

Advanced processing for recycling of iron scrap with impurities

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Abstract The present research focuses on the recycling of steel in combination with copper or aluminum alloys. To use iron scrap with a copper content in the range of 0.5 to 15%, a water atomization process was carried out, producing a rapidly solidified powder with copper of nano-order size dispersed in it. The powder was then hot rolled in the 600°C to 1000°C temperature region, where there is no liquid phase of copper, to produce a solid body. The solid bodies obtained presented a porosity of less than 1% for all the values of temperature and copper concentration, and it was established that the proposed process can be used for a wide range of concentrations of metallic impurities. The tensile strength increased with the copper content for all the temperatures, reaching stability at a copper concentration over 5%. Rapidly solidified powder was annealed and compacted at 600°C, resulting in a reduction of strength compared to non-annealed powder. The microstructure with a finely dispersed copper content seemed to have a considerable effect on the tensile strength of the compacted bodies. In the case of the use of aluminum-containing iron scrap, the results show that addition of aluminum to cast iron increased the resistance to abrasion, the high temperature oxidation characteristics, and the vibration control characteristics. When this cast iron was kept in air at temperatures ranging from 800°C to 1000°C, it was observed that the graphite on the surface was substituted by alumina.

Key words recycling • steel scrap • copper • aluminum • powder metallurgy • cast iron

General introduction

Zero-emission processes are at the core of a resources recycling society. However, the increasing technological advances and specialization of functions demand the use of composite or combined materials in the production of goods, making it difficult to achieve a high degree of recycling. As these metallic alloys and metallic parts present in discarded goods and broken components are almost impossible to separate, they end up in waste filling areas. It has become imperative, then, to develop new material processes that allow the effective use of the metallic impurities contained in the materials to be recycled which are currently impossible to separate.

Currently, the final step in the recycling process for disposed vehicles is the dismantling and shredding of the automobile, resulting in 10% to 25% of waste material. The annual amount of shredder waste is on the order of 700,000 tons, which is used for land refilling [1]. This waste product includes iron scrap with a high copper content from components, such as the cores of small motors. To separate copper that forms alloys with iron, it is necessary to use processes such as electrolysis, which are prohibitively expensive because of the large amount of energy involved. It is more economically

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sound to develop effective uses for iron scraps with a high content of copper.

The recycling of steel cans is a very efficient process in Japan, with a rate of recycling higher than 80%. However, this recycling process uses only the steel body in the steel processing plants, and the aluminum of the lid is oxidized and removed. Also, Al mass% (hereinafter, %) of iron is added to the aluminum alloys to prevent soldering in the die during casting. Copper is found also mixed with steel scrap after the shredding of small motor cores, and the bodies of steel cans are made of steel but the lids are made of an aluminum alloy. It is not easy, with the available technology, to separate iron from the aluminum alloy. The development of recycling technology that allows aluminum-containing iron scrap in the form of composites, as well as aluminum alloys with some iron content, is desirable.

In the present research, effective methods for the use of iron scrap in which copper and aluminum are present as impurities have been developed. In the case of the copper-containing iron scrap, metallurgical technology is applied to entrap the impurities inside a rapidly solidifying powder that undergoes material processing at high temperature. As for the iron scrap with aluminum as an impurity, research focused on the production of an aluminum-containing cast iron, which has a higher tolerance to impurities than steel.

Development of technologies for the use of copper-containing iron scrap

Introduction

Addition of minute amounts of copper to iron based alloys during the smelting process is a well-known method of increasing their strength. Upon heat treatment a fine structure of Cu precipitates in the iron matrix increasing the strength of the alloy. However, as the addition of copper to the steel cannot exceed 0.2%, because it promotes cracking during the hot working process, copper becomes a problem in the recycling of steel. In powder metallurgy techniques up to 5% of copper is added to iron based materials to improve sintering density of the components. However, once the copper is mixed with iron it becomes extremely difficult to separate, and a recycling method that makes effective use of iron scrap with a large amount of copper is needed.

In the present research, the application of an atomizing method to an Fe-Cu molten alloy to induce rapid solidification and trap the fine structured copper inside the powder was evaluated. It is thought that water atomization induces rapid solidification and forces the copper to solidify inside the iron. Forging is then carried out at the temperature of this powder and producing a high strength material [2, 3, 5].

Experimental

Fe-Cu alloys with a copper content of between 0 and 15% were prepared and a high-pressure water spray

was applied to these alloys, producing a powder through rapid solidification. This powder was used after it was passed through a 5 μm mesh screen. A sheath can (S45C) of 40 mm in diameter and 150 mm in height was filled with this powder and underwent vacuum degassing treatment at 480°C for 53 ks. Roll forming of this sheath can was carried out to produce solid bodies. A set of upper and lower thread rollers with an angle of 1.57 rad (90°) was used for the hot rolling process, resulting in a body with a square transversal section. The rolling was carried out at three temperatures, 1000°C, 700°C, and 600°C, with a 90% of reduction in the transversal section to 14 mm.

The microstructure on the surface of the cross-section of the formed bodies was observed. Hardness tests and a tension test were carried out. The structural observations were carried out by SEM in directions longitudinal (L) and transversal (T) to the cross-section. The micro Vickers hardness of the T and L sections was measured under a load of 500 N, applied for 15 s. Tensile strength tests were carried out using a test pieces made of rods 3.5 mm in diameter and 25 mm in length at a crosshead speed of 8.3×10^{-3} mm/s.

Results and discussion

Figure 1a shows the SEM photography of the cross-section of a rapidly solidified powder with 2% copper content. Figure 1b is an enlargement of this cross-section. Inside the powder, precipitates on the order of several tens of nanometers are homogeneously dispersed. In the results from the X-ray diffraction analysis presented in Fig. 2, peaks for fcc copper and an α -iron peak are observed, indicates that the precipitates are fcc copper.

For all the compacted powders, regardless of the temperature and of the copper content, the forming process and porosity decrease as the forming process advances, until at the last stage of forming (cross-section reduction of 90%) a dense solid body with porosity lower than 1%, is obtained. This processing technology enables the use of material with a high concentration of copper impurities. The cross-section of a body compacted at 600°C presented a pressed fine microstructure.

Figure 3 shows the relationship between tensile strength and copper content for each temperature of forming. For all the forming temperatures, the tensile strength shows a tendency to increase with copper content. Especially, there is a noticeable increase in strength for a copper content of 5%. For copper content higher than 5%, the effect of copper on the strength is not noticeable. For the three temperature zones, the highest strength of 1000 MPa corresponds to a copper content over 5%, and forming temperatures of 700°C.

Figure 4 presents the relationship between total elongation of the formed body and the copper content. Elongation shows tendency to decrease as the copper content increases, regardless of the zone of temperature. When the temperature of processing is modified, the specimen formed in the 1000°C zone of temperature shows the largest elongation. For copper content of 0.5%,

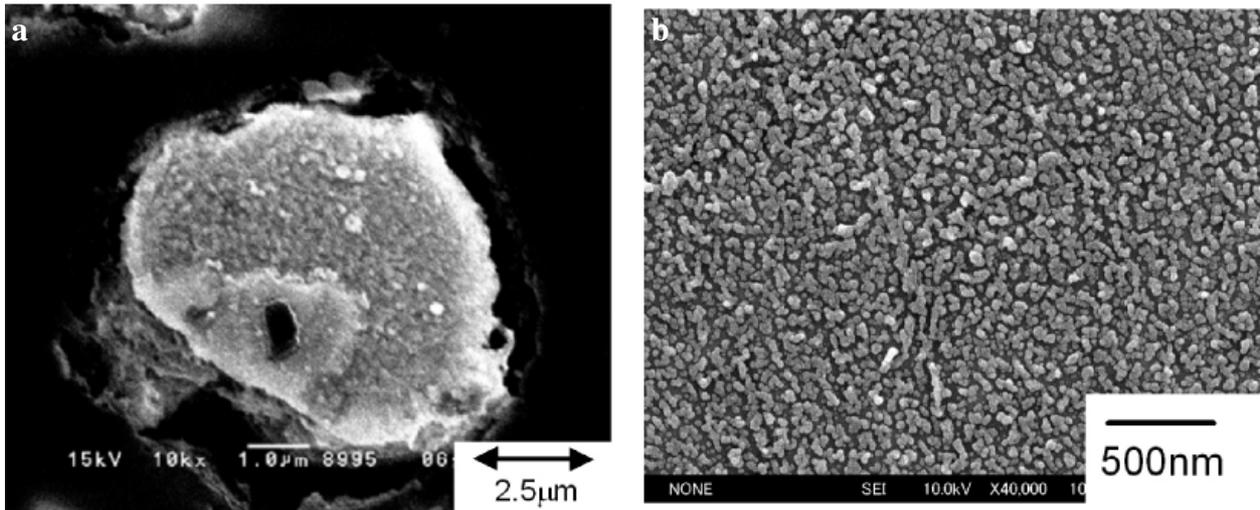


Fig. 1. SEM micrograph of the cross-section of a rapid solidification Fe-10%Cu specimen.

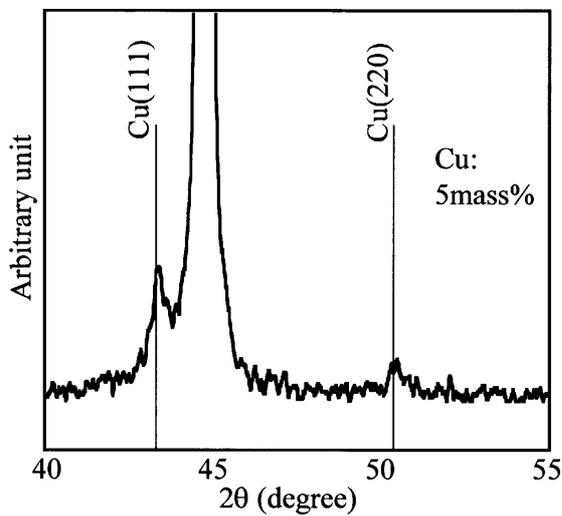


Fig. 2. X-ray diffraction pattern of the atomized powders.

the elongation was 22%; for copper content of 15%, the elongation obtained was 5.8%. Figure 5 shows the SEM observation of the fractured surface after a strength test on the specimen formed in the 700°C zone of temperature.

The Vickers hardness of the pure iron powder formed at 1000°C was Hv110. For a copper content of 5%, there was a two-fold increase in hardness to Hv220.

In the present research, when an Fe-Cu powder was used, the strength increased with the copper content. Especially in the range of temperature of 700°C, the strength reached a value around 1000 MPa for a specimen with 5% copper content. For this specimen, the grain size was 0.5 μm. It is thought that the strengthening mechanism in this range of temperature, is refining of the copper grains.

Forming at 1000°C resulted in values of tensile strength lower than at other forming temperatures. For a copper content of 0%, the specimens showed a strength similar to that of pure cast iron. As this range of temperature is higher than the transition point, A1, for iron (austenitic region), it is thought that grain growth occurs (approximately 12 μm) during forming, causing

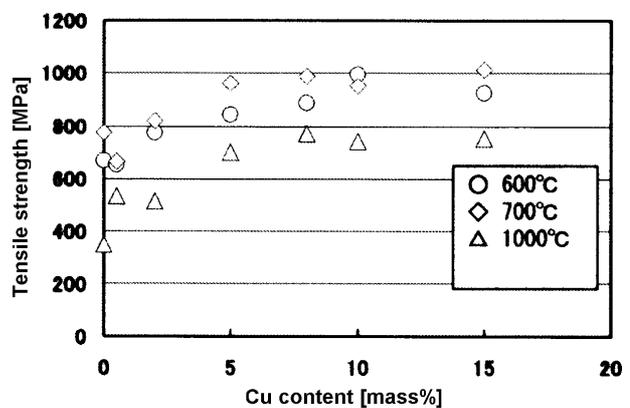


Fig. 3. Relationship between the tensile strength and the copper content of the specimen produced by heavy deformation consolidation at each temperature range.

a coarsening of the microstructure. However, the tensile strength increased with copper content. This increase in tensile strength can be attributed to the refining of the copper grains and to solid solution hardening of copper.

Elongation of the specimen decreased as the copper content increased for each working temperature. At

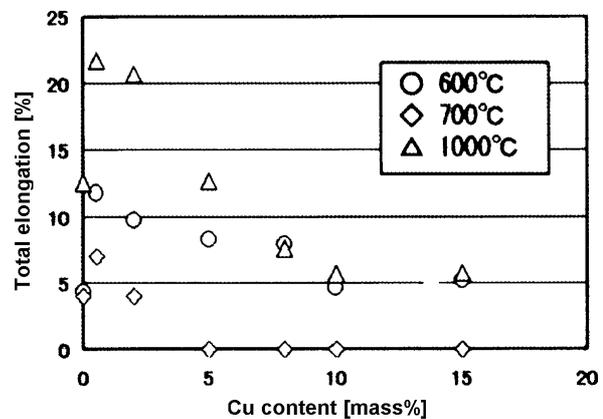


Fig. 4. Relationship between the total elongation and the copper content for the heavy forced consolidation compact.

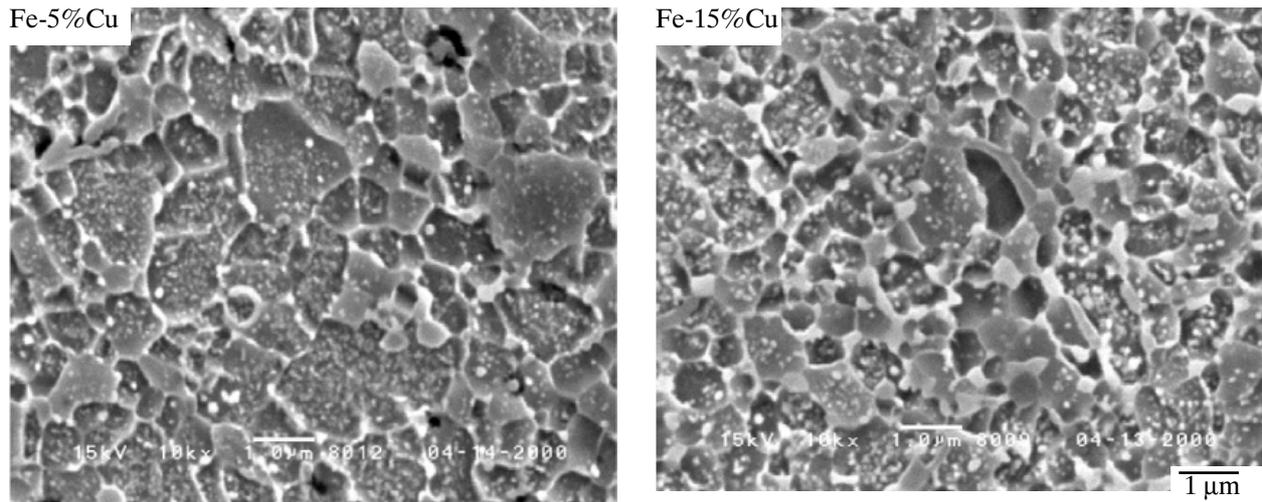


Fig. 5. SEM micrograph of the fractured surface after the tension test of the heavy forced consolidation specimen processed at 700°C.

1000°C, there was an increase in elongation which was attributed to a coarsening of the microstructure due to grain growth. For forming at 700°C, there was some elongation in specimens with a copper content of 2%, but this elongation was not homogeneous. There was no elongation when the content of copper was increased from this level. This can be attributed to the effect of oxides and to the fact that over 2% of copper, there was over saturation in the solid solution and the excess copper precipitates in the grain boundary and inside the grains, hindering elongation.

Conclusion

1. It has been established that by applying rolling forming to a rapidly solidified Fe-Cu powder with a fine structure of dispersed copper, a solid body Fe-Cu alloy with a high copper content (over 15%) can be produced without cracks or defects.
2. The fine microstructure of copper dispersed in the powder was observed in the sample formed at 600°C. The tensile strength of the solid body seems to be noticeably affected by the microstructure of the raw powders.
3. The samples formed at over 700°C showed a recrystallized structure. Copper seems to contribute to the control of the recrystallization growth.

Rapid solidification of an Fe-Cu alloy to produce powders, followed by hot forming process allows the utilization of iron scrap containing large amount of copper. The resulting material presented much better mechanical properties than those of steel materials without any copper content.

Development of technologies for the use of aluminum-containing iron scrap

Introduction

If there is a possibility of use as a material, it would open opportunities for an effective way to recycle iron-

and aluminum containing scrap. As an alloy that offers this possibility, we focused our research on the Fe-C-Si-Al system. For example, if practical application and high utility value are found for a material consisting of a cast iron with aluminum addition, it would be possible to use this kind of scrap. However, when aluminum is added to cast iron, a large amount of slag is produced when the oxidation of the melted surface in contact with the air. Moreover, this slag affects the flow of the melt, in detriment to the casting characteristics. Therefore, aluminum should be used in minute amounts as a deoxidizer, but not so much as to form iron casting alloys.

In the present research work, aluminum was added to the cast iron and the melt temperature of the melt was kept constant to study the stabilization characteristics of the structure. Also, the changes in microstructure of the cast iron were observed, and hardness and wear tests were carried out [6, 7].

Experimental

Cast iron, electrolytic iron, graphite electrodes, ferrosilicon, metallic silicon, and pure aluminum were used as starting materials. Cast iron, electrolytic iron and graphite electrodes were melted in a graphite crucible using a high frequency induction furnace. Ferrosilicon and metallic silicon were added when the temperature reached 1400°C and complete melting was achieved. The starting point 0 s was set at the point when the melt reached 1450°C. Portions of the melt were scooped by graphite crucibles at 0 s, 1.8 ks, 3.6 ks, and 7.2 ks, and were introduced into sand molds of 30 mm diameter. During this time, the slug was removed from the surface of the melt at intervals of 10 min. The target composition was 3.2%C-2.4%Si-5%Al.

To observe the changes in microstructure, cast bodies of 45 × 20 × 150 mm in dimension were prepared with the composition 3.2%C-2.4%Si-X%Al, with Al varying from 0 to 16%. Specimens were prepared for optical microscopy and for element analysis by EPMA. The hardness of the structure was evaluated by micro Vickers tests. The composition in the present work was

assumed to be 3.2C-2.4Si-6Al. In order to observe the formation process of the alumina phase, $5 \times 10 \times 20$ mm test pieces were kept in open air at temperatures of 1000°C and 800°C, using EPMA to record the changes in microstructure with time.

Pin-on-disc wear test were carried out on specimens kept at 1000°C in open air. Test pieces of 8 mm in diameter and 20 mm in length were prepared. The material carbon steel (S55C) was tempered and annealed in a furnace rotating at the relative speed of 0.5 m/s, and extruded under a pressure of 2 MPa. The wear rate was varied between 0.1 m/s to 1 m/s to observe the wearing process.

Results and discussion

For the cast iron melt kept at 1450°C, the aluminum content in the melt decreases as the aluminum reacts with the oxygen in the air. However, after 7.2 ks, an 87% aluminum content still remained, so it seems that selective removal of aluminum is not taken place.

Figure 6 shows the microstructure depending on the aluminum content in the cast and the corresponding Vickers hardness. It was determined that, for high content of aluminum, the amount of pearlite decreased and ferrite were produced. For a 4% content, the content of pearlite decreased noticeably and granule formation was observed in some regions. For 8 to 12% of Al content, Nital etching was not effective. At 8% of Al content, a dark phase composed of ferrite and a dark region of a mixed structure were observed. At 12% of Al content, this dark phase started forming dendrites. At 16% and 20%, a homogeneous phase was observed.

The Vickers hardness of these observed phases were investigated. Although the amount of ferrite and pearlite was different in the range of aluminum content from 0% to 4%, these phases were observed, and the respective hardness values were assessed. In the 8 to 12% range, the hardness of the phase that was assumed to be ferrite

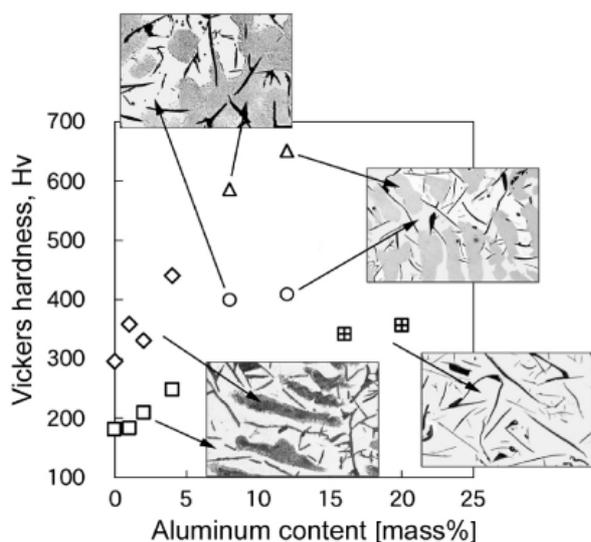


Fig. 6. Vickers hardness corresponding to the diverse microstructures formed depending on the aluminum content in the cast iron.

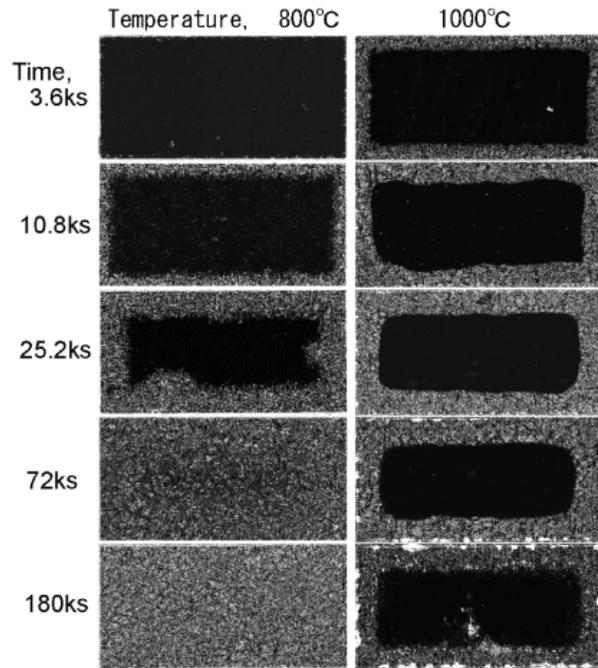


Fig. 7. Formed heat treatment process of alumina layer by EPMA analysis.

and that of the dark phase were also measured. In the 16 to 20% range, the structure looked homogeneous, therefore the hardness of the matrix was measured. Results showed that from 0 to 4% of aluminum content, both the pearlite and the ferrite phases hardened as the aluminum content increased. When the aluminum content reached 8%, there was crystallization of a very hard phase. This phase crystallized as dendrites at 12% of aluminum. It is thought that this phase was an Fe-Al carbide called the κ phase. This was identified as a double carbide formed from iron and aluminum with a carbon content of approximately 4%, which presented strong magnetic properties [8]. The composition of this phase was Fe_3AlC_x ($x = 0.5-0.69$) [4]. The alloy with an aluminum content of 16 or 20% showed the same hardness value as that with a 4% aluminum content.

Figure 7 shows the EPMA photos of the cross-section of a specimen kept in the electric furnace at 1000°C and 800°C in open air. The white portion corresponds to the high oxygen content region, which coincides with the region where alumina is present. As time elapses, the thickness of the alumina layer increases from the surrounding area. At 1000°C, there was a point where no further increase in the thickness of alumina was observed, but at 800°C, the alumina layer extended rapidly towards the interior of the specimen.

Figure 8 shows the thickness of this alumina layer plotted against time. At 1000°C, the speed at which the alumina advanced decreased with time, and beyond 72 ks there was not noticeable increase in the thickness of this layer. On the other hand, at 800°C, the increase in thickness of the alumina layer was almost proportional to the time. The precipitation of alumina in the regions occupied by graphite, coincided with simultaneous diffusion of carbon, oxygen, aluminum, and iron, and the diffusion at 800°C was assumed to be slower than at 1000°C. Diffusion of carbon was much faster

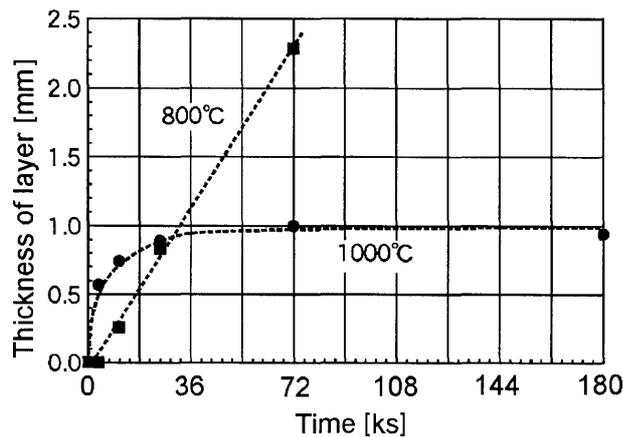


Fig. 8. Alumina dispersed layer thickness change during heat treatment in air.

than of iron. Carbon diffuses from the inside of the materials towards the outside, oxygen diffuses from the outside towards the inside of the material. If there is not presence of oxygen, it is not possible to form alumina. At 800°C the diffusion rate of iron was low, fast combustion of graphite was hindered, and absorption of oxygen became easier, promoting the formation of alumina. At 1000°C, at the same time that the combustion of carbon becomes difficult, the iron tended to diffuse to fill this space, hindering the supply of oxygen to this region. At 800°C, the alumina extended easily towards the inside the material, but at 1000°C, there was formation of alumina up to point only. The fact that the alumina phase formed at 1000°C was thicker than that formed at 800°C is also attributed to the differences in the diffusion rates.

Figure 9 shows the results from wear tests carried out on specimens kept at 1000°C in air for 180 ks. These specimens showed superb wear resistance properties in the 1.0 m/s rate region. At the beginning of the test, there was some wear, and afterwards the surface looked crushed and then became smooth, and no wear was detected. At 0.1 m/s, the wear advanced rapidly and the wear rate increased noticeably from a point. This

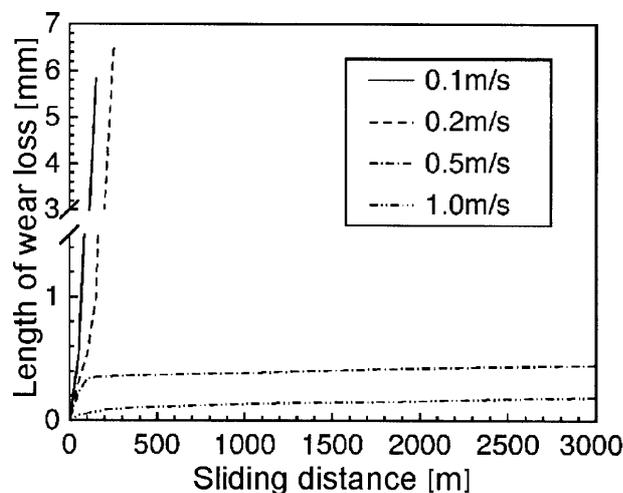


Fig. 9. Pin-on-disk test results of sample heat-treated at 1000°C for 180 ks.

indicates that the alumina containing layer was removed, exposing the region where there was not alumina present. Accordingly, in test conditions of 0.1 m/s, the region where alumina was present had much better wear resistance properties than the region without the presence of alumina.

The design and the production of an aluminum-containing cast iron is an effective method for the utilization of the scrap of iron-aluminum composites. The effect of aluminum content on this cast iron was investigated, and a material with excellent wear resistance was introduced.

Conclusion

Heat treatment in open air of a cast iron material with aluminum as additive resulted in formation of alumina in the surface vicinity. This alumina layer improves the wear resistance properties of the material. Especially, these wear resistance properties were excellent under the test condition of 1.0 m/s.

It was determined that the wear resistance properties are determined by the depth of penetration of the alumina layer into the material as well as by the wear rate. Conditions of distribution of the alumina depend on the temperature of heat treatment, time of heat treatment.

The design and production of an aluminum-containing cast iron is an effective method for utilizing of scrap of iron-aluminum composites. The effect of aluminum content on this cast iron was investigated and it was established that a material with excellent wear resistance properties can be produced.

Concluding remarks

Processing methods for the recycling of scrap material containing impurities have been developed. These processes allow effective use of iron scrap by taking advantage of the copper and aluminum impurities in the material. In the case of copper, the impurities were trapped inside a powder prepared by rapid solidification. Application of hot forming technology for this material leads to the production of a high strength material. On the other hand, use of iron scrap with high aluminum content for cast iron resulted in a material with superb wear resistance properties.

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