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The Role of Carbide Phases in the Secondary Recrystallization of Nickel-Base ODS-Superalloys

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ABSTRACT

In ODS nickel-base alloys with high γ'-content (e.g. MA760) the rate of heating to the recrystallization temperature plays an important role for the success of the recrystallization treatment. Previous results (Jongenburger et al., 1990) revealed the existence of a heating rate window for secondary recrystallization. While the lower limit of this window ($\dot{T}_{min}$) is well understood, an attempt is made in this paper to explain the upper limit ($\dot{T}_{max}$) by the influence of carbide phases. Furthermore it is shown that carbide phases may also influence the incipient melting temperature and consequently the width of the temperature window for successful secondary recrystallization.

INTRODUCTION

The formation of large elongated grains by recrystallization in oxide dispersion strengthened (ODS) superalloys has long been recognized as a crucial step for obtaining useful high temperature properties. Especially the secondary recrystallization (sRx) behavior of nickel-base alloys with high γ'-content has been studied in detail since the 1970's. After mechanical alloying and subsequent consolidation by hot extrusion, the microstructure exhibits a very fine grain size ($\sim 0.2\ \mu m$) and a low dislocation density of $< 10^{13}\ m^{-2}$ (Singer and Gessinger, 1982). Upon exceeding a specific temperature, sRx rapidly takes place, transforming the fine-grained microstructure into a structure with grains well in excess of 1 mm. For all ODS alloys investigated T_{sRx} lies in a narrow temperature range (ca. 1165...1230 °C), although the chemical compositions differ substantially (Jongenburger and Singer, 1989). Below T_{sRx} only slow, normal grain growth can be observed and even after several hours just below T_{sRx} no indications of sRx (abnormal grain growth) are observable. The abrupt occurrence of sRx upon exceeding T_{sRx} has been ascribed to γ'-solution (Hotzler and Glasgow, 1982), dispersoid coarsening (Mino et al., 1987) and to grain boundaries breaking away from segregated clouds of solute atoms (Jongenburger, 1989).
Among the parameters which are accessible by process control, the rate of heating the specimen to T_{sRx} has been found to be important for the recrystallization response. Recent investigations on several ODS alloys 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 explained by the reduction of driving force due to normal grain coarsening, a maximum heating rate could be interpreted by the presence of carbide phases. In this paper some additional results on the sRx behavior of five high γ' ODS alloys are presented and the influence of carbide phases on both the temperature window as well as the heating rate window for successful sRx are discussed.

EXPERIMENTAL

In this investigation five different high γ' ODS-alloys are compared: MA6000, MA760 (INCO, Hereford, UK) and PM3100, PM3030, PM3020 (PM Hochtemperatur-Metall, Frankfurt, FRG). The chemical compositions of these alloys are given in Table I. The following experiments were conducted on as-extruded, fine grained material.

Differential Thermal Analysis (DTA): All alloys, except PM3020, were investigated using a Perkin-Elmer DTA 1700, in an aluminum oxide crucible with specimens of 3 mm in diameter and 5 mm in height. DTA was carried out with a heating rate of 10 K/min.
Isothermal Heat Treatment: A series of specimens of the alloy PM3100 was annealed at temperatures between 900 and 1300°C. Conditions of a DTA run were simulated (sample size and shape, heating rate). The specimens were heated at 10 K/min to maximum temperature and after a 4 min hold time water quenched. All specimens were cut in half, polished, etched (perchloric acid) and examined in SEM.
Recrystallization experiments with high heating rates: Cylindrical specimens 15 mm in diameter of all five alloys were placed in an induction heating apparatus, in which heating rates up to about 18000 K/min could be achieved. Temperatures (and heating rates) were measured by PtRh/Pt-thermocouples spot-welded to the surface of the samples as well as by two optical pyrometers.

RESULTS

DTA and microstructure: Fig. 1 depicts a DTA curve of alloy PM3100 from 900 to 1300 °C, DTA and an accompanying metallographic investigation revealed the following results:
- γ'-solution terminates at about 1135 °C.
- An exothermic reaction occurs at 1186 °C; this non-

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Table I: Nominal chemical compositions (wt%) of the five high γ' ODS alloys

	Ni	Cr	Al	Mo	W	Ti	Ta	Hf	Zr	C	Y_2O_3
MA6000	bal.	15	4.5	2.0	4.0	2.5	2.0	-	0.15	0.05	1.1
MA760	bal.	20	6.0	2.0	3.5	-	-	-	0.15	0.05	1.1
PM3100	bal.	17	6.0	2.0	3.5	-	2.0	1.0	0.15	0.05	1.1
PM3030	bal.	17	6.0	2.0	3.5	-	2.0	-	0.15	0.05	1.1
PM3020	bal.	20	6.0	1.0	2.0	-	-	-	0.15	0.05	1.1.

reversible reaction (DTA) corresponds with the occurrence of sRx (metallographic observation).

- Coarsening and increase of volume fraction of carbides (carbonitrides) take place in the temperature range 950 - 1180 °C; the development of carbides as a function of temperature is readily observable by microstructural investigation, illustrated in Fig. 2; such "slight reactions" are not detectable in a DTA run.
- From the DTA curve the exothermic sRx-peak is followed by a strong endothermic reaction at about 1240 °C. Metallographic investigations of this endothermic reaction revealed carbide dissolution accompanied by localized melting (Jongenburger et al., 1990). Localized melting at sites of dissolving carbide particles takes place for PM3100 at about 60 °C below the expected incipient melting point (ca. 1300 °C). The influence of carbide dissolution on incipient melting ($T_{s(local)}$) below the solidus temperature of the matrix (T_s) is readily observed.

DTA and microstructural observations of the other alloys investigated revealed comparable behavior. Considerable differences, however, were found with respect to the carbide solution temperatures, associated with their local melting temperatures ($T_{s(local)}$). These temperatures vary for each of the alloys investigated, but are always considerably lower than the incipient melting point of the matrix, except for MA6000, where no equivalent solution reaction has been detected by DTA and microstructural observations. Table II compares DTA results for $T_{s(local)}$ and T_{sRx} for the alloys investigated. Both temperatures establish the temperature window for sRx of each alloy. Fig.3 schematically illustrates the limits of the temperature window for the alloys MA6000, PM3100 and MA760.

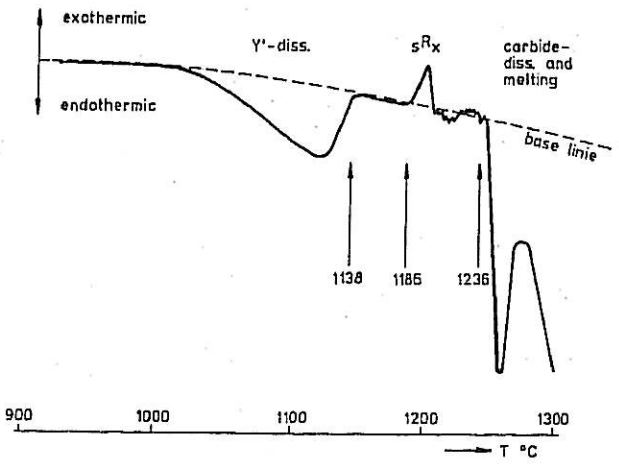

Fig.1: DTA curve of PM3100, heated at 10 K/min.

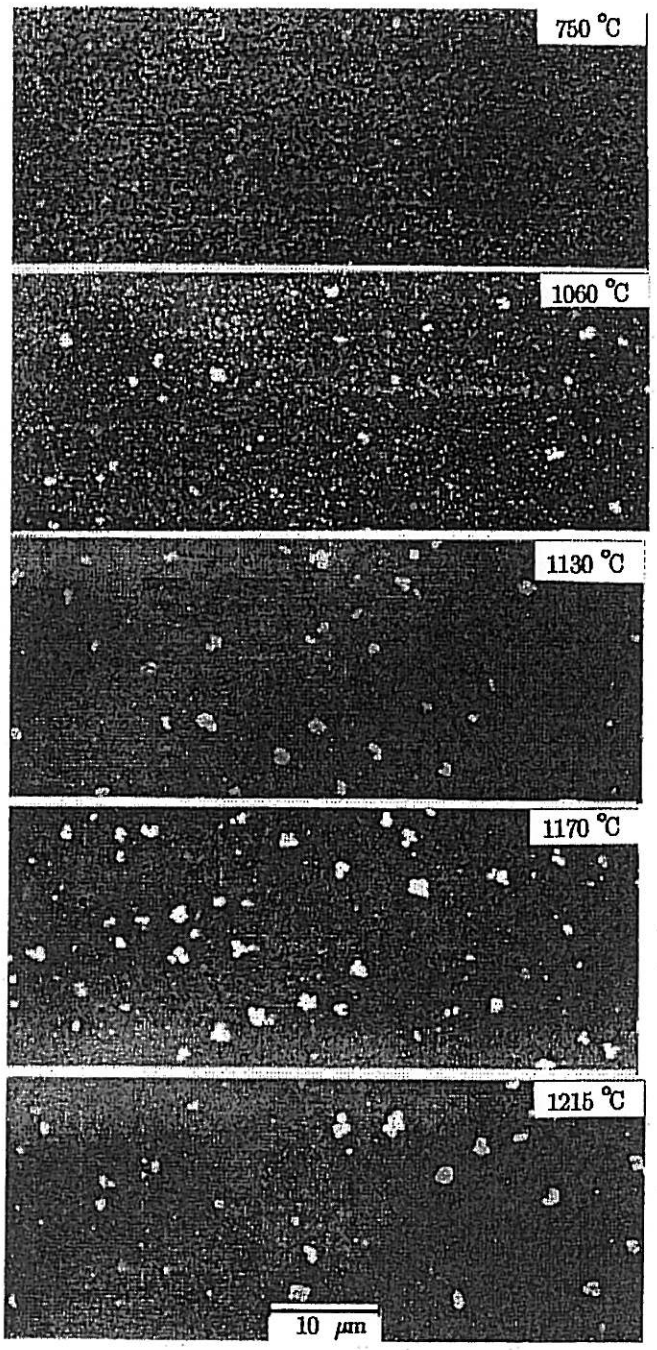

Fig.2: SEM microstructures of PM3100, heated at 10 K/min, 4 min at peak temperature, water quenched.

Table II: SRx-temperatures (T_{sRx}) and temperatures for carbide dissolution and localized melting ($T_{s(local)}$) determined by DTA (°C)

	T_{sRx}	$T_{s(local)}$
MA6000	1202	1300 [a]
PM3100	1186	1236
PM3030	1180	1222
MA760 [b]	1192	1150 [c]

a solidus temperature of the matrix, no local melting in MA6000

b data from Jongenburger et al. 1990

c not confirmed by metallographic observation; carbide dissolution temperature and local incipient melting may not overlap for MA760

Recrystallization with high heating rates:
In an earlier work the existence of an upper limit for the heating rate on the sRx temperature, i.e. a critical maximum heating rate ($\dot{T}_{max}$), was found. Values of $\dot{T}_{max}$ were reported for several alloys, e.g. MA6000 and MA760. Results of additional recrystallization treatments using high heating rates for the alloys PM3100, PM3030 and PM3020 are now included. Fig.4 compares the recrystallization response of PM3100 with that of PM3020 following heating at about 1600 K/min up to 1240 °C. Although both alloys were treated under similar conditions, the recrystallization response differs significantly: PM3020 shows a large, dark triangle-shaped region, which represents material that has not recrystallized, whereas in PM3100 the equivalent thermally-influenced region is fully recrystallized. In both cases the materials experienced the highest heating rate at sites near the specimen surface, due to the immediate vicinity of the induction coil. These results imply that $\dot{T}_{max}$ for PM3100 is higher than 1600 K/min, whereas for PM3020 $\dot{T}_{max}$ is much lower. In Table III all measured or estimated $\dot{T}_{max}$-values for several alloys are given, and the respective upper limits of the heating rate windows are schematically illustrated in Fig.5.

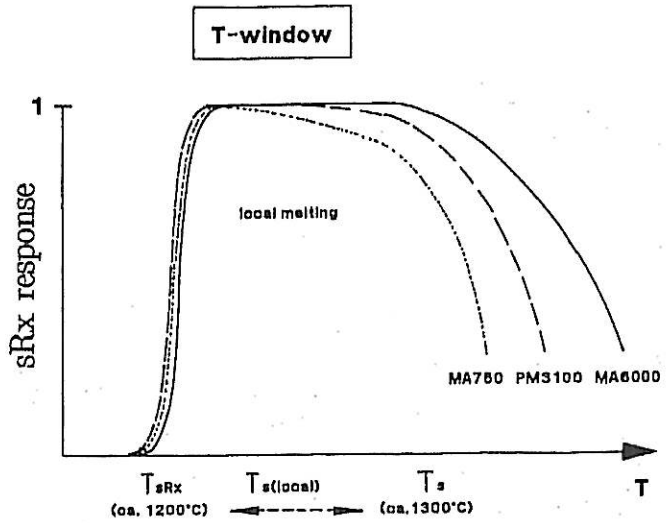

Fig.3: T_{sRx}-windows for the alloys MA6000, PM3100 and MA760.

Table III: Critical maximum heating rates ($\dot{T}_{max}$) for all alloys investigated

	$\dot{T}_{max}$
MA6000	> 15000
PM3100	2000 - 4000
PM3030	< 2500
PM3020	< 1500
MA760	< 1500

DISCUSSION

The important result of our study is that a recrystallization window exists with regard to both temperature and heating rate. The lower limit of the T-window (T_{sRx}) is nearly independent of alloy composition: For different high-γ' ODS-alloys T_{sRx} lies very close to 1200 °C (Jongenburger and Singer, 1989). The lower limit of the $\dot{T}$-window ($\dot{T}_{min}$) is also practically independent of the composition. For the alloys investigated $\dot{T}_{min}$ lies in the range 0.5 - 2.5 K/min. This critical minimum value is well explained by the necessary retention of driving force (grain boundary energy) for sRx. The reduction of grain boundary energy is due to grain coarsening by normal grain growth before abnormal grain growth (= sRx) can take place. In the following the upper limits of both recrystallization windows (T_s, $\dot{T}_{max}$) will be discussed in relation to the formation and development of carbide phases.

Precipitation of carbide phases:

Precipitation of carbides occurs both during extrusion (T_{ex} = 950 .. 1000 °C) and during heating up to the recrystallization temperature. In the alloys investigated the formation of both $M_{23}C_6$ and MC carbide-types is expected, but not M_6C since the content of Mo + W does not exceed 6 wt% (Erdös, 1973; Ross and Sims, 1987). The precipitation of both carbide-types follows the reaction

$$\gamma_1 \longrightarrow M_{23}C_6 / MC + \gamma_2 \qquad [1]$$

in which the specific carbide type depends on the temperature and alloy composition. Several superalloys, when examined in relation to their carbide-type stability as a function of temperature, show a stability field for $M_{23}C_6$ at the expense of MC at intermediate temperatures (around 900 - 1050 °C; Collins, 1968). This temperature range covers the consolidation temperature of PM- Ni-base alloys, and consequently a formation of primary $M_{23}C_6$ will be expected (in contrast to cast superalloys where primary MC will occur). At higher temperatures (> 1050 °C) the stability field of MC is reached, and preferred precipitation of MC carbides according to

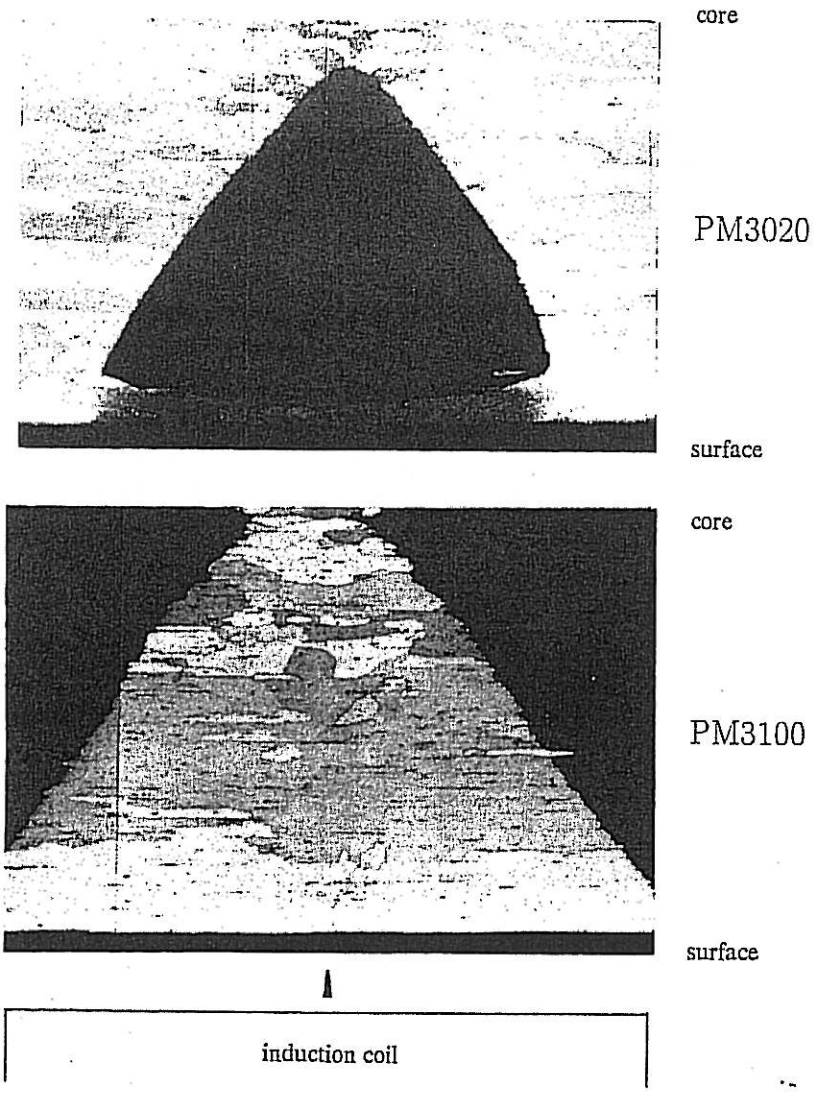

Fig.4: Microstructure (recrystallization response) of PM3020 (above) and PM3100 (below), both heated at about 1600 K/min up to 1240 °C. The highest heating rate in each specimen (round bars with 16 mm in diameter, cut in half) is located in the middle of the induction coil (see arrow), slightly below the specimen surface.

reaction [1] takes place. The MC-forming reaction depends not only on the temperature but also on the amount of strong MC-forming elements in the alloy (see below).

Coarsening and transformation of carbides:

During heating up to T_{sRx} coarsening of carbides takes place (Fig 2). It is accompanied by an increase in the volume fraction of carbides as a function of temperature up to about 1180 °C. Both coarsening and an increase in volume fraction may be explained by either Ostwald ripening of sub-microscopic particles to visible carbides (leading to an apparent volume fraction increase), or by further precipitation from the supersaturated matrix at the sites of already formed carbide particles. In the same temperature regime (> 1050 °C) transformation of the carbide phases can be expected. An already formed $M_{23}C_6$-phase will transform according to the reaction:

$$M_{23}C_6 + \gamma' \longrightarrow MC + \gamma \quad [2].$$

The balance of this reaction depends, in the same way as reaction [1], on temperature (thermal stability fields of carbides) and chemical composition, i.e. on the presence of carbide-forming elements in the alloy. The most stable MC-forming elements in Ni-base superalloys are Hf, Ta, Nb, and Ti (Ross and Sims, 1987), where the metal atoms can

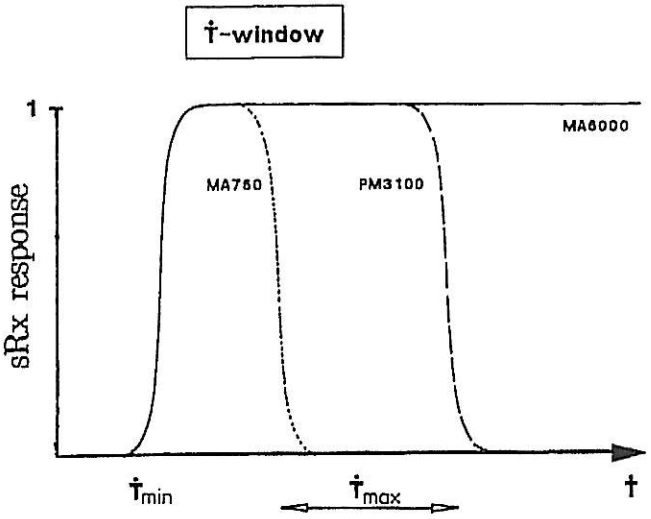

Fig. 5: Heating rate windows for the alloys MA6000, PM3100 and MA760; the width of the windows is practically determined only by $\dot{T}_{max}$.

substitute for each other. In the presence of a sufficient amount of stable MC-forming elements, reaction [2] will run to the right hand side. The higher the temperature, the more MC will be the dominating carbide phase, especially in alloys with a high amount of stable MC-forming elements. Otherwise, in the absence of these elements, $M_{23}C_6$ carbides will tend to remain (even at higher temperatures) because of the surplus Cr content. The $M_{23}C_6$ / MC reaction [2] is accompanied by a decrease of the overall carbide volume fraction, because of the considerably smaller volume associated with MC compared to $M_{23}C_6$ for the same availability of carbon. This may well be the reason for why a slight decrease in the carbide volume fraction occurs at temperatures above ca. 1180 °C (Fig 2).

Influence of carbide phases on recrystallization windows:

It stands to reason that the width of the temperature window as well as the width of the heating rate window is established by the presence of carbides. The existence of an upper heating rate limit ($\dot{T}_{max}$) is interpreted as being due to the development of different carbide phases before sRx can take place. The results of the recrystallization experiments with high heating rates show a correlation between the $\dot{T}_{max}$-effect and the amount of stable MC-forming elements, such as Ti, Ta and Hf (Fig.6): with increasing content of MC-forming elements $\dot{T}_{max}$ also increases. This means that the sensitivity to high heating rates becomes greater as the amount of MC-forming elements decreases. There exists practically no $\dot{T}_{max}$-limit for sRx in the case of MA6000, but for both MA 760 and PM3020 (PM3030) a serious restriction is observed. In several batches of MA760, $\dot{T}_{max}$-values were in fact found below 10 K/min (Jongenburger et al., 1990), in practice this means that such a batch cannot be recrystallized.

The correlation in Fig.6 may be explained by the different effects of the carbide phases: there are good reasons for expecting a stronger interaction between the moving recrystallization front and $M_{23}C_6$ rather than MC. Besides the higher volume fraction of $M_{23}C_6$, its shape and preferred position on grain boundaries may introduce a stronger pinning effect on grain boundaries. The carbide reaction [2] must therefore proceed to the right hand side before successful sRx can take place. Decomposition of $M_{23}C_6$ is not the only way to reduce the forces retarding sRx; coarsening of the $M_{23}C_6$-phase by Ostwald ripening leads also to a reduction of the drag forces on moving grain boundaries. Both transformations may occur simultaneously, but for sRx to take place the ripening process has to proceed much further in $M_{23}C_6$-dominated alloys than in MC-dominated alloys.

Depending on the amount of strong MC-formers in an alloy, the time dependent $M_{23}C_6$-decomposition will influence the degree of sensitivity to the heating rate ($\dot{T}_{max}$-effect). A lack of stable MC-formers tends to make $M_{23}C_6$-decomposition and -coarsening the time-limiting step and, thus, renders the alloys susceptible to heating rate effects. The transformation of the $M_{23}C_6$-phase competes with a further change in the microstructure: normal grain growth. Only a doubling of the mean grain diameter of the as-extruded structure can lead to an

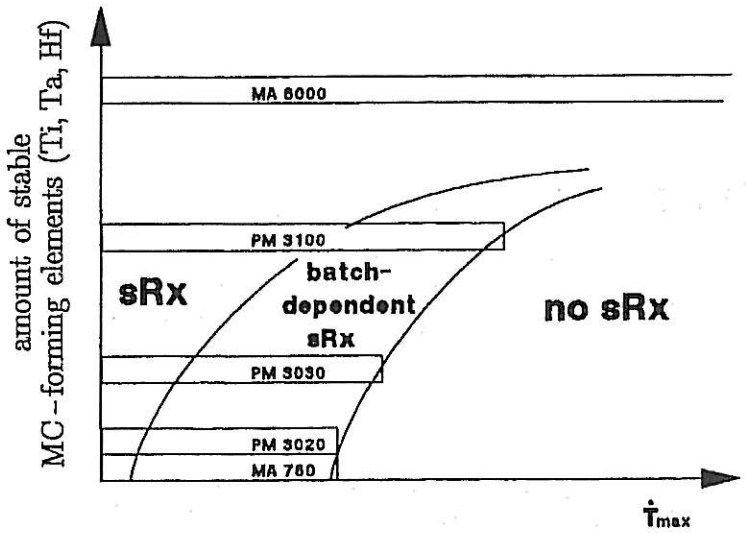

Fig.6: Schematic correlation between the amount of stable MC-forming elements and the sensitivity to high heating rates.

insufficient amount of driving force for sRx (Jongenburger, 1989). Therefore if the transformation of the $M_{23}C_6$-phase is slower than the reduction of driving force by normal grain growth, then abnormal grain growth (sRx) will never be possible.

The observed batch-to-batch variation of $\dot{T}_{max}$ for a given alloy can in principle 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 thermal profile during extrusion (temperature, hold time, cooling rate). Differences in the carbide characteristics in different batches of an alloy affect directly the value of $\dot{T}_{max}$ (see Fig.6, batch-dependent sRx response).

The different carbide phases in the alloys investigated may also be responsible for their different thermal stabilities and, consequently, the explanation for the different incipient melting temperatures ($T_{s(local)}$) of these alloys. Results of DTA and microstructural investigations revealed that for MA 6000, which contains a considerable amount of stable MC formers, no carbide dissolution is detectable. In PM3100, with a lower content of MC formers, carbides start to dissolve at about 1240 °C. In MA760, which contains no strong MC-forming elements, carbides appear to dissolve already at about 1150 °C, see Table II.

Both T_s and $T_{s(local)}$, and consequently the width of the T-window (Fig.3), may directly be affected by the carbide stability, i.e. by the ratio of MC / $M_{23}C_6$ phases in the alloy. It is suggested that the sequence of alloys with decreasing $T_{s(local)}$ (Table II) and with decreasing $\dot{T}_{max}$ (Table III) is no mere coincidence, but both correlations may result from the alloy-specific $M_{23}C_6$ / MC carbide type relation.

SUMMARY

Five high γ' ODS superalloys (MA6000, MA760, three new PM-HTM-alloys) were investigated with respect to their "recrystallizability". Results from DTA and recrystallization treatments under varying heating rates revealed the existence of a window for both the temperature and the heating rate. The width of both windows depends significantly on slight deviations in the chemical compositions of the alloys. It is shown that there exists a correlation between the carbide forming elements and the upper limits of both recrystallization windows. These correlations have been explained by the presence of two carbide phases (MC, $M_{23}C_6$) with their different influence on the recrystallization process. The more dominating the $M_{23}C_6$ phase in an alloy, the narrower the windows for successful secondary recrystallization.

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