POWDER METALLURGY CARBON FREE TOOL STEELS Fe-Co-Mo WITH VARYING Co AND Mo CONTENTS

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Abstract

Carbon-free precipitation hardened tool steels of the type Fe-Co-Mo/W have been shown to exhibit as-heat-treated hardness levels similar to those of carbidic high speed steels but markedly higher resistance to heat softening. However, the high content of expensive alloy elements is a marked disadvantage. Here, the effect of the Co and Mo contents, respectively, on hardness and microstructure has been studied. It has been shown that the Co:Mo ratio plays a major role, ratios >1 being preferable; otherwise, the material remains in the α structure during sintering and heat treatment, respectively, with resulting pronounced grain coarsening. With lower Co content, the peak hardness is attained at progressively higher aging temperatures; the absolute hardness level is however lowered. 15% Mo results in hardness levels that are 5-10 HRC higher than 10%Mo at the same Co content. Generally it must be stated that for high speed cutting applications only the materials Fe-25%Co-15% Mo and, for slightly less demanding applications, Fe-20%Co-15% Mo are promising, while lower-alloyed variants are possibly suited for cold work and hot work applications, in which case their virtually distortion-free hardening response might be a distinct advantage.

Keywords: Powder metallurgy tool steel, sintering, precipitation hardening, carbon-free alloys, temper resistance

INTRODUCTION

Tool materials, especially those used for metal cutting applications, are required to possess high hardness at elevated temperatures to withstand the thermal loading of the cutting edge [1,2]. In addition to abrasive and adhesive wear, typically resulting in flank and crater wear, respectively, thermal softening is a typical wear mechanism especially in high speed tool steels. This is due to the fact that high speed steels are not inherently hard, as are e.g. hardmetals or cutting ceramics, but can be obtained in a relatively soft, annealed "manufacturing" state, which makes machining fairly easy, and are then transformed into the hard "application" state by suitable heat treatment. The hardening mechanisms, in the case of HSS mainly precipitation hardening through fine secondary carbides, start to fail at higher temperatures, as a consequence of overaging of the precipitates, leaving only solid solution strengthening as the remaining mechanism [3]. If the cutting performance of tool materials is to be improved while the convenient "switch" from soft and machinable to hard

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and resistant is to be retained, strengthening mechanisms have to be used that remain effective up to higher temperatures.

One approach is the use of intermetallic phases as secondary hardening phase in place of carbides, these phases being less prone to overaging. This has been used for a long time in hot work tool steels which, in addition to carbides, also contain intermetallic phases. There is however no need for carbides: As early as 1932, Köster and Tonn [4-6] have shown that carbon-free alloys Fe-Co-Mo and Fe-Co-W, at that time primarily intended for hard magnetic applications, can be precipitation hardened to hardness levels >65 HRC. In the 1960s, Geller and co-workers [7-9] studied numerous carbon-free steel grades; they found that the absence of austenite stabilizers such as Ni is beneficial for temper resistance. Fe-Co-Mo and Fe-Co-W-Mo steel grades proved to be particularly well suited for machining of Ti alloys, being decidedly superior to e.g. standard HSS grade T1. Although Köster had proposed powder metallurgy manufacturing already in the 1930s [10], it took many decades until this approach was experimentally followed. In the late 1990s, Karpov et al. produced Fe-Co-W-Mo tool steel through powder metallurgy, using coprecipitated and coreduced powders [11]. Danninger et al. [12] showed that tool materials with excellent properties can be obtained also from elemental powder mixes if the sintering parameters are adjusted accordingly to result in homogeneous distribution of the alloy elements [13-15]. In particular the grade Fe-25%Co-15%Mo exhibited an excellent combination of workability and machining performance. Hardening is afforded by secondary precipitates of the μ phase $(Fe,Co)_7(Mo,W)_6$ that are generated at temperatures >350°C (see also [16-18]). However, also some μm-sized μ phases should remain during solution treatment to prevent excessive grain growth and resulting embrittlement.

One pronounced advantage of these tool steels compared to carbidic HSS is their relatively low hardness as-quenched, which enables machining and even, to some degree, cold working. Tools can be soft machined after quenching, the final hardening being an isothermal aging process at moderate temperatures, without any phase transformation. Thus, geometrical precision after hardening is much better than after the common quench- and temper treatment of carbidic HSS. Recently, the Fe-Co-Mo grade has been made commercially available by Böhler Uddeholm, under the designation “MC-90 Intermet” [19], and the applications are mainly tools for which geometrical precision is a must while hard machining should be avoided as much as possible.

A clear disadvantage of the carbon-free tool steels is however the high content of expensive alloy elements, in particular with regard to the soaring metal prices in the last years. In this work it was studied if also lower-alloyed variants of the Fe-Co-Mo grade might be feasible for producing effective cutting tools with possibly improved workability, peak hardness and aging response being taken as criteria.

EXPERIMENTAL PROCEDURE

The starting powders used were Carbonyl iron (BASF grade CN), Co powder (Umex 5-M), and elemental Mo (Plansee, <32 μm). The powders were dry blended for 60 min in a tumbling mixer and then uniaxially compacted at 400 MPa under die wall lubrication to bars of 55 x 10 x 15 mm and 100 x 12 x 15 mm, respectively. Die wall lubrication was performed since it had been found that when using admixed pressing lubricant, the high Mo content results in carbon pickup, with resulting loss of temper resistance. The compacts were then sintered in a pushtype furnace in flowing hydrogen of technical purity. Since previous experiments had shown that 2 h sintering at 1370°C had resulted in homogeneous microstructures with all materials except those containing >15%W, this sintering regime was chosen also here.

After sintering, the density was measured through water displacement, and metallographic sections were prepared by standard techniques. However, a particular feature of the materials was the retaining of grinding marks that were concealed after polishing but reemerged after etching, being visible as parallel lines. Therefore, after the first polishing step intense overetching was done to remove the deformed surface area, with subsequent careful diamond repolishing; after this treatment, with most materials clear sections without grinding marks were obtained after etching (see sections below). In all cases Picric acid was used for etching. For control purposes, the hardness was measured also in the as-sintered state.

Then the bars were heated to 1150°C in flowing N_2 and hot rolled in 6 passes, resulting in a total thickness reduction of about 50%; thus the residual porosity could be eliminated. The specimens were then solution treated at 1150°C for 30 min, oil quenched, and tempered for 60 min at varying temperatures. Rockwell hardness HRC was measured on cross sections after carefully cutting the bars using a Labotom saw with water cooling. Selected specimens were metallographically prepared using the techniques described above.

Thermodynamic calculations

For the ternary system Fe-Co-Mo, there are not too many references in the literature. In part even fairly recent books and databases show results obtained by Köster and Tonn many decades ago, apparently since there are no newer data available [20,21]. In Figure1 the isothermal section at 1300°C is shown, which gives some indication of the phases at sintering temperature, and the compositions selected for the experiments are indicated. It is evident that increasing both the Co and Mo levels in parallel does not shift the α-γ transformation too much; the exact position of the boundary lines is however questionable.

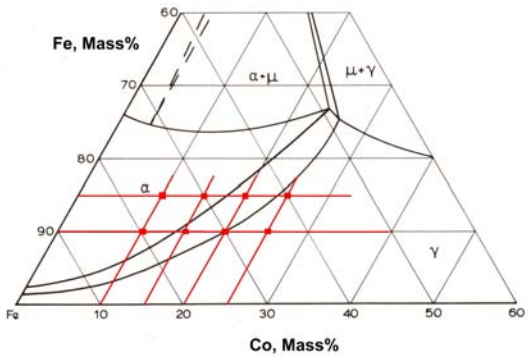
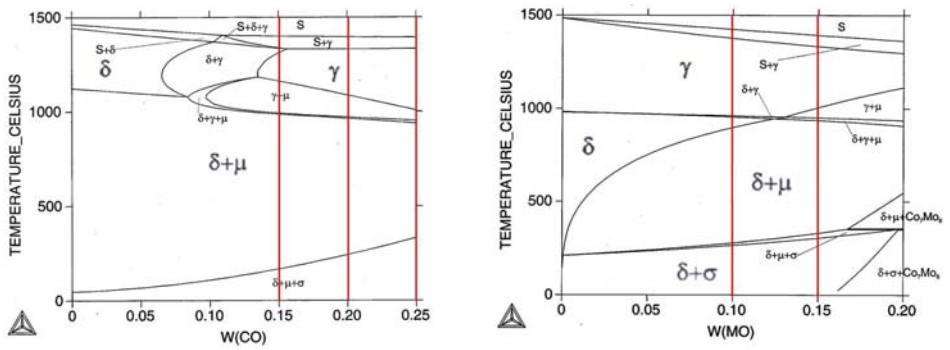


Fig.1. Isothermal section of the system Fe-Co-Mo at 1300°C ([20], after [4]); the compositions selected for the experiments are plotted.

The system was also calculated using Thermocalc™ software. The first approach, using the database TCFE, was not successful; the results obtained showed a very poor correlation with experimental results. E.g. according to these results there should be no austenite phase at all for Fe-25%Co-15%Mo, which, as shown by the experiments, definitely exists. Therefore, another database, Kaufman binary, was used, which resulted in better agreement with experiments, at least qualitatively, although e.g. the solidus temperatures are given too low. In Figures 2a, b the polythermal sections for 15% Mo and for 25% Co, respectively, are shown. The austenite-stabilizing effect of Co is clearly visible, as is the fact that the stability of the μ phase is not too much affected by the α-γ

transformation. Co seems to slightly lower the solubility of Mo. From the calculations it can be deduced that lowering the Co level should stabilize the alpha phase – with possibly beneficial effect on sintering – and increase the solubility of Mo, resulting in lower volume fraction of precipitates and thus maybe in slightly lower hardness. Lowering the Mo content would result in less precipitates and thus in lower peak hardness. Since however the quantitative agreement between calculation and experiment was still not quite satisfactory, the exact effects of changing the composition is hardly predictable, and experimental proof was necessary anyhow.



15%Mo, varying Co content 25%Co, varying Mo content

Fig.2. Polythermal sections of Fe-Co-Mo, calculated through ThermoCalc with database Kaufman; compositions studied in the present work are marked

As-sintered properties and microstructures

In Table 1 the compositions of the materials tested are given as well as the resulting density / residual porosity and as-sintered hardness data. Regarding the porosity it must be considered that this has been calculated using a theoretical density obtained through the rule of mixture, which is not necessarily applicable here. Nevertheless is it evident than in all cases near full density has been attained, those materials with a Co:Mo mass ratio of or below 1 exhibiting slightly lower porosity.

Tab.1. Properties of sintered steels Fe-x%Co-y%Mo, compacted at 400 MPa, sintered 2 h 1370°C in H_2

Composition Mass%	Sintered density g.cm^{-3}	Porosity %	Hardness HRC
Fe-25Co-15Mo	8.20 + 0.01	2.2 + 0.1	37.4 + 0.7
Fe-25Co-10Mo	7.98 + 0.01	3.7 + 0.1	41.0 + 0.8
Fe-20Co-15Mo	8.20 + 0.01	1.7 + 0.1	39.5 + 0.6
Fe-20Co-10Mo	8.02 + 0.01	2.7 + 0.1	35.6 + 0.1
Fe-15Co-15Mo	8.23 + 0.01	0.7 + 0.1	42.1 + 0.3
Fe-15Co-10Mo	8.02 + 0.05	1.6 + 0.6	36.7 + 0.3
Fe-10Co-15Mo	8.15 + 0.01	1.1 + 0.1	36.8 + 1.4
Fe-10Co-10Mo	7.99 + 0.00	1.7 + 0.0	(5.7 + 0.9)

The hardness levels are in the range of 25 to 42 HRC, there is however no defined pattern with regard to composition or porosity, i.e. “as-sintered” is similarly undefined as

"T1" for sintered aluminium. Since however the materials are not worked or used in this state, the erratic HRC values are not really of practical relevance.

In Figure3 the as-sintered microstructures are shown. Evidently there are two distinct groups of morphologies, depending on the composition: if $c_{Co} > c_{Mo}$ (Fig.3a-e), there is the typical microstructure described e.g. in [12, 15] with complex-shaped, heavily interlocked grains. In the case of $c_{Co} = c_{Mo}$ or $c_{Co} < c_{Mo}$ (Fig.3f-h) simple polygonal grains are found, and in part quite pronounced layers of precipitates can be observed at the grain boundaries, while at the Co-rich variants in part no grain boundary phases are present at all, in part they are thin and discontinuous, as typically shown in Fig.4. This can be taken as an indicator that in the ferrite, lattice diffusion of Mo to the grain boundaries to form intermetallic phases there is markedly faster than in the austenite phase. Quite similar effects have been observed with Co-free Fe-Mo alloys used for the wear loaded section of automotive rocker arms, which are subsequently carburized [24]; also in this case, polygonal grains with continuous precipitates at the grain boundaries have been obtained after sintering.

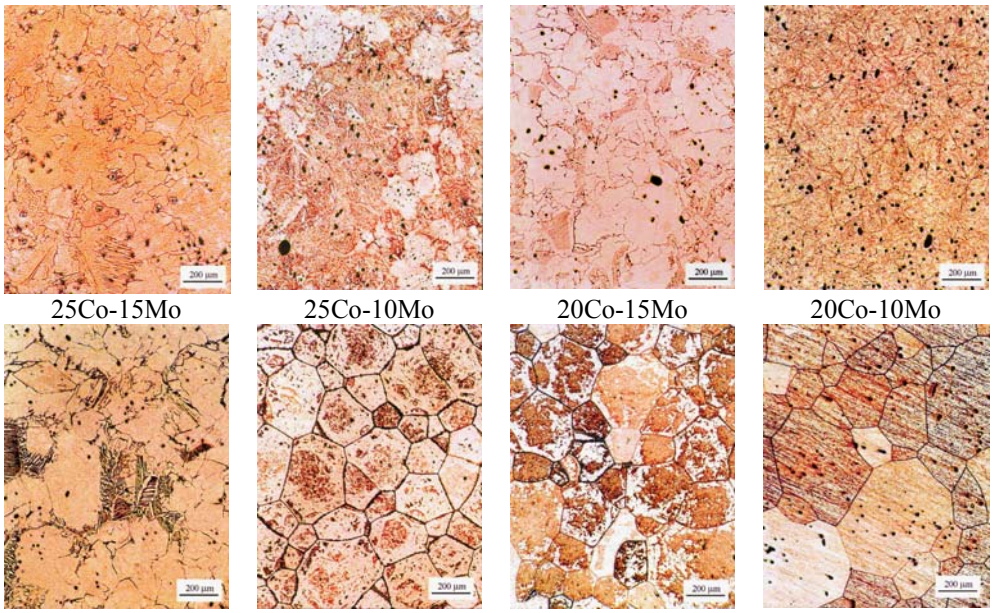
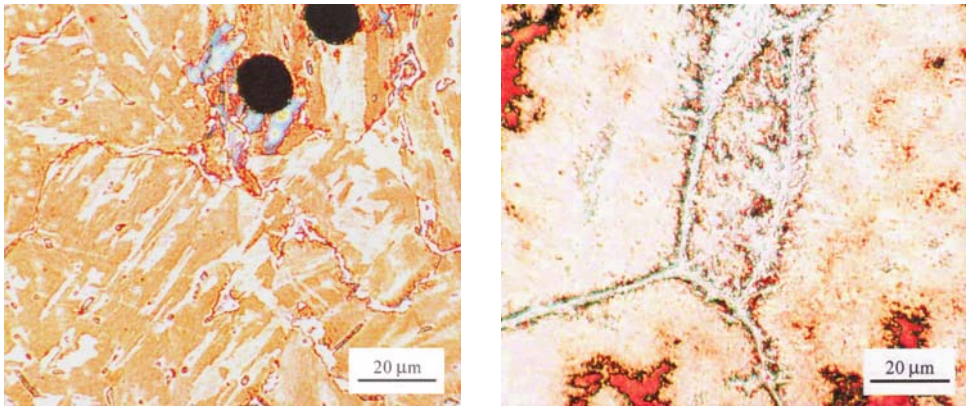


Fig.3. Metallographic sections of Fe-x%Co-y%Mo, compacted at 400 MPa, sintered 2 h 1370°C in H_2.

Taking the isothermal sections of the system Fe-Co-Mo from [20] it can be concluded that with all compositions that are located in the γ or α-γ fields, the interlocking grains are visible while those compositions in the α field exhibit the polygonal microstructure. This also agrees with the porosity data which for materials sintered in the α field (see Fig.1) exhibit slightly lower porosity, due to the well known activating effect of "alpha sintering" [25].

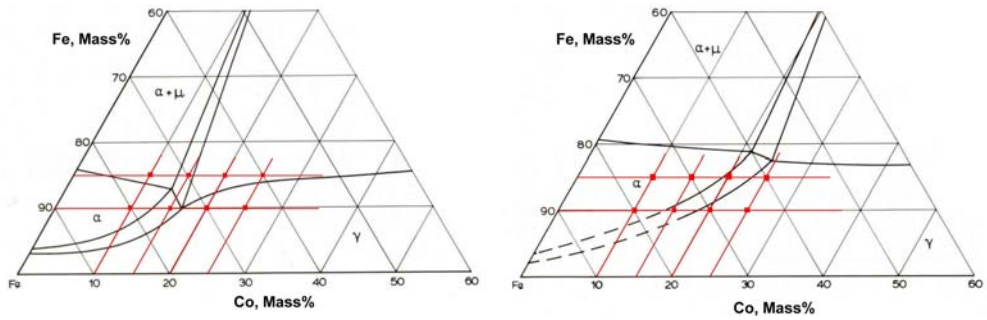


25Co-15Mo 15Co-15Mo

Fig.4. Intermetallic phases at grain boundaries in differently alloyed materials.

Heat treatment response

In Figure 5, the isothermal sections of the ternary system are shown for the temperature "window" suited for solution annealing, the compositions investigated being plotted once more in the diagrams. It is evident that at 1200°C all the materials are in the homogeneous α or γ or in the two-phase α-γ phase fields, but there is no μ phase stable any more. This means that the annealing temperature should be chosen slightly lower, in order to retain at least some of the μm-size μ phases that prevent excessive grain growth. Therefore, the intermediate temperature of 1150°C was selected for the experiments.



Section at 1100°C ([20], after [22]) Section at 1200°C ([20], after [23])

Fig.5. Isothermal section of the system Fe-Co-Mo at 1100 and 1200°C; the compositions selected for the experiments are plotted.

In Figures 6a and b, temper charts are shown for the different compositions after solution treatment at 1150°C and oil quenching. Figure 6a depicts the materials containing 10% Mo and varying amounts of Co, and Fig.6b shows the same for 15% Mo. It stands out clearly that for both Mo levels the as-quenched hardness is quite low, at or below 40 HRC, which enables soft machining. The peak hardness increases with higher Co content and the onset of precipitation hardening is shifted to lower temperatures while the drop of the hardness at higher temperatures is hardly shifted, i.e. the range of aging temperatures at which high hardness levels are attained becomes successively broader. The materials with

higher Mo content are generally more tolerant in that respect. This means that at least at technically relevant hardness levels the shifting of the α-γ transformation to higher temperatures at low Co:Mo ratio, as shown in Fig.2a, does not play a major role here, in contrast of the findings of Geller et al. for austenite stabilizers such as Ni [7-9] for which the transformation temperature is clearly related to the temperature of heat softening.

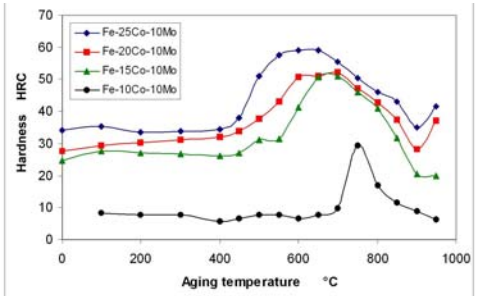


Fig.6a. Aging response of Fe-x%Co-10%Mo, solution treated at 1150°C, oil quenched, tempered 60 min

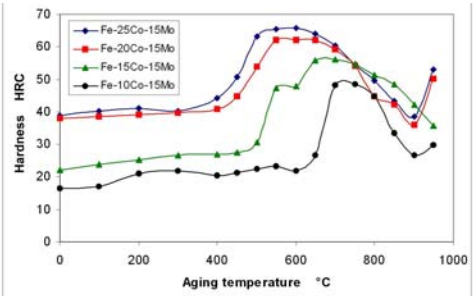
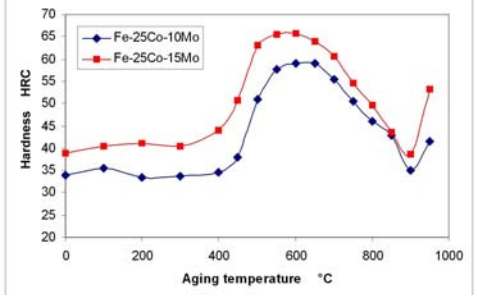
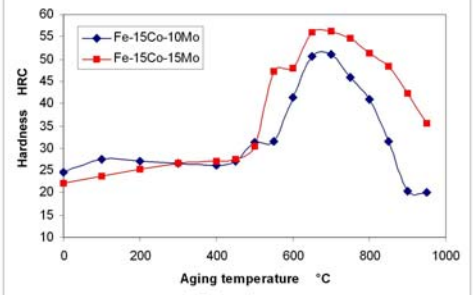


Fig.6b. Aging response of Fe-x%Co-15%Mo, solution treated at 1150°C, oil quenched, tempered 60 min

When comparing the 10% Mo and 15% Mo grades (see e.g. Figs.7a and 7b), it is evident that the higher Mo content generally results in higher peak hardness. In addition to the reference grade Fe-25Co-15Mo also the grade 20Co-15Mo seems to be attractive. Grades such as 25Co-10Mo exhibit markedly lower hardness as monolithic materials but might be interesting as matrix materials for particle reinforced MMCs in which the wear resistance, in particular against abrasion, is increased by addition of ceramic particles [26].



Fe-25%Co-x%Mo



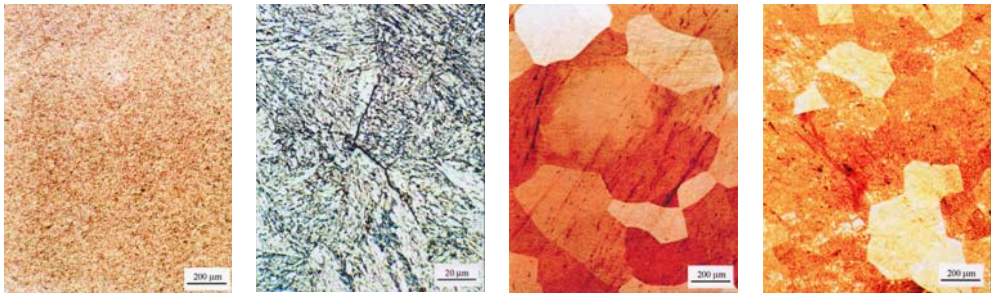
Fe-15%Co-x%Mo

Fig.7. Aging response of Fe-x%X-y%Mo as a function of the Mo content

Microstructures at peak hardness

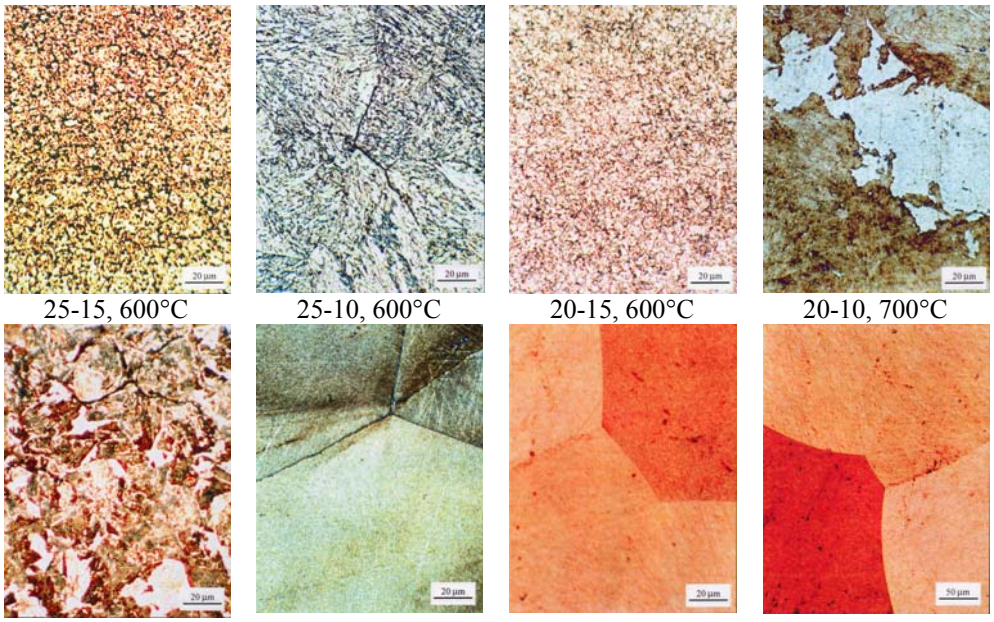
In Figure 8 the microstructures of peak aged materials with constant Mo level of 15% but decreasing Co content are shown at low magnification to give a general impression of the microstructures. It stands out clearly that also in this state the polygonal microstructure is visible for materials with Co:Mo ratio <1 while for 20:15 the fine and very regular microstructure as typical for 25-15 is revealed. Typically this latter material contains the µm size µ phases which, as stated above, are necessary for preventing excessive grain growth during solution annealing, while for the materials with polygonal

microstructure such phases are not shown, although the Mo content is the same. This indicates markedly higher Mo solubility in the latter materials, at least at 1150°C, which disagrees with the phase diagrams shown in [20] but agrees with the calculated polythermal section shown in Fig.2a, which predicts lower Mo solubility with higher Co content. At the lower Mo content, also the Co rich variants show relatively coarse grain structures, which indicates that the lack of sufficient µm-size µ phases has resulted in the austenite grain growth that had been observed at the standard 25-15 grade at high solution treatment temperatures [12, 13].



20-15, 700°C 15-15, 700°C 10-15, 700°C 10-10, 750°C

Fig.8. Metallographic sections of Fe-x%Co-y%Mo, solution treated 30 min 1150°C, oil quenched, and peak aged. Overview (Low magnification).



25-15, 600°C 25-10, 600°C 20-15, 600°C 20-10, 700°C

15-10, 700°C 15-15, 700°C 10-15, 700°C 10-10, 750°C

Fig.9. Metallographic sections of Fe-x%Co-y%Mo, solution treated 30 min 1150°C, oil quenched, and peak aged. High magnification.

In Figure 9, the microstructures are shown at higher magnification, each material being aged at the temperature at which maximum hardness has been recorded. It is evident

that once more the coarse polygonal microstructure is observed for Co:Mo <1, with hardly any structures visible within the grains. This means that the coarse microstructure is caused by annealing in the ferrite range, at which coarsening is much more rapid than in austenite, and that also the lack of µm size µ phases results in uninhibited grain growth. For the other materials the structures are much finer, and µ phases are visible which, as previously shown [12] are quite effective in preventing grain growth during the solution anneal.

CONCLUSIONS

The experiments with Fe-x%Co-y%Mo (x = 10 … 25 mass%; y = 10 ..15 mass%) have shown that through the blended elemental approach, i.e. mixing of elemental starting powders, uniaxial compaction and sintering at 1370°C, specimens with almost full density and homogeneous microstructures can be attained. The materials with Co:Mo mass ratio ≤ 1 show slightly less residual porosity, while the microstructures are relatively coarse, with polygonal grains. The other group of materials shows an interlocking grain structure. This difference can be attributed to the phases during sintering: while in the first group sintering is done in the alpha range, the second one sinters in mixed α-γ or plain γ phase.

After precipitation hardening treatment, i.e. solution anneal, quenching and aging, the materials exhibit in part hardness levels up to 65 HRC and high temper resistance. When the Co content is decreased, the peak hardness appears at higher aging temperatures while the hardness itself is lowered. The Mo content strongly affects the peak hardness: 15% Mo results in hardness levels that are 5-10 HRC higher than 10%Mo at the same Co content.

For high speed cutting applications, primarily the materials Fe-25%Co-15%Mo and, for slightly less demanding applications, Fe-20%Co-15%Mo seem to be attractive; for the lower-alloyed variants the alloying cost will probably outweigh the performance; however, at least some of them might be useful as matrix for particle reinforced metal matrix composites or for hot work application since for all these grades the virtually distortion-free hardening by isothermal anneal in the α range can be applied.

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