DEVELOPMENT OF SUBSTRUCTURE DURING MANUFACTURING OF OXIDE DISPERSION STRENGTHENED SUPER-ALLOYS

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Dedicated to Prof. Jangg at his 75th anniversary

Abstract
Oxide dispersion strengthened Ni-based alloys were produced by ball milling of elemental and pre-alloyed powders and yttria powder to study influences of the milling parameters on the alloying process and the partitioning of the yttria dispersoids. After milling, the powders were degassed, sealed in mild steel cans and hot extruded. The mechanical alloying process was characterized by X-ray-diffraction techniques and sieve analysis. Measurements of tensile strengths and elongations as well as dislocation densities and grain sizes of the as-extruded alloys were carried out to investigate the connections between milling parameters and yttria partitioning and the connections between dislocation densities, grain sizes and textures, and tensile strength and elongation. Finally, two quality control criterions are defined. The first is derived from the tensile strength-elongation functions of optimally processed alloys, the second one based upon then mutual dependence of grain sizes and dislocation densities of as milled and as extruded ODS-alloys.
Keywords: ODS-alloys, mechanical alloying, hot extrusion, thermo-mechanical treatment, substructure, tensile properties

INTRODUCTION

Oxide dispersion strengthened (ODS) superalloys are designed for long-term, high-temperature applications at high stress levels. High creep strengths will be achieved if the ODS alloy contains a fine dispersion of high-temperature stable particles (usually yttria) and if the structure consists of coarse, elongated grains. According to theoretical and experimental work, a mean particle distance between 100 and 150 nm of 10 to 20 nm yttria particles, and a grain aspect ratio of minimum 10, guarantees good high-temperature properties [1-5].

Today, ODS superalloys are produced by ball milling of metal and yttria powders, canning, degassing and powder consolidation either by hot extrusion or hot isostatic pressing. The chosen technique primarily depends on the shape of the desired product. Sheet materials are manufactured by hot isostatic pressing and rolling, while rods and wires are produced by extrusion and profile rolling. After consolidation, the alloys are worked to semifinishes, which are heat treated after the last working step. The aim of this final heat treatment is a secondarily recrystallized structure, which exhibits coarse, highly elongated grains.

Basically, the secondary recrystallization process is driven by the energy of the grain boundaries, while grain growth is hindered by the yttria particles. If the driving forces

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exceed the backstressing forces, which implies that the grain size is below the critical Zener grain size (Eq.1), secondary recrystallization is possible [6].

$$\Delta_C = 4r/3f \tag{1}$$

r particle size
f volume fraction of dispersed particles

But the desired structure of coarse, elongated grains will only be achieved if fine yttria particles are homogeneously dispersed in the metal matrix. Consequently, the metal matrix shows a narrow grain size distribution with mean grain sizes between 0.5 and 1 µm. Experimental studies of the substructures of extrudes or hot isostatically pressed and worked ODS super-alloys show that grain sizes and dislocation of such materials are connected by a boundary-line-function, which gives an additional condition for an optimal recrystallization response (Eq.2) [7].

$$\Delta = k/\rho^{0.5} \tag{2}$$

Δ grain size
ρ dislocation density
k proportion value (2.5 – 3 for optimally processed fcc-alloys)

If the ODS alloys are well processed, the calculation of the proportion value k, which is calculated by measuring grain sizes and dislocation densities by X-ray-techniques, gives approximately 2.5 for ODS-fcc-alloys and approximately 5-6 for ODS-bcc-alloys. If the values are significantly higher, the substructure is not optimal, because of cold overworking due to too low working temperatures or dynamic grain coarsening [8]. From energetic considerations, secondary recrystallization of cold overworked primary structures is possible, but it leads to fine, non-regularly shaped grains. Because the grain size of hot overworked primary structures exceeds the critical Zener grain size, no secondary recrystallization is possible. While cold overworking generally produces unsuitable materials, hot overworked structures are a suitable way to produce grain stabilized materials like dispersion strengthened copper, aluminium and noble metals.

The core of the ODS processing technology is the milling process, in which metal powders and yttria are ball milled in dry, inert atmospheres. If powder blends of pre-alloyed metal powders and yttria are milled, the milling process yields a fine and homogeneous dispersion of the yttria particles in the metal matrix. If powder blends of at least two metal components are milled, the aim of ball milling is not only a fine and homogeneous dispersion of the yttria particles in the metal matrix, but also the formation of a solid solution by mechanical alloying of the metal components.

Mechanical alloying is promoted by continuous fracturing, rewelding and deformation of the milled powder particles, which create a fine layered structure of the milled metal components. This fine layered composite structure, in which the yttria dispersoids are embedded, is continuously refined during further milling. Finally, if the interfacial area between the milled components is large enough, a true solid solution will be formed by diffusion, which is enhanced by temperature rises due to the dissipation of the kinetic energy of the ball-particle-ball-collisions.

In this article, the mechanisms of mechanical alloying, which lead to the formation of a solid solution of two milled metal components are considered first of all. Secondly, the influence of the milling parameters and the chosen raw material on the substructures and the tensile properties of ODS-NiCr20 are discussed. Finally, a generalized quality control criterion for ODS-Ni-based alloys, which bases itself upon the tensile data and the substructure parameters, is presented.

EXPERIMENTAL TECHNIQUES

To study the partitioning and homogenisation processes during mechanical alloying, Ni50W50 elemental powder blends were ball milled in a 3.5 l laboratory attritor in a dry argon atmosphere. The rotational speed of the stirrer was 600 rpm. 500-gram powder charges were milled with 5 kg 8 mm steel balls, which gives a ball to powder ratio of 1:10. Analogously, the experimental ODS-alloys (NiMo, NiCr and Ni) were produced by mechanical alloying of blended powder mixtures of yttria with an average particle size of 0.6 μm and either pre-alloyed or elemental metal powders.

After milling, the powders were degassed for 48 h at 873 K in a vacuum furnace. Then, the metal powders where canned in mild steel cans, degassed and consolidated by hot extrusion at temperatures between 1323 and 1523 K. The extrusion ratio varied between 1:4 and 1:24. Homogenisation and the development of substructure during mechanical alloying and powder consolidation were examined by X-ray-techniques. Tensile properties were measured by conventional tensile testing.

The milled powders were investigated by determination of the RRSB-powder particle size distribution and X-ray-diffraction analysis, the as extruded alloys were characterized by X-ray-diffraction and measurements of tensile strengths and fracture elongations. X-ray-diffraction was carried out using metallographic cuts of the powders and the as extruded bars. Mechanical alloying was observed by measuring the lattice parameters of the fcc-Ni-solid solution, which changes during the alloying process according to Vegard's law. Grain sizes and dislocation densities were determined by an evaluation of the profile line broadening of the reflections of the metal components. The yttria dispersion was characterized by tensile tests at room temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

Partitioning, Alloying and Homogenisation during Mechanical Alloying

Starting from elemental powders, a binary Ni50W50-model is best suitable to investigate the partitioning, alloying and homogenisation processes during milling (Fig.1).

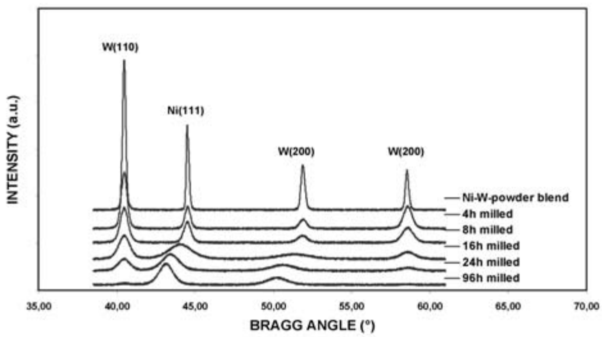

Fig.1. X-ray diffraction patterns of differently milled Ni50W50 elemental powder mixtures.

Partitioning Period

After short periods of milling, X-ray-diffraction analysis shows increasing profile line widths of the Ni- and W-reflections, which are caused by increasing dislocation densities and decreasing grain sizes due to fracturing and deformation of the powder particles.

Alloying Period

After 8 h ball milling, the interfacial area between Ni and W is large enough to start the formation of an fcc-NiW-solid solution by diffusion of W into Ni. The diffraction patterns show a shift of the fcc-Ni-profiles to lower Bragg angles, because solid solutioning of W in the Ni-matrix increases the lattice parameter of the fcc-Ni-phase (Fig.2). A significant increase of the lattice parameters of the fcc-Ni-phase is measured after 24 h of mechanical alloying. After 96 h milling, evaluation of the diffraction patterns show that the W-content of the Ni-matrix reached its nominal value of 50 wt.% (Fig.3).

After the alloying process has started, the increasing profile line width of the Ni-reflections is not only caused by high dislocation densities and small grain sizes, but also by the inhomogeneities of the Ni-phase due to the diffusion of W into the Ni-matrix, which causes locally different lattice parameters and, as a consequence, profile line widening of the Ni-reflections. The alloying process itself is driven by the diffusion of W into the Ni-matrix, while no diffusion of Ni into the W-matrix is observed.

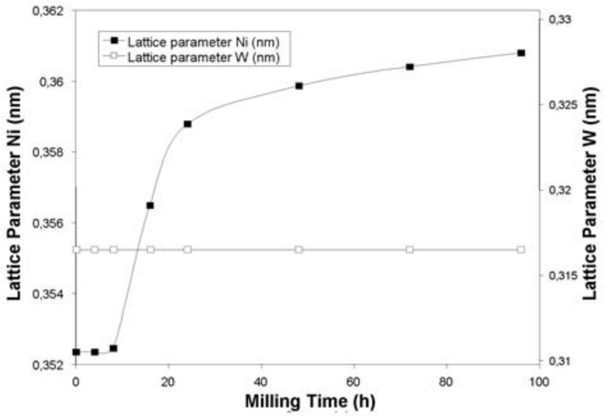

Fig.2. Changes of the lattice parameters of Ni and W during mechanical alloying.

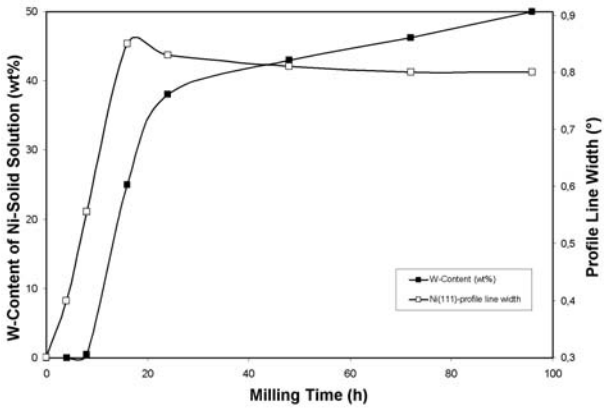

Fig.3. W-content of the fcc-Ni-solid solution and profile line width of the (111)-Ni-reflections.

Homogenisation period

The maximum line width of the Ni-reflections, which is observed after 24 h of milling, marks the beginning of the homogenisation process. Further milling yields decreasing profile line widths, because the homogeneity of the powders is improved.

Substructure

Because the profile line width of the Ni-reflections consists of a superposition of the influences of dislocation densities, grain sizes and chemical inhomogeneities, substructure parameters may only be estimated. During the first 8 h of milling, the dislocation densities increase from approximately $10^{10}/cm^2$ to $10^{12}/cm^2$, while the grain sizes decrease from the starting values in the µm-range to values below 100 nm.

Because there is no solid solution of Ni in the W-matrix, the profile line widths of the W-reflections are only caused by dislocation densities and grain sizes. Evaluation of the X-ray-reflections gives the actual grain sizes of the W-layers, which are a characteristic dimension for layer thickness in the Ni-W-composite structure (Fig.4). Considering the starting point of the alloying process, and the grain size measurements show that the critical layer thickness to start the alloying process is approximately 30 nm. When the layer thickness of the lamellar structure is reduced below this value, the interfacial area between W and Ni is large enough to start the mechanical alloying process by diffusion.

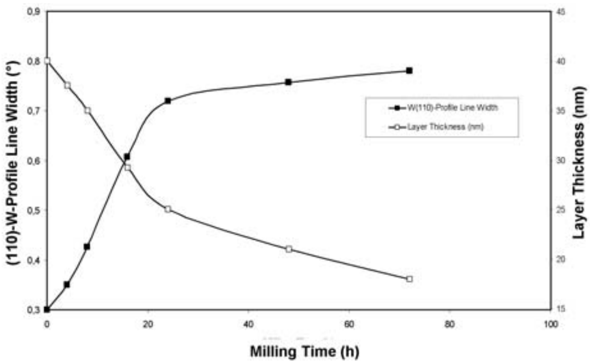

Fig.4. W-profile line width and thickness of the W-layers as a function of milling time.

Mechanical Alloying of ODS-NiCr20

Mechanical Alloying and Milling of ODS-NiCr20

Mechanical alloying of ODS-NiCr20 starts from elemental metal powders and yttria, while mechanical milling uses pre-alloyed, atomised NiCr20-powders. In analogy to the Ni-W-model system, mechanical alloying of ODS-NiCr20 shows a partitioning period, which lasts 8 h. After 8 h milling, the lattice parameter of the Ni-phase increases, which indicates the beginning of the alloying process. After 24 h milling, the profile line widths of the Ni-reflections reach their maximum values, which indicates the starting of the homogenisation period.

On the contrary, the profile line width of mechanically milled pre-alloyed powders steadily increases with increasing milling time, because further milling results in a continuous refinement of the grain sizes and increase of dislocation densities (Figs.5, 6).

Because cold-welding of NiCr20-powders predominates the milling process of pre-alloyed NiCr20 powders from the beginning, the powder particle sizes continuously increase during milling. On the contrary, mechanically alloyed elemental Ni- and Cr-powder blends remain fine during the partitioning period of the mechanical alloying process. The composite Ni-Cr-structure, which is created by fracturing and rewelding of the milled powder, acts rather brittle. After 8 h of ball milling, the brittle composite structure of Ni- and Cr-layers is gradually transformed to a ductile fcc-Ni-solid solution due to the onset of the mechanical alloying process. Consequently, the grain sizes increase due to particle welding (Fig.7).

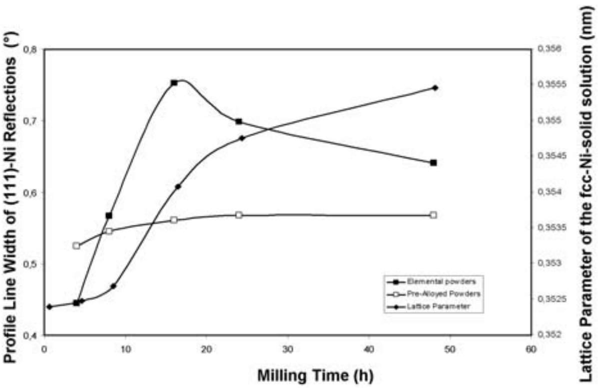

Fig.5. Changes of the profile line widths and the lattice parameter during milling of elemental and pre-alloyed powder blends as a function of milling time.

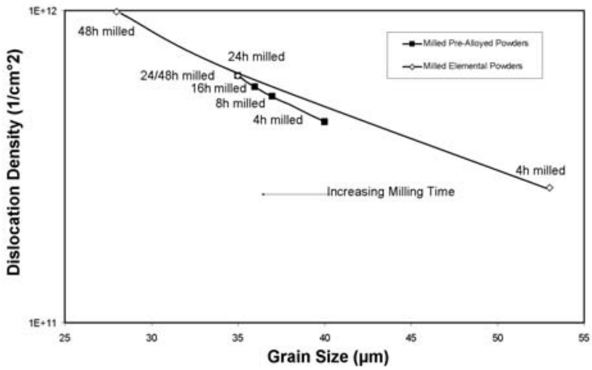

Fig.6. Connections between grain sizes and dislocation densities during ball milling.

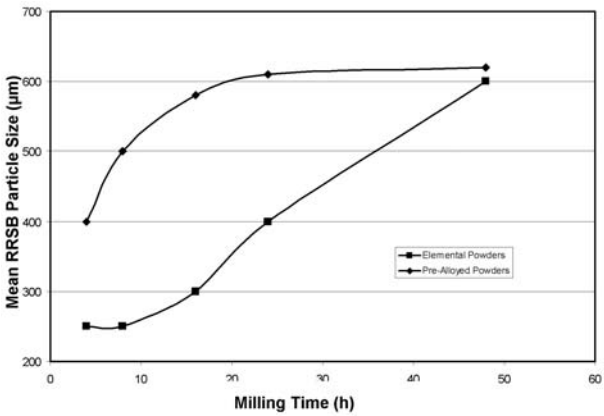

Fig.7. Mean particle sizes do.632 of milled elemental and pre-alloyed NiCr20-powder blends as a function of milling time.

Dispersoid partitioning

The most reliable method to characterize the influence of the milling parameters on the dispersoid partitioning are measurements of yield strength, tensile strength and fracture elongation of the as extruded alloy. Yield strength as well as tensile strength of ODS-alloys are controlled by the superposition of matrix strength, solid solution strengthening, strain hardening and particle strengthening (Eq.3):

$$R_P = R_0 + k_1 c^{1/2} + k_2 \Delta^{-1/2} + \alpha M G b \rho^{1/2} + 0.84 M G b / \alpha \tag{3}$$

R_0	yield stress of the pure matrix
G	shear modulus
b	Burgers vector
α	constant (usually taken as $1/2\pi$)
$k_{1,2}$	empirical constants
c	content of alloying element (at.%)
Δ	grain size
ρ	dislocation density
λ	mean particle spacing
r	particle size
f	volume fraction of dispersed particles

Strain hardening and particle strengthening of as extruded alloys are directly influenced by the yttria dispersion. Because the yttria dispersion acts as a backstress to grain coarsening at high temperatures, the more the fine grained MA microstructure is stabilized during hot extrusion, the better the distribution of the dispersoid particles during milling. Consequently, improvements of the yttria dispersion are measured as increasing yield and tensile strength.

Consideration of the tensile data of differently processed ODS-NiCr20-alloys needs a reference line of the tensile data of well processed alloys, which describes the mutual dependence of tensile strength and elongation. Higher strengths, which are caused by lower extrusion temperatures, lower extrusion ratios or higher yttria contents, are balanced by lower elongations and vice versa. The given reference line is given by the maximum values of tensile strength and elongations of ODS-NiCr20. The yttria content varied between 0.2 and 1 wt.%, the extrusion ratio between 8 and 20, and the extrusion temperature between 1323 and 1473 K.

Generally, longer milling times yield increasing yield strength. Consideration of the pre-alloyed variants shows that the tensile strength increases, while the elongation decreases with increased milling time. But tensile testing of as extruded bars, which were produced using elemental powders, shows that longer milling time raises tensile strength as well as elongation. Up to 8 h of milling, the elongations of as extruded ODS-NiCr20-bars, which were produced using elemental powders, are clearly below the values of mechanically milled and extruded pre-alloyed powders. Because the mechanical alloying process starts after 8 h milling time, the lower elongations measured at mechanically alloyed and extruded samples are caused by inhomogeneities of the milled and extruded powders. But if the alloying process is finished after 24 h of milling, tensile strengths and elongations of elemental powder variants are significantly higher than the values of equally processed powder variants (Fig.8).

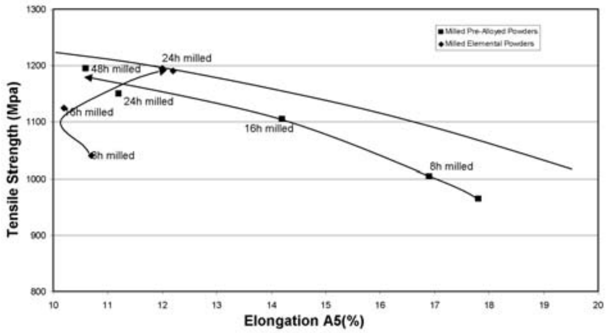

Fig.8. Influence of milling time on the tensile properties of ODS-NiCr20-alloys.

Consideration of the powder particle size data explains the lower tensile strength-elongation values of as extruded bars, which were produced via the mechanical milling of pre-alloyed powders route. Because these powders immediately coarsen during milling, sufficient partitioning of the yttria particles is hindered. On the contrary, the powder particle sizes of milled elemental Ni-Cr-powder blends remain fine during the first period of milling, which indicates a dynamic equilibrium between fracturing and rewelding, which promotes a fine and homogeneous yttria dispersion.

Comparison of powder particle sizes and tensile data, point to the fact that fracturing and rewelding are a necessary but not sufficient criterion to achieve a homogeneous partitioning of the yttria particles. Although particle welding becomes the dominant process during ball milling after 8 h milling time, the tensile strengths and elongations increase. Therefore, the dispersion of the yttria particles will be refined by deformation of the milled powders, even if the powder particle sizes of the milling products increase due to cold-welding of the powder particles.

Changes of Substructure during Milling and Hot Extrusion

Analysis of the substructure of as milled pre-alloyed NiCr20-powders, show that the dislocation densities significantly increase during the first 8 h of milling until they reach their saturation values of approximately $5*10^{12}/cm^2$. On the contrary, the grain sizes decrease steadily during milling, approaching their minimum values of 80 nm after 24 h milling time.

The milling time primarily influences the grain sizes of the ODS-alloys, which were extruded at a constant extrusion temperature if 1373 K. While the dislocation densities of as extruded bars remain at nearly constant values between 5 and $6*10^{10}/cm^2$, the grain sizes decrease from 0.5 to 0.15 µm. Up to 1473 K extrusion temperature, increasing extrusion temperatures of 48 h milled and extruded powders cause decreasing dislocation densities, which are balanced by increasing grain sizes according to the grain size-dislocation density-function. Higher extrusion temperatures yield a departure of the microstructure from the grain size-dislocation density-function of optimally processed alloys due to dynamic grain coarsening (Fig.9).

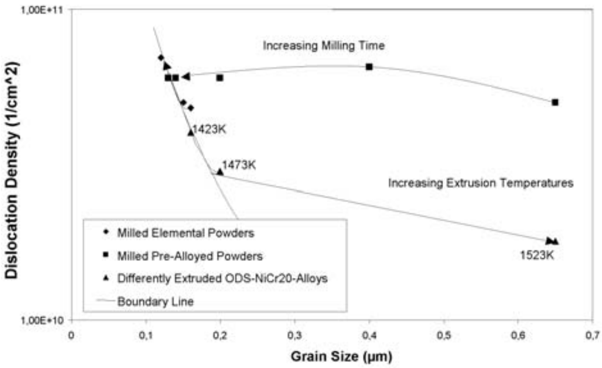

Fig.9. Influence of milling time and the extrusion temperature on the substructure of ODS-NiCr20-alloys.

Tensile properties and Substructure Parameters as Quality Control Criterion

Tensile Strength and Elongation

The determination of the tensile strength-elongation-functions is a very suitable way to control the quality of the milled powders. The finer and the more homogeneous the dispersoids are partitioned, the higher the tensile strengths. On the other hand, coarse yttria particles as well as chemical inhomogeneities decrease elongation. The better the material quality, the higher are the tensile strength and elongation.

Because the development of ODS-alloys leads to different alloy compositions, the levels of the strength-elongation functions are different due to different contributions of solid solution strengthening. A single reference line for optimally processed alloys is achieved if reduced tensile strengths are used, which is defined by the measured tensile strength minus solid solution strengthening (Eq.4).

$$R_M = C_1 \cdot A_5^{-C2} + R_S \qquad (4)$$

R_M tensile strength
R_s solid solution strengthening
0.5>A>6 C_1=1430, C_2=0.13 (Region A)
6>A>15 C_1=1800, C_2=0.26 (Region B)
15>A>23 C_1=27200, C_2=1.25 (Region C)

The reference line generally does not cover precipitation strengthened alloys. This comprises high strength ODS-NiMo15- ODS-NiMo30-alloys, the medium strength ODS-NiCr20-, ODS-NiCr30-, ODS-NiCr40-alloys as well as low strength ODS-Ni (Fig.9).

Elongation and Extrusion Texture

While the connections between tensile strength and substructures are easily explained by consideration of the different strengthening contributions given in Eq.3, the elongation may be explained in terms of the extrusion textures of the as extruded alloys. As extruded fcc-alloys usually show a double (111)-(100)-fibre texture, where the ratio of (111) to (100) orientated crystals depends on the alloy composition, the extrusion temperature and ratio and yttria content of the alloy. Higher extrusion temperatures and higher extrusion ratios (which act analogously because of the higher heat of deformation due to the higher applied and dissipated strain during the adiabatic extrusion process), which give higher elongation and lower tensile strength, favour the (100)-orientation, while lower extrusion temperatures, lower extrusion ratios and higher Cr- and Mo-contents generally promote the (111)-orientation. Due to the orientation of the (111)-gliding planes and the (110)-gliding directions in the fcc-lattice, a (100)-textured structure generally activates all gliding planes of the fcc-lattice at low stresses under tensile stress conditions. On the contrary, 8 gliding systems do not operate in the (111)-orientation, while the others begin to act under 50% higher tensile stresses. Therefore, increasing the (100)/(111) ratio increases the fracture elongation and decreases tensile strength (Fig.10).

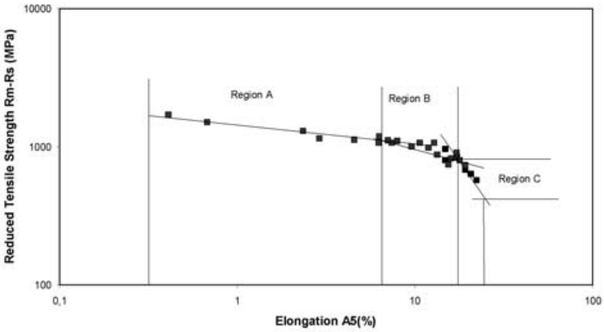

Fig.10. Reduced tensile strength-elongation function of optimally milled ODS-Ni-based-alloys.

Substructure of Optimally Processed ODS-Alloys

The measurements of tensile data refer to the quality of the as milled products in terms of the yttria partitioning. All ODS-alloys which obey the reduced tensile strength-elongation functions (Eq.4), exhibit a fine and homogeneous dispersion of the yttria particles. The dislocation of densities-grain sizes plot reflects the whole processing history, because boundary line structures, according to Eq.2, are only achieved if the milling process yields a fine and homogeneous yttria partitioning in the first case, and consolidation and working parameters are carried out in the correct temperature-strain window, which gives a secondarily recrystallized, coarse structure of elongated grains (Fig.11).

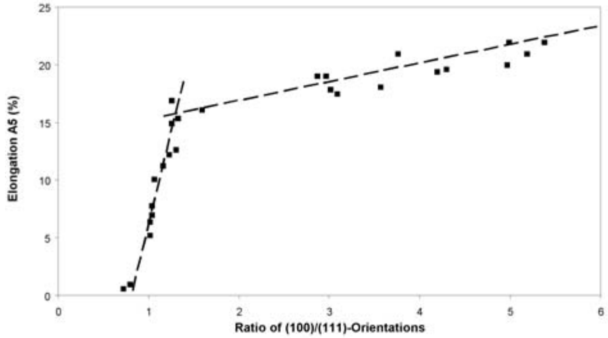

Fig.11. Influence of the (100)/(111)-ratio on the elongation of optimally milled ODS-Ni-based-alloys.

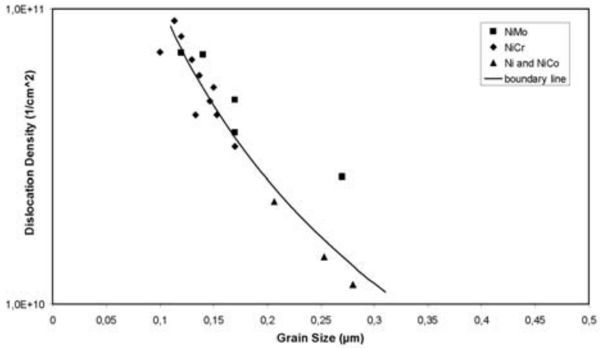

Fig.12. Dislocation density-grain size-boundary line function of optimally milled, consolidated and worked ODS-alloys.

CONCLUSIONS

Powder particle sizes and microstructures of ball milled Ni-W-model systems and NiCr-alloys were investigated to study the partitioning, alloying and homogenisation processes during mechanical alloying of ODS-alloys. As a consequence of fracturing and rewelding of the powder particles, a fine layered particle structure of the milled metal components will be created, which is continuously refined. If a critical layer thickness of approximately 35 nm is succeeded, a true solid solution of the milled metal components is formed by diffusion.

Tensile tests of differently milled and extruded ODS-NiCr20-alloys, show that the deformation of the powder particles plays a major role for the partitioning of the yttria particles. Although the powder particle sizes increase during mechanical alloying of ODS-NiCr20, which is caused by predominating welding processes, the tensile strength increases due to refinement of the yttria dispersion. Because of the predominating welding processes, fracturing of the particles does no longer contribute to the refinement of the yttria dispersion.

Refinement of the yttria dispersion, causes an approach of the measured tensile data to a tensile strength-elongation function of optimally milled powders. Elimination of the contributions of solid solution strengthening, results in a general reduction of tensile strength-elongation-function, which is valid for all investigated ODS-Ni-based alloys. This function gives the mutual dependence of reduced tensile strengths and elongations for ODS-Ni-based alloys, which exhibit a fine and homogeneous dispersion of yttria particles between 10 and 20 nm, and a mean particle distance between 100 and 250 nm.

The substructures of optimally processed alloys obey a boundary line condition, which gives the mutual dependence of dislocation densities and grain sizes of alloys, which then exhibit a fine and homogeneous yttria partitioning, and which were worked in the right temperature-strain window without cold or hot overworking.

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