

## DISSOLUTION MECHANISM FOR HIGH MELTING POINT TRANSITION ELEMENTS IN ALUMINUM MELT

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### Abstract

When added cold in aluminum melt, the alloying process for compacts of transition metal elements such as Mn, Fe, Cr, Ni, Ti, Cu, and Zn takes a sequence of incubation, exothermic reactions to form intermetallic compounds, and dispersion of the alloying elements into aluminum melt. The experiments with Cr compacts show that the incubation period is affected by the content of ingredient Al and size of compacts and by size of Cr particles. Incubation period becomes longer as the content of ingredient aluminum in compact decreases, and this prolonged incubation period negatively impacts the dissolution of the alloying elements in aluminum. Once liquid aluminum forms at reaction sites, the exothermic reaction takes place quickly and significantly raises the temperature of the compacts. As the result of it, the compacts swell in volume with a sponge like structure. Such porous structure encourages the penetration of liquid aluminum from the melt. The compacts become weak mechanically, and the alloying elements are dispersed and entrained in aluminum melt as discrete and small sized units. When Cr compacts are deficient in aluminum, the unreacted Cr particles are encased by the intermetallic compounds in the dispersed particles. They are carried in the melt flow and continue the dissolution reaction in aluminum. The entire dissolution process of Cr compacts completes within 10 to 15 minutes with a full recovery when the aluminum content is 10 to 20% in compacts.

### Introduction

Alloying of transition metal elements such as Mn, Fe, Cr, Ni, Ti, Cu, and Zn in aluminum cast shops is usually practiced by their cold addition to aluminum melt, but the effectiveness of alloying process is challenged by their high melting point and density. They may be either added as master alloys with aluminum and as compacts of their powders with aluminum, or injected as metal powders. Whatever addition methods they adopt, operators at cast shops aim at high and consistent recovery of the alloying elements within a reasonable processing time and with a minimum loss of the melt temperature. Since the introduction of UCAR aluminum additives in 1969, the compact of powders of alloying elements and aluminum has become the standard addition practice in the aluminum industry. This popularity is due to the fact that the compacts efficiently utilise the exothermic heat from the formation of intermetallic compounds with the aluminum present in the compacts and assure a high and consistent recovery with minimum attentions at cast shops. However, the recent trend in the aluminum industry is to lower the cost of the additive compacts. In response to this pressure, the constituents of the compacts have changed to reduce the content of aluminum constituent, and the industry now offers the compacts with decreasing content of aluminum in the additive agents. The compelling question is “Will they perform same?”

The dissolution of alloying elements with cold addition involves the thermal and mass transport phenomena. The thermal and mass transport properties of the additive compacts are determined by the constituents as well as physical characteristics of compacts. One of thermal properties involved is the exothermic heat from the formation of intermetallic compounds with aluminum. Thermodynamic data by Hultgren et al (1) show that the heat of formations of alloys with Al increases in the order of Cr, Mn, Fe, and Ni. Figure 1 compares the heat of formations of alloys for Cr, Mn, Fe, and Ni with Al. It shows that the thermal contribution from the heat of exothermic reactions is the least for Cr. The driving force for mass transport can be represented by the solubility of the alloying elements at saturation in aluminum melt. Figure 2 shows the liquidus of the binary systems of Cr, Fe, Mn, and Ni with Al in Al rich side taken from Massalski et al (2). The solubility of the alloying elements in liquid Al increases in the order of Cr, Fe, Mn, and Ni. It shows that the driving force for mass transport is the least for Cr. This analysis indicates that the alloying performance in Al melt under a given hydrodynamic condition is expected to be worst with Cr among the four transition metal alloying elements, and the effect of thermo-physical variables on the alloying performance is expected to be heightened with Cr. The dissolution behavior learned with the Cr compacts be helpful to further understanding the alloying performance of the compacts with the other transition metal elements.

The dissolution process of the compacts takes place by the sequence of incubation, exothermic reaction with Al, and dispersion of alloying elements. In his study with the Mn/Al compacts, Perry(3) observed that the exothermic reaction starts only after aluminum in compacts melts. The same phenomenon is expected to take place with the compacts of other transition metals. This indicates that the initial incubation period is required to transfer enough thermal energy from Al bath into compacts to raise the temperature to melt aluminum at the reaction sites. Once liquid aluminum is available at the reaction sites, the exothermic reaction takes place with Cr. As the dissolution behavior during the incubation and subsequent reactions are expected to be affected by the thermo-physical properties of the compacts, this study examines the effect of parameters such as composition and dimension of Cr compacts on the incubation period and the subsequent reactions and discusses the mechanisms for an improved alloying performance.

Experiment

Raw materials

Cr metal and Al powders were used as the ingredient for

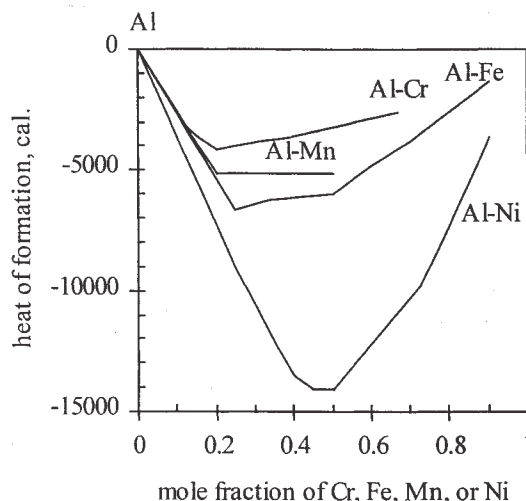


Figure 1: Heat of formation of alloys for Cr, Mn, Fe, and Ni with Al at 298K except Mn

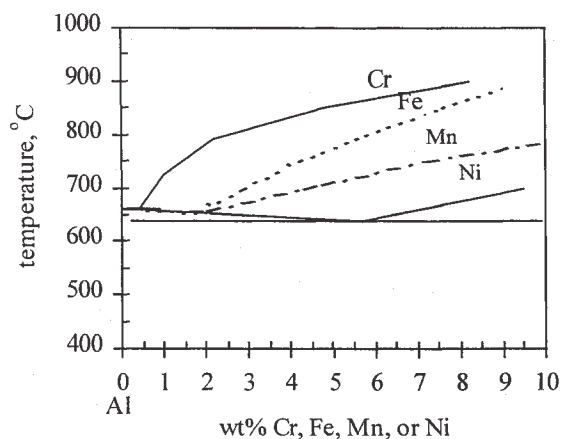


Figure 2: Solubility of Cr, Fe, Mn, and Ni in liquid Al

Table I Size Distribution of Cr and Al Powders as received

Screen size	Cr metal powder	Al powder
+30 mesh		1.2%
+40 mesh		5.0
+50 mesh	4.9%	
+60 mesh	11.48	
+100 mesh	39.85	33.8
+200 mesh	26.50	29.0
+325 mesh	10.16	17.8
-325 mesh	7.11	13.2

the compacts. Table I shows the particle size distribution for the starting metal powders. Cr metal powder was prepared by collecting particles passed through 45 mesh screen and is reported in Table I by its nominal size of 45 mesh x D. In order to examine the effect of Cr particle size, Cr metal powder of 45 mesh x D was sieved to collect the powder passed through 100 mesh screen and identified it by the nominal size of 100 mesh x D. These two differently sized Cr metal powders, 45 mesh x D and 100 mesh x D, were used to prepare the compacts. Al powder was used as received.

#### Preparation of Compacts

The ingredient Cr and Al powders were mixed by a laboratory scale PK blender for 10 minutes. In order to examine the effect of the aluminum content, the compacts were prepared at three different contents of aluminum, 0, 10, and 20%. For the experiment to examine the effect of Cr particle size, two different sized Cr particles were used to prepare the compacts at two different Al contents, 0 and 10%Al. The mixtures of powders were pressed cold into specimen bars with the dimension of 3mm x 13mm x 32mm. Compaction pressure was 520MPa (75.4 kpsi). In order to examine the effect of size of compacts, some of the specimens increased the thickness from 3mm to 13 mm. The larger sized specimens were prepared with Cr powders sized 100mesh x D at 0 and 20% Al contents. Table II summarises the combination of these variables and some other physical properties of the specimens.

#### Procedure for Examination of Incubation Period

Specimens were attached to a steel wire (1.5 mm dia.) clip and immersed into an aluminum melt at 760°C, at about 10 cm below the melt surface. Each specimen was immersed for a predetermined time period, and each immersion time was in the range of one to 600 seconds. After a predetermined immersion time, they were taken out quickly and quenched in liquid argon. The incubation time was determined by examining the quenched specimens for the sign of the reactions. Aluminum melt was not stirred during these tests.

#### Recovery Test of Cr

The alloying performance was evaluated by determining the recovery of Cr in aluminum melt by analyzing samples taken at predetermined times. The adopted procedure was designed to reflect the cast shop operation conditions.

A virgin aluminum (99.7% pure) weighing 20 kg was melted in a silicon carbide crucible using a resistance furnace. The melt temperature was controlled at 760°C,

Table II Physical Characteristics of Specimens

No	%Al	%Cr	Cr powder particle size	compacts dimension,mm	green density, g/cc
1	0	100	100 M x D	3 x13x32	5.21
2	0	100	45 M x D	3 x13x32	5.85
3	10	90	100 M x D	3 x13x32	6.01
4	10	90	45 M x D	3 x13x32	5.61
5	20	80	100 M x D	3 x13x32	4.89
6	20	80	45 M x D	3 x13x32	nd
7	0	100	100 M x D	13 x13x32	5.57
8	20	80	100 M x D	13 x13x32	4.49

\*nd: not determined

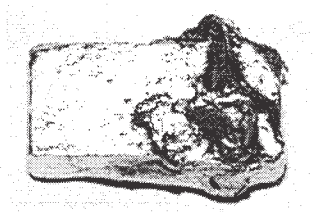
which was monitored by a K-type thermocouple. Compact specimens were weighed to have a total addition of the alloying element to 0.5% Cr in aluminum. After the initial base sample, the weighed specimens were added at once. Samples were taken every two minutes after the addition until 8 minutes processing time. After that, samples were taken at 11, 21, 30, 40, 50, 60, and 61 minutes. Melt was stirred intermittently by a graphite rod for 30 seconds one minute before the next sample taking until 30 minutes sampling time. After that, a last stirring was administered right after 60 minutes and before 61 minutes sampling time. Samples were analyzed for Cr by optical emission spectroscopy.

Only small sized compacts, 3mm x 13mm x 32 mm (No.1 to No.6 in Table II), were used to examine the recovery of Cr.

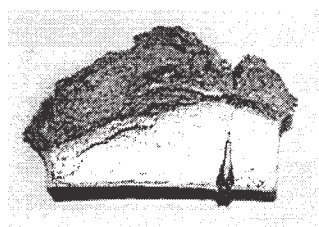
### Results

#### Incubation Period of Compacts in Aluminum Melt

The behavior of compacts during the incubation period was observed to be significantly different depending on whether they contained aluminum or not. When no aluminum was contained, compacts of Cr powder were encased with aluminum and maintained the original structural integrity and dimension of the compacts during the initial immersion period. As the immersion time increases, the compacts suddenly showed signs of localized exothermic reaction on the surfaces or edges of the compacts. Figure 3 shows such behaviors with 13mm x 13mm x 32mm sized Cr powder compacts before and after the initiation of the reactions, at immersion time of 240 and 465 seconds, respectively.



(a) Cr compact (13x13x32mm) at 240 sec



(b) Cr compact (13x13x32mm) at 465 sec.

Figure 3: Appearances of Cr powder compacts of 13mmx13mmx32mm at the immersion times of (a) 240 and (b) 465 seconds

It shows that the exothermic reaction takes place by aluminum supplied from the bath. When this happened, compacts were glowed red. However, the intensity of the glow was weak when no aluminum was contained in compacts. Soon after this, compacts were swelled and lost to the melt. A SEM examination of the reacted area showed that Cr particles are surrounded by the intermetallic compounds and the composite units of Cr particles encased by intermetallic compounds are separated each other with numerous pores among them. The energy dispersive analysis indicates that the intermetallic compounds consist of high aluminum and low chromium. The transition from the initiation of the exothermic reaction to a complete loss of compacts was quick and slightly longer with a larger sized specimens. It appears that the influx of aluminum from the bath dissolves the intermetallic compounds and the continuing reaction weakens the structural integrity of the compacts. The initiation of exothermic reaction was taken as the end of incubation period for Cr compacts.

When they contained aluminum, the compacts of Cr and Al powders were bare, i.e. not covered by aluminum, during the initial period of immersion, and their incubation periods were far shorter than that of 100%Cr compacts. When the contained ingredient Cr and Al began to exothermically react, the compact swelled and glowed red. Figure 4 shows a SEM image of the microstructure of No.8 sample containing 20%Al in Cr compact at 13 seconds of immersion time. Cr particles are shown to have reacted to form and encased by the intermetallic compounds, and

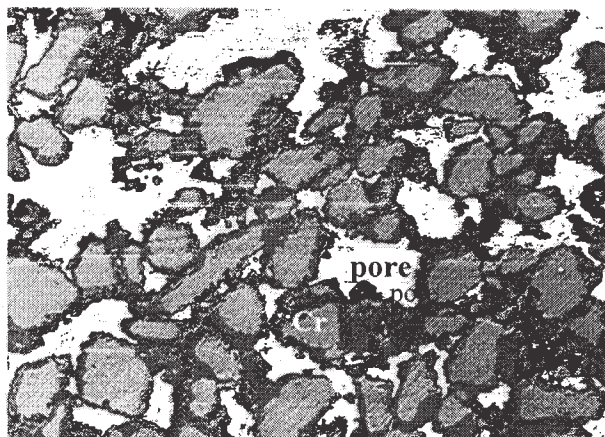


Figure 4: SEM image of No.8 20%Al Cr compact after 13 seconds of immersion time, x100

the encased Cr particles are separated each other by the intermetallic compounds and pores between them. The energy dispersive analysis shows the intermetallic compounds to consist of high aluminum and low chromium. The transformation of the microstructure results in swelling the compact with sponge like structure. This microstructure and the constituents of the intermetallic compounds are same as that was observed with 100%Cr compact as mentioned above section. Soon after this, it became weak mechanically and lost to the melt. Again, it suggests that aluminum supplied from the bath dissolves the intermetallic compounds with the result of dispersing the unreacted Cr particles in aluminum melt.

Table III summarizes the observed incubation times for the Cr-Al compacts. The incubation period is observed to be excessively long when Cr compacts do not contain aluminum as the ingredient. It decreases quickly from 167 to 221 seconds for 0%Al-Cr compact to 10 to 12 seconds for 10%Al-Cr compacts or 8 seconds for 20%Al-Cr compacts. However, its decrease is observed to be slow

Table III Incubation times for Cr-Al compacts

No	%Al	%Cr	Cr powder particle size	compacts dimension,mm	incubation time, secs.
1	0	100	100 M x D	3 x13x32	221
2	0	100	45 M x D	3 x13x32	167
3	10	90	100 M x D	3 x13x32	12
4	10	90	45 M x D	3 x13x32	10
5	20	80	100 M x D	3 x13x32	8
7	0	100	100 M x D	13 x13x32	467
8	20	80	100 M x D	13 x13x32	14

when Al content increases from 10%Al to 20, 10 to 12 seconds for 10%Al to 8 seconds for 20%Al-Cr compacts. Also, it becomes longer with the increased size of the compact specimen, and its effect is pronounced again when the compacts do not contain aluminum. As the size increases from 3 mm thickness to 13 mm, the incubation time is shown to increase from 221 seconds to 467 seconds when Cr compacts do not contain aluminum (No.1 vs. No.7 in Table III), but it is increased slightly from 8 seconds to 14 seconds with 20%Al containing compacts (No.5 vs. No.8).

An increased Cr particle size is shown to decrease the incubation times. As the Cr particle size increases from 100MxD to 45MxD, the incubation time decreases from 221 seconds to 167 seconds when Cr compacts do not contain aluminum (No.1 vs. No.2 in Table III), but its decrease becomes smaller from 12 seconds to 10 seconds when the compacts contain 10%Al (No.3 vs. No.4).

### Recovery of Cr

The recovery of Cr at various sampling times is shown in Figure 5.

When Cr compacts do not contain aluminum, the recovery of Cr is poor. The recovery is improved as the Cr particle size decreases from 45MxD to 100MxD, but a full recovery is not achieved within 60 minutes of the processing time. It was observed that some undissolved Cr compacts were found at the bottom of crucible at the end of experiment. It appears that Cr compacts settled to the bottom suffer a heavy heat loss to the crucible wall and do not accumulate sufficient thermal energy to initiate reaction with aluminum and only Cr compacts situated away from the crucible bottom appear to react with aluminum. This is a slow process and does not provide a full recovery within a reasonable processing time. This effect is observed to be greater with larger sized Cr particles.

When compacts contain aluminum, the dissolution process completes within 10 to 15 minutes of the processing time, but the behavior of the Cr recovery with time differs depending on the content of aluminum ingredient in Cr compacts. With 10%Al Cr compacts, the recovery of Cr is abruptly increased at 2 minutes sampling time and, then, returns to the normal gradual increasing pattern with the processing time. The intensity of this spike at 2 minutes sampling time is heavier with smaller sized Cr particles. The examination by SEM of the samples at 2 minutes showed that, when the Cr particle size in the compact was small (100MxD), all Cr particles were reacted to form Cr-Al intermetallic compounds and the intermetallic compounds were entrained and dissolved in aluminum stream. When the Cr particle size was larger (45MxD),

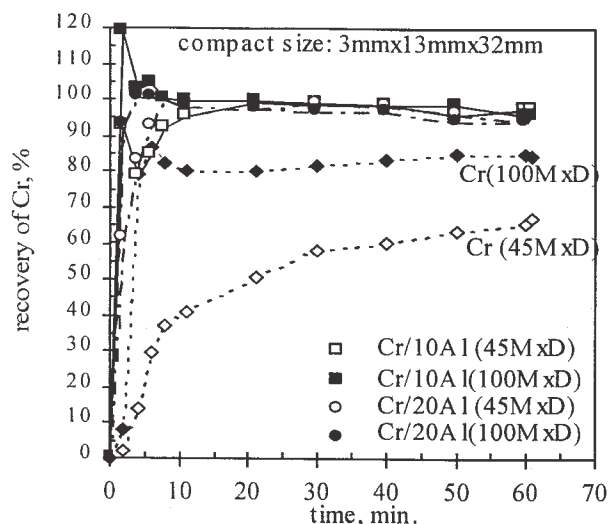


Figure 5: Recovery of Cr in aluminum melt at 760°C

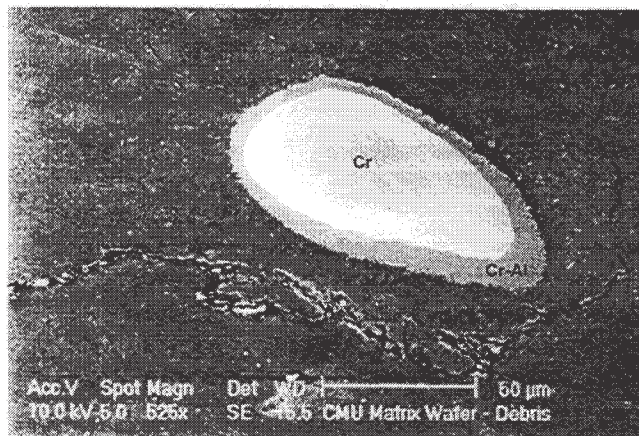


Figure 6: Entrained unreacted Cr particle in the Al sample at 2 minutes sample time for No.4 sample (20Al/90Cr, 45MxD Cr)

unreacted Cr particles were observed in the sample at 2 minutes sample time but they were encased by the intermetallic compounds and entrained in aluminum melt as a discrete composite unit. Figure 6 shows such an entrained particle observed in the sample at 2 minutes taken with No.4 Cr compacts. It appears that, when their initial size is large, the compacts do not have enough aluminum ingredient to complete the intermetallic compound formation at the end of the incubation period. As the result of it, unreacted Cr particles are encased by the intermetallic compounds, and the discrete unit of the composite particles are entrained and dispersed in aluminum melt at the processing time of 2 minutes. By this time, the size of the composite particles is small enough to continuously

entrained and to complete the dissolution in aluminum stream. This situation allows a full recovery within a short processing time.

A similar pattern is observed with 20%Al-Cr compacts, but the intensity of the spike at 2 minutes sample time is smaller than that with 10%Al Cr compacts. It appears that a higher ingredient Al content ensures a complete reaction of Cr particles at early processing time. Again, the alloying element is observed to be fully recovered within 10 to 15 minute of the processing time.

### Discussion

When a cold addition is made, the compacts need to accumulate sufficient thermal energy to melt aluminum at the reaction sites in order to initiate the exothermic reactions. The rate of heat influx during the incubation period is determined by the heat transfer coefficient of liquid aluminum in the adjacent thermal transition layer to the compact and by the thermal conductivity of the compacts. The present experimental conditions for incubation period was carried out under a condition of natural convection, and the heat transfer coefficient is not changed during the experiment. Therefore, the observed variation in the incubation period is due to the variation in the thermal conductivity of compacts. An increased thermal conductivity decreases the incubation period. The thermal conductivity of aluminum is higher than that of chromium, 2.37 W/cm-K for Al and 0.939 W/cm-K for Cr at 298K(4). Although it becomes different when the powders of Cr or Al are compacted, the thermal behavior of the compacts may be assumed to be similar to that of the elements. Then, the thermal conductivity of Cr compacts is expected to increase with the increase of Al content, and an increased Al content decreases the incubation period. This agrees with the experimental observation. The incubation time becomes shorter as the Cr particle size increases. This suggests that the thermal conductivity of Cr compacts increases with the increase of Cr particle size. When the size of compacts increases, it adds more thermal mass. Consequently, it increases the incubation time under a given heat transfer coefficient. It is judged that the excessively long incubation time observed with 100%Cr compact is the consequence of a low thermal conductivity of the compacts.

Once liquid aluminum is available at the reaction sites, the reaction between Al and Cr takes place to form intermetallic compounds exothermically. If Cr compacts do not contain aluminum, this starts at the surface of compacts and proceeds inward with the help of influx of liquid aluminum from bath. This is possible because the reacted portion of compacts swells in volume to have a sponge like structure. Perry(3) observed that the density of

25%Al-Mn compacts decreases from about 4.45-4.50 g/cc to 2.24 after the exothermic reaction. A similar volume expansion is expected to take place with Cr compacts. Figure 3(b) shows such structure developing inward from the outside of the compacts. However, a sustained reaction depends on a continued supply of liquid aluminum from bath when compacts do not contain ingredient aluminum. And it takes a longer time to complete the reaction. If the Cr compacts contain aluminum, the exothermic reaction takes place quickly. The reaction products are Cr-Al intermetallic compounds. If aluminum is deficient at the reaction sites, aluminum is depleted by the reaction with Cr, and the unreacted Cr particles are remained as the core encased by the intermetallic compounds. The formation of intermetallic compounds expands the volume of and introduces pores in the compacts. Because of these changes, the Cr particles are separated from each other and become discrete flowing units. With the influx of aluminum, they are dispersed and entrained in aluminum melt. This favorable hydrodynamic condition is promoted by the ingredient aluminum in Cr compacts and ensures a full recovery of transition elements within a reasonable processing time.

An intensified mixing activity of aluminum bath facilitates the dissolution process of the compacts through an increased heat transfer rate across the thermal transition layer and turbulent flow in aluminum bath. The increased heat transfer rate decreases the incubation time of the compacts and the increased turbulent flow promotes the dispersions of the alloying elements in aluminum bath.

### Conclusion

When a cold addition is made into aluminum melt, the dissolution process of Cr compacts takes place through the reaction sequence of incubation, exothermic reactions, and dispersion of the reaction products in aluminum melt. The same process is expected to take place with compacts of other transition metal elements.

The dissolution process of Cr compacts is observed to be slow when they do not contain aluminum as ingredient. This poor performance is due to a combination of the prolonged incubation time and the unfavorable condition for the alloying element to be entrained in aluminum stream. When Cr compacts contain 10%Al and 20%Al, the incubation period becomes shorter and the alloying element is entrained easily in aluminum stream. As the result of it, the alloying process is observed to complete within 10 to 15 minutes of the processing time.

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