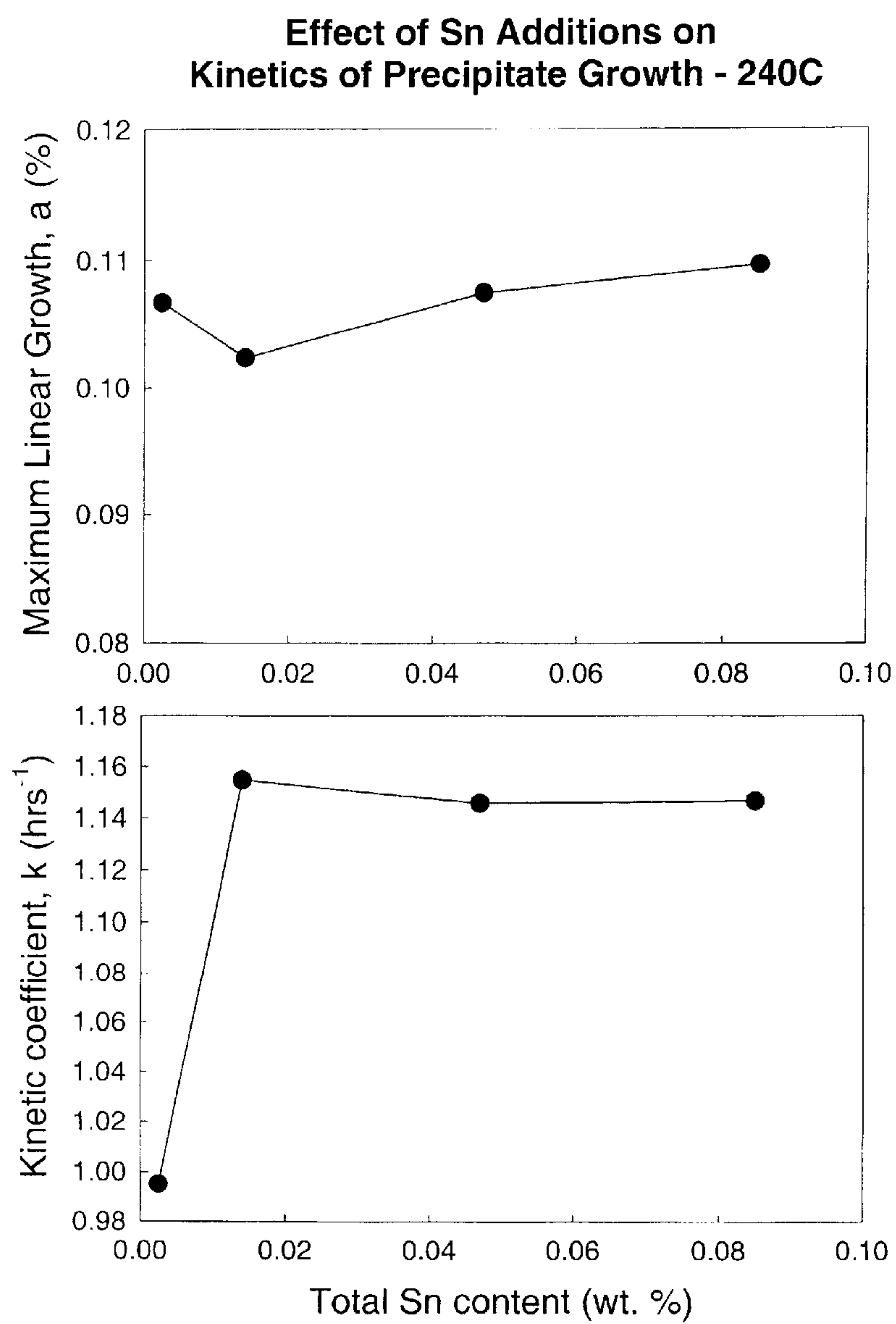


Fig. 5

**Fig. 6**

A HIGH STRENGTH CAST ALUMINUM ALLOY WITH ACCELERATED RESPONSE TO HEAT TREATMENT

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. provisional application Ser. No. 60/320,143 filed Apr. 24, 2003.

BACKGROUND OF INVENTION

[0002] 1. Field of the Invention

[0003] The field of this invention relates to cast aluminum alloys having an accelerated response to heat treatment and a method for the same.

[0004] 2. Background Art

[0005] Cast aluminum engine blocks and cylinder heads, such as those made from Al—Si—Cu—Mg alloys (e.g., a broad array of the 3xx.x class of alloys), are often heat-treated after casting to impart increased mechanical strength to the alloy via precipitation hardening. The heat treatment process usually comprises a solution treatment stage, a quenching stage, and an aging stage. During the solution treatment stage, the alloy is heated above its solubility limit to homogenize the alloy. The length of time that the alloy is heated above its solubility limit is often dictated by the amount of inhomogeneity in the alloy before heat treatment. During the quenching stage, the alloy is quenched to a relatively low temperature where the homogeneous state of the alloy solution is frozen in. During the aging stage, the precipitation-hardened alloy is aged below the solubility limit, causing precipitates to nucleate, grow and coarsen with aging time.

[0006] The yield strength of the precipitation-hardened alloy initially increases during aging, as precipitates act as obstacles for dislocation motion in the material. However, extended aging usually results in the coarsening of precipitates, which decreases the mechanical strength of the precipitation-hardened alloy. An optimum aging time and temperature exists for the precipitation-hardened alloy to achieve its highest strength before the coarsening of precipitates starts decreasing the precipitation-hardened alloy's strength.

[0007] In many precipitation-hardened alloys aged for peak strength, a macroscopic, irreversible, dimensional change has been known to occur during extended in-service, high-temperature exposure. This effect is commonly referred to as thermal growth, since the dimensional change is usually positive. It should be noted that irreversible thermal growth should not be confused with dimensional changes due to thermal expansion that can occur reversibly with temperature.

[0008] Thermal growth can cause deleterious effects on the performance of blocks and heads. Emission certification failures as well as fatigue cracks in several cylinder heads are believed to have been caused by thermal growth complications.

[0009] As a result of the deleterious effects of thermal growth, a specialized T7 heat-treatment is often devised to overage the alloy beyond its point of peak strength in order to stabilize the precipitation-hardened alloy against thermal growth.

[0010] The use of lightweight, precipitation-hardened alloy components is anticipated to increase dramatically in the following years. As a result, the automotive industry and other industries will experience an overall increase in costs associated with heat-treating precipitation-hardened alloy components. Therefore, the optimization of heat treatment of precipitation-hardened alloy components by decreasing aging times and/or aging temperatures would result in significant cost savings.

SUMMARY OF INVENTION

[0011] The present invention relates to a new alloy that provides improved heat treatment response and thus decreased aging times for engine blocks and heads, which results in significant savings of costs associated with heat treatment. This new alloy also results in decreased variability in its response to heat treatment. More specifically, under this invention, a multi-component alloy, such as the aluminum-silicon-copper-magnesium (Al—Si—Cu—Mg) alloys currently used for engine blocks and heads, is improved so that the alloy includes trace additions of tin. The inclusion of trace amounts of Sn, up to 0.1 wt. % Sn, have a significant effect on the thermal growth kinetics and thus on the heat treatment response of cast aluminum alloys. The use of Sn at relatively low levels, from 0.01 to 0.1 wt. %, can result in as much as a 50% increase in kinetic response to heat treatment, compared with a similar alloy containing less than 0.01% Sn.

[0012] Accordingly, this invention provides a new, refined alloy chemistry obtained by narrowing the currently acceptable range of Sn levels in engine block and head alloys. With this new alloy composition, one can simultaneously produce an alloy which results in a cost savings, due to improved heat treatment response and thus decreased aging times, and also decreased variability in its response to heat treatment. It is further believed that trace additions, in the range of 0.01 to 0.1 wt. %, of In, Cd and Ge also provide the requisite improved response to aging.

BRIEF DESCRIPTION OF DRAWINGS

[0013] Table 1 is a list of the chemical compositions of base alloy and Sn additions used;

[0014] FIG. 1 is a schematic of the plate geometry used in the experiment;

[0015] FIG. 2 is a graph of the measured thermal growth of W319 aged at 180° C. as a function of Sn level;

[0016] FIG. 3 is a graph of the effect of Sn levels on maximum linear growth and kinetics of precipitate growth in W319 aged at 180° C.;

[0017] FIG. 4 is a graph of the hardness curves of W319 aged at 180° C. as a function of Sn level;

[0018] FIG. 5 is a graph of the measured thermal growth of W319 aged at 240° C. as a function of Sn level; and

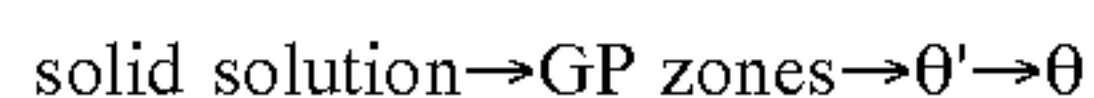
[0019] FIG. 6 is a graph of the effect of Sn levels on maximum linear growth and kinetics of precipitate growth in W319 aged at 240° C.

DETAILED DESCRIPTION

[0020] The prior art, in particular Hardy et al. detailed the influence of Sn additions on the heat treatment response of

Al—Cu alloys. Hardy et al. noted that upon artificial aging, aging at elevated temperatures, both the kinetic response and the absolute strength are substantially increased by the addition of Sn to Al—Cu alloys. However, the rate of natural aging, aging at room temperature, decreased with Sn additions. The increase of kinetic response of artificially aged alloys is dramatic. In one study, it was found that the aging time acquired to obtain peak hardness of an Al-4 wt. % Cu binary alloy at 190° C. was 24 hours. However, by adding 0.05 wt. % Sn to the alloy reduced this time to 7 hours. Similarly, the times for peak hardness at 130° C. were 58 days without Sn, but reduced down to six days with 0.05% Sn. Accordingly, very small amounts of Sn have been noted to provide a significant influence; this effect has become known as “microalloying.” Microalloying with Cd and In showed similar effects, whereas additions of Sb, Pb, Bi, or Te, showed no such effect.

[0021] Because precipitates are the structural cause of age hardening, the prior art tried to rationalize the microalloying effect in terms of the precipitates that form in Al—Cu alloys. Upon aging, Al—Cu alloys undergo a sequence of precipitate transformations involving the Cu-containing precipitate phases:



[0022] A supersaturated Al—Cu FCC solid solution may give way first to small coherent precipitates, or Guinier-Preston (GP) zones. These are plate-shaped copper-rich particles aligned crystallographically in the FCC (001) planes and often only one atomic layer thick. Upon further aging, a transition phase is formed, the Al₂Cu θ' phase, which is partially coherent with the FCC solid solution phase and forms in a slightly distorted version of the fluorite structure. The morphology of θ' precipitates tends to be (001) plates with coherency between θ' and the matrix along the broad face of the plates, and an incoherent (or semi-coherent) interface around the rim of the θ' plate. Aging even further eventually results in the formation of an incoherent equilibrium Al₂Cu θ phase.

[0023] The prior art further suggested that the Sn, In, and Cd additions enhanced the nucleation of Al₂Cu θ' precipitates. The prior art showed that the additions of Sn, In and Cd caused an increase in θ' precipitates, and that simultaneously a decrease in GP zones, thus explaining the diminished hardness during natural aging, where GP zones typically predominate, and the enhanced effect during artificial aging, where θ' is present. As a result, the prior art advocated Al—Cu alloys including Sn in an amount between approximately 0.03 and 0.05 wt. %.

[0024] With respect to this invention, it has been found that Al—Si alloys containing Cu exhibit increased response to heat treatment with the addition of trace amounts of Sn. In the prior art, there is a significant amount of literature on the hardening response and the mechanism of Sn additions to Al—Cu alloys. The prior art, however, has no studies on the effect of Sn on Cu-containing Al—Si casting alloys. Furthermore, the prior art has focused almost exclusively on hardness, and not on thermal growth/dimensional stability considerations. For many castings made from Al—Si—Cu—Mg alloys, the relevant aging time is dictated not by time to peak hardness but rather by time to dimensional stability. It further bears emphasis that microscopic thermal growth observed during elevated temperature exposure of

many Al—Si—Cu—Mg alloys is due to the kinetic growth of θ' precipitates. Therefore, as part of this invention, the effect of microalloying additions of Sn on the growth of θ' precipitates, and hence dimensional stability, were studied.

COMPARATIVE EXAMPLES

[0025] As a comparative example, an Al—Si—Cu—Mg casting alloy was selected to illustrate the concepts described here. An alloy generally conforming to but having a more limited range of composition as A320, identified as W319 aluminum, was obtained from Alchem Aluminum, Inc. Four target Sn concentrations were used for comparison: (1) “base,” (2) “0.01 addition,” (3) “0.04 addition,” and (4) “0.08 addition,” where the additions are in weight percent. These concentrations were obtained by adding 99.9% pure Sn to the W319 material. To determine the chemical compositions of the alloys, optical emission spectrometer analysis is sufficient for compositions having levels greater than 1000 ppm. However, for lower level compositions, the more accurate analysis by a glow discharge mass spectrometry is preferred. Both techniques were used for comparative purposes. Table 1, set forth below, provides the chemical composition of base alloy and Sn additions used for comparison. All reported compositions were from optical emission spectrometer analysis, except those in parentheses, which were from analysis using glow discharge mass spectrometry. Sr, Bi, and Pb levels for all of the alloys were 3.2, 11 and 90 ppm (wt.), respectively.

TABLE 1

Element (wt %)	Si	Cu	Fe	Sn	Mg	Mn	Zn
Base Alloy	7.48	3.53	0.35	0.009 (0.0025)	0.31	0.26	0.13
0.01 add.	7.46	3.47	0.34	0.018 (0.014)	0.30	0.26	0.13
0.04 add.	7.48	3.51	0.34	0.047	0.27	0.26	0.13
0.08 add.	7.50	3.48	0.34	0.084 (0.085)	0.27	0.26	0.13

[0026] Table 1. Chemical compositions of base alloy and Sn additions used.

[0027] The alloy was melted in an electric resistance furnace and two plate castings were poured, as shown in FIG. 1, from the base alloy. Sn additions were made to the melt and two plate castings were poured for each target condition. The plate casting surfaces were machined parallel and six rectangular bars of 13×10×76 mm were cut from each plate casting to serve as specimens for the dimensional growth study.

[0028] Dimensional growth measurements were taken before and after solution treatment and after the required aging times. The measurements were taken from a linear dimensional growth gauge employing an LVDT indicator; a carbide standard was used to zero the gauge before each of the measurements. Five measurements of the length were taken at each of the stages and the average of these five measurements ($\Delta L = L_f - L_o$) was used to represent the dimensional growth. $L_f(L_o)$ is the average length of the sample after (before) thermal exposure. A percent dimensional growth was calculated by dividing ΔL by L_o . The accuracy limit for dimensional growth measurements of this type is estimated to be $\pm 0.01\%$.

[0029] After machining, initial growth measurements were taken and all of the rectangular bars were subjected to an 8-hour solution treatment at 495° C. followed by an ambient water quench. Thermal growth curves were developed by thermally exposing each of the samples at 180° C. for the various exposure times: 0, 0.1, 0.5, 1, 2, 5, 10, 100 and 1000 hours. The samples with exposure times of 0.1 and 0.5 hours were thermally exposed in a 180° C. salt bath (Partherm™ 290) followed by a water quench. The samples with times exceeding an hour were thermally exposed in a tube furnace followed by a water quench. An analogous set of experiments was also done for samples solution treated at 495° C. for 8 hours, followed by aging at 240° C.

[0030] Following the completion of the thermal exposure measurements, all of the samples were tested for hardness. Each sample was measured five times by Rockwell hardness tester (Rockwell E) and the results averaged.

[0031] FIG. 2 shows the measured thermal growth of W319 during exposure at 180° C. as a function of Sn level. Each of the curves shows the expected shape: growth rises exponentially to a maximum “dimensionally stable” condition. Although the maximum growth value (after 1000 hours) does not depend on Sn level, the rise to the maximum is faster in the alloys with added Sn. The results indicated that the higher the Sn level, the faster the rise of thermal growth. These results were also consistent with the general theory that the maximum growth is a measure of the equilibrium phase fraction of θ' precipitates, which is not expected to be significantly effected by small additions of Sn. However, the kinetics of thermal growth are governed by the kinetics of the growth of θ' precipitates, which is enhanced by the addition of Sn.

[0032] To see the change in kinetic growth more clearly, the measured growth data for each Sn level was fit to a Johnson-Mehl-Avrami growth law form:

$$g(t)=g_{\max}[1-\exp(-kt)]$$

[0033] where $g(t)$ is the thermal growth of the function of time, g_{\max} is a constant indicating the maximum thermal growth for long exposure times, and k is the coefficient measuring the kinetics of growth. FIG. 3 shows the fitted maximum linear growth, g_{\max} , and kinetic coefficient, k , as a function of the total Sn level in each alloy. Not surprisingly, the fitted values of g are nearly constant as a function of Sn content. However, the kinetic coefficient showed a variation with tin content as shown in FIG. 3.

[0034] Here, it is clear that even small additions of Sn (less than 0.1 wt. %) significantly enhanced the kinetics of thermal growth, and hence the kinetics of growth of θ' precipitates. As shown in FIG. 3, the kinetic coefficient, k , increased by approximately 50% as the Sn level went from base levels to 0.1 wt. %. The current specifications of engine block and head alloys indicate only that Sn levels are to be below 0.1 wt. % and thus the allowed ranges of Sn specifications for prior art alloys exhibited a kinetic response to heat treatment that vary by 50%.

[0035] Additionally, Rockwell hardness measurements of W319 were measured during exposure at 180° C. The results are provided in FIG. 4. From the hardness curves of W319, it is clear that the addition of Sn causes no dramatic effect on peak hardness in W319, and perhaps a slight increase in hardness with Sn level can be observed. Also, there appears

to be some strengthening associated with increasing Sn levels during the early stages of aging. During the early stages of aging, solid solution strengthening as well as GP zones and other effects can be key contributors to strength. Regarding the decreased response to natural aging, there may be a connection between solute-vacancy binding and the delayed formation of GP zones.

[0036] To further clarify the role of Sn on aging response, we have conducted analogous experiments to the ones described above, but with aging at 240° C. rather than 180° C. FIG. 5 shows the measured thermal growth of W319 during exposure at 240° C. as a function of Sn level. These measured thermal growth curves of FIG. 5 were fit to a Johnson-Mehl-Avrami form, $g_{\max}[1-\exp(-kt)]$, with g_{\max} and k as fitting constants. FIG. 6 shows the fitted maximum linear growth, g_{\max} , and kinetic coefficient, k , as a function of the total Sn level in each alloy.

[0037] Again, it is clear that even small additions of Sn (less than 0.1 wt. %) significantly enhanced the kinetics of thermal growth, and hence the kinetics of growth of θ' precipitates. Even smaller levels of Sn seem to have an effect on aging at 240° C., as compared with 180° C. However, the overall response at 240° C. is somewhat less (about a 15-20% increase) than that observed at 180° C. (about a 50% increase).

[0038] In specifications for many currently used Al—Si—Cu cast alloys (e.g., 320-type or 319-type alloys), either Sn levels are not specified, or else only a maximum Sn level is specified, but not a minimum. Our results show that a minimum Sn level should be specified in cast Al—Si—Cu alloys that are subjected to overaging for dimensional stability. By using a narrower distribution of Sn levels closer to 0.1 wt. % (the current upper bound of the specification for W319), it is believed that aging times could be reduced by as much as 50%, while still retaining dimensionally stable castings. The potential cost savings associated with this invention are significant, in part because of the reduction in heat treatment time and concomitant reduction in operational costs, which together translates into significant annual cost savings for engine blocks and heads.

[0039] It is further believed that microalloying additions of Cd and In lead to the same effect as tin. It is further believed that Ge additions in W319 could potentially provide a beneficial heat treatment response.

[0040] In summary, the invention concludes that narrowing the range of allowed Sn levels allows one to simultaneously produce an alloy which results in cost savings, due to the increased heat treatment response and decreased aging times, and thus decreased variability.

[0041] In addition to cost savings, the improved alloy composition is also believed to reduce the variability in response to aging.

[0042] While the best mode for carrying out the invention has been described in detail, those familiar with the art to which this invention relates will recognize various alternative designs and embodiments for practicing the invention as defined by the following claims.

1. A method of accelerating the heat treatment response time for overaged Al—Si—Cu casting alloys, comprising:

adding a metal selected from the group consisting of Sn, Cd, In and Ge to the Al—Si—Cu alloy.

2. A method of accelerating the heat treatment response time for overaged Al—Si—Cu casting alloys, comprising:

adding a metal selected from the group consisting of Sn, Cd, In and Ge in an amount between 0.001 and 0.1 wt % to the Al—Si—Cu alloy.

3. The method of claim 2, wherein the metal selected is added to the Al—Si—Cu alloy in an amount between 0.01 and 0.1 wt %.

4. The method of claim 2, wherein the metal selected is added to the Al—Si—Cu alloy in an amount between 0.5 and 0.1 wt %.

5. An improved aluminum casting alloy for having accelerated response to heat treatment, comprising:

Si in an amount between 5 and 10 wt %;

Cu in an amount between 1 and 4 wt %; and

a metal selected from the group consisting of Sn, Cd, In and Ge in an amount between 0.0001 and 0.1 wt %.

6. The improved aluminum casting alloy of claim 5, wherein the alloy further comprises:

Fe in an amount up to 1.2 wt %;

Mn in an amount up to 0.8 wt %; and

Mg in an amount up to 0.5 wt %.

7. The improved aluminum casting alloy of claim 5, wherein the alloy further comprises:

Fe in an amount up to 0.4 wt %;

Mn in an amount between 0.2 and 0.3 wt %; and

Mg in an amount between 0.2 and 0.35 wt %.

8. An improved aluminum casting alloy for having accelerated response to heat treatment, comprising:

Si in an amount between 6.5 and 8 wt %;

Cu in an amount between 3 and 4 wt %; and

a metal selected from the group consisting of Sn, Cd, In and Ge in an amount between 0.001 and 0.1 wt %.

9. An improved Al—Si—Cu casting alloy for having accelerated response to heat treatment and decreased variability, comprising:

Sn in an amount between 0.001 and 0.1 wt %.

10. The improved casting alloy of claim 9, further comprising:

Sn is in an amount between 0.5 and 0.1 wt %.

11. The improved casting alloy of claim 9, further comprising:

Sn in an amount between 0.01 and 0.1 wt %.

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