Solid State Powder Processing

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THE EFFECT OF HEATING RATE ON THE RECRYSTALLIZATION BEHAVIOR OF HIGH γ', ODS SUPERALLOYS

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Abstract

Directional recrystallization is an essential step in the production of ODS nickel-base alloys with high γ'-content, such as MA 6000 and MA 760. The rate of heating to the recrystallization temperature plays an important role for the final grain structure. This can be explained by the development of a certain "primary" grain size during the heating period. An additional aspect is the existence of heating rate limits, which determine the success of the recrystallization. The existence of a critical minimum heating rate ($\dot{T}_{min}$) is related to normal grain growth, which reduces the driving force for subsequent abnormal grain growth. Surprisingly, recent investigations have also revealed in some cases the occurrence of a critical maximum heating rate ($\dot{T}_{max}$). In this paper an attempt is made to explain this new phenomenon, which may have important practical implications, through the formation of different carbide phases.

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1 Introduction

The formation of large elongated grains in oxide dispersion strengthened (ODS) nickel-base superalloys has long been recognized as a crucial step in obtaining optimum high temperature properties. It was observed that in investigating the transformation from fine-grained to coarse-grained microstructures a distinction should be made between ODS nickel-base alloys with a high quantity of γ' (~ 50 vol.%) and alloys without γ' or with only a low γ'-content [1]. The latter group includes alloys like TD-Ni, MA 754 and MA 753. The formation of coarse grains in this group depends solely upon the thermomechanical history and takes place over a wide temperature range (at relatively low temperatures with correspondingly low transformation rates). The high dislocation densities in the fine-grained condition makes one hesitant to describe the transformation solely with the term "secondary recrystallization" - in contrast to the other group of high γ'-forming alloys with which we will deal in this paper.

The recrystallization behavior of the alloys with a high γ'-content, such as MA 6000, MA 760, TMO-2, IN 738 + Y_2O_3 and others, has been investigated in more detail. After mechanical alloying and subsequent consolidation, the microstructure exhibits a very fine grain size (~ 0.2 μm) and a low dislocation density (< 10^{13} m^{-2}) [2]. Upon exceeding a very specific temperature, secondary recrystallization (or abnormal grain growth) rapidly takes place, transforming the fine-grained microstructure into a microstructure with grains well in excess of 1 mm. The transformation is rather abrupt and completed within a few seconds after passing the transformation temperature T_{sRx} [3]. For all ODS alloys investigated the transformation temperatures lie in a narrow temperature range (ca. 1165...1230 °C), although the chemical compositions differ substantially. Below T_{sRx} only slow, normal grain growth can be observed and even after several hours just below T_{sRx} no indications of abnormal grain growth are observable. The abrupt occurrence of abnormal grain growth upon exceeding T_{sRx} has been explained by γ'-dissolution [4], dispersoid coarsening [5] and by grain boundaries breaking away from segregated clouds of solute atoms [6,7]. Although the major alloying elements have no substantial effect on the transformation temperature, it was found that only a small increase of the boron level lowers the transformation temperature considerably.

Among the parameters which are accessible by process control, the rate of heating the specimen to the recrystallization temperature has been found to be important for the recrystallization response [8], but the reasons for this effect are not fully clear. In this paper recent investigations on several ODS alloys are described which showed that there exists a certain range for the heating rate, outside of which recrystallization does not occur. While the existence of a minimum heating rate has been recognized before, a maximum heating rate seems not to have been reported. An interpretation for this behavior, based on thermal analysis and microstructural investigations, is given and some conclusions for the practice of recrystallization are drawn.

2 Experimental Procedure

Isothermal Recrystallization Experiments

Most experiments were carried out on as-extruded fine grained MA 760 (INCO ALLOYS, Hereford, UK, Mill Batch No. EAE 0257/01) of which the measured chemical composition is given in Table I. Cylindrical specimens were taken from the core of the as-extruded bar with the long axis parallel to the extrusion direction. Both the diameter and the height of the cylinders were 15 mm. A small hole running from one of the flat faces to the center of the specimen allowed for accurate temperature measurement. The specimen was placed in a single winding medium frequency induction coil, Fig. 1, and heated to 950 °C in about one minute. From this temperature on, a constant heating rate was applied to heat the specimen to 1250 °C, which is well above the temperature for

secondary recrystallization. The constant heating rate was varied between 2 K/min and 200 K/min. The specimen was held then at 1250 °C for 5 minutes, whereafter the heating was stopped, which allowed the specimen to cool down rapidly to room temperature. The specimen was cut in half and the longitudinal section was ground, polished and etched. Some additional experiments were conducted on experimental alloys (Alloys D and Z) with small deviations in the chemical composition from MA 760.

Table I Chemical composition of MA 760 [wt.%] (Mill Batch No.EAE 0257/01)

Ni	Cr	Al	Mo	W	Fe	Y_2O_3	Zr	C	B
bal.	19.8	5.9	2.0	3.5	1.04	1.03	0.14	0.04	0.01

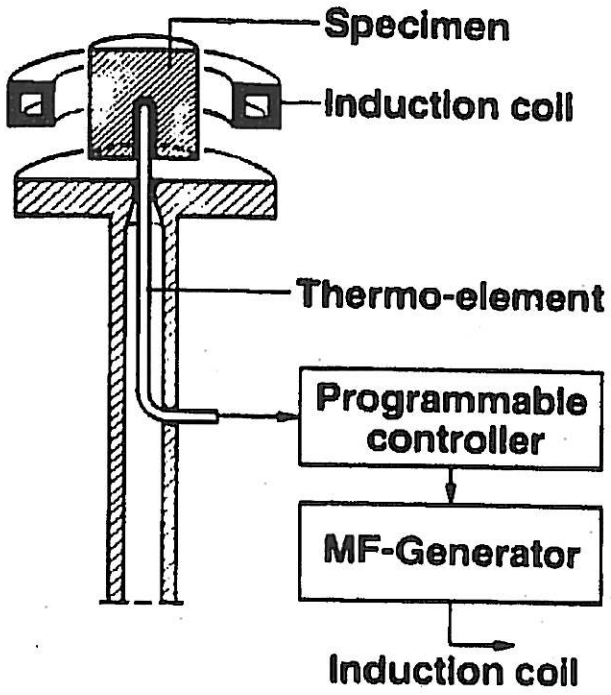


Figure 1 - Experimental set-up

Differential Thermal Analysis

DTA curves were produced for the same fine-grained material as that used in the isothermal recrystallization experiments. Two different DTA equipments were used. The alloys MA 760 and MA 6000 were analysed with a Netzsch Gerätebau Analyzer, Type STA 429. The cylindrical specimens were 5 mm in diameter and 10 mm high. A platinum crucible was used. The other alloys were investigated with a Perkin-Elmer DTA 1700, in an aluminum oxide crucible for specimens of 3 mm in diameter and 5 mm height. DTA was carried out with heating rates of 2, 5, 10 and 20 K/min. After the DTA runs the specimens were investigated metallographically in order to check the recrystallization response.

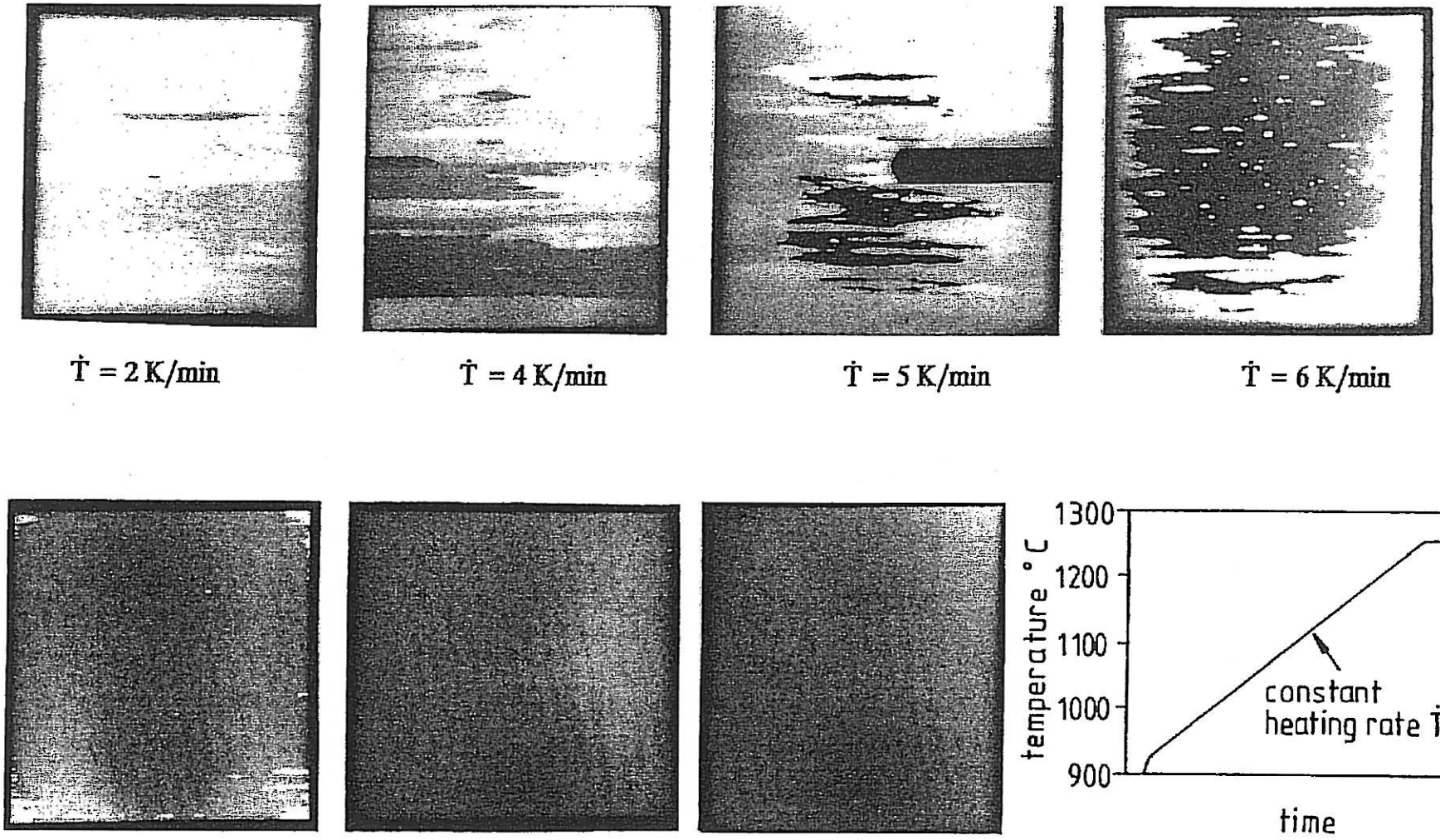


Figure 2 – Recrystallization of MA 760 as a function of heating rate Ṫ

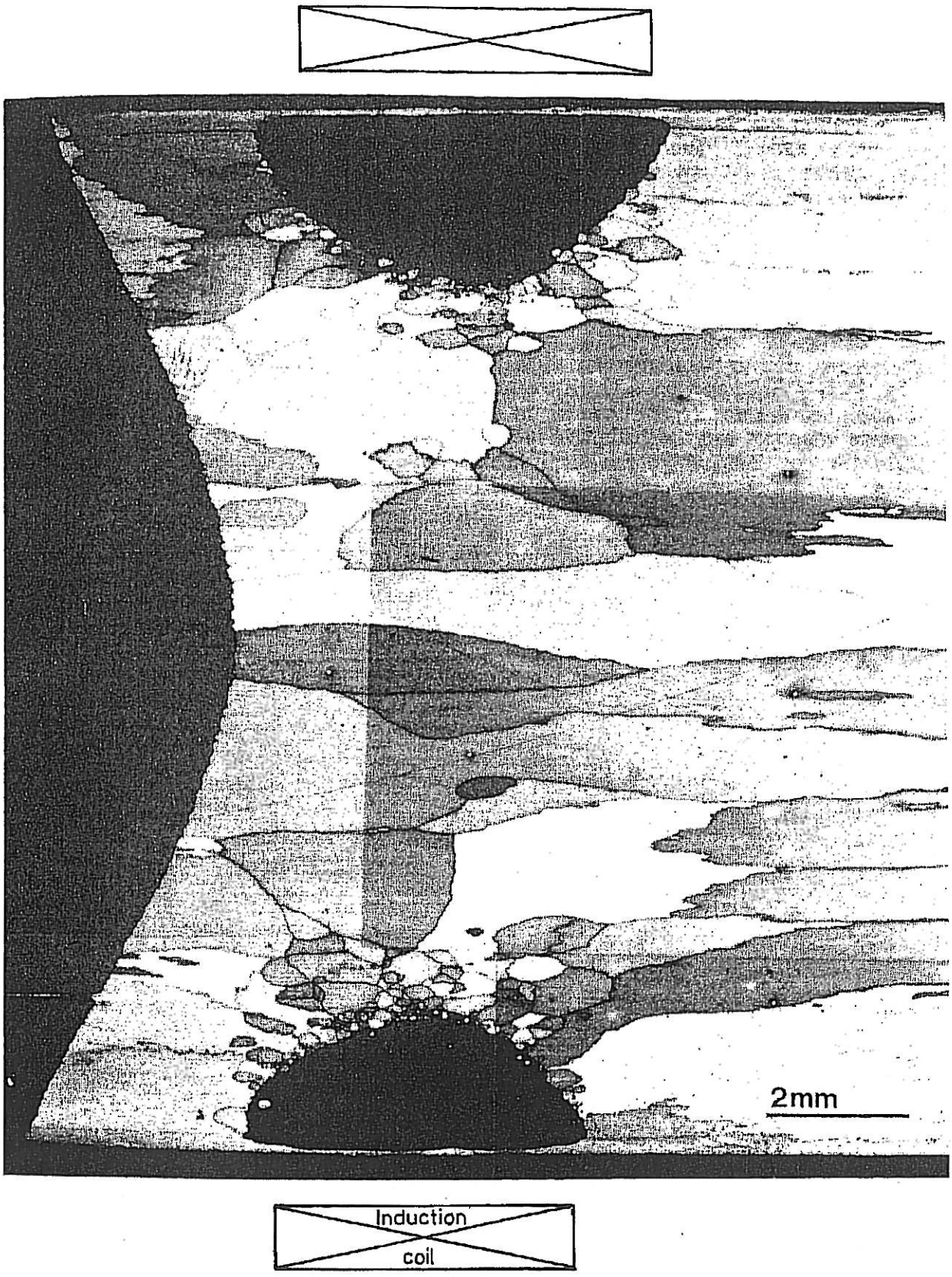


Figure 3 - Recrystallization response of Alloy Z under " continuously varied" heating rates depending on material depth at the starting position of a zone annealing run

3 Results

The influence of the heating rate on the recrystallization response of MA 760 is depicted in Fig. 2. The material showed a normal recrystallization response when subjected to heating rates of 2 or 4 K/min. The specimen that was heated with a heating rate of 5 K/min showed in the center an area that had not recrystallized. With a further increase of the heating rate this area became larger, till at 10 K/min only the very corners of the specimens showed indications of recrystallization. With 50 and 200 K/min, recrystallization did not take place anymore. Even an extension of the hold time at 1250 °C to one hour did not result in recrystallization at these heating rates.

A few batches of Alloy D showed a similar "irregular" recrystallization behavior. The critical maximum heating rates ($\dot{T}_{max}$) varied between about 8 and several hundred K/min. Alloy Z however showed a critical heating rate as high as approximately 3500 K/min. The phenomenon of $\dot{T}_{max}$ can be clearly seen in Fig. 3, which illustrates the start position of a zone annealing run of Alloy Z. The dark semi-circular areas have experienced, due to the immediate vicinity of the induction coil, the highest heating rate of ca. 3500 K/min and have therefore not recrystallized. With increasing distance from the specimen surface (corresponding to a decreasing heating rate), the recrystallization response improves and the grain size increases: the border line to the recrystallized region marks the positions where the local heating rate has first dropped below the critical heating rate; an optimum coarse grain can only be achieved in the center of the specimen where the heating rate is sufficiently low.

In Alloy Z a critical <u>minimum</u> heating rate ($\dot{T}_{min}$) is also detectable. DTA runs with various heating rates revealed recrystallization peaks at 5, 10, and 20 K/min, but not at 2 K/min. The grain structures of these DTA specimens confirm the result of the DTA curves: recrystallized coarse grain structures are produced in all specimens except the one which was heated at 2 K/min (Fig. 4).

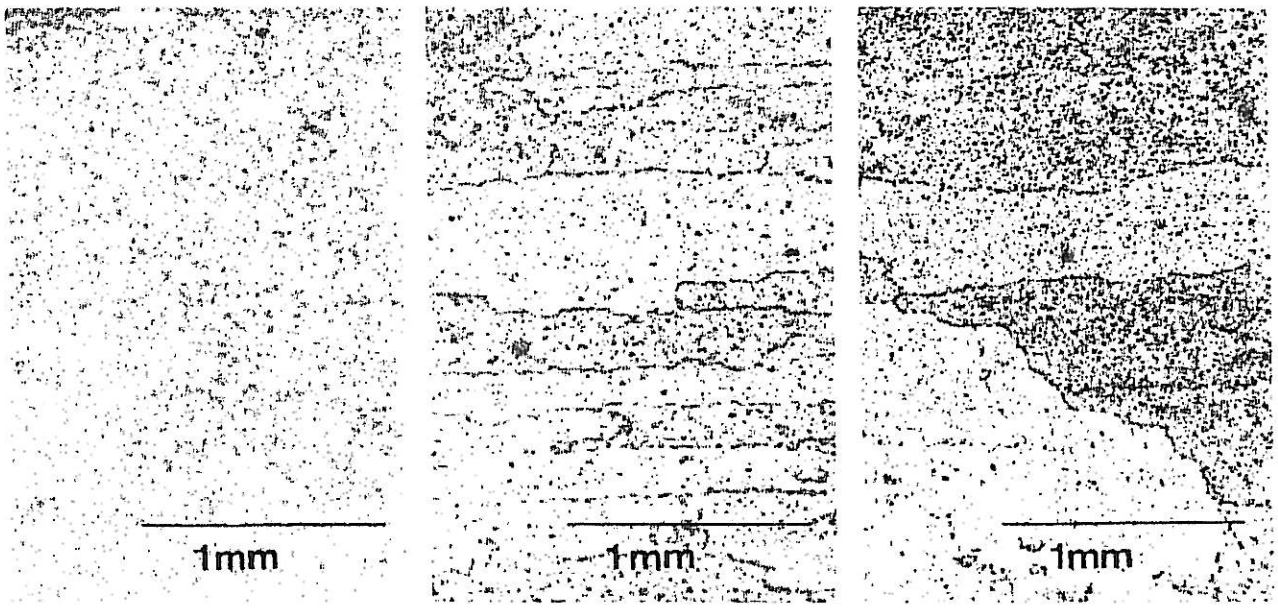


Figure 4 – Recrystallization response of Alloy Z as a function of low heating rates

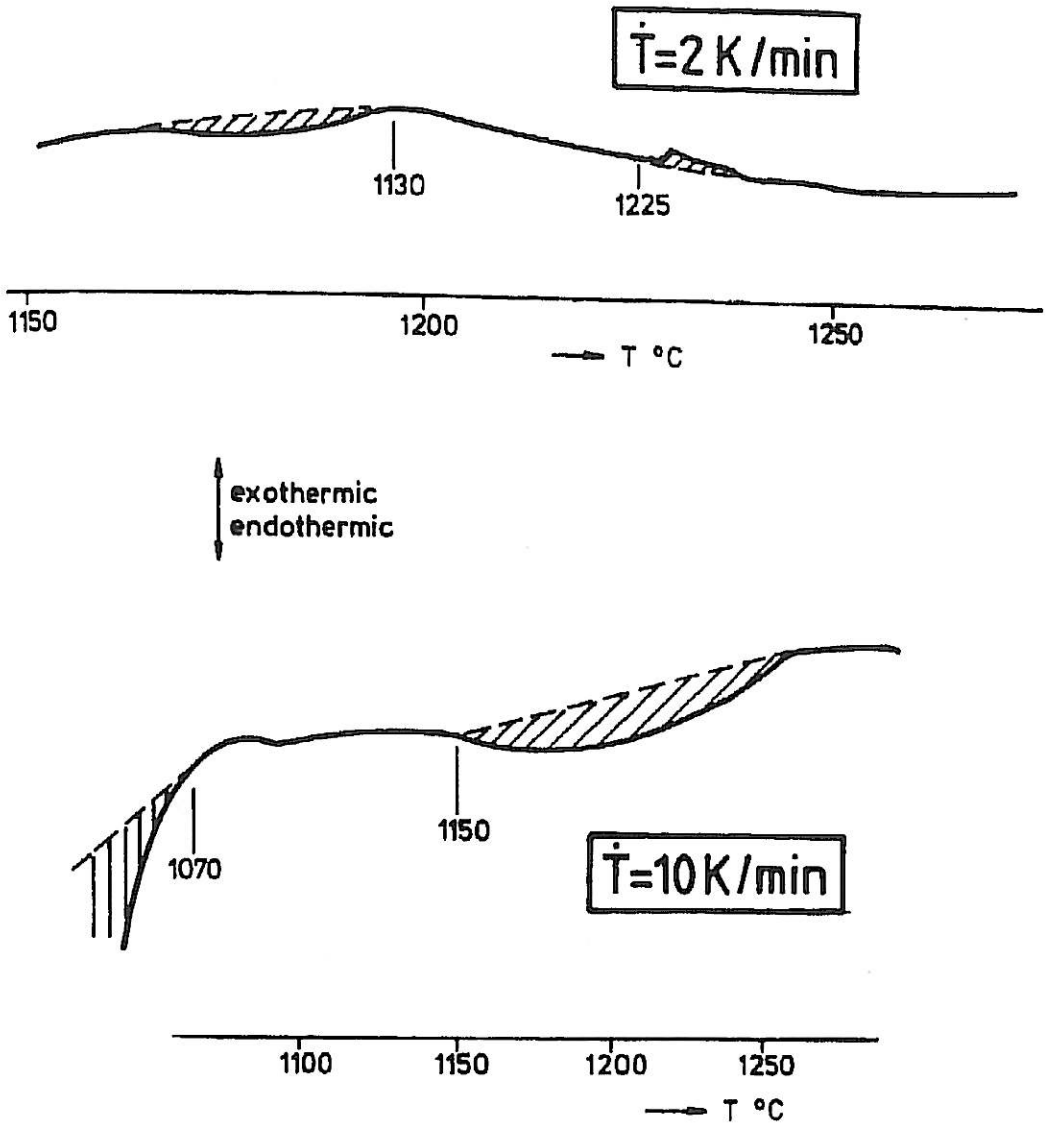


Figure 5 - DTA curves of MA 760 at 2 and 10 K/min

Fig. 5 shows two DTA curves for MA 760 heated at 2 and 10 K/min respectively. The curve for the lower heating rate shows at 1230 °C an exothermic peak which corresponds to secondary recrystallization. This peak is not present in the other curve for 10 K/min. Metallography indeed revealed that secondary recrystallization had not occurred in this specimen, in contrast to the 2 K/min specimen that had recrystallized. Another feature of the DTA curve for the higher heating rate is a shallow endothermic peak in the range between 1150 and 1250 °C.

Figs. 6 and 7 depict typical DTA curves (10 K/min) of Alloy Z and of MA 6000. Alloy Z exhibits at 1180 °C the exothermic reaction corresponding to recrystallization, followed by a strong endothermic reaction at about 1240 °C (Fig. 6). A similar behavior was found for Alloy D. Metallographic investigations of the endothermic reaction revealed carbide dissolution accompanied by localized melting. Fig. 8 shows the microstructure of Alloy Z quenched from 1250 °C after heating at 10 K/min (same conditions as in the DTA run). Partly dissolved carbide particles connected with local formation of dendritic melt structures are obvious. No equivalent reaction has been detected in MA 6000 by DTA investigations and microstructural observations.

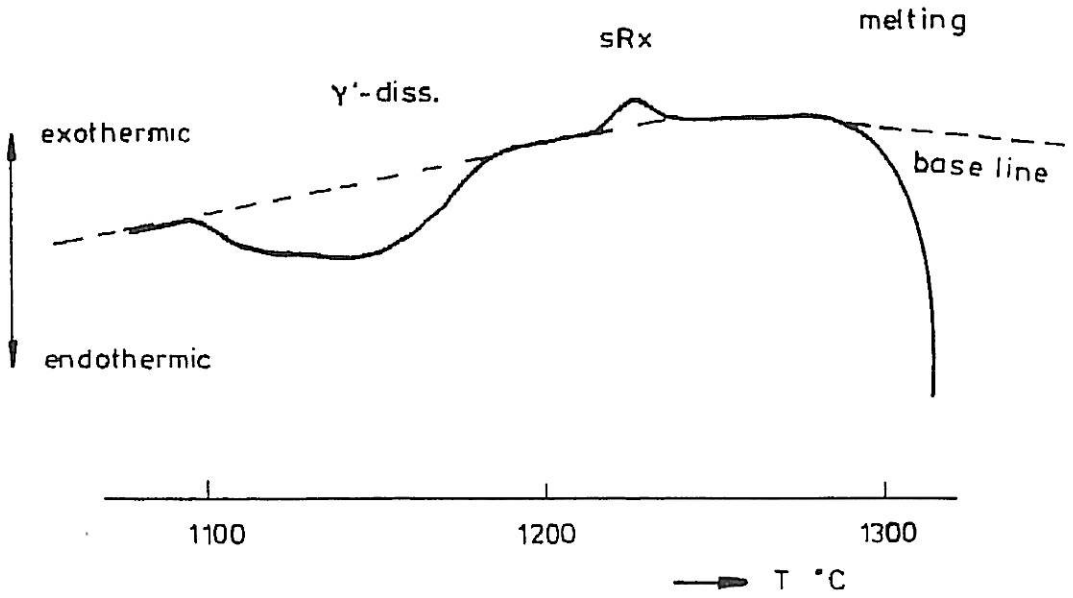


Figure 6 – DTA curve of MA 6000 at 10 K/min

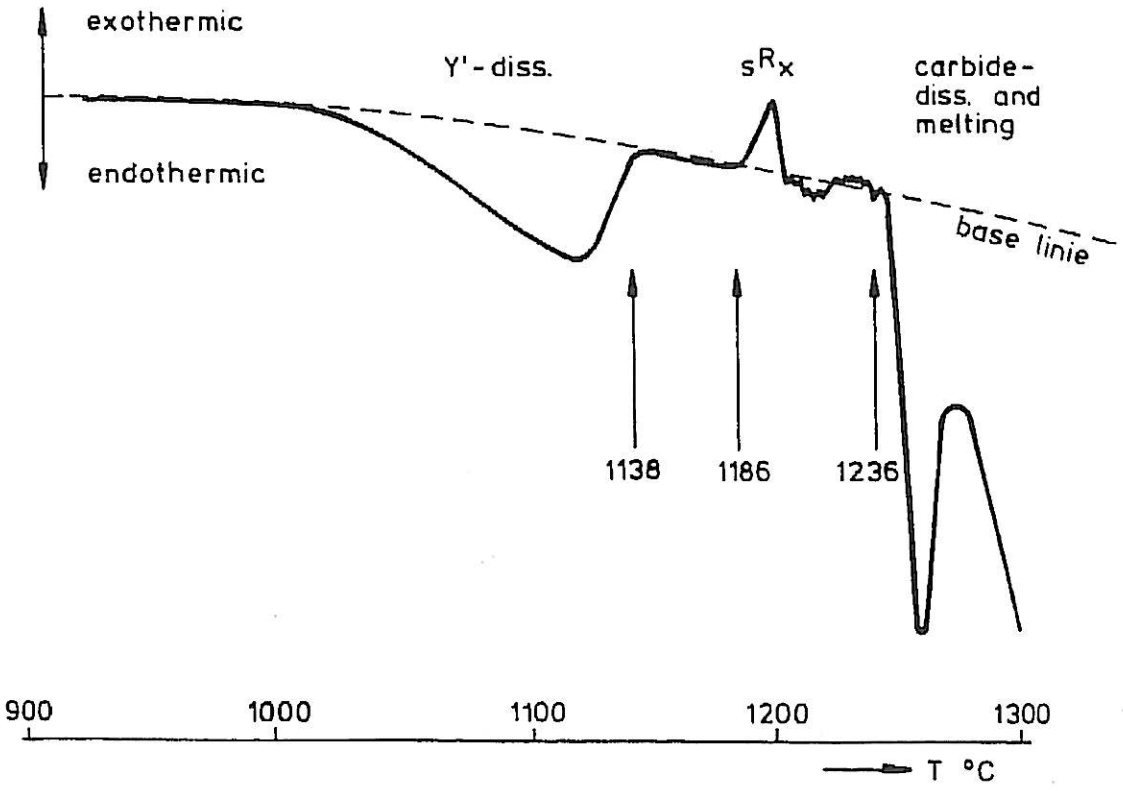
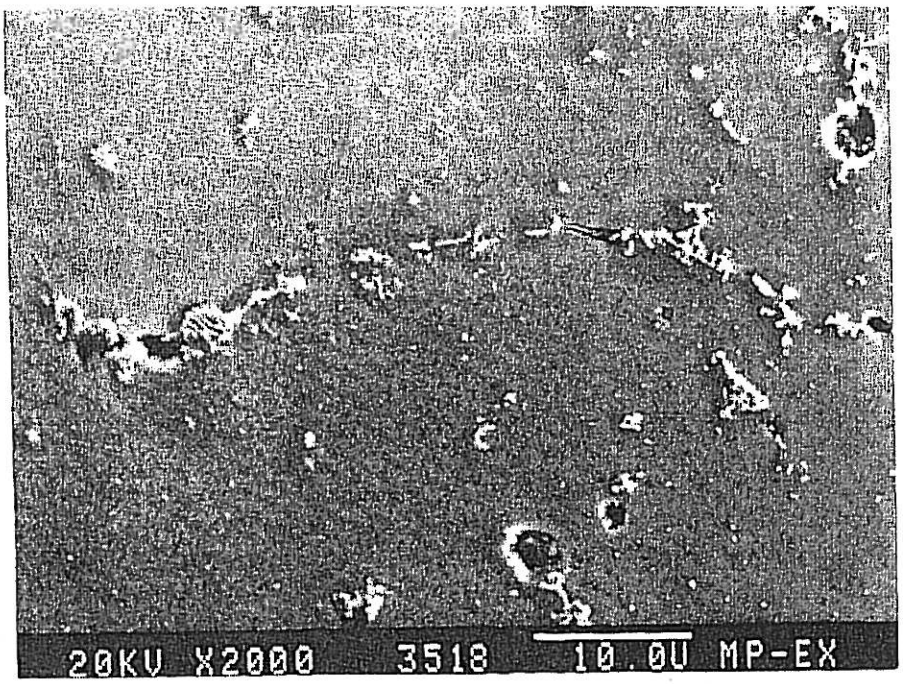


Figure 7 – DTA curve of Alloy Z at 10 K/min



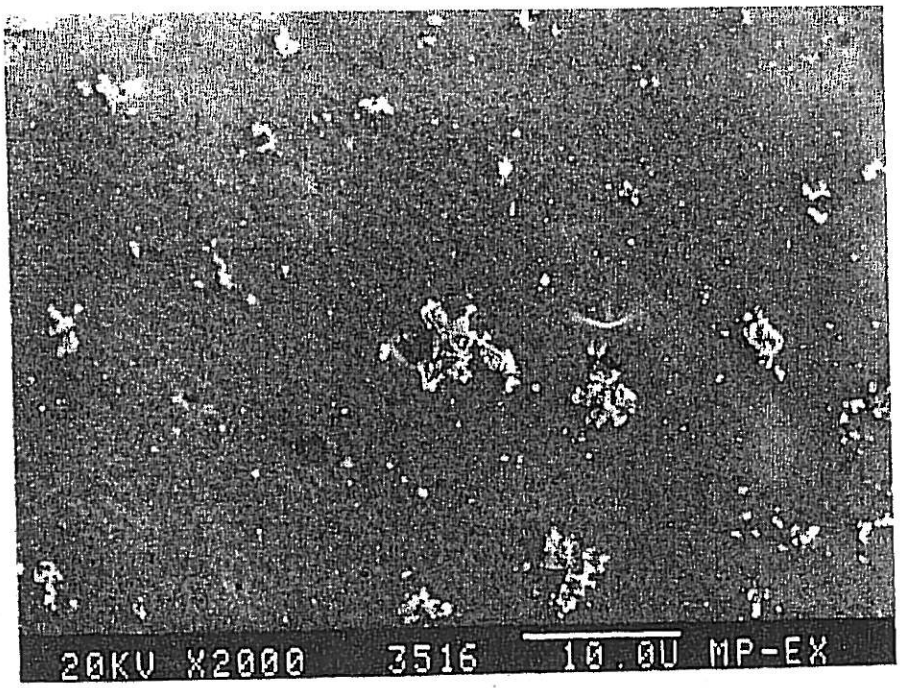


Figure 8 – Microstructures of Alloy Z after annealing at 1250 °C

4 Discussion

Studies of heating rate effects have in the past revealed only a lower limit for the heating rates leading to recrystallization. Its existence can be understood on the basis of the "primary" grain size (before recrystallization), which is determined by compaction of the mechanically alloyed powder and subsequent thermomechanical processing [2,5,9,10]. If the primary grain size exceeds a critical value, then the total amount of grain boundary energy does no longer suffice to cause subsequent secondary recrystallization. This happens, for instance, when extrusion is carried out at too high a temperature or too low a deformation rate. The potential for secondary recrystallization is destroyed, but can be regained by additional hot working under the right conditions, because this decreases the average grain size again to below the critical value. For MA 6000 this critical value is about 0.40 μm. Another way of eliminating the potential for recrystallization is prolonged heating below T_{sRx}. Normal grain growth then causes the starting grain size to increase to a value in excess of the critical grain size. Even if the temperature is subsequently raised to just below the melting point, no secondary recrystallization will take place. This effect explains also the observations made in experiments in which fine grained MA 6000 specimens were isothermally heated with a constant heating rate up to 1250 °C. If the heating rate is too low, no recrystallization will occur due to the long time the specimen resides at temperatures just below T_{sRx}. A similar observation was made in zone annealing experiments in which extremely low travel speeds were used (with a correspondingly low heating rate); recrystallization did not take place [11]. This critical minimum heating rate ($\dot{T}_{min}$), however, is about 1 K/min, which is well below the range of practical importance. Another observed heating rate effect is that the secondary grain size increases with decreasing heating rate [6,7]. Again, this is attributed to the size of the primary grains at the moment the transformation temperature is exceeded. An increase of the primary grain size leads to a decrease of the abnormal grain growth rate and of the nucleation rate (of secondary grains). The effect of the latter is of greater extent, which leads to the observed increase of secondary grain size with increasing primary grain size.

Until recently, an upper limit for the heating rate has never been observed. During isothermal recrystallization experiments on MA 6000 a normal recrystallization response was found even for extremely high heating rates (15000 K/min). Our investigations, however, showed that some alloy batches do not recrystallize if the heating rate exceeds a certain value ($\dot{T}_{max}$) and this behavior is also found in new alloy variants.

The different recrystallization behavior concerning $\dot{T}_{max}$ for different nickel-base ODS alloys could be explained by slight differences in chemical composition. It is suspected that a correlation exists between the above mentioned effect and the ratio of the carbide forming elements, as will be detailed below. Only a first tentative interpretation along this line is given here, further work to substantiate this hypothesis is presently being carried out and will be published elsewhere [12].

Table II: Contents of stable MC forming elements and $\dot{T}_{max}$-values

	MA 6000 [1]	Alloy Z [2]	Alloy D [2]	MA 760 [1]
$\dot{T}_{max}$ [K/min]	> 15000	≈ 3500	8...≈3000	5...≈2500
stable MC former [wt.%]	2.5 Ti 2.0 Ta	1.0 Hf 2.0 Ta	— 2.0 Ta	— —

[1] INCO alloys
[2] experimental alloys of PM Hochtemperatur-Metall GmbH, Frankfurt

Table II shows a comparison of $\dot{T}_{max}$-values and the elemental contents of MC carbide formers (Ti, Ta, Hf) in the alloys investigated. The sum of Mo + W in the various alloys is nearly equal, lying in the range between 5.5 - 6 wt.%. The carbon content varies also only slightly around 0.05 wt.%. Stable MC carbides in superalloys are HfC, TaC and TiC [13]. However, Mo and W can substitute in these carbides, which lowers their stability and favors a degeneration reaction to $M_{23}C_6$. Several superalloys, investigated with relation to their carbide-type stability as a function of temperature, show an instability range for MC at intermediate temperatures (around 900...1000 °C). The formation of M_6C is not expected in our alloys since the content of Mo + W does not exceed 6 wt.% [14].

Because the carbide reactions in ODS alloys have not been studied in detail, the carbide stability fields of Udimet 700 (Fig. 9) [15] are used as a rough approximation to demonstrate the principle of MC destabilisation in Mo- and W-containing alloys. For this destabilisation reaction, a limited temperature range exists whose width will depend on the amount of stable MC-forming elements. The carbide reaction

$$MC + \gamma \leftrightharpoons M_{23}C_6 + \gamma'$$

tends to run to the right hand side during extrusion, which is typically carried out at "moderate" temperatures (950 °C/1-2 h). There are good reasons to expect a relatively stronger interaction between the moving recrystallization front and $M_{23}C_6$ rather than MC. One reason is a considerably greater volume fraction of $M_{23}C_6$ with the same availability of carbon. Additionally, the shape and the preferred position on grain boundaries of $M_{23}C_6$ [15] may introduce a stronger pinning effect on moving grain boundaries during the recrystallization process. The above mentioned carbide reaction must therefore proceed in the reverse direction before successful recrystallization can take place. The recrystallization heat treatment, which is performed at higher temperatures ($T_{sRx} \approx 1200$ °C), promotes the reverse reaction resulting in the desired decomposition of $M_{23}C_6$-carbides.

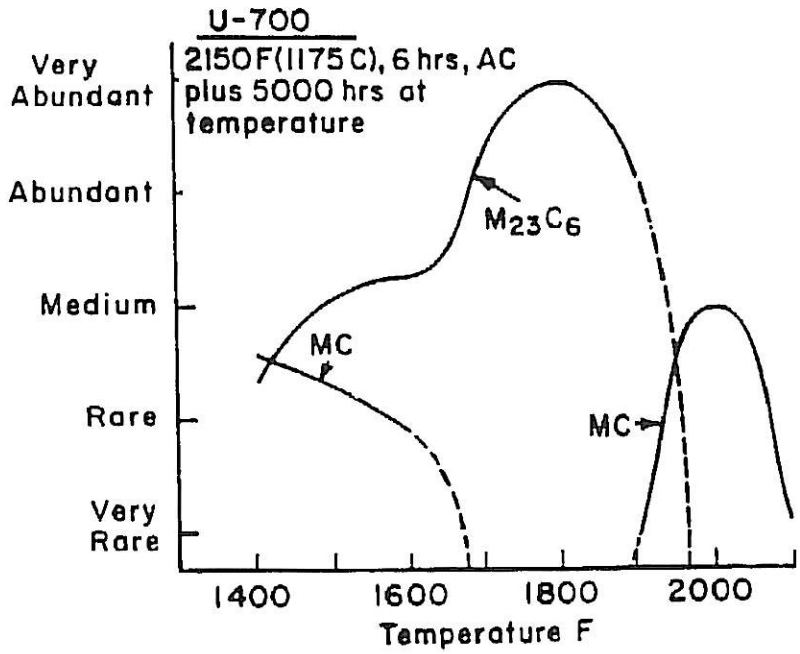


Figure 9 - Phase stabilities as a function of temperatures in Udimet-700 [15]

A fundamental difference of the carbide phase stabilities in the alloys investigated can be clearly seen by comparing the DTA curves from this point of view (Figs. 5-7): For MA 6000, which contains a higher amount of stable MC formers, no carbide dissolution reaction is detectable below the incipient melting point (≈ 1300 °C). In Alloy Z, with a lower content of MC formers, carbides start to dissolve at about 1240 °C. The corresponding endothermic reaction begins at about 1150 °C in some batches of MA 760, which contains no stable MC forming elements.

These observations lend further support to the hypothesis that the $\dot{T}_{max}$-effect in several new ODS-alloys (e.g. MA 760) may be explained by the increased occurrence of an $M_{23}C_6$-type carbide phase, which must decompose to MC during the heating period to T_{sRx} before recrystallization can take place. A lack of stable carbide formers tends to make MC formation the time-limiting step and, thus, renders the alloys susceptible to heating rate effects.

The observed batch-to-batch variation of $\dot{T}_{max}$ for a given alloy can be explained by differences in extrusion conditions. The $MC/M_{23}C_6$-ratio and the size and number of carbide particles in as-extruded material are determined by the extrusion parameters (temperature, hold time, strain, strain rate and cooling rate). Differences in the carbide characteristics affect directly the value of $\dot{T}_{max}$. This is confirmed by the observation that $\dot{T}_{max}$ in one specimen can vary from the surface to the core. It has been observed both in isothermal recrystallization and zone annealing experiments that the surface layer recrystallizes at heating rates at which the core does not recrystallize anymore. This is explained by the different thermo-mechanical processing parameters experienced by the surface layer and the core.

5 Conclusion

An "irregular" recrystallization behavior in certain alloys or alloy batches can lead to considerable practical problems. From the current point of view the possible recrystallization responses can be categorized as in Fig. 10. In this figure the recrystallized volume fraction is given schematically as a function of the constant heating rate applied between about 950 and 1250 °C. Type 1 recrystallization describes "normal" material that recrystallizes at all heating rates except very low ones (ca. < 2 K/min). Type 2 material does not recrystallize at all or only at high heating rates in the case the primary grain size is just small enough to support secondary recrystallization. Type 1 material can be transformed into Type 2 material (by heating just below T_{sRx}) or vice versa (by thermo-mechanical processing). Type 3 material displays both a minimum and a maximum critical heating rate.

While the minimum heating rate is associated with a loss of driving force due to prolonged high temperature exposure, our present results suggest that the maximum heating rate may be caused by different alloy compositions with regard to carbide formers. If our hypothesis is correct, then different alloy variants will have different sensitivities to high heating rates depending on the content of carbide-forming elements. In addition to this composition effect, different batches of a given alloy may have experienced slightly different conditions during thermo-mechanical processing before the recrystallization annealing. In order to avoid "irregular" batch-to-batch variations, temperature, hold time and cooling rate during extrusion should therefore be carefully chosen with regard to possible carbide reactions.

The presence of a maximum heating rate can have important implications for the practice and feasibility of zone annealing. Since the local heating rate in this process is determined by the travel speed of the hot zone, severe limits to the process speed can result: Our experiments indicate, for instance, a possible upper limit for MA 760 of 0.3 mm/min. The recrystallization response thus becomes an important consideration for alloy development.

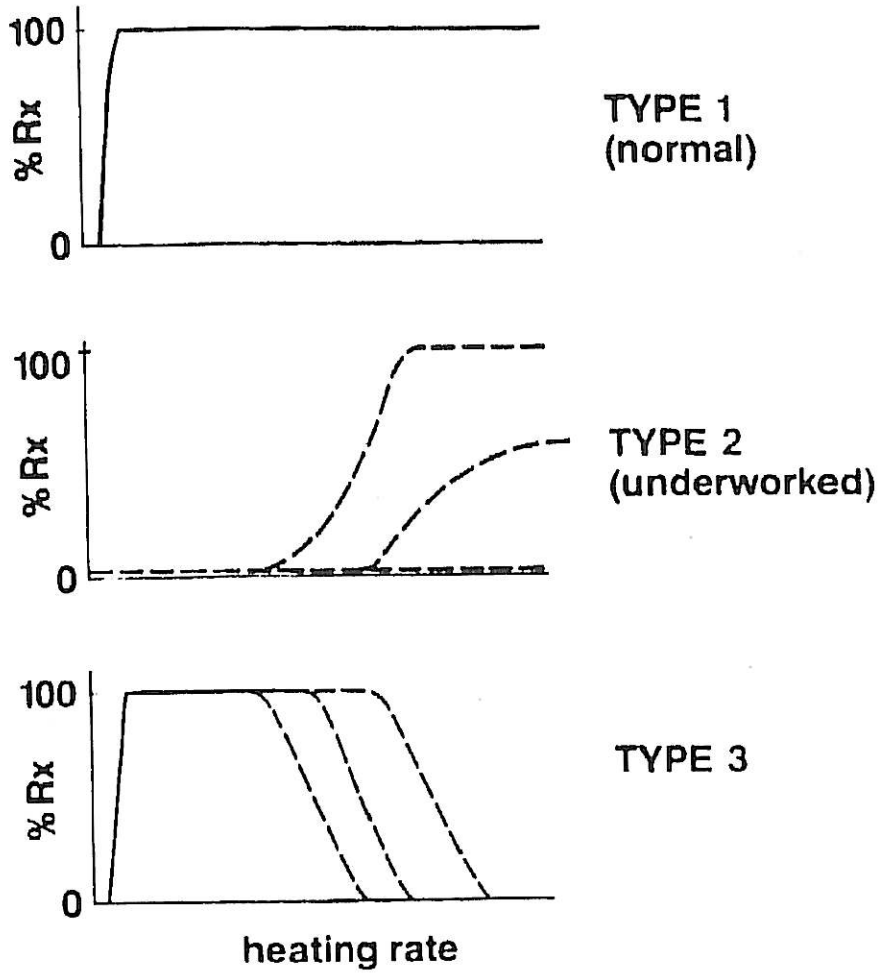


Figure 10 - Different types of recrystallization behavior in the alloys investigated

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